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HIGH-PRESSURE HYDROGENATION

STUDIES OF LIGNIN AND

RELATED MATERIALS

by

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I. CLAIM TO ORIGINAL REPEARCH

A. A new, simple and efficient method has been devised for the hydrogenation at high pressures, of small quantities of plant material and for the analysis and identification of the hydrogenated products.

B. The work of Harris, D'Ianni and Adkins (73) on the hydrogenation of methanol lignin (aspen) has been confirmed by application of same procedure to ethanol lignin (maple).

C. Each of the various groups of ethanolysis products obtained in the ethanolysis of maple wood meal, and including (1) the distillable oils; (2) the non-distillable amorphous fraction of the water-soluble oils; (3) the so-called "benzene-shakings"; (4) the non-water-soluble tar; (5) the water-insoluble ethanol lignin and (6) the residual lignin in the wood, have been hydrogenated and the resulting products separated, analyzed and very largely identified.

D. Based on these results, and on the previously published data on hydrogenation, the type of linkage (-C-C- or -C-O-C-) present in the individual fractions and the extent to which these are present, have been determined.

E. The experimental data and theoretical consideration would seem to provide a rational working theory of the mechanism of ethanolysis. F. Contrary to general belief, it was found cossible to obtain <u>simple water-soluble lignin units</u> by the <u>methanolysis</u> of maple and aspen woods. The water-insoluble <u>methanol</u> lignin (maple) has been hydrogenated and the products shown to be identical with those obtained by hydrogenation of the <u>ethanol</u> lignin (maple).

II. GENERAL INTRODUCTION

A. Definition of Lignin

In the early part of the nineteenth century various chemists and botanists discovered that woody plant tissue upon treatment with certain chemical reagents could be separated into carbohydrate and non-carbohydrate fractions. Schulze (1), for example, following the work of Payen (2), found that an aqueous solution containing nitric acid and potassium chlorate readily dissolved (at room temperature), that portion of the plant termed "incrustants" by contemporary botanists; this soluble fraction was richer in carbon than cellulose and was named "lignin".

Subsequent investigations showed that Schulze's lignin contained large quantities of carbohydrate material, and the definition of lignin was modified to include only the noncarbohydrate portion of the extracted material (3). At the same time it became apparent that the non-carbohydrate, extractable component of woody tissue was not necessarily a pure chemical compound but a mixture of substances of similar physical and chemical properties. As a consequence, the majority of chemists interested in the structural study of lignin concluded they were dealing with a class of substance capable, at that time, of being defined only by their chemical properties (4); that is to say, lignin was considered to be a chemical substance, or possibly, a mixture of closely related substances characterized by chemical reactions and composition.

The essential feature of this lignin definition was the assumed lack of chemical identity between lignin and cellulosic (cellulose, hemicellulose, and other polysaccharide plant constituents) materials with which the lignin was assumed to be closely associated or even chemically combined. As work progressed and new data accumulated concerning methods for lignin isolation two important problems arose concerning this terminology. It gradually became evident that the chemical reagents and conditions employed in the separation of lignin from the carbohydrates were so drastic that (a) the carbohydrates themselves under such treatment often underwent conversion to lignin-like materials and (b) changes in the structure of the lignin were apparently occurring.

Since carbohydrate materials yield "humins" upon treatment with concentrated acids under conditions corresponding to those employed in the isolation of acid lignins (42), and since these amorphous humins closely resemble acid lignins in physical properties, Hilpert has maintained recently (6) that the word "lignin" has no chemical significance and that all isolated lignins are derived from the carbohydrates present in the plant tissues. Hilpert's conception, however, has become untenable with the accumulation of data concerning the essentially aromatic nature of lignin.

As a result of the apparent changes taking place in the lignin during its extraction from wood, König and Rump (5)

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suggested that the term "protolignin" be applied to lignin as it exists in the plant. More recently the carbohydratefree products prepared by lignin isolation procedures have been designated as "isolated" or "derived" lignins and are generally classified by the mode of isolation and wood source used, e.g., ethanol lignin (maple).

Various investigators, nevertheless, still firmly believe, though without adequate proof, that lignins isolated by their new processes have not been changed during extraction. Consequently, the literature contains such names as "genuine" (7), "primary" (8), and "native" (9) lignin. Fortunately, however, lignin terminology in recent years has become more uniform in being based upon the "protolignin" - "isolated" lignin" system.

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B. Morphology of Wood Cells in

Relation to Lignin Content

The problem of the location of lignin in plant materials has been closely examined by botanists and chemists (10), the work of I. W. Bailey on the morphology of wood cells being of particular value. Examination of a transverse section of a wood fibre reveals the following structure:

FIGURE I.



Mature Xylem Cell

- (a) Truly isotropic intercellular substance
- (b) Primary or cambial wall
- (c) Outer layer of secondary wall
- (d) Central layer of secondary wall
- (e) Inner layer of secondary wall

All of the layers excepting the intercellular layer (a) are anisotropic and between crossed nicols, under polarized light, they are visible with varying degrees of brilliance. Apparently the intercellular layer is the only one in which cellulose is absent.

Whereas no lignin is found in the more simplified cambial cell, lignification occurs to some extent in all of the layers of the mature xylem cell. It has been known for some time that the so-called middle lamella ((a) and (b)) is highly lignified. By means of micro-dissection of Douglas fir sections A. J. Bailey (10d) isolated samples of the middle lamella which on analysis were found to contain 71.38% lignin and 14.21% pentosan (the pentosan content doubtlessly includes I. W. Bailey's polyuronides). I. W. Bailey showed that when transverse wood sections are colored with Haidenhain's hematoxylin stain (a typical one for lignin) the middle lamella appears very dark in comparison to the remainder of the cell. By treating wood sections (hardand softwoods) with 72% sulfuric acid (see page 12) the secondary wall may be dissolved (10b), leaving only a residue of the middle lamella. In the latter at least three layers are present - the two cambial walls and the intercellular material. Often five layers are discernible when the residues of heavily lignified outer layers of the secondary walls remain closely attached to the residues of the cambial cells. I. W. Bailey, at the same time presented evidence indicating the presence of polyuronides in the lignin of the middle lamella.

In addition to this study of the middle lamella, I. W. Bailey (10e) has accomplished some excellent work on

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the structure of the secondary wall. He has shown that the lignin in the latter is not distributed uniformly but concentrated in elongated intercommunicating interstices of the cellulose matrix. In heavily lignified forms either system may be dissolved without seriously modifying the structural pattern of the remaining system. The purified cellulose and the lignin residue thus reveal positive and negative images of the original structural pattern. When the lignin is dissolved the pattern remaining shows quite broad layers of compact material which is birefringent when viewed through crossed nicols. The interstices in which the lignin had existed are narrower than the remaining cellulose lamellae. When the cellulose is dissolved, the remaining lamellae are compact sheets, thin in comparison to the broader, light portions and containing a low ratio of birefringent material. In the case of heavily lignified zones of the central layers both birefringent parts leave no structural residue. Recently (10c) Bailey has devised a novel technique by which slender, elongated crystallne iodine aggregates are deposited in the elongated interstices of the cellulose matrix from which lignin had been removed. The interstices were shown to be parallel to the fibre axis in general, but fluctuations in orientation (at right engles to fibre axis or even a helical arrangement) existed.

In addition to this data concerning the location of lignin in plant cells it is also of importance to observe (a) that the quantity of lignin (degree of lignification) in a

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given cell is dependent upon its age as is shown in Table I. (10e); and (b) that the structure of the lignin (as would be expected in cell development) changes with age. The latter conclusion is exemplified by the increase in methoxyl content of young growing plants (11).

TABLE I

Lignin Content of Birches

	Klason Lignin (%)		
Cross-Section of Trunk	White Birch (29 rings)	Yellow Birch (101 rings)	
Innermost heartwood	37.44	29.84	
Heartwood 1" radius	35.14	29.14	
Annulus from 2" to 4"	23.08	22.00	
Annulus from 4" to 6"	21.26	21.28	
Annulus from 6" to periphery	19.54	21.40	

C. Isolation of Lignin

As can be seen from these cell wall studies, the isolation of lignin from woody material involves its separation from closely associated polysacoharides either by selective dissolution of the lignin or of the carbohydrate material. Since one of the primary driving forces behind investigations on lignin structure concerns the pulping of wood to produce pure, undegraded cellulose it is obvious that the commercially important processes (bisulfite, alkali, and sulfate) involve the dissolution of lignin.

Of these separation methods, the sulfite cooking process (patented by Tilghmann (12) in 1860) in which the wood is heated with an aqueous acid metallic bisulfite (calcium salt generally) under pressure is the most important industrially. Under these conditions the lignin is dissolved as water-soluble lignin sulfonic acids (13). These are employed as such in lignin investigations, since reactions involving the removal of sulphur from the lignin (13b) are so drastic as to change the structure of the lignin radically. Such preparations, carefully purified by dialysis, have been employed extensively for the purposes of lignin investigations, particularly by Klason (see p. 38), the first "lignin chemist"; Hägglund (14); and Hibbert and co-workers (see p. 28).

A second procedure of industrial importance which

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is also used as a laboratory source of lignin employs aqueous or alcoholic alkaline solutions for the dissolution of lignin. The ease with which lignin can be obtained by this method depends somewhat on the character of the lignified material; in case of cereal straws (15) and corn cobs (16) lignin fractions (not total lignin) can be obtained by treatment with alcoholic or aqueous sodium hydroxide solutions at room temperature, whereas in the case of wood a more drastic treatment is required Thus, in order to remove most of the lignin from (17). woods, heating with a 3 to 5% aqueous sodium hydroxide solution at 160-180 °C for 3-6 hours is necessary. The lignin is isolated from the "black liquor" solution by precipitation with acid. Such lignin preparations, although only partially adaptable to laboratory investigations, due to the occurrence of extensive degradation during the extraction (18) have been used frequently because they are (a) easily prepared, (b) represent an industrial waste product, and (c) are generally soluble in most organic solvents.

The application of a third process involving the isolation of lignin by heating wood with various hydroxylic solvents has become increasingly extensive in recent years thanks largely to the impetus given to such studies by Hibbert and co-workers. A wide variety of mono - and polyhydroxy alcohols and phenols have been used and the extraction process considered on the following bases:

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- (a). The extent to which lignin removal and
 cellulose degradation occurs (obviously
 due to interest in pulping possibilities).
- (b). The effect of temperature, concentration and catalyst (H⁺and OH) on yields of amorphous lignins and more soluble partially distillable oils.
- (c). The significance of concurrent alkylation of the isolated lignin by the extractant under certain conditions.
- (d). The relationship between protolignin and the isolated lignin.

Although "alcoholysis" techniques vary with different investigators, the procedures, in general, involve a refluxtemperature extraction of wood meal with an acidified alcohol followed by the concentration of the neutralized supernatant liquor. The amorphous lignin is then obtained by precipitation of the concentrate into a large volume of water.

The alcoholysis reaction will be discussed in detail later (see p. 53).

Whereas the three isolation methods mentioned above involve the solution of lignin, there are several important procedures which depend upon the removal, by hydrolysis, of the cellulose and other wood components, leaving the lignin as an insoluble residue. The essential feature of all such processes (with the exception of Freudenberg's cuproxam lignin) is concerned with the hydrolysis of all of the wood polysaccharides and polyuronides with concentrated mineral acids such as (a) sulfuric acid (64, 66 (19), and 70% (20)) to give"Klason" lignin; (b) hydrochloric acid (42-43%) (21) yielding "Willstatter" or hydrochloric acid lignin: and (c) a hydrochloric-phosphoric acid mixture (22). The dark-colored lignin residue is insoluble in water and most organic solvents and is therefore readily freed from the water-soluble sugar hydrolysis products.

Although Klason lignin is, at present, of no chemical importance since it is obtained by too drastic treatment, the isolation procedure is of primary importance in the quantitative determination of the lignin content of plant materials and wood pulp. This method for the determination of lignin varies slightly from laboratory to laboratory but it consists essentially of the following steps (23): Approximately two grams of air-dried wood meal, dried to constant weight at 105 °C, is extracted for 4 hours with benzene-alcohol; and, after removal of the solvent with water and drying, the wood meal is treated with 25 cc. of 72% sulfuric acid at 20°C for 2 hours. The resulting mixture is transferred to a large Erlenmeyer flask diluted with water to make a 3% solution and then boiled for 4 hours. The hydrolyzed residue is filtered on a tared crucible, washed with hot water, dried and weighed. Klason lignin content equals:

> Wt. hydrolysis residue Wt. oven-dried sample X 100

Due to the ease of "humin" formation from polysaccharides this procedure has been carefully standardized to yield reproducible results with little or no "humin" contamination. Possibly one of the most important results of Hilpert's (6) theories concerning the carbohydrate origin of lignin was to emphasize the necessity of careful control in lignin analysis. Whereas Klason lignin has not been used extensively

in lignin investigations, Willstätter - or hydrochloric acid lignin has been used for structural studies and its mode of isolation is the basis for an analytical method. Research on hydrochloric acid lignin has tended toward the use of modified reagents such as a mixture of phosphoric - and hydrochloric acids (22). The preparation of the various HCl lignins involves procedures quite similar to that for Klason lignin isolation.

One of the most useful and least modified of isolated lignins of this class is Freudenberg's "cuproxam" lignin, the preparation of which is based upon the solubility of cellulose in cuprammonium solution. In this process, resin-free (benzeneethanol extracted) and gum-free (5% NaOH treatment) woodmeal is first boiled with $1\% H_2 SO_4$ to remove pentosans and hemicelluloses followed by a 12 hour' shaking with Schweitzer's reagent. The reaction mixture is centrifuged and the precipitate washed successively with Schweitzer's solution, concentrated ammonia, water, dilute hydrochloric acid and again with water. The complete operation is repeated three times to give a low yield (lignin being slightly soluble in cuprammonium solution (20b,25)) of purified lignin.

D. <u>Composition and Physicial Properties of</u> Isolated Lignins

Tabulation of the data on elemantary analyses of various isolated lignins for carbon, hydrogen and oxygen content shows that poor agreement exists, due, according to Hägglund (14, p. 196) to incomplete purification of the isolated products. But even after rigorous purification procedures it is observed that a lack of agreement persists among analyses of lignins from different woods according to the method of extraction used, indicating that lignins vary from wood to wood and with the mode of isolation.

Despite these discrepencies, however, all analytical results definitely indicate that these materials are entirely different from polymerized carbohydrate; the high carbon content (63-67%) and the considerable quantity of tightly bound methoxyl groups (10-22%) prove this. Therefore, although the agreement is not perfect, it is fairly clear that lignin is as much a chemical entity as other classes of natural materials. In addition, the ratio of carbon to hydrogen (approximately $C_1 H_{1.4}$) (26) makes it unlikely that lignin is composed entirely of aliphatic or hydroaromatic groupings; instead, since reactive ethylenic bonds are not in evidence, it would appear that benzene rings (or furane or pyrane) (4b, p. 119) must be present.

Of the substituent groups in lignin, the methoxyl

group is probably the most important. This methoxyl content also suggests the presence of aromatic nuclei, since, similar to aromatic alkoxyl groups, the methoxyl groups in lignin are removed only at high temperatures by hydriodic acid (26). Apparently, however, all of the methoxyl groups in wood are not associated with the lignin, since, according to Hägglund's results (27), 0.56% of the 4.6% methoxyl content in spruce is attached to carbohydrate. Since, however, this estimation is based upon a slight decrease in methoxyl content upon extraction with hydrochloric acid and not upon isolation of methylated carbohydrates; and, since other investigators have shown that a portion of the methoxyl content, even in isolated lignins, is loosely bound (28). Hägglund's conclusion is not decisive. At any rate over 80% of the methoxyl content of wood is associated with the lignin (29).

The formation of small amounts (up to 1.2%) of formaldehyde from hydrochloric acid and Klason lignins (30), upon treatment with mineral acids according to the method of Tollens, has been interpreted by Freudenberg (24a, 31) as an indication of the existence of a dioxymethylene grouping in lignin present as a piperonyl radical. Since, however, no dioxymethylene compounds have been isolated (even from sassafras lignin (32)) from the degredation products of lignin, and since formaldehyde has been shown to probably arise from the carbohydrate content of certain isolated lignins (33) Hibbert has reasonably concluded that the presence of such a grouping is unlikely.

There are free hydroxyl groups in isolated lignins and practically complete methylation of these groups can be attained by repeated treatment with dimethyl sulfate and alkali, while approximately 50% of the hydroxyl content is diazomethane methylatable (112). From the diazomethane data it seems logical to conclude that free phenolic hydroxyl groups are present. Although Freudenberg (24b) insists that hydrochloric acid and cuproxam lignins (spruce) contain no free phenolic hydroxyl groups, the observation that certain lignin preparations, particularly the alcohol lignins, can be precipitated from aqueous alkaline solution with carbon dioxide (14, p. 199) certainly indicate their presence, as does the result obtained by Tomlinson and Hibbert, who found that alkaline cleavage of methylated ligninsulfonic acid (spruce) yielded veratraldehyde whereas the unmethylated material gave vanillin only - (34). Apparently the aliphatic hydroxyl groups are secondary and tertiary in type (4b, p. 122).

The presence or absence of a free carbonyl group in lignin has long been a debatable issue. Although it is almost certain that the aldehyde group is absent, there is considerable evidence for the presence of a keto carbonyl

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group. Hibbert and Wright (35) have shown the presence of non-enolizable carbonyl in formic acid lignin (spruce); Friedrich (8,36) has obtained condensation products of indefinite character from ethanol lignin with phenylhydrazine; and Hägglund's investigations on aromatic amine-ligninsulfonic acid compounds (37) suggest the existance of keto carbonyl groups.

Ether oxygen, other than that included in methoxyl groups, is also present, as is evidenced by comparison of the elementary analytical data with the methoxyl and hydroxyl content of isolated lignins, and it seems quite likely that it is cyclic in part; in fact, Freudenberg (4b, p. 123) assumes the oxygen-containing ring to be flanked by a benzene ring.

The presence of the ethylenic bond in lignin has not been established. Bromination data are extremely contradictory (38) and the Dimroth (39) method for ethylenic bond determination, when applied to different lignins indicates varying amounts of C=C (40), which variation has been partially explained by the observation that a portion of the lead tetraacetate addition occurs on aromatic nuclei (41,42). Apparently no positive conclusion can be drawn concerning the presence of ethylenic bonds.

Carboxyl groups are not present in lignin except in the case of certain alkali lignins (often called "lignic acids") formed when oxidation (air) occurs during the ex-

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traction with hot alkaline solutions.

It can readily be seen that evidence concerning the presence or absence of relatively simple constituent groups in lignin is oftimes conflicting. The explanation of these discrepancies is threefold in that the structure of any isolated lignin is dependent upon the plant source, the mode of isolation, and the degree of heterogeneity of the product of extraction. It, therefore, seems reasonable to expect that the actual presence of any such active substituent as the carbonyl group, phenolic hydroxyl group or ethylenic bond, will be dependent upon the type of reagent used in the extraction.

That various preparations differ from each other is shown most clearly by a comparison of physical properties, especially that of solubility. Table II graphically exemplifies this fact. (7, p.66)

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TABLE II

Solubility of Lignin Preparations

Solvent	Hydrochloric Acid Lignin	Alkali Lignin	Phenol Lignin	Ethanol Lignin (157)
Water	-	-	-	ο
Cold Sodium Hydroxide	-	+	+	+
Cold Hydro- chloric Acid	-	-	-	0 -
Ethanol	-	0	+	+
Acetone	ο	+	+	+
Ether	-	-	-	0
Benzene	-	-	-	0
Phenol	-	+	+	+

Key: + = soluble o = partially soluble - = insoluble

Such pronounced variations in solubility cannot be explained entirely on a basis of degree of polymerization of a polymeric series. Apparently the type of condensation of the building unit is dependent upon the isolation technique.

All isolated ligning are brown (light tan to black) amorphous substances of a colloidal character, which give no x-ray diffraction pattern. The colloidal nature of lignin preparations results in the typical discordancy observed in molecular weight determinations of macromolecular aggregates, especially when such procedures as the freezing-point lowering, or boiling-point elevation methods are employed. Cryoscopic measurements for example, give results varying from 400 to 3000 for the same preparation (44). Staudinger (43) has treated lignin preparations as typical, high polymeric materials and by utilizing viscometric and osmotic methods has determined their particle size. From his findings which indicated a relatively low molecular size for various phenol lignins and a lignin sulfonic acid(in comparison with cellulose and rubber) he concluded that the viscometric data could have no meaning until more was known of the structure of the lignin polymer or polymers.

Application of absorption-spectrum analysis technique to several lignin preparations has indicated (a) that a similarity in basic structure exists for different "alcohol lignins" and lignin sulfonic acid from spruce (45); and (b) that the basic component of lignin contains at least one benzene ring. More specifically, Herzog and Hillmer (46) deduced that the aromatic component of ligninsulfonic acid (spruce) has a guaiacyl nucleus.

In summarizing it may be concluded from the available analytical data and physical properties that although isolated ligning vary in structure and molecular

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,size according to the method of isolation and wood source, lignin is a chemical entity of the polymeric type derived from a basic unit, probably aromatic in part, which definitely contains methoxyl and hydroxyl groups and, in certain preparations, the carbonyl group and ethylenic bond.

E. Degradation Studies on Isolated Lignins

In attempting to obtain evidence concerning the basic composition of lignin, investigators in this field next attacked the problem of its structure by characteristic degradation experiments; namely, hydrolysis, pyrolysis, alkali fusion, oxidation and hydrogenation. Early attempts employing mild hydrolytic reagents, instead of yielding fission products, appeared to catalyze condensation and polymerization reactions; and, as a result, chemists then proceeded to use more drastic conditions to obtain the simple basic units of the more complex entities.

1. Pyrolysis (Dry Distillation) of Lignin

Hägglund (47), for example, distilled hydrochloric acid lignin (spruce) at temperatures around 500°C, and, in addition to a 45% yield of carbonaceous residue, obtained 9.6% of an oily distillate, 0.1% acetone, 0.67% methanol and 0.64% acetic acid based on the weight of the lignin used. Although much similar additional work was accomplished at this time (48) and more exact determinations made of the main fractions obtained in the vacuum distillation process (350°C) devised by Pictet and Gaulis (49)(which procedure gave 15% aqueous distillate, 20% tarry distillate, 52% residue, and 14% gas), Phillips and Goss using alkali, hydrochloric acid, and Klason lignins(from corn cobs) were the first to isolate and identify certain simpler aromatic products (50)
The following results (calculated on basis of dry alkali lignin (prepared from non-solvent extracted corn cobs) were obtained by dry distillation at 25 mm. pressure: aqueous distillate, 11.7%; oily distillate, 28.3%; carbonized residue, 50.5%; gas, 9.3%. The aqueous distillate contained acetic acid, catechol (I), phenol, o-cresol, guaiacol (II), creosol, isoeugenol (III), and n-propylguaiacol (IV); and the steam volatile "neutral" fraction of the oil, after permanganate oxidation yielded anisic acid (V).



Somewhat later, the same authors (50b) isolated catechol, guaiacol, and n-propylguaiacol by Zn dust distillation of the same lignin in a hydrogen atmosphere at 400°C.

These results, although providing valuable support for the guaiacyl nucleus hypotheses, when taken alone failed to provide positive proof of aromaticity due to the fact that the yields were very low and carbohydrates were known to yield benzene derivatives under certain pyrolytic conditions (51).

2. Alkali Fusion and Cleavage of Lignin

The treatment of isolated lignins with fused potassium hydroxide, and of ligninsulfonic acids with hot aqueous sodium hydroxide under pressure, yielded the first important positive contributions to a knowledge of the basic nature of lignin.

Fischer and Tropsch (52) fused hydrochloric acid lignin (spruce) with KOH at 240-300°C and obtained 35.5% of humin-like material ("lignin-acid") and 14.9% of ether-soluble compounds of which protocatechuic acid (VI) was one.



Among others who identified protocatechuic acid in the alkaline lignin melt were Klason (53) and Hägglund (54). Heuser and co-workers carried out extensive

fusion studies on hydrochloric acid lignin(spruce). Their results showed (a) that the volatile products were composed of protocatechuic acid, catechol, and oxalic acid; (b) that protocatechuic acid was the primary product of the combined cleavage and oxidation, the catechol being formed by elimination of carbon dioxide; and (c) that the oxalic acid resulted from secondary air oxidation of the two phenolic compounds (55). By employing an iron crucible (catalytic activity) and an atmosphere of nitrogen a maximum yield of 26% catechol was claimed.

Methylation of lignin and subsequent fusion had little effect on the character and yield of aromatic substances (56). Under similar conditions, cellulose yielded negligible quantities of aromatics (55).

Since only 50% of the protocatechuic acid recoverable when treated with fused potassium hydroxide under the conditions employed for its isolation from lignin, it was suggested by Freudenberg that the true yield of this product is that represented by the use of an appropriate "working loss factor". Also, no improvement in yield over that found with hydrochloric acid lignin (spruce) is obtained from "polymeric coniferyl alcohol", VII, by potash fusion (64).



VII

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It is of interest to note that the yields of phenols (predominantly catechol) and protocatechuic acid obtained from straw lignin vary appreciably with the means of isolation used (57a) (see Table III).

TABLE III

	Method of Lignin Isolation				
Product	Cold NaOH	R eflux NaOH	NaOH in MeOH		
Protocatechuic	6.0-7.6%	7.0-8.0	15.3		
Phenols	2.2-3.3	0.6-1.5	5.0		

Potash fusion of beech lignin at 210-215°C yielded gallic acid, VIII, (4-5%) primarily (65).



An extremely important cleavage process, both from the theoretical and commercial viewpoint, has been the aqueous alkaline cleavage of ligninsulfonic acid (spruce) to produce vanillin, IX, (58) in yields up to 7%; (34).



This process has been investigated extensively by Hibbert and co-workers and has provided valuable information concerning the aromatic components of ligninsulfonic acids. To date, no other lignin preparations have yielded more than 1-2% vanillin upon similar treatment (pressure cook of purified sulfonic acid containing 100 g NaOH per liter liquor at 160-170°C for 8-10 hours, the vanillin being isolated by benzene extraction of the neutralized liquor). It has been found that the yield of vanillin increased with the sulfur content (34, 59). The significance of the guaiacyl grouping was emphasized further by the later isolation of guaiacol (60) and acetovanillone, X, (61) from the same liquors. The latter compound established the existence of at least two carbon atoms in the side chain.

Application of this technique to hardwood ligninsulfonic acids resulted in the isolation of 3% syringaldehyde, XI, (62); 0.8% acetosyringone, XII, (63); and pyrogallol-1,3 dimethyl ether, XIII, (63); as well as approximately equal amounts of the corresponding guaiacyl derivatives. The presence of both guaiacyl and syringyl derivatives in hardwoods and the absence of the latter in softwoods led Hibbert to suggest this difference in behaviour as a chemical distinction between these two wood classes (62).



3. Oxidation of Lignin

Published results concerning the oxidation of lignin, were quite disappointing until recently in so far as their contributing to the knowledge of the structure of this substance was concerned. Ozone (66a, b, g), hydrogen peroxide (66c, 30a), potassium permangante (56, 66d) nitric acid (66e) and nitrogen tetroxide (66f) have been employed as oxidation reagents for isolated lignins as well as for ligninsulfonic acids, oxalic, succinic and malonic acids. Apparently poor choice of reagent and lack of reaction control had resulted in drastic degradation.

As the investigators became more aware of the necessity for caution and restraint in handling lignin preparations in the presence of oxidizing agents, more successful attempts resulted. Cuproxam lignin (spruce) which had been methylated with diazomethane or dimethyl sulfate, yielded 1-2% veratric acid, XIV, on permanganate

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oxidation; and powdered, diazomethane-methylated spruce wood upon similar treatment gave a 4% yield of the same acid (calculated on basis of Klason lignin content of the wood) (65). Finally, by combining the alkaline cleavage and oxidation techniques, Freudenberg found that the hydrochloric-phosphoric acid lignin (spruce), or, better the wood itself, if methylated with diazomethane, cooked for 90 minutes at 170°C with 70% potassium hydroxide, methylated with dimethyl sulfate and then oxidized with permanganate gave a yield of 10-14% veratric acid, 2-4% isohemipinic acid, XV and 3% dehydrodiveratric acid, XVI,(65-67).



Inasmuch as in a control experiment with the free acids approximately one-third of the veratric - and two-thirds of the isohemipinic acid were decomposed during similar treatment (67) Freudenberg assumed the correct yields of these compounds to be 20-21% veratric - and 6-12% isohemipinic acid; dehydrodiveratric acid being formed by secondary oxidation during the treatment.

In continuation of this trend toward milder, more specific oxidizing agents, Freudenberg (68) obtained yields of 20% vanillin from ligninsulfonic acid, hydrochloric acid lignin, and cuproxam lignin (all from spruce) and 25% from spruce wood meal by pressure treatment (160°C) with sodium hydroxide and nitrobenzene: An additional 10% yield of unidentified phenols resulted from this procedure. These results from spruce wood have been confirmed in these laboratories (96). In addition, as a result of an investigation in which the variable conditions of this reaction were modified, the yield of the syringaldehyde-vanillin mixture obtained from maple wood has been increased to 43% (plus 10% phenols and aromatic acids) of the Klason lignin content of the wood (97).

4. Hydrogenation of Lignin

As in the case of the application of oxidation reactions to the problem of the structure of lignin, the early results of high-pressure catalytic hydrogenation methods were of little value. The hydrogenation of hydrochloric acid lignin (spruce) by Fierz-David for example, produced a mixture of unidentified products containing some materials of a phenolic nature (69). Similarly the use of alumina and nickel

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oxide as catalysts (70) gave unsatisfactory results.

During the period from 1930 to 1937, however, Adkins (71) carried on an extensive investigation of high-pressure hydrogenation of organic compounds over CuCrO and Raney nickel catalysts, and he so successfully standardized apparatus design, catalyst preparation, and reaction conditions that high-pressure hydrogenation became a practical laboratory tool. Recognizing the potential applicability of this knowledge to the problem of the structure of lignin preparations, Hibbert submitted a sample of acetic acid lignin (birch) to Adkins in 1937 (72) for hydrogenation. Although this material underwent hydrogentaion over CuCrO in dioxane solution, the identification of the hydrogentaion products from lignin under such conditions was not accomplished until 1938 by Harris, D'Ianni and Adkins (73).

These investigators subjected methanol lignin (aspen) in dioxane solution to hydrogen at 250 atmospheres pressure at 250-260 °C for 12-18 hours over CuCrO catalyst and isolated methanol (28%); 4-n-propylcyclohexanol, XVII, (11.5%); 4-n-propylcyclohexanediol -1,2, XVIII, (3.8%); 3-(4-hydroxycyclohexyl)propanol-1, XIX, (25%); and a highboiling resinous residue (32%) from the reaction mixture.

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In this manner 40% of the lignin was converted into identifiable products which could be regarded as the hydrogenated basic units of lignin. In addition to these products, propylcyclohexane has been isolated from the products of lignin hydrogenation over Raney nickel in aqueous alkaline solution (74).

Not only have these conditions been successfully applied to isolated lignins, but also to wood. Godard (75) found that maple wood could be completely solubilized by hydrogenation of the suspended wood-meal in dioxane over CuCrO at 260 atomospheres pressure for 18 hours at 280°C. The colorless liquid residue, which was composed of products from carbohydrates as well as from <u>protolignin</u>, was fractionally distilled and 4-n-propylcyclohexanol (19.5%)

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and 3-(4-hydroxycyclohexyl)propanol-1 (5.8%) were identified (the percentages being based upon the Klason lignin content of the maple wood).

The hydrogenation of wood and lignin are discussed elsewhere in detail (see p.118).

5. Ethanolysis of wood.

Although the wood ethanolysis reaction is actually a lignin isolation process, on the <u>assumption</u> that protolignin is a polymeric material, certain of the reaction products may be considered fission products of lignin. Hibbert and co-workers discovered that a considerable portion of the water-soluble components obtained by the ethanolysis of spruce and maple woods were non-carbohydrate, and after a rigorous fractionation procedure the following compounds were isolated from ethanolysis oils (spruce); vanillin (77); a-ethoxypropiovanillone, XX, (78); and vanilloyl methyl ketone, XXI, (77). Using maple wood meal they were able to isolate syringaldehyde (79); a-ethoxyprop_jovanillone (80); a-ethoxypropiosyringone, XXII, (80); and syringoyl methyl ketone, XXIII, (77, 79).



F. Theoretical Considerations on Lignin Structure

1. The structure of Isolated Lignin

The data in the previous section indicated that chemical knowledge of lignin remained practically stationery from about 1890 until 1923, when suddenly a rapid accumulation of information from experimental investigations concerned with alkali fusion, oxidation, hydrogenation and ethanolysis produced positive evidence (a) that at least 50% of the lignin (protolignin and isolated lignin) was aromatic; (b) that probably all of the aromatic groups in spruce and other softwoods were guaiacyl derivatives while in maple, oak and other hardwoods both syringyl and gualacyl derivatives were present; (c) that probably all of the benzene nuclei contained n-propyl side chains in the para position with respect to the phenolic hydroxyl group of the guaiacyl and syringyl residues; (d) and that at least two of the carbon atoms in the propyl side chain were attached to carbonyl or hydroxyl oxygen.

The next important question, was the problem of the state (simple or condensed) in which these phenylpropane nuclei exist in protolignin; their manner of association (chemical or mechanical) with polyuronides and cellulose; and the mechanism by which the polymeric, amorphous isolated lignins are formed. Since approximately 90% of the work in this field has been concerned with the structure of isolated lignins, the first two problems were neglected except in so far as incidental information could be gained from the reactions of wood and procedures for lignin extraction. As a consequence they will be discussed in the sections on alcoholysis and hydrogenation and in this section will be considered only the various theories of the structure of isolated lignins.

The literature concerning the properties and reactions of lignin is now rather extensive and quite a number of constitutional formulae have been proposed. It must be emphasized at the very outset that all of these formulae (with the possible exception of the most recent one by Freudenberg) are very speculative in character although evidence of a fragmentary nature can be mustered for their support. The fact that at frequent intervals the proponents of structural formulae have found it necessary to change them is in itself an indication of the very insecure foundation upon which they rest. In addition, it must be remembered that it was not until 1935 that degradation experiments produced positive knowledge of the basic lignin units or monomers comprising the major portion of lignin.

Any one of the the many proposed structural formulae for ligninfits into one of two classes; namely, those based upon a propylguaiacyl type repeating unit or those with no particular basis other than an empirical formula and a few chemical properties. Although many structures of the latter type have been suggested (81) they have never been as popular as the former; and, now that it is known that they have no significance, they are only of historical interest.

The apparent ease with which lignin polymerizes led Klason to compare it with polymerized coniferyl alcohol: and, since coniferin (the glucoside of conifery) alcohol) was known to be present in the cambial sap of all woody species (89), he concluded that lignin also contained the same three-carbon side chain (82). Later, on the basis of a comparison of the properties of ligninsulfonic acids and sulfonic acids from polymeric coniferyl alcohol he concluded that lignin was a condensation product of coniferyl and oxyconiferyl alcohols (83). Originally the repeating units were believed by him to be united through ether-oxygen linkages (84); but later, after having conceived and discarded the possibility of a similarity existing between flavon 1s and lignin (85), the following structure XXIV, which was based upon a coniferyl aldehyde repeating unit, was proposed (86).

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This configuration was based upon the assumption that lignin was related to the tannins.

As time passed and evidence accumulated concerning the variable sulfur content of ligninsulfonic acids (66b) (for the key to all proposals made by Klason depended upon the empirical formula of spruce ligninsulfonic acid), it became apparent that a dimeric structure was unsatisfactory and Klason suggested first a paraldehydic polymer (87) and finally a hemiacetal condensation mechanism (24b,88) in which compound XXV was the monomer.



The coniferyl-alcohol-polymer hypothesis has also been advanced by Kürschner (4a, p. 77) on the experimental evidence that coniferin and spruce lignin show an analogous behaviour in several chemical reactions such as action with bisulfites and sulfurous acid, fusion with alkalis, and solubility in trichloracetic acid. The following structural formula, XXVI, was suggested by Kurschner:



The major objection to this theory, as with all theories based upon coniferyl derivatives, is that isolated lignins do not behave like true unsaturated compounds, nor do they yield the characteristically large quantities of ethyl iodide upon hydrogen iodide cleavage of the propylene side chain (89). In addition, were the benzene nuclei simply connected through ether-oxygen linkages, lignin should yield simple units when heated with hydriodic or hydrochloride acid. No such derivatives have been obtained from spruce lignin when treated in this manner (57).

Closely related to Klason's theories of oxyconiferyl alcohol, coniferyl alcohol and coniferyl aldehyde condensation products are those proposed by Freudenberg in recent years. This investigator considered the compounds XXVII to XXXII (and similar units) to be the lignin "building stones" (monomers) (90) which condensed to form a 12 unit chain called "primary lignin", XXXIII. By the polymerization of "primary lignin" "secondary lignin" XXXIV, was produced (10a, 40, 91):



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XXXIV

The latter product was formed supposedly by the condensation of "primary lignin" in the wood during the post-mortal period or during the process of the isolation of lignin in the laboratory. It was considered to be the parent substance of almost all lignin derivatives, particularly of ligninsulfonic acid, the latter substance resulting from a partial elimination of water and the addition of H - SO₃H to the newly-formed ethylenic bond.

As in the case of Kürschner's polymer, however, the conception of simple ether linkages between the "building stones" did not coincide with data from the ether cleavage reactions carried out on isolated lignins. Consequently Freudenberg abandoned his original idea (90) in favor of a benzofurane or benzopyran condensation product, XXXV and XXXVI, resembling one of the formulae proposed by Klason (XXIV).



Although these structures were originally postulated upon only the barest experimental foundation, considerable supporting avidence has accumulated for this theoretical consideration in the past five years. Freudenberg, himself, isolated isohemipinic acid (XV) (65,67) thereby indicating the presence of an alkyl residue in the meta position with relation to the methoxyl group. The essential validity of the assumption of a basic phenylpropane unit was confirmed by the lignin hydrogenation data of Adkins and Harris; and, concurrently the identification of the ethanolysis products from wood by Hibbert and coworkers established the nature of the substituents on the propyl side-chain.

In addition to this support, Freudenberg has undertaken extensive experiments paralleling those on cuproxam lignin with Erdtman's acid, XXXVIII, (67).

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This product is obtained by the oxidation of dehydrodiisoeugenol, XXXVII, (92) which, in turn, is obtained from isoeugenol by means of biochemical dehydrogenation by fungi or through gentle chemical oxidation (93). <u>the bearing on</u> The results/of this analogy are shown in Table IV.







XXXVIII

TABLE IV

	Yield o	(67)		
Substance	Veratric Acid %	Theor. Yield	Isohemip. Acid %	Theor. Yield
Erdtman's Acid	21	53	5	66
Cuproxam Lignin	14		4	
Cryst. Sulfonic Acid From Erd.'s Acid	17	39	4	40
Ligninsulfonic Acid	3		3.8	
Erd. Acid-Thioglycolli Acid Condn. Product	.0 7•4	41	3	59
Lignin Thioglycollic A	.cid 4		3	

Several important objections may be raised against this polymerization mechanism. In the first place, it seems strange that Freudenberg has not proven the structure of Erdtman's acid, for it so happens that the structure shown above for this compound is merely that of the "logical" product of a condensation reaction of somewhat doubtful mechanism. Secondly, although Freudenberg has not suggested an alternate structure for hardwood lignins, which have been shown to contain at least 50% of the aromatic residue as syringyl derivatives (96, 97), it is obvious that the presence of the second methoxyl group in this nucleus prohibits the occurrence of such a condensation (100). In the third place it is difficult to associate a 20% yield of vanillin upon relatively mild oxidation (68) of such a polymer; for, since vanillin could conceivably arise from the end guaiacyl residue only, it would mean that the isolated lignin was a tetramer whereas Freudenberg himself states that isolated spruce lignin is composed of more than twelve C9 units (10a, 40). Finally, a very recent experiment by Lautsch (95) indicates that, at best, only a part of the lignin can exist in such form. This investigator, after treatment of methanol lignin (spruce) with alcoholic mercuric acetate, replaced the added AcOHg group by iodine, The resulting iodolignin on oxidation with cobaltic hydroxide gave a 10% yield of 5-iodovanillin as the main product, indicating that a portion of the guaiacyl residues could not have been condensed through that position.

It is not to be construed that because of these objections the writer considers such a polymeric system for lignin to be irrational, for even though such a condensation mechanism is untenable for all of the lignin from syringylcontaining hardwoods, the evidence against the hypothesis in the case of spruce is far from absolute. Actually Freudenberg stated the problem quite distinctly when he said, "Although the scheme has been criticized in certain respects, a more satisfactory picture has not been presented.

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I have put forward what seems to be the most logical conception of lignin chemistry in the hope that it may stimulate those who do not agree to propose another more constructive solution to this problem."

2. Lignin as a Possible Product of Plant Respiration

According to botanical classification lignin has often been considered as a cementing or binding component in plant structure (101). Lignin chemists, in general, have either tacitly accepted this theory, or else they have ignored the functional significance of lignin entirely. With the isolation of a-ethoxypropiovanillone and vanilloyl methyl ketone from the ethanolysis products of spruce wood, however, Hibbert recognized a remarkable similarity between these compounds and a group of compounds which Szent-Györgyi has shown to constitute dehydrogenase-catalyst systems in various forms of plant life (102). As a result of a structural comparison Hibbert has suggested that lignin is derived from a series of hydrogen-transporting catalysts involved in the oxidation-reduction respiratory reactions, which catalysts during the life of the plant and in the subsequent post-mortal stage, undergo conversion into more complex condensation-polymer products (109).

In his recent Nobel Prize lecture, (102) Szent-Györgyi pointed out that, while a great deal had been learned about the mechanism of animal cell respiration, very little was known concerning that of the plant. However, as a result of a series of researches carried out with various forms of plant life, he has been able to demonstrate the existence, therein, of a number of dehydrogenase-catalyst systems such as catechol, XXXIX; ascorbic acid, XXXX; and dioxylmaleic acid, XXXXI (103).

(B) (B) (B) OH CH₂OH C(OH)-COOH -OH $c_0-C(OH)=C(OH)-CH-CHOH$ C(OH)-COOH -2H +2H -2H +2H -2H | +2H 0 CH₂OH CO-COOH СО-СО-СО-СН-СНОН =0 CO-COOH (A) (A) (A)

Each of these can function as an oxidationreduction system, the oxidized molecule being a 1,2diketone (A) and the reduced molecule (B), an "ene-diol".

XXXX

XXXIX

XXXXI

The above ene-dicls, when synthesized outside the plant, are more stable than their corresponding diketones. From these experiments and other theoretical considerations, Szent-Györgi has been led to conclude that, irrespective of any other systems which may function in plant respiration, there must be present oxidation-reduction configurations of the ene-dicl type (102).

Closely related to this hypothesis and to the possible relationship of aromatic lignin monomers to plant respiration are the results of Neuberg (104). This investigator isolated phenylacetyl carbinol, XXXXIV, and methylbenzoyl ketone, XXXXIII, from a fermenting sugar solution to which benzaldehyde had been added, a carboligase synthesis being brought about. Apparently the carboligase enzyme had catalyzed a condensation reaction between benzaldehyde and acetaldehyde, the latter compound being a product of the carbohydrate fermentation reaction. Since methylbenzoyl carbinol (a-hydroxypropiophenone) XXXXII. is readily converted to phenylacetyl carbinol in fermenting solutions which contain yeast (106), it would appear that the former compound is also a product of the carboligasecatalyzed condensation reaction. The presence of these three compounds in the same reaction mixture suggests the existence of the following combined ene-diol-oxidationreduction system:

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$$C_{6}H_{5}-CO-CHOH-CH_{3} \leftarrow C_{6}H_{5}-C(OH)=C(OH)-CH_{3} \leftarrow C_{6}H_{5}-CHOH-CO-CH_{3}$$

$$\underbrace{XXXXII}_{C_{6}H_{5}-CO-CO-CH_{3}}$$

XXXXIII

If such a reversible system is present in the fermentation reaction mixture, the possible presence of a similar system in plants (since fermentation and respiration changes are very intimately related) is suggested by the existence therein of methylvanilloyl ketone, XXI, and a-hydroxypropiovanillone, XXXXV, (actually the latter compound is isolated as the ethyl ether from the ethanolysis oils).



XXI

Since the oxidation-reduction configurations in this reversible reaction fulfil. Szent-Györgyi's requirements for a plant respiratory oxidation system, Hibbert has suggested

$$\begin{array}{cccc} c_{6}H_{5}-c_{0}-c_{H_{3}} & c_{6}H_{5}-c_{0}+c_{0}+c_{3} & c_{6}H_{5}-c_{H_{3}} \\ \underline{xxxxII} & -2H & +2H & \underline{xxxxIV} \\ & c_{6}H_{5}-c_{0}-c_{0}-c_{H_{3}} \end{array}$$

XXXXIII

If such a reversible system is present in the fermentation reaction mixture, the possible presence of a similar system in plants (since fermentation and respiration changes are very intimately related) is suggested by the existence therein of methylvanilloyl ketone, XXI, and a-hydroxypropiovanillone, XXXXV, (actually the latter compound is isolated as the ethyl ether from the ethanolysis oils).

ӉО	_CO_CHOH_CH_3	но	_C(OH)=C(OH)_CH_3
MeO		MeO	
	XXXXV	_2H	+2H

HO	_00_00_0H	HO_	_CHOH_CO_CH
MeO		MeO	

XXI

Since the oxidation-reduction configurations in this reversible reaction fulfil Szent-Györgyi's requirements for a plant respiratory oxidation system. Hibbert has suggested that they serve that purpose in growing plant cells.

In addition, on the assumption that β -hydroxypropiovanillone, XXXXVI, (an isomeric form of **a**-hydroxypropiovanillone) is present in living plant cells, Hibbert has propounded a plant dehydrogenase catalyst system which is analogous with Szent-Györgyi's fourcarbon dicarboxylic system. The latter series of compounds has been shown to be one of the principal systems active in animal cell respiration; Hibbert has proposed that the following oxidation-reduction system may play a similar role in plants (Diagram I). DIAGRAM I



In this new system it is seen that the third member (B') is coniferyl alcohol, the botanical significance of which may well be represented by this, or a similar, respiratory mechanism. Although the first member, XXXXVI, has not been isolated either from wood or from an isolated lignin, the presence of a terminal hydroxyl group in protolignin has been demonstrated by hydrogenation studies (75); and in order to determine the properties of this compound its synthesis is now being attempted (110).

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III. THE ALCOHOLYSIS OF WOOD

A. Introduction:

About 1925 chemists interested in the study of lignin began to shift from the characteristically drastic methods of lignin isolation and degradation to much milder procedures. Although there was little positive data to indicate that the reactions employed for lignin isolation were causing structural changes in the lignin itself, there were a sufficient number of informative results which suggested that chemical changes were involved in the isolation procedures. The solubilities, for example, of lignins derived by different processes varied appreciably (see p. 20); similarly, the methoxyl contents of different lignin preparations from the same wood source were not in agreement (14, p. 197). In addition, it was seemingly apparent that, if protolignin contained any very reactive substituent groups, changes would occur upon treatment with concentrated sulfuric acid. fuming hydrochloric acid, dilute sodium hydroxide, or acid metallic bisufite at high temperatures. As a consequence. lignin chemists began a study of possible isolation processes dependent more upon specific solubility of an extractant than upon preferential degradation by a reagent.

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The results from these investigations led to the development of two general methods, one of which involved the preferential dissolution of cellulose with ouprammonium solution (Freudenberg's cuproxam lignin), and the other consisted of the extraction of lignin with hydroxylic solvents. Although neither process was purely physical in that a certain amount of hydrolytic action was required, it was generally accepted that the lignins isolated by these procedures more closely approximated protolignin than did those obtained by means of the older methods. Cuproxam lignin has already been discussed; this section will deal with the preparation and properties of "alcoholysis" lignins.

Although the word "alcoholysis" has been used to describe the process by which lignin is removed from woody material by extraction, it must be emphasized that, wherein this term implies the occurrence of a molecular cleavage involving the addition of the elements of ROH to the cleavage fragments, there is no positive evidence that such a reaction actually occurs in the lignin alcoholysis extraction process. It is true that, under certain conditions the isolated lignin contains the OR group, but it is also found that under other conditions no OR addition occurs. Consequently, since the mechanism, or mechanisms, of these

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isolation methods have not been established as yet, the term "alcoholysis" as applied to lignin chemistry defines those lignin isolation procedures by which the lignin (or part of the lignin) is removed from woody material by means of solvents.

B. Survey of the Alcoholysis Process for Lignin Isolation:

The first application of the alcoholysis process in lignin chemistry was made in 1893 by Klason, (113) who found that 28-32% of spruce wood could be dissolved by boiling with a tenfold volume of ethanolic hydrochloric acid (5%) for 6-10 hours. By concentration of the supernatant liquor a resinous product was obtained which could be separated into chloroform-soluble and insoluble fractions. Klason considered the latter to be "pure lignin" without further examination of its properties. Concurrently, Mangin, a French botanist, used 20% alcoholic hydrochloric acid to effect partial dissolution of the middle lamella of cambial cells (114). Much later, another botanist, Grüss (115), found that a small amount of lignin could be isolated by boiling, with ethanol, a suspension of wood which had been moistened previously with 20% aqueous hydrochloric acid.

It was after a consideration of these preliminary experiments that various investigators attempted to isolate lignin by alcoholysis procedures. Included among the many organic hydroxylic compounds employed were primary and secondary alcohols: tertiary alcohols (116); ethylene glycol (40b, 117, 118); glycol monomethyl ether (117b, 119); glycerol monochlorhydrin (120); phenol (121); phenol homologues (122); and ethanolamine (123). In addition, several non-hydroxylic solvents (such as dioxane (116, 124), acetone (125), and chloroform (125) have been employed with varying degrees of success.

Since the same limitations of conditions and catalysts apparently apply to all of these compounds (with the exception of the use of iodine as a catalyst by Hibbert (117a) in one case), the detailed discussion of the alcoholysis process is restricted to primary and secondary alcohols.

The various procedures differ according to the alcohol employed, the quantity of water present, the type of hydrolytic agent used (if any), and the temperature and duration of the extraction. Since a change in any one of these variables affects not only the yield but also the composition of the isolated lignin, a consideration of the alcoholysis processes necessitates a detailed account of the observations which have been made. The arrangement employed by the writer to classify the available data on this subject is based upon the component or components comprising the extraction solution.

I. The Effect of Water on Wood

By cooking aspen wood with water at different temperatures for varying lengths of time, Aronovsky and Gortner

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(126) found that water had a profound effect upon wood. The starting material gave the following results upon analysis.

Analysis of Aspen Wood (126)

Moisture	10.2%
Alcohol-benzene Extractable	2.66
Lignin	26.5
Pentosan	17.5
Cellulose	62.05
a-Cellulose	46.0

The effect of the various treatments upon the wood constituents is shown in Table V.

TABLE V

The Effect of Water on the Constituents of Wood.

Material		Quantity of Material Removed by Treatment, % (a)						
	Temp. (°C)	Temp. (°C) 100 148		8	170		186	
	Time (hrs.)	12	4	12	2	8	2	8
Pentosan		5	25	45	50	90	90	97
Lignin		-	2	З	1	7	4	3
Cellulose		-	10	15	20	25	23	32
a-Cellulose			2	10	10	16	11	37

(%)a - Percentage of component present in untreated wood.
2. The Effect of Aqueous Hydrochloric Acid on Wood.

An insight into the influence of wood exerted by water, as such, is afforded by a comparison of the results described above with those of Hawley and Campbell (127). The latter investigators made an extensive study of the partial hydrolysis of Sitka spruce by aqueous hydrochloric acid solutions at 100° C for six hours. Acid concentrations of 0.05, 0.25, 1.5, 8.0, and 15.0% were employed, and it was found that considerable dissolution of cellulose and pentosans occurred. Unlike water, however, dilute hydrochloric acid removed a <u>relatively large</u> proportion of the lignin. Apparently, the hydrolytic or degradative action of the hydrochloric acid is more equally effective on all of the constituents of wood as is shown in Table VI.

TABLE VI

The Effect of Hydrochloric Acid on the Constituents of Wood.

	-	b y	
Condition Ce	llulose %(a)	Lignin %(a)	Pentosan %(a)
8% aqueous HCl (6 hrs. at 100°C)	26.0	9.9	67.0
8% HCl followed by 1% NaOH (l hr. at 100 ⁰ C)	46.5	14.0	79.0
15% aqueous HC1 (6 hrs. at 100°C)	48.0	10.2	91.0
15% HCl followed by 1% NaOH (1 hr. at 100°C)	60.0	20.5	92.9

%(a) - percent of original cellulose, lignin, or pentosan content.

By comparing the data in Table V with that in Table VI, it is apparent that $ap_{\rm P}$ roximately the same results are obtained by treating wood with water at 170° C for 8 hours as are obtained from a six-hour treatment with 8% hydro-chloric acid at 100° C. Therefore, it would appear that pure water at $170-180^{\circ}$ C is a vigorous hydrolytic agent.

3. The Effect of Alcohols on Wood

Klason was able to dissolve two percent of the material in finely-ground spruce wood by means of extraction with boiling methanol alone (128). The so-called "native lignin" which was isolated from the methanol solution had a methoxyl content of 12.5%.

These results were confirmed by Brauns (129), who obtained a similar yield of "native" lignin by allowing a water-and-ether pre-extracted spruce wood meal to stand for 3-4 days in anhydrous ethanol. After a careful fractionation of the ethanol-soluble material, this investigator isolated a product containing 14.5% methoxyl. This material was soluble in sodium bisulfite and sodium hydroxide solutions. Although this product is of considerable interest in that it was apparently isolated from wood by solvent extraction alone and not by hydrolytic action plus solvent extraction, it is obtained in such small quantities that it can hardly be considered a representative sample of this protolignin. In addition, it has been shown by Friedrich (130) that the "resin" obtained from pine by extraction with an alcohol-benzene mixture included a compound which resembled hydrochloric acid lignin in some respects.

According to Harris (131) lignin could not be extracted from freshly cut aspen wood with ethanol. However, if the wood had been air-dried, two persent of the lignin could be extracted with ethanol. In addition, with wood which had undergone attack by the fungus "blue stain", the lignin yield was increased to 3.3%. These results led Harris to conclude that the solubility of protolignin in alcohols depended upon a preliminary hydrolysis of some component in the wood. This investigator has also determined a few of the properties of this solvent-extracted lignin, and, from the data available, it appears that the isolated lignin was similar to the material isolated by Brains (129). Both Harris and Brauns have found that lignins obtained by such solvent-extraction procedures can be methylated with methanolic hydrochloric acid.

The addition of sodium ethylate to absolute ethanol was found by Campbell (143) to have no effect upon the quantity of lignin which could be extracted from wood.

4. Effect of Alcohol-Water Solutions on Wood.

From experiments dealing with the cooking of aspen sawdust with 50% aqueous solutions of aliphatic alcohols, Aronovsky and Gortner (144) concluded that primary alcohols were good "pulping agents". The results obtained by treating wood meal with various solutions at 160-175°C for 4 hours is shown in the following Table VII.

TABLE VII

The Effect of Alcohol-Water Mixtures

on the Constituents of Wood

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Extraction Agent	Wood Residue (%)	C ₆ H ₆ EtOH Extractable (%)	Lignin Content of Residue (%)	Lignin Removed (%)a	Pentosans Removed (%)a	a-Cellulose Removed (%)a
H ₂ 0	63.4	9.5	13.5	45	85	25
MeOH-H ₂ O	70.2	5.2	9 • 8	57	50	1
EtOH-H20	62.5	8.9	7.7	70	65	8
m-PrOH-H20	60.0	4.8	5.5	78	75	8
n-BuOH-H2O	54.4	0.8	3.0	88	77	18
n-AmoH-H ₂ 0	51.5	1.4	4.3	82	84	18

(%)a = Percent of component present in untreated wood

1 63

1

By comparing these results with those given in Table V, it can be seen that alcohol-water mixtures are less destructive of wood pentosans and cellulose than is water alone. When urea (10%) was added to the butanol water mixture, the extent of pentosan degradation was reduced considerably and the lignin and cellulose content of the residual wood was equivalent to that obtained by treatment with ethanol-water. The lignin isolated from the alcohol solutions (a) contained no additional alkoxyl groups and (b) was very soluble in the common organic solvents (benzene and ether excepted).

A study of the action of butanol-water solutions (158°C: 7 hrs.) on hard-and-softwoods was carried out by McMillen, Gortner, Schmitz, and Bailey (133). A marked distinction in pulping characteristics between the two classes was found, but within each class, the different woods showed similar properties (Table VIII).

TABLE VIII

Components Components Originally Present Removed Wood Pentosan Lignin Pentosan Lignin % %(a) %(a) 19.4 15.5 90 84 Aspen Silver Maple 22.2 16.9 87 82 28.2 7.0 White Spruce 60 50 Jack Pine 25.9 6.8 70 58

The Effect of Butanol-Water (50%) on Wood

%(a) = Percent of component in untreated wood

Bailey (134), in an attempt to determine the reason for this marked difference in behavior between soft- and hardwoods studied the effect of butanol-water solutions (158°C; 7 hours) on aspen and jack pine. He claimed the extracting solutions were neutral because they had been buffered at room temperature prior to use; and as a result of this neutrality, no hydrolysis occurred during the cooking treatment*. Under these conditions all of the lignin in aspen and 80% of the lignin in jack pine was removed. Since

* This claim is open to serious question in view of the appreciable lowering in pH which takes place in aqueous extracts at high temperatures. the lignin remaining in the latter wood could be isolated by means of an additional extraction with alkaline butanolwater solution, Bailey concluded that part of the lignin in softwoods and none of the lignin in hardwoods was chemically combined with cellulose. However, since cellulose and pentosans were dissolved (degraded) during the extraction with the "neutral" solution, it is apparent that hydrolysis must have occurred.

Kleinert and Tayenthal (135) carried out an extensive investigation on pulping wood with ethanol-water mixtures. By varying the water content of the alcohol-water mixture it was found that the maximum lignin removal was accomplished with a solution containing 45% ethanol at 190° in 3 hours. When wood was treated under these conditions the cellulose was only slightly decomposed. With increasing water content of the extraction liquor an increased formation of simple reducing sugars, cleavage of organic acids, and formation of furfural and other volatile products was observed. It was also found that the decrease in α -cellulose content of the wood residue was more dependent upon the water concentration than upon the temperature. Apparently changes in physical state and hydrolytic action are involved.

Since the lignin obtained from spruce contained 15.9% alkoxyl (calculated as methoxyl) and 15.6% methoxyl, no alkoxylation of the lignin had occurred.

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5. The Effect of Alcohol-Water-Alkali Solutions on Wood.

Both Bailey (136) and Kleinert (135) studied the effect of adding alkali to the aqueous-alcohol extraction medium. Mention has already been made of Bailey's work in which the presence of alkali was required to effect complete removal of the lignin from jack pine (134). This author also found that the presence of 2% NaOH in butanol-water (50%) mixtures accelerated the rate of delignification about 5-16 times (136). Pulps containing only 0.33% lignin were obtained in yields of 43-50% by cooking aspen for 15 minutes at 186°C with this squeous butanol-alkali mixture. The delignification of jack pine was less complete, since a two-hour treatment left a wood residue (37%) with a lignin content of 1.9%. The data from the jack pinepulping experiments led Bailey to conclude that the process consisted of one minor reaction (cleavage of the combined lignin from cellulose), and two major ones (condensation of butanol with lignin and hydrolysis of the cellulose). Unfortunately, this investigator published no experimental evidence indicating the formation of a ligninbutanol complex; consequently the accuracy of these conclusions is questionable.

A brief survey of the physical and chemical properties of butanol lignin has been made (135). The carbon and hydrogen contents were generally similar to those of other lignin preparations. The only functional groups present were <u>methoxyl</u> and <u>hydroxyl</u>. The methoxyl content was about 18-20% in the hardwood - and 15% in the softwood lignin. Methylation of butanol lignin (aspen) with dimethyl sulfate raised the methoxyl content from 19.7 to 31.6%. Bailey also stated that butanol lignin could be fractionated by molecular distillation, but this work has not been confirmed (136).

An ethanol-water-sodium hydroxide (pH 13) solution has been employed as a pulping reagent for bagasse (137), and the absnce of ethoxyl groups in the isolated lignin established. This latter observation confirmed a similar one obtained by Kleinert and Tayenthal (135).

Practically complete removal of the pentosans occurred in all of the above experiments.

6. The Effect of Alcohol-Water-Acid Solutions on Wood and Isolated Lignins

The addition of mineral acids to aqueous-alcoholic pulping solutions greatly accelerates the rate of decomposition of the polysaccharide constituents of wood (135). As a consequence, such solutions have been frequently employed as lignin-extraction reagents. The experimental procedure for the alcoholysis of wood when this type of

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extractant is used is generally quite different from that used with alcohol-water or alcohol-water-alkali treatment.

Instead of high temperature (170-190°C) and pressure treatments, lower alcohol-reflux-temperatures (63-120°C) at atmospheric pressure are employed.

In the method of Friedrich and Diwald (8), resin and gum-free wood meal (Pre-treated with ethanol-benzene. followed by 5% NaOH) was intimately mixed with an equal weight of 20% aqueous hydrochloric acid. After this mixture had remained at room temperature for 48 hours a large volume of 96% ethanol was added and the resulting suspension heated at reflux temperature for 8-10 hours. Only 20% of the lignin in spruce wood could be isolated. It was found that if all of the acid were removed from the wood prior to the addition of the alcohol, little or no lignin could be extracted with hot ethanol. The alkoxyl content of the lignin obtained from spruce wood was 26.9% (calculated as methoxyl), but if a sample of lignin were suspended in concentrated hydrochloric acid for several days and then washed free of acid with water, the methoxyl content dropped to 16.5%.

Later, Friedrich and Bruda (130) found that approximately 90% of the lignin in beech wood could be removed by repeated treatments with alcoholic hydrochloric acid (5%) solutions. If the extractant contained about 10% hydrochloric acid it was found that the alkoxyl content of the isolated lignin (spruce) dropped from 20.9 to 15.7% (calculated as methoxyl). These investigators isolated the beech lignin by precipitating the concentrated alcoholic extract into water. After removal of the lignin, it was shown that the aqueous solution contained only a trace of methoxyl-containing material.

The significance of the abnormally high alkoxyl content of Friedrich's lignin preparation was explained by Hagglund (30b) who established the presence of ethoxyl groups in ethanol lignin. Ethanol lignin (spruce), prepared by the method of Friedrich (130), contained 20.9% alkoxyl (calculated as methoxyl) and 12.45% methoxyl. On an ethoxyl-free basis, the latter value is increased to 14.2% which value is in agreement with the methoxyl content of Klason-, hydrochloric acid-, and alkali lignins (spruce).

Iso-butanol and iso-amylol in the presence of aqueous hydrochloric acid were used as lignin extraction agents by Hägglund and Urban. The conditions employed by these investigators differed from those used by Friedrich in that the wood was treated directly with the alcoholaqueous hydrochloric acid solution. For example, in the preparation of iso-butanol lignin (spruce), 40 g. of spruce wood meal was suspended for 2 hours in a refluxing solution which contained 400 g. of butanol and 50 cc. of 37% aqueous hydrochloric acid. Approximately 60% of the lignin was removed from the wood, and by repeated treatments a total of 85% of the original Klason lignin content of the wood was extracted (the final wood residue, however, represented only 22% of its original weight). The lignin isolated by this procedure was very soluble in acetone, acetic acid and ethanol but only very slightly soluble in ether. The abnormally high alkoxyl content found by Friedrich was confirmed by Hagglund and Urban, but the latter investigators, upon further examination of the nature of alkoxyl content, found that only a fraction was present as methoxyl groups. The total alkoxyl content was determined by the method of Zeisel (141) and the methoxyl content alone by the procedure of Willstätter and Utzinger (143). Values of 9.26% methoxyl and 16.4% butoxyl were obtained. The addition of the extraction solvent was also found to occur with iso-amyl alcohol, and this phenomenon was attributed to the formation of acetals and half-acetals between carbonyl groups in the lignin and the appropriate alcohol. These investigators interpreted these results to mean that the carbonyl groups in lignin were originally combined to hydroxyl groups in the cellulose and that the extracting agent, in the presence of hydrochloric acid, first hydrolyzed the acetal linkage

and then immediately combined with the free carbonyl to form the alkylated lignin.

Support for this theory was weakened when these same investigators later discovered that isolated acid - and alkali lignins could be partially dissolved in acidified ethanol and butanol solutions to give products containing varying quantities of ethoxyl and butoxide (190). Hydrochloric acid lignin (spruce) was separated into two fractions by means of a four-hour treatment with 3% aqueous ethanolic hydrochloric acid at 78°C. The alcohol-soluble fraction (80% of the original lignin) contained 11% methoxyl and 8.1% ethoxyl; and the alcohol-insoluble, 14.5% methoxyl and 6.0% ethoxyl. It was also found that fully-methylated (dimethyl sulfate and sodium hydroxide) hydrochloric acid lignin (spruce) (29.5% methoxyl) could be partially dissolved in an acidified solution of amyl alcohol. The insoluble portion obtained from the reaction mixture contained 20.2% methoxyl and 14,85% amyloxide. A lignin fraction with methoxyl and ethoxyl contents of 26.0 and 7.6% respectively, was obtained by the ethanolysis of fully-methylated spruce wood.

In order to avoid the necessity of analyzing lignin samples for both methoxyl - and ethoxyl-content, Friedrich replaced the ethanol solvent by methanol (125). On the assumption that spruce lignin contained 14.5% methoxyl, any

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increase in methoxyl content over that value was attributed to methylation of the lignin by the methanol-hydrochloric acid mixture. This investigation was carried out to determine (a) the conditions under which the alcoholysis procedure yielded lignin preparations with maximum alkoxyl content; (b) the influence of the absence of water on the isolation of lignin, and (c) the stability of the isolated lignin preparations toward alkali. From a series of experiments in which the water content, acid concentration, and time of treatment were varied Friedrich found that absence of water contributed only slightly toward increasing the methoxyl content of the lignin. On the other hand, the duration of the treatment with the acidified alcohol solution was of greater importance. For example, the same result was not obtained when wood was boiled with methanolic hydrochloric acid and the dissolved lignin precipitated immediately, as when the dissolved lignin was left in contact with the acidified solvent for a longer period at room temperature. The latter treatment with water-methanol (80%) yielded a product of higher methoxyl content than the former did using absolute methanol. A combination of the two treatments, i. e., absolute methanol for a long period of time, gave a maximum methoxyl content of 23.2%. The methoxyl

content of the other preparations varied from 19.5 to 22.2%. Friedrich concluded from his experimental results (a) that the addition of the alkoxyl group was a secondary reaction between the lignin already dissolved and the solvent, and (b) that this addition reached its maximum value only after 20 hours.

By treating the isolated methanol lignins with warm 1.5N sodium hydroxide solution, Friedrich found that the methoxyl content of the lignin was lowered. The quantity of methoxyl lost by this "saponification" varied with the different preparations; but, as a rule, fifty percent of the methoxyl content which had been added during the isolation process could be removed in this manner. These results led this investigator to suggest that carboxyl groups were present in protolignin, but King and Hibbert (153), by repeating Friedrich's work, found that the carboxyl groups were formed during the alkaline "degumming" pre-extraction of the wood. This oxidation did not occur, however, when an atmosphere of nitrogen was employed during the extraction process (153).

As a result of a study of the ethanolysis of Sitka spruce Campbell (143) concluded that when wood is treated with alcoholic hydrochloric acid, the hydrolysis of the polysaccharides and of a small portion of the lignin takes place independently of the action of acidified alcohol on

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the main body of the lignin. That is, in the presence of acid, alcohol reacts with a portion of the lignin to form a soluble product, the rate of formation of which does not synchronize with the rate of hydrolysis of the polysaccharides. The observations of Friedrich (125) which indicate that a decrease in water content of the alcoholysis reagent resulted in an increase of alkoxyl content of the isolated lignin was confirmed by Campbell.

7. The Effect of Anhydrous Alcohol-Hydrogen Chloride Solutions on Wood and Isolated Lignins

Since it is practically impossible to remove all of the water from wood, no ethanolysis reaction has ever been run under absolutely anyndrous conditions. Although this condition has been approached by several workers, the major proportion of the investigations have been carried out by Hibbert and co-workers.

Brauns and Hibbert (112), were able to extract twenty-five percent of the lignin from wood by treating carefully-dried spruce wood meal with anhydrous methanolic hydrogen chloride (2%) at 80-90°C for 80 hours. At the end of this treatment the lignin was isolated by precipitating the concentrated methanol solution into a large excess of water. Analysis of the lignin preparations from different experiments gave methoxyl contents varying from 21.6 to 22%. The mother liquors from the methanol-water precipitationswere evaporated to a thick syrup (40% of the original weight of wood) which was found to be essentially carbohydrate in nature. Further examination of this syrup showed the presence of a component having a methoxyl content of 17.5%; this material was not investigated, however.

Preparation of methanol lignin by the method of Brauns and Hibbert, on a larger scale than that employed previously, disclosed the presence of a second fraction which was soluble in ether-dioxane (154). The original methanol lignin (21.0% methoxyl) and this new fraction (23.9% methoxyl) were separated by solvent fractionation with dioxane and benzene, and two fractions were obtained, in approximately equal proportions. However, in a methanolysis run at 70-75°C (instead of 90-100° as in the previous example), the yields of the ether-soluble fraction was very small (154). Apparently the use of a higher temperature in the first example resulted in the formation of a relatively large proportion of a more soluble form of methanol lignin.

An extraction of methanol lignin carried out in an open flask at 66°C with anhydrous methanolic hydrogen chloride (2%) gave a poorer yield of a crude methanol

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lignin containing 22.7% methoxyl (112).

Brauns and Hibbert (121k) also found that hydrochloric acid lignin (14.5% methoxyl), diazomethanemethylated hydrochloric acid lignin (21.2% methoxyl), diazomethane-methylated cuproxam lignin (20.2% methoxyl), and fully-methylated cuproxam lignin (30.1% methoxyl) would dissolve almost completely in 2.5% methanolic hydrogen chloride when treated at 80-100°C for 20-50 hours. The lignin preparations thus obtained contained 22.4, 24.4, 25.4, and 29.7% methoxyl, respectively. Fully-methylated spruce wood meal (38.8% methoxyl) yielded a lignin preparation which contained 29.7% methoxyl when treated in the same manner.

It is of interest to note that all of the methylated lignin preparations mentioned above were insoluble in methanol prior to the methanolysis reaction. In fact, the methylated lignin preparations were insoluble in all organic solvents. The methanol-soluble fractions obtained from the methanolysis reaction, however, were soluble in dioxane and acetone as well as methanol.

8. Summary of Data on the Alcoholysis of Wood

The following summary of the data presented herein seemingly indicates that the alcoholysis process can be divided into two types; in one process, alcohol-water

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solutions (with or without dilute alkali) are used, and in the other, alcohol-acid solutions (with or without water) are employed.

(a). Lignin can be removed from wood by alcohols when (a) an approximately equal volume of water is present and temperatures of about 180°C are employed or (b) when mineral acids are present and temperatures of 65-120°C are used.

(b). Practically all of the pentosan content of the wood is extracted by either process.

(c). In addition to the pronounced difference in yields of isolated lignin obtained by the alcohol-water and the alcohol-acid extraction processes, it is also observed that the extent and direction of the polysaccharide hydrolysis varies considerably. In general, it is found that all of the pentosans and only a portion of the cellulose is extracted by means of a treatment with alcohol-water. On the other hand, when alcohol-acid solutions are employed the pentosan loss may be as low as 70% and the cellulose dissolution as high as 40%. In other words, when wood is extracted with alcohol-water solutions a relatively high yield (60%) of pulp containing only small amounts of lignin (hardwoods, 1-3%; softwoods, 10-13%) and practically no pentosan material is obtained. When alcoholacid solutions are used, the wood residue generally contains a considerable quantity of lignin (hardwoods 8-17%; softwoods, 15-25%) and small quantities of pentosan material (1-3%). In addition, in the latter case, the a-cellulose content is usually very low. (d). Approximately 90% of the lignin can be removed from hardwoods and 60-70% from softwoods with aqueous alcohols. The addition of dilute alkali to the extraction solution facilitates the complete removal of lignin from softwoods.

(e). Alkoxylation of the isolated lignin does not occur during the alcohol-water or alcohol-water-alkali extraction process.

(f). <u>Identical</u> results are not obtained when⁽¹⁾wood is heated at 180°C with water, followed by an alcohol-benzene extraction (40% of the lignin dissolved) as when⁽²⁾the wood is treated with 50% aqueous ethanol (70% of the lignin is extracted). However, in view of the fact that the alcoholbenzene extraction is carried out at 80°C as compared to 180°C for the ethanol-water treatment, it would appear that the alcohol-water alcoholysis procedure is composed of two main reactions. The first is one of hydrolysis of all of the pentosan material and swelling and hydrolysis of the cellulose by the water; and the second, one of dissolution of the lignin by the alcohol.

(g). All of the lignin cannot be removed from wood by means

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of the alcohol-acid (1-2%) procedure. In order to isolate the lignin from an ethanolysis wood residue it is necessary to employ concentrated acid solutions (preferably aqueous). The latter treatment causes a pronounced degradation of cellulose.

(h). The extent to which alkoxylation of the isolated lignin occurs in the presence of acid varies directly with the duration of the treatment and inversely with the concentration of water.

(1) The alcohol-acid process cannot be separated into two distinct reactions since, apparently, the simultaneous presence of both the acid and the alcohol is required.
(j) A possible mechanism for the acid-alcohol process is as follows: When wood is extracted with an alcohol-acid solution at least two main reactions take place simultaneously. First there is hydrolysis of the carbohydrates, influenced by the presence of the alcohol, and secondly, there is the interaction between protolignin and alcohol (solution and combination) influenced by the hydrogen chloride. Both reactions are influenced in turn by the presence of water.

(k) Alcohol insoluble lignins and methylated lignins upon treatment with alcoholic-acid solutions, are partially transformed into alcohol-soluble alkylated lignins. In the case of the acid methanolysis of fully-methylated spruce

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lignin the final product has the same methoxyl content as the original insoluble product; therefore, it would appear that the change in solubility is due to a structural change in the lignin.

C. The Ethanolysis of Wood According to Hibbert

The belief that lignin (isolated and protolignin) existed only as highly-polymerized, complex substances led investigators to conclude that the water-insoluble amorphous product obtained by means of the customary extraction methods was the only form in which lignin could be isolated. Precipitation into water from concentrated alcohol, acetic acid, or dioxane solutions has been practically an invariable step in the isolation of lignin and its purification; and the efficiency of an extraction process has been almost always judged by the amount of water-insoluble product formed.

Prior to the development of the ethanolysis lignin-extraction procedure by Hibbert and co-workers, the aqueous precipitating liquors had been examined only twice; namely, by Friedrich (130) (methanolysis of beech) and by Brauns and Hibbert (112) (methanolysis of spruce). The former investigator isolated a small amount of lignin which apparently had been suspended in the water as a sol, and only minute traces of methoxyl-containing material were found in true solution in the concentrated aqueous liquors. Brauns and Hibbert also found only a small quantity of methoxyl-containing material in these liquors.

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When it was observed, however, that the sum of the weight of water-insoluble, amorphous alcohol lignin plus the weight of Klason lignin present in the alcoholysis wood residue was almost always less than the weight of the Klason lignin in the original untreated wood, Hibbert became interested in the reason for this discrepancy. The solution of this problem was found when Cramer, Hunter, and Hibbert (78, 80) showed that this loss in weight was due (in the case of the ethanolysis of spruce and maple woods) to the water-solubility of a large proportion (12% of the total lignin, spruce; 30-35%, maple) of the methoxylcontaining materials.

As a result of this important observation an extensive series of investigations was started immediately in these laboratories to determine (a) the structure of the components of the water-soluble fraction, (b) the factors involved in the formation of this fraction, (c) the significance of the simple compounds isolated therefrom with relation to the structure of the amorphous, water-insoluble ethanol lignin, and (d) the significance of the simple units with relation to photosynthesis, plant respiration, and the formation of protolignin.

The essential features of the ethanolysis procedure are shown in Flow Sheets I, II, and III (see p.167).

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It is noteworthy that the sum of the weights of the lignin fractions obtained by means of the Sthanolysis procedure represents about 120% of the Klason lignin content of the original wood. This apparent discrepancy is readily explained by the fact that ethoxylation (or ethylation) of the lignin occurs to an appreciable extent. For example, the ethoxyl content of water-insoluble, ethanol lignin (Fraction B in Flow Sheet I) is about 9.1%.

The ethanolysis extraction procedure, when extended to Douglas fir, redwood, red oak, bamboo, jute, cornstalks, and rye straw, gave rise to the typical ethanolysis products, viz., ethanol lignin and a mixture of distillable oils (152). The yields of these products were of the same order of magnitude as those obtained from spruce and maple woods. The establishment of the presence of the syringyl radical in the volatile oils from jute, rye, corn, and red oak confirmed Hibbert's hypothesis that this grouping was common to all angiosperms. Brown, Heddle, and Gortner confirmed the results obtained by Hibbert and co-workers by applying the ethanolysis reaction to a group of western softwoods (148)

The question of whether the C_6-C_3 units could be obtained from an isolated lignin was settled by Peniston, McCarthy and Hibbert (147). These investigators refluxed an acetylated oak lignin with anhydrous ethanolic hydrogen chloride (2%) for 15 hours. The reaction products were isolated in the manner already described. The crude oils, which amounted to 36% of the acetylfree lignin content of the starting material (acetylated lignin), were separated into four fractions whose characteristics were very similar to those obtained by the action of ethanolic hydrogen chloride on maple wood.

A study of the effect of ethanolic hydrogen chloride on the amorphous ethanolysis products obtained from maple wood has been made by West, Hawkins and Hibbert (149-150). One-gram samples of Fractions B, C, and F (See Flow Sheets I and III) were treated with ethanolic hydrogen chloride (2%) according to the standard ethanolysis procedure (151). The oily residue obtained by concentrating the neutralized alcoholic extract was dissolved in 10 cc. of acetone, and this acetone solution was then precipitated into 60-70° petroleum ether. The results obtained by means of this treatment are shown in Table IX.

TABLE IX

The Effect of Ethanolic-Hydrogen Chloride (2%)

Ethanolysis Fraction	Reduced Viscosity (a)	Petrol Soluble (b) %	Petrol Insoluble (c) %	Viscosity of Pet. Insol.
В	600	10	90	
C	4 69	22	75	541
F	389	30	69	538

on Ethanolysis Fractions

(a) Reduced Viscosity = $\frac{\text{Specific Viscosity}}{\text{Concentration}} \times 10^5$

(b) Contains the distillable oils.

(c) Equivalant to Fractions B, C and D, combined. "See Flow Sheet I"

It has already been mentioned that the extent to which alkylation occurs during the alcohol-acid extraction process increases with the duration of the treatment. In addition Hewson, McCarthy and Hibbert (150) have found that the ratio of water-soluble ethanolysis oils to water-insoluble, amorphous ethanol lignin increases with increased duration of the alcoholysis (up to 48 hours).

Summary of Ethanolysis Data

1. All plant materials which have been studied thus far undergo the ethanolysis reaction and yield distillable water-soluble lignin derivatives. 2. The amorphous, water-insoluble ethanol lignin fractions also yield distillable, water-soluble compounds when treated with ethonolic hydrogen chloride (2%).

3. The ratio of the distillable fraction to the non-distillable fraction obtained from non-distillable ethanolysis products by treatment with ethanolic hydrogen chloride (2%) increases with (a) decrease in viscosity and (b) increase in solubility of the original non-distillable materials.

4. This same ratio increases with the duration of the ethanolysis treatment (up to 48 hours).

IV. THE HIGH-PRESSURE HYDROGENATION OF ORGANIC COMPOUNDS IN THE PRESENCE OF COPPER-CHROMIUM OXIDE AND RANEY

NICKEL CATALYSTS

Hydrogenation processes have been steadily increasing in size, variety and importance, and the unit process of hydrogenation is becoming one of the most useful and widespread in organic synthesis. A discussion of even a few of the many important industrial hydrogenation processes is out of place in this thesis, instead the discussion in this section is limited to hydrogenation reactions adaptable to laboratory investigations. Even more specifically, this discussion is concerned with those phases of high-pressure catalytic hydrogenation reactions and technique which bear specifically on its utilization as a tool in the investigation of the structure of lignin.

Hydrogenation is correctly defined as reduction by means of molecular hydrogen; actually, however, the term has grown to include the reduction by means of molecular hydrogen <u>in the presence of a catalyst</u>. In addition, catalytic hydrogenation or, more commonly, hydrogenation may be divided into two classes; namely, high pressure (above 50 atmospheres) and low pressure by hydrogenation.

A. Variables (Physical Factors) Affecting Hydrogenation

The most difficult problem involved in the application of hydrogenation technique to industrial or laboratory problems has been the determination of the optimum conditions for the production of a desired product. In the study and application of hydrogenation reactions it is essential to realize that the reactions are reversible. Thus Raney nickel, (168) which is one of the best catalysts for the reaction:

Benzene + $3H_2$ = Cyclohexane

is also one of the best dehydrogenation catalysts for the production of aromatics from hydroaromatics (169). Similarily, catalysts containing copper and copper oxide which are especially useful in the reduction of aldehydes to alcohols (71, p. 50) are used commercially for the production of aldehydes from alcohols (170, p. 431). It is for this reason that changes in any given variable are so important in hydrogenation.

Of the many variables involved, the most important (exclusive of choice of catalyst) are temperature, pressure, time, solvent, concentration and quantity of catalyst.

I. Temperature

For the most part, the temperatures used for hydrogenation reactions are usually below 400°C, except in cases where pyrolytic decomposition occurs concurrently with hydrogenation as in the hydrogenation of coal at 500°C (171). It may be mentioned at this point that hydrogenolysis, which, like hydrolysis, is a cleavage of a molecule by hydrogen in the presence of a catalyst is not to be confused with pyrolysis, or cleavage due to heat energy.

Practically every hydrogenation reaction can be reversed by increasing the temperature high enough (170, p.411); obviously, then, it is desirable to work at as low a temperature as possible. On the other hand, increasing the temperature increases the speed of the reaction. It therefore becomes necessary to balance the less favorable equilibrium position with the faster rate of reaction. Fortunately, in recent years, knowledge of catalysis has been so extended that satisfactory reaction rates are possible at lower temperatures where a more favorable equilibrium condition prevails.

Concerning the temperature coefficient of hydrogenation reactions, almost none fit the generalized statement that the speed of a reaction may be doubled every 1-15° rise in temperature, a change of 50° or more being usually necessary.

In general, the noble metal catalysts, such as Pt or Pd are used from room temperature to 150°; catalysts of the Ni and Cu type, from 150 to 250°; and various

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combinations of metals and metal oxides, from 250-400°.

2. Pressure

Pressure, like temperature, can affect both the rate of reaction and the equilibrium position. The equilibrium, however, is only noticeably affected when there is a decrease in the reaction volume as it proceeds (Le Chatelier's principle). Increase in rate with pressure increase is generally observed due to concentration effect. If the reaction is in the gas phase the concentration of one of the reactants has been increased; if in the liquid phase, the solubility of hydrogen in the liquid is increased, thereby increasing the effective hydrogen concentration. Several other factors are also involved, for there appears to be a considerable difference between compounds with respect to the effectiveness of increased pressure in accelerating the reaction rate. The following figures for the hydrogenation of aniline, phenol and acetoacetic ester (AAE) over Ni(K) (Ni on Kieselguhr) illustrate this condition (172): (TABLE X).

_		Extent of React	ion (%) in	Specified Time
	Pressure (Atm.)	Benzene (0.5 hr.)	Aniline (6 hrs.)	AAE (0.5 hr.)
	30	40	29	40
	200	68	60	72
	350	75	75	100

TABLE X

Of major importance, however, is that increase in pressure is almost always desirable.

3. Time

The importance of the time factor lies chiefly in the fact that all other variables remaining constant, the time necessary for a hydrogenation may vary from a few seconds to several hours depending upon the material being hydrogenated. In the laboratory this factor is outstanding chiefly as an additional means of promoting a selective hydrogenation.

4. Solvent

When a solid material is to be hydrogenated, the choice of solvent becomes an important one. Obviously, a given solvent must be stable to hydrogenation conditions and be used below its critical temperature. That the solvent can and does affect the rate of hydrogenation was shown by Adkins in the case of ethyl nicotinate at 165° over RaNi (Raney Nickel) where the solvents were ethanol, methylcyclohexane, ethyl ether and dioxane. The hydrogenation times were 3, 1.5, 5, and 1 hour and the yields of product were 58, 80, 80 and 77%, respectively (173). With CuCrO and RaNi, ethanol, dioxane, ethyl ether and methylcyclohexane have been found quite satisfactory as solvents (70, p.25).

5. Concentration

Changes in concentration of a solid in solution effect the hydrogenation to a marked extent only if the material is complex and side reactions are possible. It is of interest to note, however, that whereas a 10% solution of ethanol lignin in dioxane hydrogenated readily at 250°C, an 18% solution underwent a slight change only (174).

Of considerable interest in this respect are the results obtained by Cooke, McCarthy and Hibbert (174) in the hydrogenation of veratraldehyde, XXXXVII, at 180°C at 1100 psi. hydrogen pressure. When this reaction was run with a solution containing 43.2 g. of veratraldehyde in 150 cc. of dioxane (350 cc. void), three products were obtained; namely, veratryl alcohol XXXXVIII, (55%), homoveratrol XXXXIX (40%), and a trace of a crystalline compound (2%) melting at 74-75°C of the probable structure represented by L (175). When the concentration of veratraldehyde (from the same preparation) was increased to 66 g., however, only two products were obtained; namely, veratraldehyde (55%) and the crystalline compound (40%).

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6. Ratio of Catalyst to Acceptor

Although one might expect the concentration of catalyst to play a minor role in hydrogenation this is not found to be the case. This condition is due to the fact that all hydrogenation catalysis is based upon surface activation and is therefore dependent upon the amount of surface. Adkins makes the following statement "500 g of compound with 25 g of a catalyst will be hydrogenated very much more rapidly than would 50 g of a compound with the same ratio of catalyst (2.5 g) (71, p.22). It has been observed frequently in these laboratories that an increase in quantity of catalyst will appreciably increase the rate of a hydrogenation reaction (174, 176). It may be of interest to note that in a typical lignin hydrogenation the ration of lignin to CuCrO is 15/8. For simple

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compounds such as acetone or benzene, however, the amount of catalyst generally ranges from 2-8% of the weight of acceptor. The following table shows the change in hydrogenation rate of benzaldehyde over Pt; 21.2 g of benzaldehyde was used and the time to 100% reduction determined (177).

TABLE XI

of The Effect/Catalyst Concentration on

Duration of Hydrogenation

Weight of	
g•	<u> </u>
0.0288	5.5 hrs.
0.0575	60.0 min.
0.115	34 . 0 "
0.23	23.0 "

B. Hydrogenation Catalysts

1. Principles Concerning Hydrogenation Catalysts

(a). Surface

Hydrogenation catalysts are solids consisting of metals, metal oxides, or metal sulfides which are prepared in such a manner that a highly extended surface is obtained. A consideration of the nature of surface catalysis is out of place in this thesis*; but it is of importance to note that this extensive surface is only effective when obtained by chemical and not mechanical means. In other words the phenomenon of adsorption plays a very important role and a porous material whose particles are of atomic size is essential. A good example of a catalyst preparation is that for Raney nickel (157). In this procedure the catalyst is prepared by alloying equal parts of nickel and aluminum and then dissolving out the latter with aqueous sodium hydroxide. The principle is quite clear; firstly, the aluminum atoms are removed from a solid "solution" of nickel-aluminum, leaving an atomic latticework composed of nickel, secondly, this very reactive form

*An excellent review on the subject of hydrogenation catalysis is presented in the "Twelfth Catalysis Report", Wiley (1940) of the (U. S.) National Research Council (1-131) of nickel is protected from oxidation by the presence of the hydrogen formed during the dissolution of the aluminum. This catalyst is stored in a liquid (water, ethanol, etc.) to prevent reaction with the air, for as soon as it becomes dry in the presence of oxygen it oxidizes with explosive repidity (176).

(b). Mixed Metal Catalysts

Catalysts are easily poisoned and must be prepared very pure, although it has been found that when completely pure, some catalysts have a reduced activity. By careful study of this problem by many investigators it has been found that certain metals in the presence of a catalyst produced promoting effect. For example a small amount of chlorine or sulfur will render a copper catalyst used for the dehydrogenation of methanol completely inactive (178), while the addition of about 3% of zinc oxide to a pure copper catalyst will increase the activity threefold (179). The use of mixed metal catalysts, or promoted catalysts, has been extended rapidly in recent years. More common mixtures of the wellknown types of catalysts are Ni-Cu (184), NiAl 203 (186), Cu-ZnO (187), Cu-CrO (188), ZnO-CrO (185). However, the recent chemical and patent literature describes the use of practically every metal and metallic oxide in the periodic table.

The number of catalysts capable of effecting hydrogenations is large, and in addition many types of hydrogenation are possible. Practically any type of unsaturated material can be hydrogenated catalytically. It will be pointed out that hydrogenation may involve the saturation of C=C, C=C or C=O linkages; the reduction of a carbalkoxyl, hydroxyl, nitro and cyano groups, and also the cleavage of C-C and C-O bonds. In general, however, hydrogenation catalysts may be classified as follows:

(a). Violent Hydrogenation Catalysts

These catalysts are usually characterized by the fact that they carry the hydrogenation to the fullest possible extent so that the maximum addition of hydrogen to a compound occurs under the particular operating conditions. Thus in the case of the simple aldehydes the reduction will pass beyond the alcohol stage and end at the saturated hydrocarbon. Even here, the tendency to saturate the carbon atoms may be sufficiently great to cause cracking, or to break the C-C bond so that still more hydrogen can be added, the final result being CH₄. Cracking tendencies are usually associated with these violent hydrogenation catalysts, although through control of the variables of temperature and pressure, the cracking reactions can usually be suppressed. Common catalysts belonging to this class usually consist of the iron, cobalt and nickel compounds (189, p.107) and oftimes of molybdenum and tungsten sulfides and oxides (189, p.111).

(b). Mild Hydrogenation Catalysts

The term mild should not be confused with activity. These catalysts will effect hydrogenations just as rapidly as the violent hydrogenation types, but they are able to effect only one step at a time in a hydrogenation, or at least they do not permit the reaction to proceed to the hydrocarbon stage. A great many catalysts belong to this class, and more are being developed rapidly. These catalysts will easily reduce an aldehyde or ketone to the corresponding alcohol, or an acid or ester to an alcohol. The large number of catalysts developed for the direct synthesis of methanol from carbon monoxide belong to this class and they usually contain Cu, ZnO, CrO and MnO (182) and may include some of the rarer elements as promoters. In addition, the noble metal catalysts platinum and palladium. or their oxides are placed in this category.

(c). <u>Catalysts with Properties other than those</u> Associated with Hydrogenation

The synthesis of higher alcohols from carbon monoxide involves a condensation as well as hydrogenation.

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These so-called "higher alcohol" catalysts are usually of the mild hydrogenating type but contain some more alkaline materials such as sodium, calcium or barium carbonates or aluminum and magnesium oxides (181). Other types of catalysts are capable of splitting out water from a molecule along with the hydrogenation but do not possess any appreciable cracking tendencies. These usually are of the violent type but contain considerable, and sometimes even preponderating quantities of dehydrating catalysts such as alumina, thoria, tungstic oxide, or chromic oxide (189, p.127). They serve to effect such reductions as phenol to benzene and cresols to aromatic hydrocarbons and convert various hydroxylic compounds to hydrocarbons with little or no other changes in the molecular structure.

C. Types of Reaction with Hydrogen

In laboratory high-pressure hydrogenation technique (specifically in these laboratories) two catalysts are generally employed - one from the "violent" category, RaNi; the other from the "mild" division, CuCrO. This section will be devoted essentially to the behaviour of various type compounds over these two catalysts.

1. Hydrogenation (Reduction)

(a). Hydrogenation of Ethylenic (C=C) Linkage

The hydrogenation of an ethylenic to a paraffinic linkage can be accomplished readily, usually in the presence of a Ni or Ni-containing catalyst. In general, the hydrogen pressure need not be high, except when the hydrogenation is slow, and then increased pressure usually speeds up the reaction. With RaNi it is safe to say that relatively few alkenes would resist hydrogenation at 100°C. and 100 atmospheres pressure. CuCrO is also an active catalyst for the hydrogenation of alkene linkages, but since higher temperatures (100-175°) are required, there appears to be little advantage in its use for hydrocarbons except where some other group such as carbonyl or carbethoxyl is to be hydrogenated. It is often advantageous to combine the two hydrogenations and use CuCrO to bring about both effects.

Exam	oles	:
------	------	---

Substance	Press. Atm.	Temp. oC.	Time Min.	Catalyst	Product	
Styrene	3	20	75	N i (K)	Ethylbenzene	(190)
Styrene	34	20	25	Ni(K)	Ethylbenzene	(190)
Styrene	34	125	7	CuCrO	Ethylbenzene	(190)
Cinnamyl Ethyl Ester	200	250	180	CuCrO	3-Phenyl- propanol-1	(191)

In general, the alkene linkage is saturated at so low a temperature, and so rapidly, that other unsaturated groups such as benzoid, furanoid, pyridinoid and carbethoxyl are not acted upon by hydrogen under the conditions necessary for reduction of the C=C bond. Care must be exercised in hydrogenating unsaturated aldehydes, ketones, cyanides, oximes, etc. or both functional groups will be hydrogenated.

(b). Hydrogenation of Carbonyl (C=O) Linkage

The carbonyl group in aldehydes and ketones is readily hydrogenated. This group can be reduced either partially, to give an alcohol, or entirely to give a hydrocarbon. The partial reduction is obviously characterized as a "mild" hydrogenation and CuCrO is the appropriate catalyst. Acetone may be converted to isopropyl alcohol over RaNi at room temperature and 2-3 atmospheres pressure, but much more rapid reaction is obtained at higher temperatures and pressures. Apparently the great majority of aldehydes and ketones may be hydrogenated to the corresponding carbinols over either catalyst at temperatures not greater than 150°C and pressures not greater than 100 atmospheres, the yields of alcohols being practically quantitative. Keto- and aldo-alcohols and esters are hydrogenated almost as readily and they give yields of the same order as those from unsubstituted ketones and aldehydes. If a phenyl or pyrryl group is adjacent to the carbonyl group then the hydroxyl group first formed may undergo a secondary hydrogenolysis to a methylene group (see page 108). Since the alkene linkage is hydrogenated under conditions similar to those used for the hydrogenation of carbonyls, both reactions can be carried out in a single operation.

Substance	Press. Atm.	Temp. °C.	Time Min.	Catalyst	Product
Acetophenone	100	110	10	R aNi	91% Ø*-Me-carbinol (192)
Acetophenone	100	150	30	CuC r0	95% Ø-Me- carbinol (192)
Heptaldehyde	***	150	240	RaNi	92% heptanol-1 (192
Glucose	-	160	240	CuCrO	97% sorbitol (184)
Benzalacetone	-	175	12	CuCrO	97% 4-Ø-butanol-2 (157)
Acetoacetic ester	100	150	180	CuCrO	97% ethylOH- butyrate (183)

Examples:

^{*} ∅ = Phenyl.

The benzenoid nucleus requires distinctly more drastic conditions for its complete hydrogenation than do the alkene, carbonyl, cyano or imino groups. CuCrO is seldom used for these reactions since high temperatures and pressures over a prolonged period are required. Over RaNi, however, benzene can be rather rapidly hydrogenated in the vicinity of 125°C at 100 atmospheres pressure. The phenols are more rapidly hydrogenated than other derivatives of benzene; the amino, carbethoxyl, ether and hydrocarbon groups definitely retard hydrogenation. In the case of the amino and carbethoxyl derivatives of benzene the yields of the corresponding cyclohexyl derivative are above 90%, but with ethers, hydrogenolysis occurs resulting in only 50-70% yields of the cyclohexyl ethers.

Substance	Temp. oc	Time Hrs.	Catalyst	Product
Benzene	150	1.0	RaNi	100% Cyclohexane (190)
Toluene	175	0.12	RaNi	100% Me-cyclohexane (190)
Benzene	125	0.25	Ni(K)	100% Cyclohexane (190)
Di-Ø-methane	150	7.0	N i(K)	100% Dicyclohexyl- methane (193)
Phenol	150	3.0	N i (K)	Cyclohexanol (194)
Anisol	200	4.4	RaNi	60% (S)-OCH ₃ (195)
Aniline	200	9.0	N1(K)	80% cyclohexylamine (194)
Ethyl salicyl- ate	175	9.0	Ni(K)	96% 2-OH-cyclohexyl acetic ethyl ester (196)

Examples:

(d). Hydrogenation of the Furanoid Nucleus

The hydrogenation of the furanoid nucleus occurs under somewhat milder conditions than those used for the benzenoid ring, and also differs in that the former is an unsaturated cyclic ether, hence is subject to hydrogenolysis. Over RaNi, however, the furyl derivatives have been hydrogenated in yields of 80-97% to the corresponding tetrahydro compounds (197). (For reactions over CuCrO see page 110)

2. Hydrogenolysis (Cleavage)

(a). Hydrogenolysis of the C-C Bond

(1). C-C Cleavage in Hydrocarbons

Hydrocarbon cleavage occurs most commonly at very high temperatures over the "violent type" catalyst (RaNi) although the writer suspects that with certain groupings C-C cleavage may occur over CuCrO.

Some examples are:

Pentaphenylethane RaNi 125°C Tricylohexylmethane + Dicyclohexylmethane (193)

Pentaphenylethane
$$\frac{CuCrO}{2000C}$$
 Triphenylmethane + Diphenylmethane
(193)
HO- $\not{\rho}$ - C - $\not{\rho}$ -OH $\frac{Ni-Bi}{175^{\circ}C}$ $\not{\rho}$ -OH + $\not{\rho}$ -CH (198)
CH₃ CH₃

On the other hand the hydrogenated phenylethanes are completely stable toward hydrogen at 200°C; it is thus evident that the phenyl group is very much more effective than the cyclohexyl group in facilitating C-C cleavage. It is interesting to note, however, the effect of loading a carbon atom with alkyl groups in regards to stability towards C-C cleavage; and then to consider the similarity of these compounds to the structure which Freudenberg considers to be a lignin building unit. (see page 43).

(2). C-C Cleavage in Alcohols

Primary alcohols react with hydrogen over RaNi at 250°C:

$$RCH_2OH + 2H_2 \longrightarrow RH + CH_4 + H_2O$$

Thus:

$$S CH_2-CH_2-CH_2OH \xrightarrow{\text{RaNi}}_{250\circ\text{C}} 80\% S CH_2-CH_3 (199)$$

Secondary alcohols undergo hydrogenolysis preferentially at the C-O bond rather than the C-C bond (199).

No example of this reaction being catalyzed by CuCrO could be found in the literature.

(3). C-C Cleavage in Glycols

The hydrogenolysis of C-C linkages in alcohols, referred to above, takes place slowly even over RaNi at 250°C: however, if the hydroxyl groups in a glycol are in the 1,3- positions, and, in addition, if there are alkyl substituents in the 1,2 or 3 position, then hydrogenolysis at the C-C becomes a very important factor and occurs readily even over CuCrO ($200-250^{\circ}C$).

A sufficient accumulation of hydroxyl groups, even without alkyl substitution, makes hydrogenolysis of C-C linkages possible.

(4). C-C Cleavage in Diketones

These compounds behave similarly to 1,3 glycols in being labile toward hydrogenolysis (202).

(b). Hydrogenolysis of the C-O Bond

(1). C-O Cleavage in Alcohols

The hydroxyl group in primary and secondary alcohols and in phenols is extremely resistant to hydrogenolysis below 250°C except where R contains a phenyl, furyl, pyrryl, hydroxyl, carbonyl, or carbethoxyl group. Thus, if there is an ethylenic bond or carbonyl group in the β position with respect to the C-O linkage, the latter is readily broken. This tendency is even found in the β position and to a lesser extent in the δ .

Examples:

∲-СH ₂ OH	RaNi 125°C 10 min.	88%	Ø-CH3 (18	4)
Ø-СН2-СН2О Н	CuCrO 250°C 5 hr.	95%	Ø-СН2-СН3	(184)
Ø-c0-ø	CuCrO 175°C 1 hr.	97%	Ø- СН2- Ø	(183)
Ø-CO-CH2-CH2-CO2Et	CuCrO 250°C 1 hr.	9 4 %	Ø-(CH2)3-C	H ₂ OH (183)
S OH	CuCrO 250°C 6 hr.	20%	S-OH	(203)
ся сн	200°C CuCr0	95%	S -он	(203)
но- сл	<u>CuCr</u> 0 250°C	5%	S-OH	(203)



(2) C-O Cleavage in Ethers

Over RaNi the benzyl ethers undergo hydrogenolysis at lower temperatures than do others (effect of G=C-C···O) and benzyl-aryl ethers cleave at lower temperatures than do benzyl-alkyl ethers. Di-aryl ethers are somewhat more stable to hydrogenolysis than benzyl-alkyl ethers since the former cleave around 150-200°C. Aryl-alkyl ethers are more stable toward hydrogenolysis than other ethers. Where the alkyl group is large, hydrogenation occurs, otherwise the principal change is one of hydrogenolysis at 200°C. Di-Alkyl ethers are quite stable toward hydrogenolysis at 200°C; at temperatures sufficiently high to cleave dialkyl ethers over RaNi a C-C cleavage would also occur.

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The situation is probably very much the same over CuCrO, although only little work has been reported in this field. Interestingly enough, especially in regard to proposed lignin structures, most of the work on CuCrO on ether cleavage has been done on furane and

Examples:

benzofurane compounds.



4%

n-heptanol







It is important to note, however, that tetrahydrofurane, prepared by RaNi hydrogenation of furane, is extremely resistant to hydrogenolysis over CuCrO. Thus again, the influence of a conjugated system in labilizing a C-O bond to hydrogenolysis is apparent.

3. Hydrogenation Accompanied by Hydrogenolysis

The most important reaction of this type is that of the preparation of alcohols and glycols from esters, a process which is becoming very valuable in the laboratory for the synthesis of alcohols from acids (200, 204).

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As might be expected the yields decrease as the ideal situations for C-O hydrogenolysis are approached (e.g. proximity of phenyl, carbonyl, furyl or hydroxyl groups (204). However, even though hydrogenolysis of the resulting C-OH group does occur, the yields, with only a few exceptions, are large enough to make the transformation of preparational value.

4. Selective Hydrogenation

Although very few examples are mentioned in this thesis, an immense quantity of data is to be found in the literature on the conditions for reaction of hydrogen with various functional groups; in other words, the problem of catalyzing the reaction of hydrogen with various functional groups has been in large part solved during the past forty years. The critical problem to-day is not that of finding <u>better</u> but <u>more selective</u> catalysts, and of obtaining more complete knowledge of the influence of one functional group on the hydrogenation of another. At the present time a great deal of work is being accomplished in this line.

By selective hydrogenation is meant the hydrogenation of one functional group in the presence of another which remains unreduced. Selective hydrogenation, at least at present, depends primarily upon the selection of a catalyst,

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temperature and duration of reaction, and, secondarily, upon the medium of reaction. For example, CuCrO is relatively inactive toward the benzenoid nucleus, hence pyridinoid rings, aldehydes, ketones, and esters containing an aryl group may be hydrogenated to the corresponding alcohols or amines containing the unchanged benzene ring.. RaNi is inactive toward carbalkoxy groups, so that compounds of these types containing aryl groups may be converted to the corresponding cyclohexyl derivatives.

A very good example of careful selection of catalyst to induce selective hydrogenation is shown by the remarkable hydrogenation of an unsaturated ester to the unsaturated alcohol. It will be recalled that the C=C bond is hydrogenated under as mild conditions as any other group, even at room temperature and atmospheric pressure over RaNi or Pt-Pd catalysts. In contrast to this, the ester group requires a temperature of over 200°C and hydrogen pressures greater than 100 atmospheres for its conversion to a carbinol group over CuCrO, the most active catalyst for this reaction. The C=C bond in butyl oleate is hydrogenated at a much lower temperature than the carbethoxyl group over CuCrO so that the saturated alcohol is obtained. Yet, this seemingly hopeless task is readily accomplished in 35% yields over ZnCrO at 300°C (185).

Selective hydrogenation is most commonly attained, however, through careful control of temperature and reaction time. This is possible because of a peculiar (and fortuitous) feature of hydrogenation reactions, namely, the pronounced tendency for hydrogenation to proceed stepwise; that is, for one functional group to be completely hydrogenated before action with another commences. Generally the most reactive group will hydrogenate at a somewhat lower temperature, and the reaction is controlled by cautiously raising same until the reaction just begins, then maintaining this, or a lower temperature until the reaction is complete. If the two groups react at about the same temperature the technique is to slowly raise the temperature until the reaction just begins and then rapidly cool the bomb by immersion in cold water. An example of this method is the preparation of β -phenylethyl alcohol from phenylethyl acetate:

The optimum yield (about 60%) is obtained only by interrupting the hydrogenation before all of the ester has undergone the first reaction. (203)

An excellent example of the relative hydrogenations of various groups in one molecule was found in

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the hydrogenation of α -ethoxypropriovanillone (XX) over CuCrO by Cooke, McCarthy and Hibbert (174). Fifteen grams of a-ethoxypropriovanillone were treated with hydrogen at 220 atmospheres pressure over CuCrO (8.0 g) at 250°C. The products of this reaction were water. ethanol, methanol and 4-N-propylcyclohexanol. The stepwise curve, Figure II, obtained by plotting the hydrogen in broad outline concentration versus time distinctly indicates/that the following reactions occurred. First, the carbonyl group adjoining the benzene ring was completely reduced to the approximately methylene group with the absorption of $/2^{-1}$ moles of hydrogen; secondly, the ethoxyl group was cleaved with the absorption of "one mole" of hydrogen; and thirdly, the benzene ring was saturated and the methoxyl group cleaved with the absorptof about ion of / four moles of hydrogen.



In considering a selective hydrogenationa it is important to note, however, that the relative rates of reaction of two compounds with different functional groups taken separately is not always a safe basis for prediction as to the relative rates of hydrogenation of the two compounds in a mixture, or of the two groups when both are in the same molecule. For example. d-am pinene is much more rapidly hydrogenated than is cinnamic acid, yet in a mixture of the two, cinnamic acid is completely hydrogenated before the former takes up any hydrogen (205). A reducible substance not undergoing hydrogenation may greatly accelerate the hydrogenation of another compound. Thus, pure pinene, which is much more rapidly hydrogenated than pure allyl alcohol was found to increase the rate of hydrogenation of allyl alcohol almost sevenfold, without itself being hydrogenated to any considerable extent.

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D. Review on the Hydrogenation of Lignin

The first successful hydrogenation of an isolated lignin to produce identifiable products was reported by Harris, D'Ianni and Adkins (73) in 1938. Although lignin had been treated with hydrogen under various conditions prior to this time, no compounds were isolated and identified. Consequently, these earlier investigations will not be described in detail in this thesis. The following workers have attempted to gain knowledge of the structure of lignin by means of its hydrogenation. Fischer and Schrader, (206); Fierz-David, (207); Fierz-David and Hannig (69); Bowen and Nash (70); von Wacek, (208); Lindblad, (209); Ipatieff and Petrov, (210); Trefliev and Filaterov, (211); Moldavsky and Vainstein, (212); Freudenberg, (213); and Hibbert and Moore (214).

Harris, D'Ianni and Adkins (73) hydrogenated methanol lignin (maple) over CuCrO at 255°C at a hydrogen pressure of 5,000 psi. The hydrogenation products isolated and identified were methanol (28%); 4-n-propylcyclohexanol, <u>XVII</u>, (11.5%); 4-n-propylcyclohexanediol-1,2, <u>XVIII</u>, (3.8%); 3-(4-hydroxycyclohexyl) propanol-1, <u>XIX</u> (25%); and a highboiling resinous residue (32%).

This process has been extended to other lignins by Harris and Adkins (215). The results obtained by these investigators are shown in Table XII.

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TABLE XII

THE HYDROGENATION OF VARIOUS LIGNINS OVER COPPER-CHROMIUM OXIDE

(215)

	Proportion of	Methoxyl	Products Isolated					
Lignin	Total Lignin in Wood	Content of Lignin	Me OH %	XVII %	XVIII %	IX %	R esidue %	Total Return %(a)
Methanol (Aspen)	6.0	27.0	26.5	11.0	3.2	24.0	22.0	86.7
Klason (Spruce)	30	20.6	19.0	6.0	2.0	15.0	48.0	90.0
Alkali (Aspen)	60	11.6	10.5	4.0	1.4	9.0	66.0	90.9
Methanol (Spruce)	25	23.0	15.0	7.0	2:.0	12.0	52.0	88.0
Alkali (Black Gum) 6.0	11.8	11.0	5.0	1.0	14.0	60.0	91.1

(The following results were reported by Harris, D'Ianni, and Adkins (73))

Methanol (Aspen) 90 ---- 28.0 11.5 3.8 25.0 32.0 100.3 %(a) = Percentage of original weight of lignin At a later date Harris (216) reported the hydrogenation of these same lignin preparations under the same conditions to give the products shown in Table XIII.

TABLE XIII

THE HYDROGENATION OF VARIOUS LIGNINS

OVER COPPER-CHROMIUM OXIDE (216)

Products Isolated

Lignin	Nater %	М ө О Н %	n-Propylcyclo- hexane and its Derivatives %	High- Boiling Resin %	Total Return %(a)
Methanol (Aspen)	11.0	26.5	38.2	22.0	97.7
Klason (Spruce)	9.0	19.1	23.0	48.0	99.1
Alkali (Aspen)	9.0	10.5	14.4	660	99.9
Methanol (Spruce)	10.3	15.0	21.0	52.0	98.3
Alkali (Black Gum)10.5	11.0	20.0	60.0	101.5

%(a) = Percentage of original weight of lignin

It is interesting to observe the changes that have taken place in the published yields of the hydrogenation products from lignin. It might be mentioned at this point that the paper containing the data on water as a hydrogenation product was not submitted for publication until after the criticism made by McCarthy and Cooke (220).

Apparently the yields reported by Harris and Adkins (215) for 3-(4-hydroxycyclohexyl) propanol-1 are open to question. This is particularly true with regard to yields reported in the case of soda lignin (aspen and black gum); namely 9 and 14%, respectively. Adkins has found recently (72) that soda lignins from hardwoods yield only <u>traces</u> of this glycol, and this investigator emphasized the fact that Harris "had given no substantial evidence that he had isolated or characterized the glycol among the products of their hydrogenation of soda lignin". In addition, it will be seen later in this thesis that this glycol is obtained in only very small yields from the hydrogenation products of ethanol lignin.

The resins obtained in the hydrogenation of lignin have been studied by Harris, D'Ianni and Adkins (73). These investigators found that the resinous residue obtained in the hydrogenation of methanol lignin (aspen) contained 73% carbon and 10.8% hydrogen. This residue was dehydrated with alumina and the unsaturated hydrocarbons thus obtained were rehydrogenated over Raney nickel to yield saturated hydrocarbons containing 86.6% carbon and 12.5% hydrogen. From the physical properties of these hydrocarbons (particularly boiling point) Adkins

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concluded that, since the minimum number of carbon atoms present in the simplest hydrocarbon was fifteen, the original lignin was composed, at least in part, of units containing more than fifteen carbon atoms.

A more detailed investigation of the resins was made by Adkins, Frank and Bloom (72). The high-boiling residue obtained in the hydrogenation of alkali lignin : (hardwoods), which contained 79.9% carbon and 11.4% hydrogen, was dehydrated with oxalic acid and then rehydrogenated. The hydrocarbons thus obtained were carefully fractionated and analyzed. The results indicated that: (a) The soda lignin was converted to alcohols and glycols related to polycyclic hydrocarbons having 20 to 70 (or more) carbon atoms in the molecule. (b) Although high molecular weight compounds were also obtained from methanol lignin (13), they were present in smaller amounts and were more oxygenated than the products of similar physical properties obtained from soda lignin. (c) The products from methanol lignin contained one oxygen atom per six carbon atoms, while the products from soda lignin had one oxygen per average of 13.5 carbon atoms.

Harris, Saeman and Sherrard (74) have hydrogenated methanol lignin, alkali lignin, sulfuric acid (Elason) lignin and cellosolve lignin in an aqueous medium in the presence of Raney nickel. The reaction products were stated to include methanol, propylcyclohexane, hydroxy derivatives of propylcyclohexane and resins. No yields or properties of these products were reported.

E. Review on the Hydrogenation of Wood

The only investigators to report the isolation and identification of propyloyclohexanol derivatives from wood hydrogenation mixtures are Godard, McCarthy and Hibbert (217). These workers treated maple wood meal with hydrogen at 400 atmospheres pressure in presence of CuCrO at 280°C for 19 hours, and isolated 4-npropylcyclohexanol (19.5%) and 3-(4-hydroxycyclohexyl) propanol-1 (5.8%) (The yields are based upon the Klason lignin content of the wood).

Harris (216) recently claimed to have isolated a high yield of protolignin hydrogenation products by hydrogenation of wood (maple, aspen and spruce) over Raney nickel catalyst in an aqueous alkaline medium. Thirty grams of aspen wood suspended in 300 cc. of 1% aqueous sodium hydroxide were treated with hydrogen (300 atmospheres pressure) at 175°C for four hours. The yields of products (percentage of original woods) were: pulp, 40%; methanol, 5.1%; propanol, 16%; propylcyclohexane derivatives, 20%; resin, 14%; unidentified residue, 2%; total recovery, 97%. Since aspen wood contains 20-22% lignin (218), it would appear that the quantity of propylcyclohexane derivatives isolated by Harris account for about 100% of the Klason lignin content

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of the wood. Since, according to the results obtained by Zartman and Adkins (201), carbohydrate materials yield considerable quantities of water upon hydrogenation, it is difficult to conceive of a 97% recovery of hydrogenation products which do not include water. Brewer, McCarthy and Hibbert (176) have been unable to duplicate the work of Harris (219).

An excellent general review of the early literature on the hydrogenation of cellulose and wood was given in 1935 by Boomer and Edwards (219).

V. OBJECTIVES OF THE INVESTIGATION

From the survey concerning the present status of the structure of lignin which has been presented above, it is apparent that:

1. Of the various lignin isolation procedures, the Hibbert ethanolysis extraction process has produced more valuable data than has any other, that is to say, not only has this process been useful as a means of removing lignin from wood, but it has also made possible the isolation of the first $C_6 C_3$ units which contained substituent groups on the propyl side-chain.

2. The various lignin degradation reactions such as high-pressure hydrogenation over CuCrO, controlled oxidation with alkaline-permanganate, and mild oxidation with nitrobenzene have each yielded valuable information concerning the basic structure (guaiacylpropane and syringylpropane units) of lignin.

3. Since the structures of the simplest products of ethanolysis have been definitely proven (a-ethoxypropiovanillone, vanilloylmethyl ketone, and their syringyl homologues), and in addition, since the presence of a large amount of phenylpropane derivatives in lignin has been established by hydrogenation studies, it was decided to apply high-pressure hydrogenation technique firstly to the simple monomolecular ethanolysis lignin units and secondly to the amorphous lignin fractions obtained by treating maple wood with ethanolic hydrogen chloride (2%). By means of such a study it was hoped to obtain information concerning:

(a) The quantity of aromatic material in the isolated amorphous lignin fractions.

(b) The manner in which the C_6C_3 ethanolysis "lignin units" are combined in the polymeric amorphous protolignin and extracted lignin fractions.

(c) The chemical relationships existing between the various fractions with regards to their structure.

(d) The bearing of these various factors on the structure of "protolignin" and "extracted lignins".

VI. DISCUSSION OF EXPERIMENTAL RESULTS

A. Alcoholysis of Hardwoods

1. The Ethanolysis of Maple Wood

One kilogram of solvent pre-extracted maple wood meal was treated with anhydrous ethanolic hydrogen chloride (2%) according to the standard ethanolysis procedure (151). The experimental conditions used and the yields of ethanolysis fractions are shown in Flow Sheets I, II, and III. This ethanolysis was carried out in order to isolate alcoholysis lignin fractions for hydrogenation studies. The yields of the products obtained by means of this experiment were in agreement with those reported previously in the literature (151).



ETHANOLYSIS OF MAPLE WOOD MEAL



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FLOW SHEET II



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FLOW SHEET III

FRACTIONATION OF "WATER-SOLUBLE OILS" (FRACTION E)

Scheme No.2

75 g. Fraction E

Pptn. of acetone soln. into 30-50° pet. ether



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2. The Methanolysis of Hardwoods

(a) Introduction:

Investigations on the methanolysis of wood have been made by Friedrich (spruce) (125), Hibbert and coworkers (spruce) (112, 121k, 153, 154, 223, 234), and Harris and co-workers (black gum and aspen) (73, 76). Friedrich failed to report either lignin analyses of his starting material and wood residues or the actual vield of lignin so that it is impossible to evaluate his results. Harris (73) has implied that all of the lignin removed from aspen wood on treatment with methanolic hydrochloric acid is isolable as an amorphous, water-insoluble product. By refluxing solvent pre-extracted aspen sawdust (450 g.), containing 22% lignin (99 g. lignin in the wood), for three days with 4.5 liters of methanol containing 3% (by weight) hydrogen chloride, he was able to dissolve 65 g. of lignin (65% of the total lignin) from the wood. This was isolated by concentrating the methanol solution (no data on the pH of this was given) and pouring the concentrate into 10 liters of cold water. By repeated treatments of the residual aspen wood meal with methanolic hydrogen chloride the yield of waterinsoluble lignin could be increased to 90 g. (91% of the total Klason lignin). Although Harris has claimed that 90%

of the lignin in <u>hardwoods</u> can be removed as <u>water-</u> <u>insoluble</u> lignin by repeated treatment of the wood meal with methanolic hydrogen chloride (3%), <u>all</u> other investigators <u>in the field of alcohol-acid</u> <u>extraction of wood</u> have reported that not more than 60-70% is isolated by such treatments (pp. 68 to 81) (150). In addition to this discrepancy in the quantities of lignin removable, there is the very important observation of many other investigators that <u>all</u> of the lignin removed from the wood is <u>never</u> recovered quantitatively as water-insoluble lignin (36, 111, 112, 139, 140, and 150).

Dorland and Hibbert (222) have shown that propanol and butanol can be substituted for ethanol in the Hibbert alcoholysis process, to give the same alcoholysis type of lignin fractions (amorphous, waterinsoluble lignin; water-insoluble, non-distillable tars and oils) as obtained by the <u>ethanolysis</u> of wood. An early attempt to substitute methanol for ethanol, however, was unsuccessful (223).

Finally, Harris, D'Ianni and Adkins (73) have shown that the highest yields of propylcyclohexane derivatives obtained by the hydrogenation of lignin are those obtained from methanol lignin (aspen). In order to check the observations that (1) acid methanolysis of wood yields no appreciable quantities of water-soluble materials; (2) practically all of the lignin (90%) can be removed from hardwoods by repeated treatment with methanolic hydrogen chloride (3%); and (3) methanol lignins are converted to propylchclohexanol derivatives in a very high yield by means of hydrogenation, a short study was made of the methanolysis of maple and aspen woods.

(b) Experimental results

(1) Methanolysis of Maple Wood

Using the conditions employed by Harris for the methanolysis of aspen wood (73) the following results were obtained when applied to both maple and aspen woods (TABLE XIV):

TABLE XIV

Wood	Lignin in Methanolysis Wood Residue %(a)	Water Insoluble Methanol- Lignin %(a)	Tars (b) %(a)	Water Soluble Oils %(a)	Total Lignin Return %(a)
Maple (20.8% lignin)	27.8	42.8	8.2	26.1	104.9
Aspen	29.4	47.9	19.1	11.9	106.3

Methanolysis of Maple and Aspen Woods

(2) Methanolysis of the Methanolysis Wood Residue

The maple methanolysis wood residue was re-treated twice with methanolic hydrogen chloride (3%) with results as detailed below.

lst Treatment (A): 373 g. of maple wood (1.1% moisture; 20.8% lignin; 77.0 g. lignin) yielded 202 g. of a methanolysis wood residue containing 0.8% moisture and 10.6% lignin (21.4 g. lignin); loss in lignin 56.6 g. or 72.3%.

2nd Treatment (B): 50 grams of the air-dried methanolysis wood residue (4.5% moisture and 10.6% lignin; 5112 g. lignin) from (A) yielded 45.0 g. of a methanolysis residue containing 0.7% moisture and 9.15% lignin (4.12 g. lignin). <u>3rd Treatment (C):</u> 40 grams of the methanolysis wood residue (3.66 g. lignin (B) yielded 37.7 g. of a methanolysis wood residue containing 0.8% moisture and 9.12% lignin (3.45 g. lignin).

These results are summarized in (TABLE XV).

TABLE XV

Effect of Repeated Methanolyses on the Lignin Content of Maple Wood

Treatment	R esidue %(a)	Lignin Content of Wood Residue	Quantity of Lignin Removed %(b)	
First	21.2	10.6	72.2	
Second	91.1	9.16	5.6	
Third	94.6	9,13	, 1. 3	

%(a) = Percent of wood or wood residue treated.
%(b) = Percent of lignin in original untreated wood.

(ĉ) Conclusions

From the data given in TABLE <u>XIV</u> and <u>XV</u> it is apparent that when hardwoods are treated with methanolic hydrogen chloride (3%), according to the conditions employed by the writer:

(1) A portion of the lignin is isolated in a water-soluble form (TABLE XIV).

(2) A large portion of the lignin is very slightly soluble in water (tars which precipitated upon concentration of the aqueous extraction liquors). (TABLE XIV). (3) The quantity of lignin which can be removed from maple wood on repeated treatment with methanolic hydrogen chloride rapidly reaches a limit. Apparently this limit is approximately 78-80%. (TABLE XV).

Since methanol reacts in the same manner as do ethanol, propanol, and butanol in the Hibbert alcoholysis procedure, it is apparent that this reaction is a general one, at least, for primary alcohols. The question as to whether the simple units obtained from a wood alcoholysis reaction mixture are derived from simple protolignin units or from a condensed polymer type of lignin is unknown, but there is considerable evidence indicating that the simpler ethanolysis derivatives are degradation products. West, Hawkins and Hibbert, for example, have shown (Table <u>IX</u>, p.86) that the water-insoluble ethanolysis fractions can be partially converted to distillable lignin derivatives by re-treatment with 2% ethanolic hydrogen chloride. The theory for the mechanism of the Hibbert alcoholysis reaction will be described in detail in the following section.

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B. <u>HYDROGENATION STUDY OF ETHANOLYSIS LIGNIN</u> FRACTIONS FROM MAPLE WOOD

<u>1. Hydrogenation of Monomolecular Lignin Units</u> (a) Study of A -Ethoxypropiovanillone.

(1) <u>Introduction</u>

As mentioned previously (see p. 35), Hibbert and coworkers have isolated \triangle -ethoxypropiovanillone (<u>XX</u>), vanilloylmethyl ketone (<u>XXI</u>) and their syringoyl homologues (<u>XXII</u>) and (<u>XXIII</u>) from the water-soluble ethanolysis products of maple wood while Adkins and co-workers (see p. 32) isolated 4-npropyl cyclohexanol (<u>XVII</u>), 4-n-propylcyclohexanediol-1, 2 and 3-(4-hydroxycyclohexyl)propanol-1 (<u>XIX</u>) from the hydrogenation products of methanol (aspen) lignin. The striking relationship which would appear to exist between these two series of compounds suggested that at least two of the hydrogenation products (<u>XVII</u> and <u>XVIII</u>) would probably be formed by hydrogenation of the above Hibbert ethanolysis products (<u>XX</u>, <u>XXI</u>, <u>XXII</u> and XXIII).

On the basis of observations made by Adking concerning the hydrogenation of organic compounds over copper-chromium oxide catalyst (see pp. 101-112), vanilloyl methyl ketone should undergo the following successive reactions I and II when treated with hydrogen at 300 atmospheres pressure and 250° C in the presence of copper-chromium oxide. - 139 -



In the case of *d*-ethoxypropiovanillone, however, there are no good examples in the literature on which to base theoretical speculations concerning the successive steps of its hydrogenation under the above conditions. The following reactions are possible:



(2) Experimental Investigation and Results

Fifteen grams of $\not{\prec}$ -ethoxypropiovanillone was hydrogenated over CuCrO at 250° at a hydrogen pressure of 5000 psi. The hydrogen absorption curve is shown in Figure II (pp. 115 and 116) and the hydrogenation results in Table IV.

TABLE IV

Hydrogenation Products from *A*-Ethoxypropiovanillone

Product	Yield	Yield % (a)	Yield (% of theoretical) (b)
Methanol	1.15 (0)	7.66	55
Ethanol	2.50 (c)	17.20	86
Water	1.57 (c)	10.40	130
4-n-Propyl- cyclohexanol	7.00 (d)	46.59	78
Residue	0.60	4.06	

- (a) Calculated on weight of original <-ethoxypropiovanillone.
- (b) Based upon reaction (III) above.
- (c) Determined by quantitative analyses.
- (d) Identified by physical properties and derivatives (phenyl- and *A*-naphthyl urethanes)

The following observations can be made on these results:

(1) No cyclohexane derivatives containing either ethoxyl

or isopropanol groups were present in the reaction products, so that reactions (<u>IIIa</u>) and (<u>IIIb</u>) could have been no more than intermediate reactions. (2) No cyclohexanediol-1,2 derivative was present.

(3) The yield of water was high and the yields of methanol, ethanol and 4-n-propylcyclohexanol were low in the light of reaction (<u>III</u>c) as representing the principal hydro-genation mechanism.

(3) Conclusions and Deductions

(\checkmark) An ethoxyl group in the β position with respect to an aromatic ring undergoes hydrogenolysis readily; so that all substituted groups on the propyl side-ohain of the simple units thus far isolated from the ethanolysis should undergo readily conversion to 4-n-propylcyclohexanol upon hydrogenation. It would appear that the guaiacyl nucleus is not the pre-(B) cursor of the hexane-1,2-diol found among the hydrogenation product from lignin, since only the monohydroxy cyclohexane derivative was obtained from the hydrogenation of A-ethoxypropiovanillone. Also, while on the other hand, only 55% of the theoretical quantity of methanol was isolated, on the other, water amounting to 130% was obtained. This result finds a satisfactory explanation in the assumption of a partial occurrence of reaction (IIb) to give 4-n-propylcyclohexanediol-1,2 and methane, followed by the hydrogenolysis of the hydroxy groups (see p. 106) thus formed to yield 4-n-propylcyclohexanol and water:

HO 5)-OH2-OH2-OH3 + H20 CH2-CH2-CH3CuCro HO-8 HO

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 (Υ) A similar reaction mechanism might possibly explain a portion of the loss of ethoxyl content, since the recovery of the ethoxyl groups was not quantitative. Should a hydroxyl group be formed during the hydrogenolysis of the ethoxyl group the former would unquestionably be subsequently reduced to the methylene group (see p. 105). The apparent ease with which the ethoxyl group is cleaved is probably due to the proximity of the aromatic ring. It was emphasized during the discussion of typical hydrogenolysis reactions that the phenyl group, as well as the hydroxyl, carbonyl, and carbethoxyl groups and unsaturated bonds labilize adjacent C-O-C linkages towards hydrogenolysis.

 (δ) Of considerable interest is the fact that the yield of 4-n-propylcyclohexanol was only 80% of theory. This result is not surprising when it is realized that considerable C ... O hydrogenolysis had occurred during the reaction. Probably an appreciable amount of C ... C cleavage also took place. Unfortunately there is very little data in the literature concerning C · · · C hydrogenolysis over CuCrO, but that it can and does occur is known (71, pp. 79 to 86). Although the investigations in this laboratory have been concerned chiefly with the application of hydrogenation reactions to a comparative study of isolated lignins and protoligning, some work has been done on analysis of the gaseous hydrogenation products (225). Preliminary investigations have shown the presence of at least 6-10% (calculated on the weight of lignin treated) of hydrocarbons in the bomb gases after a lignin hydrogenation.

(4) Observations of Importance with Regard to Hydrogenation of Non-distillable Ethanolysis Lignin Fractions

If \checkmark -ethoxypropiovanillone is considered to be the simplest lignin unit, or if the amorphous ethanolysis products (Flow Sheets I, II, III) are considered to be condensation polymers of this, or of an isomeric unit, then the hydrogenation products obtained from it should be representative of the first member of the polymeric series in which the benzene-insoluble ethanol lignin (Fraction B, Flow Sheet I) is the highest member. Since, however, Hibbert and co-workers have shown that hardwood ligning contain the guaiacyl and syringyl nuclei in approximately equal proportions (61, 62, 63, 97) the theoretical yield of 4-n-propylcyclohexane from the simplest unit (a mixture of A-ethoxypropiovanillone and -syringone) should be 55% of the weight of the starting material, instead of 59%, while the yield of 4-n-propylcyclohexanol actually obtained would, theoretically, be changed from 50.8 to 48.1% for a gualacy1syringyl group mixture (1:1).

2. <u>Hydrogenation Study of Ethanol Lignin: Ethanolysis</u> <u>Fraction B</u>

In order to make a preliminary comparison of the hydrogenation products obtainable from ethanol lignin with those obtained by Harris, D'Ianni and Adkins (73), ethanol lignin in dioxane solution was hydrogenated over CuCrO at 250°C with hydrogen at 6,000 psi. When the fractionation was carried out according to the scheme employed by Adkins it was possible to isolate and identify (by means of derivatives) methanol, ethanol, water, 4-n-propylcyclohexanol, and 4-n-propylcyclohexanediol-1,?. Instead of obtaining 3-(4-hydroxylcyclohexyl) propanol-1, however, a fraction which analyzed for $C_{1g}H_{34}O_{3}$ was obtained in the same boiling range (125-127°C at 1 mm. pressure). After considerable experimentation, it was found that this fraction was a constant boiling mixture, one component of which was soluble in water.

By separating the ethanol lignin hydrogenation products boiling above 101°C (the boiling point of the solvent, dioxane) into water-soluble and water-insoluble fractions it was possible to separate the components of the constant boiling mixture. The component present in the water-soluble fraction was shown to be 3-(4-hydroxycyclohexyl)propanol-1. The component insoluble in water is believed to be a new compound having a refractive index (25°C) of about 1.4975, a boiling point of 130-132°c at 1 mm. pressure, and a carbon and hydrogen content of 50.2 and 12.3% respectively.

The presence of this constant boiling mixture in the hydrogenation products form ethanol lignin (maple) and its absence in those reported by Adkins using methanol lignin (aspen) is explained by the fact that, in the case of the former, 3-(4-hydroxycyclohexyl)propanol-1 is obtained in small yields, (2-3%) whereas from methanol lignin (aspen) it is found in a 25% yield. The unidentified component of the mixture (ethanol lignin) was also present (2-3%).

It is noteworthy that the earliest published recognition of the fact that water is a major product of lignin hydrogenation was made by the writer (226). The water is isolated from the hydrogenation reaction mixture as a component of a binary azeotrope with dioxane $n_D^{25} = 1.4705_p$ b.p. = 87.0 at 760 mm. pressure.

A summary of the yield of products isolated and positively <u>identified</u> (excepting the resin) from the ethanol lignin (maple) hydrogenation is shown in Table <u>XVI</u>:

TABLE XVI

Hydrogenation Products from Ethanol	Lignin	(Maple)
Product	Yield g.	Yie ld % (a)
Methanol	10.6	10.0
Et han ol	5.4	5.1
Water (minimum yield)	క .0	7.5
4-n-propylcyclohexanol	8.5	8 . 0
3-(4-hydroxycyclohexyl)propanol-1	3.0	2.7
Compound of $n_{D}^{25} = 1.4975$	2.8	2.6
Residue	34.2	32.0
	Total	70.9

(a) Percentage of yield based on original ethanol lignin.

The following observations can be made:

(1) Similar products to those obtained by Harris, D'Ianni and Adkins in the hydrogenation of methanol lignin (aspen) have been obtained in the hydrogenation of ethanol maple lignin when subjected to a similar treatment.

(2) The author's results differ from those of the former investigators in that ethanol lignin, on hydrogenation yields ethanol, water and <u>only</u> a small quantity of 3=(4-hydroxycyclohexyl)propanol-1.

The ethanol is probably formed as a hydrogenation product of the ethoxyl groups known to be present in ethanol lignin. Since the presence of carbonyl groups in ethanol lignin has not been established it would appear that water may result from the hydrogenolysis of ether linkages and possibly hydroxyl groups. The only explanation of the small yield of 3-(4-hydroxycyclohexyl)propanol-1 is that difference in structure exists between ethanol lignin (maple) and methanol lignin (aspen).

3. <u>Comparative Hydrogenation Study of Amorphous</u>, <u>Non-Distillable Ethanolysis Maple Lignin</u>, <u>Fractions (Flow Sheets I, II, and III)</u>

(a) <u>Procedure for Identification of Products from Small-</u> <u>Scale Hydrogenations</u>.

In order to make the hydrogenation studies on the ethanolysis fractions strictly comparable it was necessary to devise a technique for the quantitative determination of the entire hydrogenation products obtained from relatively small samples of ethanolysis fractions. Up to the present time it has been necessary to hydrogenate from 100 to 500 g. of an isolated lignin in order to obtain enough material for analysis by fractional distillation. Since certain of the ethanolysis fractions are obtained in yields of only 6-20 g. from 1 kilogram of wood, a lengthy and expensive program of preparative work would have been necessary to obtain enough material for hydrogenation studies. However it was found possible to develop a method of hydrogenation by which satisfactory analytical values could be obtained by the use of only 10 g. of starting material. This procedure involved the application of quantitative analytical methods to the determination of the low boiling components (methanol, ethanol, and water), and a combination scheme of sclvent and distillation fractionation for the high boiling components (4-n-propylcyclohexanol, 4-n-propylcyclohexanediol-1,2, 3-(4-hydroxycyclohexyl)

propanol_1, and an unidentified compound with a refractive index (25°C) of 1.4975).

The quantitative analytical methods included:

(a) Determination of water by estimation of the acetylene formed by interaction with calcium carbide. The acetylene was isolated as copper acetylide, and determined volumetrically with potassium permanganate.

(b) Determination of methanol by conversion into methyl iodide by the action of hydriodic acid and precipitation as tetramethylammonium iodide. The latter was determined gravimetrically by conversion to silver iodide.

Recently a more simplified volumetric method (iodimetric) has been devised by the writer for the determination of the methoxyl content of alkoxyl-containing materials which presumably will supersede the older and less convenient gravimetric procedure.

(c) Determination of ethanol by quantitative oxidation to acetic acid with acid potassium dichromate. Any methanol was oxidized quantitatively to formic acid. Since the methanol content was already known, the ethanol content could be determined by difference.

Each of these methods represents a semi-micro procedure, so that by their application it is possible to determine, accurately, the total low-boiling hydrogenation products obtained from as little as 7-10 g. of lignin. The details of the procedure and the data concerned with their development are included in Experimental Section B, 7, (a). In the analysis of the high-boiling components (boiling above 101°C at 760 mm. pressure these were first separated into water-soluble and water-insoluble fractions. The basis for this fractionation was the previous observation (see section B, (1), above) that 4-n-propylcyclohexanediol-1,2 and 3-(4-hydroxycyclohexyl)propanol-1 which are water soluble could be separated from the water-insoluble 4-n-propylcyclohexanol, from the compound of $n_D^{25} = 1.4975$, and from the high-

boiling resins. Since the water-soluble (glycol) fraction rarely amounted to more than 700 mg. in the small-scale investigations it was carefully distilled through a modified Podbielniak fractionating column, the description of which is given in Experimental Section B, 7, (b).

This entire analytical procedure, carried out on the hydrogenation products from 10-15 g. samples of the ethanolysis lignin fractions, was standardized by reference to the behavior of the products obtained using 15 g. of <u>ethanol lignin</u>. A comparison of the yields from the various hydrogenation products using this amount and employing the above treatment, with those found by using fractional distillation separation of all the components from a 100 gram sample of lignin is given in TABLE XVII.

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TABLE XVII

Comparison of Yields of Hydrogenation Products

from Fifteen Grams of Ethanol Lignin with

Those From & Larger One-Hundred and Nine Gram Sample

Product	109 g. Run Yield %	15 g. Run Yield %
Nother of	10.0	77 (
Methanol	10*0	1)+0
Ethanol	5.1	4.9
Water	7.5	8.7
4-n-propylcyclohexanol	8 . 0	8 .1
4-n-propylcyclohexanediol-1,2	1.9	
3-(4-hydroxycyclohexyl)propanol-1	3.3	2•4
Compound of $n_D^{25} = 1.4975$	3.3	2.1
High Boiling Resin	32.0	29.5
Total	71.1	72.3

(b) Hydrogenation Results from Ethanolysis Fractions B. C, D and F (Ethanol Lignin, Benzene Shakings, Red Tars and Non-Distillable Phenols) (Flow Sheet I, II and III)

(1) Experimental Results

The following ethanolysis lignin fractions were hydrogenated in dioxane solution over CuCrO at 250°C with hydrogen at 5000 to 6000 psi. The hydrogenation data are given in Table XVIII.

TABLE XVIII

Hydrogenation Data for Ethanolysis

Maple Lignin Fractions

(Flow Sheets I, II, III)

	Ethanolysis Fraction	Weight of Fraction g.	Time to Complete Hydrogenation hrs.	Moles H ₂ consumed per 100g. of fraction
в	Ethanol Lignin	15.0	16.0	3.90
C	Benzene Shakings	12,2	5 .0	3.80
D	Red Tars	15.0	4.8	3.68
F	Non-Distillable Phenols	9.5	4.0	3.80
	Ethoxypropio- vanillone	15.0	3.5	3.40

The yields of methanol, ethanol and water have not been determined, as yet, for Ethanolysis Fractions C, D and F. The yields obtained from Fraction B were given in Table XVII.

The hydrogenation products boiling above 101°C at 760 mm. were separated into water-soluble and water-insoluble fractions. The latter were fractionally distilled through the modified Podbielniak column, and the distillation results are summarized in graphical form in Figures III, IV, V and VI.









The yields of the distillable (Figures III, IV, V and VI) and non-distillable (resins) portions of the water-insoluble hydrogenation products, as well as the yields of water-soluble glycols, from the various ethanolysis fractions are given in Table XIX.

TABLE XIX

Comparison of Yields of Hydrogenation Products

from	Ethanolysis	Lignin	Fractions
	TU.	riald	

	Fraction	Yield Nater - Soluble	Distil- lable Water - Insoluble	Yield Water Insoluble Resin	Total Yield Water- Insol. %	(a)
в.	Ethanol Lignin	5.4	16.0	29.5	45.5	1/0.55
с.	Benzene Shakings	5.2	27.4	14.8	42.2	1/1.9
\mathtt{D}_{ullet}	Red Tars	6 .0	32.5	14.6	47.1	1/2.4
F.	Non-distillable phenols	5.9	42.7	6.0	48.7	1/7.1
α-	ethoxypropiovanillone. syringone	0.0	48 .0	2.0	50.0	1/2.4

(a) Ratio of Distillable Waterinsoluble to Resin. - 157 -

(2) Review of Experimental Results

From the hydrogenation and fractionation data it can be seen that:

(\prec) The ease with which an ethanolysis lignin fraction undergoes hydrogenation (and hydrogenolysis) increases with increase in solubility of the fraction (Tables XIX and XX). A distinct difference is observable between the rates of hydrogenation of the first two fractions, B and C (ethanol lignin and benzene shakings).

 $(\beta$) The shapes of the four fractional distillation ourves are essentially identical, the only marked differences in the four distillations being: (1) increase in yields of distillable products with increase in solubility of the ethanolysis lignin fraction; (2) conversely, decrease in yield of non-distillable resin with increase in solubility of the fraction; and (3) rapid increase throughout the series in the ratio of distillable to non-distillable materials.

(γ) The <u>total</u> yield of water-insoluble and water-soluble hydrogenation products for the entire series remains practically constant.

(S) Within the boiling point range $(95^{\circ}-97^{\circ}C \text{ at } 7 \text{ mm.})$ of 4-n-propylcyclohexanol $(n_D^{25} = 1.4600, 1.4675)$ two flat portions or "plateaus" are observed. The refractive index of the lower-boiling component varies slightly among the various lignin fractions $(n_D^{25} = 1,4605 \text{ to}$ 1.4675) whereas that of the higher-boiling component is constant $(n_D^{25} = 1.4675)$.

(ϵ) Examination of the four distillation curves (Figures III, IV, V and VI) shows that a slight elevation in refractive index is observable at the initial point of a fraction "plateau". Since the size of this elevation has been shown to be dependent upon the rate of distillation it is reasonably certain that this phenomenon is due to the fact that insufficient time had been allowed for the liquid and vapor of the new fraction, to reach true equilibrium.

(5) Except for the fact that no water-soluble glycol fraction is obtained, the results predictable from the hydrogenation of a theoretical mixture containing A-ethoxypropiovanillone and -syringone fit nicely into the lignin fraction series. (The data used for this theoretical fraction are the values (see Section B, 1, above) obtained from A-ethoxypropiovanillone "corrected" for a hypothetical A-ethoxypropiovanillone-A-ethoxypropiosyringone mixture.

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(3). Conclusions Concerning the Structure of the Ethanolysis Lignin Fractions and the Mechanism of the Ethanolysis Reaction

(α) Introduction

It seems advisable first to summarize all the available data concerning the physical and chemical properties of the lignin fractions. The pertinent data are given in Table XX.

TABLE XX

Lignin Fraction	Reduced Viscosity	OMe Content %	OEt Content %	Yield of Distillable Oils upon EtOH-HCl treatment	Reduced Viscosity of non-dist. residue left- after EtOH-HC1 treatment
В	600	19.0	8.8	10	÷
C	469	18.0	12.3	22	541
F	389	19 .9	13.0	30	538

The following information concerning the

hydrogenolysis of C-C and C-O bonds and the structure of the non-distillable resin fraction obtained in the hydrogenation of lignin is also essential to the discussion. (i) The hydrogenolysis of the C-C bond occurs to a very limited extent over CuCrO and this is especially true for the short hydrogenation time employed with ethanolysis Fractions C, D and F. On the other hand, hydrogenolysis of C-O bonds occurs readily over CuCrO at 250°C (see pp. 106-111).

(ii) Adkins has shown conclusively that the lignin hydrogenation resins are composed of compounds having <u>hydrocarbon</u> nuclei which contain a minimum of fifteen carbon atoms.

(iii) 4-n-Propylcyclohexanol and 3-(4-hydroxycyclohexyl)propanol-1 are obtained in yields of 20 and 6%, respectively by hydrogenation of <u>maple</u> wood over CuCrO at 280°C for nineteen hours. (217).

(iv) It must be emphasized that while the lignin structures proposed by Freudenberg (pp.43-47), in which the C_9 units are connected jointly by C-C and C-O bonds, are applicable to softwood lignins, the fact that in hardwoods (maple) at least 50% of the aromatic nuclei consist of syringyl groups circumscribes their usefulness to this extent.

(3) <u>Conclusions Regarding the Structure of the</u> <u>Amorphous Ethanolysis Products from Wood</u>

From a comparison of the hydrogenation data obtained by use of ethanolysis lignin fractions, as well as from the available data of other investigators summarized in the preceding section, it may be concluded:

(i) The observed physical (solubility and viscosity) and chemical (ethanolysis and hydrogenation data) differences associated with these lignin fractions are due to differences both in chemical structure and degree of polymerization. (See Tables XIX, XX).

(ii) The difference in chemical structure is primarily one of a difference in mode of linkage between the C_6C_3 units comprising the lignin polymers. At least two types of union are involved in the maple ethanol fractions; in one there exists a C-C bond between adjacent C_6C_3 units while others are united by means of an oxygen linkage.

(iii) The extent to which the C-O-C type linkages occur in a given ethanolysis fraction is indicated by the solubility of the fraction. That is, the watersoluble, non-distillable phenols contain the C-O-C bond almost exclusively, whereas, the water-, ethanol-water-, benzene-, and ether-insoluble ethanol lignins are composed mainly of C_6C_3 units connected with C-C bonds. (Compare Adkins' data pp.106-111 and Table XIX).

(iv) In addition, it would seem that both the C-C and C-O-C types of isolated ethanolysis lignins

differ in structure from protolignin. The only basis for this conclusion at the present time is that 3-(4-hydroxycyclohexyl)propanol is obtained from maple wood in 6% yield, whereas for ethanol lignin the yield is less than 3%. This appears to indicate that the structure in the plant giving rise to 3-(4-hydroxycyclohexyl)propanol-1 had either undergone condensation or a rearrangement during the ethanolysis extraction process. (Compare Table XIX and data of hydrogenation of wood by Godard, p124).

(Y) Conclusions Regarding the Mechanism of the Ethanolysis Reaction

Certain hitherto inexplicable changes connected with the ethanolysis of hard- and softwoods would seem to find a satisfactory explanation in the light of the preceding discussion. Chief among these are the now well-established reversible character of certain of the ethanolysis reaction products and the non-reversible type shown by others.

Thus while the simple ethanolysis spruce lignin units, such as \checkmark -hydroxypropiovanillone, on refluxing with ethanol-HCl, are converted into irreversible, higher molecular weight lignin polymers, on the hand other/certain of the lower-molecular weight lignin ethanolysis fractions (non-distillable phenols) are

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changed into readily distillable oils when subjected to the same treatment. In agreement with the theoretical views of Freudenberg and of Hibbert the first type (irreversible) is exemplified in the -C-C model of condensation polymer such as exists in benzofurane groupings etc., while the latter (reversible) presupposes an ether or acetal linkage as the connecting link between the lignin units.

That these two types have a very definite existence in different fractions of ethanolysis lignins is evident on the one hand from the hydrogenation data in Table XX, and from the previously mentioned data of Adkins' (see p.120) on the much greater resistance to fission of a C-C as compared with a C-O-C linkage over CuCrO, together with that author's data concerning the structure of the resin obtained by the hydrogenation of lignin (see p.122-123).

Hägglund has shown (pp. 71-72) that the alkoxyl group added on during ethanolysis, can be readily removed, at least in large measure, by the action of hot dilute acid, a behaviour which led him to conclude that acetal formation has occurred.

This conclusion finds support in the formation of α -methyl mannoside during the methanolysis of spruce wood, as found by Compton, Greig and Hibbert (15a) and in the recent discovery of the presence of a ketal grouping in the <u>neutral</u> ethanolysis fraction.

Possibly the reversible type of ethenolysis, associated with an acetal union, may be connected with changes involving a primary half-acetal (ethylal) formation between the carbonyl group in the lignin unit side chain and the solvent followed by a further intermolecular half-acetal union between two moles of the primary half-acetal to give a "mixed" acetal as shown below:

$$R = C = OHOH = CH_3$$

$$R = C = O$$

Dilute acids would bring about removal of ethanol and formation of a C-C linked, irreversible polymer from the liberated "activated" lignin units. On the other hand any re-union of two molecules to give an ether type -CO-CH-O-CH-CO- would give a product capable CH₃ CH₃

of hydrogenolysis into two moles of the individual lignin units, but incapable of being cleaved by ethanolic hydrogen chloride. This point of view finds confirmation in the close relationship indicated (Table XX) in the comparable yields, shown to exist between the amounts of monomolecular lignin units formed on ethanolysis of the various ethanol lignin fractions and the yields of distillable products found on hydrogenation.

Recent unpublished work of Hewson, McCarthy and Hibbert (150) in which it is shown that repeated successive ethanolysis of a maple wood ethanol lignin gives two products, namely water-soluble oils and an ethanol-insoluble lignin, also provides additional support for the theory of reversible and non-reversible polymer formation as well as the work of West, Hawkins and Hibbert on the action of ethanolic HCl (2%) on vanilloylmethyl ketone and α -hydroxypropiovanillone whereby amorphous lignin-like materials are formed(110).

VII. EXPERIMENTAL SECTION

A. Alcoholysis Experiments

1. The Ethanolysis of Maple Wood

The ethanolysis of 1000 g. of maple wood meal was carried out according to the standard procedure as described by Pyle, Brickman, McCarthy and Hibbert (151). The products shown in Table <u>x x</u> were obtained (See Flow Sheet <u>I</u>).

TABLE XXI

The Ethanolysis of Maple Wood-Lignin Balance

(1000 g. untreated wood meal contained 215 g. lignin)

	E	thanolysis Fraction	Yield g.	Portion of Original Lignin in Wood
A	_	Wood Residue (565 g. 12% lignin)	68	32.0
В	-	Ethanol Lignin	ଞଠ	37.0
C	-	Benzene Shakings	38	17.7
D		Red Tars	6	2.3
E	-	Water-Soluble Oils	76	35.5
				Total 119.5

The water-soluble oils (Fraction E) were separated according to the method outlined in Flow Sheet <u>III</u>. Instead of separating
FLOW SHEET I

ETHANOLYSIS OF MAPLE WOOD MEAL



FLOW SHEET II





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FLOW SHEET III

FRACTIONATION OF "WATER-SOLUBLE OILS" (FRACTION E)

Scheme No. 2

75 g. Fraction E

Pptn. of acetone soln. into 30-50° pet. ether



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the non-distillable-from the distillable phenols by distillation, however, a solvent fractionation procedure was used (See Flow Sheet <u>II</u>). By precipitating 300 cc. of a benzene solution containing 29.7 g. of "alkali-soluble oils" into 6 liters of 30-50° petroleum ether, it was possible to isolate 9.6 g. of amorphous "water-soluble lignin" (non-distillable phenols).

2. The Methanolysis of Maple Wood

Maple wood meal (40 mesh) was first air-dried and then extracted for 48 hours with a 1:1 mixture (by volume) of absolute ethanol and benzene, then with absolute ethanol for 24 hours, and finally washed with hot, running water for 12 hours. After air-drying, the wood meal was dried in the vacuum oven (20 mm. pressure) for 48 hours at 50°C. The wood meal, upon analysis, showed a Klason lignin content of 20.8%, and a moisture content of 1.1%.

The maple wood meal (382 g.) and dry methanol (3.82 liters) containing anhydrous hydrogen chloride (94 g., 3% by weight) were placed in a flask equipped with a mercury-sealed stirrer and a reflux condenser. The contents were refluxed, with stirring, for 50 hours. At the end of this time the mixture was cooled, filtered, and the residual wood meal washed with hot anhydrous methanol (1.5 liters). The wood residue, after air-drying, weighed 211.5 g. and contained 4.5% moisture and 10.6% Klason lignin.

The combined methanol liquors were neutralized with

solid sodium bicarbonate, the sodium bicarbonate-sodium chloride precipitate removed by filtration, and the methanol filtrate concentrated at 100 mm. pressure to a volume of 500 cc. The methanol concentrate was dropped in a very fine stream into vigorously-stirred distilled water (9 liters) and the precipitated methanol lignin was filtered and washed well with water. The methanol lignin was air-dried over night and then reprecipitated from a methanol solution (800 cc.) into 12 liters of distilled water. The amorphous precipitate was removed from the aqueous liquor by filtration, washed carefully with distilled water, and then air-dried. The air-dried methanol lignin weighed 33 g.

The combined precipitation liquors and washings were concentrated to a small volume (1.2 liters) at 50°C under reduced pressure (40-50 mm.). During the concentration process 6.3 g. of a tar-like material was precipitated from solution. The tar-free aqueous concentrate was exhaustively extracted with benzene, the benzene removed, leaving 19.96 g. of a viscous oil.

A summary of the yields of methanolysis products from maple wood is given in TABLE XXII.

TABLE XXII

THE METHANOLYSIS OF MAPLE WOOD-LIGNIN BALANCE

(373 g. untreated wood meal contained 77.0 g. lignin)

Methanolysis Fraction	Yield g.	Porti Lig	on of Original min in Wood %
Wood residue (202 g., 10.6% ligni	21.4 n)		27.8
Methanol Lignin	33.0		42.8
"Red Tars"	6.3		క .2
Water-Soluble Oils	20.0		26.1
		Total	104.9

3. The Methanolysis of Maple Methanolysis Wood Residue

Fifty grams of the air-dried wood residue (4.5% moisture; 10.6% lignin) from the methanolysis of maple wood was again refluxed with boiling 3% methanolic hydrogen chloride (500 cc.) for 36 hours. The mixture was cooled, filtered and the residual wood meal washed with hot, anhydrous methanol. After drying in the vacuum oven for 24 hours the residue weighed 45 g. (9.15% lignin).

Forty grams of this residue was subjected to an additional methanolysis reaction. The vacuum-oven-dried wood meal residue weighed 37.7 g. and contained 9.12% lignin.

4. The Methanolysis of Aspen Wood

Aspen⁺ wood meal (150 g.) was extracted with 30-50° petroleum ether (24 hours), ethyl ether (24 hours), ethanol (6 days), and 1:1 ethanol-benzene (48 hours) in the order given. After air-drying, the wood meal was dried in the vacuum oven (20 mm. pressure) for 5 hours at 50°C. The wood meal, upon analysis, showed a Klason lignin content of 17.5% and a moisture content of 4%.

The aspen wood meal (150 g.) was treated in exactly the same manner as was the maple wood (see preceding section). A summary of the yields of the methanolysis products from aspen wood is given in TABLE <u>XXIII</u>.

TABLE XXIII

THE METHANOLYSIS OF ASPEN WOOD-LIGNIN BALANCE

(150 g. of untreated wood meal contained 25.1 g. lignin)

Methanolysis Fraction	Yield g.	Portion of Original Lignin in Wood
Wood Residue (89 g., 8.7% lignin)	7.4	29.4
Methanol Lignin	12.0	47.9
Red Tars	4.8	19.1
Water-Soluble O <u>j</u> ls	3.0	11.9 Total 106.3

⁺ The aspen wood was obtained from a three-year old tree; therefore the quantity of lignin present in the wood was relatively low (see p.8).

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B. Hydrogenation Experiments

1. Apparatus, Catalysts and Solvents

(a) Apparatus

The following pieces of equipment were used in the hydrogenation experiments.

One 500 cc. capacity high-pressure reduction apparatus manufactured by the Parr Instrument Company and described in Bulletin E-44 published by that company.

One 2500 cc. capacity high-pressure hydrogenator, No.406-DLa, described in Catalog 406 of the American Instrument Company. Temperature control was maintained with this electrically heated apparatus by the use of a Type 100 Variac manufactured by the General Radio Company.

One hydrogen pressure "booster" pump, No.406-135, also manufactured by the American Instrument Company.

Both hydrogenation units were connected to the booster pump in such a manner that hydrogenations could be run simultaneously or separately. Voltages were measured with a simple slide-wire potentiometer. The arrangement of the hydrogenation equipment is shown in Figure \underline{VI} .

FIGURE VII

HYDROGENATION APPARATUS



- A. Parr Apparatus
- B. Aminco Apparatus
- C. Booster Pump
- D. Slide-wire Bridge

Themol lighth (15 g.) was discolved in absolute dioxanal (150 cc.) and placed in the Part bomb with 8.8 g. of CuCrO catalyst. Hydrogen was similted at a pressure of 3200 psi. (pounds per square inch). The shaker was then started and the bomb (supersture was rapidly increased to 250°C. The (b) Catalysts

Copper-chromium oxide (156) and Raney nickel (157) catalysts were prepared according to the methods of Adkins. The activity of the CuCrO catalysts was tested with acetone (71, p.50); the Raney nickel, with acetone and with benzene (71, p.50 and 57).

(c) Solvent

In order to eliminate the catalyst-poisoning content of commercial dioxane, the solvent was purified by refluxing in an all-glass apparatus with sodium for 36 hours. During the treatment a thick sludge always formed on the bottom of the reaction vessel. At the end of the heating treatment the purified anhydrous dioxane (b.p. $101^{\circ}C$; $^{25} = 1.4202$) was separated by distillation at atmospheric pressure. It was not necessary to use a fractionating column.

2. <u>Hydrogenation of Ethanol Lignin (Fraction B,</u> Flow Sheet I); Series I

(a) Experiment No.1 (The Effect of HCl Contamination)

Ethanol lignin (15 g.) was dissolved in absolute dioxane (150 cc.) and placed in the Parr bomb with 8.8 g. of CuCrO catalyst. Hydrogen was admitted at a pressure of 3200 psi. (pounds per square inch). The shaker was then started and the bomb temperature was rapidly increased to 250°C. The reaction was allowed to proceed for 18 hours, at the end of which time 0.6 moles of hydrogen per 100 g. lignin had been absorbed. The heating was stopped, the bomb allowed to cool, and the bomb contents transferred to a 400 cc. beaker. The bomb was washed carefully with absolute dioxane, and the combined reaction mixture and washingsfiltered with suction through a sintered glass funnel (Jena, No.4). The catalyst residue was dark red, and the filtrate dark brown in color.

The fact that (a) the catalyst was red in color, (b) that the hydrogen consumption was only 0.6 moles hydrogen per 100 g. lignin (Adkins (73) reported 4.0 moles hydrogen per 100 g. methanol lignin), and (c) that the dioxane solution was not colorless indicated that the reaction had not gone to The color of the catalyst suggested that it had completion. been poisoned; and since hydrochloric acid had been used in the preparation of the ethanol lignin, it appeared that traces of acid had destroyed the catalyst. A sample (1 g.) of the lignin was heated for one hour with 10 cc. of boiling water to which had been added 2 drops of concentrated nitric acid. At the end of the two-hour heating period the suspension was filtered, and 1 cc. of a 10% silver nitrate solution was added to the filtrate. An appreciable precipitate of silver halide was obtained.

In order to remove all traces of hydrochloric acid from the ethanol lignin which was to be used for hydrogenation experiments, a large quantity (300 g.) of this material was

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reprecipitated three times from ethanol solution into water. The lignin thus purified gave no test for the Cl⁻ ion. The test for Cl⁻ was always made prior to the hydrogenation of a given lignin preparation.

(b) Experiment No.2 (Successful Hydrogenation of Ethanol Lignin)

A sample of the Cl⁻ ion-free ethanol lignin (15 g.) was hydrogenated according to the procedure described in Experiment No.1. During the reaction 3.88 moles of H_2 per 100 g. of lignin were absorbed, the catalyst residue was black, and the dioxane solution of the hydrogenation product was colorless.

(c) Experiment No.3

A hydrogenation, duplicating Experiment No.2, was made in the 2500 cc. Aminco apparatus with 90 g. of Cl⁻ -ionfree lignin.

3. <u>Separation and Identification of Hydrogenation</u> Products Obtained from Experiments Nos. 2 and 3

(a) Preliminary Fractionation of Hydrogenation Products

The combined dioxane solutions obtained in Experiments Nos. 2 and 3 (1.4 liters) were placed in a 2-liter round-bottomed flask and fractionated through a 30 mm. Widmer fractionating column packed with 1 cm. lengths of 1 mm. glass tubing. A total of 145 g. of material (Fraction <u>I</u>) boiling from 63° to 101°C at atmospheric pressure was collected and placed over "drierite".

The dioxane in the remainder of the solution was removed at atmospheric pressure at 101°C. This material upon refractionation through the same column distilled constantly at 101°C.

After the dioxane had been removed at atmospheric pressure, the orange-colored residue (66.6 g.) was placed in a 125 cc. Claisen flask and distilled at reduced pressure (10-12 mm.) and a bath temperature of 105°C. The distillate had a constant refractive index (25°C) of 1.4204, which is the value for pure dioxane. The residue (Fraction II) weighed 55.5 g.

(b) <u>Fractionation and Identification of Products Boiling Below</u> 101°C (Fraction I)

The material boiling below 101°C, which was allowed to stand over "drierite" for 3 days, was fractionated carefully in a 24" Widmer column containing a glass spiral 18 inches long and 1/2 inch in diameter. The following fractions were isolated:

Fraction Ia (Methanol):

Boiling point, 63-66°C at 760 mm. pressure $n_D^{25} = 1.3520$. Identified as methanol by means of the α -naphthyl urethane derivative, m.p., 123-124°C. Mixed melting point with an authentic sample, 123-124°C. Yield, 10.6 g.

Fraction Ib (Ethanol):

Boiling point, $78-79^{\circ}$ C at 760 mm. pressure. $n_D^{25} = D^{1.3670}$. Identified by means of the α -naphthyl urethane, m.p., 69-80°C. Mixed melting point with authentic derivative of ethanol, 79-80°C. Yield, 5.4 g.

Fraction Ic (Dioxane-Water Azeotrope):

Boiling point, $\$6.9 - \7.2° C at 760 mm. pressure. $n_D^{25} = 1.4079$. A positive test for water was obtained with anhydrous CuSO₄. After the addition of several small pieces of anhydrous CaCl₂ to 1 cc. of Fraction Ic, the refractive index of the liquid gradually increased to 1.4200, the value for dioxane. This result indicated that the fraction was an azeotropic mixture of water and dioxane. The indication was verified by the following experiment:

Distilled water was added from a burette to 50 cc of pure dioxane until the refractive index (25°C.) of the dioxane-water solution reached 1.4079 (11.5 cc. of water required). The solution was then fractionally distilled through an 18" Widmer column; the entire quantity distilled at \$7.2°C and samples of the distillate taken at frequent intervals all had the same refractive index of 1.4709 (25°C).

Therefore Fraction Ic consisted of water and dioxane as an azeotropic mixture. Since a portion of the water was probably absorbed by the "drierite", the yield of S.O g. of water represented a minimum value.

(c) <u>Fractionation and Identification of Products Boiling</u> above 101°C (Fraction II)

The products boiling from 97°C at 7 mm. pressure to 185°C at 0.65 mm. pressure (21.76 g.) (Fraction II) were refractionated carefully from a 35 cc. vacuum jacketed Widmer-Claisen flask. This flask has been described by Perry and Hibbert (185).

Fraction IIa (4-n-propylcyclohexanol):

Boiling point, 93-95°C at 7 mm. pressure. $n_D^{25} = 1.4630$. Identified by means of the phenyl- and α -naphthyl urethanes (m.p. 129-130°C and 133-134°C, respectively). Mixed melting point with the phenyl urethane from a synthetic sample of 4-n-propylcyclohexanol, 129-130°C. Yield, 7.5 g.

Fraction IIb (4-n-propylcyclohexanediol-1,2):

Boiling point, 106-110°C at 1 mm. pressure. $n_D^{25} = D$ 1.4820; $n_D^{60} = 1.4709.$ Identified by means of the α -naphthyl urethane, m.p. 218-219°C. Adkins reports a melting point of 218-219°C for this derivative (73). Yield, 0.92 g.

Fraction IIc (Product X):

Boiling point, $126-129^{\circ}C$ at 1 mm. pressure. n⁶⁰ = D 1.4842. Yield, 6.1 g.

In addition, three small intermediate fractions, each containing two of the above materials were collected. They

Resinous Residue:

It was impossible to obtain a refractive index of the viscous (almost solid) resinous residue on the Abbé refractometer. The resin gave the following results upon analysis:

> C = 73.6, 73.8H = 10.8, 10.9 Yield, 33.0 g.

(d) Summary of Results from the Hydrogenation of Ethanol Lignin

A summary of the products obtained in the hydrogenation of 107 g. of ethanol lignin (maple) is shown in Table \underline{YXIV} Note that the yields of 4-n-propylcyclohexanol, 4-n-propylcyclohexanediol-1,2, and Product X include the material isolated in the intermediate fraction.

TABLE XXIV

Compound	Boiling Point °C	Weight	Yield %(a)
Methanol	63-66° (760 mm.)	10.6	10.0
Ethanol	7 8-79° (760 mm.)	5.4	5.1
Water (minimum)	87°(azeotrop (760 mm.)	e) 8.0	7.5
4-n-Propylcyclohexanol	93-95° (7 mm.)	8.5	క.0
4-n-propylcyclo- hexanediol-1,2	106-110° (1 mm.)	2.0	1.9
Product X	126-129° (1 mm.)	7.0	6.6
Residue	$130+^{\circ}$	34.21	32.0
		Tota	al=71.1

ETHANOL LIGNIN HYDROGENATION PRODUCTS

%(a) = Percentage yield on basis of original ethanol lignin

(e)	Exa	mi	nation	of Proc	luct	y	<u> </u>		
		(:	1) <u>Ana</u>	lytical	Dat	a			
Found	<u>i:</u> C	н	73.5,	73.3%;	H	=	11.6,	11.	7%

Rast molecular weight = 236, 232

Grignard Analyses:

Moles active hydrogen Mole compound (C18) = 2.01, 2.13

Carbonyl = 0.0

Calc. for C₁₈H₃H₃H₃H₃:

C = 73.05; H = 11.5%. Mol. wt. = 297.

(2) Derivatives of Product X

(a) Dichloracetyl Ester of Product X

The preparation of this derivative was carried out according to the method of Bell (159).

A benzene solution (l cc.) containing 0.53 g. of dichloracetyl chloride was added dropwise to a well-stirred and cooled (- $\$^\circ$ C) solution of Product X (0.3 g.) in 2.2 cc. of anhydrous pyridine.

After all of the dichloracetyl chloride had been added, the reaction mixture was allowed to stand at 0°C for 3 hours. A l:l mixture (10 cc.) of benzene and water was then added to the reaction mixture, the water layer removed in a separatory funnel, and the benzene layer washed 3 times with 5 cc. portions of water. The benzene layer was then allowed to stand over "drierite" for 10 hours. Upon removal of the benzene under reduced pressure in a vacuum desiccator, a light reddish-colored oily residue was obtained.

Attempts to obtain a crystalline product from ethanol, chloroform, ethyl acetate and benzene solutions were unsuccessful, consequently the material was distilled at reduced pres-A sample of the oily derivative (200 mg.) was placed sure. in the first bulb of a three-bulb micro, vacuum distillation apparatus (constructed from a single length of 7 mm. pyrex glass tubing) (160). In the distillation, carried out at 10 microns pressure, 150 mg. of material distilled smoothly from the first to the second oulb at a bath temperature of 125-140°C. The second bulb was then heated slightly and two drops of material were distilled into the third bulb. The latter material had a refractive index (25°C) of 1.4915. Since the refractive index (25°C) of the main portion of the distillate (in the second bulb) was 1.4919, it was assumed that the distillate was A Stepanow analysis on 120 mg. of the disa pure compound. tillate indicated a chlorine content of 27.3%. The theoretical value for the bis-dichloracetyl derivative of a dihydroxy compound, $C_{18}H_{34}O_{3}$, is 27.4% chlorine.

(β) Other Derivatives of Product X

The 3,5-dinitrobenzoyl ester of Product X was prepared according to the method of Reichstein (161). The phenyl- and α -naphthyl urethanes were prepared according to the method of French and Wirtel (162). The trityl derivative was prepared in the same manner as the 3,5-dinitrobenzoyl ester (161). All attempts to isolate derivatives in a crystalline form by methods suggested by Morton (160) were unsuccessful.

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(3) Refractionation of Compound X

An additional supply of this material was obtained by the hydrogenation of 90 g. of ethanol lignin (maple). By means of a fractional distillation in a Perry flask a material having the following properties was isolated:

> b.p. $(1 \text{ mm.}) = 122-125 \circ 0$ $n^{25}_{D} = 1.4970$ $n^{60}_{D} = 1.4846$ 0 = 73.6, 73.7%H = 11.6, 11.6\%

It can be seen that these results compare favorably with those for the original Compound X.

Upon redistillation from a Perry flask, the same refractive index was found for the distillate, e.g., $n_{D}^{60} = 1.4848$.

A portion of this material was then fractionally distilled through a modified Podbielniak column (See Experimental Section <u>II</u>,6,(b)) with the following results:

· · · · ·	n	60 D	Poiling		
Fraction	A(a)	B(b)	Point °C	Pressure mm.	Weight
1	1.4784		117	1.6	0.164
2	1.4861		117	1.6	0.117
3	1.4861		117	1.6	0.154
4	1.4861		121	1.8	0.910
5	1.4839	1.4892	124-128	1.8	0.166
6	1.4832	1.4893	128.5	1.8	0.147
7	1.4822	1.4900	128.5	1.8	0.209
g	1.4825	1.4893	130	1.9	0.602
9	1.4825		132	2.0	0.365
10	1.4825		125	2.0	0.289
11	1.4829			2.1	0.259
12	1.4838		-	-	0.279
Residue	-			-	0.106

(a) Bottom Liquid Layer(b) Top Liquid Layer

Fractions 5, 6, 7 and 8 separated into two distinct layers, indicating the presence of at least two components in those fractions.

4. Hydrogenation of Ethanol Lignin; Series II

(a) Experiment No.1

Two-hundred and fifty grams of ethanol lignin were hydrogenated in three portions in the Aminco apparatus. The hydrogenation conditions and the method of preliminary fractionation of the hydrogenation products were carried out according to the procedures described in Experimental Sections <u>II</u>,2,(b) and <u>II</u>,3,(2), respectively.

Fraction <u>II</u> (Experimental Section <u>II</u>,3,(a)), composed of compounds boiling above 101°C, was dissolved in an equal volume of ether (400 cc.), and the ether solution extracted 10 times with 100 cc. portions of water. The residual ether solution, Fraction <u>III</u>, was dried over Na₂SO₄.

The combined aqueous extracts were then concentrated to a volume of 300 cc. by distillation through an 15" Widmer column. The distillate, which contained ether, dioxane and water, was not examined further. The residue was saturated with sodium sulfate and extracted continuously with ether for 45 hours. After drying the ether extract over Na_2SO_4 for 10 hours, the ether was removed under reduced pressure, leaving 6.5 g. of a viscous oil (Fraction <u>IV</u>).

(1) Fractionation of Water-Soluble Oils (Fraction IV)

Fraction <u>IV</u> (6.0 g.) was fractionally distilled through the modified Podbielniak column at 0.5 mm. pressure. The following fractions were collected:

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Fraction	n ²⁵ D	n ⁶⁰ D	Boiling Point °C	Pressure mm.	Weight
1	1.4820		105	1.0	0.470
2	1.4822		106-118	0.7	0.781
3	1.4840	1.4742	121.5	0.6	0.948
24	1.4842	1.4744	121.5	0.6	1.137
5	1.48	1.4744	120	0.5	0.649
6	-	-	121	0.5	0.561
				Total =	4.30

Residue = 1.59 g.

Fractions 1 and 2, which were clear, colorless oils, apparently consisted of 4-n-propylcyclohexanediol-1,2 $(n_p^{25} = 1.4821)$.

(2) Identification of 3-(4-cyclohexyl)propanol-1

Fractions 3, 4, 5, and 6 were semi-crystalline so that once the material had changed from a viscous to a crystalline paste it was impossible to obtain satisfactory refractive index measurements. Attempts to separate the crystalline portion from the oil were unsuccessful. Upon analysis, a sample from Fraction 4 gave the following values:

C = 68.2; H = 11.5%

Calc. for 3-(4-hydroxycyclohexyl)propanol-1:

C = 68.3; H = 11.5%

Oxidation of Fraction 4 to 4-keto-cyclohexane propionic acid:

A sample of Fraction 4 (500 mg.), dissolved in a mixture containing 1.1 g. of CrO_3 , 10 cc. glacial acetic acid, 5.3 cc. water and 10 cc. benzene was shaken at room temperature for 8 hours. At the end of this time the benzene layer was removed and the green aqueous layer extracted three times with 4 cc. portions of benzene. The combined benzene extracts were then extracted with three portions of 10% Na₂CO₃ solution, the Na₂CO₃ solution then acidified with dilute HCl (no precipitation), the acidified solution saturated with sodium sulfate and back extracted with six 10 cc. portions of benzene. After drying the combined benzene extracts over "drierite" for 15 hours, the benzene was removed at reduced pressure (20 mm.). The light yellow viscous residue weighed 250 gm. Yield, 50% of theoretical.

Two hundred milligrams of the oxidation product was then distilled in a micro-distillation bulb at 25 microns pressure. The distillate (130 mg.) solidified to a camphor-like m² terial upon standing. Melting point, 62-64°C.

Preparation of the semicarbazone of the keto-acid:

The keto-acid (100 mg.), dissolved in 0.8 cc. of 40% aqueous ethanol was added to a solution of 100 mg. of semicarbazide in 1.5 cc. of a buffered (pH 5) aqueous solution. Precipitation occurred immediately, and the precipitate after two recrystallizations from water melted at 201-202°C. Mixed melting point with the semicarbazone of the synthetic keto-acid, 201-202°C.

(3) Fractionation of Water-Insoluble Oils (Fraction III)

The material (102 g.) in Fraction <u>III</u> (water-insoluble products boiling above 101°C, 760 mm.) was separated into four fractions by rapid distillation (not fractionation) from a 260 cc. Claisen flask. The following four cuts were made:

raction	<u>IIIa</u> :	B.p., below 105°C at 1 mm.
18	<u>IIIb</u> :	B.p., 100-140°C at 1 mm. (boil- ing range for Product X)
11	IIIc:	B.p., 140-150°C at 1 mm.
11	<u>IIId</u> :	Residue, 59.2 g.; n_{D}^{25} greater than 1.4978

Fractionation of Fraction IIIc:

F

Fraction <u>IIIc</u> (15.6 g.) was refractionated in the Podbielniak column. The following fractions were obtained:

Fraction	n 25°0	D 60°C	Boiling Point °C	Pressure mm.	Weight
1	1.4833	1.4700	110-116	0.9	0.855
2	1.4947	1.4816	116-125	0.9	0.479
3.	1.4974	1.4842	126-138	0.8	1.697
4	1.4993	1.4860	139	0.8	0.615
				Tota	1 = 3.67

Undistilled portion = 11.5 g.

No material corresponding to Compound X was thus present in the hydrogenation products from this experiment (II,4,(a) -Experiment No.1) but on extracting with water the compound 3-(hydroxycyclohexyl)propane-1 was isolated.

5. <u>Comparative Hydrogenation Studies of Ethanolysis</u> Fractions

(a) Hydrogenation Study of a-Ethoxypropiovanillone

α-Ethoxypropiovanillone (15.0 g.), dissolved in 150 cc. of absolute dioxane, was hydrogenated over CuCrO catalyst (18.5 g.) at 250°C with hydrogen at a pressure of 5000 psi. Seven moles of hydrogen per mole of compound were absorbed over a period of 6 hours (see p.116).

The hydrogenation products were separated from the catalyst and dioxane according to the procedure described in Experimental Section II,3(a) and gave two fractions, Fraction I, boiling below 101°C and Fraction II, boiling above 101°C.

Fraction I was analyzed for methanol, ethanol and water according to the procedure described in Experimental Section II,6,(a).

Fraction II was distilled in a Perry flask at 7 mm pressure and gave 6.9 g. (78% yield) of pure 4-n-propylcyclohexanol; $n_D^{25} = 1.4615$ (refractive index constant throughout the distillation). The 4-n-propylcyclohexanol was further characterized by conversion to its phenyl- and α -naphthyl urethanes, m.p., 128.5-130°C and 131-132°C, respectively. When it was found that 4-n-propylcyclohexanol (1.0 g.) upon heating at 140°C for 8 hours yielded a small quantity of resinous product (200 mg.), it was assumed that at least a portion of the residue obtained above was due to the polymerization of 4-n-propylcyclohexanol.

The results of the hydrogenation of α -ethoxypropiovanillone are shown below:

Product	Weight g.	Portion of Theo- retical Yield
Methanol	1.15	55
Ethanol	2.58	ଞ୍ଚ
Water	1.57	130
4-n-propylcyclohexanol	7.40	78

Total weight = 12.59 g. Total return = 84%

(b) <u>Hydrogenation Studies on Amorphous, Non-distillable</u> <u>Ethanolysis Products</u>

(1) <u>Procedure</u>:

Ten to fifteen gram samples of each of the amorphous, non-distillable fractions isolated from the ethanolysis of maple wood (see below) were dissolved in 150 cc. of absolute dioxane and hydrogenated at 250°C with hydrogen at a pressure of 5000-5500 psi. The hydrogenation products were separated according to the method employed in Experimental Section \underline{II} ,4,(a). In brief, the low boiling hydrogenation products (Fraction \underline{I}) and dioxane were removed by distillation through a Widmer column. The products boiling above $101^{\circ}C$ (Fraction \underline{II}) were then separated into water-insoluble (Fraction \underline{III}) and water-soluble (Fraction \underline{IV}) fractions.

Fraction <u>IV</u>, which was shown to contain 3-(4-hydroxycyclohexyl)propanol-1 and <math>4-n-propylcyclohexanediol-1,2 (Experimental Section <u>II</u>,4,(2),(2)) was never found to contain more than 4-5% by weight of the total material hydrogenated. Since it was impracticable to fractionate 500 mg. samples, the yield of these two compounds were combined under the heading "Propylcyclohexane Glycols".

Fraction <u>III</u> (generally 40-50% of the weight of the starting material) was fractionally distilled through the Podbielniak column. This fraction contained 4-n-propylcyclohexanol and the high boiling resins. In addition, the presence of a compound or compounds having a refractive index (25°C) of about 1.4950-1.5000 was indicated by the fractionation curves. Approximately 100 mg. of material remained (liquid holdup) in the column after each fractionation and this quantity was added to the weight of the distillable portion.

The fractional distillations in the Podbielniak column were carried out in all cases at a distillation rate of 100 mg. per hour. The initial distillate pressures were approximately 20 mm., and were gradually lowered during the period of a fractionation (24-36 hours) to 1 mm. pressure. The fractions in

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FLOW SHEET IV

METHOD of SEPARATION and IDENTIFICATION of PRODUCTS from

SMALL_SCALE LIGNIN HYDROGENATIONS (See p. 194)



the $n_D^{25} = 1.4600-1.4700$ range distilled uniformly at a temperature of 122°C at 20 mm. pressure. The fraction in the $n_D^{25} = 1.4900-1.5000$ range distilled uniformly at a temperature of 130°C at 1 mm. pressure. The wire spiral in the column generally became completely dry between the $n_D^{25} = 1.4600-1.4700$ range and the 1.4900-1.5000 range.

The maple wood ethanolysis fractions studied according to this procedure were (Flow Sheets I, II and III): Ethanolysis Fraction A, the ethanolysis wood residue; <u>B</u>, benzene-extracted, water-insoluble lignin, commonly called "ethanol lignin"; <u>C</u>, benzene-soluble, water-insoluble fraction commonly called "benzene shakings"; <u>D</u>, the ethanol-water soluble fraction commonly called "red tars"; and <u>F</u>, water-soluble, 30-50°C petrolinsoluble lignin commonly called "higher-boiling phenols".

(1) <u>Hydrogenation Study on Fraction A (Ethanolysis</u> Wood Residue)

Due to the fact that this fraction was chiefly carbohydrate in nature, the experimental procedure varied slightly from that described above.

Carefully washed (Cl⁻free) maple ethanolysis residual wood meal (150 g.) containing 12.2% Klason lignin (18 g. lignin) was suspended in 950 cc. of dioxane with 89 g. of CuCrO and hydrogenated at <u>280°C</u> for 16 hours with hydrogen at a maximum pressure of 6,000 psi. A hydrogen absorbtion of 2.97 moles per 100 g. of wood was observed. The higher-boiling hydrogenation products were separated from the catalyst, the low-boiling alcohols and the dioxane according to the standard procedure. The materials boiling above lol°C and having a refractive index (25°C) higher than 1.4500 were rapidly distilled in a loo cc. Claisen flask at 1 mm. pressure (final bath temperature of 220°C). The resin obtained at this point weighed 5.96 g. and the distillate, 38.69 g. The distillate was then separated into water-insoluble and waterinsoluble fractions. The water-soluble fraction has not been examined as yet.

The water-insoluble fraction (25.2 g.) was then fractionally distilled through the Podbielniak column with the following results:

Fraction	Weight g.	Portion of original material	f 1 n ²⁵ 1 D
1234 567890 10	0.300 .400 .150 .300 .156 .147 .564 .302 .280 .236	0.194 .258 .100 .194 .100 .095 .364 .195 .181 .152	(Two layers (present (in Fractions (1 to 4 1.4092 1.4111 1.4168 1.4173 1.4171 1.4174

(continued)

Fraction	Weight g.	Portion of original material	n ²⁵ n _D
123456789012222222222233333333333901234444444444445678901234555555555555555555555555555555555555	0.22547355600903007 273802245662660950041322222	0 = 142 184 1572 1282762 1252 1252 125894 172511 12541 12541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1541 1522 1542 1522 1541 1522 1542 1522 1542 1522 1542 1522 1252 1	111111111111111111111111111111111111

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(continued)

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Fraction	Weight g.	Portion of original material	n ²⁵ D
5789012345678	0.254 .267 .240 .207 .321 .198 .254 .239 .254 .239 .221 .189 .129 .129 .206 .095	0.164 .173 .155 .134 .207 .136 .174 .164 .152 .129 .086 .141 .065	1.4614 1.4610 1.4617 1.4616 1.4676 1.4693 1.4709 1.4709 1.4711 1.4710 1.4733 1.4780

Total=16.90 g.

At the end of this fractionation the residual resin weighed 1.4 g. The material collected in the cold trap weighed 5.8 g.

Fractions Nos.50 to 62 (3.19 g.) were recombined and refractionated with the following results:

Fraction	Weight g.	n ²⁵ D	
1	0.191	-	
2	.155	1.4348	
3	.090	1.4369	
4	.095	1.4382	
5	.105	1.4402	
6	.100	1.4402	
7	.104	1.4298	
8	.112	1.4298	
9	.106	1.4254	
10	.090	1.4247	
11	.090	1.4248	
12	.090	1.4250	

The remainder of this material (1.62 g.) was collected in the cold trap. Apparently the compounds boiling in this range were too volatile to be distilled at such a low rate of distillation (100 mg. hour) at 100 mm. pressure (boiling point of 92°C).

Fractions Nos. 15 to 29 (3.06 g.) were also recombined and refractionated with the following results:

Fraction	Weight g.	Portion of original material %	n ²⁵ D
1234567890112345678901222222222222222222222222222222222222	0.040 .083 .092 .035 .180 .050 .064 .101 .092 .138 .070 .087 .100 .075 .100 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .075 .077	0.026 .05626 .05654250 .0054250 .0054250 .005666994787776449 .005776449 .0057662 .0057662	1.4420 1.45120 1.4570511 1.455811 1.455911 1.455911 1.455911 1.4559911 1.4559911 1.4559911 1.46613311 1.4661901 1.466108 1.466108 1.46602

(continued)

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Fraction	Weight	Portion of original material	n ²⁵ D
26	0.086	0.058	1.4635
27	.078	.052	1.4635
28	.098	.066	1.4638
29	.100	.067	1.4642
30	.102	.068	1.4653
31	.120	.080	1.4660

Total = 2.89 g.

(2) Hydrogenation Study on Fraction B (Ethanol Lignin)

Fifteen grams of ethanol lignin were hydrogenated according to the procedure described above. The hydrogenation was complete in 14 hours, and 3.98 moles of hydrogen were absorbed per 100 g. of lignin.

The water-soluble fraction (Propylcyclohexane Glycols) weighed 0.82 g., or 5.3% of the weight of the lignin.

The water-insoluble fraction was fractionally distilled through the Podbielniak column with the following results:

Fraction	Weight g.	Portion of original material %	n ²⁵ D
123456	0.077 .183 .153 .195 .195 .196 .129	0.513 1.22 1.02 1.30 1.04 0.860	1.4608 1.4634 1.4634 1.4635 1.4635 1.4633

(continued)

Fraction	Weight g.	Portion of original material	n ²⁵ D
7 9 10 11 12 13 14	0.115 .1015 .0942 .134 .0745 .0876 .0842	0.766 0.676 0.628 0.893 0.496 0.584 0.562	1.4658 1.5679 1.4680 1.4678 1.4680 1.4697 1.4703
15 16 17 18 19 20 21 23 24 23 25	.0610 .0539 .0783 .1168 .0943 .0943 .0915 .0749 .0939 .0166	0.406 0.359 0.495 0.628 0.610 0.499 0.626 0.119	1.4701 1.4701 1.4795 1.4923 1.4940 1.4940 1.4940 1.4965 1.4982

The distillable portion weighed 2.56 g., or 17.0% of the weight of the lignin.

The undistilled residue weighed 4.40 g., or 29.5% of the weight of the lignin.

Samples from those fractions in the center of a group of fractions of constant refractive index were analyzed for carbon and hydrogen content:
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Fraction	% C	% H
4	75.6	12.7
<u>4</u>	76.1	12.9
9	76.0	12.6
9	76.2	12.7
(Calc. for	4-n-propy C = 76.1, H	lcyclohexanol = 12.7%)
23	80.4	12.3
23	80.2	12.2

(3) <u>Hydrogenation Study on Fraction C ("Benzene-</u> <u>Shakings</u>"

:

A sample of the "benzene-shakings" (12.2 g.) was hydrogenated according to the procedure described above. The hydrogenation was complete in 5 hours and 3.5 moles of hydrogen were absorbed per 100 g. of material.

The water-soluble fraction (propylcyclohexane glycols) weighed 0.48 g., or 5.2% of the weight of the original material.

The water-insoluble fraction was fractionally distilled through the Podbielniak column with the following results:

Fraction	Weight g.	Portion of original material	n ²⁵ D
123456789012345678901222222222222222222222222222222222222	0.061 .141 .195 .196 .197 .195 .197 .167 .157 .105 .105 .005 .005 .05	$\begin{array}{c} 0.50\\ 1.12\\ 1.60\\ 1.53\\ 1.11\\ 1.42\\ 5.8\\ 1.97\\ 1.11\\ 1.25\\ 1.97\\ 1.11\\ 0.58\\ 1.97\\ 1.11\\ 0.680\\ 9.66\\ 0.89\\ 1.26\\ 9.53\\ 1.64\\ 1.64\\ 1.64\\ 1.65\\ 0.64\\ 1.65\\ 0.64\\ 1.65\\ 0.64\\ 1.66\\ 0.65\\ 0.64\\ 1.66\\ 0.65\\ 0.64\\ 1.66\\ 0.65\\$	$\begin{array}{c} 1.4560\\ 1.4560\\ 1.4625\\ 1.4625\\ 1.4625\\ 1.4625\\ 1.4625\\ 1.46625\\ 1.46673\\ 1.46673\\ 1.4673\\ 1.4673\\ 1.4673\\ 1.46992\\ 1.4900\\ 1.4900\\ 1.4986\\ 1.4997\\ 1.4986\\ 1.4997\\ 1.4997\end{array}$

Tota1=3.347

The distillable portion weighed 3.347 g. or 27.4% of the weight of the starting material.

The residue weighed 1.69 g., or 13.8% of the weight of the starting material.

(4) Hydrogenation Study of Fraction D ("Red Tars")

Fifteen grams of the "red tars" were hydrogenated according to the procedure described above. The hydrogenation was complete in 48 hours, and 3.68 moles of hydrogen were absorbed per 100 g. of starting material.

The water-soluble fraction weighed 0.90 g. or 5.96% of the weight of the starting material.

The water-insoluble fraction was fractionally distilled through the Podbielniak column with the following results:

Fraction	Weight g.	Portion of original material %	n ²⁵ D
12 74 56 78 9012 34 56 78 9012 34 56 78 9012 34 56 78 9012 22 22 22 22 22 22 22 22 22 22 22 22 2	0.051 .135 .0253 .1355 .2210 .1607 .1607 .1607 .16093 .16924 .10806 .108592 .16806 .108592 .16806 .109528 .109000 .000000 .00000 .00000 .00000 .00000 .00000 .000000 .000000 .000000 .000000 .0000000 .0000000 .000000000000 .000000000000000000000000000000000000	0.3460.0280.021.021.001.001.0000.0000.0000.00	1.45834 1.45994 1.466218 1.46616616 1.46616616 1.4661661 1.4661661 1.4661661 1.4661668 1.46668 1.46677 1.46668 1.4888 1.488 1.49996 1.5032 1.5032 1.5032

The distillable portion weighed 4.96 g. or 33.10% of the starting material.

The residue weighed 2.17 g. or 14.55% of the weight of the starting material.

(5) <u>Hydrogenation Study of Fraction F (Higher-</u> <u>Boiling Phenols)</u>

A sample of the "higher-boiling phenols" (9.6 g.) was hydrogenated according to the procedure described above. The hydrogenation was complete in 4.0 hours and 3.80 moles of hydrogen were absorbed per 100 g. of starting material.

The water-soluble fraction weighed 0.56 g., or 5.9% of the starting material.

The water-insoluble fraction was fractionally distilled through the Podbielniak column with the following results:

Fraction	Weight g.	Portion of original material %	n ²⁵ D		
1 2 3 4 5 6 7 8 9 10	0.152 201 .153 .090 .157 .213 .364 .126 .133 .269	1.60 2.12 1.61 0.97 1.72 2.33 4.00 1.39 1.47 2.96	1.4532 1.4501 1.4545 1.4565 1.4598 1.4608 1.4604 1.4604 1.4604		

(continued)

Fraction	Weight g.	Portion of original material %	ⁿ²⁵ D
11 12 13 14 15 16 17 18 19 20 21 22 23 24	0.290 .176 .170 .133 .147 .080 .076 .111 .153 .030 .247 .159 .179 .115	3.20 1.95 1.86 1.46 1.61 0.875 0.73 1.21 1.67 0.33 2.68 1.73 1.95 1.25	1.4604 1.4604 1.4665 1.4693 1.4676 1.4674 1.4720 1.4826 1.4876 1.4898

The distillable portion weighed 4.035 g. or 42.2% of the weight of the starting material.

The residue weighed 0.58 g. or 6.1% of the weight of starting material.

6 Hydrogenation Study of Methanol Lignin (Maple)

Fifteen grams of methanol lignin (maple) were hydrogenated according to the procedure described above. The hydrogenation was complete in 16 hours and 4.4 moles of hydrogen were absorbed per 100 x. of lignin.

The water-soluble fraction (Propylcyclohexyl Glycols) weighed 0.50 g. or 3.5% of the weight of the original lignin. In concentrating the aqueous solution containing the "Glycol" fraction entrainment apparently occurred. As a result the aqueous distillate, instead of having the correct refractive index (25°) of 1.3330, had a value of 1.3960. The material isolated from the aqueous concentrate doubtlessly was only a fraction of the actual quantity of "glycols" The given value, therefore, is open to question and must be confirmed.

The water-insoluble fraction was fractionally distilled through the Podbielniak column with the following results:

Fraction	Weight g.	Portion of original material %	n ²⁵ D
1234567890112345678901123456789011234567890112234	$\begin{array}{c} 0.121\\ .055\\ .104\\ .111\\ .105\\ .114\\ .115\\ .114\\ .116\\ .119\\ .098\\ .109\\ .109\\ .109\\ .122\\ .120\\ .109\\ .113\\ .122\\ .120\\ .109\\ .109\\ .114\\ .009\\ .107\\ .144\\ .065\end{array}$	- 800 - 366 - 680 - 740 - 700 - 760 - 765 - 781 - 755 - 781 - 755 - 781 - 755 - 781 - 755 - 781 - 755 - 765 - 755 - 755	1.4652 1.4610 1.4630 1.4620 1.4607 1.4609 1.4609 1.4605552 1.4665552 1.4665552 1.4665552 1.4665552 1.4665594 1.49322 1.493350 1.49350 1.49350 1.49350
Tota	1 = 2.04		

The distillable portion weighed 2.63 g. or 17.6% of the weight of the lignin. (0.80 g. or 5.3% of the low boiling components with $n_D^{25} = 1.4650$ and lower collected in the cold trap.) The undistillable residue weighed 2.10 g. or 14.0%

of the weight of the lignin.

7. Development of Technique for Identification of Products from Small-scale Lignin Hydrogenations

(a). Quantitative Procedure

(1) Determination of Water in Organic Solutions

The following procedure for the quantitative determination of water in organic solutions was based upon the work of Ilosovoy (163a), Willstätter and Maschmann (163b), Schütz and Klauditz (161c), and Barellini (161d).

(A). Reagents

<u>N/10 KMnO₄</u>: Dry analytical KMnO₄ (3.3 g.) was dissolved in one liter of distilled water and heated on the steam bath for one hour. The cool solution was filtered through a sintered glass funnel, and the filtrate was stored in a clean, glass-stoppered bottle. The KMnO₄ solution was standardized against oxalic acid.

<u>Copper Absorption Solution</u>: $Cu(NO_3)_2 \cdot 5H_2O$ (1 g.) was dissolved in a small amount of distilled water in a 50 cc. volumetric flask. To this solution, 4 cc. of 20% NH_AOH were added dropwise, and then a saturated solution of NH₂OH.HCl and distilled water was added to make a total volume of 50 cc.

Acid Fe⁺⁺⁺ Solution: To a suspension of Fe₂(SO₄)₃ in 300 cc. of distilled water in a one liter volumetric flask was slowly added 110 cc. of concentrated H_2SO_4 . The solution was maintained at room temperature during the addition of the H_2SO_4 by cooling the flask in a stream of cold water. After the addition of the H_2SO_4 , the solution was diluted to a volume of 1 liter by the addition of distilled water. Upon standing for about 30 minutes the suspension changed to a clear solution.

(β). Apparatus

The apparatus consisted of a 25 cc. ground-glass round-bottomed flask, a reflux condenser equipped with a male ground at the bottom, and an absorption train consisting of 3 test tubes (8" tube, 5" tube, and 3" tube, in that order). The condenser was placed in a vertical position (reflux) and was fitted with a two-hole rubber stopper at the top. Through one hole was passed a fine capillary tube which extended 2/3 the length of the condenser and through which tube was passed dry, CO_2 -free nitrogen. The other hole was connected to the absorption train with glass tubing.

(γ) . Procedure

Enough sample was weighed into the <u>dry</u> flask to give 18-72 mg. of $H_{2}O(0.5 - 1.0$ g. sample containing 3-10% $H_{2}O$). The sample was diluted with 5 cc. of 98% ethanol and 0.15 - 0.20 g. of finely ground calcium carbide was added. The flask was then immediately attached to the condenser; a small quantity of Fisher stop-cock grease was used at the very top of the joint. The solution was then refluxed at a bath temperature of 95-100°C for 50 minutes with a steady stream of nitrogen (1 bubble per second) passing through the apparatus, and with the ethanol condensing just below the nitrogen inlet. At the end of this time, the cooling water was drained from the condenser and a portion of the ethanol was allowed to reach the absorption train.

The contents of the absorption flask were then washed into a 250 cc. Erlenmeyer flask and the copper acetylide precipitate filtered through a Jena, G/4 sintered glass funnel and washed free of chlorides. Since the precipitate was quite flocculent, it was found that 1.0 - 1.5 liters of distilled water was required. Since copper acetylide is very slightly soluble in cold water it is advisable to use the same volume during the determination as was used during a blank determination. After having been washed (care being taken to prevent drying of the acetylide), the precipitate was dissolved on the filter with 40 cc. (two portions; one of 25 cc., and one of 15 cc.) of the acid-Fe⁺⁺⁺⁺ solution. The filtrate was then titrated with N/10 KMnO₄ according to the reactions:

 $Cu_2C_2 + Fe_2(SO_4)_3 + H_2SO_4 \longrightarrow 2FeSO_4 + 2CuSO_4 + C_2H_2$ 10FeSO₄ + 2KMnO₄ + 8H₂SO₄ == Fe₂(SO₄)₃ + K₂SO₄ + 2MnSO₄ + 8H₂O

One cc. of N/10 $KMnO_4$ is equivalent to 0.0018 g. of water.

Dryness of the apparatus and accuracy of technique was indicated by constant values for a series of blanks run on 5 cc. portions of ethanol. The conditions employed in running the blanks duplicated those of the actual experiment as closely as possible (including the opening of the reaction flask to the humid air of the balance room).

(δ) . Development of Procedure

(i) Choice of Diluent

It was decided that a diluting agent was necessary for two reasons; (1) a sufficient volume of liquid was necessary to establish efficient refluxing, and (2) a liquid was required to make possible the running of blank determinations. The test solution contained 4.87% water, 3.95% methanol and 4.698% (by weight) in dioxane solution.

Liquid	Blank (cc. of N/10 KMnO ₄)	H ₂ O Found In Test Solution
Dry Dioxane (10 cc.)	1.81 1.89	3.8 2.8
Dry Methanol (10 cc.)	2.60	-
Dry Methanol (10 cc.)		4-7
Dry Methanol (10 cc.)		4.6
Stock Ethanol (5 cc.)	5.1	
Stock Ethanol (5 cc.)	5.2	
Stock Ethanol (5 cc.)		4.6
Stock Ethanol (5 cc.)		4.9
Stock Ethanol (5 cc.)	-	5.7(?)
60-70°C Petrol (10 sc.)	1.2	
60-70°C Petrol (10 cc.)		4.5
60-70°C Petrol (10 cc.)	49	4.7

Although the use of ethanol is described in the procedure, 60-70°C petrol is probably a better diluent since the blank is smaller. The results obtained with dioxane were probably low due to the fact that the water-dioxane

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azentropic mixture boils at a lower temperature than does dioxane (87°C as compared to 101°C.)

(ii) Choice of Absorbing Solution

Schütz and Klauditz suggested the use of acetone in the absorbtion train, but the writer found that acetone did not absorb acetylene quantitatively at room temperature. For example, when an 8" tube containing acetone was backed up by a 6" tube containing the copper solution. considerable precipitation of copper acetylide took place during a determination using the standard solution described above. With two tubes containing the copper solution only a very slight precipitate of copper acetylide formed in the third tube so that the use of three tubes containing copper solution gave a satisfactory margin of safety with respect to complete absorbtion.

(2). Quantitative Determination of Methanol <u>in Organic Solutions Containing Dioxane</u>, Ethanol, Water and Methanol

The following procedure for the quantitative determination of methoxyl is based upon the procedure for the determination of methoxyl and ethoxyl groups as described by Willstätter and Utzinger (192). (α) Reagents

The reaction flask was filled with a charge consisting of 15.0 cc. of constant boiling HI.H₂O (b.p. 127^oC) and 7.5 g. of recrystallized analytically pure phenol. This charge was sufficient for six determinations.

Scrubber Solution: The scrubber was filled with a 1:1 solution of 5% $CdSO_4$ and 5% $Na_2S_2O_3$. This solution was renewed at the same time as the HI-phenol charge.

Absorption Solution: The absorption solution consisted of a 10% solution of trimethylamine in absolute ethanol.

AgNO₃: A silver nitrate solution approximately N/10 was used.

(B) Apparatus

The apparatus consisted of a modified Zeisel apparatus equipped with a reflux condenser as described by Peniston and Hibbert (164).

(V) Procedure

A sample containing 2-4 mg. of methoxyl (80-150 mg. samples for liquids containing 2-4% MeOH) is weighed into a micro container made from a 2 cm. section of 2.5 mm.(I.D) glass tubing by sealing off one end. The container with the sample and a short piece of nichrome

wire is placed in the flask which is then heated to $135-140^{\circ}$ C. For the first five minutes the condenser is maintained at a temperature of $10-20^{\circ}$ C and a slow stream of dry CO_2 (at a rate just sufficient to prevent loss of liquid through the CO_2 inlet) is passed through the apparatus. At the end of this time the condenser temperature is raised to $45-50^{\circ}$ C and the CO_2 flow is increased to 1.5 bubbles per second. Complete absorption of CH_gI is obtained in 45-50 minutes, the total time of operation being approximately one hour. The absorbing solution, containing crystals of tetramethylammonium iodide was then carefully transferred to a 100 cc. beaker (the absorption tubes being washed with absolute ethanol) and allowed to stand at room temperature for 24 hours.

At the end of this time the solution was evaporated almost to dryness on the steam bath, and then completely dried in a vacuum desiccator for 8 hours. The solid crystalline residue was now extracted with three portions (3 cc., absolute ethanol, 3 cc., and 2 cc.,) respectively, of/the supernatant liquor being removed each time by means of a medicine dropper with suction. The solid on the filter paper was washed into the beaker with distilled water, 4 drops of aqueous nitric acid (1:1) were added, and the iodide precipitated by the addition of an excess of N/10 silver nitrate. The precipitate of AgI was coagulated by heating, and then filtered

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through a tared sintered glass filter. The precipitate was washed with water until free of Cl⁻ions and then with a small quantity of acetone prior to drying at 110°C for 1 hour.

One mole of AgI is equivalent to one mole of methoxyl.

(δ) Development of Procedure

(i) Choice of Apparatus

The ordinary Zeisel methoxyl apparatus could not be used because a portion of the methanol was volatilized before it had an opportunity to react with the HI.

Two determinations made on a solution containing a methanol content of 3.95% gave values of 3.2 and 3.3% when analyzed in a Zeisel apparatus, according to the procedure described above.

With the Peniston apparatus, however, according to the same procedure a value of 3.90% was obtained.

(ii) Choice of Absorption Solution

Due to the presence of the dioxane in the solution to be analyzed it was impossible to determine the total ROH content (MeOH EtOH), by means of the Viebock and Schwappach (165) method (volumetric determination of RI by absorption in a Br_2 -KOAc-HOAc solution). It was found that dioxane alone, when treated with HI in the Peniston apparatus (Br_2 solution as the absorbent) was cleaved by HI to yield varying quantities of RI (or possibly $C_2H_4I_2$). For example, 500 mg. samples of dioxane gave results indicating the presence of 8.2, 6.7 and 10.2 mgs. of ROH.

(iii) Preparation of the Sintered-Glass Filters

Since a finely divided suspension of AgI passed through the pores of a sintered-glass filter (Jena- G-4) it was necessary to prepare these filters by partially filling them with a large quantity of AgI and then washing continuously with about 4 liters of water to remove all finely divided particles from the pores. Filters thus prepared could be used for an indefinite number of analyses.

(E) Analytical Results Obtained with a Known Solution

A known solution containing water, ethanol, methanol and dioxane was analyzed for methanol according to the procedure described above. The solution contained 3.95% methanol; four analyses were made and the following results were obtained:

MeOH (%) = 3.90, 3.80, 3.92 and 3.87.

(3). <u>Quantitative Determination of Ethanol and</u> <u>Methanol in Solutions Containing Water and</u> <u>Dioxane</u>

The following procedure for the quantitative determination of methanol and ethanol in solutions containing water and dioxane was based upon the work of Harris (166).

(a) Reagents

 $N/5 K_2 Cr_2 O_7$: Pure, analytical potassium dichromate (9.8074 g.) was dissolved in 200 cc. of distilled water and diluted to 1 liter with water. The solution was standardized against standard ferrous sulphate (iron wire) or standard Mohr's salt (ferrous ammonium sulfate).

Mohr's Salt: Pure, analyzed ferrous ammonium sulfate was required.

Indicator: One small crystal of pure potassium ferricyanide was dissolved in 30 cc. of distilled water. Fresh indicator was prepared for each set of analyses.

() Procedure

A sample containing 0.0 - 0.5 mg. moles of alcohol (methanol and ethanol) was placed in a 100 cc. pressure bottle which contained 25 cc. of water, 2.0 cc. of concentrated sulfuric acid, and a measured excess of N/5 potassium dichromate (about 15 cc.). The pressure bottle was sealed and the contents heated on a steam bath for 30 minutes. At the end of this time the bottle was cooled in a stream of cold water, and then a weighed quantity of Mohr's salt (in excess over unused dichromate) was added. The excess ferrous ammonium sulfate was back-titrated with N/5 dichromate. (If insufficient dichromate had been added originally, more was added at this point and the procedure repeated). Under these conditions methanol and ethanol each required four equivalents of dichromate, methanol having been oxidized to formic acid and ethanol to acetic acid.

 $\frac{(cc. K_2 Cr_2 O_7)(N)}{(4)(wt. sample)} = mg. moles alcohol per gram of sample.$

Having determined the quantity of methanol by the procedure described previously, the ethanol was determined by difference.

() Development of Procedure

Harris (166) reported that a reaction mixture containing 20 ml. of water plus sample, 10 ml. of 10% sulfuric acid, and the required amount of dichromate would oxidize methanol and ethanol completely in 25 minutes at 100°C. When the writer treated a known sample containing 36 mg. moles of alcohol per gram of sample according to Harris' conditions he obtained values of 2.10 and 2.24 mg. moles ROH per gram of sample. In addition, a sample known to contain 0.505 mg. moles of ethanol gave a value of 0.288 moles under the same conditions. A study was then made of the effect of changes in the sulfuric acid concentration on the extent of the oxidation of the alcohols to the respective acids.

The following results were obtained (25 cc. of water and 15.0 cc. of N/5 $K_2Cr_2O_7$ were present in each oxidation). The time of heating at 100°C was 30.0 minutes in each case.

	Sample	m.g. moles ROH	cc. Conc. Hg SO4 add- ed ml.	mg. moles found
1.	EtOH	0.602	1.0	0.498
2.	EtOH	0.615	1.5	0.535
3.	EtOH	0.680	2.0	0.672
4.	МеОН	0.729	2.0	0.727
5.	МеОН	0.592	2.0	0.590
6.	Dioxane	0.000	2.0	0.07
7.	Dioxane	0.000	2.0	0.09
8.	EtOH,MeOH, Dioxane	3.60	2.0	3.69
9.	EtOH,MeOH, Dioxane	3.60	2.0	3.67

(δ) Further Investigations on Dichromate Oxidation of Alcohols

In addition Harris reported that after the total alcohol had been determined, a further known excess of

together dichromate was added/with 10 ml. of concentrated sulfuric acid. The solution was then refluxed for 15 minutes. cooled, partially neutralized and the excess dichromate determined in the usual manner. In this phase of the procedure, the formic acid (from MeOH) was supposedly oxidized quantitatively to CO_2 and H_2O .

These conditions were examined by adding 10 cc. of concentrated sulfuric acid to Sample #5 (above) and refluxing the solution for 15 minutes. Only 2.45 cc. of dichromate were used; 5.05 cc. was the theoretical value. Therefore, under these conditions only 48% oxidation occurred.

In addition, a sample containing 0.573 mg. moles of methanol was treated with 19 cc. of concentrated sulfuric acid, 70 cc. of water and 20 cc. of N/5 potassium dichromate for 30 minutes. A value of 0.512 mg. moles of alcohol, on the basis of complete oxidation to CO_2 and H_2O was obtained.

A third experiment, employing 18 cc. of H_2SO_4 , 50 cc. of water and a reflux of 30 minutes gave 98% oxidation of methanol to H_20 and CO_2 . In a similar experiment containing only dioxane and water in the sample 1.4 cc. of N/5 dichromate (equivalent .150 mg. moles) was reduced.

(b). Design and Construction of Fractionating Columns

(1) Column #1

(α) Details of Column Construction

The design of the fractionating column used for the fractional distillation of the products from small-scale lignin hydrogenation was based upon the columns described by Podbielniak (167).

The column proper consisted of a 3.8 mm (I.D.) pyrex tube 92 cm. long.packed with a gold-plated wire (20 gauge) spiral with a 1/8" pitch. The spiral was prepared by winding the wire tightly on a stiff steel wire of 1/16" diameter. The tight coil was then slowly stretched until the spiral fitted snugly in the pyrex tube. The column head (partial condenser), which is sealed directly on to the 3.8 mm. column, made of 8 mm. I.D. tubing, had a height of 4 cm. and was equipped with a thermocouple well (made of 2 mm. I.D. tubing inserted to a depth of 1.5" from the top of the column). The side-arm, or delivery tube, which projected from the top of the column head with a negative slope of 45° was equipped with a small, all glass condenser. The base of the column consisted of a standard #12/18 male pyrex ground.

The column was wrapped with 1/16", 36 gauge nichrome ribbon, having a resistance of 3.4 ohms per foot, in a spiral

of approximately 3/16" pitch. The column head was wound with a continuation of this heating element. The total resistance of the wire was 29 ohms.

The column proper was surrounded with a 37"evacuated pyrex jacket (vacuum of less than $1 \ge 10^{-4}$ mm.) which was constructed from 15 mm. and 21 mm. pyrex tubing. The column was supported within the jacket by means of a rubber stopper at the top and by cork wedges at the bottom. The area between the ground glass connection at the bottom of the column and the vacuum jacket was heat-insulated with a thick layer of asbestos. The exposed area at the column head was protected from drafts by means of a moveable asbestos shield.

The flasks used for the distillation were pyrex and pear-shaped. They were originally equipped with an open side-arm through which a capillary bubbler was inserted, but in the more recent fractionations smooth distillation has been maintained by the presence of glass-wool within the flask. Several flasks of various sizes from 15 cc. capacity to 100 cc. capacity were constructed and equipped with pyrex standard #12/18 female grounds.

The distillate receiver is shown in Figure VII.

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FIGURE VIII

Distillate Receiver for Podbielniak Column



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This receiver was constructed from a cylinder of 60 mm. pyrex tubing, 180 mm. long and flanged at each end. The ends were closed by means of #13 rubber stoppers. The stopper at the top was equipped with three holes, the center one of which contained a glass bearing (12 mm. tubing) to accomodate the end of the brass turning rod,

and two off-center holes containing the vacuum inlet and the fractionating column delivery tube respectively. This entire unit was mounted rigidly. The lower stopper contained one hole in the center through which was passed the lubricated (glycerine) brass turning rod. On this rod were mounted three brass discs 54" in diameter. The lowest of these discs was solid while the two upper ones were equipped with 12 holes arranged evenly in a circle. The receiving tubes (constructed from 4 mm. I.D. soft-glass tubing) were inserted through three holes and were supported by the bottom disc. With this arrangement it was possible to collect twelve (50 to 500 mg.) fractions at reduced pressure without stopping the distillation.

Electrically heated oil baths were used. These were made from 400 and 600 cc. beakers which were wrapped with a layer of asbestos, then with 1/16" nichrome ribbon and finally with asbestos. The total resistance of the heating wire was 50 ohms for the 400 cc. vessel and 60 ohms for the 600 cc. bath.

The electrical system was a simple parallel set-up, that is, the heating circuits (column and bath) were placed in parallel with a variable resistance, which in the case of the column circuit had a total resistance of 45 ohms and was constructed from 24 gauge nichrome wire (1.5 ohms per foot). The latter wire (30 feet) was

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wrapped tightly around a 1/4" glass rod and then drawn out to such a length that the wire spiral had a 1/8" pitch. This spiral was then spirally wound around a one foot length of 1" glass tubing which had been wrapped with asbestos. The variable resistance (120 ohms) for both circuits was made in the same manner. The resistance in each circuit was varied by moving a battery-clip contact along the resistance spirals.

The quantity of electricity to be applied to the column or bath was determined by a voltmeter which was placed in parallel with either of the circuits by means of a double-throw switch.

The distillation temperature was determined by use of a thermocouple-potentiometer set-up. Actually, the column was run at such a slow rate under reduced pressure that true boiling points were not determined. The reflux head of this column, as with all Podbielniak columns, was of the partial-condensation type; consequently the quantity of vapor and liquid at the uppermost portion of the column was only occasionally large enough (at a distillation rate of 100 mg. per hour) to **completely** wet the thermocouple tube. The thermocouple voltage was actually of inestimable value in indicating the quantity of liquid in the head, and, therefore, the approximate rate at which the material would distil. As was mentioned in the preceding paragraph, the distillations under reduced pressure were run at a rate of 100-150 mg. per hour; and, generally, the column was run in 24 hour stretches.

The vacuum system consisted of a mercury diffusion pump backed up by a Cenco Hyvac or a water pump, thus it was possible to obtain pressures from 760 mm. to 15 microns. Pressure measurements were made on a barometertype manometer or a McCleod gauge, depending upon the pressure. To eliminate charges arising from slight changes in pressure, a 6 liter flask was placed between the mercury pump and the system. Satisfactory pressure control was maintained with the use of a hand-operated "bleeder" stop-cock.

The fractionating unit is shown in Figure IV.

FIGURE IX

Modified Podbielniak Fractionating Column



fractio lesign exception was designed for the ties of material. The lumn \$1 with two 13 de. long. and eatly to the column.

 (β) Efficiency of Column

The number of theoretical plates in this column was determined according to the method described by

Morton	(160,	p.87)	using	a	mio	cture	of	benzene	and
carbon	tetra	chlorid	le wit	h	the	follo	owir	ng result	js.

Rate of Distillation	n_{D}^{25}		· 0	Cl4 %)	Theor.	H.E.T.P.
(drops/min.)	Vapor	Liquid	Vapor	Liquid	Plates	(cm.)
2	1.4690	1.4775	71.5	50.8	7.9	11.6
2	1.4710	1.4785	68.0	47.0	7.9	11.6
2	1.4688	1.4776	72.0	50.2	8.1	11.3
4	1.4695	1.4747	70.2	50.8	6.5	14.1
6	1.4761	1.4788	54.5	47.0	2.7	34.0

(2) <u>Column #2</u>

Later an additional column was designed for the fractionation of even smaller quantities of material. The design was identical with that of column #1 with two exceptions; (1) the column was only 42 cm. long, and (2) the vacuum jacket was sealed directly to the column. The gold spiral was a portion of the spiral used in column #1, and the column head, delivery tube and fraction receiver were of the same design as in column #1. The outside of the evacuated jacket was heated (when necessary) with 1/16" nichrome ribbon (36 ohms) and the entire column was shielded from drafts with an 18" length of 40 mm. pyrex tubing (air jacket).

The following results were obtained by means of

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an efficiency determination according to the same procedure used with column #1.

Rate of n ²⁸ Distillation			CC	Theor.	ዘ. ፑ. ጥ. ₽.	
(drops/min.)	Vapor	Liquid	Vapor	Liquid	Plates	(cm.)
Total Reflux	1.4710	1.4789	6 7.5	47. 0	7.3	5.75
0.5	1.4729	1.4791	62.5	46.2	6.1	6 . 89
2.0	1.4731	1.4786	62.2	47.5	5.2	8.10
2.2	1.4751	1.4815	62.0	41.8	5.8	7.30
3.5	1.4752	1.4810	57.1	42.5	4.9	8.60
14	1.4739	1.4739	59.0	59.0	0	-

8. Synthesis of Compounds used for Identification Purposes in Lignin Hydrogenation Studies

(a). Synthesis of 4-n-Propylcyclohexanol

4-n-Propylcyclohexanol was synthesized according to the procedure of Harris, D'Ianni, and Adkins (73) and embodying the following reactions(Fries Rearrangement);



(b). Synthesis of 3-(4-hydroxycyclohexyl)propanol-1

3-(4-hydroxycyclohexyl)propanol-1 was synthesized by the procedure of Adkins, Frank, and Bloom (72), according to the following reactions:











The mode of synthesis, as described by Adkins, was found satisfactory with the exception of reaction III and the physical properties of the product of reaction $V_{,}$ 4-(propionylethylester)cyclohexanol.

Reaction III:

According to Adkins the hydrogen iodide cleavage of p-methoxyhydrocinnamyl ethyl ester is carried out at <u>moderate</u> temperatures. It was found that this compound (25 g.) when heated with constant boiling hydriodic acid (b.p. 127°C)(50 cc.) for 45 minutes gave 17 grams of p-methoxyhydrocinnamic acid. On esterification with absolute ethanol containing a trace of concentrated sulfuric acid, 16 grams of p-methoxyhydrocinnamyl ethyl ester $(n_p^{25} = 1.5143)$ was obtained.

A second alkoxyl cleavage was run on 9.6 g. of p-methoxyhydrocinnamyl ethyl ester, using 25 cc. of constant boiling HI (d = 1.7) and carried out in a 125 cc. ground-glass flask. The flask was equipped with a vertical condenser, the top of which was connected to a dry-ice trap. The reaction mixture was heated at 95°C for 40 minutes in an attempt to follow Adkin's instructions to "heat gently until iodides are removed". At the end of the period <u>complete solution of the ester layer had occurred</u>. The reaction mixture was then boiled (bath temperature = 145°C) for twenty minutes. The hot solution was poured into a beaker and the product crystallized from the aqueous acid solution on cooling. The crystalline product was filtered and washed with ice-water. The yield of yellow crystalline product was 7.5 g. (93% of theory). The yield of iodide collected in cold trap was ll.l g. A portion of this product when recrystallized from water melted at 125-127°C (Adkins reported 128-129°C for a sample recrystallized several times.).

Reaction V:

p-Hydroxyhydrocinnamyl ethyl ester (39 gm.), dissolved in 10 cc. of ethanol, was treated with hydrogen at 200 atmospheres pressure and 210°C over RaNi catalyst (5 g.) for three hours. A yield of 37 g. of a liquid distilling at 118°C at 0.6 mm., $n_D^{25} = 1.4690$, $d_{25}^{25} = 1.0310$ was obtained. (Adkins reported b.p. 102-103°C at 0.2 mm; $n_D^{25} = 1.5661$; $d_{25}^{25} = 1.0309$).

> Molecular refractivity (Cooke's results) = 53.9 Molecular refractivity (Adkins' results) = 63.2 Theoretical molecular refractivity = 53.87

Reaction VI:

The ester (37 g.)(with a refractive index of 1.4690) was hydrogenated over CuCrO (3 g.) at 250°C using hydrogen at 250 atmospheres pressure for 2 hours. Twentyfive grams (89% of theory) of a material boiling at 132-134°C at 0.7 mm. $(n_D^{25} = 1.4878)$ just before solidification) which solidified into a wax-like white product was obtained.

Oxidation of 3-(4-hydroxycyclohexyl)propanel_1_ 4-keto-cyclohexylpropionic acid:

The oxidation of the glycol (2.3 g.) to the ketoacid (0.99 g.) was carried out according to the method described in Experimental Section B, 4, (a), (2).

Acid Equivalent:

Found = 169.5, 172.1

Theoretical = 170.1

The semi-carbazone of the keto-acid (a new derivative) was prepared as follows: The keto-acid (100 mg.) in 0.8 cc. of 40% EtOH-H₂O was added to a solution of 100 mg. of free semi-carbazide (m.p. $94-95^{\circ}$ C) (not the hydrochloride) in 1.5 cc. of a buffered (pH 5) aqueous solution. Precipitation occurred immediately, and after two recrystallizations from water gave a product melting at $201-202^{\circ}$ C.

Acid Equivalent of Semi-carbazone:

Found: = 224.

Theoretical: = 227.2

Analytical Results on Semi-carbazone:

Found: % C = 52.2, 52.4; % H = 8.0, 8.1.Theoretical: % C = 52.6; % H = 7.9.

VIII SUMARY

A. A new, simple and efficient method has been devised for the hydrogenation at high pressures, of small quantities of plant material and for the analysis and identification of the hydrogenated products.

B. The work of Harris, D'Ianni and Adkins (73) on the hydrogenation of methanol lignin (aspen) has been confirmed by application of same procedure to ethanol lignin (maple).

C. Each of the verious groups of ethenolysis products obtained in the ethanolysis of maple wood meal, and including (1) the distillable oils; (2) the non-distillable amorphous fraction of the water-soluble oils; (3) the so-called "benzene-shakings"; (4) the non-water-soluble tar; (5) the water-insoluble ethanol lignin and (6) the residual lignin in the wood, have been hydrogenated and the resulting products separated, analyzed and very largely identified.

D. Based on these results, and on the previously published data on hydrogenation, the type of linkage (-C-C- or -C-O-C-) present in the individual fractions and the extent to which these are present, have been determined.

E. The experimental data and theoretical consideration would seem to provide a rational working theory of the mechanism ethanolysis. F. Contrary to general belief, it was found possible to obtain <u>simple water-soluble lignin units</u> by the <u>methanolysis</u> of maple and aspen woods. The water-insoluble <u>methanol</u> lignin (maple) has been hydrogenated and the products shown to be identical with those obtained by hydrogenation of the <u>ethanol</u> lignin (maple).
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