

[CONTRIBUTION FROM THE DEPARTMENT OF SOIL MICROBIOLOGY, RUTGERS UNIVERSITY, AND NEW JERSEY AGRICULTURAL EXPERIMENT STATION]

Investigations Concerning Phenol Lignin and Methoxy Glycol Lignin from Spruce Wood¹

BY WALTER FUCHS²

On heating spruce wood with phenol (or methoxy glycol, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$), in the presence of hydrochloric acid, phenol lignin³ or methyl glycol lignin⁴ is obtained, respectively. Phenol lignin may be regarded as a mixture of at least two substances, since Wedekind and his co-workers,⁵ as well as Brauns and Hibbert,⁶ found it to be partly soluble in ether. Fuchs and Daur⁷ have shown that methoxy glycol lignin or abbreviated methylin also consists of a number of different complexes.

In the present paper a convenient method for preparing large amounts of phenol lignin from spruce wood is reported. It is further shown that phenol lignin is a complex mixture of a variety of substances. Phenol lignin in alcoholic solution is, in part, adsorbed by activated carbon. The portion adsorbed may be extracted with various solvents and thus yields a number of fractions. The phenol lignin which is not adsorbed can be separated into two fractions by means of ether extraction and these can be still further fractionated by treatment with ethyl acetate and shaking the ethyl acetate solutions with sodium carbonate solutions. Figure 1 contains a survey of the procedure. By the use of chloroform instead of ethyl acetate, methoxy glycol lignin can also be separated into a number of different fractions.

Even the fractions thus obtained were not uniform as shown by results reported below. However, it was decided to subject the main fractions to an investigation as applied in the case of uniform substances. Therefore, the fractions have been characterized by analysis, determination of oxygen functions, determination of equivalent weights and basicity and breakdown experiments. Attention might be called to the following particulars.

(1) Journal Series Paper of the Department of Soil Microbiology, New Jersey Agricultural Experiment Station.

(2) Research Professor, Rutgers University; present address, The Pennsylvania State College, State College, Pa.

(3) See Fuchs, "Chemie des Lignins," Berlin, 1926. (American Ed. in preparation.)

(4) Fuchs, *Ber.*, **62**, 2125 (1929).

(5) Wedekind, *et al.*, *Cellulosechem.*, **12**, 163 (1931).

(6) Brauns and Hibbert, *Can. J. Research*, **13B**, 28 ff. (1935).

(7) (a) Fuchs and Daur, *Cellulosechem.*, **12**, 103 (1931); (b) *Brennstoff-Chem.*, **12**, 266 (1931).

Figure 1
FRACTIONATION OF PHENOL LIGNIN
The raw product is dissolved in alcohol and treated with activated carbon

Solution concentrated, precipitated with dilute HCl precipitate treated with ether			Residue
Insoluble in ether Fraction 1	Soluble in ether Fraction 2		
Fr. 1 and 2 extracted with ethyl acetate			adsorbed Fraction 3 Successive extraction with various solvents: Fractions 3a, b, c
Residue Fraction 1c	Solution	Solution	
	The solutions shaken with a solution of sodium carbonate		Trace
Fr. 1a remains in ethyl-acetate Fr. 1d separates out	Fr. 1b soluble in sodium carbonate	Fr. 2a remains in ethyl-acetate	Fr. 2b soluble in sodium carbonate

(a) **Analysis.**—The methoxyl determination of methoxy glycol lignin and similar substances has met with the criticism that glycol derivatives may falsify the results in the usual procedure. Brauns and Hibbert⁸ studied the subject and proposed a certain correction of the values. It is, however, to be emphasized that glycol or methoxy glycol in combination with lignin are not split off to a great extent under the conditions of the methoxyl determination. Furthermore, a modification of the usual procedure has been found which is described in the experimental part, and which renders the conditions of the determination still milder. The uncorrected values are, therefore, probably much nearer to the truth than any corrected ones.⁹

(b) **Oxygen Functions.**—Phenol lignin, as well as methoxy glycol lignin, easily gives acetyl derivatives which are soluble in cold benzene and insoluble in dilute alkali, indicating complete acetylation, as well as the absence of COOH groups in both substances. According to Wede-

(8) Brauns and Hibbert, *Can. J. Research*, **13B**, 35 (1935).

(9) The modification consists of heating the sample, using 5 cc. of acetic acid and 5 cc. of hydriodic acid, instead of 10 cc. of hydriodic acid, as applied hitherto. It has been found to be apparently generally applicable and since it also cuts down the cost of the methoxyl determination, it might be recommended for general use.

kind and co-workers,⁵ acetyl phenol lignin is insoluble in cold benzene; if, however, the outline given below is followed, a preparation is obtained which is just as easily soluble in benzene as the acetyl methoxy glycol lignin and which most closely resembles that substance.

(c) **Equivalent Weight and Basicity.**—An attempt was made to determine the combining weights of methoxy glycol lignin and phenol lignin by ascertaining the exact amount of substance necessary to neutralize a dilute solution of standard alkali. For methoxy glycol lignin, Fraction 1a gave a value of 460, a result which fits very well

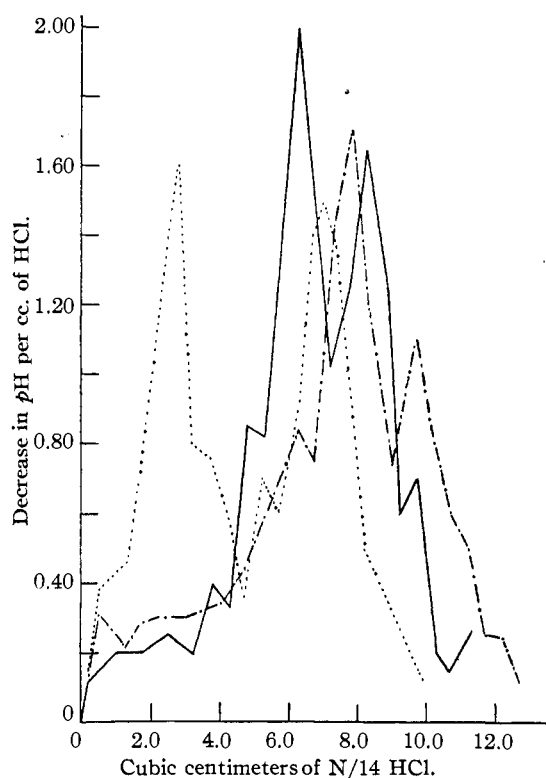


Fig. 2.—Methylin 1a, ·····; phenol lignin 1a, ———; phenol lignin 2a, ·····.

with the conclusion reached in 1929⁴ that the substance contains two acid OH groups in a stoichiometric molecule of approximately 930. The values obtained for phenol lignin comprise figures such as 260 for Fraction 1a and 130 for Fraction 2a. These figures indicate either that the substances in question contain from 4 to 8 acid OH groups in their molecules or represent one of the contradictions not infrequently met with in lignin chemistry. In this connection it might be mentioned that Wedekind and Katz,¹⁰ by osmotic

(10) Wedekind and Katz, *Ber.*, **62**, 1172 (1929).

pressure measurements, obtained similar contradictory results which still await explanation.

The solutions obtained on determining the equivalent weights were used for potentiometric titrations. In Fig. 2 the values are plotted in the differential form of $\Delta pH / \Delta n$ against n (cc. of acid consumed).¹¹ The curves thus obtained suggest the presence of a mixture of acid substances in either case. Thus, another proof of the complexity of the fractions in question is secured.

Recently, King, Brauns and Hibbert¹² have published the results of potentiometric titrations of lignin sulfonic acid. By plotting n (cc. of acid consumed) against the pH values observed, they obtained a rather smooth curve. However, it seems that by applying the method of plotting used in Fig. 2, a curve of very similar form would result.

(d) **Linkage of Phenol in Phenol Lignin.**—Hägglund¹³ was unable to achieve a cleavage of the phenol introduced into phenol lignin and therefore assumed an essential difference between phenol lignin and the various aryl lignins. This assumption, however, is erroneous. The phenol introduced into phenol lignin may be split off, at least in greater part, by heating the substance with a mixture of acetic acid and hydrobromic or hydriodic acid, preferably in the presence of small amounts of reducing agents, such as phosphorous or hypophosphorous acid. Phenol begins to split off at a comparatively low temperature, but the action is greatly accelerated by an increase in heat and pressure. On heating the substance with hydrobromic acid, in addition to phenol, a sugar-like substance originates. These methods were suggested by a consideration of the properties of euxanthic acid,¹⁴ as well as anthocyanins.¹⁵ Euxanthic acid, it may be recalled, is a glucoside having the unique property of being hydrolyzed only under conditions of relatively high pressure and temperature; the anthocyanins, on the other hand, are glucosides of extraordinary sensitivity to hydrolysis.

The cleavage of the phenol lignin definitely proves, at least for the phenol split off, either an acetal linkage as previously postulated by the writer,⁴ or an ether linkage as assumed by Hibbert.⁶

(11) The writer is indebted to Dr. Paul S. Roller for help and criticism.

(12) King, Brauns and Hibbert, *Can. J. Research*, **13B**, 88 (1935).

(13) Hägglund, *Cellulosechem.*, **11**, 30 (1930).

(14) Rosenthaler *et al.*, in Klein, "Handbuch der Pflanzenanalyse," Verlag Julius Springer, Wien, Vol. II, Part 1, 1932, p. 989 ff.

(15) Karrer, *ibid.*, p. 941 ff.

The phenol split off amounts to 20% in the case of phenol lignin Fraction 1a, and 26% in the Fraction 2a. However, since the particular spruce wood contained 27% lignin, while a yield of 40% of phenol lignin was obtained, it is to be computed that the actual amount of phenol introduced was at least 30% of the phenol lignin prepared. The results established by ultimate analysis of the preparation point to the same conclusion.

(e) **Breakdown Experiments.**—Alkali fusion and oxidation with nitric acid both give rise to definite crystalline breakdown products. In carrying out the alkali fusion of the preparations at a somewhat higher temperature than previously described,^{7a} *p*-oxybenzoic acid is obtained in addition to protocatechuic acid and other products already recorded. A quantitative determination of the *p*-oxybenzoic acid was developed. That acid originates, in part, from the phenol introduced, and, in part, from the lignin itself as shown by the results obtained with methylin. *p*-Oxybenzoic acid was first established by Phillips¹⁶ as a breakdown product of lignin preparations.

On oxidizing phenol lignin and methyl glycol lignin with nitric acid, picric acid and benzene carbonic acids are obtained in both cases. The latter were established qualitatively by decomposing with hydriodic acid in a sealed tube and identifying the benzene formed.

It seems probable that continued fractionation studies may lead eventually to the isolation of uniform and possibly even crystalline preparations. At present, improved methods for the determination of chemical and physical properties and for studying the breakdown and fission products appear to offer the most promising approach. It has been suggested¹⁷ that the formulation of a hypothetical substance, the properties of which are consistent with what is known of spruce lignin and its fission products, may be of value. That formulation is represented in Fig. 3.

The analytical data agree fairly well with Formula I. Formulas II and III represent possibilities concerning the formulation of phenol and methoxy glycol derivatives. In this respect the following contradiction is observed: acetals of

simple substances are easily formed and easily decomposed; ethers are more difficult to obtain and also harder to hydrolyze. Since the products in question are obtained easily, but not easily decomposed, both possibilities are apparently conceivable. In the author's opinion, however, the evidence for acetal formation by ring splitting is stronger.

As to the breakdown experiments, catechol derivatives may be traced to ring 8, phenol derivatives to ring 2 and benzene derivatives to the system comprising rings 5, 2, 3, 4 and 6. Thus, Formula I seems to be a good means of summing up the results obtained and of suggesting new experimental procedures.

Experimental Part

1. **Preparation of Phenol Lignin.**¹⁸—The mechanical device used for this purpose consisted of an S-shaped rubber-coated stirrer which revolved at 60 revolutions per

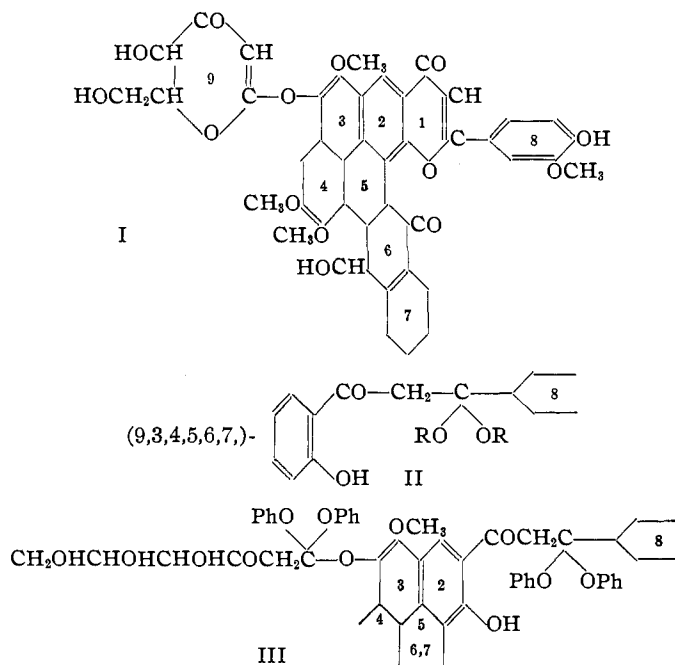


Fig. 3.

minute in a 20-liter earthenware crock. In accordance with results of a series of preliminary experiments, 5000 g. of phenol was placed in the crock and heated to 85 to 90° in a boiling water-bath. Then 500 g. of spruce wood flour was introduced, the stirrer set at work and 50 cc. of concentrated hydrochloric acid was added at once. The addition of both 500 g. of wood flour and 50 cc. of hydrochloric acid was repeated twice during thirty minutes; stirring and heating were continued for two hours. When the wood flour came in contact with the phenol and the hydrochloric acid, it immediately assumed a dark green

(16) Phillips and Goss, *THIS JOURNAL*, **55**, 3466 (1933).

(17) Fuchs, Symposium on Wood, San Francisco Meeting of the A. C. S., 1935.

(18) In collaboration with I. J. Hutchings.

color which, after a few minutes, transformed into a purple-brown.

After two hours of stirring, the doughy mixture was allowed to cool and poured under constant stirring into 60 liters of water. One hour later the supernatant phenol solution was siphoned away and the operation repeated until the material had a granular consistency. Then the decomposed wood was brought on a suction filter, thoroughly washed until the filtrate was neutral and then dried between 50 and 60° in circulating air. The dried and pulverized material was ground by means of a Wiley mill and then treated at 50° with four liters of alcohol, again filtered by suction and washed with two liters of hot alcohol in small portions. The alcoholic filtrate was poured under constant stirring into 60 liters of water containing 5-10 cc. of hydrochloric acid. The bright yellowish precipitate was collected on an earthenware suction filter and carefully washed until the filtrate was neutral, then it was dried between 50 to 60° in circulating air; yield, was nearly 600 g.

In a second experiment certain additional data were collected. Starting with 1500 g. of spruce sawdust, 1475 g. of water-insoluble material was obtained. After grinding in a Wiley mill, the material was extracted with about 8 liters of 95% alcohol in successive portions at 50°. The cellulosic residue was retained and dried. Methoxyl determinations were made on the alcoholic extract, the cellulosic residue and the original to determine the losses during the operation. The results together with the yields are given in Table I.

TABLE I
YIELDS AND METHOXYL CONTENTS DURING PREPARATION OF PHENOL LIGNIN

Substance	Yield, g.	Methoxyl, %	Total methyl alcohol, g.
Original wood	1500	4.93	74.70
Wood after treatment	1475
Cellulosic residue	650	1.05	6.86
Alcoholic extract	850	7.86	66.81
Raw phenol lignin	600	9.20	55.20

Obviously, the alcoholic extract referred to in Table I contains condensation products of carbohydrates with phenol; these, however, seem to remain in solution on precipitating.

2. Separation of Phenol Lignin into Fractions.¹⁹—

In preliminary experiments, the alcoholic solution containing phenol lignin and other substances, as obtained above, was treated in various ways with activated carbon and the light absorption capacity studied colorimetrically. The results are given in Table II. (The values of the last column were calculated by use of the rule of allegation.)

In order to prepare greater quantities of the fractions, 100 g. of phenol lignin was dissolved in one liter of alcohol, 100 g. of activated carbon was added, the mixture shaken for thirty minutes and then filtered by suction. The filtrate was filtered once more, then concentrated to 500 cc. and finally poured while stirring into 10 liters of water containing some hydrochloric acid. The precipitate was collected on a Büchner funnel and carefully washed with

(19) 2, 3, 4 and 6 in collaboration with T. C. Cordon.

TABLE II
YIELDS AND LIGHT ABSORPTION CAPACITIES ON TREATING PHENOL LIGNIN SOLUTIONS WITH ACTIVATED CARBON (DECOLORIZING CHARCOAL MERCK)

Charcoal, g. per liter	Temp., °C.	Time of treatment, min.	Subs., g. per liter	Colorimetric reading	Light absorption g. in soln./g. original	g. removed/g. original
None			106.4	100	100.0	...
37	20	30	95.6	66	73.4	400.9
50	80	1	84.5	33	40.3	317.2
100	80	1	66.0	22.8	32.5	69.3
150	80	1	59.5	18.0	27.1	66.7

water. The yield was 75-80 g.; 20-26 g. was in part adsorbed by the activated carbon, in part lost with the filtrate and wash waters.

The precipitated product was dried and the lumps extracted four to five times with dry alcohol-free ether by boiling under a reflux condenser. After 4-5 extractions the ether appeared only slightly yellow; at this point, extraction was continued in a Soxhlet apparatus until the ether was practically colorless.

The collected ether extract solutions were brought to dryness, the residue dissolved in alcohol to form a 4% solution and this solution poured into 25 times its volume of acidulated water. The part insoluble in ether was termed fraction 1, the part soluble in ether fraction 2, and the part adsorbed on the charcoal fraction 3. The relative yields of the fractions 1 and 2 varied somewhat, fraction 2 amounting to about 20% of fraction 1.

3. Treatment of the Activated Carbon.—The activated carbon was extracted with 800 cc. of boiling alcohol. The alcoholic filtrate was concentrated to about 100 cc. volume and then precipitated by pouring into one liter of slightly acidulated water, giving a yield of 3 g. After this treatment, the remaining activated carbon was treated with 800 cc. of boiling alcohol which contained 5 cc. of concentrated hydrochloric acid. The solution was concentrated and precipitated as above, giving a yield of 1.5 g. The activated carbon was then extracted with boiling 2% sodium hydroxide solution. The solution was precipitated with hydrochloric acid, the precipitate collected on a filter and carefully washed with water; the water was rather dark. The precipitate was redissolved in about 50 cc. of alcohol and precipitated by pouring in 500 cc. of acidified water; yield 3.5 g. There was still some substance left on the adsorbent.

4. Further Fractionation of Fraction 1 and Fraction 2.—Ten grams of fraction 1 was treated with 125 cc. of ethyl acetate in a 250-cc. weighed Erlenmeyer flask and, with occasional shaking, left at room temperature overnight. A certain amount of substance (fraction 1c) remained undissolved. The clear solution was poured into a separatory funnel; the residue in the flask (fraction 1c) was washed with fresh ethyl acetate, dried and weighed.

The combined ethyl acetate solutions in the separatory funnel were shaken with 150 cc. of an aqueous solution of 1 g. of sodium carbonate and 1.5 g. of sodium chloride. After standing overnight the layers could be separated, and the aqueous and the ethyl acetate solutions were run through filters into dry weighed bottles. In the separatory funnel a resinous substance (fraction 1d) remained.

The bulk of the original fraction 1 was contained in the

ethyl acetate. This part was termed fraction 1a, isolated by distilling off the solvent and weighed after drying in an oven at 50°. The sodium carbonate solution was acidified and the precipitate collected, washed, dried and weighed.

The above-mentioned resins (1c and 1d) were dissolved in alcohol to form approximately 10% solutions, and these solutions were precipitated by pouring them into 10 times their volume of acidulated water. The precipitates were carefully washed and dried. It may be added that fraction 1a was purified in the same way.

Ten grams of fraction 2 was fractionated by following exactly the same procedure as outlined for fraction 1. In contradistinction to fraction 1, no resins were observed. To purify the bulk of fraction 2 present in the ethyl acetate solution the final residue (fraction 2a) was dissolved in alcohol to form a 4% solution and reprecipitated by pouring into 25 times its amount of acidulated water.

TABLE III

SUBDIVISION OF 10 G. PHENOL LIGNIN, FRACTIONS 1 AND 2

Fraction	1a	1b	1c	1d	2a	2b
Yield, g.	7.0	0.1	1.7	2.0	9.5	0.2
	(7.0)	(0.1)	(1.5)	(1.9)	(9.5)	(0.2)

The weights of the reprecipitated fractions 1a and 2a were 6.1 and 8.4 g., respectively.

5. Preparation of Methoxy Glycol Lignin.—Five hundred grams of spruce wood meal, 2000 g. of methoxy glycol and 25 cc. of concentrated hydrochloric acid were placed in a large beaker, well mixed, covered with a Petri dish, and heated in an autoclave at 15 lb. steam pressure (121°) for several hours. The mixture was then diluted with 2 liters of alcohol, solution and solid were separated by suction and the residue extracted several times with hot alcohol. The weight of the remaining solids was 288 g. That residue contained about 10 g. of a lignin soluble in alkali, but not in the organic solvent.

The combined filtrates were concentrated to 1200 cc. volume and then precipitated by pouring into 12 liters of water slightly acidified with hydrochloric acid. The yellow precipitate was collected on a filter—the filtrate was of a decidedly orange color—washed with distilled water to neutrality and then dried, first in the air at room temperature and finally under a moving fan in an oven at 50°; yield 100 g.

Fifty grams of raw methoxy glycol lignin was dissolved in 1000 cc. of acetone, filtered—3 g. remained undissolved—and 50 g. of activated charcoal added to the solution. The mixture was shaken for thirty minutes and the solution was filtered twice. The acetone solution was poured while stirring into 10 liters of water slightly acidulated with hydrochloric acid; the precipitate was collected, washed and dried under a moving fan at 50° giving a yield of 30 g.

Twenty-five grams of that product was completely extracted with ether in a Soxhlet. The undissolved portion, fraction 1, amounted to 19 g., while fraction 2 (6 g.), was recovered as a brown semi-solid resinous mass by evaporating the ether.

Ten grams of fraction 1 was dissolved in 100 cc. of chloroform and filtered; a negligible residue remained on the filter. The solution was shaken with 150 cc. of an aqueous solution containing 1 g. of sodium carbonate and 1.5 g.

of sodium chloride. After standing overnight, the layers could be separated, and the aqueous and the chloroform solution were run through filters into dry bottles. A resinous substance (fraction 1d) remained in the separatory funnel, while the bulk of the original fraction 1 remained in the chloroform. The clear chloroform solution was poured into 10 times its volume of benzene. The precipitate was filtered, washed several times with benzene, dried and weighed; yield 6.5 g. (fraction 1a). A small amount was contained in the sodium carbonate solution (1b).

Ten grams of fraction 2 was treated in almost the same way. The chloroform solution was extracted with a solution of sodium carbonate as above. After separation of the layers and filtration, the chloroform extract was poured into 10 times its amount of petroleum ether. About 50% of the substance contained in the solution was precipitated while the rest (fraction 2e) remained in solution. Table IV contains a survey of the results.

TABLE IV

SUBDIVISION OF 10 G. OF METHOXY GLYCOL LIGNIN, FRACTIONS 1 AND 2

Fraction	1a	1b	1c	1d	2a	2b	2c	2d	2e
Yield, g.	6.4	0.2	trace	3.1	4g	0.3	trace	trace	rest

6. Analytical Data Concerning Phenol and Methoxy Glycol Lignin Fractions.—These are compiled in Table V. For the determination of the methoxyl content a modification of the method of Zeisel was employed consisting in using instead of 10 cc. of hydriodic acid reagent for each determination, a mixture of 5 cc. of hydriodic acid and 5 cc. of glacial acetic acid. No additional substance is necessary, the reaction taking place easily, quickly and without difficulties. With known substances such as vanillin or anisic acid, the experimental values obtained corresponded closely to theoretical values.

TABLE V

COMPOSITION OF PHENOL AND METHOXY GLYCOL LIGNINS

Designation	C, %	H, %	O, %	OCH ₃ , %
Phenol lignin 1	70.60	5.91	23.59	10.2
Phenol lignin 2	74.60	6.57	18.83	5.0
Phenol lignin 1a	69.75	5.88	24.37	10.0
Phenol lignin 2a	74.90	6.98	18.12	4.2
Methoxy glycol lignin				
1a	64.78	6.32	28.90	17.45

7. Acetylation.—Ten gram-portions of the substances were dissolved in 30 cc. of acetic acid anhydride, the solution diluted with 20 cc. of this reagent containing 0.2% concentrated sulfuric acid, and kept for six hours on a boiling water-bath. The mixture was then poured on 400 g. of ice suspended in 100 cc. of a 20% sodium acetate solution and decomposed. When the ice was melted, the mixture was placed in a separatory funnel, shaken with benzene, the aqueous solution drained off, and the benzene layer completely neutralized by shaking with a solution of sodium carbonate. The benzene solution was then dried with sodium sulfate evaporated and the residue isolated by dissolving in acetone to make a 10% solution and pouring in a large excess of slightly acidulated water. The preparations were bright yellowish powders insoluble in alkali and water, and soluble in acetone, acetic acid and benzene.

8. **Some Physico-Chemical Properties.**—If the individual fractions are dissolved in organic solvents such as alcohol, acetone or acetic acid to form 10% solutions and these solutions are poured into 10 times their amount of water, colloid solutions exhibiting strong Tyndall phenomena are obtained. In these solutions, the lignin shows the properties of a lyophobic and organophilic colloid; the solutions are not viscous, and on adding more organic solvent, the Tyndall phenomena disappear. Phenol lignin fraction 1 in alcoholic solution is moderately transparent beyond 3650 and absorbs in the violet. Phenol lignin fraction 2 absorbs relatively more beyond 3650 and relatively less in the violet. With the apparatus used, no structure in the absorption spectra could be established. In the ultraviolet both show a yellowish fluorescence.

9. **Equivalent Weights.**²⁰—The material was introduced from a weighed container into a wide-mouthed, glass-stoppered bottle containing in some cases 50 cc. of 1/14 *N* sodium hydroxide and in other cases 100 cc. of a 1/28 *N* sodium hydroxide solution. After shaking, further material was added until a slight excess was present. In each case 1% sodium chloride was added. The solutions were shaken at intervals for twenty-four hours.

The undissolved material was finely divided and settled to the bottom of the bottle. The excess was then filtered off and washed with a 1% sodium chloride solution to avoid colloidal phenomena. It was then dissolved in acetone, the acetone evaporated and the residue weighed. In this manner the exact amount of substance in solution was determined. The solutions were filled to 250 cc. volume with 1% sodium chloride solution and used for pH determinations and potentiometric titrations by means of a Leeds and Northrup potentiometer type 7657 and the Leeds and Northrup glass electrode No. 7685. The solutions obtained in the case of the phenol lignin fractions 1 and 1a and the corresponding methoxy glycol lignin were brown but clear, and hardly showed a Tyndall phenomenon; the solutions of the phenol lignin fractions 2 and 2a, however, were rather bright, but difficult to filter and showed a strong Tyndall phenomenon. Most probably due to this interference; the results in the case of fractions 2 and 2a did not check as well as in the case of fractions 1 and 1a. In the blank experiment an amount of sodium chloride was added equal to that contained in the other solution.

TABLE VI
EQUIVALENT WEIGHTS

Material	Solvent NaOH, Cc. <i>N</i>	Amount dissolved	Eq. wt.	Average	% error
Phenol lignin					
Fr. 1	50 1/14	0.8727	244.4	244.0	0.2
Fr. 1	100 1/28	.8697	243.6		
Fr. 2	50 1/14	.5735	160.0	149.0	8.0
Fr. 2	100 1/28	.4931	138.0		
Fr. 1a	50 1/14	.9600	268.8		
Fr. 2a	50 1/14	.4550	127.4		
Methoxy glycol lignin					
Fr. 1a	50 1/14	1.6536	463.0		

The solutions obtained above were further subjected to

(20) In collaboration with D. M. Goss.

potentiometric titration; the data are represented by the curves in Fig. 2.

10. **Cleavage of Phenol from Phenol Lignin.**—The results of experiments run in order to split off the phenol introduced into lignin are reported in Table VII. In each of the experiments 1-9 and 13, 1 g. of phenol lignin, 0.2 g. of red phosphorus and a mixture of hydriodic acid and acetic acid were applied. The mixture was finally poured into 100 cc. of water, the precipitate was isolated by suction and the quantity of the precipitate soluble in ether as well as the amount of the phenol present in the filtrate were established. In the experiments 10-12 and 14-16, 0.125 g. substance was treated with 10 cc. of acetic acid, 5 cc. of hydrobromic acid and 1 cc. of hydriodic acid containing hypophosphorus acid. The most complete cleavage was obtained by working from one to two hours at 250-300°.

TABLE VII
CLEAVAGE OF PHENOL FROM PHENOL LIGNIN

No.	Fraction	Temp., °C.	Time min.	Reagent, cc. HI	AcOH	Precipitate soluble in ether, %	Phenol, %
1	1	100	30	5	5	15	2.4
2	1	100	240	5	5	25	5.2
3	1	130	30	5	5	25	7.6
4	1	130	240	5	5	31	10.3
5	1	130	240	15	5	26	9.5
6	1	130	240	10	10	47	12.1
7	1	130	240	5	15	46	10.1
8	1	150	240	10	10	60	12.5
9	1	170	240	10	10	55	13.1
10	1	250	60				15.9
11	1	300	60				17.3
12	1	300	120				19.8
13	2	170	240	10	10	55	19.1
14	2	150	60				16.6
15	2	200	60				19.3
16	2	250	60				26.5

In order to determine the phenol, the contents of the tubes were washed with water into a distilling flask, neutralized with sodium carbonate and after addition of a small amount of zinc dust distilled to a very small volume. The distillate was collected in a ground-glass stoppered bottle, and the phenol determined volumetrically as tri-bromophenol. To the solution in the ground-glass stoppered bottle 50 cc. of 0.1 *N* bromate solution was added, the mixture shaken, 5 cc. of 1:1 hydrochloric acid introduced, the mixture again shaken and kept for fifteen minutes. Two grams of potassium iodide was then added and the separated iodine titrated with a 0.1 *N* sodium thio-sulfate solution. The same results may be obtained with a variety of hydrolyzing agents applied in acetic acid. In a series of blank experiments it was established that the total procedure results in the recovery of about 95% of the phenol present.

In the aforesaid process not only phenol is split off but also the lignin proper is attacked, *i. e.*, in a number of preliminary experiments using amounts of 10 g. there were found to be present organic crystallizing substances other than phenol. Some of these substances showed certain characteristics of coumarins; these experiments, however, were not brought to completion.

As to the ether-soluble part of the precipitate mentioned in Table VIII, it was, if obtained up to 150° or a lower temperature, completely soluble in alkali and gave in alcohol an intensive emerald-green reaction with iron chloride; if obtained at or above 150° it was insoluble in alkali and gave no iron chloride reaction.

11. **Alkali Fusion.**²¹—Ten grams of the substance was introduced into a mixture of 50 g. of potassium hydroxide and 10 cc. of water heated in a nickel crucible to about 250°. The temperature was then raised slowly. The phenol lignin first formed a cake floating on the surface of the melt and went into solution at about 270–280°, yielding a very viscous doughy mass. The temperature was kept for about fifteen minutes and then raised above 300°. At this stage the melt was dark, homogeneous, rather liquid and covered with a foam consisting of small bubbles. After sixty to eighty minutes the melt became mud-like and eventually dried up and started to burn.

After cooling, the melt was dissolved in water, acidified with concentrated hydrochloric acid, and the precipitate collected on a filter. The filtrate was decolorized as follows: 500 cc. of water and 10 cc. of hydrochloric acid were brought to boiling, 5 g. of activated carbon (charcoal decolorizing Merck) was introduced and the boiling continued for five minutes. The activated carbon was filtered off and kept for immediate use. The acidified filtrate of the alkali fusion, amounting to about 500 cc., was brought to boiling, the carbon added and the solution kept boiling for one minute, then filtered and brought to dryness. The ether solution was concentrated to about 20 cc. volume, thus separating the bulk of the oxalic acid. The solution contained now but little oxalic acid; it was poured off, evaporated and the residue weighed. The residue was then extracted with benzene. The results are reported in Table VIII.

TABLE VIII
ALKALI FUSION OF PHENOL LIGNIN (1–5) AND METHOXY
GLYCOL LIGNIN (6–7)

No.	H ₂ O, cc.	KOH, g.	Time, min.	Precipitate, g.		Extract	
				Total	Ether soluble	Total	Benzene sol.
1	20	50	30	3.0	2.4	2.50	0.15
2	20	50	45	2.5	2.0	2.75	.15
3	20	75	45	1.8	1.5	2.90	.20
4	20	75	60	1.6	1.3	2.95	.20
5	20	75	75	0.6	0.15	1.60	.25
6	20	75	45	3.0	1.8	2.4	.05
7	20	75	70	0.7	0.2	1.4	.05

By washing with benzene, catechol and an acid with a reddish-violet iron chloride reaction (perhaps benzene-1-hydroxy-2,4-dicarboxylic acid) were removed from the ether extract. The crystalline breakdown products were now dissolved in benzene-alcohol 1:1, and the solution allowed to stand until crystallization began. The first crystalline fraction consisted mainly of *p*-hydroxybenzoic acid, while later protocatechuic acid separated. Both products are identified by melting point, mixture melting point and reactions. The yields of pure acids were poor, partly because of the well-known difficulties connected with such work, partly because the two acids in question form a double compound which decomposes none too easily.

(21) In collaboration with A. Paeyna.

The ether extract obtained after washing with benzene served also for the quantitative determination of oxalic acid, protocatechuic acid and *p*-hydroxybenzoic acid. A weighed amount of the substance was dissolved in water, adjusted by means of potassium hydroxide to a certain pH (preferably between 5 and 6), and after the addition of a 1% iron chloride solution made up to 100 cc. volume, the color was compared in a colorimeter with the color of a standard solution adjusted to match the same conditions.

In order to determine the amount of *p*-hydroxybenzoic acid present in the ether extract 0.25 g. of the yield was heated with 10 cc. of hydriodic acid, sp. gr. 1.7, in a sealed tube for six hours, at 160–170°. The liquid was transferred to a distilling flask, the hydriodic acid neutralized with sodium bicarbonate, some zinc dust added and the mixture distilled until its volume amounted to about one-fifth of the original volume. A phenol determination was made on the distillate. From the amount of phenol obtained the amount of *p*-oxybenzoic acid was calculated. Experiments with pure *p*-hydroxybenzoic acid established that by this procedure 95–98% of the acid appeared as phenol in the final distillation. The results are given in Table IX.

TABLE IX
YIELDS OF PROTOCATECHUIC ACID AND *p*-OXYBENZOIC ACID
FROM PHENOL LIGNIN (2–5) AND METHOXY GLYCOL LIGNIN
(6, 7)

No. (Table VIII)	Protocatechuic acid		<i>p</i> -Oxybenzoic acid	
	% extract	% lignin	% extract	% lignin
2	54.0	14.7	31.7	8.7
3	56.0	16.1	37.8	11.0
4	55.0	15.9	37.6	10.9
5	27.0	4.3	29.7	4.8
6	31.0	7.5	5.4	1.3
7	30.5	4.3	5.5	0.8

12. **Oxidation with Nitric Acid.**—Ten grams of phenol lignin or methylin, respectively, were dissolved in 50 cc. of acetic acid, 50 cc. of nitric acid were added and the mixture kept for several hours, first in the cold and then on a water-bath and finally evaporated to dryness.

The residue was treated with water, thus giving a solution and an insoluble substance. The latter was collected on a filter and washed with water; it proved to be partly soluble in ether, as shown in Table X.

The aqueous solution was, in part, neutralized by the addition of 2 g. of calcium carbonate, the oxalate was removed by filtration, the filtrate completely neutralized with calcium carbonate, brought to boiling, filtered again, concentrated to 50 cc. and then precipitated by adding a solution of 10 g. of silver nitrate in 10 cc. of water. The silver salts were collected on a suction filter. The filtrate was acidified with hydrochloric acid, the silver chloride formed filtered off and the filtrate hereof extracted with ether. The ether solution was washed with a few cc. of a calcium acetate solution, dried with sodium sulfate and finally evaporated. The residue thus obtained consisted mainly of picric acid which, after purification, could be recognized by melting point, mixture melting point and reactions.²² Table X contains a survey of the work.

The silver salts were decomposed with hydrochloric acid. The clear acid solution obtained after removing

(22) Rosenthaler, "Nachweis org. Verbindungen," 1921.

TABLE X

PRODUCTS OF TREATMENT OF LIGNIN WITH NITRIC ACID			
Substance		Phenol lignin	Methylin
Residue, g.	Total	9.5	6.5
	Water insol.	2.0	1.5
	Water, ether insol.	1.2	0.3
Silver salts		9.5	6.5
Raw picric acid		0.6	0.2

the silver chloride was concentrated to a very small volume, extracted with ether and the ether solution brought to dryness. The partly crystallized residue was dissolved in 20 cc. of concd. hydriodic acid and the solution kept in a sealed tube for six hours at 170–180°. On cooling the solution became turbid. The liquid was neutralized with sodium bicarbonate and then extracted with ether. The ether contained benzene, as established by applying the routine procedure.

Acknowledgment.—Acknowledgment is made to Dr. S. A. Waksman, of the Department of Soil Microbiology, New Jersey Agricultural Experiment Station, New Brunswick, New Jersey, who made possible the execution of this work.

Summary

1. A convenient method for preparing phenol lignin has been devised.
2. Phenol lignin and methoxy glycol lignin are

closely related substances and represent mixtures which may be separated into several fractions, following the procedure developed.

3. These fractions have been characterized by chemical and physical determinations. As shown by potentiometric titrations, they are still mixtures consisting of several compounds.

4. A method for splitting off the phenol introduced into the phenol lignin has been developed.

5. On fusing with alkali, phenol lignin as well as methoxy glycol lignin give rise to protocatechuic acid and *p*-oxybenzoic acid; procedures of approximate quantitative determination have been devised for both of these acids.

6. On oxidizing with nitric acid, both phenol lignin and methoxy glycol lignin give rise to picric acid and benzene carboxylic acids; the latter were qualitatively established by decomposition, yielding benzene.

7. A formula has been given representing an ideal substance to which all chemical experiences collected in the investigation of spruce lignin may be traced and from which possibilities of further experimental work may be derived.

STATE COLLEGE, PENNSYLVANIA

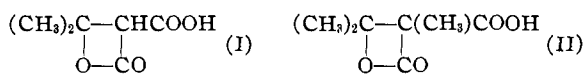
RECEIVED JANUARY 14, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Carbon Syntheses with Malonic Acid and Related Compounds. II. Aromatic Aldehydes

BY ARTHUR MICHAEL AND NATHAN WEINER

A large literature¹ exists on the use of malonic acid for the synthesis of α,β -unsaturated acids by condensation with aldehydes. Acetone does not show an analogous reaction; however, Meldrum² observed that the addition of a small amount of sulfuric acid to the mixture brought about an aldolization, involving the carbonyl group of the ketone, followed by an intramolecular esterification of the formed β -hydroxy acid to β,β -dimethyl- β -propiolactonic acid, (I). Ott³ found the yield of



lactonic acid considerably increased, if the sulfuric acid is first added to a suspension of malonic

acid in acetic anhydride, the formed acetic acid and excess of anhydride removed by distillation *in vacuo* and the residual mixed malonic-acetic anhydride allowed to react with acetone. In this manner, Ott prepared α,β,β -trimethyl- β -propiolactonic acid, (II), from acetone and methylmalonic acid. By the Meldrum method, Khandiah⁴ condensed malonic acid with di-isopropyl ketone, cyclopentanone and cyclohexanone and obtained the corresponding β -propiolactonic acids. Recently, Michael and Ross¹ showed that aliphatic aldehydes may be substituted for acetone in the Meldrum-Ott β -lactone synthesis. The present paper deals with the use of several aromatic aldehydes, *viz.*, benzoic, salicylic, acetylsalicylic and cinnamic aldehydes. These aldehydes cannot be used successfully in the Meldrum method, since

(1) See Michael and Ross, *THIS JOURNAL*, **55**, 3684 (1933).

(2) Meldrum, *J. Chem. Soc.*, **93**, 605 (1908); for explanation, see Michael and Ross, *ref. 1*, p. 3692.

(3) Ott, *Ann.*, **401**, 151 (1913).

(4) Khandiah, *J. Chem. Soc.*, 1215 (1932).