by recrystallization from glacial acetic acid. It decomposes above 320°.

Anal. Calcd. for $C_8H_{10}O_4N_2$: N, 14.14. Found: N, 14.12, 14.06.

5-Oxymethyl-4-methyluracil IV.—A small amount of this pyrimidine IV (0.1 g.) precipitated immediately upon dissolving the chloropyrimidine II (0.5 g.) in cold water (10 ml.). It was purified by recrystallization from boiling water, dried in a vacuum desiccator and analyzed. It melted with decomposition at 313–315°.

Anal. Calcd. for $C_6H_8O_3N_2$: N, 17.96. Found: N, 18.03, 18.05.

Since this pyrimidine IV is unstable when heated with hydrochloric acid, concentration of the mother liquor did not result in the isolation of more of this pyrimidine, but only in its conversion to bis-(4-methyl-2,6-dipyrimidyl-5)-methane.

The following procedure was found to be more successful for this transformation: 0.5 g. of the chloropyrimidine II was dissolved in 15 ml. of cold water and 0.1 *N* sodium hydroxide added until the solution was neutral to litmus. After concentrating the solution, 0.37 g. of the pyrimidine IV (83%) crystallized. After recrystallization from boiling water it melted at 314–315°.

Anal. Calcd. for $C_6H_8O_3N_2$: N, 17.96. Found: N, 17.96, 17.93.

5-Ethoxymethyl-4-methyluracil VII and 5-Methoxymethyl-4-methyluracil VIII.—These two pyrimidines are most conveniently prepared by dissolving 5-chloromethyl-4-methyluracil in absolute ethanol and methanol, respectively. Solution of 1 g. of the pyrimidine II in 10 ml. of boiling absolute ethanol yielded on cooling 0.68 g. of the 5-ethoxypyrimidine VII. This yield was increased by 0.27 g. by neutralization of the free hydrochloric acid with the required amount of sodium ethylate and then evaporating the solution to dryness. The ethoxypyrimidine was then separated from the sodium chloride by extraction with acetone. This pyrimidine is soluble in boiling absolute ethanol (1 g. in 30 ml.), less soluble in boiling dioxane and acetone and insoluble in ether. The pyrimidine crystallizes from absolute ethanol in plates which on heating grow moist at 195–200° and finally decompose with effervescence to a yellow oil at 312–315°.

Anal. Calcd. for $C_8H_{12}O_3N_2$: N, 15.22. Found: N, 15.20, 15.27.

A quantitative yield of the 2-methoxypyrimidine VIII was obtained when the chloromethylpyrimidine II was treated with absolute methanol and sodium methylate (as above).[10] This compound crystallized from boiling methanol in the form of needles. These show a change, on heating, at 235° and finally decompose to a yellow oil above 330°. The pyrimidine is moderately soluble in dioxane and acetone, and insoluble in ether.

Anal. Calcd. for $C_7H_{10}O_3N_2$: N, 16.39. Found: N, 16.42, 16.50.

Summary

1. Chloromethyl ether interacts with 4-methyluracil in a sealed tube to give 5-chloromethyl-4-methyluracil.

2. This chlorinated pyrmidine is very reactive due to the high activity of the chlorine atom. Its reactions with water, absolute ethanol and methanol, concentrated hydrochloric acid and silver acetate are described.

[10] Dioxane proved to be a better solvent than acetone for extracting the methoxypyrimidine from the sodium chloride.

NEW HAVEN, CONNECTICUT RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LI. The Solvent Fractionation of Maple Ethanol Lignin

BY R. F. PATTERSON,[1] KENNETH A. WEST,[2] EDWIN L. LOVELL, W. LINCOLN HAWKINS AND HAROLD HIBBERT

Lignins obtained by the various available methods of isolation vary widely in physical characteristics such as solubility, homogeneity and average molecular complexity. The heterogeneous nature of certain isolated lignins, for example birch formic acid lignin, has been demonstrated by Lieff, Wright and Hibbert.[3] These authors fractionated their lignins by continuous solvent extraction, in this way obtaining several fractions having different solubility characteristics. Chemical analysis of the fractions showed marked differences in chemical composition, notably in the methoxyl and hydroxyl contents. Bailey[4] from his studies on aspen butanol lignin concluded that the isolated product was not homogeneous, and succeeded in fractionating this and other isolated lignins by use of the molecular still technique. His attempts to use solvent fractionation methods, however, were unsuccessful. Loughborough and Stamm[5] made a com-

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[1] Holder of a Studentship awarded by the National Research Council of Canada, 1940–41.

[2] Holder of a Canadian Pulp and Paper Association Research Scholarship, 1940–41.

[3] Lieff, Wright and Hibbert, THIS JOURNAL, **61**, 1477 (1939).

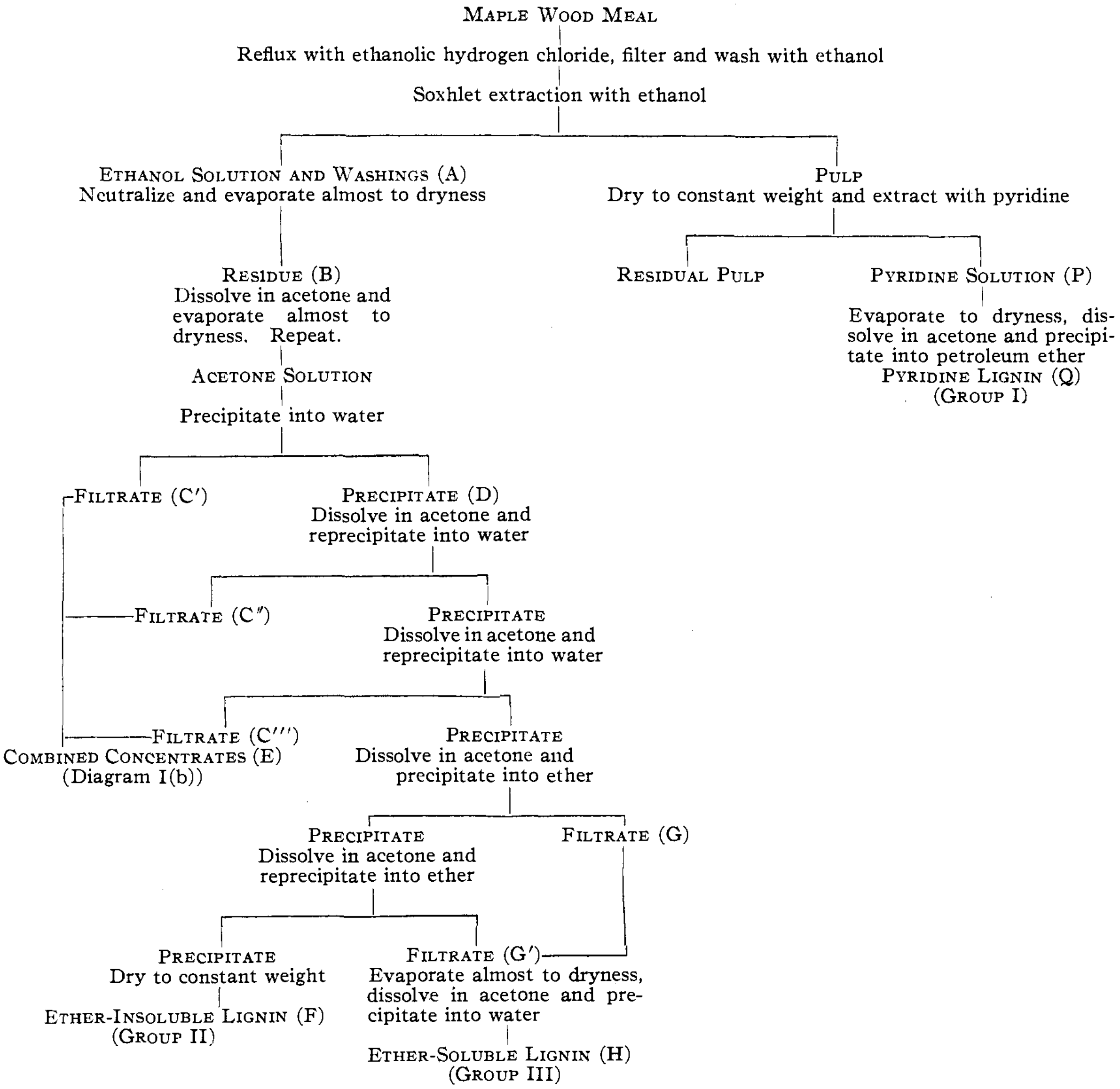
[4] Bailey, *Paper Trade J.*, **111**, 27 (no. 7) (1940).

[5] Loughborough and Stamm, *J. Phys. Chem.*, **40**, 113 (1936).

DIAGRAM I(a)

ETHANOLYSIS OF MAPLE WOOD MEAL

SEPARATION OF THE ETHANOL LIGNIN INTO SOLVENT GROUPS



prehensive investigation of the physical properties of soluble fractions of several maple lignins, isolated under widely varying conditions and concluded that the molecular size of each such fraction was approximately the same. However, several of their lignins were isolated by extraction methods which removed only a small portion of the total lignin present in the wood.

A study of maple ethanol lignin has now been made with the object of determining the extent of its heterogeneity. It is the ultimate purpose of this investigation to fractionate maple ethanol and other lignins into their homogeneous constituents, as far as possible, and to determine the chemical structures and interrelationships of these various polymers. This is all the more necessary in view of the implied assumption, made by different workers,[6] that the materials used in their investigations were homogeneous in character. Until true homogeneity has been established, attempts to assign chemical formulas to isolated lignins would seem to have only a limited significance.

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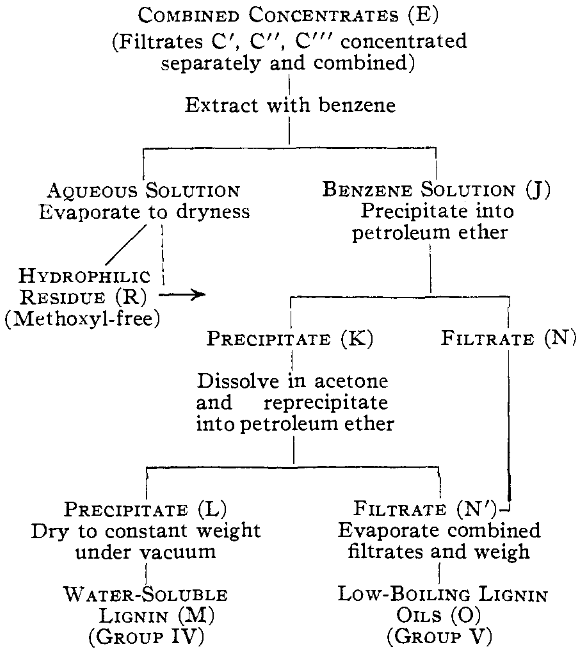
[6] (a) Freudenberg, "Annual Review of Biochemistry," Vol. VIII, 1939, p. 92; (b) Brauns, THIS JOURNAL, **61**, 2120 (1939).

DIAGRAM I(b)



Discussion of Results.—The ethanolysis of maple wood has previously been shown to give rise to a variety of simple products, among which have been identified vanillin,[7a,d] vanilloyl methyl ketone,[7b] α-ethoxypropiovanillone,[7c] syringaldehyde,[7d] syringoyl methyl ketone[7b,e] and α-ethoxypropiosyringone.[7f] In addition to these oils, large amounts of amorphous lignin are obtained. Investigation of the latter material has now shown that this is a heterogeneous substance, capable of separation into a further number of products on the basis of solubility in selected solvents. These solvents are ethanol, pyridine, water, petroleum ether, ethyl ether and benzene, their application being shown in the following flow-sheets (Diagrams Ia and Ib). All the lignin groups separated in this manner are readily soluble in acetone, and this solvent was therefore preferred for use throughout the procedure.

It can be seen that the total amount of ethanol–hydrogen chloride extracted material from the maple wood meal has been separated into three distinct lignins, referred to in the above Diagrams (Ia and Ib) as "water-soluble," "ether-soluble" and "ether-insoluble" respectively, together with the "petroleum-ether soluble, readily distillable oils" previously mentioned, and a "hydrophilic part." The latter is an extremely hygroscopic material not extractable from its aqueous solution by benzene, and showing on isolation a zero lignin content by the usual Klason lignin determination. In addition a further lignin-like product has been obtained from the residual wood meal after ethanolysis, by continuous extraction with pyridine, the Klason lignin content of the wood meal being reduced in this treatment by an amount corresponding to that of the lignin-like product isolated. The following table shows the yields of each lignin group, including a comparison with the amount of Klason lignin present in the original wood meal. The weight of oils isolated in this process agrees well with that expected on the basis of earlier methods of isolation.[7c,f] The yields of the various amorphous lignins are also fully reproducible (as shown by the duplicate runs (B) and (C)), provided that the temperature at which the various operations are carried out does not exceed 40° at any time.[8]

Characterization.—The series of lignin solubility groups (I–IV, Diagrams Ia and Ib) isolated in this manner would appear to comprise (with the exception of Group I (Table II)) a series of closely-related compounds presumably having a chain-molecular structure. This is shown by a study of their solution viscosities (Table II). In the cases of Expt. (a), the viscosities were measured in two different solvents, and at two different concentrations; it was found that neither variable had an appreciable effect on the value of the reduced viscosity η_{sp}/c which, therefore (at the concentration used, namely, 20 mg./cc.), may be taken as a measure of the chain-length of the solute,[9] on the very probable assumption that we are dealing with a linear type polymer.

The Staudinger constant for the homologous lignin series is *6*, obtained by utilizing the molecular weight and viscosity data of Stamm[5] and confirmed by the present authors' viscosity determinations on the "monomer." This evidence for regularly-increasing molecular weights of the lignin is supported by determinations of the precipitabilities of each group, in two solvents where

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[7] (a) Tomlinson and Hibbert, THIS JOURNAL, **58**, 345 (1936); (b) Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940); (c) Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939); (d) Hawkins, Wright and Hibbert, *ibid.*, **59**, 2447 (1937); (e) Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939); (f) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); (g) Brickman, Hawkins and Hibbert, *Can. J. Research*, **B19**, 24 (1941); (h) Leger and Hibbert, THIS JOURNAL, **60**, 565 (1938).

[8] A number of experiments in this Laboratory have shown that the viscometric chain-lengths of lignins may be changed considerably merely by refluxing in neutral organic solvents.

[9] Lovell and Hibbert, THIS JOURNAL, **61**, 1916 (1939).

TABLE I[f]

Group	Product[c]	Weight isolated A[a]	B[b]	C[b]	% of total Klason lignin[d] A	B	C
	Pulp	106.0	46.0	..	..	..	..
	Residual pulp	102.5	44.3	..	..	..	..
	Lignin in residual pulp	3.0	..	..	..	..	..
I	Pyridine lignin	3.5	1.7	..	7.3	7.1	..
II	Ether-insoluble group	9.1	9.2	8.7	18.3	37.0	35.2
III	Ether-soluble group	18.5	5.5	5.7	37.2	21.1	22.0
IV	Water-soluble group	4.2	3.3	3.2	8.4	12.8	12.3
	Total amorphous solids	31.8	18.0	17.6	63.9	70.9	69.5
	Hydrophilic part[e]	48.0	..	..	..	..	..
V	Low boiling oils	11.0	4.1	3.9	..	..	..

[a] From 200 g. of fully dried wood meal by the alternative method (II). [b] From 100 g. of wood meal by method (I). [c] See flow-sheet—diagrams Ia and Ib. [d] Ethoxyl-free basis. [e] Zero Klason lignin. [f] The total lignin recovery (Expt. B) was 1.7 + 9.2 + 5.5 + 3.3 + 4.1 = 23.8 g. Ethoxyl-free basis = 90.4% of Klason lignin.

TABLE II

Properties	Group 1 a	b	Group 11 a	b	c	Group 111 a	b	c	Group IV a	b	c
Ash, %	0.5	3.4	0.0	0.3	1.5	1.1	0.4	0.1	1.7	0.5	0.3
Carbon, %[a]	51.6	63.0	62.7	63.4	62.8	63.0	65.4	64.2	61.4	59.8	60.7
Hydrogen, %[a]	6.2	5.8	6.0	5.8	6.0	6.1	6.4	6.3	6.5	6.5	6.6
—OCH_3, %[a]	10.0	14.4	21.0	19.2	19.3	21.8	17.8	18.4	21.8	20.1	19.9
—OC_2H_5, %[a]	4.9	7.0	9.3	9.1	8.4	8.7	13.2	11.5	10.8	13.6	13.1
Carbon (alkoxyl free), %[a,b]	52.8	67.2	70.3	70.3	69.3	70.8	73.5	71.8	68.5	66.6	67.7
Reduced viscosity $\eta_{sp}/c \times 10^5$	920	755	640	600	600	470	445	450	389	379	340
Precipitability in pyridine[c]	68.9	..	73.7	..	..	82.1	..	..	..	..	..
Precipitability in dioxane[c]	..	..	52.2	..	..	62.1	..	..	..	..	..
Melting point (av.), °C.	Chars	Chars	180	Chars	Chars	148	125–129	121–125	68	72–74	..

[a] Calculated on an ash-free basis. [b] Carbon content of alkoxyl-free material. [c] Volume per cent. of water referred to 0.2% solutions.

possible, and using water as the precipitant. The data (Table II) show a regular increase in this property with decreasing viscometric chain-length, as would be expected if the chains involved are the same, or similar, chemically.

The melting points, showing an average range not greater than 5°, exhibit from group to group a similar, regular increase.

Although the separate lignin solubility groups may well be heterogeneous, both as to chain-length and chemical nature (this is being further investigated), elementary analyses and also alkoxyl determinations have been made on each, principally as a means of characterization. It would appear from these analyses, also, that the lignin groups II, III, IV are chemically closely related compounds. Group I, however, differs markedly from them in its elementary composition, particularly with regard to the alkoxyl content.

Method of Separation.—The technique of the separation of lignin into distinct solubility groups involves essentially the precipitation of suitably concentrated lignin solutions into an excess of another organic solvent which has the property of being a non-solvent for a part or parts of the total dissolved lignin, the conditions being so arranged as to bring about the reprecipitations. The proportion of solvent to non-solvent in the final mixture must also be sufficiently small to prevent any increase in solubility of the precipitating fraction as precipitation proceeds. A ratio of 1:20 is recommended as being a safe margin for most combinations of solvents, using an original solution concentration of 10%. This precipitation technique is in contrast to the extraction technique applied by Bailey[4] to butanol lignin and which he describes as giving highly contradictory results, these depending to a marked extent on the physical state of the lignin samples. The success of fractional dissolution procedures seems to be limited to fibrous material such as cellulose, whereas it would now appear that the solubility of macromolecular substances in a given solvent may, in general, best be determined by precipitation into an excess of that solvent, rather than by attempts at direct dissolution. The separation of lignin into groups on the basis of their differing solvent-affinities has thus been accomplished by avoiding the errors inherent in the extraction procedure.

Finally, it is noteworthy, in view of the present results, that Loughborough and Stamm[5] failed to find any viscosity differences in fractions of a "soluble" lignin prepared by absorbing one-half of the material on charcoal. Furthermore, according to their viscosity data for methanol–hydrogen chloride lignin, the molecular chain-length of their products are of the same order of magnitude as those found by the authors for the highest fractions of ethanol lignin.

Acknowledgment.—The authors wish to thank Mr. Joseph Colucci for his kind assistance in carrying out much of the analytical work for this investigation.

Experimental Part

Ethanolysis of Maple Wood.—Maple wood meal (50-mesh, 4% moisture) was first extracted for forty-eight hours with a mixture of equal volumes of ethanol and benzene (400 cc. mixed solvent/100 g. wood meal), then for twenty-four hours with ethanol (400 cc./100 g.), and finally washed for twelve hours with water to remove fats, waxes, carbohydrates, resins and tannins. The residual wood meal was allowed to dry in air for several days and then further dried in a vacuum oven for forty-eight hours (60°/20 mm.), leaving a product containing 2% moisture and 23.3% Klason lignin.

Extracted wood meal (100 g.) and absolute ethanol (800 cc.) containing 2% anhydrous hydrogen chloride (16 g.) were placed in a 2 liter flask equipped with reflux condenser, mechanical stirrer and carbon dioxide inlet. The reaction mixture was refluxed for forty-eight hours in an atmosphere of carbon dioxide. An inert atmosphere was also maintained in all subsequent operations, and ground glass apparatus was used throughout the procedure, since previous experiments had shown the need for avoiding oxidation and also the introduction of impurities from corks and rubber stoppers. The ethanolysis mixture was cooled, filtered and the residual wood meal extracted with ethanol (500 cc.) for ten hours in a Soxhlet apparatus, these extracts being added to the main ethanol filtrate (A) (see Diagrams Ia and Ib covering these designations).

Separation of the Ethanolysis Products

Method I.—The acidity of the combined ethanol solutions (A) (1300 cc.) was reduced to *p*H 6 by the slow addition, with constant stirring, during the course of about four to five hours, of solid sodium bicarbonate. The mixture was then filtered to remove the sodium chloride. The ethanol was removed in an atmosphere of nitrogen at a temperature below 25° (20 mm.). The dark, tarry residue (B) was dissolved in acetone (500 cc.) and the solvent removed at 25° (20 mm.). This procedure was repeated twice in order to remove the last traces of ethanol and water, and then the residue, without being desiccated, was dissolved in anhydrous acetone (500 cc.). (In this procedure only the final products were vacuum-desiccated; intermediate residues were merely sucked dry on the filter.)

The water-insoluble material was first precipitated by running the acetone solution through a fine orifice into twenty times its volume of cold distilled water, with vigorous stirring. The dark brown amorphous precipitate (D) was separated by decantation and filtration (filtrate C'), washed several times with water and then, without drying or further treatment, dissolved in acetone, and reprecipitated twice into water using the same relative amounts of lignin, solvent and precipitant. (The same ratio of 1 g. of lignin:10 cc. of solvent:200 cc. of precipitant was employed in all the precipitations of this separation procedure, independent of the type of solvents and precipitants used.) This water-insoluble lignin was then further subdivided into ether-insoluble (F) and ether-soluble groups (H) by first dissolving it in acetone (*ca.* 150 cc.), then precipitating into twenty times the volume of cold, anhydrous diethyl ether, filtering and repeating the treatment. The final brown, amorphous, ether-insoluble precipitate (F) was vacuum-dried to constant weight. The combined filtrates (G, G') from the ether precipitations were evaporated almost to dryness, the residue dissolved in acetone (*ca.* 60 cc.), and this solution run into water. The precipitated, light brown, amorphous material (H) was washed with water and dried to constant weight.

Extraction of Water-Soluble Lignins.—The three aqueous filtrates C', C'', C''' left after removal of the brown amorphous lignin (D) were united and concentrated at 40° (20 mm.) in an atmosphere of nitrogen to a volume equal to one-third of the original amount. During this concentration, a small amount of solid material separated out. This was filtered off, precipitated from acetone solution into water (1:10:200 ratio as before) and then divided into separate ether-soluble and ether-insoluble fractions in the manner already described.

The clear aqueous concentrate (*ca.* 5 liters) (E) was extracted with benzene (200 cc.) in a ground glass liquid extractor operating under reduced pressure, the receiving flask being maintained at 30°. A series of control experiments indicated that the time required for removal of the water-soluble material by benzene under these conditions was considerably less than had previously been supposed.[10] It was found that the color of the refluxing benzene solution in the receiving flask (which was changed periodically) was a reliable indication of the extent of extraction and this was the criterion used to determine completion (usually eight to ten hours).

The benzene solution (J) was concentrated to approximately 100 cc. and then precipitated into twenty times its volume of 30–50° petroleum ether. After decantation, the residue (K) was dissolved in acetone and again precipitated into petroleum ether. The final residue (L), termed "water-soluble lignin," was dried to constant weight (M) by prolonged vacuum desiccation. The petroleum ether solutions (N), (N') were evaporated to dryness at 30° (14 mm.) leaving the "low-boiling lignin oils" as an orange-brown, syrup-like material (O).

The aqueous solution remaining after the benzene-extraction of (E) was evaporated at 40° (14 mm.) leaving a sirupy, hydrophilic, methoxyl-free residue (R).

In addition to the ethanol–lignin fractions (F), (H), (M), (O) obtained from the ethanolysis liquor, a further lignin fraction (Q) was obtained from the residual wood meal

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[10] Brickman, Pyle, McCarthy and Hibbert, THIS JOURNAL, **61**, 868 (1939).

(Klason lignin 8%) by extracting with pyridine. The residual wood meal (68.7 g.) was continuously extracted for six hours with anhydrous pyridine in a carbon dioxide atmosphere at 60° (20 mm.). The pyridine solution (P) (500 cc.) was evaporated to dryness, below 60°, leaving a dark brown residue (2.3 g.) (P). This was dissolved in acetone (25 cc.) and precipitated into 30–50° petroleum ether (500 cc.). The precipitate was centrifuged and dried at 40° (20 mm.) for twelve hours. Klason lignin content of final residual pulp was 6.7%.

Method II.—This run ((A) Table I and (a) Table II) was performed in an alternative manner on another sample of maple wood meal. Here the low-boiling oils were removed directly from the original ethanol solution (A) by first removing the ethanol (20° (12–14 mm.)) then dissolving the residual product in chloroform and running the chloroform solution into petroleum ether (30–50°), using the same solvent ratios as in Method I (1:10:200). The subsequent procedure also differed somewhat in the choice of solvents, but it can be seen (Table I) that the same group types are obtained in comparable yields. It is to be expected that different samples and types of wood will contain a somewhat different distribution of these groups. The first method is that recommended as a general standard procedure for plant products. Application of this to maple wood meal gave average yields, based on the amount of Klason lignin present in original wood and on an ethoxyl-free basis, of 13.2%, 12.5%, 21.5%, 36.1% and 7.1% for the low-boiling oils (Group V), water-soluble lignin (Group IV), ether-soluble lignin (Group III), ether-insoluble lignin (Group II) and pyridine-soluble lignin (Group I), respectively, and representing a combined lignin recovery of 90.4%.

Summary

1. A new method is given for the fractionation of the lignin ethanolysis products from maple wood, by which the isolated lignin components, amounting to a total of 90–95% of the original (Klason) lignin, are divided into five groups comprising (1) pyridine-soluble; (2) ether-insoluble; (3) ether-soluble; (4) water-soluble; (5) monomolecular low-boiling oils. The fractions differ from one another, in possessing, in the order named, a successively decreasing molecular complexity.

2. The scheme is proposed as one probably applicable to a wide variety of plants.

MONTREAL, CANADA RECEIVED MAY 2, 1941

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. LII. New Method for the Fractionation of Lignin and Other Polymers

BY EDWIN L. LOVELL[1] AND HAROLD HIBBERT

The remarkable progress made recently in the field of high molecular weight polymers has emphasized clearly the necessity for new methods of fractionation, whereby "distribution coefficients" of the various chain length fractions in any given polymer can be determined. The following new method, it is hoped, will prove helpful in this connection.

Isolated soluble lignins, such as maple ethanol lignin,[2] are most commonly prepared as amorphous brown powders, having a strong tendency to form oils in the presence of organic solvents. For this reason it is now customary[3] to prepare such samples by precipitation, from a weak solution of the lignin, into an excess of some precipitant; in this way the formation of an oil may often be avoided. There are some indications[4] that isolated lignins are not necessarily homogeneous substances, and in the preceding paper[5] the authors have shown that it is possible to separate maple ethanol lignin into different groups based on selective solubility in different organic solvents. But it is still not revealed by this method whether or not the groups so isolated are themselves uniform in respect to either chemical nature, or chain length, or both. It is therefore very desirable to be able to fractionate further each of these groups to determine their degree of uniformity and the possibility of isolating a pure compound from the mixture for analytical and structural purposes. With lignins, the ordinary methods of fractional precipitation from mixed solvents[6] appear invariably to produce oils, which are difficult to separate from the dissolved fractions. It is necessary to devise some means of overcoming this difficulty if a clean separation of the component parts of amorphous lignins is to be effected.

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(2) Brickman, Pyle, McCarthy and Hibbert, THIS JOURNAL, **61**, 868 (1939).

(3) See, for example, Brauns and Hibbert, *Can. J. Research*, **B13**, 28 (1935).

(4) Lieff, Wright and Hibbert, THIS JOURNAL, **61**, 1477 (1939).

(5) Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941).

(6) See, for example, Spurlin, *Ind. Eng. Chem.*, **30**, 538 (1938).