(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.

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[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).

Such a method[7] has now been found, and some experiments of a preliminary nature indicate that a successful fractionation of lignin[8] is possible with the new method; the experimental technique is relatively both simple and rapid. A valuable new tool is thus provided for investigating the homogeneity of lignin preparations, a fact which should discourage the use of preparations of unproven uniformity as the basis for assigned lignin formulas.[9]

Method.—This depends on the fact that substances of different chemical structure are distributed in different amounts between two nonmiscible solvents, *i. e.*, the distribution constants are not likely to be identical, especially so for polymer homologs of different chain lengths. With a two-layer solvent system, in which the solvent ability (with reference to the solute) of one layer can be progressively decreased, it becomes possible to extract, from the dissolved mixture, portions of the solute which differ in composition or molecular weight, or both.

The best solvent system for lignins is the combination chloroform – water – methanol – carbon tetrachloride. The initial choice of solvents, while largely empirical, is based on certain general principles which determine the possibility of a successful fractionation with the chosen system.

Common organic solvents, in general, are mutually miscible in all proportions and, in order to permit the formation of two layers, water must be one component of the system, and one of the organic solvents must be non-miscible with water (such as chloroform or ethyl acetate). In the simplest case, the solute is soluble in both layers, water and the immiscible organic solvent; the solute distribution may then be controlled by the addition of a water-insoluble precipitant. *Lignin* is water-insoluble so that a system of water and an immiscible non-solvent, together with a solvent of high solvent-power distributed between the two layers, can be employed (for example, benzene–water–acetone, the acetone having the strong solvent action). If *two* "good" organic solvents are used, or if the distribution of the one good solvent is very one-sided, then the extraction of the solute during the fractionation will be very inefficient or even quite negligible, as with the system benzene–water–acetone where the amount of lignin extracted over a wide range of acetone is too small to be practicable. The same was found to be true for other systems such as chloroform–water–acetone, and carbon tetrachloride–water–acetone. Finally, in the system carbon tetrachloride–water–methanol the addition of *chloroform* can be used to control the solute distribution within the range of complete solubility in the "aqueous" layer (when no chloroform is present) to complete solubility in the "non-aqueous" layer—presumably by preferential solution of the chloroform (a good lignin solvent) in the carbon tetrachloride (a lignin nonsolvent). Furthermore, it was possible to judge the amount of chloroform required for, say, 10% extraction, by the depth of color in the chloroform layer.

Experimental

The fractionation of lignin samples from various sources may be carried out in general as follows: The lignin (contained in a round-bottomed flask) is dissolved in fifty times its weight of methanol and the resulting solution diluted with water equal to 20% of the volume of methanol. To this is added carbon tetrachloride equal to one-half of the methanol used. Chloroform is next added carefully with thorough mixing of the two layers until the desired color difference is attained (this is usually a volume of chloroform equal to that of the water previously added). These operations are most conveniently carried out by using a number of burets to contain the various solvents.

The two-layer system is then very thoroughly mixed by vigorous mechanical stirring for thirty minutes. After a further ten minutes to allow the layers to reform, the *bottom* layer is separated by gently siphoning into a small Erlenmeyer flask. This is done with a glass tube of small diameter (1 mm.) bent to form two right angles, and with one end (drawn down) dipping into the solution, the other extending down through a rubber stopper into a micro-bell jar containing the receiving flask. By controlling the pressure through the side arm of the bell jar, the separation of the two liquid layers may be made very accurately. The dividing line eventually appears clearly in the narrow glass tube even although it may be completely invisible in the dark lignin solution.

After the separation the lignin fraction may be recovered from the chloroform solution merely by removing the solvent. This is done by directing a slow stream of filtered air, carbon dioxide or nitrogen over the surface of the solu-

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[7] This method should also be applicable, with appropriate changes in the solvent system used, to other high-polymeric materials such as cellulose derivatives. Work on this phase is proceeding. As a fractionation technique the method has the advantage of being completely free from the most important defects of precipitation and dissolution methods, namely, adsorption (of the low members by higher members on precipitation) and peptization (of higher members by lower adsorbed members).

[8] Since this work was completed, a paper has appeared [Schulz and Nordt, *Z. physik. Chem.*, **155**, 115 (1940)] which describes this method of fractionation by distribution between immiscible solvents as applied to hemicolloidal polyoxyethylene glycols. This is an especially simple and ideal case, since the polyglycols are water-soluble.

[9] Compare Brauns, This Journal, **61**, 2120 (1939).

tion in the flask placed under the bell jar, suction being applied to pull the inlet gas through a glass funnel passing through the top opening. The residual fraction is finally dried at room temperature in a desiccator (over solid potassium hydroxide) maintained at about 100 microns pressure. It can then be powdered and analyzed.

Further fractions are then obtained from the aqueous methanol layer by adding another portion of carbon tetrachloride and chloroform, using one-half the amounts added in the first extraction. The rest of the procedure remains the same.

Viscosity measurements were carried out in the Ostwald-type viscometer described previously.[10]

Application

The actual fractionation of a number of selected lignins was carried out to test the applicability of the method for the extraction of lignins, possessing different properties, from maple ethanol lignin solubility groups.[5,11] All of the experiments reported here were carried out using the solvent ratios described above, and with amounts of lignin varying from 300 mg. to 2.0 g., depending on the number of fractions desired. The loss of material during handling was always very small, due to the simplified method of separation of the layers and isolation of the lignins by direct evaporation of the solutions.

Table I gives the results of fractionation of an ether-soluble maple ethanol lignin.[5] The sample was first divided into four fractions and the solution viscosities in dioxane determined. It is seen that there is a definite increase in the viscometric values as the extractions proceed, the lowest fraction being present in the smallest amount. The last two fractions had identical viscosities, and hence the residue should be a chain-uniform material, incapable of yielding further fractions of differing viscosity. This was shown to be the case by a refractionation of this residue, giving two further fractions of identical viscosity.

TABLE I

FRACTIONS FROM AN ETHER-SOLUBLE MAPLE ETHANOL LIGNIN

Extraction number	Yield, %	$\eta_{sp}/c \times 10^5$
1	12	405
2	31.5	435
3	20	470
Residue	36.5	470
Refractionated residue	13	470
Final residue	87	470

In Table II are shown the results of fractionating an ether-insoluble lignin[5] (G. II lignin) and a water-soluble lignin[5] (G. IV), products of widely different solubility properties but still both readily fractionated by the standardized method outlined above. This ether-insoluble lignin appears to contain a high-viscosity fraction and one of low viscosity in almost equal parts; the water-soluble lignin on the other hand is comparatively uniform in composition.

TABLE II

FRACTIONATIONS OF TWO DIFFERENT MAPLE ETHANOL LIGNINS

Extraction number	G. II Lignin (ether-insoluble) Yield, %	$\eta_{sp}/c \times 10^5$	G. IV Lignin (water-soluble) Yield, %	$\eta_{sp}/c \times 10^5$
1	20	555	28.5	360
2	43	565	42.5	360
Residue	37	640	29.0	350

In all these cases, it was noted that the fractions showed a definite gradation of color of the (2%) solutions used for viscosity determinations, the lightest-colored fractions being those extracted first.

Fractions from a lignin extracted from aspen wood by pure ethanol (without the use of catalysts or high temperature) were examined as regards their methoxyl values. These results are shown in Table III. The fractionation is seen to have led to the separation of materials having methoxyl contents somewhat higher and lower, respectively, than the average value obtained for the total original material.

TABLE III

FRACTIONATION OF AN ASPEN LIGNIN

Extraction number	Yield, %	Methoxyl, %	$\eta_{sp}/c \times 10^5$
1	3.5	..	...
2	8.6	..	...
3	32.8	16.0	...
4	24.1	17.7	482
Residue	31.0	18.4	523
Methoxyl value of original lignin		17.5	

Finally, Table IV shows the result of dividing an ether-soluble maple ethanol lignin (prepared with many precautions to avoid polymerization during and after isolation) into nine fractions. This material would seem to be relatively uniform viscometrically (presumably therefore also uniform with respect to chain length) but to contain substances of differing chemical composition.[12] In only one case (extraction 6) did the yield of material fall considerably below that expected;

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[10] Fordyce and Hibbert, THIS JOURNAL, 61, 1912 (1939).

[11] The resulting data are not presented as showing any conclusive results regarding the composition of maple ethanol lignin groups, but only to illustrate the possibilities of the new fractionation method.

[12] Further investigation of these fractions is being carried out.

otherwise the yields were uniformly in the range 8 to 15%.

TABLE IV

FRACTIONATION OF AN ETHER-SOLUBLE MAPLE ETHANOL LIGNIN

Extraction number	Yield, %	$\eta_{sp}/c \times 10^5$	Methoxyl, %
1	6.5	545	..
2	15.0	540	..
3	14.5	540	25.2
4	9.8	540	24.8
5	8.0	550	..
6	5.6	545	..
7	12.1	540	23.1
8	13.0	545	..
Residue	15.5	550	26.3

Summary

1. A new method is described for the fractionation of lignins, which involves the distribution of the lignin between two immiscible layers of solvent in the system methanol–water–chloroform–carbon tetrachloride. By varying the concentration of chloroform, the percentage of lignin extracted into the non-aqueous layer may be controlled over a wide range of values.

2. This new method should, it is suggested, be applicable to a wide variety of high polymeric substances.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Many-Membered Ring Compounds by Direct Synthesis from Two ω,ω'-Bifunctional Molecules

BY ROGER ADAMS AND L. N. WHITEHILL[1]

Only two methods have been employed successfully in the synthesis of many-membered ring compounds. The first consists of a ring closure within an ω,ω'-bifunctional molecule making use of the high dilution principle.[2] Here two active groups at the ends of long chains are allowed to react in a solution so dilute that the rate of linear polymerization is slowed down sufficiently to permit formation of monomeric large rings. The other and less general method[3] is a depolymerization process and involves a series of mutually dependent and quantitative reversible reactions where constant removal of the more volatile cyclic compound leads ultimately to complete conversion to this product.

By the high dilution technique, many-membered cyclic lactones from ω-hydroxy acids,[4] iminonitriles from ω,ω'-dinitriles,[5] and phenolic ethers from ω-bromoalkoxyphenols[6] have been synthesized.

The depolymerization process[3] has been used in the preparation of macrocyclic esters and anhydrides. The method used by Ruzicka[7] to prepare large ring ketones, the heating of the calcium, thorium, cerium and yttrium salts of ω,ω'-aliphatic dibasic acids, possibly follows this same course.[8]

The adaptability of the dilution process for synthesizing many-membered rings is limited by the difficulty of obtaining molecules of appropriate size with ω,ω'-functional groups capable of interaction. Theoretically, it should be possible to form macrocyclic rings by allowing two bifunctional molecules to react with each other at high dilution provided the proper physical conditions are established. To illustrate in a general way a synthesis of this nature, the reaction between an ω,ω'-glycol and ω,ω'-dibasic acid may be considered. The first reaction that must take place regardless of the dilution is between one molecule of glycol and one molecule of dibasic acid. The ω-hydroxy-ω'-carboxy dimer (I) will then react either with a molecule of glycol or of dibasic acid to form a trimer (II) or (III) which, in turn, may react further to give the tetramer (IV). The tetramer may also be produced from two mole-

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(1) An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Ruggli, *Ann.*, **392**, 92 (1912).

(3) Carothers and Hill, THIS JOURNAL, **55**, 5023, 5031 (1933).

(4) Stoll and Rouve, *Helv. Chim. Acta*, **17**, 1283 (1934); Stoll, Rouve, and Stoll-Comte, *ibid.*, **17**, 1289 (1934).

(5) Ziegler and Aurnhammer, *Ann.*, **513**, 43 (1934); **528**, 114 (1937).

(6) Lüttringhaus and Ziegler, *ibid.*, **528**, 155 (1937); Ziegler, Lüttringhaus and Wohlzemuth, *ibid.*, **528**, 162 (1937); Lüttringhaus, *ibid.*, **528**, 181, 211, 223 (1937); *Ber.*, **72**, 887 (1939); Lüttringhaus and Kohlhaas, *ibid.*, **72**, 897, 907 (1939); Lüttringhaus and Bucholz, *ibid.*, **72**, 2057 (1939); Lüttringhaus and Gralheer, *Naturwissenschaften*, **28**, 255 (1940).

(7) Ruzicka, Brugger, Pfeiffer, Schintz and Stoll, *Helv. Chim. Acta*, **9**, 499 (1926); Ruzicka, Brugger, Seidel and Schinz, *ibid.*, **11**, 496 (1928); Ruzicka, Stoll and Schinz, *ibid.*, **11**, 670 (1928); Ruzicka, Schinz and Pfeiffer, *ibid.*, **11**, 686 (1928).

(8) Carothers and Hill, THIS JOURNAL, **55**, 5043 (1933).