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A symposium sponsored by the Division of Cellulose, Wood, and Fiber Chemistry at the 150th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13–14, 1965.

Joseph Marton, *Symposium Chairman*

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Lignin is one of the most abundant natural products constituting about one-fourth of the woody tissue in plants. Nature has chosen a unique synthetic technique to prepare this cross-linked polymeric material from coniferyl alcohol and related substances. The mechanism of lignin formation is not completely known yet, and the structural characterization of lignin has been only partially successful despite considerable research.

The modern concept of lignin structure took its more definitive form at the last Lignin Symposium of the American Chemical Society in 1956. The highlights of that meeting included a new method for extracting representative lignin samples from milled wood (Björkman), the chemical and functional group analysis of milled wood lignin (Adler), and for preparing and characterizing a biosynthetic lignin (DHP of Freudenberg). Elaboration of these and other basic results has dominated the literature of the past 10 years. Progress has been considerable. The results of these efforts permitted construction of constitutional schemes for lignin based on more critical experimental data. New research tools have been applied to lignin research, and important details of the fine structure were detected. The discussion of these results and evaluation of the present status of lignin research motivated the organization of the present meeting of lignin chemists.

At this symposium 18 papers were presented, concerning topics of current research on lignin structure and reactivity. Renowned authorities from different parts of the world contributed to its success. Half of the authors also presented papers at the previous Lignin Symposium. The other half are newcomers, which is a promising sign for the vitality of lignin chemistry. It would be premature to assess the significance of the information presented here. However, quinonemethides clearly emerged as the most important reactive intermediates in lignin formation and reactions. It became clear that the current presentation of lignin structure is oversimplified. Although the main features of the structural conception are sharper than ever, new fine details are constantly being added. The door is still open, and more ingenious work is needed to establish the sequence of units—the most prominent singular task of future lignin research. Some promising information in this direction has been revealed at this meeting. With regard to the scientific, technical, and commercial importance of lignin, it is advantageous that these papers have been published in one volume.

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Two great personalities of the lignin-chemical research reached important milestones in their lives in close timing with the symposium. Karl Freudenberg celebrated his 80th birthday while Erich Adler celebrated his 60th. It is most appropriate that the papers of this volume are dedicated to these two giants of lignin research, honoring their contributions and wishing them further success and many happy returns.

Charleston, S. C.
January 1966

JOSEPH MARTON

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Dedication

ERICH ADLER

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At this symposium attention has been directed to present knowledge, recent views, and new ideas which may lead to future developments in lignin chemistry. I would like to focus on the long history of this subject. There are several decisive events which could have been celebrated this year. A period of 125 years has passed since Anselme Payen treated wood alternately with nitric acid and caustic soda, obtaining a product which he called "cellulose." By analyses, he concluded that a material differing from cellulose by a considerably higher carbon content had been removed from the wood. This material he considered an incrusting material, in which the fiber-forming cellulose was imbedded. Payen's "incrustation theory" marks the beginning of the history of what later was named "lignin."

Another important event could have been chosen on which to base a centennial—the invention of the sulfite pulping process by the Tilghman brothers in Philadelphia. Although dated as 1866 when a British patent for the process was issued, successful laboratory experiments had been made in 1865. In their attempts to adapt the new method to commercial scale, the Tilghmans tried to develop a continuous process but unfortunately could not solve the technical problems involved. A few years later, at the beginning of the 1870's, experiments on sulfite pulping were taken up in several places in Europe, and in 1874 the first sulfite pulp was produced commercially by C. D. Ekman in a Swedish mill.

This event not only marked the start of a new industry but also the opening of a new epoch of lignin research, although slow and hesitating. For decades sulfite pulping as well as the alkaline pulping processes, based on the pioneering work of Watt and Burgess, were carried out with no knowledge and even with wrong ideas about the basic principles involved in these processes. The chemistry of lignin was still a mystery. As late as 1890 Benedikt and Bamberger found that lignified materials, but not cellulose, contained methoxyl groups—another discovery which would merit a 75th anniversary celebration.

However, the rapid development of the young wood pulping industry, especially in Sweden, finally stimulated the interest of scientists in

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problems related to the chemistry of the pulping reactions and thus in the chemistry of lignin and its behavior in pulping.

In 1893, Peter Klason, at the Royal Institute of Technology in Stockholm, published his first two papers dealing with the composition of black liquor from the kraft process and with sulfite waste liquor. For more than 40 years he devoted much of his interest to lignin chemistry and to practical problems of wood utilization. Many of his procedures were valuable in later lignin research, and his method of lignin determination is still used. Although many of his hypotheses and conclusions were often based on weak experimental evidence, his imagination and intuition led him on the right track.

By 1897 he had advanced the idea that lignin was built up from coniferyl alcohol. Although his experimental arguments were meager, this idea was not merely a rough guess. Klason's reasoning was simple and logical. In 1875 Tiemann, who had clarified the structure of the plant glucoside, coniferin, had suggested that coniferin might be a simple transformation product of what he called "the aromatic atom complex" present in wood. Obviously, with this "aromatic atom complex," he referred to lignin. In his first paper on sulfite waste liquor, Klason found that part of the sulfurous acid which was bound to lignin could be split off again by heating with barium hydroxide whereas another part was bound in a stable way. He proposed that the loosely bound sulfurous acid was added to a carbonyl group whereas the alkali-resistant part had been added to an ethylenic double bond. Now, Tiemann's coniferyl alcohol was an aromatic compound which contained methoxyl and had an ethylenic double bond. Moreover, when heated with calcium bisulfite solutions, it yielded a sulfonic acid whose composition seemed similar to that of lignosulfonic acid. Klason also observed that treating wood with mineral acids changed the lignin so that it no longer gave a soluble sulfonic acid, a behavior comparable with the resinification of coniferyl alcohol by acids reported by Tiemann and Haarmann.

The coniferyl alcohol idea remained the basis of Klason's continued work on lignin behavior and structure, and he was strongly convinced of its correctness. At the beginning of the 1930's, Holger Erdtman, while working in the laboratory of Bror Holmberg, was asked by Prof. Emeritus Klason, "What are you working with, my young friend?" "I am working with the lignin problem," Erdtman answered. "Oh," said Klason, "there is no lignin problem any more; it's all solved."

In the 1920's, a new generation of Swedish wood chemists had grown up, represented by Bror Holmberg, Erik Hägglund, and Carl Kullgren. The broad and versatile work of these men became the basis for understanding the chemistry of the pulping processes.

From the viewpoint of lignin structure and reactions, the work of Holmberg deserves special attention. Initially interested in extracting

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lignin from wood by boiling alcoholic hydrochloric acid (which had been briefly reported by Klason), he found in the thioglycolic acid method a new way of isolating lignin in the form of a derivative. He explained the behavior of lignin in these reactions as well as in the sulfite process by assuming that lignin contained reactive alcoholic and ether groups in a benzyl position, and he supported this idea by model experiments. Holmberg's view regarding the nature of the reactive groups in lignin, which he advanced in the middle of the thirties, became a strong stimulus to modern lignin research.

Meanwhile, Freudenberg had entered the field of lignin chemistry. It is a true pleasure for all of us to have Prof. Freudenberg, with us. This gives us an opportunity to address him personally with the prospect of his 80th birthday which he is going to celebrate on January 29, 1966.

The first lignin work from his laboratory, at the Technische Hochschule in Karlsruhe, appeared in 1926. That same year Heidelberg became the place of his continued work on tanning agents and catechins, stereochemistry, sugars, cellulose and starch, blood group substances, insulin, and last but not least, on lignin. He and his co-workers investigated various methods for isolating lignin from wood and characterizing the preparations by careful analytical examination. On the basis of this work he stated in 1928 that in this amorphous, apparently unordered material, there was some kind of a structural order, a principle of continuously connected building stones. He also visualized that this building principle could not be as simple and clear as he had postulated in 1921 for cellulose. Rather, the building stones of lignin would be variations of a structure possibly containing a phenylpropane skeleton, and the connecting principles would be both ether linkages, preferentially alkyl aryl ether linkages, and carbon-carbon linkages. In the middle of the 1930's he introduced successful procedures for oxidative degradation, which gave substantial amounts of aromatic carboxylic acids and aromatic aldehydes. There could no longer be any doubt regarding the aromatic nature of lignin, which had been denied by certain workers as late as 1936.

The view that the lignin molecule was made up of building stones with a guaiacyl-syringyl propane skeleton was supported by the brilliant work of Hibbert on ethanolysis and that of Adkins and Harris on the pressure hydrogenation of wood and isolated lignin preparations.

However, it was still impossible to discuss the structure of lignin in any detail. A new approach to the problem was needed. In Stockholm Holger Erdtman in the early 1930's, was studying the dehydrogenation of phenols and found that a dehydrogenation product of isoeugenol had the structure of a phenylcoumaran. Similar structures had been proposed by Freudenberg as being present in lignin, and in 1933 Erdtman said that lignin might be formed in nature by dehydrogenation of phenylpropane compounds carrying an oxygenated side chain.

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Freudenberg realized the importance of investigating this possibility. In 1937 he found that dehydrogenation of coniferyl alcohol with ferric chloride seemed to proceed in a way comparable with that of isoeugenol, and in 1943 he started his studies on the enzymatic dehydrogenation of coniferyl alcohol. It would not be possible here to give even a brief survey of the outstanding work which he has done since then.

In a paper (*Naturwiss.* **8,** 903 (1920)) on recent results in the field of tanning agents, Freudenberg wrote about his teacher's, Emil Fischer's, work on hydrolyzable tannins: "... er hat, wie in ähnlichen Fällen, auch hier nach kurzer analytischer Einführung durch eine mit beispielloser Energie aufgebaute Synthese den Weg in das vorher ungangbare Gebiet dieser amorphen Naturstoffe erzwungen."

Mutatis mutandis. This also applies to Freudenberg's work on the biogenesis of lignin. Similarly, never-ceasing energy, creative imagination, and a masterful use of experimental tools enabled him to disclose the way in which lignin is formed in nature from its cinnamic alcohol precursors. Successful analytical and degradative work supplement his biosynthetic studies. Thanks to his admirable contributions our picture of lignin formation and lignin structure now has attained a high degree of reality and exactness.

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(Opposite) Watercolor by Karl Kratzl, made at the symposium to depict centers of activity in lignin research.

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Analytical and Biochemical Background of a Constitutional Scheme of Lignin

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A schematic formula for lignin has evolved from analytical observations and from studies of biochemically duplicated lignin and its intermediates. By dehydrogenation, coniferyl alcohol alone forms more than 30 intermediates (oligolignols) which give detailed information about the constitution of lignin. Most of the intermediates have been isolated and elucidated. They are listed here. Recently, it became evident that rather labile benzyl aryl ether links occur in lignin. This led to experiments on the mild hydrolysis of lignin. Several oligolignols have been isolated from wood, some of which are identical with the intermediates; others supplement them. Work done in Heidelberg during the last 12 years is reported. Results from other laboratories are mentioned only when they apply directly to these topics.

A constitutional scheme for spruce lignin was given previously (*9*) and will be discussed further. There are still some uncertainties in our lignin formula (*9*, *10*, *11*, *20*), especially regarding the content of ketonic groups. The nature of some of these (about 1 for every 12 units) is fairly well established, and the validity and nature of a similar amount are still under discussion. Part of the residual carbonyl content of lignin is apparently related to quinonoid substances. When attempts were made to fit some ketonic groups into the β-positions of the C_3 side chains in the lignin scheme—such groups are postulated by Adler (*1*)—the compositional and structural balance was difficult to establish because β-ether links must decrease. (Note: the lignin scheme of the earlier papers (*10*, *11*) is incorrect with regard to units 13b and 14b. These units should be replaced by formula XXXIII of this paper with one correction: one of the two phenolic hydrogen atoms of XXXIII should be removed).

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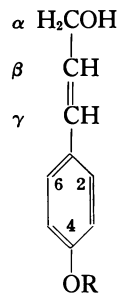
Our constitutional scheme is based on different kinds of information. The first type of information comes from an analytical study of milled sprucewood lignin prepared according to Björkman (*3*). The analytical data considered comprise the elemental composition of lignin, its content of methoxyl groups and other ether bonds, the types and amount of its different hydroxyl groups, carbonyl, and lactone groups, and the kind and number of its biphenylyl linkages and other bonds in which the benzene nucleus is involved. The work that led to data of this kind has been carried out in various laboratories and has been described previously (*9,11*).

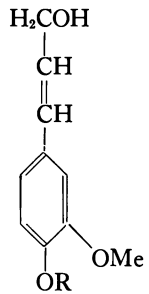
Products from the direct oxidation of lignin that give information about its structure include acetic, oxalic, and succinic acids, vanillin, vanillic acid, and dehydrodivanillin. Regarding lignin constitution, they are of only minor interest, but the yields in which they are obtained are significant. For vanillin and its derivatives the total yield is about 33% of spruce lignin (*24*, *36*, *37*, *38*). Two extraordinary products of this direct oxidation deserve special attention—i.e., benzenepentacarboxylic (*45*) and tricarballylic acids (*47*), (XXIX) and (XXX). They will be mentioned later in connection with lignenolide (XXVII).

The second type of data is derived from biochemical experiments related to the three cinnamyl alcohols—*p*-coumaryl alcohol (I), coniferyl alcohol (II), and sinapyl alcohol (III) and their phenolic glucosides—*p*-glucocoumaryl alcohol (IV), coniferin (V), and syringin (VI). These and the following formulas do not differentiate between cis and trans isomers.

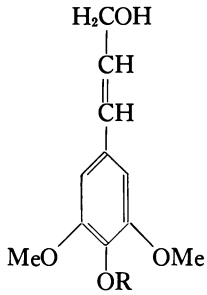
The three glucosides (IV–VI) are present in the cambial sap of spruce, V being by far the most abundant (*19*). Furthermore, spruce cambial sap contains very small amounts of coniferyl alcohol (I), coniferaldehyde (VII), the dilignols (XVII), (XIX), (XXII), and the trilignol (XXXVI) (*19*). Other lignols are present but in amounts too small for convenient identification. Extensive work has been done to examine the pathway of lignin formation in vivo and in vitro.



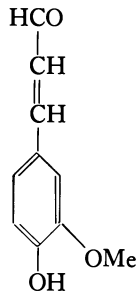
(I) R=H, *p*-Coumaryl alcohol
(IV) R=$C_6H_{11}O_5$ Glucocoumaryl alcohol



(II) R=H, Coniferyl alcohol
(V) R=$C_6H_{11}O_5$ Coniferin



(III) R=H, Sinapyl alcohol
(VI) R=$C_6H_{11}O_5$ Syringin



(VII) Coniferaldehyde

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In plant cells where lignification occurs, the glucosides encounter a β-glucosidase (*8*, *29*). (The rate of β-glucosidase action decreases quickly with falling temperature. Since the location of the timberline depends largely upon temperature (*48*), a mutual dependency of these two phenomena seems possible.) The *p*-hydroxycinnamyl alcohols are liberated and dehydrogenated by either laccase or peroxydase in the presence of air or a hydroperoxide. Metastable free radicals are formed which combine and finally build up lignin.

By using the same phenolic aglycons and the same enzymes as those present in the cambium for experiments in vitro, it has been proved that the mechanism of lignification is the same or at least very similar both in nature and in the laboratory; the same is true for the similarity between natural and artificial lignin. Numerous arguments support these conclusions (*9*, *11*).

The third approach that gave insight into the structure of lignin was its degradation with strong alkali, methylation, and oxidation (*12*). The many methoxylated benzenecarboxylic acids obtained from both natural and artificial lignin were identical in both structure and yield. Recently, the dicarboxydiphenyl ether (VIII), the dimethoxyphenyl ether of vanillic acid (IX), and a new biphenic acid (X) (*13*) were found among these acids. When using lignin preparations labelled on the side chain in this degradation, we encountered some unexpected irregularities which may indicate some rearrangement in the C_3 side chain.

These and many other facts must be considered when constructing a constitutional scheme for lignin, but they are by no means sufficient for building up such a formula. Special constitutional information is given by the structures of the lignin-building stones described in the following sections. These form the major content of this paper and are described in detail.

The experiments mentioned above allow one to estimate the relative amounts of the three cinnamyl alcohols which serve as building stones for

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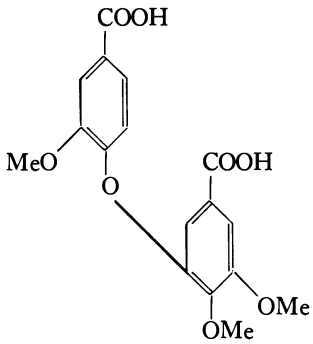
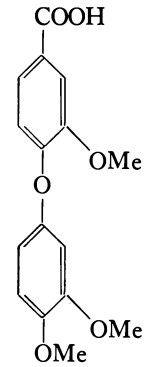
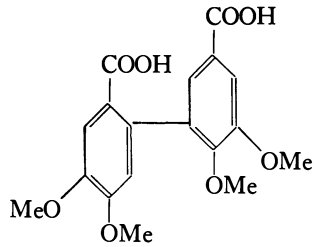


(VIII) 4,3′-Dicarboxy-2,5′,6′-trimethoxydiphenyl ether



(IX) 6,3′,4′-Trimethoxy-4-carboxydiphenyl ether



(X) 3,4,5′,6′-Tetramethoxybiphenyl-6,3′-dicarboxylic acid

spruce lignin (*6*, *7*, *8*, *12*). The starting materials of spruce lignin are *p*-coumaryl alcohol (I), coniferyl alcohol (II), and sinapyl alcohol (III) in molar proportions of about 14, 80, and 6%, respectively.

When this mixture is dehydrogenated by phenol dehydrogenases until 1.5–2 hydrogen atoms per unit are lost, natural spruce lignin is truly duplicated. When only 1.0–1.2 atoms of hydrogen are removed, many intermediates are obtained (*6*, *25*). This mixture is very complex and extremely difficult to separate. The problem can be simplified by using only one alcohol at a time for the experiment. Although we chose coniferyl alcohol, the number of products obtained on dehydrogenation was overwhelming. Paper chromatograms indicated that at least 30–40 substances were formed. When isolated, either by countercurrent distribution or column chromatography, many of these substances, which seemed to be individual species, were seen to be mixtures also. Nevertheless, it has been possible to isolate about 30 individual substances and to elucidate their constitution. Most of them are formed in yields of 1% or less, some of a few percent, and a few in up to 15% yield. We call these substances monolignols, dilignols, oligolignols, and polylignols. A complete list has not been given for several years, and the number of identified lignols has increased since. It may be expedient therefore to give an updated

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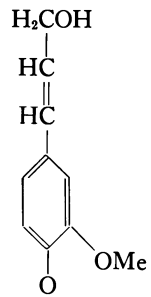
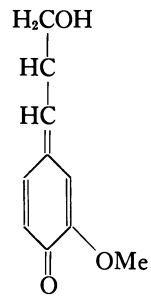
list of these intermediates of artificial lignin formation for they undoubtedly also give valid information about the formation of natural lignin. In nature, of course, the number of intermediates is probably greater, owing to the admixture of the other *p*-hydroxycinnamyl alcohols. They intercombine—preferably with coniferyl alcohol—just as coniferyl alcohol does with itself. However, *p*-coumaryl alcohol tends to intercombine more frequently and sinapyl alcohol less frequently owing to their lower and higher methoxyl contents.

Monolignols

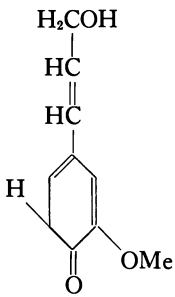
When coniferyl alcohol is dehydrogenated, it loses its phenolic hydrogen atom to form first an aroxyl radical R_a (XI), which is in effect also present as the mesomeric radicals R_b (XII), R_c (XIII), and R_d (XIV). Of these limiting structures, R_b is the most favored. The existence of the radicals in these forms is recognized by their reaction products. In very dilute dioxane-water solution (1:1 vol.), the half-life of the radicals is about 45 seconds (*13*).



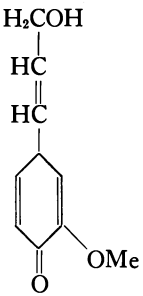
(XI) R_a



(XII) R_b



(XIII) R_c



(XIV) R_d

This is not very different from the conditions of our in vitro dehydrogenation (0.2% solution in water, 20°C., pH 5.5 in the presence of laccase plus air or peroxidase plus hydrogen peroxide (*6*)).

Other monolignols formed during the dehydrogenation of coniferyl alcohol are coniferaldehyde (VII), *trans*- and *cis*-ferulic acid (XV, XVI), vanillin (traces), and vanillic acid (traces).

Dilignols

At a certain stage during the dehydrogenation, the dehydrodiconiferyl alcohol (XVII) produced comprises about 15% of the total lignols formed (*22*). It arises by combination of R_b (XII) and R_c (XIII). Since it also originates from R_a, it is optically inactive as are all the other lignols and

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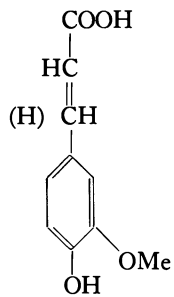
lignin itself. No isomeric or stereomeric form of XVII has ever been encountered. The hydrogen atoms in the hydrofuran ring are cis-oriented (*2*). This dilignol is present to a small extent in spruce cambium sap and has been isolated from spruce lignin in crystalline form (*13*).

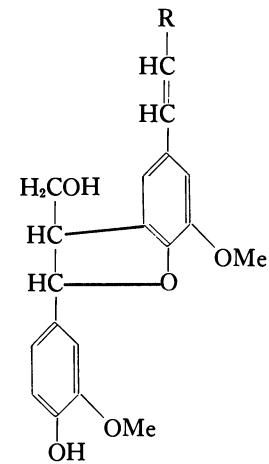
Dehydrodiconiferaldehyde (XVIII) (*25*) is an unsaturated aldehyde corresponding to XVII and is formed partly by condensation of free radicals derived from coniferyl alcohol and coniferaldehyde.

DL-Pinoresinol (XIX) (*27*) is formed when two R_b radicals combine to build a twofold *p*-quinonemethide in which each half has the same configuration. This means that a racemate is formed (*RR* + *SS*). By intramolecular prototropy a double tetrahydrofuran system originates, two new asymmetric carbon atoms being thereby created. In pinoresinol these are again equal to each other (*4*) in such a way that the benzene rings are in the equatorial position (*32*). This means that, when two R_b radicals combine, a transition state is developed in which the racemoid approach is more favored than the mesoid-producing approach, probably owing to some interaction between the hydroxyl and quinonoid groups. For stereochemical reasons, mesoid (*RS*) condensation of the two R_b radicals would allow closure of only one ring. Such a product has not yet been found. Pinoresinol occurs in about the same amount in the lignol mixture as dehydrodiconiferyl alcohol (XVII). DL-Pinoresinol has also been found in spruce cambium and has been isolated from spruce lignin in crystalline form (*13*).

DL-Epipinoresinol (XX) accompanies the DL-pinoresinol in a small amount (*25*). Here the configuration at one benzyl carbon atom is inverted to form an axial-equatorial system (*35*).



(XV) (XVI) *trans-cis-* Ferulic acid



(XVII) Dehydrodiconiferyl alcohol R=CH_2OH

(XVIII) Aldehyde of XVII R=CHO

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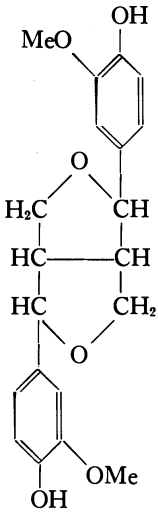
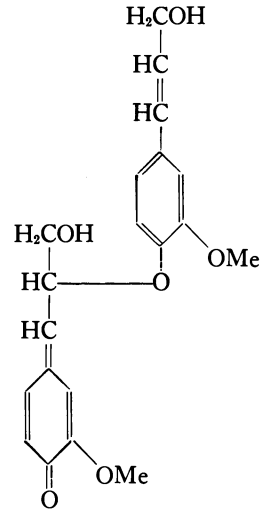


(XIX) DL-Pinoresinol and its epimer (XX) DL-Epipinoresinol



(XXI) Quinonemethide

The quinonemethide (XXI) (*31*) is formed by combination of R_a and R_b. It is the prototype of many other similar quinonemethides, especially ones with higher molecular weights. It is yellow and can be recognized easily by its absorption maximum at 312 mμ and intense absorption extending into the start of the visible range.

The same chromophore is present in the *p*-quinonemethide precursors of DL-pinoresinol (twice) and dehydrodiconiferyl alcohol (once). Measurements in a fast-recording ultraviolet spectrometer (Cary apparatus) indicated a half-life of the quinonemethides of about 1 hour (dilute solution in 70% aqueous dioxane at 20°C. and pH 5.5) (*5*, *18*). They may also become stabilized to a small extent by polymerization (*see* XLIV). Since the quinonemethide (XXI) has no opportunity to become stabilized by intramolecular prototropy, it adds on external electrolytes, particularly hydroxyl compounds and preferably water (*31*).

The yield of guaiacylglycerol β-coniferyl ether (XXII) (*31*) probably surpasses even pinoresinol (XIX) and dehydrodiconiferyl alcohol (XVII). So far it has not been obtained in crystalline form, possibly because of its labile benzyl alcohol group. A derivative has been obtained in the crystalline state and has also been synthesized (*15*). Guaiacylglycerol β-coniferyl ether also occurs to a small extent in spruce cambium and has been isolated from spruce lignin as a crystalline derivative (*42*).

Guaiacylglycerol β-coniferaldehyde ether (XXIII) (*25*) contains an α,β-unsaturated aldehydic group and is formed partly at least by com-

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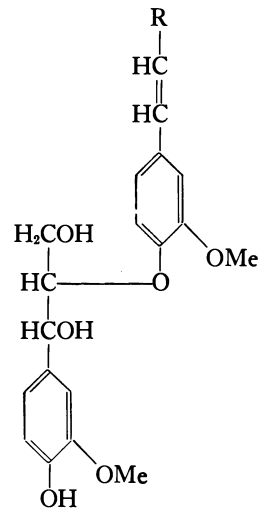
bination of R_b with a coniferaldehyde aroxyl radical with subsequent addition of water onto the resultant quinonemethide.

Dehydrobisconiferyl alcohol (XXIV) (*28*) is a very labile substance formed by the interlinking of two R_e radicals. It can be isolated only as its tetrahydro derivative which is stable. Corresponding biphenyl derivatives are formed preferentially from lignols with saturated side chains. The same must be assumed for systems with a 5,6-biphenylyl bond (cf. X). The occurrence in lignin of compounds with such a structure is indicated by isolating the acid (X) from the degradation products of lignin.

Diconiferyl ether (XXV) has not yet been isolated, but its presence among the dilignols is not inconceivable (*28*). Undoubtedly, diaryl ether derivatives are also preferably formed by dehydrogenation of preformed oligolignols which contain saturated side chains. The occurrence of diaryl ethers in lignin has been proved by its oxidative degradation since the acid VIII is also formed.



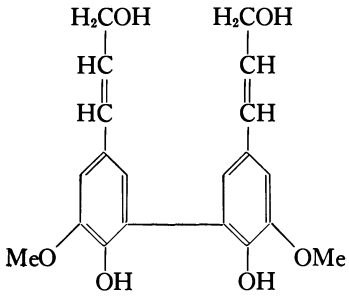
(XXII) Guaiacylglycerol β-coniferyl ether R = —CH_2OH

(XXIII) Aldehyde of (XXII) R = —CHO

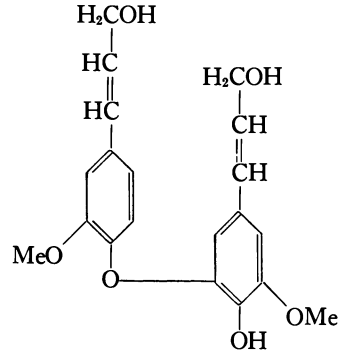
Pinoresinolide (XXVI) (*17*) and lignenolide (XXVII) (*17*, *40*) are lactones which are obtained in a small yield from the mixture of intermediates. Both arise from combinations of dehydrogenated ferulic acid and R_b. They are crystalline and are responsible for the weak lactone band in the infrared spectrum of lignin.

The lignenolide (XXVII) may undergo a condensation between its double bond and position 2 or 6 of the other nucleus to form a cyclolignan, a tetrahydronaphthalene derivative which can give rise to benzenepenta-

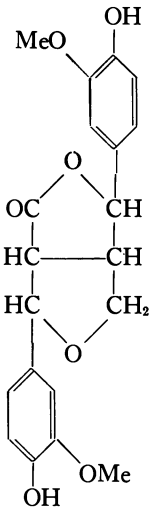
In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.



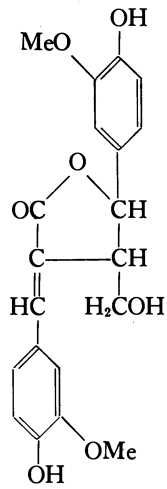
(XXIV) Dehydrobisconiferyl alcohol



(XXV) Hypothetical diconiferyl ether



(XXVI) Pinoresinolide



(XXVII) Lignenolide

carboxylic acid (XXIX) on oxidation. Read and Purves (*45*) obtained benzenepentacarboxylic acid in a yield of 0.2% of the lignin. This is the only benzenepolycarboxylic acid occuring among the oxidation products of *uncondensed* lignin. It can originate from the lignenolide unit after cyclization to a hypothetical cyclolignan (XXVIII). Another cyclolignan, podophyllotoxin, also yields this acid on oxidation (*49*). A further oxidation product of lignin, tricarballylic acid (XXX) (*46*), may originate from the same cyclolignane. Substances XXIX and XXX are listed here despite the fact that they are not dilignols.

Here, another possible explanation for the origin of the acids XXIX and XXX must be mentioned. Sprucewood contains about 0.3%

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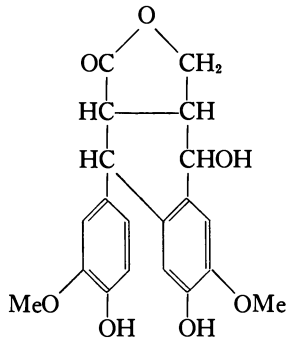
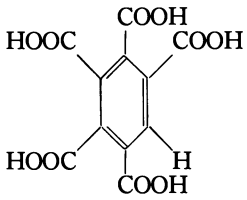
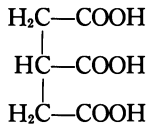


(XXVIII) Hypothetic cyclolignane

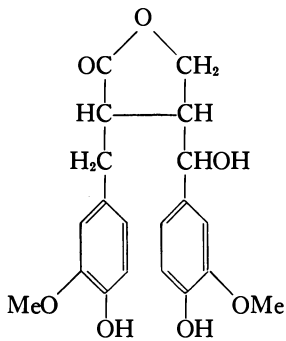


(XXIX) Benzenepentacarboxylic acid

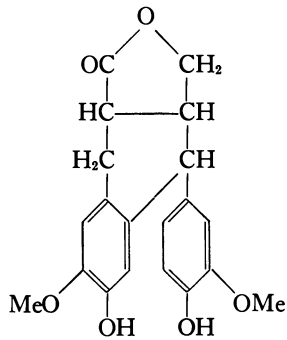


(XXX) Tricarballylic acid

hydroxymatairesinol (XXXI) (*23*) which, because of its optical activity, is assumed to belong to the resin system of sprucewood and not to be a lignin intermediate. Nevertheless, it is present to a small extent in what we call "cambial sap." Therefore, we do not exclude the possibility that some of it may be incorporated into lignin. This substance is transformed easily by weak acids into α-conidendrin (XXXII) (*23*). On oxidation the latter may yield benzenepentacarboxylic as well as tricarballylic acids. This question deserves special investigation.



(XXXI) Hydroxymatairesinol



(XXXII) Conidendrin

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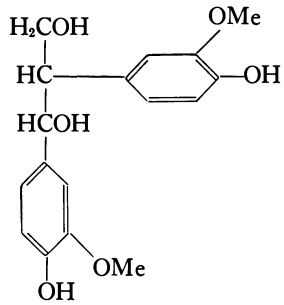
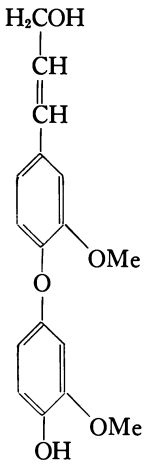
1,2-Diguaiacylpropane-1,3-diol (XXXIII) (*13*) is a crystalline substance that may be included in the list of the dilignols since it originates from two monolignols—namely by combination of R_b and R_d with simultaneous elimination of the side chain of R_d. Its presence among the intermediates of artificial lignin has so far been indicated only by chromatography (*26*). The substance appears among the products of mild hydrolysis of spruce lignin (*13*) (*see* below).



(XXXIII) 1,2-Diguaiacylpropane-1,3-diol



(XXXIV) Hypothetical coniferyl alcohol guaiacyl ether

Coniferyl alcohol guaiacyl ether (XXXIV) has not yet been isolated from the intermediate mixture, but the presence of an ether of this kind must be concluded from the formation of the acid (IX) on treating lignin with alkali, followed by methylation and oxidation (*13*). Its origin can be explained by combination of R_a and R_d followed by loss of the side chain of R_d.

Trilignols

The first six members of this group originate from combination of R_b with an aroxyl formed from a dilignol by loss of phenolic hydrogen. The quinonemethide initially formed is stabilized by adding water. The trilignols formed in this way include guaiacylglycerol β-dehydrodiconiferyl ether (XXXV) (*33*) and guaiacylglycerol β-pinoresinol ether (XXXVI) (*26*). The latter trilignol is present to a larger extent than any of the others; and it has also been detected in spruce cambium sap. Other trilignols are guaiacylglycerol β-epipinoresinol ether (XXXVII) (*26*), bisguaiacylglycerol coniferyl ether (XXXVIII) (*33*), guaiacylglycerol diguaiacylpropane-

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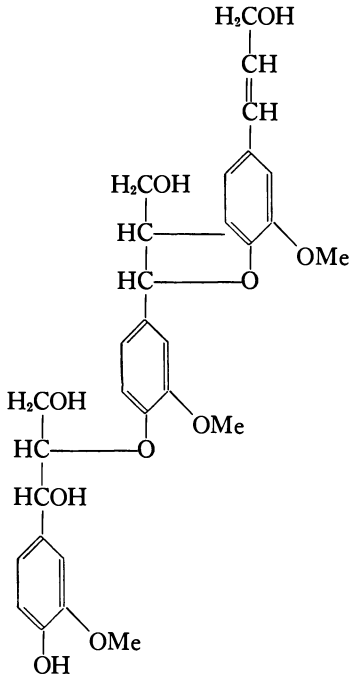
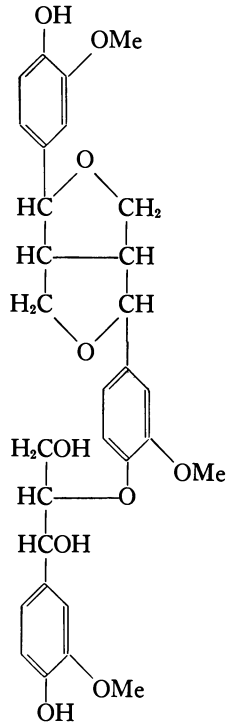


(XXXV) Guaiacylglycerol β-dehydrodiconiferyl ether



(XXXVI) Guaiacylglycerol pinoresinol ether

(XXXVII) Guaiacylglycerol epipinoresinol ether

diol ether (XXXIX), and its isomer, guaiacylglycerol β-diguaiacylpropanediol ether (XL). The two last substances have actually been found only among the products of mild hydrolysis of spruce lignin, but possibly they are present among the intermediates. However, their separation from each other and from other intermediates is difficult. Possibly XL is a stereoisomer of XXXIX.

Dehydrotriconiferyl alcohol (XLI) (*39*) is another trilignol whose formation among the intermediates can be explained by interaction of R_b and a corresponding R_c radical of dehydrogenated dehydrodiconiferyl alcohol (XVII).

Guaiacylglycerol β,γ-bisconiferyl ether (XLII) (*16*) is a labile trilignol formed by addition of coniferyl alcohol onto the dimeric quinonemethide (XXI). It readily loses a molecule of coniferyl alcohol by hydrolysis but is stabilized somewhat as soon as its phenolic group is etherified by further dehydrogenation and interaction with other radicals.

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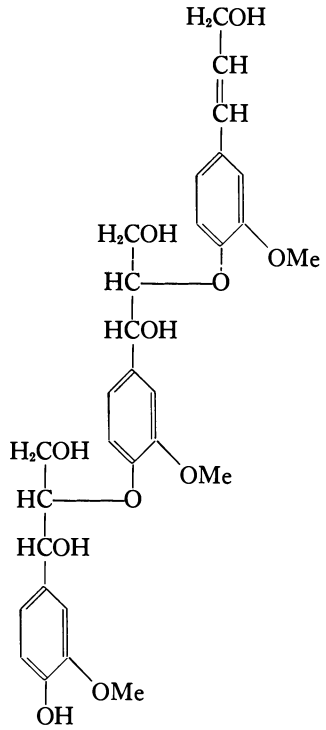
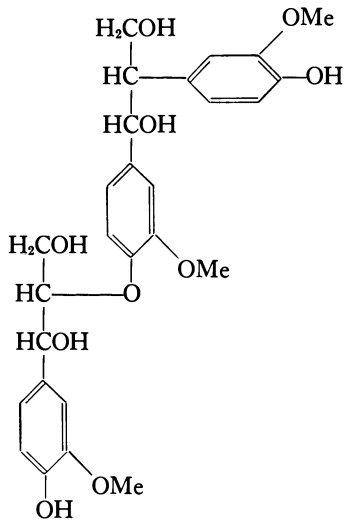
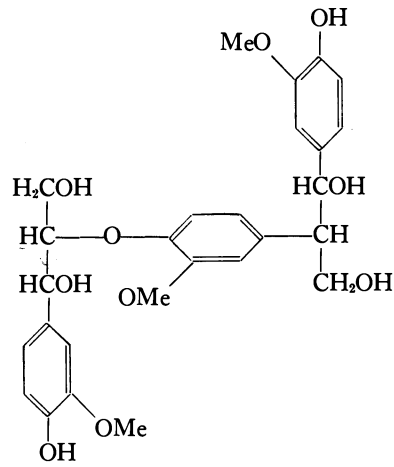


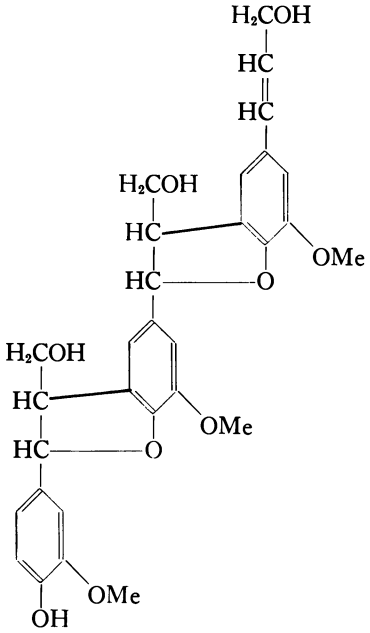
(XXXVIII) Bisguaiacylglycerol
β-coniferyl ether



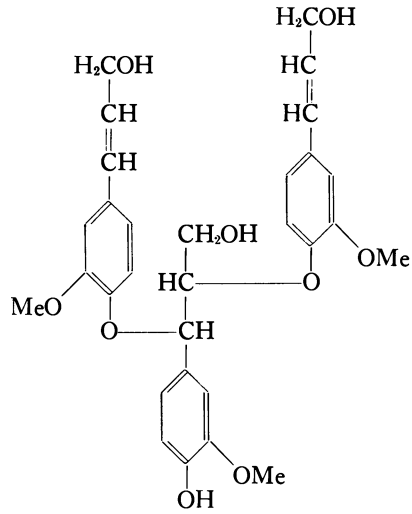
(XXXIX) Guaiacylglycerol
diguaiacyl propanediol



(XL) Isomer of XXXIX



(XLI) Dehydrotriconiferyl alcohol



(XLII) Guaiacylglycerol β,γ-bis-coniferyl ether

Higher Oligolignols

Guaiacylglycerol β-coniferyl-γ-dehydrodiconiferyl ether (XLIII) (*16*) is a tetralignol of the same kind as the last trilignol and originates by addition of preformed dehydrodiconiferyl alcohol (XVII) onto the dimeric quinonemethide (XXI). It is more stable as the trilignol (XLII).

Both XLII and XLIII are *p*-hydroxybenzyl aryl ethers; so is the polymerization product (XLIV) (*21*) of the quinonemethide (XXI) mentioned above. Such benzyl aryl ether bonds are not very rare in lignin and are easily attacked by acids or nucleophilic reagents containing sulfur.

Bisdehydropinoresinol (XLV) (*30*) is a crystalline tetralignol formed by biphenyl coupling on dehydrogenation of two molecules of pinoresinol and occurs to a small extent among the dehydrogenation products of coniferyl alcohol. There is no doubt that such 5,5′ bondings occur frequently between other oligolignols in which the side chain is saturated, thus making the formation of R_b-type radicals impossible.

The occurrence of the acid (X) (*13*) among the products of robust degradation of lignin proves that 5,6′-biphenylyl bonds also occur in lignin.

The pentalignol (XLVI) (*34*) is a labile amorphous substance and is probably a mixture of isomers and stereoisomers. It seems to consist mainly of the guaiacylglycerol β-ether of the tetralignol (XLIII).

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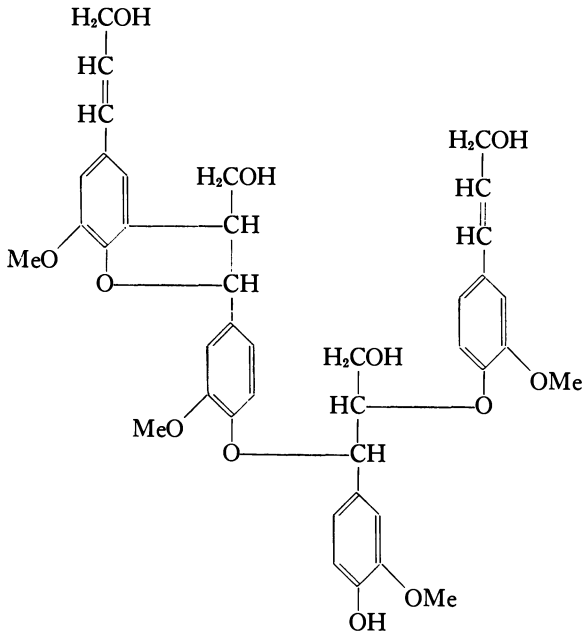
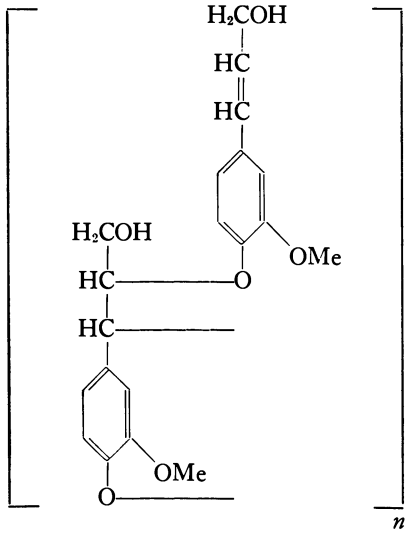
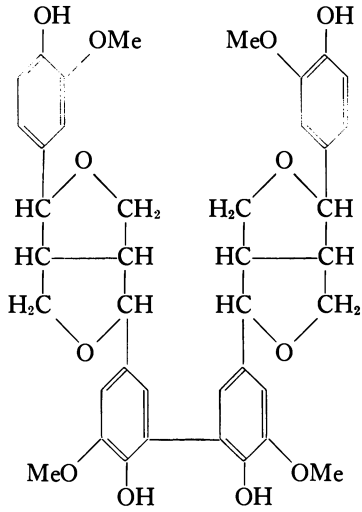


(XLIII) Guaiacylglycerol β-coniferyl-γ-dehydrodiconiferyl ether



(XLIV) Polymer of XXI



(XLV) Bisdehydropinoresinol

The hexalignol (XLVII) (*34*) is an amorphous product that is more stable than the pentalignol (XLVI) but consists of a mixture of stereoisomers. It is probably an adduct of the tetralignol (XLIII) onto the

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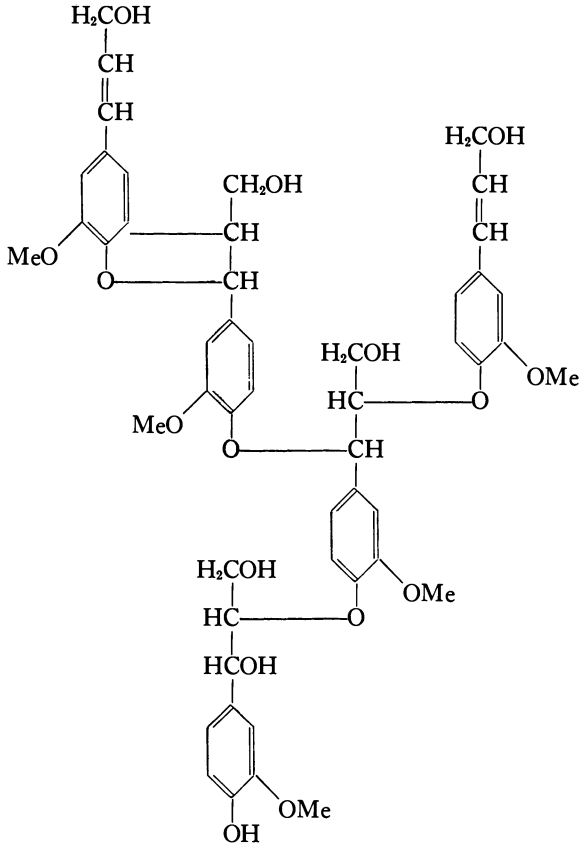
quinonemethide (XXI). It can also be regarded as the adduct of dehydrodiconiferyl alcohol (XVII) onto a tetrameric zwitterion or diradical formed by dimerization of the quinonemethide (XXI).



(XLVI) Pentalignol, guaiacylglycerol β-ether of XLIII

Once more the reactivity of the *p*-quinonemethides that occur as intermediates in these reactions must be emphasized. Their main representative (XXI) has been found able to add on not only water and phenols but even carbohydrates. The result is a new type of carbohydrate compound—namely, a carbohydrate *p*-hydroxybenzyl ether (e.g., XLVIII). These are about as sensitive towards hydrolysis by acid as cane sugar. Such a carbohydrate lignol ether is a phenol and can be incorporated into the lignin molecule after dehydrogenating the phenol group, thereby becoming more stable. This is undoubtedly the main way in which lignin is grafted onto the carbohydrates of the cell wall.

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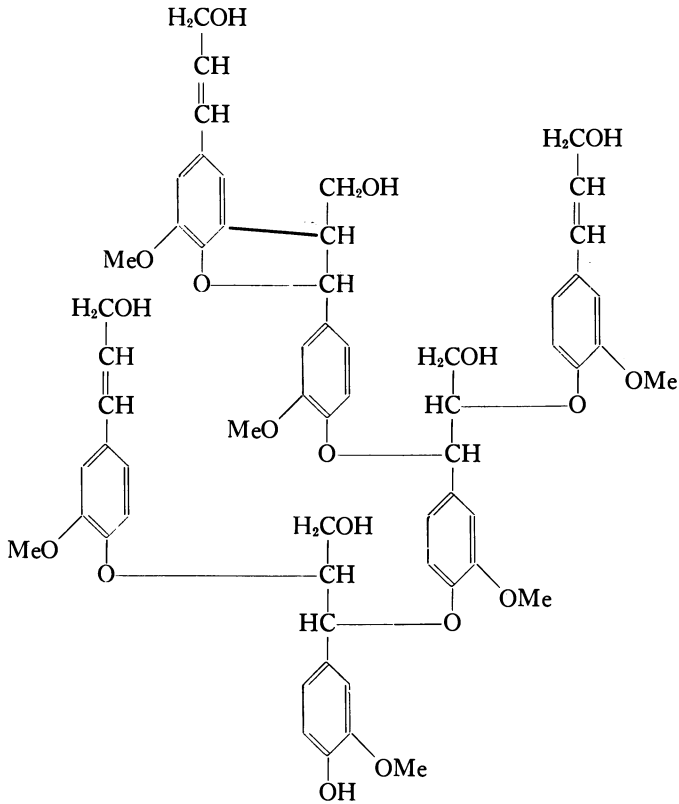

(XLVII) Hexalignol

As mentioned above, a number of substances can be isolated from acetone-percolated sprucewood meal by very mild hydrolysis. Hot water is generally sufficient. It hydrolyzes the benzyl aryl ethers but avoids recondensation or other alterations of the degradation products which normally occur when the lignin is more aggressively attacked. Lignin is a highly branched material. Mono-, di-, and trilignols can be isolated by mild hydrolysis if they are attached by benzyl aryl ether bonds at the periphery of the bulky lignin molecule. Obviously the yield of such small lignin hydrolysis products must be poor. Nevertheless, these substances are remarkable because they are chemically unaltered lignin degradation products and because undoubtedly larger amounts of these products are present inside the lignin molecule but are not split off under such mild conditions. Some of them have also been found among the intermediates of in vitro lignification. They are mentioned above as building stones of spruce lignin. They comprise coniferyl alcohol (II), coniferaldehyde (VII), ferulic acid (XV), dehydrodiconiferyl alcohol (XVII), DL-pino-

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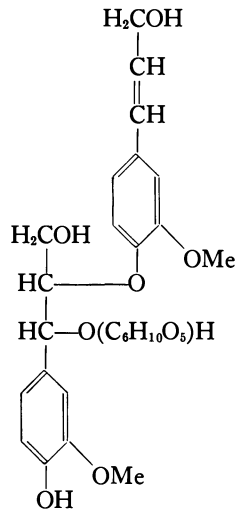
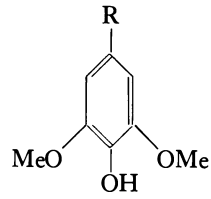
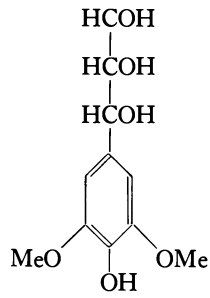


(XLVIII) Polysaccharide ether of XXII



(XLIX) R = —CH=CH—CHO Sinapyl aldehyde

(L) R = —CHO Syringaldehyde



(LI) Dimethylpyrogallyglycerol

resinol (XIX), guaiacylglycerol β-coniferyl ether (XXII), 1,2-diguaiacylpropane-1,2-diol (XXXIII), and the two guaiacylglyceroldiguaiacylpropanediols (XXXIX) and (XL) or a stereoisomer of XXXIX.

Beech Lignin. The ratios of *p*-coumaryl, coniferyl, and sinapyl alcohols in beech lignin are estimated to be about 5:49:46. When carefully pre-extracted beechwood powder (*Fagus silvatica*) is extracted with hot water or dilute acetic acid, coniferyl alcohol (II), coniferaldehyde (VII), sinapyl alcohol (III), sinapaldehyde (XLIX), syringaldehyde, dimethylpyrogallylglycerol (LI), DL-syringaresinol (LII), 1-guaiacyl-2-(dimethylpyrogallyl)-propane-1,3-diol (LIII), and 1,2-di(dimethylpyrogallyl)propane-1,3-diol (LIV) are obtained. Of these substances (XLIX), and the diols occur in yields of a few percent. The total yield of degradation products may be 12–15% of the beechwood lignin. Other substances are still under investigation.

DL-Syringaresinol can be isolated also when sinapyl alcohol is carefully dehydrogenated (*14*). It is easily attacked by further dehydrogenation to form dimethoxy-*p*-quinone. The latter substance has a high melting point and seems to be a trimeric form.

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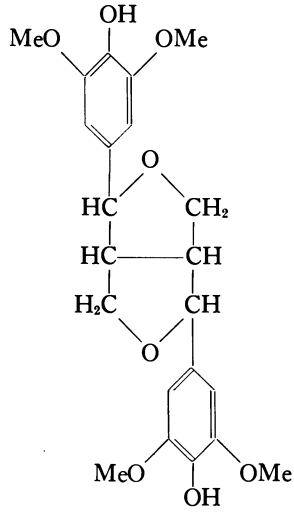
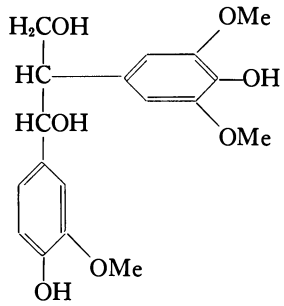
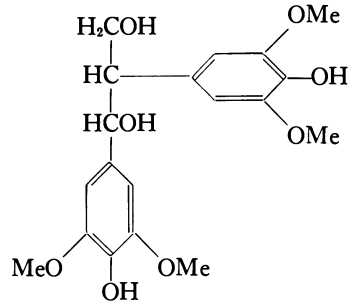


(LII) Syringylresinol



(LIII) 1-Guaiacyl-2-(dimethyl-pyrogallyl)-propane-1,3-diol



(LIV) 1,2-Di-(dimethylpyrogallyl)-propane-1,3-diol

It has been possible to construct a tentative constitutional scheme for spruce lignin based mainly on the results described above. Such a scheme satisfactorily accommodates many other facts of lignin chemistry which are not mentioned here (*9*, *10*, *11*, *20*). The lignols which originate during lignin formation, together with the products of mild hydrolysis, reveal the different ways in which the C_6C_3 units are combined in lignin. It is impossible to combine these polylignols on paper at random. In order to obtain a reasonable constitutional scheme representing a true fragment of the lignin polymolecule, it is necessary, while combining the oligolignols, to apply the rules we are taught while studying their constitution.

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2

The Structure and Reactivity of Lignin

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Degradation of Björkman spruce lignin by "acidolysis" (4 hours refluxing with 0.2M HCl in dioxane-water) followed by fractionation on dextran and silica gel columns results in isolating several products containing one or two guaiacyl groupings. The monomeric main product (6%) was ω-hydroxyguaiacylacetone (XII) originating from arylglycerol β-aryl ether systems (II). Isolation of phenylcoumarone (XXII) and the o,p'-dihydroxystilbene (XXIII) reveals the occurrence in lignin of the trimeric sequence (XXVIII). Furthermore, the p,p'-dihydroxystilbene (XXV) and the α-methyldesoxybenzoin (XXVI) were isolated and shown to originate from a 1,2-bisguaiacyl-1,3-propanediol system (XXXIV) either present in lignin or formed on acidolysis from a cyclohexadienone precursor (XXXII). For a fifth dimeric product, structure (XXIV) (d,l-3,4-divanillyltetrahydrofuran) is proposed; its origin is still obscure.

For several years, studies regarding the behavior of lignin on "acidolysis," —i.e., heating with 0.2*M* hydrogen chloride in dioxane-water 9:1— have been carried out in our laboratory. Analytical examination of the changes incurred by this treatment, and more recently, the isolation of various degradation products helped to elucidate some basic structural features of the lignin molecule.

Strong analytical support for the presence of the phenylcoumaran system (I) in lignin was obtained a few years ago (*5*) (Figure 1). Under the conditions of acidolysis, models for system I, namely dihydrodehydrodiconiferyl alcohol (III) (*13*) and its methyl ether (III, OCH_3) were converted into phenylcoumarone derivatives (VIII and VIII, OCH_3). The structure of the phenolic coumarone (VIII) was established by an inde-

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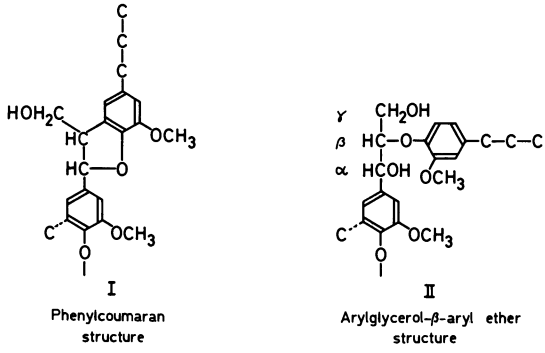

Figure 1. Structure of phenylcoumaran (I) and arylglycerol β-aryl ether (II)

pendent synthesis (*29*). Its yield on acidolysis of III was 75%. The conversion (III) → (VIII) may be understood as a sequence of reactions involving ring opening with the formation of the benzylium ion (IV), formation of the cinnamyl alcohol (V) (full line arrows) and the allylium ion (VI), allylic rearrangement with reclosure of the hydrofuran ring to give VII, and finally, migration of the exocyclic double bond of VII (Figure 2).

As a by-product of the acidolysis reaction, the *o,p'*-dihydroxystilbene (IX) was formed, obviously by the loss of a molecule of formaldehyde from the benzylium ion intermediate (IV) (broken line arrows), a reaction to be regarded as a reverse Prins reaction (*29*).

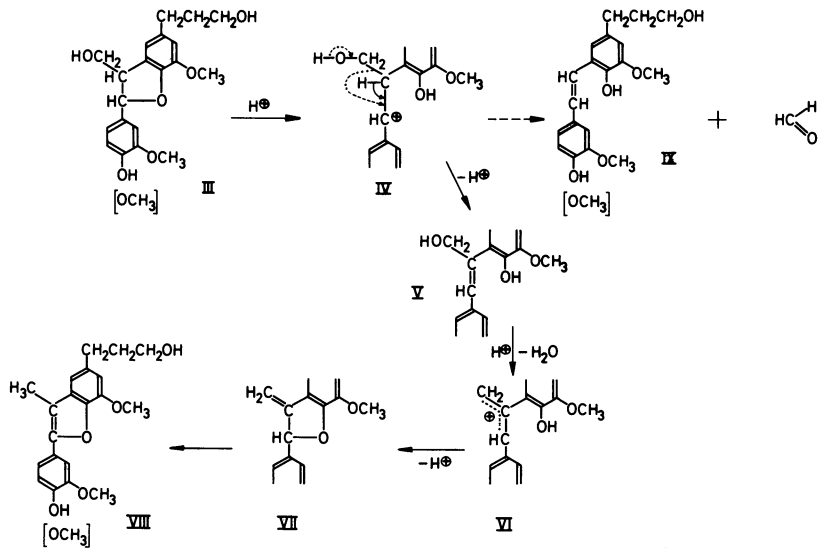

Figure 2. Acidolysis of dihydrodehydrodiconiferyl alcohol

Phenylcoumarone (VIII) has a characteristic ultraviolet and ionization-$\Delta\epsilon$ spectrum, which enabled us to detect dimeric structures of this type in reaction mixtures obtained when Björkman spruce lignin was subjected to acidolysis for 20 hours. From the spectrophotometric estimation of the amount of the phenylcoumarone systems formed, we concluded that from a total of 100 phenylpropane units of Björkman lignin, about 20 are involved in phenylcoumaran systems (I); in other words, about every 10th phenylpropane unit is linked to one of its neighbors by the cyclic benzyl aryl ether linkage characteristic of I.

Acidolysis was also used in our earlier, mainly analytical studies regarding the arylglycerol β-aryl ether system (II). (The usual designation of the C atoms of the propane side chain, as given in (II), is retained. The reversed numbering recently used by K. Freudenberg (*16*) seems to be appropriate only for the (unsaturated) cinnamyl side chain (cf. (*21*)).

After 48 hours acidolysis, model substance X (R = H) (*3*, *22*) yielded (*6*) a mixture of α-hydroxypropioguaiacone (XV), vanilloyl methyl ketone (XVI), and guaiacylacetone (XVII) in addition to guaiacol (XIII). Products XV–XVII were detected by paper chromatography after similar acidolysis of Björkman lignin, analogous to the results obtained by Hibbert on ethanolysis of wood, which gave the ethyl ether of ketol (XV) as well as the ketones (XVI) and (XVII). The nonphenolic model compound X (R = CH_3) (*4*) reacted in a similar way (*6*), the essential feature of the acidolysis reaction of the model substances thus being the liberation of guaiacol and the formation of C-methyl groups. Analogously, acidolysis of Björkman lignin resulted in liberating free phenolic hydroxyl groups as well as forming C-methyl groups. The increase in the amounts of these groups indicated that one-fourth to one-third of the phenylpropane units of spruce lignin has the structure of an arylglycerol, in which the β-hydroxyl group is etherified with the phenolic hydroxyl group of the adjacent unit, as represented by formula II (Figure 3).

The course of the acidolysis reaction of model compound X was then studied in greater detail (*1*, *2*, *24*, *27*, *28*). We found that ω-hydroxyguaiacylacetone (XII, R = H) and its methyl ether (XII, R = CH_3) are intermediates in the acidolysis of guaiacylglycerol β-(2-methoxyphenyl) ether (X, R = H) and its methyl derivative (X, R = CH_3), respectively. Obviously, their formation is caused by an initial dehydration (step *a*) and the hydrolysis of the resulting enol aryl ether (step *b*). Ketol (XII) is further converted by allylic rearrangement of (XIIa) and subsequent enol-keto rearrangement (step *c*) (*17*, *18*, *33*) into an equilibrium mixture (*28*, *29*) of the isomeric secondary ketols (XIV and XV). Finally, oxidoreduction of the latter ketols (R = H) provides vanilloyl methyl ketone (XVI) and guaiacylacetone (XVII). It may be pointed out that this oxidoreduction is not given by the nonphenolic ketols (XIV and XV, R = CH_3) (*8*), which seems to indicate that the quinonemethide derived

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from the phenolic benzyl alcohol (XIV, R = H) is involved in the reaction. Traces of vanillin (XVIII) and vanillic acid (XIX) were detected as by-products in the acidolysis of the phenolic starting material (X, R = H).

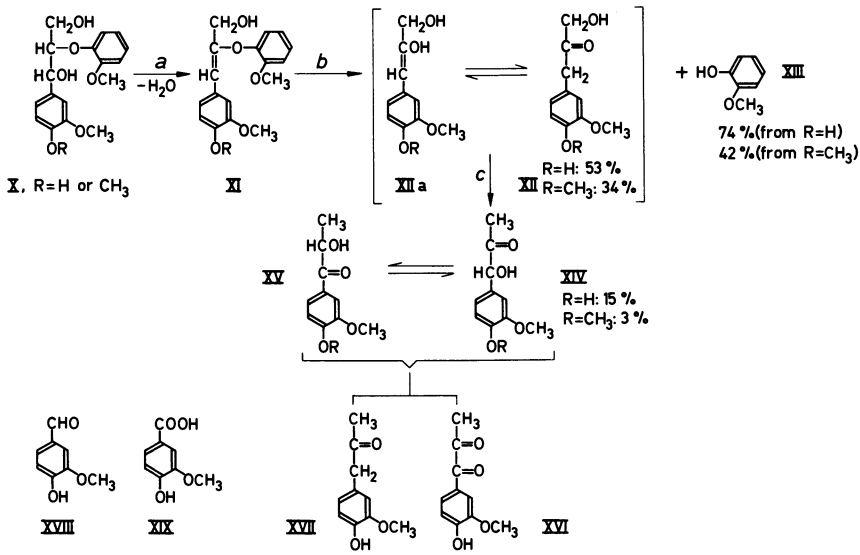

Figure 3. Acidolysis of arylglycerol β-aryl ether model compounds. Conditions: 0.2M HCl in dioxane-water, 9:1, refluxed for 4 hours.

In the acidolysis of the phenolic β-aryl ether model (X, R = H) Reaction *b* was much faster than the initial step *a*; furthermore, Reaction *c* was appreciably slower than *a*. Therefore, the primary ketol (XII) accumulated in the acidolysis mixture during the first few hours of heating and could be isolated after 4 hours of acidolysis of X (R = H) in a yield of 53%; only 15% of the starting material had been converted further into the mixture of (XIV) and (XV). The total β-aryl ether cleavage was 74%, as indicated by the yield of guaiacol (XIII). (The nonphenolic model compound X (R = CH_3), reacted at an appreciably lower rate, the corresponding yields after 4 hours of acidolysis being 34% XII (R = CH_3), 3% XIV and XV (R = CH_3), and 42% guaiacol.)

On the basis of these model experiments we expected that 4 hours of lignin acidolysis would produce ω-hydroxyguaiacylacetone (XII, R = H) as a reaction product of arylglycerol β-aryl ether structures (II) containing arylglycerol moieties with an uncondensed aryl group. In fact, Lundquist (*25*) was able to isolate the ketol XII (R = H), which had not been obtained previously from lignin, in a yield of about 6% of the Björkman lignin used, by fractionating the acidolysis mixture on silica gel columns.

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The crude Björkman lignin acidolysis mixture contained both polymeric material and a number of more or less low molecular, chromatographically visible products in addition to ketol (XII) and was considered to be a potential source not only of further monomeric but also of dimeric and oligomeric degradation products. The polymeric material was readily removed by filtering the crude mixture of reaction products through a short silica gel column (solvent, dioxane-benzene 1:3).

To separate the products of lower molecular weight present in the filtrate, gel filtration on dextran (Sephadex) columns proved to be very helpful. The use of polar organic solvents or their mixture with water suppressed the undesirable adsorption effects previously encountered when gel filtration was applied to aromatic compounds in aqueous solution, and fractionation according to molecular size (molecular sieving) was accomplished. This is illustrated in Figure 4 which shows the behavior of a model mixture containing three monomeric compounds (XV; XVIII; XII, R = H), three dimeric compounds (X, R = H; XXVII; (+)-pinoresinol) and Björkman lignin on filtration through Sephadex G 25, dioxane-water 1:1 being used as eluant (*31*).

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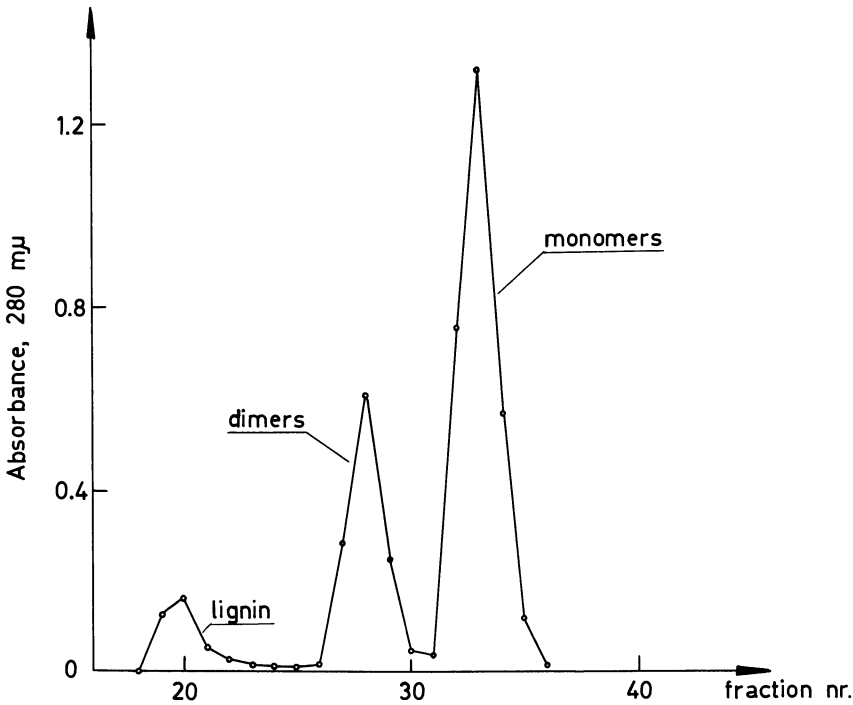

Figure 4. Gel filtration of model mixture. Conditions: Sephadex G25, dioxane-water, 1:1.

If a reaction mixture obtained after 4 hours acidolysis of Björkman lignin (spruce), after neutralization and removal of the polymeric material, were filtered through a Sephadex G 25 column, the elution curve (Figure 5) exhibited three peaks (*26*). The effluent fractions corresponding to peaks A and B were subjected to further fractionation by chromatography on silica gel columns. We found that fraction A contained only monomeric products while fraction B was a mixture of dimeric products (Figures 6 and 7).

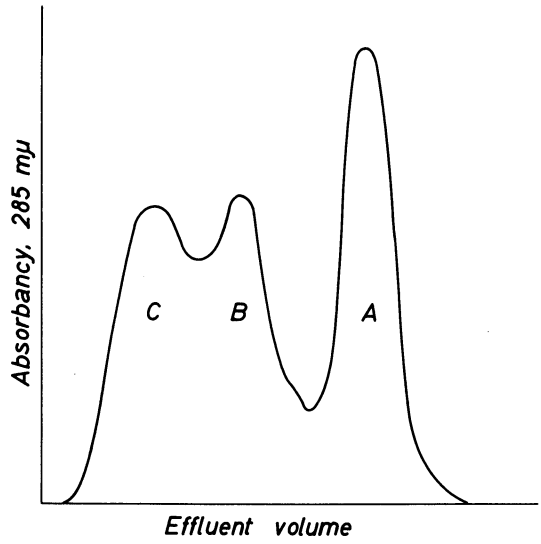

Figure 5. Elution curve of reaction mixture

In fraction A, which contained 12% of the lignin used the main constituent was the expected ω-hydroxyguaiacylacetone (XII), which again was isolated in a yield of 6% of the lignin. It was accompanied by minor amounts of its two rearrangement products (XIV, XV) (*25*, *26*) and their two oxidoreduction products (XVI, XVII) as well as small quantities of vanillin (XVIII) and vanillic acid (XIX). These "monomeric" lignin degradation products are identical with those obtained on acidolysis of the β-aryl ether model (X, R = H) as reported above, and their relative amounts, especially the relative abundance of the primary ketol (XII), also agree with the results of the model experiment.

In our opinion, these results constitute decisive proof that the arylglycerol β-aryl ether structure (II) occurs in lignin.

Recently, small amounts of guaiacylglycerol β-coniferyl ether have been isolated by Nimz (*35*) after percolating pre-extracted sprucewood for 8 days with 2% aqueous acetic acid at 100°C. This particular β-aryl

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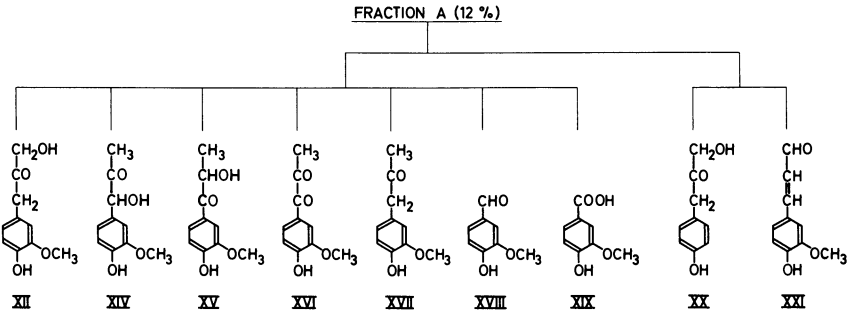

Figure 6. Effluent fraction A

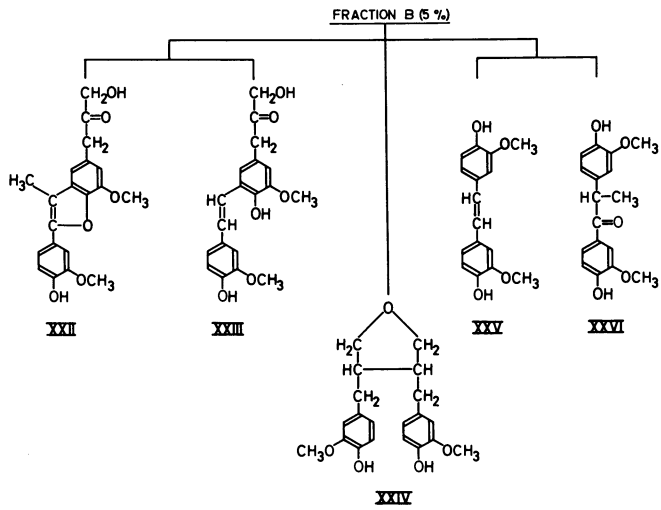

Figure 7. Effluent fraction B

ether must be present in lignin as an end group, bound to the rest of the molecule by an easily hydrolyzable linkage, presumably a benzyl aryl ether linkage. The arylglycerol β-aryl ether linkages may remain largely unaffected by the hydrolytic extraction method of Nimz whereas cleavage of such linkages will occur throughout the whole lignin molecule in the considerably more drastic acidolysis procedure (0.2*M* HCl) used in our work.

Therefore, isolating 6% ω-hydroxyguaiacylacetone (XII) from Björkman lignin also provides quantitative information. If this yield is compared with the yield of XII from the model compounds X, considering the fact that only the noncondensed arylglycerol units of lignin can give rise to free ketol (XII), it tends to indicate that about 25% of the phenylpropane units of lignin are arylglycerol units connected to an adjacent unit by a β-aryl ether link. This figure, which would include both noncon-

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densed and condensed arylglycerol units, agrees with our previous estimate (*6*) which was based on purely analytical data. However, it may well be considered as a lower limit, since C—C condensation between benzyl alcoholic groups and phenolic nuclei may occur during the acidolysis reaction, which would result in a decreased yield of ketol (XII). Although in the 4 hours of acidolysis of the model X such condensation seems to be negligible (cf. the high yield of guaiacol, XIII), it may be favored in the acidolysis of lignin by closer vicinity of the reacting groups.

A small amount of the previously unknown *p*-hydroxyphenyl-ω-hydroxyacetone (XX), obviously derived from *p*-hydroxyphenylglycerol β-aryl ether elements, was also isolated from fraction A, and its structure was established by synthesis (*26*).

Finally, coniferaldehyde (XXI) was found (*26*) in fraction A in a quantity of about 0.5% of the lignin. The major portion of XXI probably originates from coniferaldehyde end groups linked to the lignin molecule by hydrolyzable ether bonds—i.e., α- and β-aryl ether bonds. In agreement with this view, we found that borohydride-reduced Björkman lignin, when subjected to acidolysis, gave only traces of coniferaldehyde.

The fraction of the Sephadex eluate, which corresponded to peak B (Figure 5), contained 5% of the weight of the Björkman lignin used in the acidolysis experiment. We expected it to contain dimeric acidolysis products. So far, five pure compounds (XXII–XXVI) have been obtained from fraction B.

Structure (XXIV) (3,4-divanillyltetrahydrofuran) for one of these products, although still awaiting final confirmation, is proposed on the basis of ultraviolet, infrared, and mass spectra of the substance and of further analytical data.

The (−)-enantiomer of compound (XXIV) (m.p., 117°C.) has been prepared by Freudenberg and Knof (*14*) from *d*-pinoresinol, and on the basis of chromatographic evidence it was suggested as being present in the extractives of sprucewood. Since the acidolysis product has m.p. 135°C., it is apparently not identical with the substance described by Freudenberg and Knof; the possibility that our product might be the racemate of XXIV was then examined by synthesizing the latter from *d,l*-pinoresinol. In fact, the synthetic *d,l*-divanillyltetrahydrofuran had the same melting point as the acidolysis product, the mixed melting point showed no depression, and the two products were similar with respect to all other properties examined. If structure XXIV (*d,l*-form) is correct and if the substance actually is a degradation product of Björkman lignin, it constitutes the only acidolysis product found so far which does not fit directly into the coniferyl alcohol dehydrogenation picture (Figure 7). The degree of oxidation of its phenylpropane units actually is lower than that of coniferyl alcohol, and its formation in lignin synthesis therefore would require some oxidoreduction process.

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Of the four remaining "dimeric" products, the phenylcoumarone (XXII) (m.p., 110°C.), isolated in a yield of about 0.5% of the lignin, and the *o,p'*-dihydroxystilbene (XXIII) obviously are genetically interrelated; both must be derived from a phenylcoumaran structure, as already shown above in the acidolysis of dihydrodehydrodiconiferyl alcohol.

The structure of the phenylcoumarone (XXII) (*26*) was derived from analytical and spectral investigation and was confirmed by a synthesis (*29*) starting from dehydrodiconiferyl alcohol (XXVII). The latter compound (XXVII) was converted by monoperphthalic acid into an epoxide whose side chain was equivalent to that of an arylglycerol. By properly performed acidolysis, the epoxide side chain therefore was converted into the primary ketol structure, and at the same time the hydroxymethyl-substituted phenylcoumaran system (*see* XXVII) was converted into the methyl-substituted phenylcoumarone system of XXII (Figure 8).

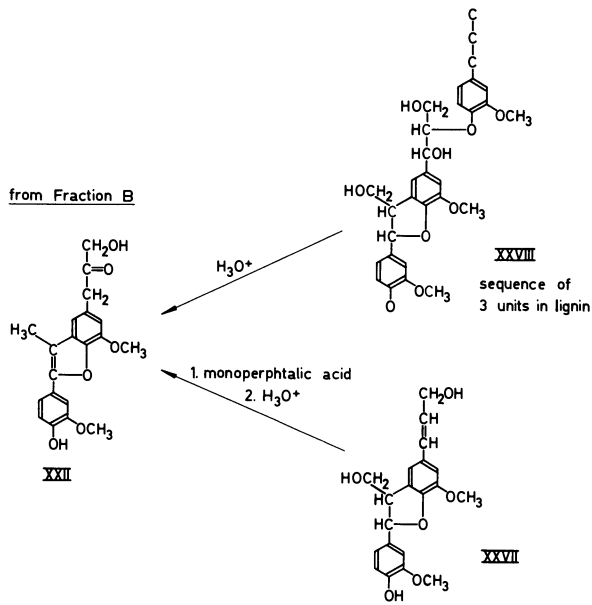

Figure 8. Synthesis of phenylcoumaran (XXII) and its formation from a trimeric structure in lignin

To our knowledge, the coumarone ketol (XXII) is the first crystalline dimeric lignin degradation product with two complete phenylpropane skeletons which has been reported in the literature (*26*). On the basis of the model experiments discussed above, the presence of the ketol side chain as well as the phenylcoumarone system in (XXII) indicates that the origin of the product is a sequence of three phenylpropane monomers (XXVIII) in lignin, involving a phenylcoumaran system carrying a gly-

cerol side chain, to which the third unit is linked by a β-aryl ether linkage. Thus, isolating degradation product XXII proved directly that the phenylcoumaran system as well as the arylglycerol β-aryl ether system occur in lignin. In the glycerol side chain, the benzylic hydroxyl group may be etherified (*12*), which would add a fourth phenylpropane unit.

Recently, Freudenberg and co-workers (*11*) briefly reported the isolation of small amounts of dehydrodiconiferyl alcohol (XXVII) from the methanolysis of wood at room temperature. By this procedure, again, only benzyl aryl ether-linked terminal dimers can be obtained whereas acidolysis liberates (α- and) β-ether-linked phenylcoumaran systems from the core of the lignin molecule as well.

The remaining pair of acidolysis products isolated from Sephadex fraction B, as already mentioned, consisted of 4,4′-dihydroxy-3,3′-dimethoxystilbene (XXV) and 1,2-bisguaiacylpropanone (XXVI). The stilbene (XXV) was isolated several years ago from sulfite-spent liquor which had been heated with alkali (*37*) as well as from alkali-heated wood (*37*, *39*, *40*); it has also been detected in kraft liquor (*10*). The structure of the previously unknown ketone (XXVI) (m.p., 121–122°C.) was derived from analytical and spectral data and established by synthesis (*30*).

Both products could be considered to originate from dimeric phenylpropane systems by losing one of the propane side chains; in addition, the stilbene (XXV) then had lost the terminal carbon of the remaining propane side chain. One therefore had to look for an appropriate dimeric phenylpropane structure which could explain the formation of these products on acidolysis.

The loss of a terminal carbinol group with the formation of a stilbene had been encountered previously as a side reaction in the acidolysis of the phenylcoumaran system. By analogy, stilbene (XXV) could be assumed to arise by the loss of formaldehyde (reverse Prins reaction) from the benzylium ion (XXXV), which, in turn, could be derived only from the corresponding benzyl alcohol (XXXIV, R = H) or a corresponding benzyl ether. 1,2-Bisguaiacyl-1,3-propanediol (XXXIV, R = H) was therefore synthesized, and its behavior on acidolysis investigated (*30*). (The synthesis of XXXIV (R = H) yielded the two possible diastereoisomers; one of these crystallized (m.p., 158°–159°C. (*37*); tetraacetate, m.p., 134°–135°C.).) We found that it yielded not only the expected stilbene (XXV) but also the diarylpropanone (XXVI) (Figure 9). As a matter of fact, the formation of the latter product by a sequence of proton-catalyzed reactions, starting from the benzylium ion (XXXV), had also been predicted, being quite similar to the conversion of phenylcoumaran (III) to phenylcoumarone (VIII) as well as to the reactions leading from the arylglycerol β-aryl ether (X) to the Hibbert ketones.

In addition to stilbene (XXV) and the propanone derivative (XXVI) at least one further phenolic product was formed, whose structure has not

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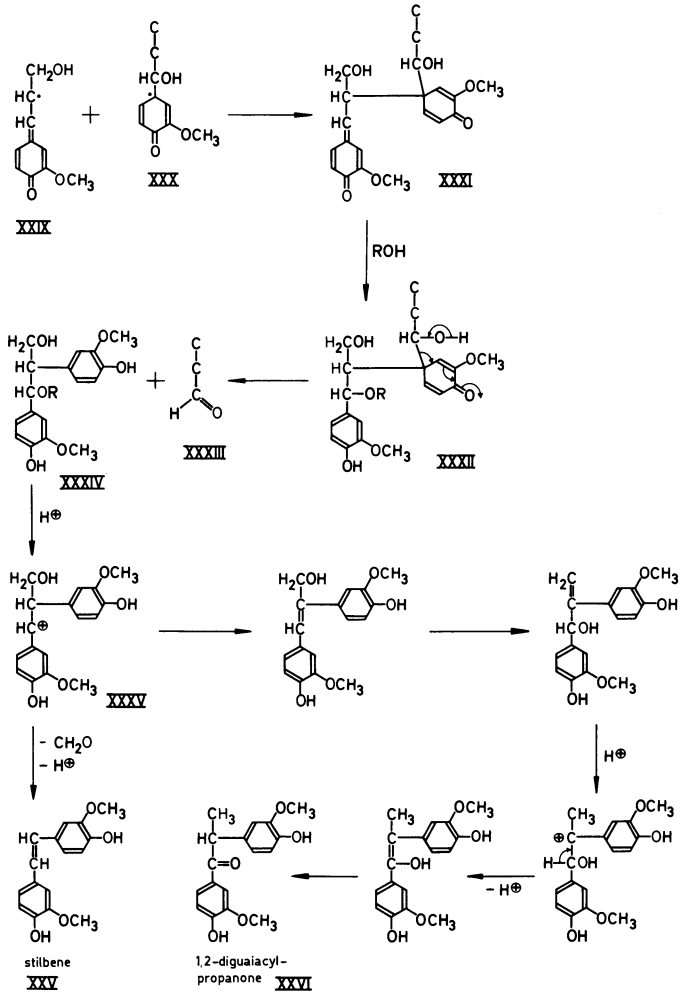

Figure 9. Genesis of propanediol in the lignin molecule and acidolysis of this system

been definitely established. It contains a nonconjugated carbonyl group and is probably formed from one of the intermediary benzylium ions by aryl migration (Wagner-Meerwein rearrangement). This phenolic product was also detected in fraction B of the lignin acidolysis mixture. This product has been found to be 1,1-bisguaiacyl-2-propanone, isomeric with the 1,2-bisguaiacyl propanone (XXVI). In other words, the same group of three degradation products (XXV, XXVI, and a third phenolic compound) were formed on acidolysis of lignin as well as on acidolysis of the synthetic bisguaiacylpropanediol (XXXIV). This demonstrates conclusively that Björkman lignin contains the 1,2-bisguaiacyl-1,3-propanediol

system or, possibly, a precursor structure, from which the diol system is formed on acidolysis.

Regarding the genesis, in the growing lignin molecule, of the propanediol (XXXIV) or its precursor system, the following assumptions can be made (*30*). A coniferyl alcohol radical (XXIX) couples with a mesomeric radical (XXX) formed by dehydrogenation of a phenolic end group to give the quinonemethide (XXXI) which in the β-position is substituted by a 2,5-cyclohexadienone system. (The possibility of such a β,4-coupling has been suggested previously by Freudenberg and Lehmann (*15*).) Stabilizing the quinonemethide structure in XXXI by adding water or a phenolic hydroxyl group (*12*) (ROH, R = H or aryl) would yield system XXXII. On acidolysis, the latter system would be degraded via the 1,2-bisguaiacylpropanediol XXXIV (R = H) to the end products XXV and XXVI. It is also possible that in the wood, system XXXII decomposes spontaneously to give the diarylpropanediol system (XXXIV), which could be linked to the lignin molecule as a benzyl aryl ether (R = aryl) and/or through one or both of the phenolic hydroxyl groups. Again, acidolysis would degrade such systems to XXV and XXVI.

The conversion of the hypothetical precursor system XXXII into the aromatic system XXXIV would involve the removal of a carbon substituent from the cyclohexadienone moiety. In general, cyclohexadienones tend to stabilize themselves by migration of one of the geminal substituents into an adjacent ring position (dienone-phenol rearrangement). Removal rather than migration of a carbon substituent, however, has been reported (*9*, *19*, *23*, *32*, *34*) in the case of 2,4,6-tri-*tert*-butyl-6-hydroperoxy-2,4-cyclohexadienone—the 6-*tert*-butyl group being expelled as isobutene. Furthermore, removal of the isopropyl substituent from 2-isopropyl-*o*-quinol acetates was described by Zbiral (*41*).

The following mechanism is suggested as operating in the conversion of XXXII to XXXIV. If the radical (XXX) is assumed to be generated from a *p*-hydroxybenzyl alcoholic end group, the cyclohexadienone system (XXXII) would carry an α-hydroxyl-substituted side chain. Removal of the latter as an aldehyde (XXXIII) might then occur, as indicated by the arrows in formula (XXXII).

The occurrence of a similar reaction has recently been indicated by studies carried out in this laboratory (*7*). If *p*-hydroxybenzyl alcohol (XXXVI) was oxidized with sodium bismuthate, the spirocyclic epoxycyclohexadienone (XXXVII) was obtained. The epoxide ring of this compound was hydrolyzed almost instantaneously by 2*N* aqueous hydrochloric acid and in a few hours by 10% aqueous acetic acid. However, the expected glycol (XXXVIII) could not be isolated since it decomposed immediately into equimolar amounts of hydroquinone and formaldehyde. (Attempts are now being made to prepare compounds analogous to XXXVIII but containing, in addition to the $HOCH_2$ group, a carbon sub-

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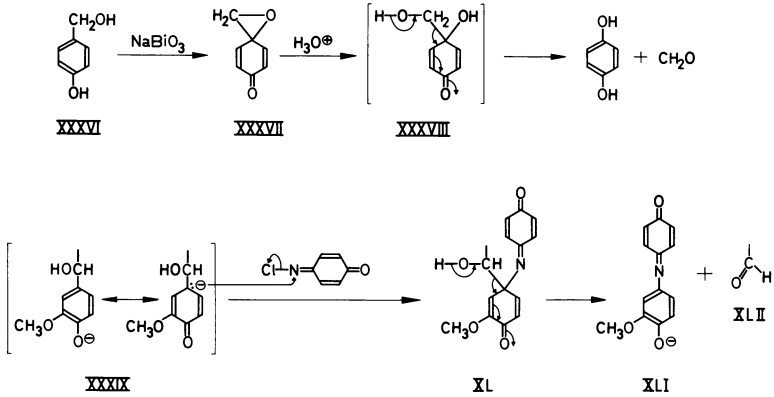

Figure 10. Reactions of 2,5-cyclohexadienones

stituent rather than a hydroxyl group and thus being more similar to the cyclohexadienone (XXXII) (Figure 10).)

Similar removal of an alcoholic substituent is found in the indophenol color reaction of *p*-hydroxybenzyl alcohols (XXXIX) with *N*-chloroquinoneimide (Ziegler and Gartler (*42*, *43*), Gierer (*20*)). If the quinamine type compound (XL) is assumed as an intermediate in this reaction, its decomposition to the indophenol (XLI) and the aldehyde (XLII) (*42*, *43*) would be analogous to the decomposition of XXXII postulated above.

Independently of the isolation of the acidolysis products XXV (*26*) and XXVI (*30*) and the studies (*30*) reported above regarding their origin from a 1,2-bisguaiacyl-1,3-propanediol system (XXXIV) or its precursor XXXII in lignin, Freudenberg and Nimz (*see* reference (*11*)) succeeded in isolating the syringyl analog of XXXIV (R = H) as well as the guaiacyl compound XXXIV (R = H) after mild hydrolysis of wood. (A detailed paper by H. Nimz (*36*) on the isolation of the syringyl compound from beechwood appeared after this manuscript had been written.)

Acknowledgment

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3

Repeating Units in Spruce Lignin

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The prevailing opinion today is that lignin is a statistical polymer for which no structural formula in the true sense can be presented but only a structural scheme of the type proposed by Adler and Freudenberg. Careful fractionation of the lignosulfonates and other compounds that are dissolved in the liquor in a sulfite cook shows, however, that the lignosulfonic acids may not be derived from a statistical polymer but from an ordered polymer composed of repeating units, and that sprucewood contains appreciable amounts of aromatic compounds which are related to true lignin as hemicellulose is to cellulose. We believe that it is necessary in lignin studies to be sure that the lignin preparation studied does not contain any of these hemilignin components.

We have studied the properties of spruce lignin by first dissolving the lignin and hemilignin from the wood by sulfite cooking liquors of varying composition under different experimental conditions and then fractionating the formed lignosulfonates by gel filtration. From the fractions resulting on gel filtration through a column of Sephadex G-25, 25 ft. long, we have isolated a series of nine low molecular weight lignosulfonates that form a homologous series. We have concluded from analytical data for these lignosulfonates that spruce lignin is composed of repeating units, each consisting of 16 guaiacylpropane units and two *p*-hydroxyphenylpropane units. The repeating unit has four carbon atoms which can be sulfonated without previous hydrolysis. Sulfonating these carbon atoms leads to the formation of undissolved lignosulfonic acids in the wood. The repeating units are bound to each other by ether bonds that are partially broken by hydrolysis during the cook. They are further bound to carbohydrates by four ether bonds that are hydrolyzed and at least partially sulfonated during the cook. The smallest complete lignosulfonic acid is composed of only one repeating unit. Further hydrolysis and sulfonation of this acid lead to the successive liberation of eight guaiacylpropane units and hence to the isolated series of homologous lignosulfonates, each of which comprises one incomplete repeating unit composed of 15 to eight guaiacylpropane units and two *p*-hydroxyphenylpropane units.

In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

The theoretical composition deduced for spruce lignin was confirmed by analytical data for several low sulfonated, high molecular weight lignosulfonate fractions. The results of these studies are presented in detail in *Paperi Puu* **47**, 443 (1965).

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4

Reactivity of Lignin in Electrophilic Displacement Reactions

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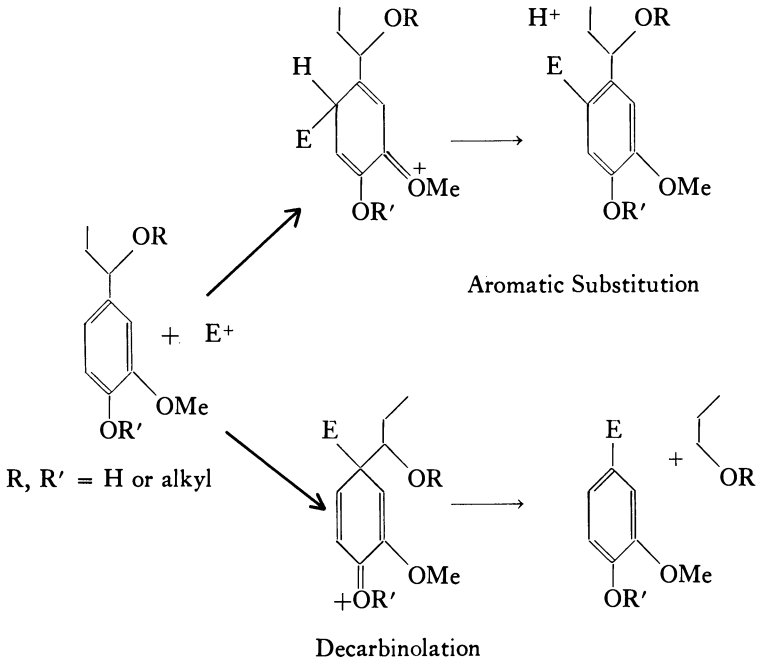
Estimating the reactivity of various aromatic nuclei in lignin involves studies to determine the protodedeuteration rates of certain selectively deuterated model compounds. The combined effects of hydroxyl, methoxyl, and side-chain substituents are approximately additive in guaiacyl models while syringyl models show significant deviation from the predicted behavior. The reactivity of the position meta to methoxyl groups is higher while those of the ortho and para positions are lower than anticipated on the basis of combined substituent effects.

Lignin macromolecules undergo electrophilic displacement reactions easily owing to the reactivity of the aromatic nuclei that are activated by several electron-releasing substituents. These reactions include ordinary aromatic substitutions involving the displacement of a hydrogen from the ring as well as side-chain displacements. The latter reactions have been shown to occur during chlorination (*3*, *4*, *16*) and nitration (*7*) and are particularly facilitated if the side chain contains a carbinol group adjacent to the ring. The reaction scheme below illustrates both types of displacement reactions.

Some of the most important electrophilic displacement reactions of lignins are listed in Table I with the reactive species indicated. In general, the complexity of the products from these reactions makes structural evaluation extremely difficult. Therefore, an approach using model compounds related to lignin appears desirable.

A typical lignin C_6C_3 unit (*see* reaction scheme below) contains a side chain at position 1, a methoxyl at position 3, and a phenolic hydroxyl or phenol ether group at position 4. Another methoxyl group or a condensed

In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.



side chain may be linked to position 5. Alternatively, no methoxyl groups may be attached to the aromatic nucleus. To what degree, then, is it possible to predict the reactivities of the unsubstituted aromatic sites towards various electrophilic displacement reactions?

This question could be answered more easily if we knew that the C_6C_3 units conformed with the principle of additivity. This principle can be formulated as follows. If the introduction of each of two substituents alters the free energy of activation at a particular position by amounts x and y, the presence of both substituents would alter the free energy of activation by an amount $(x + y)$. If this relationship holds, it allows one to predict the reactivities of the individual positions in disubstituted benzene derivatives from the rate data obtained for the corresponding monosubstituted ones. The partial rate factor for a given position of a

Table I. Electrophilic Displacement Reactions of Lignin

	Reactive Species
Halogenation and halodecarbinolation	Cl_2, Cl^+, Br^2, Br^+, etc.
Nitration, nitrosation, nitrodecarbinolation	NO_2^+, N_2O_5, NO^+, N_2O_4
Hydroxylation	RCO_3H
Hydrogen exchange	HA (DA)
Various condensations	R_3C^+
Mercuration	$Hg(OAc)_2$, $Hg(NO_3)_2$
Diazonium coupling	$Ar N_2^+$

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disubstituted compound would equal the product of the rate factors for the two monosubstituted compounds. By extending this principle further, the partial rate factors for the three positions of a trisubstituted aromatic compound can be predicted; each partial rate factor in this case is obtained as the product of three individual partial rate factors.

According to the definition, the partial rate factors express the ratio of the rate constant of a particular substitution reaction at a given site to the rate constant of a single site in an unsubstituted benzene nucleus. To illustrate, this principle would predict that the partial rate factor for position 6 in 4-hydroxy-3-methoxytoluene is equal to the product $f_m^{OH} \times f_p^{OMe} \times f_o^{Me}$.

The validity of the additivity principle has been tested so far in relatively few cases, but it has been notably successful in predicting correctly the rates of halogenation (*12*) and hydrogen exchange (*9*) reactions of polymethylbenzenes.

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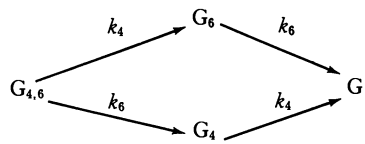
Protododeuteration. A previous paper (*6*) pointed out that a protododeuteration reaction has several advantages in determining partial rate factors. To use this method, deuterium is introduced into a particular position in the aromatic ring, and the rate of back-exchange to protium is determined in an aqueous mineral acid solution of suitable strength. The rate determinations are conveniently carried out by infrared spectrophotometry.

In other substitution reactions, such as halogenation, the reactivity determinations are necessarily based on the quantitative analysis of product mixtures. The results can often be dubious, especially if individual site reactivities show a wide spread. Protodedeuteration is not subject to this limitation because the reactivities of individual positions are determined in separate experiments.

Under suitable conditions, even dideuterated derivatives can be used for kinetic studies as long as the deuterium substituents do not occupy adjacent sites. Ericsson *et al.* (*6*) showed that estimating the reactivities of positions 4 and 6 in general is feasible from a single kinetic run on 4, 6-dideuteroguaiacol ($G_{4,6}$). The dedeuteration process proceeds as follows:

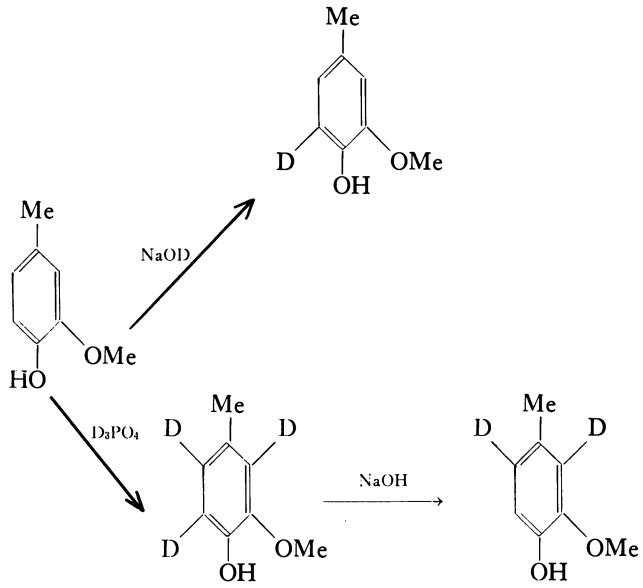


By using a mathematical treatment formally analogous to that of Spurlin (*19*) for the substitution of cellulose derivatives, the following equations are derived for the mole fractions of individual deuterated guaiacols as a function of time:

$$G_{4,6} = e^{-(k_4+k_6)t}$$
$$G_4 = e^{-k_4 t} - e^{-(k_4+k_6)t}$$
$$G_6 = e^{-k_6 t} - e^{-(k_4+k_6)t}$$
$$G = 1 + e^{-(k_4+k_6)t} - (e^{-k_4 t} + e^{-k_6 t})$$

In this particular case, it is convenient to determine $k_4 + k_6$ from the rate of disappearance of the $G_{4,6}$ species, and k_6 from the decay of the G_6 species after the reaction has proceeded to the point where the concentration of the $G_{4,6}$ species is insignificant. Other approaches are, of course, possible.

Specifically deuterated derivatives of phenols can be prepared conveniently by using appropriate combinations of acid- and base-catalyzed exchange reactions. Treating with NaOD (or NaOH) causes exclusive exchange in positions ortho and para to the phenolic group while D_3PO_4 deuterates all available aromatic sites. As an example, the conversion of 4-hydroxy-3-methoxytoluene to 5-monodeutero- and 2,6-dideuteroderivatives is illustrated below.



Protodedeuteration reaction has, however, some limitations. It cannot be used to study compounds subject to secondary condensation in acidic medium, such as certain benzyl alcohol and benzyl ether derivatives. Moreover, the partial rate factors depend greatly on the medium used because different acids show different degrees of selectivity. For instance, the reported partial rate factors for the para position of toluene (f_p^{Me}) range from 170 (in sulfuric acid at 65°C.) (*13*) to 4000 (in hydrogen bromide) (*22*).

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Results and Discussion

Partial Rate Factors for Protodedeuteration in Perchloric Acid Solution. All lignin model compounds studied contained hydroxyl, methoxyl, and methyl groups as the only substituent groups. Table II summarizes what the authors believe are the most reliable partial rate factors for these substituents in perchloric acid solution. All partial rate factors are based on determinations in 57% perchloric acid solutions. The partial rate factors for ortho and para positions of methyl and methoxyl groups are based on later work by Suzuki (*21*). The partial rate factors for phenol were calculated from data on 2, 4, 6-trideuterophenol (*6*) using the value 9.1×10^{-5} hr.$^{-1}$ for monodeuterobenzene by Suzuki (*21*) and assuming 1:3.2 ortho to para ratio.

Comparing the partial rate factors in perchloric acid with those obtained in other mineral acids, it is interesting to note that they are, in general, slightly lower than those observed for sulfuric acid solutions. For instance, the partial rate factors in sulfuric acid for the ortho, meta, and para positions of toluene are, under comparable conditions, 250, 5, and 250, respectively, (*5*) while the corresponding values for anisole in the same medium have been reported to be 2.3×10^4, 0.25 and 5.5×10^4 (*18*). This suggests that perchloric acid medium is probably slightly less selective in protodedeuteration than sulfuric acid.

Deuterated Model Compounds and Protodedeuteration Rate Measurements. Protodedeuteration rate studies were outlined for 2,4,6-trideuterophenol and 2,4,6-anisole, 3,5-dideutero- and 4,6-dideuteroguaiacols, 3,5-dideuteroveratrole, 5-deutero-4-hydroxy-3-methoxytoluene, and 2,6-dideutero-4-hydroxy-3-methoxytoluene (*6*). Using appropriate combinations of acid- and base-catalyzed deuterium exchange reactions, the following deuteroderivatives were prepared in this study; 3,5-dideutero- and 4-deutero-2,6-dimethoxyphenols, 4,6-dideutero- and 5-deutero-1,2,3-trimethoxybenzenes, and 2,6-dideutero-4-hydroxy-3,5-dimethoxytoluene.

Table II. Partial Rate Factors for Protodedeuteration in Perchloric Acid Solution

Substituent	f_o	f_m	f_p
CH_3	82	2.5	80
OCH_3	1.4×10^4	—	5.5×10^4
OH	8.5×10^3	—	2.6×10^4

As a rule, 36% perchloric acid at 25°C. was found to be the most convenient medium for protodedeuteration rate studies. Again, infrared spectrophotometric determinations on samples recovered from the protodedeuteration medium after appropriate reaction times were used to determine the rate constants.

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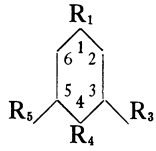
Table III summarizes the observed rate constants, some of which were determined in 57% perchloric acid solution. It is interesting to note that the ortho and para positions of phenol are slightly less reactive towards protodedeuteration than those of anisole. In most electrophilic displacement sections the reverse order is observed.

Table III. Summary of Protodedeuteration Rate Constants

Numbering System:



Rate Constants, $k \times 10^{-3}$, hr.$^{-1}$

R_1	R_3	R_4	R_5	k_1	k_2	k_3	k_5	k_6
H	H	OH	H[b]	6.04	—	1.93	1.93	—
				2400[a]	—	770[a]	770[a]	—
H	OMe	OH	H	2.73	0.20	—	0.87	0.63
				1460[a]	310[a]	—	470[a]	880[a]
Me	OMe	OH	H	—	11	—	2.73	86
H	OMe	OH	OMe	15.9	3590	—	—	3590
Me	OMe	OH	OMe	—	18000[c]	—	—	18000[c]
H	H	OMe	H[b]	7.47	—	2.47	2.47	—
				3430[a]	—	1130[a]	1130[a]	—
H	OMe	OMe	H	580[a]	190[a]	—	190[a]	580[a]
H	OMe	OMe	OMe	1.27	1610	—	—	1610

[a] Rate constants determined in 57% perchloric acid; all others determined in 36% perchloric acid.
[b] *o/p* ratios assumed to be the same as in guaiacol.
[c] Experimental error likely to be somewhat larger than in other measurements because of the exceptionally fast rate.

In order to determine the applicability of the additivity principle for polysubstituted models, the rate data in Table III have been expressed in terms of partial rate factors of individual substituent groups in Table IV. The partial rate factors for polysubstituted compounds are calculated on the same basis as those of monosubstituted ones. For instance, the partial rate factors in guaiacol refer to the factors by which the rate constants of phenol are modified in positions 3, 4, 5, and 6 by introducing a methoxyl group in position 2. Likewise, the partial rate factors for methoxyl in 4-hydroxy-3,5-dimethoxytoluene indicate how the protodedeuteration rates of 4-hydroxy-3-methoxytoluene at positions 2 and 6 are modified by inserting a methoxyl group at position 5.

If the protodedeuteration rates were governed strictly by the principle of additivity, the partial rate factors would be independent of the degree of substitution, except for the rate factors for ortho positions flanked by two substituent groups. Examples of such factors are f_o^{MeO} for 4-hydroxy-3,5-dimethoxytoluene and f_o^{Me} for the position 2 of 4-hydroxy-3-methoxy-

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toluene. In these cases enhanced steric hindrance effects should lower the partial rate factors.

The data in Table IV demonstrate both reasonable agreement and substantial deviations from the principle of additivity discussed in detail below.

Table IV. Comparison of Partial Rate Factors Between

Substituent Group	*Compound Used for Determination*	*$HClO_4$, %*
—OMe	Anisole[a]	57
	Guaiacol	36
		57
	Veratrole	57
	2,6-Dimethoxyphenol	36
	1,2,3-Trimethoxybenzene[c]	36
	4-hydroxy-3,5-dimethoxytoluene	36
—OH	Phenol	57
	Guaiacol	57
		36
—Me	Toluene[a]	57
	4-hydroxy-3-methoxytoluene	36
	4-hydroxy-3,5-dimethoxytoluene	36

[a] Data by Suzuki (*21*).
[b] Value given by Satchell for sulfuric acid solution (*18*).
[c] The partial rate factors refer to the methoxyl at position 1 (or 3).
[d] f_o^{Me} for position 2.

Partial Rate Factors of Methoxyl and Hydroxyl Groups. Partial rate factors for the meta positions of phenol and anisole have not been determined in perchloric acid media. The unavailability of such data is a handicap in interpreting the rate data on guaiacol and veratrole. To obtain approximate values for f_o^{OH} and f_p^{OH} for guaiacol, it was assumed that the partial rate factor 0.25, determined for the meta position of anisole in sulfuric acid (*18*), closely approximated the corresponding factor in perchloric acid.

A comparison of f_o^{OMe} and f_p^{OMe} values of different compounds shows that 1,2-disubstitution in veratrole causes a distinct but minor lowering of these rate factors. A further lowering is observable in the 1,2,3-substituted 2,6-dimethoxyphenol, although the deviation even in this case is not very large. The conformity with the additivity principle is, as a matter of fact, much better than that estimated by Satchell (*17*), who based his conclusions on the reactivity of 3,5-ditritio-2,6-dimethoxyphenol.

Like 2,6-dimethoxyphenol, 1,2,3-trimethoxybenzene represents a situation of adjacent trisubstitution, but the deviation from the additivity

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principle is substantially greater. Since the central methoxyl in the latter compound requires more space than a hydroxyl group, it seems reasonable to ascribe the observed deviations to steric crowding which interferes with the relay of resonance effects. Whatever the interpretation, increasing the number of substituent groups to give a 1,2,3,5-tetrasubstitution pat-

Mono- and Polysubstituted Compounds

f_o	f_m	f_p
14 $\times 10^3$	0.25[b]	55 $\times 10^3$
—	0.45	—
—	0.60	—
8.4 $\times 10^3$	0.13	26 $\times 10^3$
5.7 $\times 10^3$	5.8	18 $\times 10^3$
1.3 $\times 10^3$	1.0	3.8 $\times 10^3$
0.21 $\times 10^3$	—	1.6 $\times 10^3$
8.5 $\times 10^3$	—	26 $\times 10^3$
21 $\times 10^3$	.26	64 $\times 10^3$
—	.08	—
82	2.5	80
136	3.2	—
55[d]		
5.0	—	—

tern, such as in 4-hydroxy-2,5-dimethoxytoluene, causes a further lowering in partial rate factors.

Unexpectedly, the partial rate factors f_o^{OH} and f_p^{OH} were larger in guaiacol than in phenol. While the differences are not large, the higher values observed for guaiacol are probably significant and may be caused by hydrogen bonding between the adjacent hydroxyl and methoxyl groups. Two separate possibilities may be considered in this connection. Either partial hydrogen bonding in guaiacol facilitates the transition to the sigma-complex intermediate or the hydrogen bonding contributes more to the stability of the intermediate than to that of guaiacol itself, making the transition energetically more favorable. These proposals receive added support from a later discussion on the anomalous f_m^{CMe} value of 2,6-dimethoxyphenol.

At first glance, the partial rate factors for the meta positions appear rather irregular. It should be noted, however, that the calculation of f_m^{OMe} values is based on the assumption that the partial rate factors for the ortho and para positions of a hydroxyl group are the same in all com-

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pounds studied, and this assumption was doubted by the results on guaiacol. On this basis, the apparently large f_m^{OMe} values observed for guaiacol and, particularly, 2,6-dimethoxyphenol, should not be understood in terms of diminished meta deactivation of the methoxyl group but rather in terms of the enhanced activation of the *p*-hydroxyl group, caused by the hydrogen bonding interaction of the latter group with adjacent methoxyl groups. If this argument is accepted, the value 0.13 for veratrole ought to be more characteristic of the meta deactivation effect.

The foregoing argument does not explain the anomalous f_m^{OMe} value for 1,2,3-trimethoxybenzene which appears to be more than four times too high. One would rather anticipate a deviation in the opposite direction since the activation by the central methoxyl group, as a consequence of flanking by two ortho substituent groups, ought to be less than in veratrole. As a matter of fact, steric retardation effects of this kind have been observed in the bromination of 2,6-dimethylphenol and anisole (*1*). To explain the observed anomaly, one might consider the possible enhancement of nonconjugative relay of resonance effects (*20*) from the 1- and 3-methoxyls to position 5 as a consequence of steric crowding. In addition, the mutual distances of the three methoxyl groups are slightly increased in the transition to a sigma-complex intermediate involving position 5, and some of the nonbonded interaction between these groups in the initial state may thus be relieved.

Partial Rate Factors of a Methyl Group. Comparison of the f_o^{Me} and f_m^{Me} values of toluene with those of 4-hydroxy-3-methoxytoluene does not reveal significant differences. The second f_o^{Me} value that was determined for position 2 in the latter compound is lower than that for position 6 owing to steric inhibition effects caused by two ortho substituents. Consequently, the additivity principle appears valid for the 1,3,4-trisubstitution pattern.

The two remaining aromatic positions in 4-hydroxy-3,5-dimethoxytoluene are analogous to the 2-position in 4-hydroxy-3-methoxytoluene, and the additivity principle would predict f_o^{Me} values of equal magnitude. The observed values differ, however, by a factor of 10. The lower reactivity of the former compound is again related to the sterically crowded substitution pattern.

Conclusions

To summarize the conclusions from the foregoing data, which of course are not sufficient for broad generalizations, we found that the additivity principle predicts reactivities of a correct order of magnitude for 1,2-disubstituted and 1,3,5-trisubstituted compounds. In general, the observed reactivities were somewhat lower than the predicted ones, with the exception of sites located para or ortho to a phenolic hydroxyl adjacent

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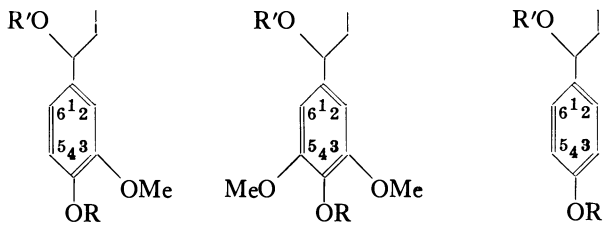
to a methoxyl group. Increasing the number of substituent groups to 1,2,3-trisubstitution and 1,3,4,5-tetrasubstitution patterns resulted in distinct deviations from the principle of additivity.

Reactivity of Aromatic Sites in Lignin. It is of considerable interest to estimate the significance of the protodedeuteration data in predicting the reactivities of the phenylpropane units in lignin.

As shown below, the C_6C_3 units present in lignin are of three basic types, differing from each other in the number of methoxyl groups in positions 3 and 5. Since the partial rate factors for the ortho and para positions of methoxyl groups all lie in the range 10^2–10^4, demonstrating the strong activating effect of these groups on all levels of substitution, the sequence of reactivities for the 2 and 6 positions is easy to predict, and the same sequence of reactivities is likely to be valid for displacements other than protodedeuteration.



k_1 (III) > k_1 (I). If R = H, k_1 (II) > k_1 (I)
k_2 (II) ≫ k_2 (I) > k_2 (III)
k_5 (III) > k_5 (I)
k_6 (I) ≫ k_6 (III) = k_2 (III)

The prediction, k_5 (I) > k_5 (III), probably holds for protodedeuteration, but its applicability to other displacements is less certain. As far as the displacement of the side chain at position 1 is concerned, it was already pointed out that, in protodedeuteration, side-chain condensation is more likely to occur. Side-chain displacement is common, however, in halogenation and nitration, and it seems reasonable to assume that the rates of these reactions may be controlled by the same factors controlling the displacement of hydrogen. On this basis unit III ought to be the most reactive in side-chain displacement while the reactivities of I and II are likely to be of the same order of magnitude.

It may be recalled that for 4-hydroxy-3-methoxytoluene the sequence of reactivities was found to be $k_6 > k_2 > k_5$ (Table III). The same sequence of reactivities is the most probable one for guaiacyl propane units

In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

(I), regardless of the presence of a hydroxyl or an ether group at position 4. This sequence is not, however, applicable to other displacement reactions. For instance, for the chlorination of an etherified guaiacyl propane unit, model experiments suggest the sequence $k_6 > k_1 > k_5 > k_2$ (*15*) while a hydroxyl group at position 4 modifies the sequence to $k_5 > k_6 > k_1 > k_2$ (*3*). These differences may be rationalized in terms of three factors: (a) lower *o/p* ratio in molecular chlorination; (b) enhanced steric inhibition limiting the reactivity of position 2; (c) in halogenation reactions, the partial rate factors for positions ortho and para have been found to be roughly 100 times larger than those of a methoxyl group (*1*) while in protodedeuteration, they are approximately equal.

Position 5 is also the most reactive in the nitration of guaiacyl propane units containing a free phenolic hydroxyl group and in analogous model compounds (*7*). By contrast, acid-catalyzed condensation reactions appear to proceed more rapidly at position 6 (*15*) and in this respect resemble the protodedeuteration reactions.

Base-catalyzed displacement reactions, such as base-catalyzed halogenation, hydrogen exchange, and condensation reactions, belong to a separate class of reactions. The reactive species, in this case, is the phenolate ion rather than unionized phenol, and the reactive positions are limited to those ortho and para to the hydroxyl group. In a guaiacyl propane unit, no reaction occurs at positions 2 and 6, and displacement at position 5 will generally proceed more rapidly than the displacement of the side chain.

Obviously then, the relative reactivities of the aromatic positions in lignin units do not fit a uniform pattern but depend largely on the specific nature of the electrophile. Consequently, the information obtainable from protodedeuteration data is somewhat limited at the moment. Since the protodedeuteration rate constants can be determined conveniently and precisely, they can probably be used better in the future to predict reactivities in other electrophilic displacements as the interrelations between these reactions become more thoroughly understood.

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Experimental

Selective Deuteration. Methods outlined earlier (*6*) were used. NaOD was used to deuterate selectively positions ortho and para to a free phenolic group, D_3PO_4 to deuterate all aromatic sites, and NaOH to remove selectively deuterium from positions ortho and para to a free phenolic group.

The 5-deutero and 4,6-dideutero derivatives of 1,2,3-trimethoxybenzene were prepared by methylating the corresponding deuterated 2,6-dimethoxyphenols with dimethyl sulfate in 10% NaOH at room temperature.

4 - Hydroxy - 3,5 - dimethoxyphenol. 2,6 - Dimethoxyphenol was converted to 4-hydroxy-3,5-dimethoxybenzyl alcohol by reaction with

formaldehyde in cold alkali (*8*). This compound, isolated in 60% yield, melted at 135°–136°C. A sample of 6 grams of the latter compound was dissolved in 400 ml. of glacial acetic acid and hydrogenated using Pd-charcoal as catalyst under 45 p.s.i.g. hydrogen pressure at room temperature for 17 hours. After vacuum distillation of the product, 4-hydroxy-3,5-dimethoxy phenol was isolated in 55% yield. Recrystallized from ethanol, the product melted at 29°–30°C. (*2*).

Kinetic Experiments. The experimental arrangement differed slightly from that used earlier (*6*). Aliquots of 0.1 gram each of the deuterated compounds were carefully weighed in reaction tubes each containing 10.0 ml. of 36% perchloric acid at 25°C. The tubes were immersed in a thermostat held at 25°C. for prescribed reaction periods, after which they were immediately diluted with ice water. The solutions were extracted with ether, the ether extracts washed with bicarbonate, dried, and distilled. The infrared spectra were generally measured in cyclohexane using 0.5-cm. cells. With crystalline compounds, carefully prepared KBr pellets could be used as well for kinetic measurements. Maxima at the following wave-numbers ($cm.^{-1}$) were used for kinetic measurements; 4-deutero-2,6-dimethoxyphenol:669; 5-deutero-1,2,3-trimethoxybenzene:680; 3,5-dideutero-2,6-dimethoxyphenol:660; 4,6-dideutero-1,2,3-trimethoxybenzene:995, and 2,6-dideutero-4-hydroxy-3,5-dimethoxytoluene:630.

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Stable Free Radicals in Lignin and Lignin Oxidation Products

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Electron paramagnetic resonance (EPR) spectrometry has revealed the presence of stable free radicals in lignin preparations. Fungal and chemical attack of native lignins increase the radical content; hardwood lignins have higher spin contents than softwood lignins. The EPR behavior of lignins in alkali is characteristic of quinhydrone systems and indicates that the extent of quinone character is directly related to radical content. Experiments with model phenols reveal that α-carbonyl syringol derivatives can be oxidized to remarkably stable radicals in solution. Guaiacol analogs do not form radicals under similar conditions. When disyringylmethane is oxidized, a purple, solid, stable free radical is formed, which may be the species responsible for the high radical content of hardwood kraft lignin.

In 1963 we began to investigate lignin preparations by electron paramagnetic resonance (EPR) spectrometry. This technique can detect paramagnetic species, particularly organic free radicals. The types of information available from EPR measurements can be summarized as follows:

(1) Number of radicals.
(2) Change in the number of radicals as a function of chemical, physical, or biological change.
(3) Molecular structure of radical.

Item 3 depends upon the extent of hyperfine resolution of the EPR spec-

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In Lignin Structure and Reactions; Marton, J.;
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trum, and with complicated heteropolymers such resolution is difficult to obtain. However, important structural insights may be inferred from items 1 and 2.

Examining a number of lignin preparations showed that all contained stable radical species. Table I lists the spin contents (number of unpaired electrons per gram) of these species.

Table I. Spin Contents of Various Lignin Preparations

Sample	*Spins/gram* $\times 10^{17}$
Sprucewood meal	0.04
Vibratory spruce meal	0.80
Brauns native spruce lignin[a]	0.5
Björkman lignin, spruce[a]	1.0
Klason spruce lignin[a]	0.4
Decayed western hemlock wood meal[a]	0.9
Softwood kraft lignin[a]	3.0
Hardwood kraft lignin	8.0
Kraft-treated native spruce[a]	4.0

[a] *See* Ref. (*23*).

The results could also be expressed as unpaired electrons per OCH_3; on this basis, native lignin would have 0.000017 unpaired electrons per OCH_3.

These data indicate that mechanical, chemical, and biological attack of lignin create radical centers. We turned our attention next to an EPR analysis of chemically modified lignins. Reducing a number of samples (*23*) with $NaBH_4$ seemed to have very little effect on the spin content. However, when samples were converted to their metal salts, a marked increase in free radical centers was observed. Acidification of the salts returned the spin content to its original level.

Table II. Spin Content of Lignins and Their Salts

	Spin Content $\times 10^{17}$		
Sample	*Acid Form*	*Salt*	*Reacidified Lignin*
Brauns native spruce[a]	0.5	50	1.1
Softwood kraft[a]	3.0	100–300	3.0
Kraft-treated native spruce lignin[a]	4.0	70	
Hardwood kraft	8.0	550 (sodium salt)	
	8.0	880 (barium salt)	

[a] *See* Ref. (*23*).

These results indicate that kraft treatment modified the lignin structure to permit enhanced radical formation upon basification. Signifi-

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cantly, hardwood kraft lignins have higher spin contents than softwoods up to 0.05 unpaired electrons/OCH_3.

Fungal attack also increases the stable radical content of woods. A study of wood decay caused by brown and white rots revealed a two- to threefold change in spin content over a period of time (Figures 1 and 2). Again, decayed hardwood species have higher spin contents than decayed softwoods.

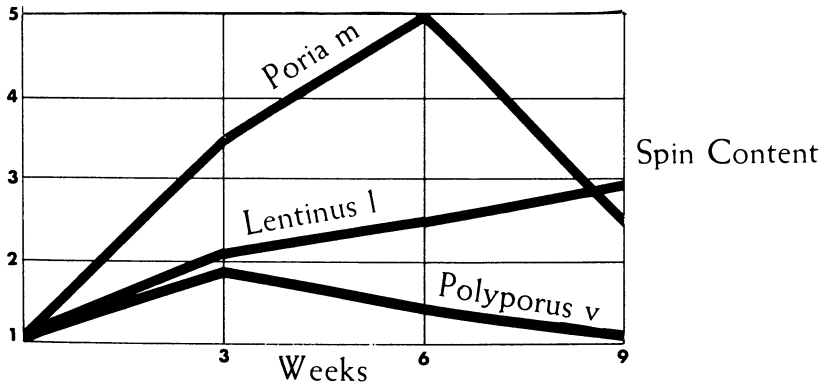

Figure 1. Free radical content of fungally decayed sweet gum

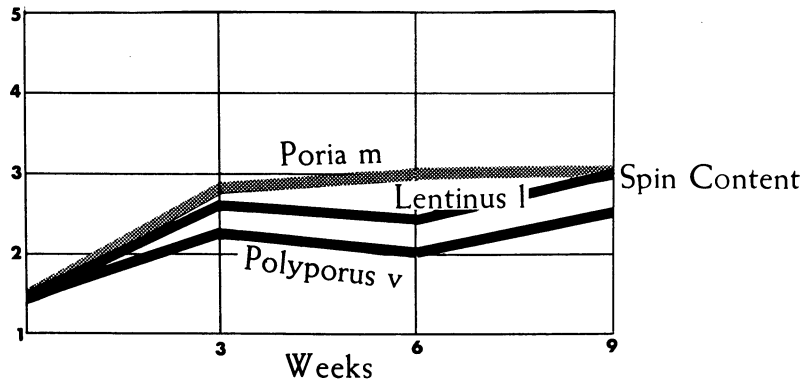

Figure 2. Free radical content of fungally decayed southern pine

A reasonable model has been proposed to accommodate these results (*21*, *23*). The presence of quinoid functions in lignin would give rise to electron donor-acceptor complexes with existing phenolic groups. These complexes, like quinhydrone, would form stable radical anions (semiquinone anions) on basification, according to the scheme shown below. Both biological and chemical oxidation would create more quinone moieties, which in turn would increase the contribution of Reactions 1 and 2. Alternately, enzymatic (*8*) and/or alkaline demethylation (*16*) would produce

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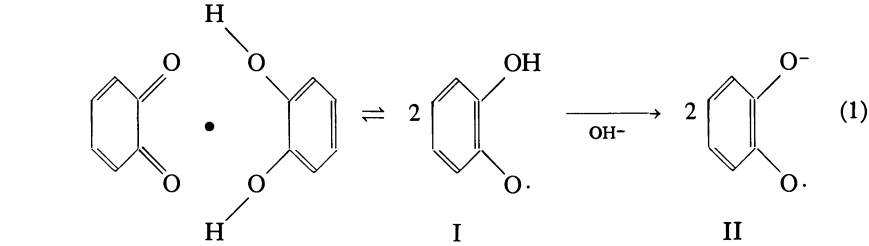
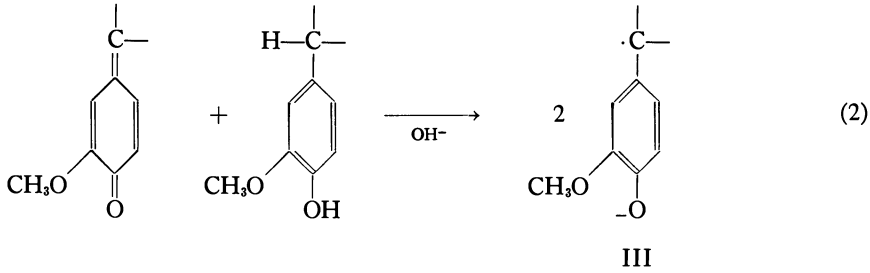


(1)

or

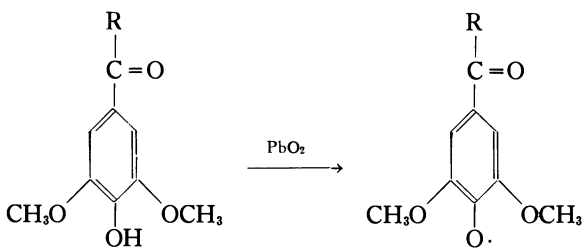


(2)

substituted catechols, which would be oxidized readily to orthoquinones. The latter would participate in the quinhydrone system.

Thus, a small concentration of ortho- or parabenzoquinone species in an environment of phenolic functions could explain the radical enhancement upon basification. The "residual" spin content of the neutral or acid form of lignin is almost nil in whole wood, very small in native lignins, but significant in kraft and other chemically modified lignins. Such a stable free radical could be attributed to (a) the small equilibrium concentration of I in Equation 1, (b) a semiquinone polymer patterned after synthetic models (*4*, *25*) containing donor and acceptor groups, or (c) radicals entrapped and stabilized in a polymeric matrix (*5*, *15*).

This last possibility appeared to offer the most fruitful line of investigation. Therefore, we decided to determine what kinds of structural features would confer unusual free radical stability on simple model phenols which had been oxidized. Several phenols were oxidized in benzene solution by one-electron oxidants such as PbO_2, alkaline ferricyanide,



IV R = H
V R = CH_3
VI R = C_2H_5

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and acidic ceric sulfate and examined by EPR spectrometry. The following phenols did not form stable radical species: vanillin, acetovanillone, and 4-propyl-6-methylguaiacol. Syringol derivatives with an α-carbonyl substituent, however, did form phenoxy radicals whose half-lives were five hours in benzene (*20*) at room temperature. Figure 3 shows the EPR

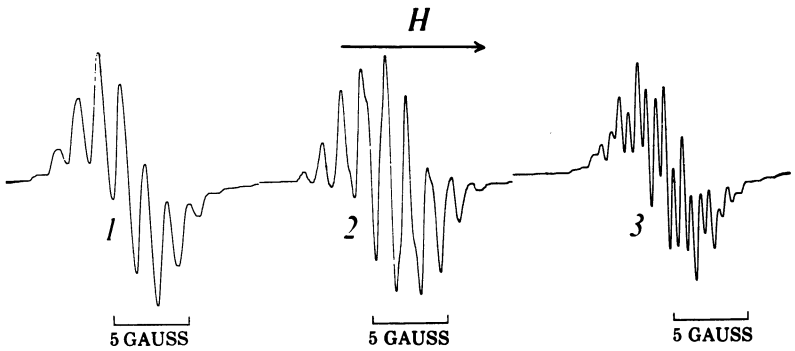

Figure 3. First derivative EPR spectra of syringol radicals. (1) syringaldehyde radical, (2) acetosyringone radical, (3) propiosyringone radical

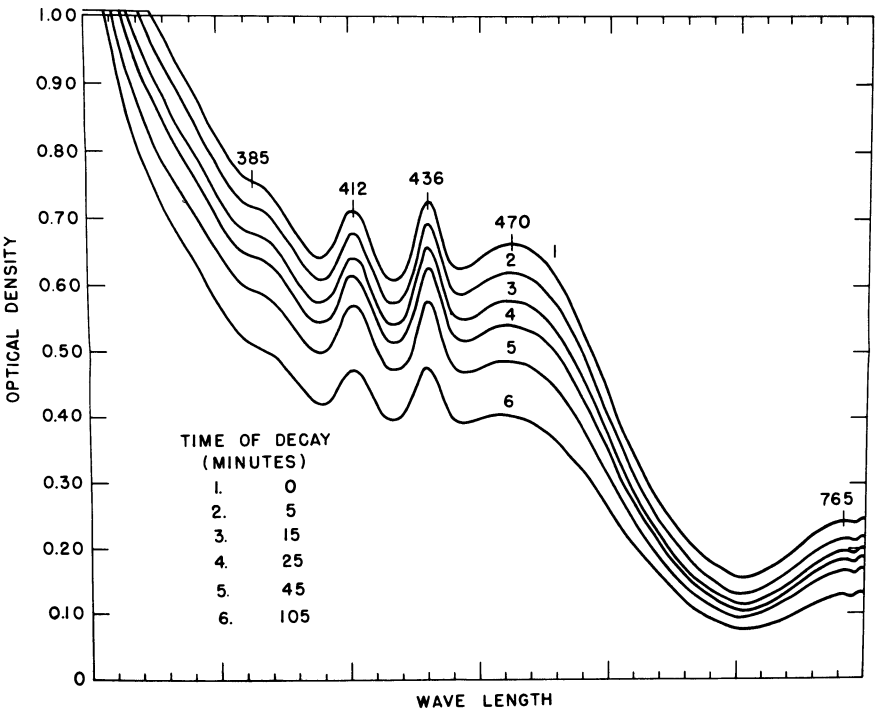

Figure 4. Visible spectrum of propiosyringone radical

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spectra of these radicals. Apparent first-order decay rates were observed for these radicals. They appeared to decay to orthoquinone species, probably analogous to those observed by Adler (*1*). The visible spectrum (Figure 4) of the oxidized phenols seems to support this assumption. The solid, obtained by evaporating the radical solution to dryness, is not paramagnetic. No doubt, it contains dimers of the phenoxy species, formed by processes outlined in Figures 5 and 6.

Thus, α-carbonyl syringols can be oxidized to relatively stable phenoxy radicals in contrast to guaiacol derivatives. The latter probably dimerize

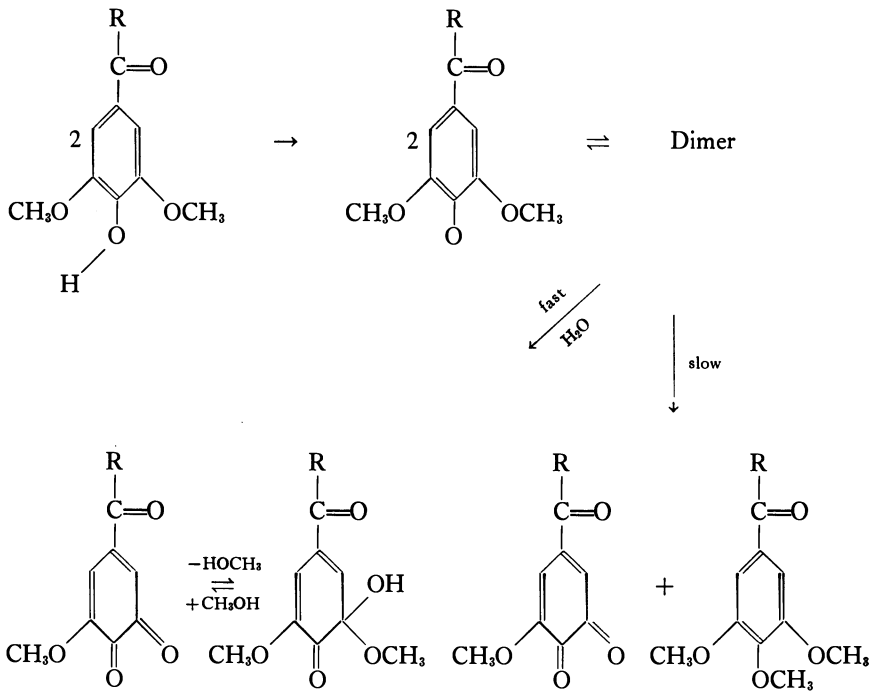

Figure 5. Mechanism of decay of syringyl radical

rapidly at the free 5-position as reported by Pew (*18*) and others. One would anticipate, on the basis of these observations, that hardwood lignins (high syringyl content) would contain more stable free radicals than softwoods (high guaiacol content). This has been noted previously in our measurements of kraft lignins and fungally decayed woods. While these phenoxy radicals have been generated under highly artificial conditions (benzene solvent, nitrogen atmosphere) to secure long-lived species, stability and longevity under biological or industrial conditions could also be obtained by entrapment in a polymeric network such as lignin or cellulose.

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To ascertain whether syringyl derivatives IV, V, and VI could be converted to phenoxy radicals under biological conditions, we treated water solutions of the phenols with hydrogen peroxide and peroxidase. All three phenols formed transient green species in contrast to the vanillin compounds (which yielded brown precipitates). The aqueous solutions turned red within a few minutes after initial reaction. If these solutions were quickly frozen in liquid nitrogen a few seconds after the reactants had been mixed, a blue solid was obtained. When the solid was examined by EPR spectrometry, radicals were observed whose half-lives were estimated at 30–60 seconds. The radicals appeared to be identical to those generated in benzene.

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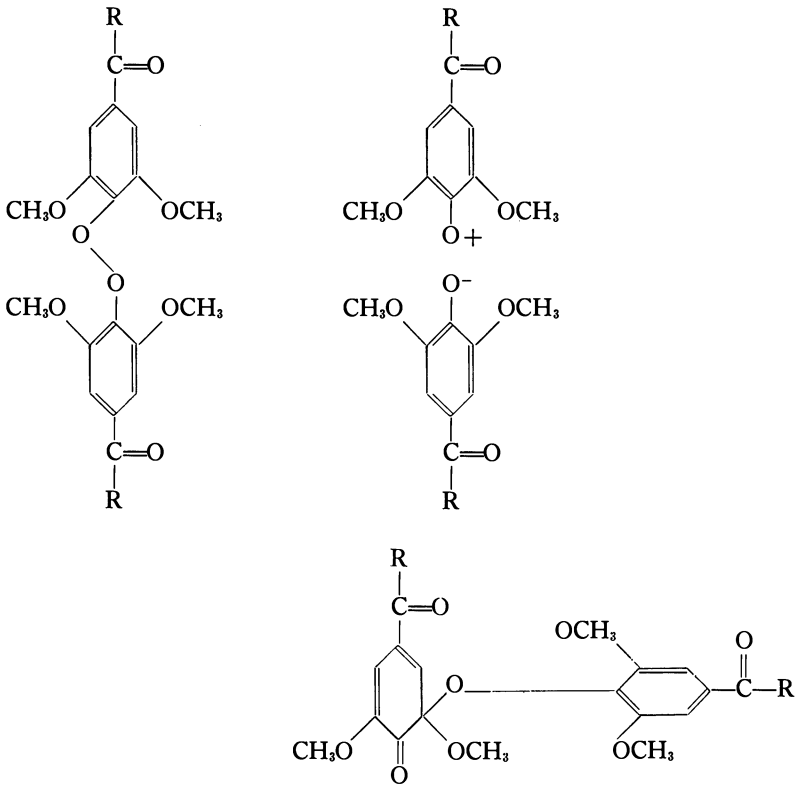
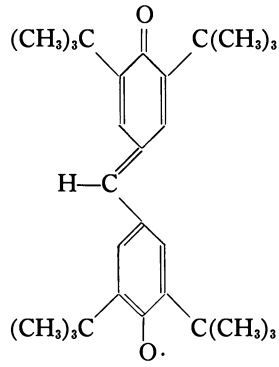


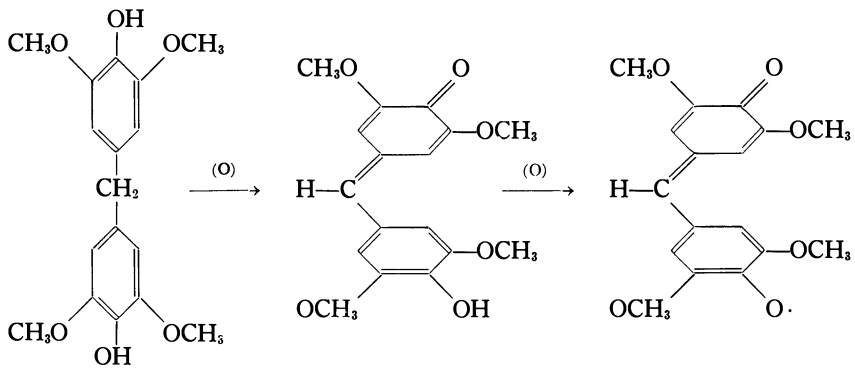
Figure 6. Proposed dimers as decay products of syringyl radicals

An intriguing problem still remained: could a simple, solid, stable free radical be prepared, whose structure would be consistent with lignin models? Our attention was directed to the compound galvinoxyl (VII),



VII

a well-known solid standard for EPR measurements (*6*, *12*, *24*). By substituting OCH_3 groups for the *tert*-butyl groups in this molecule, one would arrive at an oxidized quinonemethide (VIII) from disyringylmethane (X) via the intermediate quinonemethide (IX). Freudenberg and Harkin (*10*) have proposed that structural elements related to VIII, IX, and X exist in lignins (*see* Figure 7), and the presence of disyringylmethanes in lignin degradation products have been reported by others (*11*, *14*, *17*, *19*).



X IX VIII

When disyringylmethane was oxidized in dichloromethane with PbO_2, a violet compound was obtained. This was a 66% radical (based on molecular weight of disyringylmethane) and in the solid form under nitrogen had a half-life of one week. Under oxygen, the half-life in an open vessel was two days. It constitutes the first relatively stable, solid free radical model for hardwood lignins (*22*). Its EPR spectrum in CH_2Cl_2 has 25 principal lines, each of which is split into five subsidiary lines. The spectrum is analogous to that of galvinoxyl (Figure 8). The following

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coupling constants have been assigned to the radical; a synthetic spectrum based on these constants is almost identical with the experimental spectrum. The twelve methoxyl protons do not interact equivalently with the unpaired electron. Six of them have a coupling constant twice the value of the other six (Table III). This might be expected from the asymmetrical nature of the molecule at room temperature. We have assigned the trivial name syrinoxyl to this radical.

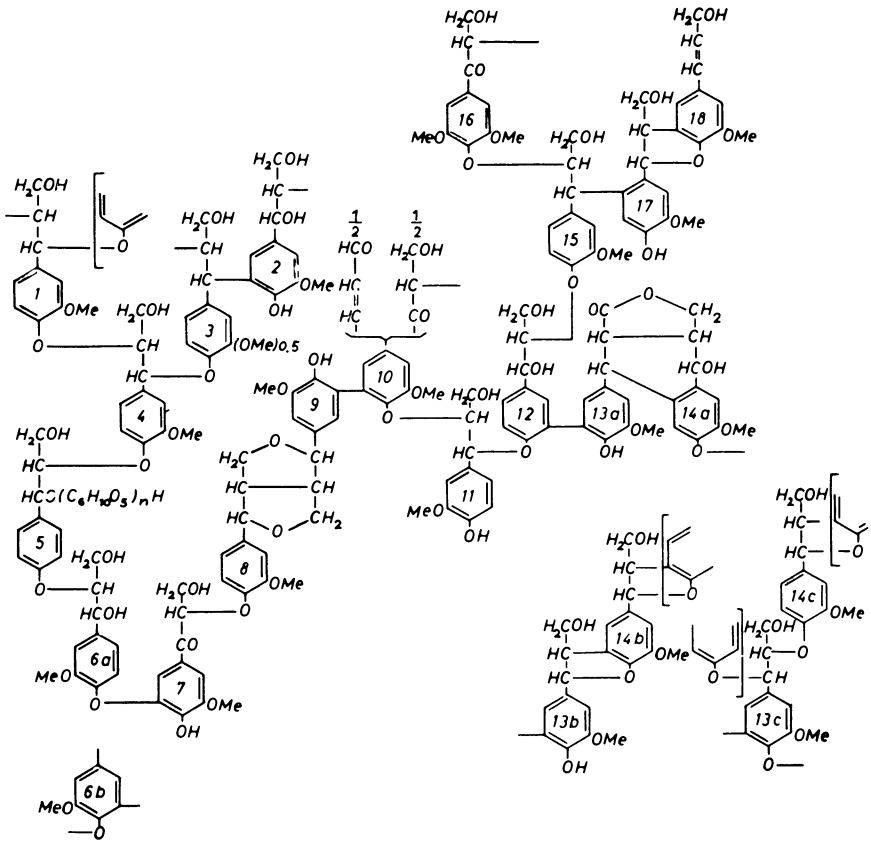

Figure 7. Constitutional scheme for lignin (after Freudenberg)

An interesting color reaction gave additional support to our assignment of VIII to syrinoxyl. When this radical was dissolved in aqueous base, an immediate blue color developed (259 mμ, 285 mμ, 613 mμ (intense)). When disyringylmethane was mildly oxidized with air or PbO_2, a yellow color was observed in neutral solution (275 mμ, 281 mμ, 319 mμ, 434 mμ (intense)) which is most likely the quinonemethide IX. Upon basification, this yellow solution turned deep blue with the same

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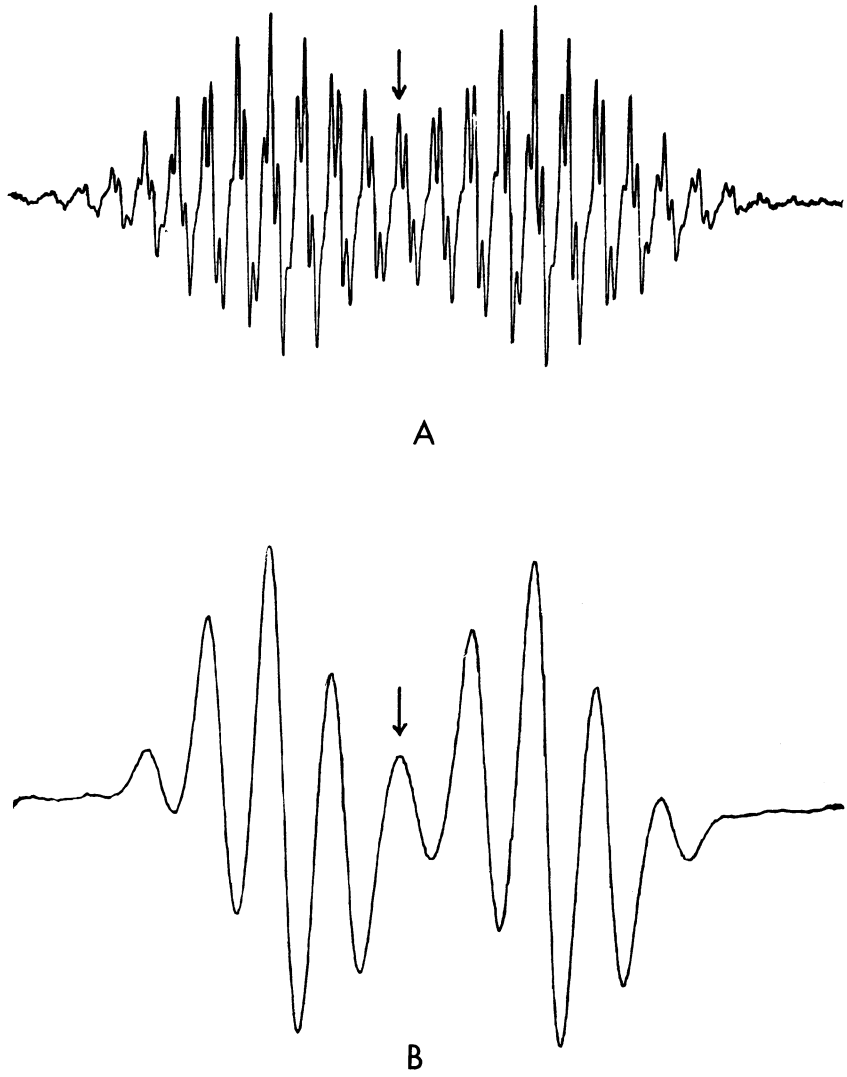
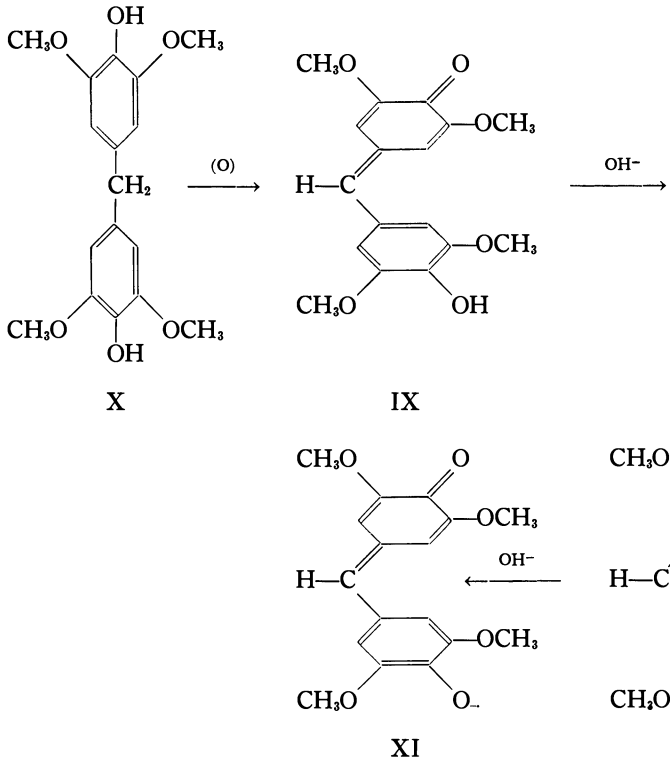


Figure 8. First derivative EPR spectra of (A) syrinoxyl in CH_2Cl_2, g = 2.0060 (arrow) and (B) galvinoxyl in CH_2Cl_2, g = 2.0044 (arrow). Distance between dark lines is 18 gauss in both spectra.

spectral bands as those of syrinoxyl in base. The blue compound is probably the anion XI. The results are summarized below. The results parallel those reported by Kharasch and Joshi (*12*) for galvinoxyl and its diphenylmethane precursor.

In conclusion, we have shown that the paramagnetism of lignin is probably caused by very small amounts of trapped phenoxy radicals or oxi-



dized products of diphenylmethanes. The enhancement of radical centers upon basification (also observed by Kleinert (*13*)) is caused by quinhydrone-like (electron donor-acceptor) elements. The concentration of both types of radicals increases with chemical and biological oxidation, probably owing to an increase in quinone or quinonemethide elements.

In addition, EPR spectrometry seems particularly suitable for studying the mechanism of biological and chemical oxidation of lignin, its precursors, and its degradation products.

Table III. Coupling Constants for Syrinoxyl[a]

Proton	A^H (*gauss*)	*Number of Protons*
Methide	5.60	1
Ring	0.14	4
OCH_3 (a)	0.70	6
OCH_3 (b)	1.40	6

[a] Assumed line width = 0.125 gauss (*22*).

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Experimental

EPR Measurements. All intensity measurements were made with a Varian 4500 (100 kc. field modulation) spectrometer. Spin concentrations were estimated by comparison with solid diphenylpicrylhydrazyl. The number of radicals was assumed to be proportional to signal height times signal width squared.

Syrinoxyl Spectra. The EPR spectrum of syrinoxyl was taken using a specially modified Varian spectrometer (*3*, *22*).

Sodium Salts. The sodium salts of lignins were made by precipitation from an aqueous alkaline solution with absolute ethanol as previously described (*21*).

Barium Salts. To a solution of lignin in 0.1*N* NaOH we added 0.1*M* $BaCl_2$ until precipitation was complete. The solid barium salt was dried under vacuum for 24 hours at room temperature.

Fungal Decay of Woods. Blocks of sweet gum and southern pine sapwood were inoculated with test fungi by the standard soil-block method (*7*). The test fungi were the brown rots *Poria monticolla* and *Lentinus lepidius* and the white rot *Polyporus versicolor*. As a control, one block of pine and one block of gum were left in the sterilized soil-block chambers in which the fungus had been started on feeder blocks and then sterilized.

At intervals of three, six, and nine weeks after inoculation, the test blocks from each wood species were removed, the fungus washed off, the blocks sterilized and dried at 30% relative humidity. They were then ground in a Wiley mill to pass a 40 mesh screen.

Disyringylmethane. Disyringylmethane was prepared by the method Bailey (*2*) used to prepare diguaiacylmethane. To 52 ml. of water we added 19.2 grams of 2,6-dimethoxyphenol, 6 ml. of 40% formaldehyde, and 4.8 grams of solid NaOH. The mixture was stirred under nitrogen and heated to reflux. A pale yellow solution resulted. After 10 minutes of reflux, a white solid started to separate. Refluxing was continued for 2½ hours. The reaction mixture was cooled, diluted with an equal volume of water, and rapidly filtered. A deep blue color appeared on exposure to air. The white residue was dissolved in a large quantity of water and neutralized with glacial acetic acid. The resulting yellow slurry was filtered and recrystallized twice from boiling ethanol-water to which a pinch of $NaHSO_3$ had been added to discharge the color. Yield: 3.8 grams (19%); m.p., 111°–111.5°C. Analysis: C, 63.92; H, 6.21; calc. for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. From the filtrate we obtained 31% more crystalline material, identical with the above. Spectra: (λ_{max}) 273 mμ (3200), 281 mμ (2800). NMR (deuterochloroform): τ3.59 (4H singlet), τ4.57 (2H, singlet) and τ6.17 (14H, singlet). The integrated intensities were consistent with the assignments of four aromatic protons, two hydroxyl protons and 14 protons (2 methylene and 12 methoxyl).

Syrinoxyl [2,6-dimethoxy-4-(3,5-dimethoxy-4-oxo-2,5-cyclohexadiene-1-ylidenemethyl)-phenoxyl]. To 15 ml. of benzene we added 80 mg. of disyringylmethane. PbO_2 (1 gram) was added, and stirring under nitrogen was begun. After 1 hour, another gram of PbO_2 was added, and stirring was maintained for 15 minutes, during which time a purple solid

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precipitated out of the benzene. The mixture was filtered by suction under nitrogen, and the filtrate was evaporated to dryness leaving a yellow-orange solid. This was assumed to contain the quinonemethide (IX) and was discarded.

The reaction flask containing the PbO_2 purple solid mixture was washed with dichloromethane, yielding a purple solution. When this was filtered and evaporated to dryness, a purple-black solid with a metallic luster was deposited. It sintered at 190°C. and slowly melted in the range 240°–250°C. Spectra: (λ_{max}): 270, 286, 413 (intense), 459 (sh), 650 (sh), and 850 mμ (infl). In the infrared, no OH bands were detected, and intense bands were observed at 6.15, 6.35, and 6.45μ. An EPR intensity measurement showed the solid to be 66% radical.

Phenoxy Radicals in Solution. Benzene, toluene, or dichloromethane solutions of syringol compounds were placed in 4 mm. o.d. quartz EPR tubes and frozen. A small amount of PbO_2 was placed in the tube, which was then thawed and placed in the EPR cavity. Identical spectra were also obtained by using $K_3Fe(CN)_6$ (alkaline) or $Ce(HSO_4)_4$ (acidic) as the oxidants.

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6

o-Quinonemethides as Tentative Structural Elements in Lignin

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During lignification, addition of phenols onto p-quinonemethides leads to labile free or etherified p-hydroxybenzyl aryl ethers. These rearrange slowly in situ or rapidly on treatment with acids or alkalies—e.g. during pulping—to o-hydroxydiphenylmethanes with free or etherified p'-hydroxyl groups. These groupings can be readily dehydrogenated either by enzymes (e.g., during lignification) or oxidizing agents (e.g., during pulping or bleaching of pulps) to give stable o-quinonemethides. Structures involving o-quinonemethides may be responsible for part of the carbonyl and part of the free radical contents of lignin and for some of the color in pulps. Pertinent models have been prepared, and their properties have been examined.

Adler and Marton have made a careful study of the carbonyl content of spruce lignin (*1*, *2*, *18*, *19*). Values for some types of carbonyl groupings known to be present in lignin were determined accurately by various direct methods, but the value given for unconjugated carbonyl (*1*) was derived by subtracting the sum of these values from the value for the total carbonyl content of lignin. However, the value for the total carbonyl content of lignin is questionable since different amounts are reflected by different methods of assay (*13*, *19*). Hence, the value for the content of unconjugated carbonyl groups in lignin also appears to be somewhat unreliable. Unconjugated carbonyl groups can occur only in the β-position of the C_3 side chain of the arylpropanoid units in lignin. A simple bio-

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In Lignin Structure and Reactions; Marton, J.;
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gentic mechanism leading to the formation of β-ketonic groups in lignin is hard to conceive, and including the amount of β-carbonyl postulated by Adler and Marton (*1*) in the formula scheme for lignin designed by Freudenberg (*4*, *5*, *9*) constrains the formula owing to the concurrent reduction in the possibilities of forming β-aryl ether bonds, the most frequent type of interunitary bonding in lignin (*6*).

Therefore we looked for other possible types of carbonyl groupings in lignin which might be more compatible with the current theory about the mode of its biogenesis. Pew *et al.* (*23*, *24*) have shown that benzyl alcohol derivatives are produced in biphenyl-coupled and diphenyl ether lignin models by the action of peroxidase and hydrogen peroxide, one enzyme known to be involved in lignification. *p*-Quinonemethides are thought to be intermediates in this reaction. Continued dehydrogenation of the *p*-hydroxybenzyl alcohols (*23*, *24*) leads to the corresponding ketones (α-ketones). Similar observations have also been made by the present author with several lignin models—e.g., the biphenyl-coupled dehydro dimers of vanillyl alcohol, apocynol, dihydroconiferyl alcohol, guaiacylpropane-1,3-diol, and guaiacylglycerol-β-coniferyl ether; the production of carbonyl groups was followed by infrared spectroscopy (*15*). However, even α-ketones, like β-ketones, are relatively weak chromophores and can hardly account for the strong coloration of isolated lignins. Other, stronger chromophores seem to be indicated.

Ether Groups in Lignin

It was recently demonstrated that spruce lignin contains approximately 4% free *p*-hydroxybenzyl aryl ether I and about 6% etherified *p*-hydroxybenzyl aryl ether II (*10*). Compounds containing this type of grouping have been made by polymerizing *p*-quinonemethides (*11*) and have been isolated as intermediates of the in vitro biosynthesis of lignin (*8*). Such ethers are readily cleaved in the cold by mild acids or alkalies or slowly by water alone. Heating accelerates this hydrolysis. Fast cleavage of the free *p*-hydroxybenzyl aryl ethers and the slow cleavage of the *p*-alkoxybenzyl aryl ethers in lignin by the mild alkalinity of sodium borohydride (*15*) tend to make the values of 0.21–0.24 CO per C_9 unit determined for spruce milled wood lignin using the $NaBH_4$ assay method (*15*, *19*) too high.

Generally, the hydrolysis of such *p*-hydroxy- or *p*-alkoxybenzyl aryl ethers is accompanied by condensation of the benzyl carbon atom with unsubstituted positions in a neighboring benzene ring and release of the etherified phenolic hydroxyl group. However, when provisions are made to prevent these condensation reactions—e.g., by conducting the reaction in anhydrous methanol (*15*) or by removing the compounds liberated before they can condense using a mild percolating system (*20*)—small amounts of low molecular weight hydrolysis products can be isolated from lignin

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(*7*). Dissolution of almost 40% of powdered beechwood in this way (*20*) suggests that the benzyl aryl ether content of beech lignin is much higher than that of spruce lignin.

The hydrolysis and condensation of *p*-hydroxy- or *p*-alkoxybenzyl aryl ethers lead to derivatives of hydroxydiphenylmethane—e.g., structures of type III. There is evidence that this process occurs to some extent in the tree without the interference of external reagents. This may result from the natural acidity of wood and may represent a sort of aging process, causing greater condensation and strengthening of the lignin. The same type of condensation must take place to a greater extent when lignin comes into contact with acids—e.g., during the isolation of lignins by acidic hydrolysis of the wood polysaccharides—or with alkalies—e.g., during alkaline pulping processes.

Any hydroxydiphenylmethane structures formed in this way would be prone to oxidation, either by the phenol dehydrogenases involved in lignification while *in situ* in the wood, by redox processes during pulping, or by oxidizing agents during pulp bleaching. Therefore, we prepared some dihydroxydiphenylmethanes and studied their behavior towards oxidizing agents.

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p,p'-Dihydroxydiphenylmethanes

p,p'-Dihydroxydiphenylmethanes are readily prepared using a slight adaptation of Pearl's method. He observed the formation of diguaiacylmethane as a by-product during the oxidation of vanillin to vanillic acid (*21*).

Method. Vanillin was hydrogenated in ethyl acetate using Raney nickel to give vanillyl alcohol (IV, R = H, m.p., 115°C.), in quantitative yield. The alcohol was then refluxed with silver oxide under nitrogen for 24 hours to give diguaiacylmethane V, R = H, m.p., 109°–110°C. as the major product. The material was purified by chromatography on deactivated silica gel using chloroform:acetone (9:1 v/v) as eluant. The formaldehyde eliminated during the above reaction is oxidized by the silver oxide to formic acid, and hence condensations of the phenol formaldehyde type are avoided; the formation of polymeric products is thus suppressed. Boiling vanillyl alcohol with excess alkali alone for 1 hour (*21*) does not afford quantitative yields of diguaiacylmethane but a mixture of several products plus unchanged vanillyl alcohol.

The corresponding syringyl derivative was prepared as follows. Vanillin was converted into 5-iodovanillin, m.p.181°–182°C., which was then converted with sodium methoxide and copper powder (*22*) into syringaaldehyde, m.p.109°–110°C. A trace of free iodine promotes the catalyst in this reaction. The aldehyde was again reduced quantitatively with Raney nickel in ethyl acetate to syringyl alcohol (IV, R = OCH_3, m.p.134°–5°C.) which on treatment with alkali and Ag_2O as above gave a high yield of bis-3,5-di-*O*-methylpyrogallylmethane (V, R = OCH_3, m.p.112°–3°C). Dehydrogenation of V with laccase in air or peroxidase

and hydrogen peroxide or with neutral inorganic oxidizing agents—e.g., MnO_2, PbO_2, heavy metal salts, and air, or potassium persulfate—led to a yellow-colored solution containing some of the *p*-quinonemethide (VI).

Results. This solution exhibits a high molar extinction with λ_{max} at 400 mμ; the carbonyl absorption in the infrared appears at 6μ. The crude quinonemethide (VI) can be prepared in aqueous solution or in almost any organic solvent. When its solution is made alkaline with sodium carbonate or when V is oxidized in weakly alkaline solution—e.g., with potassium ferricyanide or simply with air, a permanent violet color is formed with λ_{max} at 345 and 575–580 mμ. The violet color is caused by the formation of the highly conjugated phenoxide ion VII. If caustic alkali is used, the violet color is only transient, owing to nucleophilic addition of hydroxyl ion onto the *p*-quinonemethide to form the corresponding benzhydrol derivative VIII. The *p*-quinonemethide VI exhibits the normal reactions of *p*-quinonemethides—e.g. decoloration by electrolytes such as mineral or organic acids, phenols or methanol owing to addition reactions. Already during its preparation (e.g., by shaking solutions of V in dioxan with manganese dioxide), some further dehydrogenation of the quinonemethide VI occurs, leading to the free semiquinone radical (IX), which can be detected in the solution of the crude oxidized product by EPR spectroscopy. The mixture obtained on dehydrogenation of V thus contains some unchanged V, some of the *p*-quinonemethide VI, and some of the free radical IX; it is therefore impossible at present to give definite values for the molar extinctions of the quinonemethides or quantitative data on the free radical concentrations.

Other Lignin Models

More lignin-like models were made following the method of Gierer *et al.* (*14*). The yields were improved by applying the dilution principle. Dilute solutions of vanillyl alcohol (X, R = R′ = H) or syringyl alcohol (X, R = OCH_3, R′ = H) were added slowly dropwise to refluxing 66% aqueous ethanol containing creosol (XI) with 1% HCl as catalyst. In this way intermolecular condensation of the alcohols is circumvented. The products consist of mixtures of about 80% 6-vanillylcreosol (XII, R = R′ = H, m.p.112°–5°C.) plus a little 5-vanillylcreosol (VIII, R = R′ = H, m.p.114°–5°C.) or 80% 6-syringylcreosol (XII, R = OCH_3, R′ = H, m.p.121°–2°C.) plus about 10% 5-syringylcreosol (XII, R = OCH_3, R′ = H). The syringylcreosol described by Gierer *et al.* (*14*) is actually the 6-isomer XII and not the 5-isomer XIII. This agrees with the findings of Sarkanen for electrophilic substitution of creosol (*3*, *25*). With acidic catalysts, a benzyl carbonium ion derived from the vanillyl or syringyl alcohol makes an electrophilic attack on the creosol nucleus. Under alkaline conditions the condensation leads to 5-vanillylcreosol

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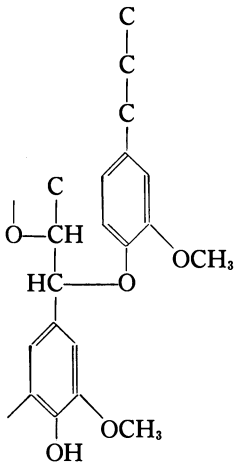

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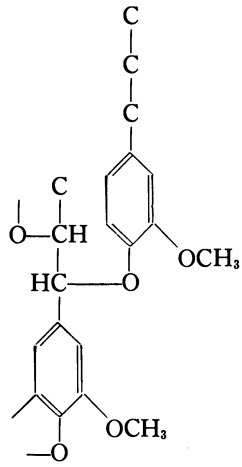

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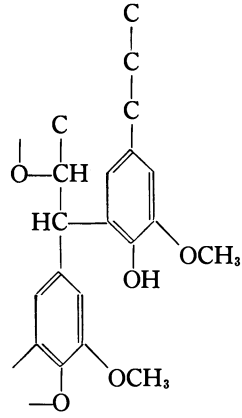

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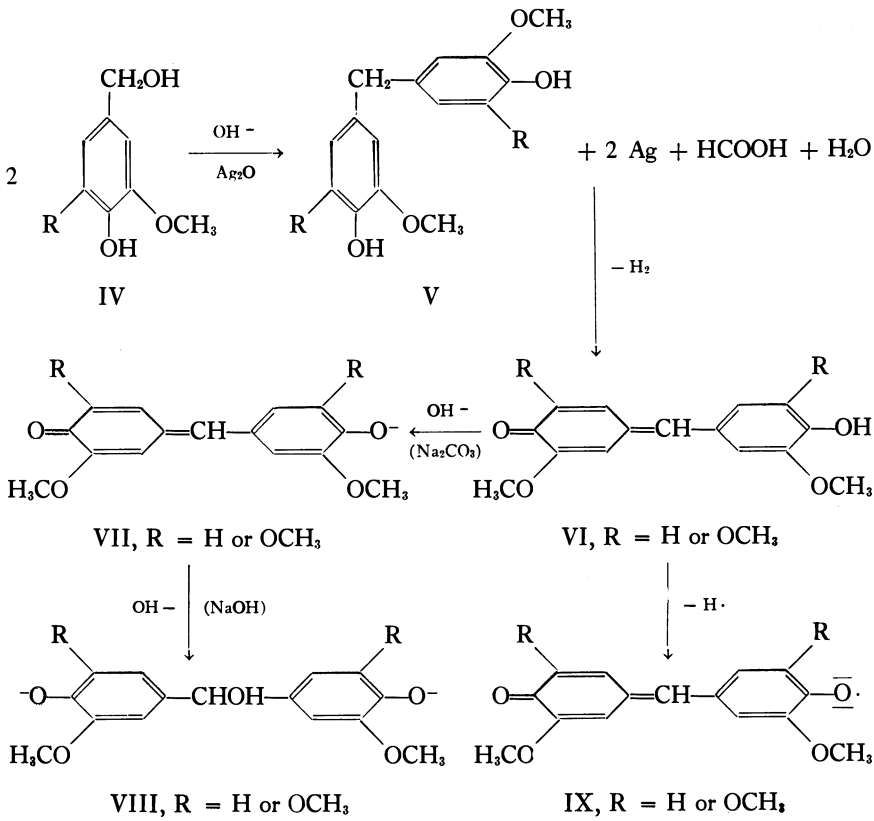

IV V

VII, R = H or OCH_3 VI, R = H or OCH_3

VIII, R = H or OCH_3 IX, R = H or OCH_3

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(XIII) as the predominant product; little 6-isomer (XII) is formed. Dehydrogenation of 6-vanillylcreosol (XII, R = R′ = H) or 6-syringylcreosol (XII, R = OCH_3, R′ = H) with enzymes or inorganic oxidants gives rise to yellow solutions of the *p*-quinonemethide (XIV). Only a slight bathychromic shift occurs when alkali is added to this solution, owing to the formation of the nonconjugated phenoxide ion (XV). Continued dehydrogenation of the quinonemethide can lead to the nonconjugated semiquinone radical (XVI).

Chromophores in Lignin

Dehydrogenation of the 5-isomer (XIII) leads to quinonemethides (XVII) that may be tautomeric between the *o*-quinonemethide and *p*-quinonemethide forms. The yellow solutions of these quinonemethides absorb with high molar extinctions with λ_{max} at 400 mμ. In alkali, the solution becomes intensely red owing to the formation of the conjugated phenoxide ion, which is mesomeric between the *o*- and *p*′-positions. Here no absorption appears at 575–580 mμ; λ_{max} is at 345 mμ; the extinction is greatly intensified, and the long wave side of the absorption band stretches out far into the visible region. Again partial dehydrogenation of the phenolic hydroxyl group remaining in the quinonemethide (XVII) occurs during the production of XVII from XIII giving rise to a stable mesomeric semiquinone radical (XIX) which can be detected by EPR spectroscopy. Again no precise values can be given for the molar extinctions or free radical concentrations of these compounds, for absolutely pure isomers have not yet been obtained and the dehydrogenation again leads to a mixture of unchanged phenol, quinonemethide, and free radical. The free radical content of lignin (*9*, *27*) may be caused partly by structures of types XIX, XVI, or IX.

The crude vanillylcreosols were purified by vacuum distillation (*14*), recrystallization, and zone melting (*26*). Although 5-vanillylcreosol is stable enough to be purified by zone melting slightly above its melting point, it decomposes with spontaneous loss of hydrogen on heating to about 170°C. in air. One product formed is the quinonemethide (XVII), which can be detected by its characteristic spectrum and red coloration when alkali is added. If *o*,*p*′-dihydroxydiphenylmethanes (XIII) are formed during pulping, they may be dehydrogenated to the strong quinonemethide chromophores merely by the effect of the heat alone, especially if traces of heavy metals are present to act as catalysts. The spontaneous formation of XVII from XIII also occurs in strong sunlight. The oxidation of V is even easier; the purple color of VII appears as soon as air is admitted to alkaline solutions of V. XIII is not as readily oxidized by air in alkaline solution.

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Models for diphenylmethane structures derived from *p*-alkoxybenzyl aryl ethers II in lignin were made by condensation of veratryl alcohol (X, R = H, R′ = CH_3) or 3,4,5-trimethoxybenzyl alcohol (X, R = OCH_3, R′ = CH_3) with creosol (XI). The resultant 5-veratrylcreosols and 5-trimethoxybenzylcreosols (XIII with R′ = CH_3, R = H or OCH_3) were again readily dehydrogenated by enzymes or inorganic oxidizing agents to give only *o*-quinonemethides (XX) with λ_{max} at 400 mμ. As expected, their spectra were completely unaltered by adding alkali.

The mesomeric quinonemethides and *o*-quinonemethides described above are somewhat more stable than the simple *p*-quinonemethides whose properties are already well known even from classical studies. The *o*-quinonemethides XX and XVII do not add on water even in solution in aqueous organic solvents; their solution in dioxane/water is stable for months. They do not add on methanol or higher alcohols and react only slowly with phenols and organic acids. The addition of water is not catalyzed by mild alkalies; the red color of the phenoxide ion (XVIII) prevails for weeks in soda solution. Addition of water occurs more rapidly in strongly alkaline solution. The addition of mineral acids and reduction by sodium borohydride are instantaneous. The addition of HCl is rapid even at pH 4.0, the conditions used for determining the carbonyl content of lignin by the hydroxylamine hydrochloride reaction (*13*).

The last observation served to indicate that mesomeric or *o*-quinonemethide groups may be present in spruce milled wood lignin. When a solution of Björkman lignin is added to a solution of hydroxylamine hydrochloride at pH 4.0, the pH rises briefly owing to the addition of HCl onto quinonemethides. The pH then falls off below 4.0 owing to the release of HCl when the carbonyl groups in lignin react with the hydroxylamine. As a rough estimate, a content of 0.03 stable quinonemethide group per C_9 unit in lignin is suggested by this method. Thus, the value of 0.15–0.16 carbonyl per C_9 unit in spruce milled-wood lignin found by the hydroxylamine hydrochloride method (*12*, *13*, *15*) may be slightly low.

Another indication that quinonemethide chromophores are present in Björkman lignin is given by its ionization difference ($\Delta\epsilon$) spectrum in the visible region. A slight difference between the spectrum in neutral and alkaline solution suggests a small content of quinonemethides with a free hydroxyl group in the second benzene ring (cf. type XVII). This difference disappears when the lignin is reduced with sodium borohydride. Quinonemethides substituted by a *p*-alkoxyphenyl group (cf. type XIII, R′ = CH_3) would not be indicated by this method since their spectra are identical in neutral and alkaline solution.

The quinonemethide content of chemically modified lignins may be much higher. If quinonemethide precursors (—e.g. structures of type III) are present in high yield pulps in residues of condensed lignin attached to the fibers, attempts to bleach the pulps with oxidizing agents may lead

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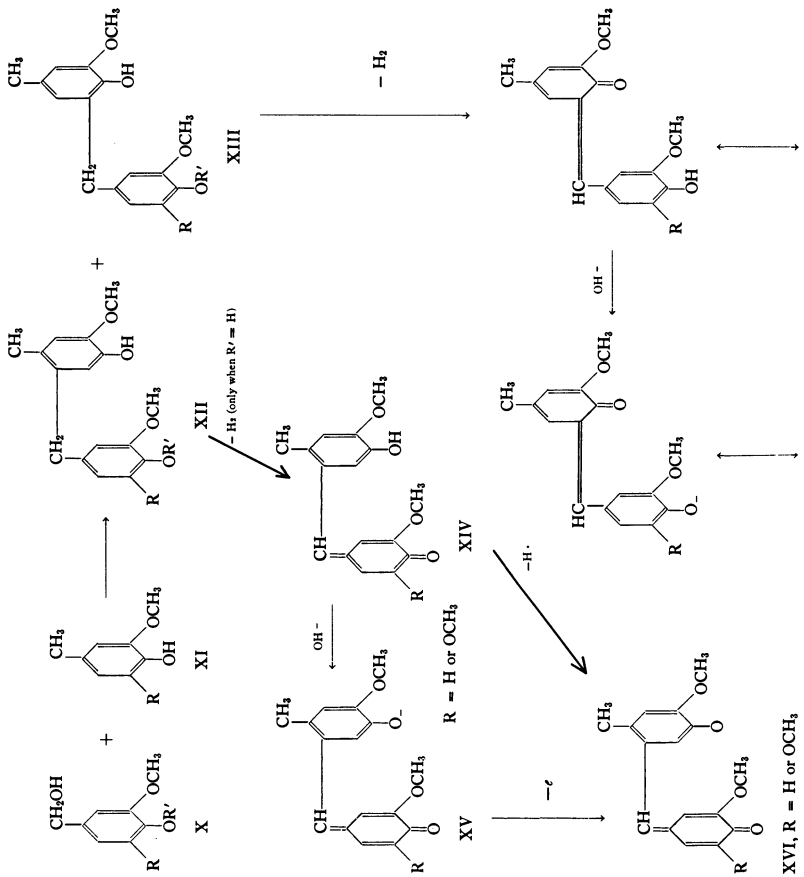

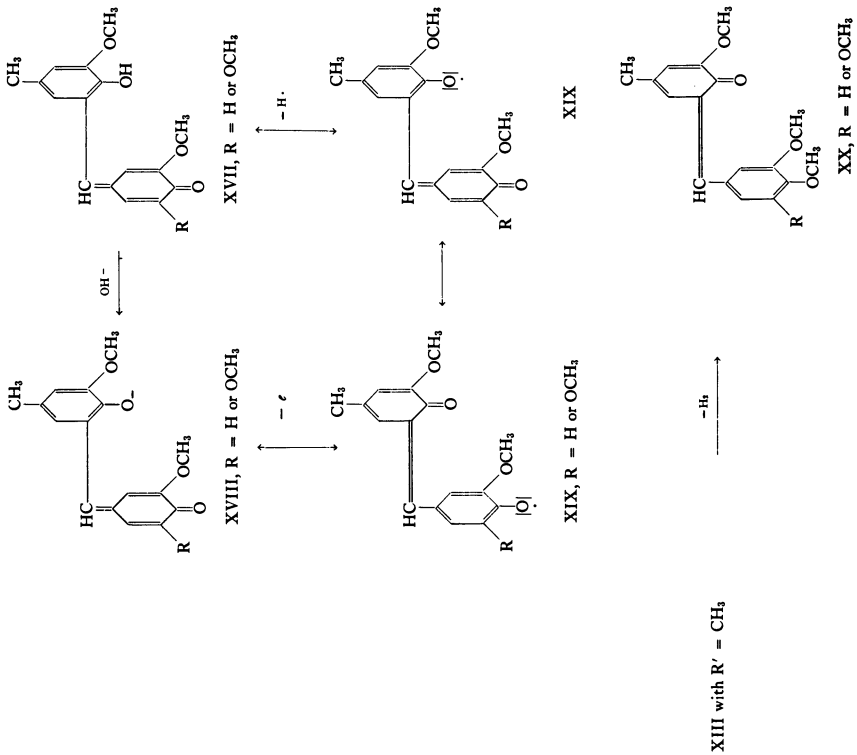

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to pulp darkening instead of brightening. The hydrogen released so readily from the quinonemethide precursors may be responsible for some of the reduction reactions observed during pulping—e.g., reduction of sulfate to sulfide—and may be responsible for some of the free radicals observed by Kleinert (*16*, *17*) on heating wood impregnated with cooking chemicals in an EPR spectrometer. This and other problems suggested by the possible presence of dihydroxydiphenylmethane and quinonemethide structures in lignin are currently being investigated.

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7

Chromophores in Kraft Lignin

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Potential chromophoric systems in kraft lignin are evaluated on the basis of light adsorption and reflectance properties of the lignin, direct determination of chromophores, and the results from kraft cooking of lignin models. The exact nature of the color-causing structures of kraft lignin is uncertain, but the following chromophores may contribute to the color: (1) CH=CH double bonds conjugated with the aromatic ring; (2) quinonemethides and quinones which also may serve as oxidative species creating further chromophoric structures; (3) chalcone structures; (4) free radicals; (5) metal complexes with catechol structures. The three latter structures are likely to contribute to the color of kraft lignin only to a minor extent.

The well known reddish-brown color of kraft paper was the subject of many early investigations. Pigman and Csellak (*34*) showed that residual kraft lignin is the likely coloring matter in kraft pulp. At present, little is known about the chemical nature of the color-causing structures of the kraft lignin itself. This paper discusses some of the potential chromophoric systems in kraft lignin, using three different approaches:

(1) Determining chromophores and auxochromic groups in kraft lignin.

(2) Evaluating spectral changes on oxidation, reduction, or other treatment of the kraft lignin.

(3) Interpreting results from the kraft cooking of lignin models.

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The Color of Kraft Lignin

The color of kraft lignin as compared with the untreated Björkman milled wood lignin (spruce) is demonstrated by the curves for the Kubelka-Munk reflectance function $F(R_\infty)$ *vs.* the wavelength (Figure 1). The shoulder at around 500 mμ is particularly interesting since it is in the visible region. Sodium borohydride reduction of kraft lignin causes a certain

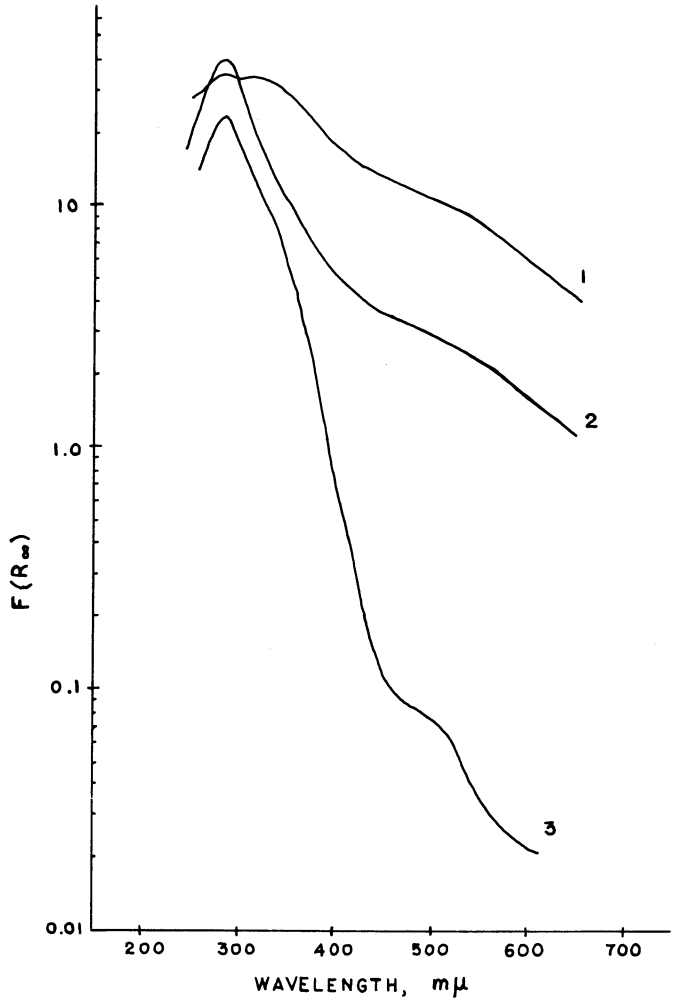

Figure 1. Kubelka-Munk reflectance functions
(1) Softwood kraft lignin, (2) $NaBH_4$-reduced softwood kraft lignin, (3) Björkman spruce milled wood lignin

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decrease in the color of the dry lignin. However, part of the reduction in the reflectance function may be attributed to the somewhat smaller particle size of the sodium borohydride-reduced material and likely higher scattering coefficient (*24*).

The light absorption curve of kraft lignin (Figure 2) shows the aromatic maximum at 280 mμ, a shoulder around 340 mμ which will be discussed later, and a steady reduction in the absorption in the visible region. The nature of the latter part of the spectrum indicates that several chromophoric systems should be involved and that the number or absorption intensity of the color structures responsible for the absorption in a particular wavelength region is decreasing relatively rapidly with increasing wavelength.

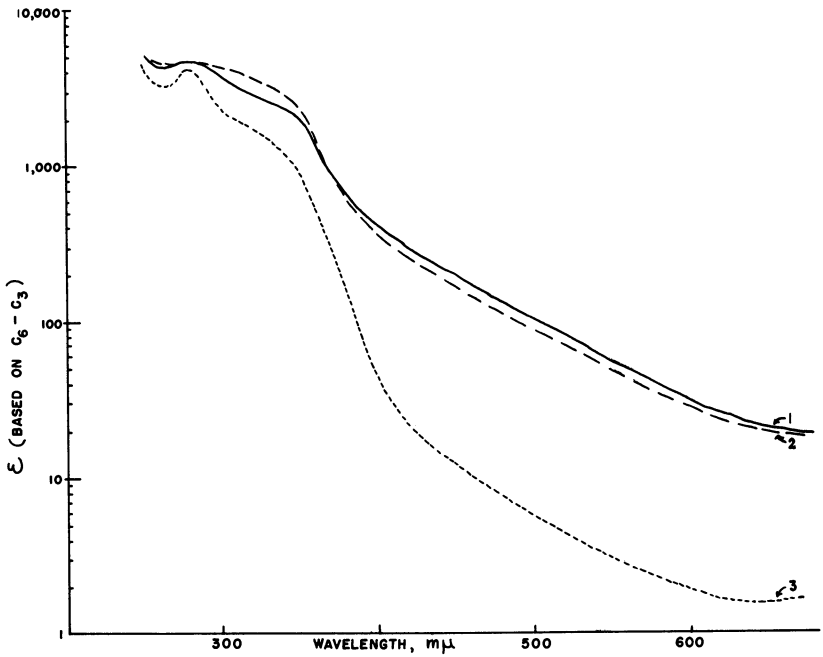


Figure 2. Absorption curves for softwood lignins

(1) Kraft lignin (Indulin AT), (2) kraft-cooked Björkman spruce milled wood lignin, (3) Björkman spruce milled wood lignin. Solvent: methylcellosolve-ethanol, 1:1.

A series of composite chromophoric systems is assumed to be present in kraft lignin. Some simpler chromophores are only absorbing within the ultraviolet (UV) region, and some of those which have a color are only hypothetical. Nonetheless, we considered it necessary to include a num-

ber of potential chromophoric structure types. A single one is unlikely to be solely responsible for the light absorption in the long wave region.

The different types of chromophores, auxochromic groups, and originating reactions which will be discussed are:

(1) Formation of —CH=CH— double bonds conjugated with the aromatic ring

(2) Condensation reactions with formation of chalcones or of easily oxidizable structures such as *p,o'*-dihydroxydiphenylmethanes

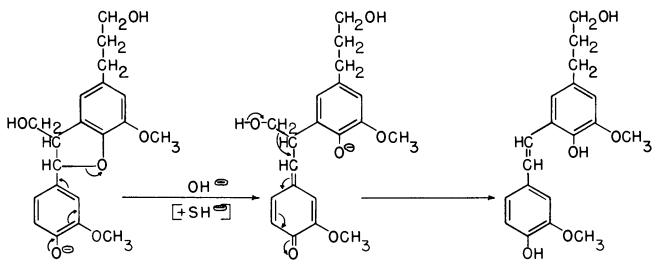
(3) Oxidative dehydrogenation with formation of quinonoid structures

(4) Homolytic reactions or electron abstraction with formation of free radicals

(5) Complex formation with heavy metals

Stilbenes and Other Unsaturated Groups

Kraft cooking of dihydrodehydrodiconiferyl alcohol (I) as a model for the phenylcoumaran system shown to be present in native lignin (*1*, *2*), resulted (*3*, *13*) in the opening of the hydrofuran ring and splitting off of formaldehyde, probably through a reverse aldol condensation of an intermediate quinonemethide (*17*, *18*). The resulting *p,o'*-dihydroxystilbene



(III), which was obtained in a yield of 76%, showed a strong blue fluorescence in UV light, and the medium intensity infrared (IR) band at 960 cm.$^{-1}$ indicated the trans configuration for the —CH=CH— grouping. The UV absorption spectrum in ethanol showed a maximum at 327 mμ with ϵ = 26600 (Figure 3). The spectrum is similar to that of *trans*-4,4'-dihydroxy-3,3'-dimethoxystilbene (IV) which Enkvist (*11*) showed is present in kraft liquor. Richtzenhain (*35*) earlier isolated the same stilbene from spent sulfite liquor. Other *trans*-stilbenes without any substituents in the α,α'-positions have also been found to have similar absorption spectra (*7*, *26*, *36*). The *o*-hydroxystilbene (V), prepared by Lundquist (*1*, *2*) has its absorption maximum located at 300 mμ. The OH and OCH_3 groups thus have a considerable auxochromic effect. Substitutions in the α-positions have been found (*26*, *36*) to cause a pronounced hypsochromic

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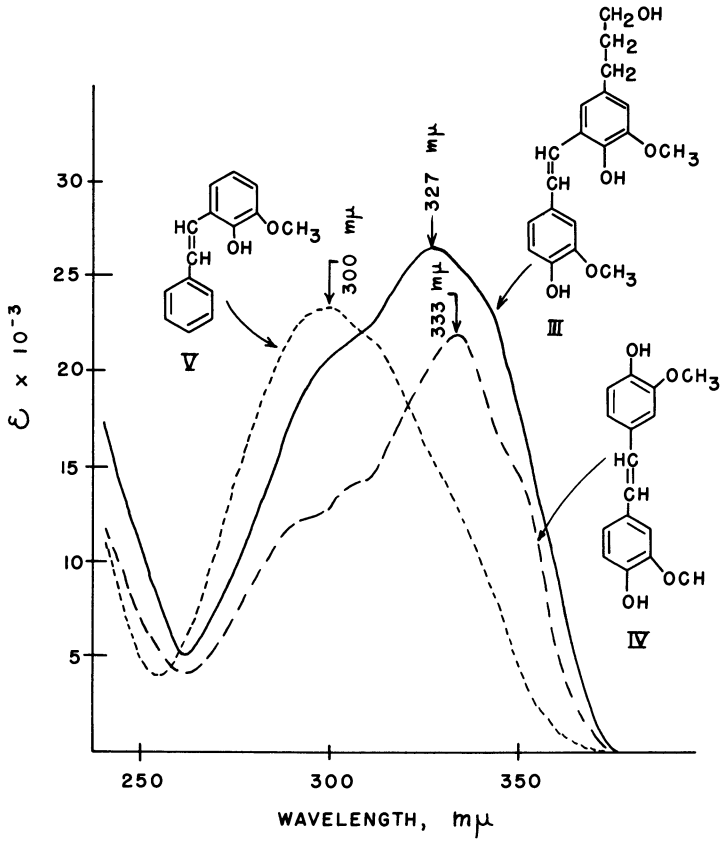

Figure 3. Ultraviolet absorption curves. Solvent: ethanol.

displacement of the long wave absorption band which is attributed to the N → V transitions in the stilbene chromophore. This effect is particularly great if substituents also are present in the neighboring 2-position because of the sterical hindrance for coplanarity of the molecule. Thus, the elimination of the methylol group in I during the kraft cook is important for the light absorption of the resulting stilbene.

The ionization $-\Delta\epsilon$ ($\Delta\epsilon_i$) curve for stilbene III (0.1*N* NaOH) showed a maximum at 378 mμ, $\Delta\epsilon_i$ = 24300 (Figure 4). In alkaline solution the stilbene was extremely sensitive to light, and the UV absorption was therefore recorded within 1 minute after NaOH was added. The cause of the photochemical reaction, which also occurs in the absence of air, has not been elucidated.

The ionization $-\Delta\epsilon$ curve for untreated Björkman spruce milled wood lignin has a maximum at 357 mμ (Figure 5) which is attributed to phenolic α-carbonyl structures (*31*). Kraft-cooked Björkman lignin, however, has

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a strong maximum at 372 mμ. The long wave $\Delta\epsilon_i$-maximum for alkali lignin has also been assumed previously to be caused at least partly by phenolic α-carbonyl structures (*10*). Earlier estimates of α-carbonyls in kraft lignin were based on the $\Delta\epsilon_i$ and $\Delta\epsilon_r$ methods (*21*, *29*, *30*). UV irradiation reduces the long wave $\Delta\epsilon_i$ maximum for kraft lignin; thus, carbonyl structure determination based on spectrophotometric methods may give biased results with kraft lignin. The spectral data for some α-carbonyl structures show that structures VII and IX could possibly explain the long wave $\Delta\epsilon_i$ maximum of kraft lignin.

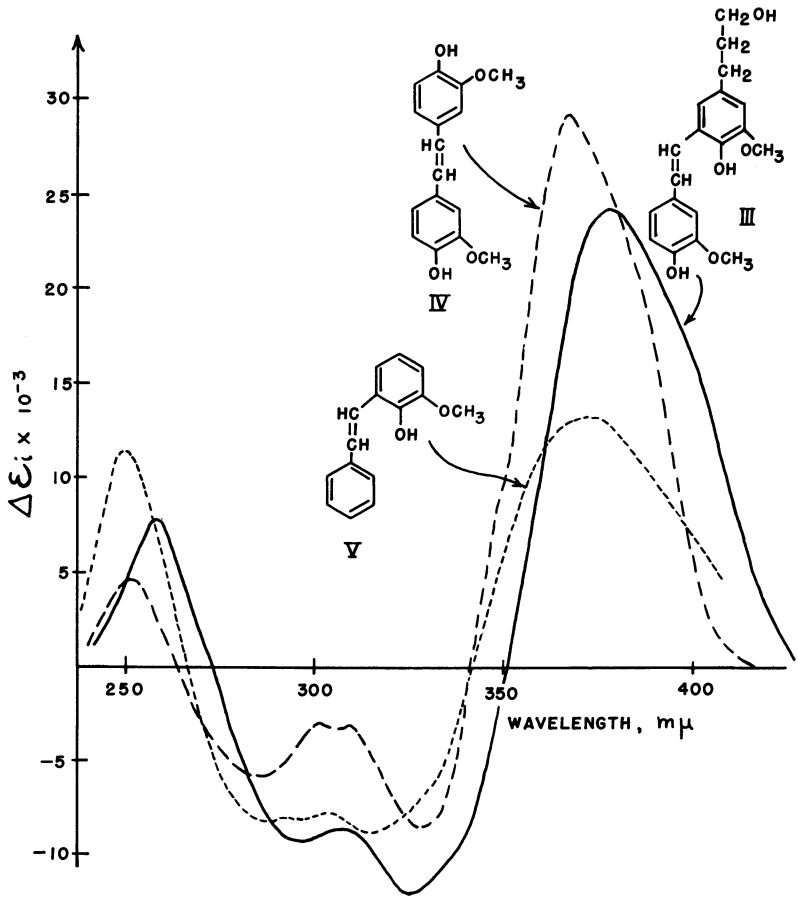

Figure 4. Ionization $\Delta\epsilon$ *curves. Solvents: ethanol and 0.1N in ethanol-water, 1:1.*

Structure IX was unstable during the kraft cooking, but the presence of catechol, α-CO, or other highly conjugated carbonyl structures could

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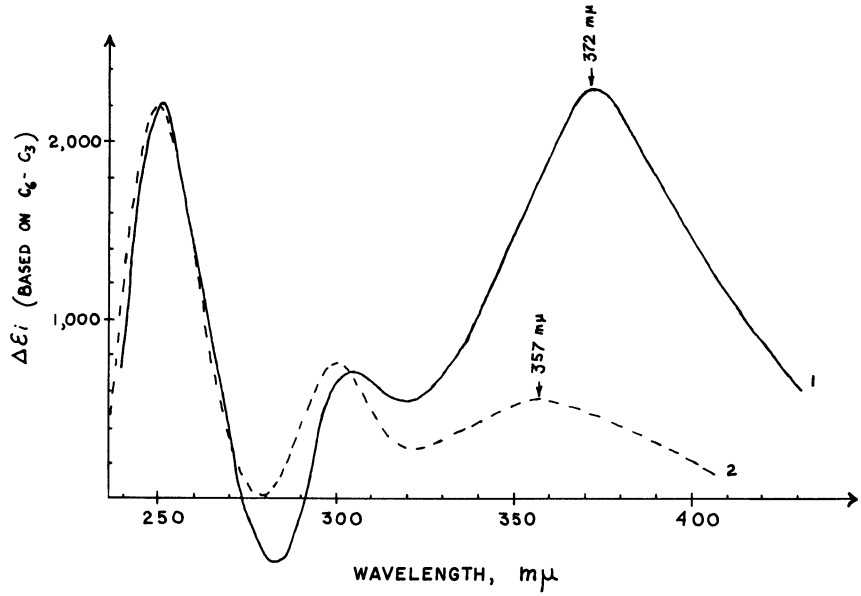
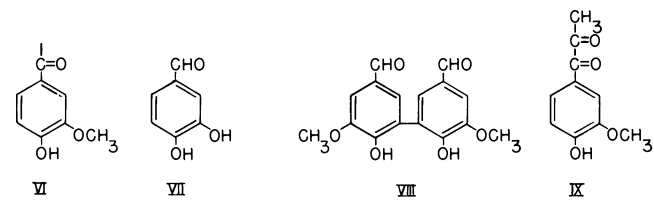


Figure 5. Ionization Δε curves

(1) Kraft-cooked Björkman spruce milled wood lignin, (2) Björkman spruce milled wood lignin. Solvents: methylcellosolve-ethanol, 1:4 and 1N NaOH in methylcellosolve-ethanol-water, 2:3:5. Curves recorded within 2 minutes after mixing the solutions.

not be immediately excluded. However, reducing kraft Björkman lignin with $LiAlH_4$ did not remove the long wave $\Delta\epsilon_i$ maximum (Figure 6) but caused a slight bathochromic displacement to 378 mμ—i.e., the same location as for the stilbene III. The intensity of the $\Delta\epsilon_i$ maximum of the $LiAlH_4$-reduced kraft Björkman lignin, when compared with the intensity



of the corresponding maximum of the model stilbene III, indicated the presence of 0.07 stilbene structures per C_6-C_3 unit in the kraft lignin. If the $\Delta\epsilon_i$ curve of the $LiAlH_4$-reduced kraft lignin is subtracted from the $\Delta\epsilon_i$

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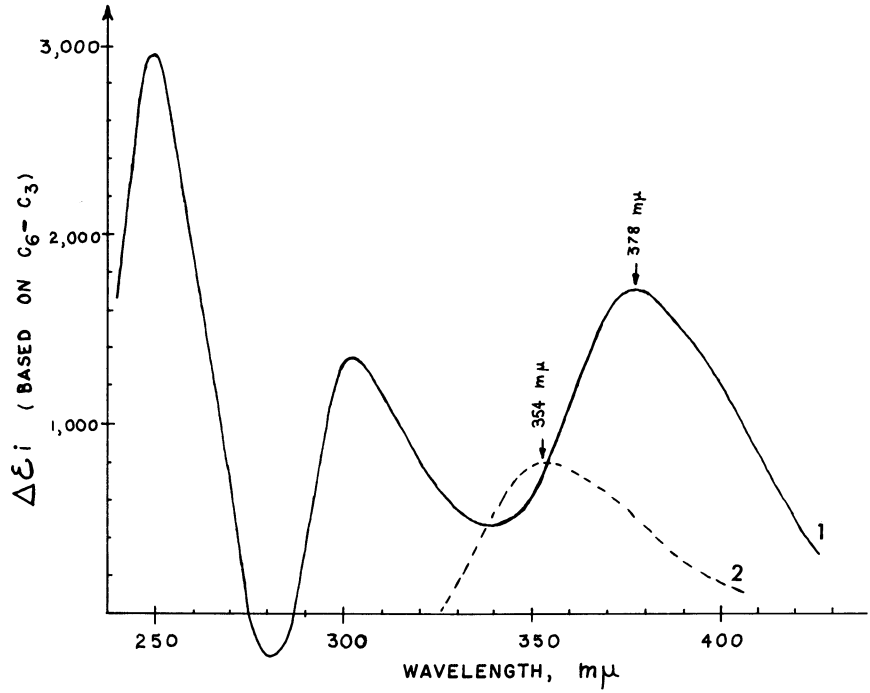

Figure 6. Ionization $\Delta\epsilon$ curves

(1) $LiAlH_4$-reduced, kraft-cooked Björkman spruce milled wood lignin, (2) difference between nonreduced and $LiAlH_4$-reduced kraft-cooked Björkman spruce milled wood lignin, $\Delta(\Delta\epsilon_i)$ curve. Solvents: methylcellosolve-ethanol, 1:4 and 1N NaOH in methylcellosolve-ethanol-water, 2:3:5. Curves recorded within 2 minutes after mixing the solutions.

curve of the nonreduced kraft lignin, a $\Delta(\Delta\epsilon_i)$ curve is obtained with a maximum at 354 mμ which may be attributed to phenolic α-carbonyl structures. This subtraction would indicate the presence of about 0.03 such structures per C_6-C_3 in kraft Björkman lignin, which can be compared with 0.05 α-CO groups suggested for pine kraft lignin (*29*, *30*).

The amount of *p*,*p*′-dihydroxystilbene structures in kraft lignin was estimated at 0.005 per C_6–C_3 by oxidation with H_2O_2 in the presence of Cu^{+2} (*4*) to the stilbenequinone structure (X) which has a high intensity absorption maximum at 478 mμ with $\epsilon = 40300$.

The *p*,*o*′-dihydroxystilbene III does not give any quinone on oxidation with H_2O_2/Cu^{+2}, but the stilbene is destroyed. Neither do simple catechols give any significant color under the oxidation conditions used. Recently (*15*, *28*) structures of type XI, or precursors of dienone type, have been demonstrated in Björkman lignin. Kraft cooking of XI presumably

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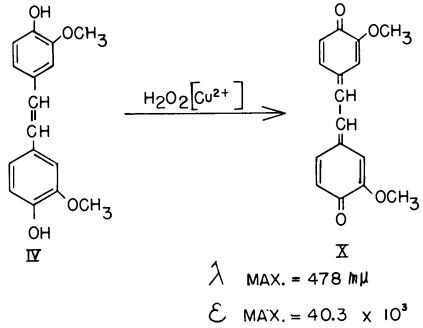
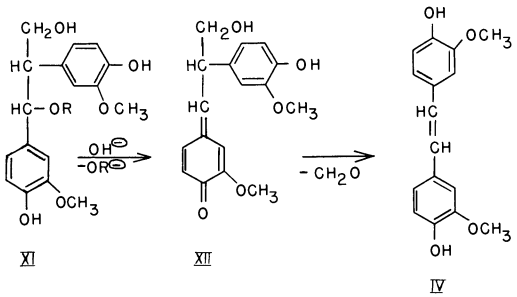
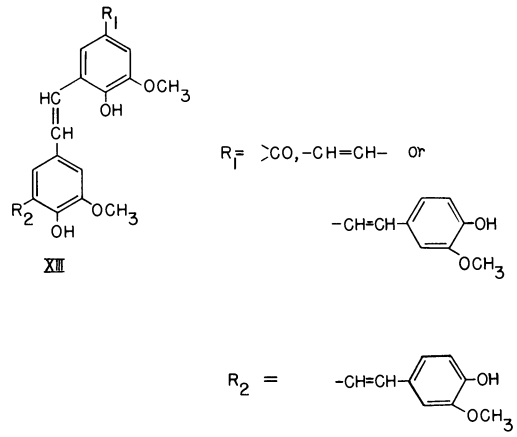


leads to the formation of the *p,p'*-dihydroxystilbene (IV), analogous to the formation of the *p,o'*-dihydroxystilbene (III) from the phenylcoumaran (I).



Thus, we can assume that two types of stilbene structures contribute to the chromophoric systems of kraft lignin. If further double bonds or carbonyl groups are conjugated with the stilbene as in XIII, the resulting structure is likely to have absorption within the visible region of the spectrum.



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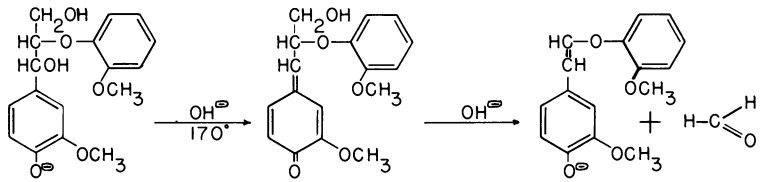
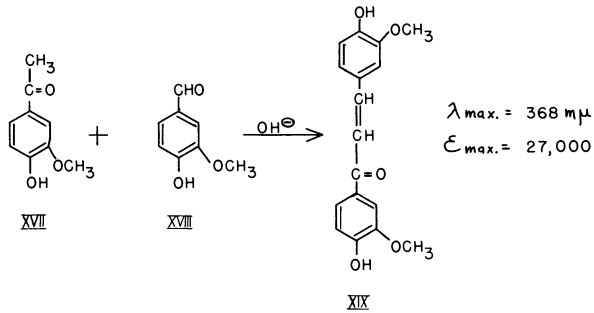
Other types of —CH=CH— double bonds may also form in the kraft cook. It has been found that kraft cooking of the phenolic guaiacylglycerol β-aryl ether (XIV) gave rise to formation of an enol ether (XVI) (*6*, *19*) in a yield of about 30%.



Analogous to the proposed mechanism of the kraft cooking of the phenylcoumaran (I), the enol ether (XVI) is assumed to be formed through intermediate formation of the quinonemethide (XV) which would undergo a reverse vinylogous aldol condensation, splitting off formaldehyde, and would then stabilize as the enol ether (XVI). In the NaOH-cook of model XIV the yield of the enol ether is still higher (*18*) than in the presence of sulfide ions. On the other hand, the veratrylglycerol β-aryl ether type of lignin groups does not give any enol ether (*18*). Thus, the alkali-stable enol ether is likely to be present, although not as a dominant structural feature of kraft lignin.

Condensation Reactions

Condensation reactions of lignin have been mentioned (*22*) in connection with sulfite pulping as being responsible for color formation. However, most of the likely condensation reactions occurring during a kraft cook do not lead directly to chromophore formation. One potential condensation reaction which would give a chromophore is the formation of a chalcone (XIX) from vanillin and acetoguaiacone, both of which have been isolated by Enkvist (*12*) from black liquor.



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Björkman lignin contains (*5*) 0.06 α-CO groups which may participate in chalcone condensation. The chalcone XIX is best prepared by acid catalysis (*33*), but alkaline catalysis has been effective (*38*) in preparing other chalcones. Zentner (*42*) found that the chalcone XIX undergoes a reverse aldol condensation to a certain extent under kraft cooking conditions. In order to investigate the possible formation of chalcone structures during the kraft cook, mixtures of acetoguaiacone and vanillin were cooked for 4 hours at 170°C. and 32% sulfidity. The chalcone XIX has a high intensity absorption maximum in neutral solution (ethanol) at 368 mμ (yellow color) with $\epsilon = 27000$. The formation of the chalcone was followed spectrophotometrically. At kraft cooking conditions the yield was found to be of the order of 1%. Decreasing temperature and increasing alkalinity increased the yield of the chalcone.

The most likely lignin condensation reaction during the kraft cook is the formation of diphenylmethane structures (*29*, *30*). These structures are also proposed (*14*) as being already present in native lignin. Phenolic diphenylmethanes do not exhibit any color, but they can easily be dehydrogenated to quinonemethides (*20*, *23*) or quinonemethide radicals (*9*).

Oxidative Dehydrogenation to Quinonoid Structures

It has been proposed that quinonoid structures (*8*) contribute to the color of kraft lignin. If quinonoid groups are present, they must have been formed in an oxidative process whose nature is unknown.

Oxygen or the presence of carbohydrates is not a prerequisite for the formation of chromophores in lignin during the kraft cooking. This is demonstrated by kraft cooking of Björkman spruce lignin in a nitrogen atmosphere which gave a kraft lignin similar in color and with almost identical long wave absorption spectrum (Figure 2) as a commercial kraft lignin. It seems quite possible that quinonemethides which have been assumed as intermediates in the alkaline pulping (*3*, *6*, *17*), could act as oxidative agents. The formation of quinonemethides and stilbenequinones was observed early in the studies of phenol formaldehyde resins (*16*, *32*, *41*, *43*), and it was suggested (Scheme A) that a disproportionation reaction was taking place with the formation of a stilbenequinone (XXII) and a dihydroxydiphenylethane (XXIII) from the quinonemethide XXI derived from a methylolphenol (*41*).

Another alternative (Scheme B) would be that an intermediate quinonemethide (e.g. XXV) dehydrogenates an easily oxidizable species, such as dihydroxydiphenylmethane, catechol, or *p,p'*-dihydroxystilbene. The dehydrogenation of phenolic diphenylmethanes to highly colored quinonemethides has been reported by Harkin (*20*) and Rothenberg and Luner (*37*). The resulting ionized quinonemethide XXVII is likely to be quite stable because of the resonance stabilization.

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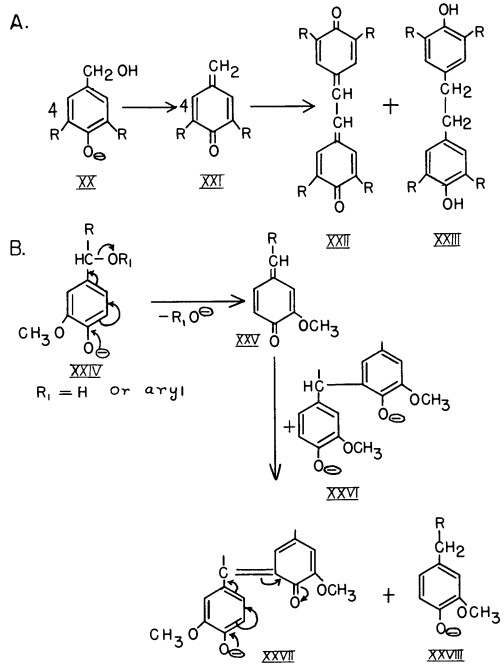

Metal Complexes with Catechol Groups

The amount of complexing structures in kraft lignin has been estimated by using a colorimetric method which is a modification of earlier methods (*25*, *27*). Catechols and kraft lignin give a blue-colored complex with $FeSO_4$ in the presence of tartrate at pH 8.1. In the experiments with kraft lignin 5 ml. of a 5-mmolar sulfite solution and 5 ml. of a 0.1*M* (based on C_6-C_3) dimethylsulfoxide solution of the lignin were pipetted into a 100-ml. volumetric flask; 5 ml. 5-mmolar $FeSO_4$ solution (containing the tartrate) and 20 ml. Na_2HPO_4 buffer (*27*) were added, and the flask was filled to 100 ml. with air-free distilled water. Care had to be exercised in order to avoid the presence of oxygen in the solutions. The presence of sulfite prevents the oxidation of Fe^{+2} to Fe^{+3}. The visible absorption spectrum was determined with a lignin solution (containing all chemicals except $FeSO_4$) as blank. By applying this difference technique, the softwood kraft lignin gave an absorption curve with a maximum at 560 mμ and $\epsilon = 66$. Catechol, pyrogallol-1-methyl ether, *p*-methylcatechol, and 3,5-dimethylcatechol gave maxima at 560–590 mμ and an average $\epsilon = 1100$ in the same test. It can be assumed that catechol structures are mainly responsible for the complexing and color formation of kraft lignin with Fe^{+2}. Based on the ϵ values obtained for the models and the kraft lignin,

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the amount of catechol structures in kraft lignin can in such a case be estimated as 0.06 per C_6-C_3 unit.

It is likely that iron and other heavy metal ions are present in the raw water used in the kraft process, and possibly the kraft lignin is complexing these metals with the formation of color.

Potential Chromophores in Kraft Lignin

The native Björkman milled wood lignin has a very slight yellow color and a low absorption in the visible part of the spectrum (Figure 2). If quinonemethides are present in the native lignin, as suggested by Harkin (*20*), the amount of such structures must be exceedingly small.

The light absorption curve of kraft lignin (Figure 2) gives certain indications about the amount of chromophores that could be present. The shoulder at around 340 mμ is likely to be caused mainly by the stilbene structures. The amounts of *p,o'*-dihydroxy- and *p,p'*-dihydroxystilbene structures in kraft lignin were estimated to be 0.07 and 0.005 per C_6-C_3, respectively. The absorption in the visible region is likely to be caused by a number of chromophores. It is important to realize that not many structures have to be present to explain the color of kraft lignin. The ε value of kraft lignin in the short wave region of the visible spectrum, between 400 and 550 mμ, changes from 400 to 50. This means that of a chromophore with an ε value of 30,000 as little as about 0.002–0.013 such structures per C_6-C_3 would explain the color within the region mentioned.

Stilbene structures as a part of further conjugated systems (XIII) are likely to contribute to the color of kraft lignin. The amount of such conjugated systems cannot, however, presently be estimated with satisfactory certainty.

Quinonoid structures (quinonemethides, stilbenequinones and *o*-quinones) may be formed during the kraft cook, but in such a case it seems likely that they are further converted into colored polymerization products. Chirkin and Tischchenko (*8*) claimed recently that kraft lignin contains many *o*-quinone groups (0.3 per structural unit). Steelink (*39*) has estimated the amount of quinonoid structures as 0.01 per OCH_3 in the kraft lignin, which would only explain a minor part of the absorption at 400 mμ. *o*-Quinones generally have an absorption band in the region of 400 mμ with an ε-value of about 1700 (*40*). Stilbenequinones have considerably higher ε values (ε = 40300 for model X). Complete oxidation of the *p,p'*-dihydroxystilbenes in kraft lignin to stilbenequinones more than doubles the absorption at 480 mμ. There is, however, as yet no concrete evidence on the presence of stilbenequinones in kraft lignin. Ionized quinonemethides (XXVII) are likely to be the most stable of the quinonoid structures considered.

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The free radical content in kraft lignin has been determined by Steelink (*39*) as about 0.0001 per OCH_3. Even with a model ϵ value of 200,000 as obtained for a tetra-*tert*-butylquinonemethide radical (*9*), only about 7% of the absorption of kraft lignin at 420 mμ would be explained.

Chalcone structures are probably formed to a small extent during the kraft cooking, but they are likely to contribute to the color even less than the free radicals.

Complexes between heavy metals and catechol structures in the kraft lignin could theoretically contribute to the long wave absorption, but it is unlikely that their contribution to the color of the kraft lignin is very important.

Estimating the contributions of the different potential chromophores to the color of kraft lignin will be the subject of further investigations.

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8

Formation of Colored Compounds in the Reaction of Lignin Model Compounds with Alkali and Oxygen

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The reaction products of syringyl alcohol and vanillyl alcohol with alkali in air were investigated to elucidate the nature of the chromophoric groups formed during the cold soda pulping of hardwoods. The products identified thus far are bis-4-hydroxy-3,5-dimethoxyphenylmethane, 2,6-dimethoxyquinone, and syringaldehyde. It is suggested that syringyl alcohol reacts initially to form bis-4-hydroxy-3,5-dimethoxyphenylmethane which then reacts with oxygen to form 2,6-dimethoxyquinone, syringaldehyde, and a quinonemethide derivative, 2,6,3',5'-tetramethoxy-4'-hydroxyphenyl - 4 - methylene-2,5-cyclohexadiene-1-one. Vanillyl alcohol reacts to form products that are analogous to those identified from the reaction of the hardwood lignin model. These reaction products, especially the quinone-methide derivative, could account for the color in the cold soda pulping of hardwoods.

Although color is developed in most chemical pulping processes, it is usually formed to the greatest extent in alkaline operations. For example, in the cold soda pulping of hardwoods, a characteristic yellow color (*5*) is generally formed, which is a limiting factor in its commercial acceptance. We investigated the problem of color formation under alkaline pulping conditions to gain information about the types of chromophoric structures involved and the mechanisms of their formation.

During the last decade or so, many researchers have studied color formation in pulps from the various existing processes, indicating the grow-

In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

ing realization of the importance of unbleached brightness, especially for high yield pulps. In a brightness study of cold soda pulps, Luner (*18*) proposed a mechanism for the formation of quinones through a free radical attack on lignin by oxygen. He emphasized the role that oxygen could play in color formation in wood and pulp.

Giertz (*12*) stated that high yield pulps cannot be bleached with retention of lignin, using bleaching agents such as chlorine, hypochlorite, and chlorine dioxide because these agents form colored substances with lignin. On the other hand, peroxides can be used to bleach high yield pulps because they do not form colored substances when they react with lignin.

Ivancic and Rydholm (*14*) noted changes in lignosulfonate from a Mitscherlich cook upon various types of treatments by recording ultraviolet and visible spectra. Hydrochloric acid condensation of the lignosulfonate resulted in increased absorption throughout both spectra, and absorption increased with increased reaction time. Thus, the increase in color is reflected by structural changes recorded in the ultraviolet region.

Additional results showed that spectra of the condensed lignosulfonate reduced with sodium bisulfite or zinc powder in hydrochloric acid approached the visible spectrum of the uncondensed lignosulfonate, although, in all instances, possessing increased absorption. Oxidizing the reduced lignosulfonate with sodium peroxide destroyed some of the aromatic system.

In a study of pH changes of the lignosulfonate, the same authors showed that as the pH increased the absorption in the visible region increased. Increasing pH on the acid side resulted in small changes in increased absorption whereas pH changes on the alkaline side resulted in large increases in absorption in the visible region.

Croon and Swan (*6*) studied lignin chromophoric groups in semichemical spruce bisulfite pulps. Their results from bleaching experiments and the lowering of methoxyl content during pulping suggest that pyrocatechol groups, easily oxidizable to quinonoid structures, may be present in the pulp and the lignosulfonate from the spent liquor. Another phase of the study showed that the visible spectra of milled wood Björkman lignin possessed increased light absorption after being treated under various sulfite-pulping conditions. They showed that the sensitivity of the pulp to heavy metal ions during bleaching and storage affected color and advised adjusting the pH of the finished pulp to 4 in order to obtain good brightness stability.

In a later paper (*7*) they discussed the treatment of some lignin model compounds (e.g., vanillic acid and vanillyl alcohol) with sulfite liquors under varying pulping conditions. Their results indicated that pyrocatechol groups may be formed in lignin during semichemical sulfite pulping.

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The presence of stilbene structures, leading to stilbenequinones, in sulfate Björkman lignin has been suggested by Falkehag (*8*). Using spectral analyses, he showed that the ionization $\Delta\epsilon$ curves of reduced sulfate Björkman lignin and an *o,p'*-dihydroxystilbene structure are similar, possessing peaks at almost identical wavelengths. Furthermore, it seems that those peaks of the ionization $\Delta\epsilon$ curves located in the 370–380 mμ region are caused by stilbene structures and not by carbonyl groups because infrared measurements show that carbonyl groups are either absent or present in only minor quantities. Falkehag concluded that stilbene structures are formed in sulfate Björkman lignin by the opening of phenylcoumaran elements, such as those present in the dihydrodehydrodiconiferyl alcohol units of the untreated lignin. Gierer *et al.* (*10*) have suggested that the mechanism for the alkaline cleavage of the hydrofuran ring proceeds through the formation of a quinonemethide structure.

Simulating alkaline cooking conditions, Hästbacka (*13*) noted that, during the treatment of the lignin model compound, vanillyl alcohol, with sodium hydroxide solution in a nitrogen atmosphere, the reaction mixture became orange. After opening the reaction vessel to the air, the color became dark red within a few minutes. However, he did not attempt to account for the formation of the dark red color but concluded that the product, diguaiacylmethane, was formed by the reaction between a quinonemethide molecule, characteristically yellow, and a vanillyl alcohol molecule.

This research was undertaken to study aqueous alkaline reactions of monomeric structures, similar to polymeric wood constituents, from which color would be formed. Since hardwood pulps were of the greatest immediate interest, the reaction of syringyl alcohol, representing the hardwood lignin structure, in aqueous alkaline solution at room temperature has been studied extensively up to the present time, but the reactions of vanillyl alcohol and α-methylvanillyl alcohol, representing the softwood lignin structure, have also been studied to some extent under the same reaction conditions.

Generally we allowed various model compounds to react with alkali for varying lengths of time and then separated the reaction products by paper chromatography. For identification, the products were eluted from the paper, and spectral analyses were made of the eluates.

Experimental

Preparation of Compounds. Methyl Ether of α-Methylvanillyl Alcohol. This compound was prepared using a modified procedure for preparing vanillyl ethyl ether as described by Adler and Hernestam (*2*). A 4% solution of dry hydrogen chloride in absolute methanol (210 ml.) was added dropwise in 2½ hours to a solution of α-methylvanillyl alcohol (9.5 grams) in methanol (200 ml.). During the addition, the solution was cooled at 0°C. and stirred continuously. After the mixture

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had reacted for 1 day at room temperature, it was neutralized to pH 7 by first adding slightly less than the equivalent amount of base from an aqueous sodium hydroxide solution. The final adjustment to pH 7 was made by addition from an aqueous saturated sodium bicarbonate solution. The methanol was distilled off, and a dark-colored oil separated from the aqueous layer. This mixture was extracted with chloroform and dried over sodium sulfate. The solvent was removed by distillation, and the oil was distilled between 107°–108°C. at 2–3 mm. pressure. The distillate crystallized in the receiver as a white product which slowly changed to a light blue color. The crystalline product was recrystallized from diethyl ether-petroleum ether in 18% yield, m.p.56°–57°C. Analyses found: C, 65.27; H, 7.72; OCH_3, 33.28. Calculated: $C_{10}H_{14}O_3$: C, 65.91: H, 7.74; OCH_3, 34.06.

METHYL ETHER OF VANILLYL ALCOHOL. This compound was prepared using the same procedure described above. After the chloroform was removed by distillation, the oil was distilled between 113°–115°C. at 2 mm. pressure. A yield of 53.9% was obtained; n_D^{22} = 1.5389, tungsten light source. (Lit. n_D^{22} = 1.5407 (*17*)). Analyses found: C, 64.15; H, 7.36; OCH_3, 36.46. Calculated: $C_9H_{12}O_3$: C, 64.27; H, 7.19; OCH_3, 36.90.

METHYL ETHER OF SYRINGYL ALCOHOL. This compound was also prepared by the procedure described above. A 0.07% solution of dry hydrogen chloride in absolute methanol (190 ml.) was added dropwise in 2½ hours to a solution of syringyl alcohol (8.6 grams) in methanol (180 ml.). The cooled solution (0°C.) was stirred continuously during the addition. The solution was allowed to react at room temperature for 89 hours, and it was then neutralized to pH 7 by adding aqueous sodium hydroxide; the final adjustment was made by adding an aqueous saturated sodium bicarbonate solution. After distilling off the methanol, an oil separated from the water layer. The mixture was extracted with chloroform, and the chloroform solution was dried over sodium sulfate. The solvent was removed by distillation, and the oil was vacuum distilled between 142.5°–144°C. at 2 mm. pressure. A product in 53.2% yield was obtained. n_D^{22} = 1.5462, tungsten light source. Analyses found: C, 59.99; H, 7.04; OCH_3, 46.32. Calculated: $C_{10}H_{14}O_4$; C, 60.59; H, 7.12; OCH_3, 46.97.

BIS-4-HYDROXY-3,5-DIMETHOXYPHENYLMETHANE. This compound was prepared using a modification of a procedure suggested by Parker (*19*), in which the product was obtained in 20% yield.

A mixture of 5 grams of zinc chloride, 10 grams of syringyl alcohol, and 22 grams of 2,6-dimethoxyphenol was added to a solution of 15 grams of sodium hydroxide in 300 ml. of water. This mixture was refluxed for 48 hours, carefully avoiding bumping. After cooling, a large amount of organic material appeared in the solid phase. After the reaction mixture was acidified and the solid phase was filtered off, both phases were extracted with diethyl ether. The ether solutions were dried over magnesium sulfate, and the ether evaporated. Since the crystals from the solid phase appeared purer than the crystals from the liquid phase, the former was recrystallized from a 1:1 mixture of benzene-cyclohexane, and pure white crystals were obtained with a melting point of 111°–112°C. (Lit. m.p. 113°C. (*21*)). A mixed melting point with authentic bis-4-hydroxy-3,5-dimethoxyphenylmethane was not depressed.

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Effect of Oxygen on the Reaction of Syringyl Alcohol with Alkali. Ethanolic solutions of syringyl alcohol (0.0545*M* in 5 ml.) and sodium hydroxide (0.0923*M* in 5 ml.) were placed separately in each leg of an inverted Y-tube. After the system was exhaustively evacuated, the solutions were mixed and allowed to react at room temperature. For comparison, an identical experiment was conducted in the presence of air.

Preparation of Reaction Solutions. In general, the reaction solutions of the aromatic alcohols (syringyl alcohol, vanillyl alcohol, and α-methylvanillyl alcohol and their ethers were prepared by adding aromatic alcohol or ether (usually 2.5×10^{-4} mole) to the solvent (water or ethanol) in a 10-ml. volumetric flask. After the model compound was dissolved, the calculated amount of a sodium hydroxide solution was added to make the reaction solution 1:1 molar (model compound to alkali). The solution was then made up to the 10 ml. mark by adding solvent. These solutions were allowed to react at room temperature for given periods.

At the end of the reaction periods, the solutions were acidified to pH 4 with aqueous hydrochloric acid or ethanolic hydrogen chloride, depending on the reaction solvent.

Preparation and Development of Paper Chromatograms. The paper chromatograms were developed on Whatman filter paper No. 1, chromatography grade, using sheets 6″ x 22½″ in size, with development of the chromatograms in the machine direction of the paper.

The solvent system used in developing the chromatograms was a modification of the procedure of Freudenberg and Lehmann (Fr-L II system) (*9*). After the sheets were rolled in cylindrical form and tied with a string, they were then dipped in an ethyl acetate-formamide mixture (8:2) in a 500-ml. graduated cylinder for 15 minutes, removed, and dried with forced air at approximately 35°C. Immediately after the sheets were dry, the solutions of the reaction mixture and reference compounds were spotted at points on the origins of the chromatograms. Approximately 185 gamma of the reaction mixture (based on the unreacted model compound) was placed on the chromatograms, because the development of preliminary chromatograms showed that there were several products in small quantities. When the reaction products were eluted from the chromatograms for spectral analyses, larger quantities of the reaction mixtures were spotted.

After the chromatograms had been prepared for development, they were placed in a chromatography box, and the developing mixture (Fr-L II; xylene: dimethylformamide, 9:2) was added for descending chromatography. Good separation occurred when the chromatography system was free from developing solvent vapors at the start of the experiments. The developing solvent was allowed to move 18–19 inches on the sheets, and then the sheets were removed and dried in a hood.

The visible spots and those detected under short and long wave ultraviolet light were recorded initially. The sheets were then sprayed with an 0.5% aqueous solution of Fast Red Salt GG, and after drying for 30 minutes they were sprayed again with a saturated solution of sodium carbonate.

Elution of Products Separated by Paper Chromatography. In the experiments where the reaction products were eluted for spectral analyses, the chromatograms were initially washed with distilled water

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overnight. This was necessary to prevent high interfering absorption by compounds present in the paper itself (*16*) and not by solvents used in the experiments. The papers were washed efficiently by placing them in a chromatography box and by using the technique of descending chromatography but replacing the developing solvent with distilled wash water. Since absorbing compounds are re-formed in the paper after washing, the chromatographic development and elution of compounds were accomplished as rapidly as possible.

The separated compounds from the reaction mixture, reference compounds, and paper blanks were cut from the developed chromatograms, and the aqueous eluates were received in volumetric flasks under a closed glass system.

Spectral Determination of Terminal Ring *o*-and *p*-Quinones. A modification of Sawicki's method (*22*) was used to help prove that 2,6-dimethoxyquinone was a product of the reaction of syringyl alcohol with aqueous alkali. The coupling of the quinone and 1-ethylquinaldinium iodide to form a dye, measured by spectral absorption in the 725 mμ region, was done as follows.

The 2,6-dimethoxyquinone spots, representing the product from the reaction mixture and the reference compound, and a paper blank were eluted with water from the chromatogram so that each eluate totaled 0.6 ml. Then, 1 ml. of a 1-ethylquinaldinium diodide solution (4 mg./10 ml. 2-methoxyethanol, freshly prepared) was added to each of the three eluates. The volumes of the three solutions were made up to 5 ml. with 2-methoxyethanol and, after mixing, were allowed to set for 9 minutes. At the end of this period, 0.1 ml. of a 2.5% aqueous tetraethylammonium solution was added to each of the reaction solutions.

Immediately afterward, visible spectra were recorded of each of the sample solutions against the paper blank solution and of the paper blank solution against a blank solution excluding the paper eluate.

Results and Discussion

Color Characteristics of the Reaction Mixtures. Initial experiments in air involving the reactions of syringyl alcohol, vanillyl alcohol, and α-methylvanillyl alcohol with alkali showed both visually and spectrophotometrically that the reaction mixture of syringyl alcohol, the hardwood lignin model, and alkali was more intensely colored than either of the reaction mixtures of the guaiacyl compounds and alkali.

The color characteristics of the reaction mixtures in aqueous and ethanolic solutions were also interesting. In ethanol, the mixture of syringyl alcohol and alkali turned pale violet within 15 minutes after preparation, and the color slowly became more intense with time until a deep violet color was formed, which persisted for approximately 2 months; after this time, the violet color slowly faded, and the solution became brown. Concomitant with the appearance of the brown color, a brown polymeric substance settled out of solution. The same reaction mixture in aqueous medium turned yellow in about 15 minutes and then slowly changed to

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violet, to blue, to green, and finally to brown with the formation of a brown precipitate. Acidifying the solutions to pH 4 in both solvent systems resulted in yellowish to brownish colors of varying intensities.

Effect of Oxygen on the Reaction of Syringyl Alcohol with Alkali. Preliminary experiments (*18*) on the reaction of white birchwood meal with alkali in the presence and absence of oxygen indicated that in the presence of oxygen a red-brown color was formed while in its absence (total pressure 1×10^{-4} mm.), the reaction mixture was yellow-brown.

Therefore, we thought it important to determine the role of oxygen in color formation during the reactions of the model compounds and alkali. Syringyl alcohol and alkali were allowed to react in ethanolic solution after the air had been removed in a high vacuum for a prolonged period. During the 14 months in which the solution was examined at intervals, it remained colorless. In comparison, when oxygen was not excluded from the reaction mixture, the solution became colored within 15 minutes; the visible spectrum of such a solution after a reaction period of 24 hours is shown in Figure 1. Although the same experiment was not repeated in aqueous medium, it is reasonable to assume that such an aqueous mixture would also be colorless in the absence of oxygen. Neutral solutions of the three lignin models in both aqueous and ethanolic mediums remain colorless for substantial periods of time before they become pale yellow.

Thus, similarities in color formation exist between the treatment of hardwood meal with alkali and the treatment of syringyl alcohol with alkali. In either instance, when oxygen is absent or suppressed, color formation is minimized. It may be concluded then, that oxygen is necessary for color formation when wood is pulped under alkaline conditions, and that units of the lignin component can be responsible for the color.

Effect of Blocking Reactive Sites in Lignin Model Structures. The lignin model compounds selected for this study possess two functional groups, a phenolic hydroxyl group, and an aliphatic hydroxyl group located on the side chain para to the phenolic hydroxyl group. Experiments were performed to determine the effect of blocking each of these two sites relative to the formation of chromophoric structures.

Phenolic Hydroxyl Group. An ethanolic solution of 3,4,5-trimethoxybenzyl alcohol (4-*O*-methylsyringyl alcohol) and sodium hydroxide was prepared, and ultraviolet spectra of the solution were recorded immediately and 3 days after preparation. These spectra were compared with the spectrum of the model compound in neutral ethanol. The three spectra were identical with the absorption curve possessing a broad maximum in the 270–280 mμ region. Further visual observation of the alkaline solution for 2 weeks revealed no color formation. This suggests that phenoxide ion formation may be a necessary initial step in reactions leading to the development of chromophoric structures from lignin model compounds.

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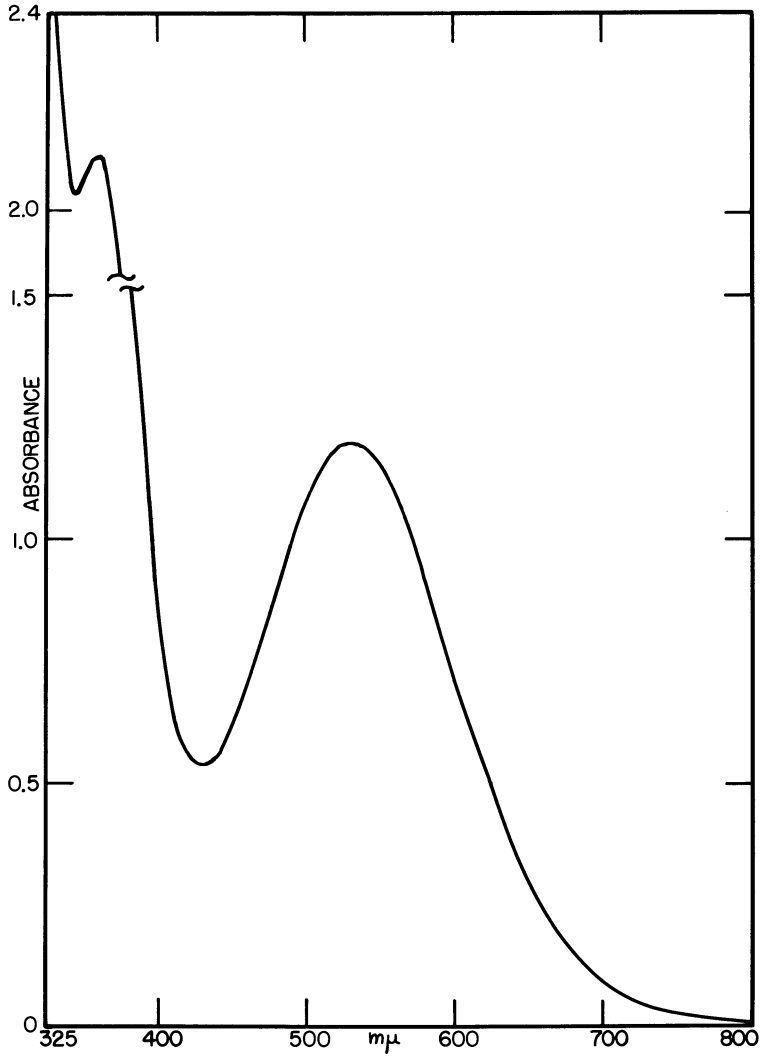

Figure 1. Visible absorption spectrum of an ethanolic reaction mixture (0.008M syringyl alcohol and 0.008M NaOH, 24-hour reaction period)

ALIPHATIC HYDROXYL GROUP. The methyl ethers of syringyl alcohol, vanillyl alcohol, and α-methylvanillyl alcohol were treated with alkali under the same conditions as those used in studying the reaction of syringyl alcohol with alkali. For the reactions of each of the three compounds with alkali, spectral analyses showed that colored products had been formed in each instance, indicated by general ultraviolet absorption tailing into the visible region. It is interesting to note that in all three reactions, as in

the reaction of syringyl alcohol with alkali, some of the new material formed was reducible with sodium borohydride, as determined by spectral analyses.

From these results, it can be concluded that blocking the aliphatic hydroxyl groups does not inhibit the reactions of the model compounds in alkaline solutions leading to color formation.

Products from the Reaction of Syringyl Alcohol with Aqueous Alkali. Table I shows the locations on the paper chromatogram of products from the reaction of syringyl alcohol with alkali in aqueous medium. The chromatograms were developed using a modified FR-L II system (*see* Experimental), and the R_f values were compared with the R_f values of reference compounds also shown in Table I.

BIS-4-HYDROXY-3,5-DIMETHOXYPHENYLMETHANE. Table I shows, the reference compound, bis-4-hydroxy-3,5-dimethoxyphenylmethane, had an R_f value of 0.41 and was blue when sprayed with the location sprays. Table I also shows that the syringyl alcohol reaction mixture contained a

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Table I. Reaction of Syringyl Alcohol with Alkali

Comparison of R_f Values of Reaction Products and Reference Compounds

Reaction Mixture				
R_f	*Color*[a]	*Reference Compounds*	R_f	*Color*
0.00	Blue[b]			
		Syringic acid	0.00	Blue
		2,6-Dimethoxyhydroquinone	0.00	Blue
0.00	Yellow[b]			
		Coerulignone	0.00	Yellow
0.13	Blue			
0.20	Blue			
0.26	Violet	Syringyl alcohol	0.27	Violet
0.40	Blue	Bis-4-hydroxy-3,5-dimethoxy-phenylmethane	0.41	Blue
0.58	Violet[c]	Syringaldehyde	0.58	Violet[c]
		2,6-Dimethoxyphenol	0.68	Violet
0.73	Yellow[d]	2,6-Dimethoxyquinone	0.73	Yellow[d]
		4,4′-Dihydroxy-3,3′,5,5′-tetra-methoxystilbene (fluorescent)	0.82	Pink → Yellow

[a] After spraying with an 0.05% aqueous solution of Fast Red Salt GG followed by spraying with a saturated solution of Na_2CO_3 (*20*).

[b] Although the color was sea-green, it appeared that it was formed from at least two compounds, one or more being blue and one or more being yellow.

[c] Color as seen under long wave ultraviolet light after sheet has been sprayed with location reagents and dried.

[d] Original color of compound itself.

product at an R_f value of 0.40 which was also colored blue with the same location sprays.

After the reaction product at the R_f value of 0.40 was eluted with water from the chromatogram, its spectrum in neutral solvent and its ionization $\Delta\epsilon$ curve were recorded. The neutral spectrum and the ionization $\Delta\epsilon$ curve of bis-4-hydroxy-3,5-dimethoxyphenylmethane in 47.5% ethanol were also recorded; the wavelengths of the ultraviolet absorption maxima of the two compounds—eluted product and reference compound—are given in Table II. The spectra of the compounds possess maxima at nearly identical wavelengths. Thus, paper chromatography and ultraviolet spectroscopy indicate positively that bis-4-hydroxy-3,5-dimethoxyphenylmethane is a product of the reaction of syringyl alcohol with alkali in aqueous solution.

Table II. Wavelength Locations of Ultraviolet Absorption Maxima of Bis-4-hydroxy-3,5-dimethoxyphenylmethane

Bis-4-hydroxy-3,5-dimethoxyphenylmethane	*Solvent*	*Neutral Solvent*		*Ionization $\Delta\epsilon$ Curve,*		
		λ_{max}, $m\mu$	*Log* ϵ	λ_{max}, $m\mu$		
Reference compound	47.5% Ethanol	273	3.45	226[a]	258	290
Reaction product	Water	272	—	219[a]	257	289

[a] The location of these maxima do not agree exactly. However, this slight difference is explained by background absorption owing to solvents which may be in the paper eluates.

2,6-DIMETHOXYQUINONE. Table I shows that the reference compound, 2,6-dimethoxyquinone, had an R_f value of 0.73, and the color of the spot on the chromatogram was yellow. A product from the reaction mixture of syringyl alcohol and alkali had a similar R_f value and color (Table I).

After this reference compound and reaction product were eluted with water from the chromatogram, their neutral spectra were recorded. In addition, the neutral spectrum of an aqueous 2,6-dimethoxyquinone solution was obtained; the locations of the maxima of the three spectra are given in Table III which shows that the ultraviolet spectra of the three compounds in aqueous solution possessed maxima at the identical wavelength of 289 mμ.

Sawicki *et al.* (*22*) showed that terminal ring *o*- and *p*-quinones are characterized by a coupling reaction with 1-alkyl quinaldinium salts while inner ring *o*- and *p*-quinones do not couple with these salts. The type of dyes formed in the coupling reaction absorb in the 635–775 mμ region. Using a modification of Sawicki's procedure, the eluted reference compound, 2,6-dimethoxyquinone, the reaction product at the R_f value of 0.73 and a paper blank were treated with the quinaldinium salt. The three

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spectra showed that the solutions of both the reference compound and reaction product possessed maxima at 725 mμ while the solution of the blank possessed very slight general absorption. Therefore, the spectral results confirm the reaction product at the R_f value of 0.73 as 2,6-dimethoxyquinone.

Table III. Wavelength Locations of Ultraviolet Absorption Maxima of 2,6-Dimethoxyquinone

2,6-Dimethoxyquinone	*Aqueous Neutral Solvent* λ_{max}, mμ		*Log ε*
Spectrum of reference compound	—	289	4.13
Spectrum of reference compound eluted from chromatogram	225[a]	289	—
Spectrum of reaction product eluted from chromatogram	225[a]	289	—

[a] These maxima have been assigned to background absorption caused by chromatographic solvents which have not been entirely compensated for by the blank.

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SYRINGALDEHYDE. Table I shows that the reference compound, syringaldehyde, is located at an R_f value of 0.58 and that one of the products of the reaction of syringyl alcohol with aqueous alkali is also located at the same R_f value. These compounds were located on the chromatograms most easily using a long wave ultraviolet lamp after applying the location sprays, and they appeared as violet spots under these conditions.

Syringaldehyde and its corresponding R_f value compound were eluted from the chromatogram, and their spectra in neutral aqueous solutions were recorded. Table IV shows that the maximum at 307 mμ for both spectra is located at the same wavelength as the maximum of the spectrum of syringaldehyde in aqueous neutral solution recorded by Aulin-Erdtman and Hegbom (*4*). Furthermore, the ionization Δε curve of the eluate of the product from the reaction mixture located at the R_f value of 0.58 possessed maxima at 252 and 365 mμ, which correspond very well to the locations of the maxima of the ionization Δε curve of syringaldehyde (*4*), given as 249 and 365 mμ (Table IV). Therefore, a third product, syringaldehyde, has been identified as a product of the reaction of syringyl alcohol with aqueous alkali.

In addition to the products discussed above, Table I shows that there are other reference compounds for which there are no corresponding reaction products. Experimental evidence has indicated that 3,3′,5,5′-tetramethoxy-4,4′-diphenoquinone (coerulignone), 4,4′-dihydroxy-3,3′,5,5′-tetramethoxystilbene and 2,6-dimethoxyphenol are not products of the reaction of syringyl alcohol with alkali while additional experimental work

Table IV. Wavelength Locations of Ultraviolet Absorption Maxima of Syringaldehyde

Syringaldehyde	*Aqueous Neutral Solvent* λ_{max}, $m\mu$	*Ionization* $\Delta\epsilon$ *Curve (Aqueous)*, λ_{max}, $m\mu$	
Reference compound	307	—	—
Reaction product	307	252	365
Aulin-Erdtman and Hegbom (*4*)	307	249	365

is necessary to provide conclusive evidence as to whether or not syringic acid and 2,6-dimethoxyhydroquinone are products of the reaction.

UNKNOWN REACTION PRODUCTS. The three compounds identified thus far as reaction products of syringyl alcohol with aqueous alkali are located at R_f values of 0.40 or greater while syringyl alcohol is located at an R_f value of 0.27 (Table I). From an R_f value of 0.20 down to the origin, the number and location of additional spots or compounds become more difficult to determine. Those spots close to the origin tend to overlap, and it becomes more difficult to separate them from one another. The amount of tailing from the origin also increases as the time of reaction increases. However, it appears that the longer the syringyl alcohol solution reacts, the greater will be the number and intensity of such spots or reaction products.

Notwithstanding these difficulties, initial attempts have been made to separate and identify these compounds. They have been labeled unknowns IV, V, VI, and VII, with the lowest numbered unknown having the highest R_f value, and the other unknowns following in consecutive order. Unknown VII, further identified as the material at the tip of the tail which starts at the origin, fluoresces under long wave ultraviolet light.

Table V lists the location of the maxima of the spectra in aqueous neutral solvent and the ionization $\Delta\epsilon$ curves of the four unknown compounds.

The maxima in the 305 mμ region, representing conjugated carbonyl groups, were overlooked initially, because they appeared only as weak shoulders and not as distinct peaks. However, the ionization $\Delta\epsilon$ curves for Unknowns IV and VI show distinct peaks at 364 mμ which also represent conjugated carbonyl groups, and this would support the presence of the maxima in the 305 mμ region for the corresponding spectra in neutral solvent.

However, the spectra of unknowns V and VII in aqueous neutral solution also have similar weak shoulders; hence, their ionization $\Delta\epsilon$ curves should normally possess peaks in the 364 mμ region. Initial experiments have not shown this to be true, and this question needs further examination.

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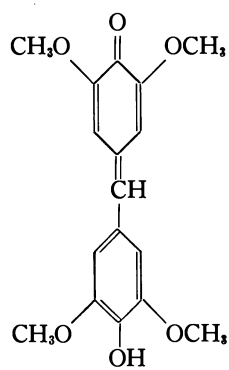
Table V. Wavelength Locations of Ultraviolet Absorption Maxima of Unknowns IV–VII

Unknown Compound No.	*Aqueous Neutral Solvent,* λ_{max}, $m\mu$		*Ionization* $\Delta\epsilon$ *Curve (Aqueous),* λ_{max}, $m\mu$			
IV	278	304	226	256	291	364
V	279	308	221	256	292	—
VI	275	305	225	256	293	364
VII	273	303	225	256	294	—

Table V also shows that the spectra of the unknowns in neutral solvent possess peaks in the 273 mμ region, similar to the location of the peaks of the spectra representing the syringyl nucleus (Table II). The presence of the syringyl nucleus is also suggested by the maxima at 225, 256, and 292 mμ for the ionization $\Delta\epsilon$ curves as shown in the same tables.

These sparse but enlightening spectral data might fit a structure such as Structure A′ which is discussed under Suggested Reaction Mechanisms. Kharasch and Joshi (*15*) have shown that the anion of a similar type of compound (*tert*-butyl groups in place of methoxyl groups in Structure A′) absorbs very strongly at 575 mμ (log ϵ = 5.34 in ethanol). Thus, the anion of Structure A′ should also absorb very strongly at approximately the same wavelength. Evidence of the presence of such a species in this study might be the maximum at 531 mμ exhibited by the spectrum in Figure 1.



Structure A′

Products from the Reaction of Vanillyl Alcohol with Aqueous Alkali. Table VI shows the results of a paper chromatography experiment comparing the R_f values of compounds formed by the reaction of vanillyl alcohol and sodium hydroxide with R_f values of reference com-

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pounds, diguaiacylmethane, methoxyquinone, vanillin, and vanillic acid (Fr-L II System).

DIGUAIACYLMETHANE. The reference compound, diguaiacylmethane, is located at an R_f value of 0.58, and one of the products of the reaction mixture is located at an R_f value of 0.55 (Table VI). Both compounds are violet after the location sprays are applied.

Table VI. Reaction of Vanillyl Alcohol with Alkali

Comparison of R_f Values of Reaction Products and Reference Compounds

Reaction Mixture				
R_f	*Color*[a]	*Reference Compounds*	*R_f*	*Color*[a]
0.00	Rust			
0.16	Blue-violet			
0.30	Pink-violet	Vanillyl alcohol	0.30	Pink-violet
0.39	Violet			
		Vanillic acid	0.39	Pink-violet
0.47	Yellow[b]	Methoxyquinone	0.47	Yellow[b]
0.55	Violet	Diguaiacylmethane	0.58	Violet
0.67	Light violet	Vanillin	0.68	Light violet

[a] After spraying with an 0.05% aqueous solution of Fast Red Salt GG followed by spraying with a saturated solution of Na_2CO_3 (*20*).
[b] Original color of compound itself.

Spectra of the two eluted compounds in neutral solvent and their ionization $\Delta\epsilon$ curves were recorded, and the locations of their maxima are shown in Table VII.

The maxima of the spectra of the eluted reference compound, diguaiacylmethane, and of the reaction product are located at almost identical wavelengths for both the neutral solvent and ionization $\Delta\epsilon$ curve, as shown in Table VII. Furthermore, in both cases, the locations of the maxima of the ionization $\Delta\epsilon$ curves agree well with the locations of the maxima of the ionization $\Delta\epsilon$ curve of an ethanolic diguaiacylmethane solution (Table VII). Thus, paper chromatography and spectral analyses indicate that diguaiacylmethane is a product of the reaction of vanillyl alcohol with sodium hydroxide under aqueous reaction conditions.

METHOXYQUINONE. Although methoxyquinone has not been definitely established as a product, the experimental work to date strongly indicates its presence. Table VI shows that the reference compound, methoxyquinone, is located at an R_f value of 0.47 and that there is a corresponding compound at the same R_f value from the reaction mixture of vanillyl alcohol and alkali. Both compounds appear as yellow spots on the chromatogram.

Further evidence indicating the presence of methoxyquinone as a product is shown by the neutral aqueous spectra of the eluted compounds

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Table VII. Wavelength Locations of Ultraviolet Absorption Maxima of Diguaiacylmethane

Diguaiacylmethane	*Solvent*	*Neutral Solvent*, λ_{max}, $m\mu$		*Ionization* $\Delta\epsilon$ *Curve*, λ_{max}, $m\mu$	
Spectrum of reference compound eluted from chromatogram	Water	229	281	254	299
Spectrum of reaction product eluted from chromatogram	Water	229	281	250	299
Spectrum of reference compound	Ethanol	—	—	251	300

possessing maxima at 278 mμ for the reference compound and at 273 mμ for the product from the reaction mixture.

VANILLIN. Table VI shows that the reference compound, vanillin, is located at an R_f value of 0.68, and the spot is light violet after applying the location sprays. There is a corresponding compound at an R_f value of 0.67 for the reaction mixture of vanillyl alcohol and alkali, and it is also light violet when sprayed similarly.

Table VIII compares the locations of the maxima of the spectra of the eluted vanillin, reference compound, the locations of the maxima of the spectra of the corresponding eluate of the reaction mixture, and the locations of the maxima of the spectra of vanillin as given by Aulin-Erdtman and Hegbom (*4*).

Table VIII. Wavelength Locations of Ultraviolet Absorption Maxima of Vanillin

Vanillin	*Aqueous Neutral Solvent*, λ_{max}, $m\mu$			*Ionization* $\Delta\epsilon$ *Curve* (*Aqueous*), λ_{max}, $m\mu$		
Reference compound	231	280	308	248	292	347
Reaction product	235	282	310	248	290	342
Aulin-Erdtman and Hegbom (*4*)	230	279	309	248	—	348

Thus, the wavelengths of the maxima of the spectrum in neutral solvent and of the ionization $\Delta\epsilon$ curve of the vanillin reference compound agree well with the wavelengths of the maxima of similar spectra of the corresponding reaction mixture compound. As Table VIII also shows the locations of the same maxima agree with those given by Aulin-Erdtman and Hegbom (*4*) for the spectra of vanillin. Thus, paper chromatography and spectroscopy have helped to verify vanillin as a product in the reaction of vanillyl alcohol with aqueous alkali.

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VANILLIC ACID AND UNKNOWNS. The vanillic acid reference spot has an R_f value of 0.39 (Table VI) as does one of the compounds from the reaction mixture. However, as Table VI shows, the colors of these spots, after applying the location sprays, have been recorded as being slightly different. Therefore, although the results so far indicate that vanillic acid might be a product of the reaction of vanillyl alcohol and alkali, spectral analyses of the eluates of the chromatographic spots at the R_f value of 0.39 is necessary for confirmation.

Table VI also shows that the mixture from the reaction of vanillyl alcohol and alkali contains at least two more unidentified compounds. These are represented by the spots located at the origin and at the R_f value of 0.16. It is possible that more than one compound, represented by the rust color, is located at the origin, but additional experimental work is necessary to verify this fact. These unknown compounds located at the low R_f values could be similar in structure to unknowns IV, V, VI, and VII, discussed previously.

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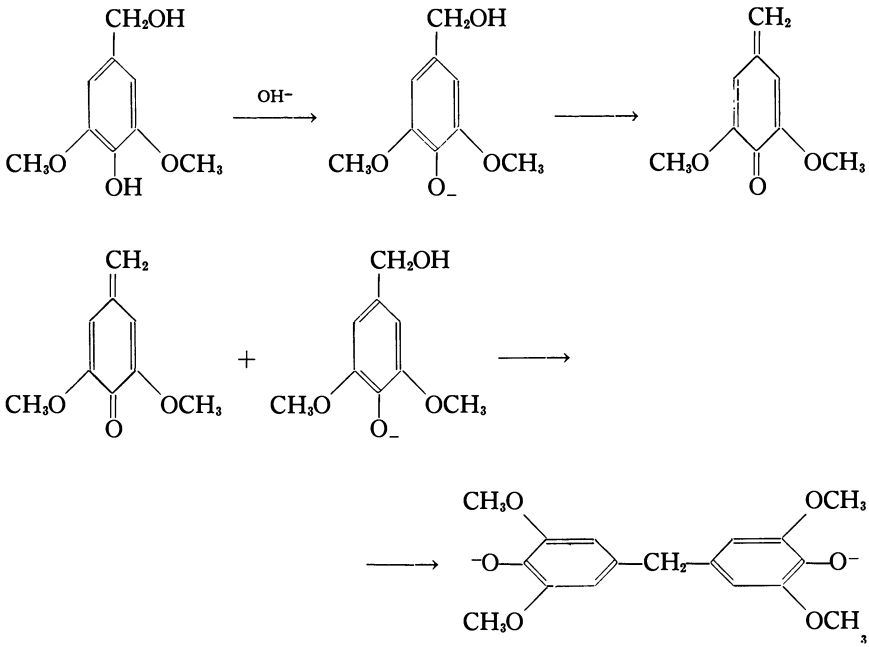
Suggested Reaction Mechanisms

At present the only colored product that has been identified in the reaction of syringyl alcohol with aqueous alkali is 2,6-dimethoxyquinone. No evidence exists that dimeric chromophoric structures such as a diphenoquinone or a stilbenequinone, which have been found to be products in the oxidative reactions of phenols in other studies (*1*, *3*, *15*, *23*), are also products of this reaction. However, with the identification of 2,6-dimethoxyquinone and the two colorless products, bis-4-hydroxy-3,5-dimethoxyphenylmethane and syringaldehyde, one of the logical pathways for the reaction is suggested and discussed.

Hästbacka (*13*) proposed the first stage in the reaction between vanillyl alcohol and aqueous sodium hydroxide as the formation of the quinonemethide from vanillyl alcohol. Subsequently, a molecule of quinonemethide reacts with a molecule of vanillyl alcohol forming diguaiacylmethane.

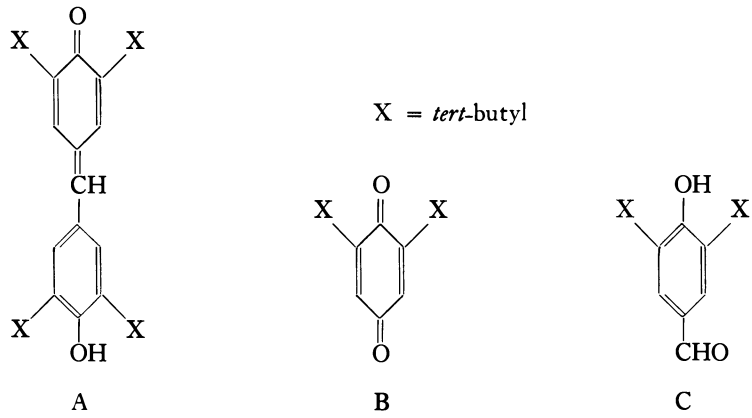
The same mechanism is proposed for the reaction between syringyl alcohol and aqueous sodium hydroxide to form bis-4-hydroxy-3,5-dimethoxyphenylmethane under the conditions used in this study. This mechanism is shown in Scheme I.

Kharasch and Joshi (*15*) have shown that when 4,4′-dihydroxy-3,5,3′,5′-tetra-*tert*-butyldiphenylmethane is treated in ethanolic potassium hydroxide under oxygen, A, B, and C are products. (The aforementioned compound differs from bis-4-hydroxy-3,5-dimethoxyphenylmethane, possessing *tert*-butyl groups in place of the methoxyl groups of bis-4-hydroxy-3,5-dimethoxyphenylmethane.)



Scheme I. Suggested mechanism for the formation of bis-4-hydroxy-3,5-dimethoxyphenylmethane from syringyl alcohol and aqueous sodium hydroxide

Since structures analogous to B and C have already been separated and identified in this study and since spectral analyses of separated but unidentified products indicate the possibility of structures similar to A, Scheme II is proposed for the reaction of bis-4-hydroxy-3,5-dimethoxyphenylmethane under these alkaline conditions forming A′, B′ and C′.



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The validity of the reaction presented in Scheme II has been partially proved at this time. When bis-4-hydroxy-3,5-dimethoxyphenylmethane reacts with aqueous alkali under conditions similar to the reaction between syringyl alcohol and aqueous alkali in this study, 2,6-dimethoxyquinone and syringaldehyde are found among the reaction products.

Additionally, Kharasch and Joshi (*15*) observed that during the absorption of oxygen, the reaction mixture acquired a dark purple color which was discharged upon neutralization, forming a yellow color. They showed that the dark purple color was caused by the anion of A and suggested that the intensity of absorption probably was associated with resonance stabilization.

We noted earlier that the color reactions of an ethanolic reaction solution of syringyl alcohol and sodium hydroxide (Figure 1) and also an aqueous reaction solution of the same components are similar to the color reaction noted by Kharasch and Joshi in their study. In other words, the longer wavelength colors of the alkaline reaction solutions are discharged with the formation of a yellow color when the solutions are neutralized.

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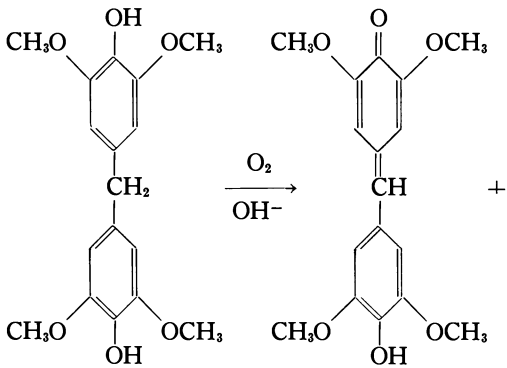
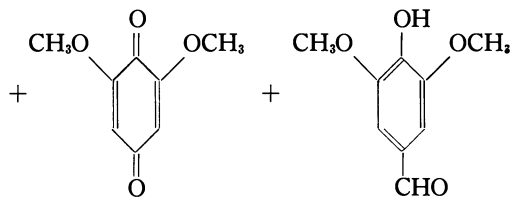


Bis-4-hydroxy-3,5-dimethoxyphenylmethane

A′

2,6,3′,5′-Tetramethoxy-4′-hydroxyphenyl-4-methylene-2,5-cyclohexadiene-1-one



B′
2,6-Dimethoxyquinone

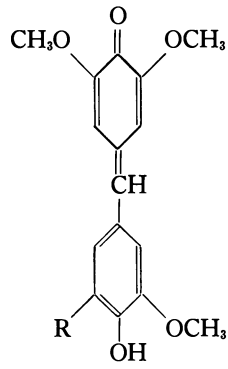
C′
Syringaldehyde

Scheme II. Suggested mechanism for the reaction of bis-4-hydroxy-3,5-dimethoxyphenylmethane under alkaline conditions

Thus, Structure A′ in Scheme II, which might be representative of unknowns IV–VII, could be responsible for the color changes of the reaction mixture of syringyl alcohol and alkali under varying pH conditions.

The question may arise whether diphenylmethane derivatives—e.g., bis-4-hydroxy-3,5-dimethoxyphenylmethane and diguaiacylmethane, are realistic lignin models. Pertaining to this study, the models are realistic if they occur in lignin *in situ* or if they are artifacts formed in any of the various alkaline pulping processes.

In summarizing the conclusion of other workers, Gierer *et al.* (*11*) state that 2,4′-dihydroxydiphenylmethane and 4,4′-dihydroxydiphenylmethane are thought to arise in lignin during alkaline cooking by condensation of *p*-hydroxybenzyl alcohol or *p*-hydroxybenzyl alkyl ether structures with phenolic units at their free 5-position and with other *p*-hydroxybenzyl alcohol structures, respectively. Recently, Parker (*19*) has obtained evidence by vapor phase chromatography that bis-4-hydroxy-3,5-dimethoxyphenylmethane is a dimeric reaction product in the alkaline hydrogenation of maplewood. Thus, the results of several lignin researchers support the view that diphenylmethane derivatives are realistic structures which may be formed when wood is treated under alkaline conditions.



AA

From a practical viewpoint, perhaps diphenylmethane derivatives are formed at the extremities of lignin fragments in alkaline pulps. The derivatives might then react as shown in Scheme II, forming colored products such as AA, in which R represents the remainder of the lignin fragment.

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samples of methoxyquinone, vanillic acid, 2,6-dimethoxyquinone, and 3,4,5-trimethoxybenzyl alcohol. The authors wish to express their appreciation to J. Smid for his cooperation in conducting the reaction of syringyl alcohol and alkali.

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The experimental work involving the determination of products in the reaction of vanillyl alcohol and sodium hydroxide was performed by William B. Mucklow.

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9

Infrared Spectroscopy of Lignins. IV

Isolation of Lignins by Solvolysis in Acetals

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Simple acetals of acetone (2,2-dimethoxypropane and 2,2-diethoxypropane), with HCl in dioxane, extracted 50–60% of the Klason lignin from both spruce- and birchwood by a continuous (Soxhlet) procedure. Infrared spectra of the isolated lignins suggested the presence of acetal groups. Relative rates of extraction revealed that the mechanism was different from hydrolysis, alcoholysis, and acetonolysis and that the extent of degradation of the wood cellulose affected neither the reaction rate nor lignin yield. Hence, the extraction required breaking covalent bonds between lignin and carbohydrate, and the results were consistent with the hypothesis that the links might be acetal groups.

At the present stage of development of lignin chemistry, there is little need for inventing new laboratory methods for extracting lignin from wood. However, the mechanism of extraction merits intensive study since little is known about how lignin and carbohydrate are joined in their natural state. In fact, none of the existing ideas of possible lignin-carbohydrate bonds or of lignin structure could have predicted our main findings —i.e., that extracting wood with anhydrous dioxane containing an acetal and hydrogen chloride would produce a higher yield of lignin and at a much greater rate than hydrolytic, alcoholytic, or acetonolytic reactions in dioxane.

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In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

In all extractions, we used dioxane as the extracting solvent. However, dioxane alone or even anhydrous dioxane and hydrogen chloride will not extract appreciable quantities of lignin from wood. Rather, the extraction depends upon the presence in dioxane of both an acid catalyst (usually hydrogen chloride) and any of the various solvolytic agents—water, alcohols, ketones, and now acetals. Hence, the term "dioxane lignin" as commonly used is probably a misnomer, and more correct terminology might be hydrolysis, alcoholysis, ketonolysis, or acetalolysis lignins, depending upon the solvolytic agent employed.

We studied the reactions of wood with various solvolytic agents because our earlier investigation suggested (*2*, *5*) that isolating lignin by hydrolytic methods required breaking a covalent bond which generated a new keto group in the lignin. The bond might be an acetal, such as proposed 40 years ago by Holmberg and Runius (*17*), or a benzyl ether, as found by Freudenberg (*12*, *13*) in his biosynthetic experiments. Our conclusions had been drawn from the results of infrared spectroscopic studies of both bound and isolated lignins.

Infrared spectra of isolated lignins exhibit an absorption band in the region 1700–1720 cm.$^{-1}$ While doubt still exists as to precisely which groups in dioxane or milled wood lignins are responsible for this absorption, clearly (*16*) there is at least some contribution from nonconjugated keto groups in the β-position of the phenylpropane side chain.

In contrast, differential infrared spectra of lignins in woods and pulps exhibit no absorption bands at 1700–1720 cm.$^{-1}$ (*2*, *5*). This observation has been confirmed recently by Michell, Watson, and Higgins (*21*). Thus, unconjugated β-keto groups (II) (Figure 1) arise only during isolation, and the mechanism of formation from Freudenberg's benzyl ether lignin-carbohydrate bond (I) with a guaiacyl (or any other) ether group on the β-carbon (*1*), might be: (1) Hydrolysis to the benzyl alcohol; (2) Dehydration to form an enol-ether; (3) Further hydrolysis to produce a β-keto group (II). The postulated dehydration step, occurring in an aqueous medium under mild conditions, is open to criticism. A similar mechanism would operate if the carbohydrate were joined to lignin on the β-carbon (III), but the presence of such a structure is far less likely than the benzyl ether (I).

The simplest interpretation might be that the lignin and carbohydrate are joined through a straightforward acetal link (IV) (*17*), but no direct evidence has ever been found for the existence of acetal groups in lignin. Nevertheless, in our work we have continued to consider the acetal bond as an alternative explanation of the observations.

Of course one cannot neglect the possibility that the keto group may arise, not from a bond between lignin and carbohydrate but from the hydrolysis of internal bonds in the lignin (*21*), and we intend to pursue this point in later studies. However, since there seems to be a relationship

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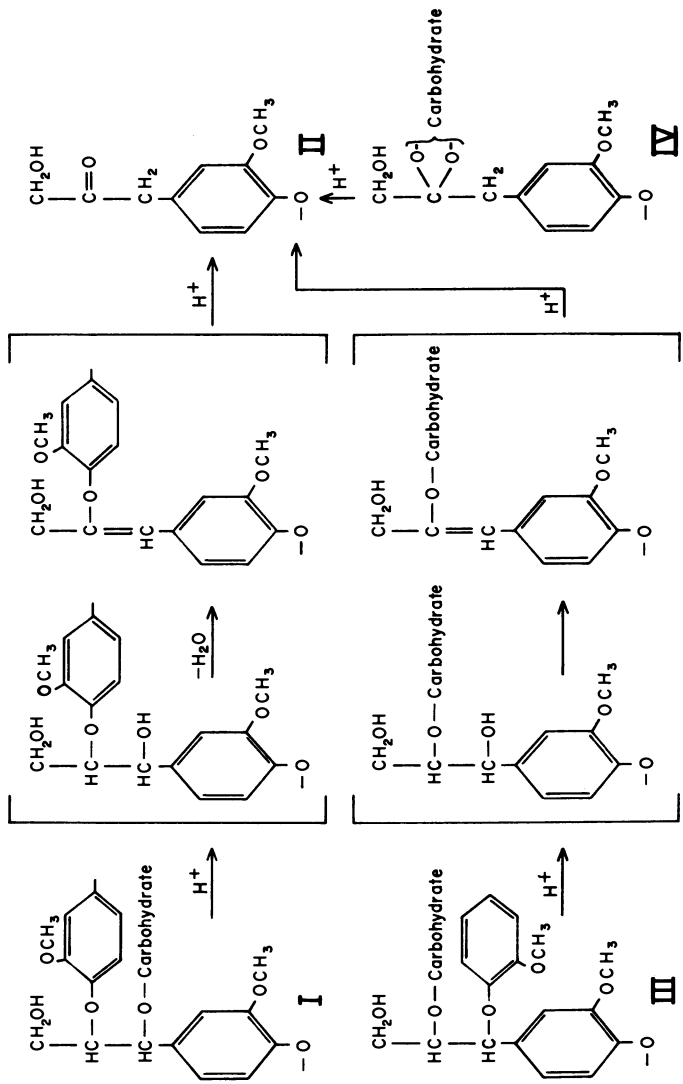

Figure 1. Proposed mechanism for the formation of β-keto groups

between the process of isolation and the generation of the keto group, we tend to favor the notion of the keto group's being involved in a lignin-carbohydrate bond.

Searching for evidence on the nature of the bond, we conducted a spectroscopic study of lignins isolated from wood by ethanolysis (*9*) and found, as expected, that β-keto groups did not appear in the lignins until

they had been hydrolyzed. So far, a quantitative analysis of ethoxyl groups introduced by ethanolysis has not produced any clear-cut results which might favor either the benzyl ether or the acetal bond hypothesis of the lignin-carbohydrate link. However, further consideration of the possibility of an acetal bond led to the suggestion that it should break on solvolysis in aldehydes or ketones and should undergo transacetalization with other acetals. Whether the benzyl ether bond might do the same is not self-evident, and we are undertaking suitable model experiments.

Experimental

Analytical Methods. Microanalyses ($C_xH_yOCH_3$, $C—CH_3$) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Methoxyl and ethoxyl were determined simultaneously, using the method (slightly modified) developed by Cobler, Samsel, and Beaver (*10*) for determining alkoxyl groups in alkyl cellulose ethers. A quantity of 20–30 mg. lignin was suspended in a solution of 2 grams of phenol and 6 ml. of HI, and the mixture was heated at 150°C. for 1 hour in an atmosphere of nitrogen. Liberated alkyl iodides were distilled through a washing device, containing water, to a trap containing 2 ml. of 2,2,5-trimethylhexane cooled by dry ice in acetone. Of this solution 50 μl. were used for analysis on the gas chromatograph (Perkin-Elmer vapor fractometer, model 154) on a column of diisodecyl phthalate (Perkin-Elmer column A) at 75°C. Curves for quantitatively measuring ethyl and methyl iodides had been prepared previously by using the following as standards: methyl iodide, ethyl iodide, *p*-methoxyphenol, *p*-ethoxyphenol, and vanillin.

Infrared spectra were determined on a Unicam SP-100 prism-grating spectrometer. Spectra of solid samples were measured by the KBr disc technique in discs of 16 mm. diameter. Each disc contained 1.6 mg. of sample in 400 mg. of KBr.

Viscosities of samples of cellulose were measured as 0.5% solutions in cupriethylenediamine by the viscosity pipet method (*28*).

Reagents. All reagents except 2,2-diethoxypropane were commercial products and were dried and distilled before use. The 2,2-diethoxypropane was prepared by the method of Claisen (*7*, *9*).

Extracting Lignin with Benzaldehyde. A solution of the required normality of acid (*see* Table I) was prepared by passing dry HCl gas into dioxane. To 90 ml. of this solution, 10 ml. of benzaldehyde and 5 grams of sprucewood (previously extracted with alcohol-benzene then with hot (60°C.) running water, and dried in vacuo over P_2O_5) were added, and the mixture was heated with stirring at 90°C. for 2 hours in a nitrogen atmosphere. The mixture was allowed to cool, then was filtered, and the filtrate was concentrated under vacuum. The residue was dissolved in about 10 ml. of dioxane and poured into 100 ml. of ether to precipitate the lignin, which was then separated by centrifugation. Purification was conducted by repeating the precipitation procedure three times, after which the product was dried in vacuo.

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Table I. Preliminary Experiments on Black Spruce[a]

No.	*Solvolytic Agent*	*Solvent*	*Acid*	*Concentration of Acid, N*	*Reaction Time, hrs.*	*Extract Yield, %[b]*
1	Benzaldehyde	Dioxane	HCl	0.2	2	3
2	—	Dioxane	HCl	0.2	2	3
3	Benzaldehyde	Dioxane	HCl	0.02	5	0.5
4	Benzaldehyde	Dioxane	*p*-tosyl H	0.05	2	0.8
5	2,2-Dimethoxypropane	Dioxane	HCl	0.2	5	5
6	2,2-Dimethoxypropane	DMSO[c]	HCl	0.5	3	7
7	2,2-Dimethoxypropane	DMSO	HCl	0.1	5	6

[a] All extractions were done at 90°C.
[b] As % of original wood.
[c] DMSO = dimethyl sulfoxide.

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Continuous Extraction of Lignin. The extraction vessel was a three-necked 500-ml. round-bottomed flask, with a Soxhlet extractor fitted to the center neck. Above the extractor a condenser was attached vertically, and at its top end a glass tube led to a pair of wash bottles in series. The wash bottle farthest from the condenser contained concentrated H_2SO_4; its purpose was to prevent moisture from entering the system. One side neck of the flask held a capillary tube which led dry nitrogen into the solution. The second side neck contained a Claisen head adapter through which a glass tube extended into the bottom of the flask, and led, at its other end, through a stopcock to a flask which could be evacuated through a side arm in order to draw the extract from the extraction flask without disturbing the system.

A sample of 5 grams of wood meal (100 mesh, dry, extractive-free) was placed in the cup of the extractor, and the entire system was flushed with nitrogen to displace the air. Then a solution of 0.95 gram of dry HCl in 130 ml. of dioxane (0.2*N*) and 20 ml. of the required solvolytic agent were placed in the extraction flask through a dropping funnel in the side arm of the Claisen adapter. With a constant flow of dry nitrogen through the system, the extracting solvent was heated by an electric mantle to effect extraction. During the extraction the temperature of the solution at the reaction site (i.e., in the wood meal) was measured as 80° ± 3°C., and the acidity of the solvent in the flask decreased because of differences in relative volatility and absorbability in wood meal. The acidity at the reaction site was measured several times, and the highest value was found to be 0.33*N*.

After 1–2 hours of extraction, the extract was sucked into the side flask, and fresh extractant was added. Extraction was then continued for the required time (Table II).

The extracts were combined, a large excess of sodium bicarbonate was added, and the mixture was filtered through sintered glass. The dark, clear solution was concentrated in vacuo at a temperature less than 50°C., to a volume of about 20 ml., and the concentrate was poured with stirring into

150 ml. of petroleum ether (b.p. 30°–60°C). After centrifugation, the precipitated lignin was stirred with 10 ml. of dioxane, and the insoluble portion was separated and washed with 5 ml. of dioxane. The combined dioxane solutions were added to 150 ml. of petroleum ether, and the resulting suspension was centrifuged.

Two final purification steps involved precipitation, first in ether (150 ml.) then in water (150 ml.), both times from 15 ml. of a clarified dioxane solution.

The suspension obtained from dioxane-water required high speed centrifugation (10,000 r.p.m. for 30 minutes) to separate the lignin. The product was dried in vacuo over P_2O_5.

Table II. Continuous Extraction of Black Sprucewood with Dioxane (0.2*N* HCl)

	Solvolysis Agent		
	Water	*Methanol*	*Acetone*
Extraction time, hrs.	5	5	3
Yield of Klason lignin, %	14	33	25
Methoxyl[a] in isolated product, %	13.8	16.3	14.6

[a] Gas-liquid chromatography method; modified Zeisel.

Determining the Rate of Extraction. The extraction rates were determined at 90°C. under conditions of batch extraction with stirring under nitrogen. Samples of 5 grams each of dry sprucewood meal were used. The solvent mixture contained 130 ml. of dioxane and the specified amount of solvolytic agent (*see* Figure 2) and was made 0.2*N* in HCl by adding the gas. The mixture was brought to temperature as quickly as possible; 2-ml. aliquots were removed at 10-min. intervals, transferred immediately to centrifuge tubes, and centrifuged. A quantity of 10 μl. of the clear supernatant was diluted with 3 ml. of methanol, and optical density was read at 280 mμ in the Beckman DU spectrophotometer against a reference of 10 μl. of pure solvent mixture in 3 ml. of methanol.

Degradation of Cellulose. Cotton cellulose, purified by a standard method (*11*) was used as the starting material. The procedure was the same as for the continuous extractions of lignin from wood.

Hydrolysis of 2-Methyl-2-benzyl-1,3-dioxolane. A sample of 1 gram of the dioxolane was suspended in 20 ml. of 50% dioxane which contained enough HCl to make it 0.5*N*. The suspension was heated at 60°C. and became a clear solution in 1–2 minutes. Total heating time was 5 minutes. The product was identified as 3-phenyl-2-propanone by the properties of its 2,4-dinitrophenylhydrazone and semicarbazone derivatives.

Hydrolysis of the "Acetal" Lignins. The lignins (400 mg.) were dissolved in a solution of 28 ml. of dioxane and 12 ml. of water acidified with hydrochloric acid to a concentration of 0.5*N*, and the solution was boiled under reflux for 2 hours. After cooling, the solution was poured into water (about 200 ml.), the precipitate was separated by centrifugation and purified by reprecipitation from dioxane (15 ml.) into water (150 ml.). After centrifugation the lignin was dried in vacuo over P_2O_5 at 65°C.

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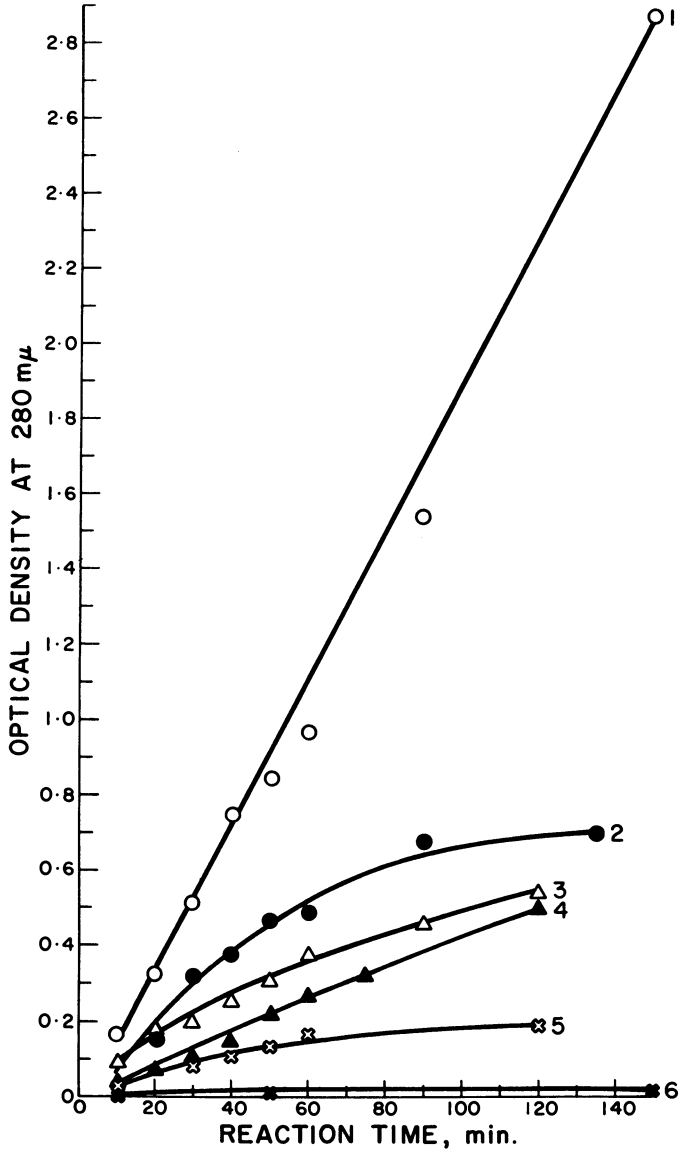

Figure 2. Relative rates of lignin extraction as measured by the optical density at 280 mμ. All reactions under nitrogen at 90°C and with 0.2N HCl in dioxane.

1. *Dimethoxypropane (13 vol. %)*
2. *Water (13 vol. %)*
3. *Methanol (13 vol. %)*
4. *Acetone (13 vol. %)*
5. *Methanol (2 vol. %)*
6. *Dimethoxypropane (13 vol. %), no HCl*

Results and Discussion

The Reaction and its Product. To study extraction by aldehydes, benzaldehyde was chosen as the solvolysis medium in preliminary experiments because it was known to be a solvent for dioxane lignin (*23*) and because it had no α-hydrogens which might enable it to polymerize in the presence of hydrogen chloride. The possibility that benzaldehyde might condense with lignin (*22*) was considered negligible because in these experiments the concentration of acid was low and the temperature was no higher than 90°C. Under these conditions, lignin was, in fact, extracted from wood. However, the crude product contained an appreciable amount of entrained, free benzaldehyde and proved difficult to purify. Ultimately, only a small amount of lignin, relatively pure as judged from its infrared spectrum, was obtained.

An unsuccessful attempt was next made to simplify the problem of purifying the product by using dioxane as the extracting solvent with only enough benzaldehyde for solvolysis. Finally, on the assumption that an acetal should be as effective in transacetalization as an aldehyde or ketone, the benzaldehyde was replaced by 2,2-dimethoxypropane. In several experiments the hydrogen chloride was replaced by *p*-toluenesulfonic acid; also, dimethyl sulfoxide was tried instead of dioxane. All these experiments are summarized in Table I, and they lead to the following conclusions:

(1) Using benzaldehyde did not give any higher yields than dioxane alone (Experiment 3) and was probably entirely without effect;

(2) Using *p*-toluenesulfonic acid as a catalyst offered no advantage over hydrogen chloride;

(3) Using 2,2-dimethoxypropane gave better yields of product, and the lignin was easy to purify;

(4) Dimethyl sulfoxide offered no advantage over dioxane.

In the three experiments with 2,2-dimethoxypropane, the yield of extract, based on Klason lignin, was 15–20%. While this was comparable with yields obtained from sprucewood by the conventional dioxane-water extraction when low concentrations of acid are used (*24*), consideration of transacetalization as an equilibrium process led to the idea that a continuous extraction might give higher yields by removing the liberated lignin from the reaction site. Accordingly, the extractions were then performed under nitrogen in a Soxhlet extractor, arranged so that water could not enter the system.

Paralleling our use of the Soxhlet extractor, Perrenoud (*25*) performed a series of sequential wood extractions with dioxane containing aqueous hydrochloric acid. After seven treatments, he isolated 92% of the lignin that had been in the original wood. We have not tried to duplicate his experiments but instead have conducted several extractions with dioxane-HCl and water, methanol, and acetone, respectively, in the Soxhlet ex-

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tractor; the lignin yields ranged from 14% (water) of Klason lignin in the wood to 33% (methanol) (Table II). In contrast, yields of pure lignin extracted by dioxane-acetal-HCl in the Soxhlet extractor were from 50–60% (Table III).

Table III. Continuous Extraction of Wood with Dioxane, Acetals, and 0.2*N* HCl

Species	*Black Spruce*		*White Birch*	
Solvolysis agent	*2,2-Dimethoxypropane*	*2,2-Diethoxypropane*	*2,2-Dimethoxypropane*	*2,2-Diethoxypropane*
Extraction time, hrs.	10	5	3	3
Yield, of lignin, purified with dioxane-ether, %[a]	86.3	89.9	~80	~80
Yield of lignin, purified with dioxane-water, %[a]	~50	57.5	—	—
Analysis of Lignins, %				
Carbon	62.24	61.05	59.27	58.62
Hydrogen	6.29	6.47	6.44	6.85
Methoxyl by G.L.C.[b]	18.75	12.56	21.28	15.49
Ethoxyl by G.L.C.	trace	6.38	trace	5.23
Total alkoxyl by G.L.C.	18.75	18.94	21.28	20.72
Methoxyl by microanalysis[c]	14.42	14.24	20.85	19.67
C-methyl	4.76	6.09	3.64	5.73

[a] As % of Klason lignin.
[b] Gas-liquid chromatography method; modified Zeisel.
[c] Conventional Zeisel determination.

The results from analyzing the "acetal" lignins for carbon and hydrogen (Table III) fell within a reasonable range, and the values for methoxyl, as determined by the conventional micromethod, gave the impression that methoxyl might neither have been lost nor gained. However, we had anticipated some increase in alkoxyl, and in order to determine its extent, we had used diethoxypropane in some experiments in place of the dimethoxy compound; we then analyzed the products by a gas-liquid chromatography. The results of these latter experiments suggested that some of the original methoxyl in the lignin had been lost while some additional alkoxyl had been taken up from the solvent.

It was to be expected that gas-liquid chromatography would give higher values for alkoxyl than the conventional micromethod because in the latter the percentages had been calculated as though all the alkoxyl had been methoxyl. When the alkoxyls by gas-liquid chromatography were recalculated as methoxyl, there was good agreement in the values found for the birch lignin (19.1% by G.L.C.; 19.67% by the conventional method). However, in the case of spruce lignin, we cannot explain the differences between the results found by the two methods; the likelihood

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of experimental error is small because there was no change when both the microanalysis and the gas chromatographic analysis were repeated.

The content of C-methyl groups was analyzed (Table III) to determine whether or not acetone had condensed with the lignin. The values recorded are to be compared with the value of 3.72% given in the literature for "acetone lignin" (*29*).

Mechanism of Isolation. In view of our correct prediction that acetals of acetone would extract lignin from wood, we were tempted to conclude that the hypothesis had some degree of validity. However, we have overlooked completely the possibility and the supporting evidence (*6*, *14*, *15*, *18*, *19*, *20*) that lignin and carbohydrate are joined through glycoside bonds. Such bonds are a form of acetal and might be expected to undergo the type of transacetalization we have performed. We have no evidence to offer on this point but plan to study it through reactions of appropriate model compounds.

In any event, the first difficulty in explaining the reaction in terms of our prediction is that it failed with benzaldehyde; this suggests that extraction with acetals may have occurred by a mechanism other than the one postulated.

Possibilities include (a) the hydrolysis of the lignin-carbohydrate bond by small amounts of water present in the wood despite all precautions to make the system anhydrous, (b) the dehydration of carbohydrates under these conditions to produce water and hence hydrolytic conditions, (c) transacetalization of the extracting acetal with carbohydrates to liberate alcohol and create conditions of alcoholysis, and (d) transacetalization of the extracting acetal with free or bound keto groups in the wood to liberate acetone and create conditions of acetonolysis.

To investigate these points we performed a series of batch extractions, each with a different pair of solvents, and determined the rates of lignin extraction by measuring the ultraviolet absorption (at 280 mμ) of aliquots of solution taken at time intervals. The results (Figure 2) showed clearly that the rate of lignin extraction by reaction with dimethoxypropane was far greater than with water, methanol, or acetone. Furthermore, the rate was linear for 3 hours while reactions with other reagents showed decreasing rates during the same period. Thus, the mechanism of lignin extraction with dimethoxypropane must be completely different from the mechanism when the other reagents are used.

However, these results do not prove that a chemical bond is being broken between lignin and carbohydrate for we must consider the hypothesis developed in modern terms by Pew (*26*, *27*).

Pew found that the residue, mainly lignin, from unground wood digested by cellulytic enzymes was insoluble in 2*N* sodium hydroxide while the residue from finely ground wood was freely soluble (*26*). Also, spruce periodate lignin, normally insoluble in methyl cellosolve and in 0.1*N*

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sodium hydroxide, became somewhat soluble in both after milling (*27*). From this and other evidence, Pew concluded that protolignin is insoluble but may be rendered soluble by grinding or by a degradative reaction. In his words: "Spruce lignin as it exists in wood, regardless of its association with other wood components, *is a highly insoluble substance and is not likely to dissolve in any solvent with which it does not react chemically*" [his italics]. Pew's results and arguments support the "incrustation" or "snake cage resin" effect as the important factor in binding lignin to carbohydrate.

The idea of lignin's reacting chemically to become solubilized has some support in our own unpublished work (*4*) in which periodate lignins from various sources were extracted with acidic aqueous dioxane, whereupon they dissolved to a considerable extent, and the soluble portion, after precipitation, showed all the characteristics (analytical and spectroscopic) of the corresponding dioxane lignins, including enhanced absorption at 1710 $cm.^{-1}$

In this work we have, in a preliminary way, extracted periodate lignin by the continuous dioxane-dimethoxypropane-HCl procedure and obtained only about 11% of a soluble material which had the same infrared spectral characteristics as the lignin isolated from wood. The gel-like residue showed evidence of having undergone the same reaction but remained insoluble. This seemed to indicate that the reaction alone was not enough to confer solubility.

By analogy to Pew's grinding procedure we considered the possibility that lignin was being released because the cellulose was hydrolyzed, and we examined this point by determining the effect of the reaction on the viscosity of cellulose. When we extracted pure cotton cellulose with dioxane-dimethoxypropane-HCl for 3 hours, we found that viscosity decreased greatly.

Moreover, we found that the viscosity loss was equally great (Table IV) when methanol, acetone, or water were used in place of dimethoxypropane, or even when dioxane and HCl were used alone. (Despite large decrease in viscosity, the loss in weight of the cellulose was always only about 1–2%). If the extraction of lignin by dioxane depended only upon the breakdown of the carbohydrate, we might have expected that equal degrees of degradation would have produced more nearly equal rates of extraction, but they did not.

We believe that all these results mean that the snake-cage resin hypothesis does not explain our reactions, and we have eliminated it from further consideration. Thus, the idea that an actual chemical bond between carbohydrate and lignin must be broken in order to liberate the lignin became a stronger possibility.

Determining the nature of the bond involves determining the reaction site on the lignin molecule, and to attempt this, we have recorded infrared spectra of the products.

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Table IV. Viscosity of Cotton Cellulose Extracted with Various Reagents[a]

Reagent Mixture	*Viscosity[b]*
None (starting material)	42.2
Dimethoxypropane-dioxane-HCl	2.8
Acetone-dioxane-HCl	2.5
Methanol-dioxane-HCl	1.9
Water-dioxane-HCl	2.4
Dioxane-HCl	2.7

[a] Extraction time, 3 hrs., conc. HCl, 0.2*N*.
[b] Centipoise; 0.5 C.E.D.

The main differences in the infrared spectra of spruce lignin (I in Figure 3) isolated by means of dimethoxypropane and of conventional dioxane lignin (II in Figure 3) are three new absorption bands in the former: a strong band at 1085 cm.$^{-1}$ and two weak but sharp bands at 892 and 875 cm.$^{-1}$ We had previously encountered the band at 1085 cm.$^{-1}$ in differential spectra of protolignins (III in Figure 3) but suspected then that it was an artifact (*5*). More recently, we found the same band in spectra of lignins extracted from wood by anhydrous ethanol and hydrogen

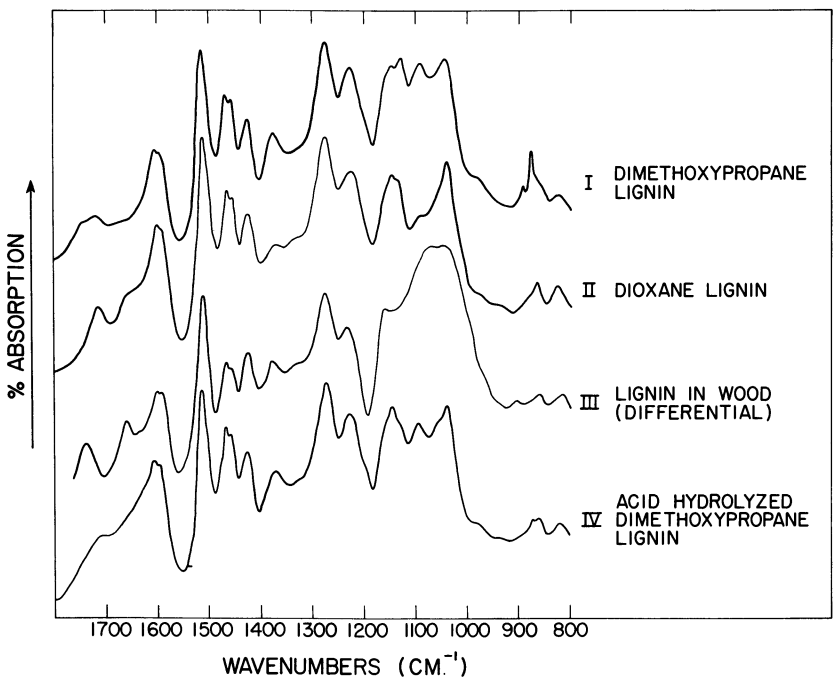

Figure 3. Infrared spectra of lignins

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chloride, and of dioxane lignins subjected to ethanolysis (*3*); we concluded that it might represent an ether or acetal bond absent from milled wood lignins, conventional dioxane lignins, or other isolated lignins. As a model experiment we hydrolyzed the ethylene glycol acetal of phenylacetone, which has no absorption band at 1720 cm.$^{-1}$ but has a strong band at 1095 cm.$^{-1}$ The hydrolysis product, phenylacetone itself, has a strong band at 1720 cm.$^{-1}$ and none at 1095 cm.$^{-1}$ (Figure 4). Although not proof, all these results considered together suggest that the band at 1085 cm.$^{-1}$ in the spectrum of lignin may be caused by an acetal grouping of the type and at the location postulated.

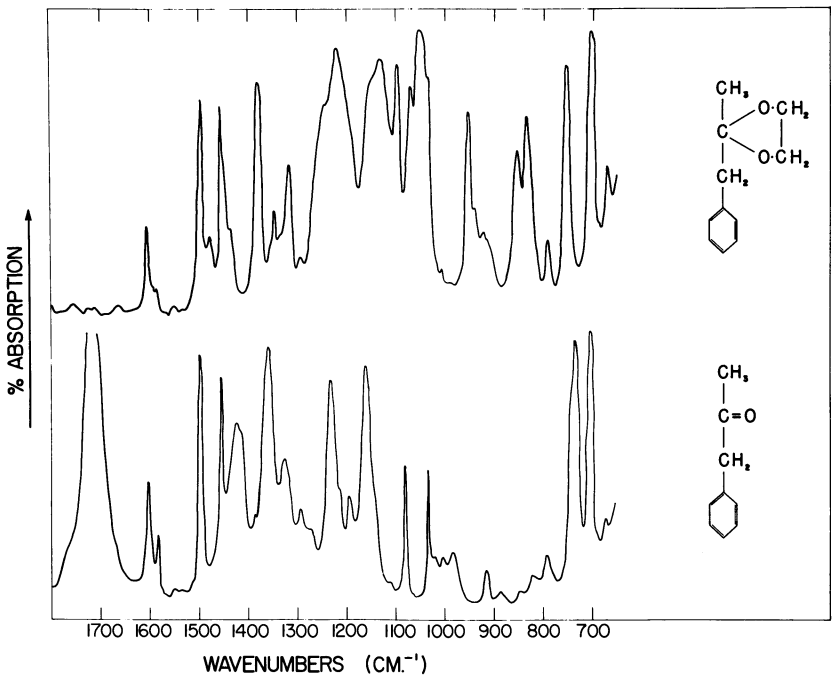

Figure 4. Infrared spectra of model compounds

However, if the band is caused by an acetal group, then we might expect it to be removed readily by hydrolysis in aqueous acid. Treating the dimethoxypropane lignin with 0.5*N* HCl in aqueous dioxane at reflux temperature did reduce the intensity of the band at 1085 cm.$^{-1}$ (IV in Figure 3) while the absorption at 1715 cm.$^{-1}$, ascribed to the nonconjugated keto carbonyl, increased. Yet the intensity of absorption at 1085 cm.$^{-1}$ was not reduced to the level of dioxane lignin.

The interpretation was further complicated when we measured the alkoxyl contents of the lignins before and after hydrolysis in aqueous acid.

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Table V. Hydrolysis of Acetal Lignins (Alkoxyl Measurements)

	Dimethoxypropane Lignin, %	*Diethoxypropane Lignin, %*
Methoxyl on isolation	17.05	12.06
Methoxyl after hydrolysis	16.80	15.58
Ethoxyl on isolation	0.1–0.2	7.32
Ethoxyl after hydrolysis	1.01	4.02

As Table V shows, the diethoxypropane lignin lost only half of its ethoxyl content and gained a corresponding amount of methoxyl. The increase in methoxyl may perhaps be explained if, in future studies of the soluble hydrolyzate we find large fragments of lignin without methoxyl. The apparent retention of ethoxyl may be related to a similar unexpected finding in our earlier studies on ethanolysis of lignins which also apparently failed to give up all of their ethoxyl on hydrolysis (*3*, *8*). Since the method had been carefully checked with known compounds and found to be accurate, we suspect that in these hydrolysis products something other than true ethoxyl is being measured. Our suspicion is strengthened by the observation (Table V) that the methoxyl content of dimethoxypropane lignin decreased only by 0.25% on hydrolysis, and analysis of the hydrolyzed lignin showed 1.01% ethoxyl where no ethoxyl existed before, or could have been expected to exist. We are investigating the possibility that lignins which have undergone extraction and hydrolysis may contain side-chain groupings capable of undergoing retroaldol reactions in the presence of hydrogen iodide to release acetaldehyde which might then become reduced and converted to ethyl iodide (*8*).

Despite the anomalies, one key point does emerge when this work is compared with alcoholysis studies. Ethanolysis lignin has a much higher ethoxyl content than diethoxypropane lignin (spruce ethanolysis lignin contains 14.6% ethoxy (*3*, *8*)), and this is additional proof that lignin isolated by acetals is different from lignin isolated by alcohols.

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Conclusions

Our conclusions may be summarized as follows:

(1) Acetals such as dimethoxypropane and diethoxypropane with hydrogen chloride in dioxane extract lignin from wood much more rapidly than methanol, acetone, or water. When the extraction is performed in a Soxhlet extractor, unusually high yields of lignin are obtained.

(2) Although carbohydrate is extensively degraded during the extraction, this degradation does not play any role in the extraction mechanism. Rather, cleavage of an acid-labile bond between lignin and carbohydrate seems to be involved in facilitating the extraction.

(3) Spectroscopic evidence suggests that the bond cleaved may be an acetal, but the possibility of a benzyl ether is not eliminated.

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(4) The spectroscopic evidence is complicated by the results of alkoxyl analysis, which, in fact, appear anomalous.

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Alkali-Catalyzed Reactions of Formaldehyde with Lignins

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Formaldehyde reacts with lignins in the presence of alkali both by substituting free 5-positions in the phenolic (guaiacyl) nuclei, and by Tollens reaction of the side chains bearing carbonyl groups. The distribution and location of hydroxymethyl groups were determined by comparing the reactivities of the lignins and their sodium borohydride-reduced and diazomethane methylated derivatives, respectively. CH_2OH (0.15 mole per OCH_3) was introduced into 5-positions of the guaiacyl units of milled wood spruce lignin—i.e., about half of the phenolic nuclei are uncondensed and reactive with alkaline formaldehyde. Kraft pine lignin took up 0.5 mole CH_2OH per OCH_3, mainly into ring positions, indicating that about one-third of the phenolic nuclei are uncondensed in 5-position. The phenol alcohols formed were determined colorimetrically.

As early as 1929 Ross and Hill (*32*) observed that wood meal previously soaked in formalin completely dissolved in 72% sulfuric acid. By dilution with water a formaldehyde lignin precipitated. The solubility of the formaldehyde lignin in concentrated sulfuric acid suggested (*33*) that formaldehyde occupied active centers of lignin which otherwise con-

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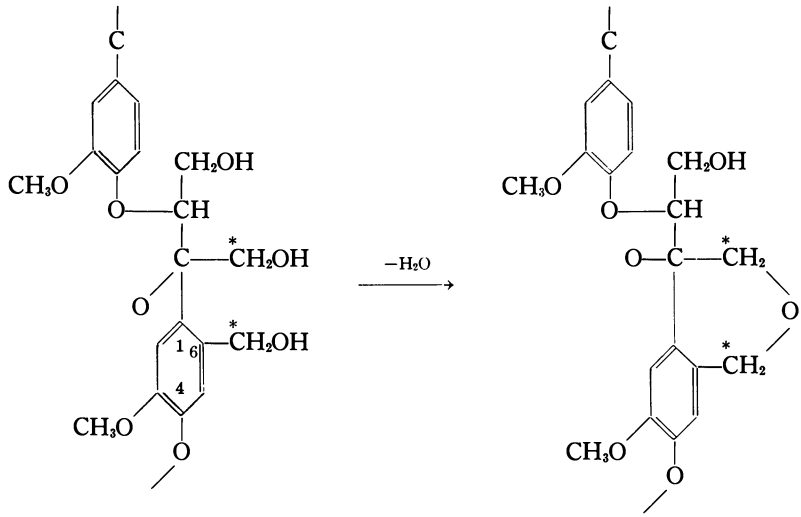
densed with each other to form the insoluble Klason lignin. Eisenbraun and Purves (*10*) found strong indication that formaldehyde lignin probably is substituted in the α-position of the side chain and in the 6-position of the ring.



The condensation of kraft lignin with formaldehyde in the presence of alkali was the subject of many early attempts to use this lignin as a Bakelite-type resin (*22*). Mikawa and co-workers (*30*) studied the reactions of some lignins and formaldehyde at various pH and found them to be approximately second order. Kraft softwood lignin and soda lignin had the highest reactivity, nitrolignin and chlorolignins reacted only slightly suggesting that nitration or chlorination substituted the formaldehyde-reactive centers of lignin. The structure of formaldehyde lignins was not investigated further.

The alkali-catalyzed reaction of lignin as a polyphenolic material with formaldehyde is the subject of this paper.

Reactive Sites in Lignin

On the basis of our present concept of lignin structure, generally two types of condensation reaction are expected to occur: A and B.

(A). Introduction of hydroxymethyl groups into position ortho to the phenolate groups—i. e., reaction with the activated free 5-positions of phenolic nuclei (Lederer-Manasse reaction) is expected to be the main reaction in alkali.

In the acid-catalyzed formaldehyde condensation, position 6 appeared to be the most reactive since in acid solution the relative electron density is

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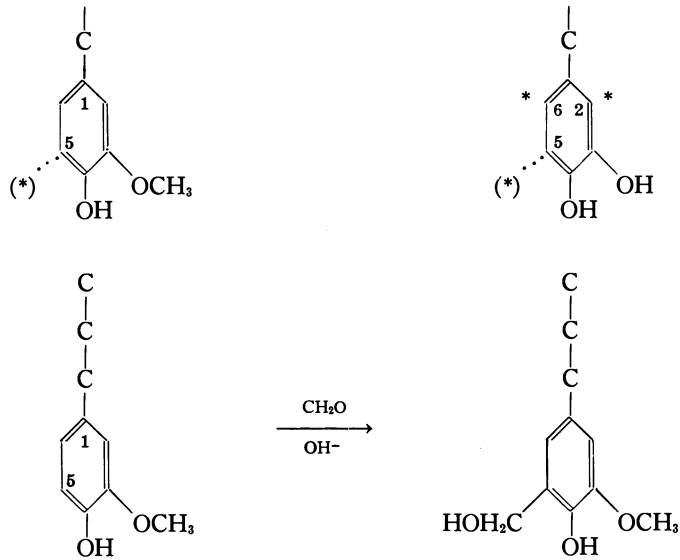
highest in position meta to the phenolic hydroxyl (cf. (*34*)). Also, it was immaterial for the reactivity of position 6 in acid solution whether the phenolic hydroxyl was free or it was connected to a C atom of another unit. Eisenbraun and Purves (*10*) estimated that just about every aryl propane unit of their spruce periodate lignin preparation took up a mole of formaldehyde in the ring 6-position. In alkali, however, only the phenolic portion of lignin is reactive, and there is a further restriction that the 5-position should not be substituted or condensed. Some lignins like kraft lignin also contain a few catechol units (*13*, *26*). In these units the 2- and/or 6-positions of the ring also can be activated.



(B). Lignin contains carbonyl groups in various positions of the side chain. Hydroxymethyl groups can be introduced into the neighboring positions by substituting their activated hydrogen atoms (Tollens reaction).

One of the main goals of this investigation was to differentiate between these two reaction possibilities in lignin.

Two lignin preparations were used in these experiments, milled wood spruce lignin (M.W.L.) prepared according to Björkman (*8*), and a kraft pine lignin fraction. Both preparations were characterized earlier (M.W.L., (*1*, *8*) kraft lignin (*26*)). Some pertinent data are given in Table I.

The groups are expressed as groups per 100 aryl propane units. The C_6-C_3 units are calculated from analytical composition. It is assumed that one aryl propane unit contains approximately one OCH_3 group in M.W.L. With kraft lignin the situation is more complicated. There are reasons to believe (*26*) that the average composition of the units should be

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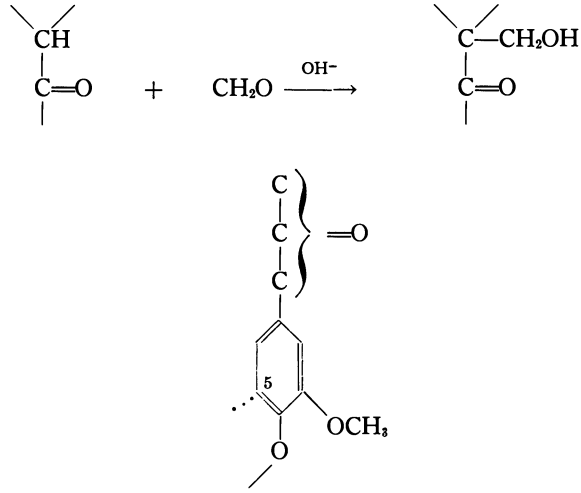

between C_6-C_2 and C_6-C_3. As an approximation we will compare here the reactivity of both lignins by using a common C_6-C_3 basis.

M.W.L. contains free phenolic (guaiacyl) hydroxy groups in about every third unit; kraft lignin contains about twice as much. In addition, probably about every 15th unit of kraft lignin has a catechol ring structure (*2*, *13*).

The side chains of lignins contain carbonyl groups as determined by NH_2OH, HCl reagent (*1*), and volumetric KBH_4 method (*21*, *28*). The distribution of the CO groups among different locations of the side chain was determined by spectrophotometric reduction $-\Delta\epsilon$ method (*6*). The

Table I. Some Structures in Lignin

Groups per 100 C_6-C_3 Units	*M.W.L. Spruce*	*Kraft Pine*	*Method Used*	*Method Ref.*
Calculated C_6-C_3 units	$C_9H_{8.8}O_{2.4}$ $(OCH_3)_{0.96}$	$C_9H_{7.9}O_{2.1}S_{0.1}$ $(OCH_3)_{0.82}$	Elemental Analysis	*26*
Total OH	120	120	Acetylation	Experimental
Guaiacyl OH	30	60	$NaIO_4$ Oxid.	*4*
2 × Catechol		12	Fe^{+2}, Colorim.	*2*, *13*
Total CO	20	15	NH_2OH, HCl Titr.	*21*, *28*
Coniferaldehyde	3	—	Volum. KBH_4	*21*, *28*
α-CO	7	5	Red. $\Delta\epsilon_r$	*6*
β-CO	10	10		
Free 5-positions of phenolic units	(a) 50%	(b) 25–40%	(a) Fremy salt oxid. (b) Mannich React.	*5* *31*

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amount and distribution of the CO groups is rather similar in M.W.L. and kraft lignins with two main exceptions: (a) the coniferyl aldehyde groups of the milled wood lignin have been destroyed during the alkaline cook, and (b) kraft lignin contains the α-CO groups almost exclusively in phenolic units while the opposite was true with M.W.L.

By means of Fremy salt oxidation, Adler and Lundquist (*5*) estimated that about half of the phenolic units contain free 5-positions in M.W.L. Mikawa (*31*), by Mannich reaction, obtained evidence that about 25–40% of the phenolic units in his sulfate lignin preparation contained no substituent in 5-position. In this investigation we also conclude that at least one-third of the phenolic units in our kraft lignin preparation has free 5-positions.

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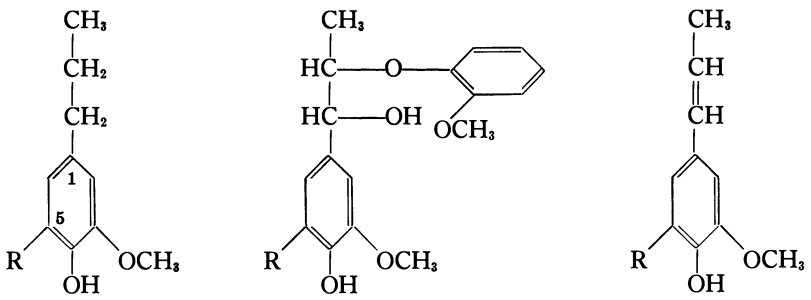
Model Reactions

To interpret the lignin-formaldehyde reaction properly, a series of comparative experiments was carried out to elucidate the behavior of model substances representing structural features of lignin possibly involved in this reaction.

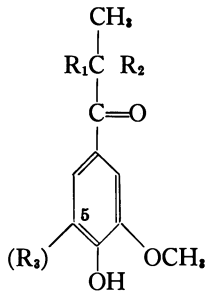


I II III

R = H, CH_2OH

Under optimum conditions (2 moles of CH_2O, 1 mole of NaOH per mole of phenol, 0.8 to 1*N* sodium hydroxide concentration, 3–4 days at room temperature) crystalline hydroxymethyl derivatives (R = CH_2OH) were obtained in very good yield from the simple guaiacyl-1-propane (I) as well as from the dimeric β-aryl ether model (II). The reaction products gave the blue color reaction with $FeCl_3$, characteristic of *o*-phenol alcohols. The reaction of isoeugenol (III) with formaldehyde gave an oily mixture; chromatographic investigation indicated that the hydroxymethyl derivative may have formed in about 50% yield. The conjugated C=C double bond deactivates somewhat the aromatic ring; a conjugated C=O in side chain α-position almost completely inhibits the reaction in position 5.

To find the best conditions for Tollens reaction, several model compounds were used containing CO groups in α- or β-side chain positions.



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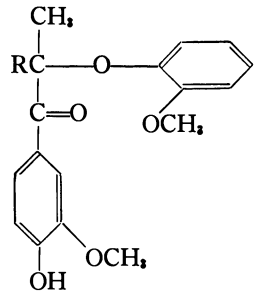

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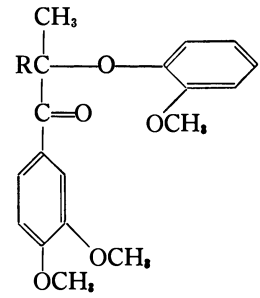

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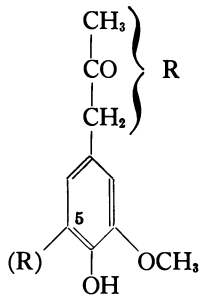
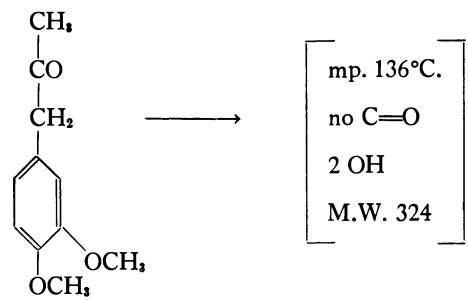
R, R_1, R_2 = H, CH_2OH



VII



VIII

The reaction in almost every case led to a mixture of hydroxymethyl substituted compounds (R = CH_2OH) unless only one hydrogen was available for carbanion formation. Also, more severe conditions were needed for optimal results (2 moles of NaOH, large excess of CH_2O, 2*N* sodium hydroxide concentration, 4–5 days at room temperature). From the dimeric models V and VI, having CO group in α-position, crystalline monohydroxymethyl derivatives were obtained with partial conversion but in good yield. The products did not give any $FeCl_3$ color reaction. Infrared evidence indicated that the hydroxymethyl groups are in the β-position. There was no principal difference between the mode of substitution of the phenolic and nonphenolic dimeric models, though the conversion of the phenolic V was definitely the higher. Hydroxymethylation of propioguaiacone (IV) resulted in a mixture, containing probably all three of the possible hydroxymethyl compounds. A dimethylol derivative (IV, R_3 = H, R_1 = R_2 = CH_2OH) crystallized out in small yield, and its structure was ascertained by oxidative degradation and infrared spectrum. One

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component of this mixture gave positive $FeCl_3$ reaction ($R_3 = CH_2OH$), indicating that the deactivating effect of CO group was suspended probably by the (double) CH_2OH substitution in the neighboring position.

Hydroxymethylation of guaiacyl acetone (VII) yielded an amorphous solid, probably a self-condensation product after being methylolated in several positions. Veratyl acetone (VIII) gave a crystalline product in good yield which had no CO group. It can be assumed that the CO group was reduced by a crossed Cannizzaro reaction, and a dimeric product was formed, whose structure is not known yet.

Summarizing the results of model studies, we found that phenolic models react easily with formaldehyde in Lederer-Manasse type of reaction unless the side chain contains conjugated electron-attracting groups. Double bonds in the α-position somewhat deactivate the ring, and α-CO groups definitely decrease the reactivity of a ring 5-position towards electrophilic substitution. However, carbonyl groups activate the neighboring side chain positions. The extent and rate of Tollens reaction was, however, less than that of Lederer-Manasse reaction under comparable conditions. Carbonyl groups in β-position may be reduced by the formaldehyde especially in nonphenolic models less reactive towards hydroxymethylation.

Hydroxymethylation of Lignins

When lignins were treated at room temperature with aqueous formaldehyde and alkali, a maximum of about 15 CH_2OH groups were introduced into milled wood lignin and about 40 CH_2OH groups into kraft lignin, based on 100 arylpropane units. The amount CH_2OH introduced was estimated from the increase of OH number, determined by acetylation.

Two relatively simple ways are given to determine the location of formaldehyde-reactive centers in lignin. In a lignin preparation whose carbonyl groups had been removed by $NaBH_4$ reduction, only the phenolic nuclei are expected to react with (alkaline) formaldehyde. On the other hand, in a diazomethane-methylated lignin, in which the phenolic hydroxyl groups had been etherified, only the carbonyl-containing side chains will be able to react with formaldehyde.

The amount of CH_2OH groups introduced into the $NaBH_4$-reduced M.W.L. indicates (Table II) that about half of the phenolic nuclei could take up formaldehyde presumably into the free 5-positions. This is a further proof that about half of the phenolic (guaiacyl) units are noncondensed in M.W.L. The $NaBH_4$-reduced kraft lignin preparation took up formaldehyde apparently into almost half of its phenolic units. If we correct this number by assuming that the units with catechol hydroxyls may have taken up two CH_2OH groups, the result would indicate that at least about one-third of the phenolic units is uncondensed in pine kraft lignin.

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Table II. The $-CH_2OH$ Groups Introduced[b] per 100 C_6–C_3

Preparation[a]	*M.W.L. Spruce*	*Kraft Pine*
Lignin	16	39 ± 2
$NaBH_4$–Lignin	13	30 ± 3
CH_2N_2–Lignin	[c]	9 ± 1

[a] Reaction conditions, *see* Experimental.
[b] Estimated from increase of OH number by acetylation.
[c] Δ OH = 15, *see* text.

Since diazomethane-methylated lignins are not soluble in aqueous alkali, aqueous dioxane was used as solvent. Methylated kraft lignin reacted only with a reduced amount of formaldehyde. The sum of the methylol groups introduced into the side chains of methylated lignin and of the methylol groups attached to the rings in $NaBH_4$-reduced kraft lignin is in excellent agreement with the amount found by the reaction of untreated kraft lignin (Table II).

Diazomethane-methylated milled wood lignin (OCH_3 = 18.90%) contained 1.15 OH per OCH_3 originally present. (Before methylation this lignin analyzed for 1.40 OH per OCH_3, not corrected for carbohydrates). After treating with formaldehyde the OH content increased to 1.30 OH per OCH_3 originally present. This lignin preparation has thus gained 0.15 OH/OCH_3 as a result of the formaldehyde treatment which superficially might indicate that a similar number of CH_2OH groups have entered the side chains. This conclusion would, however, contradict the previous findings from the CH_2O treatment of M.W.L. and of $NaBH_4$-reduced M.W.L., in which the side chains obviously could not react with formaldehyde.

This apparent contradiction might however be accounted for as follows. The conditions used for the formaldehyde reaction of methylated lignin differed from the conditions of non-methylated lignins. Based on the findings with models, in the former case 2 moles of NaOH and 7 moles of CH_2O were used per C_6-C_3 equivalent of lignin; the alkali concentration also was higher. Under these conditions a crossed Cannizzaro reaction may have occurred with the formaldehyde, which would give rise to the formation of new OH groups rather than CH_2OH groups. The similar behavior of veratryl acetone (VIII) as a model for the side chains of methylated M.W.L. having β-CO groups (0.10 per C_6-C_3) tends to support the assumption that the considerable increase of OH groups after formaldehyde treatment of methylated M.W.L. may have been caused mainly by the reduction of keto groups rather than by the introduction of hydroxymethyl groups into the side chains of this lignin.

It is obvious that OH determination cannot serve as sole evidence to judge the reactivity of lignin with formaldehyde. While reduction by

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crossed Cannizzaro reaction would lead to overestimating the reactivity based on increase of OH number, condensation of phenol alcohols resulting in —CH_2— bridge formation would decrease the OH groups available for acetylation. The conditions of formaldehyde treatment of lignin were carefully selected to avoid this complication which could be minimized but not completely excluded. Molecular weight determinations (*29*) indicated a slight unaccounted increase of $\overline{M}_n$ after formaldehyde treatment.

Studies reported earlier on reactions of phenol alcohols and lignins with methanolic hydrochloric acid (*27*), chlorocresol (*25*), and with urea (*25*) suggested that the difference in reactivity of hydroxymethylated lignins and starting lignin preparations may serve as an analytically convenient indication for estimating the amount of CH_2OH groups introduced by formaldehyde treatment. The condensation with 4-chloro-*m*-cresol just as the methanol-hydrochloric acid treatment are proton catalyzed reactions; it is expected that the acid-catalyzed self-condensation of phenol alcohols will reduce the extent of these reactions even under the mild conditions used. The condensation with urea is, however, catalyzed by base (pH 8–9). It was previously shown (*25*) that side chain hydroxymethyl groups (such as those in compounds V and VII) are nonreactive in these reactions. The results in Table III support these expectations: the more acidic the conditions, the more significant the self-condensation. The data obtained for increased reactivity owing to the presence of new phenol alcohol groups confirm our previous conclusions.

Table III. Evidence for Hydroxymethylation of Kraft Pine Lignin

Method	*In Original Lignin*[a]	*Increase*
OH Determination	120	37–41
Reaction with: CH_3OH, HCl	7	21–23
chlorocresol, H^+	23	26
urea, OH^-	7	29
Phenol alcohol color reaction		32–34
Kinetic expts., side-chain reactions		9

[a] Amount of groups, calculated for 100 C_6-C_3 units.

The *o*-phenol alcohols give a characteristic blue color reaction with $FeCl_3$, which is used widely to identify phenol alcohols. Our problem was how to stabilize the color in polar solvents capable of dissolving lignin. It was found (*2*) that if the $FeCl_3$ solution were made up in DMSO-pyridine (4:1), and one part of this solution were added to four parts of a methyl cellosolve solution containing the lignin, very stable colors could be produced. Probably, the DMSO with its strong solvating properties, takes

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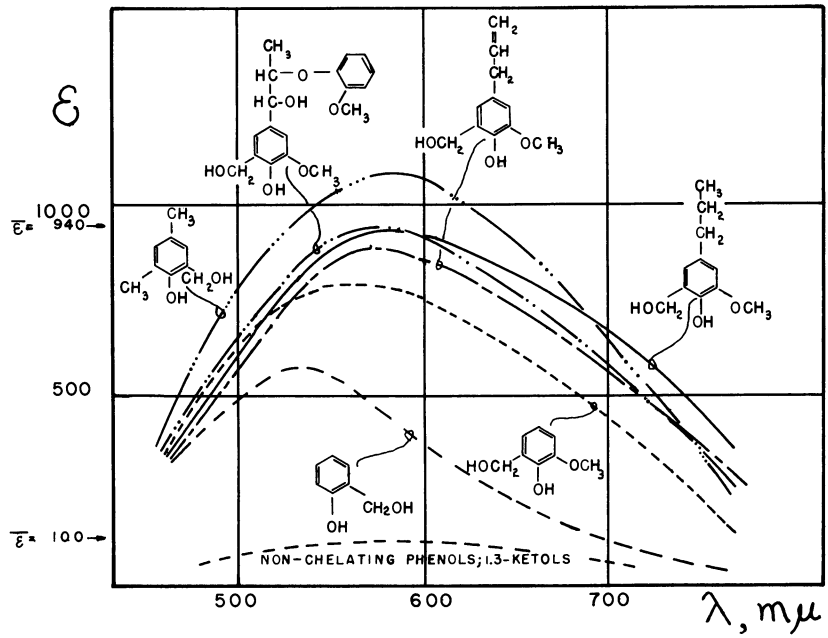

Figure 1. $FeCl_3$ test of model substances

part in the formation of the chelate complex thus increasing the stability of the color.

Figure 1 shows the absorption curves of some of the representative phenol alcohol models (*2*). The absorption maximum is centered around 590 mμ; the ε value for the dimeric model II (R = CH_2OH) is about 950 per mole. Simple phenols like guaiacol or the parent phenol of compound II (R = H) give only a very faint color, with $\epsilon \approx 100$ at around 590 mμ. 1,3-Ketols, like compound VI (R = CH_2OH) do not give color reaction; thus, side chain hydroxymethyl groups probably do not interfere with the $FeCl_3$ test.

o-Dihydroxy compounds also develop color with $FeCl_3$ showing broad absorption maximum around 750 mμ. Color formation with ferrous sulfate is the basis of a colorimetric method used to estimate the amount of catechol structures in kraft lignin (*2*, *13*). The number of catechol groups found in kraft pine lignin probably is small (6 per 100 C_6-C_3 units); by applying a difference technique, this interference is minimized. Another source of error may be the probably somewhat different absorption of hydroxymethylated catechol structures not yet investigated.

When untreated lignins are subjected to the $FeCl_3$ test (*2*), they also give color with a very broad maxium around 550 mμ owing to the phenolic

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structures; at 590 mμ ϵ/OCH_3 is about 580 for kraft lignin and 320 for Björkman lignin. The color of methylol complex is superimposed on this background absorption in formaldehyde-treated lignins.

Figure 2 shows a difference curve obtained from methylol kraft lignin when untreated lignin was used as reference. The difference curve has a distinct maximum at 590 mμ, characteristic of the phenol alcohol structures formed. By comparing the absorbance at 590 mμ with the molar absorbance (ϵ) of models investigated, the amount of phenol alcohols in lignin can be estimated. The numerical values depend somewhat on the ϵ value of the model chosen. In this study a value of $\epsilon = 840$ was used, the increase found at 590 mμ between the molar absorbances of the dimeric phenol alcohol and its parent phenol of model II.

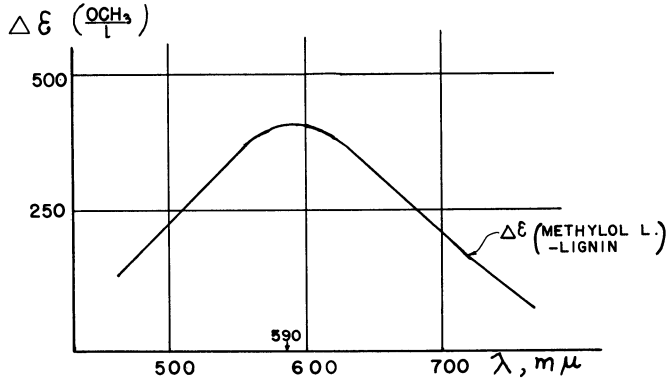

Figure 2. $FeCl_3$ test of methylol kraft lignin

Regarding these uncertainties the agreement of phenol alcohols found in kraft lignin with $FeCl_3$ test and other methods is very reassuring. This colorimetric method is less applicable for M.W.L. preparations in which only a small amount of phenol alcoholic groups can be formed.

From a theoretical viewpoint the alkaline lignin-formaldehyde system is rather complicated (Table IV). Lignin can take up formaldehyde into different reactive positions; the hydroxymethyl groups once introduced may further react with unchanged lignin or rather with each other to form diphenylmethane-types of cross-linked structures. Formaldehyde is subject to a disproportionation reaction in alkaline medium (Cannizzaro reaction), causing CH_2O loss as formic acid and methanol, or sugar derivatives can be formed by CH_2O self-condensation.

This paper deals mainly with the lignin structural aspects of the alkali-catalyzed reactions of lignin with formaldehyde; thus, the technique used will be illustrated briefly with two experiments (Figures 3 and 4).

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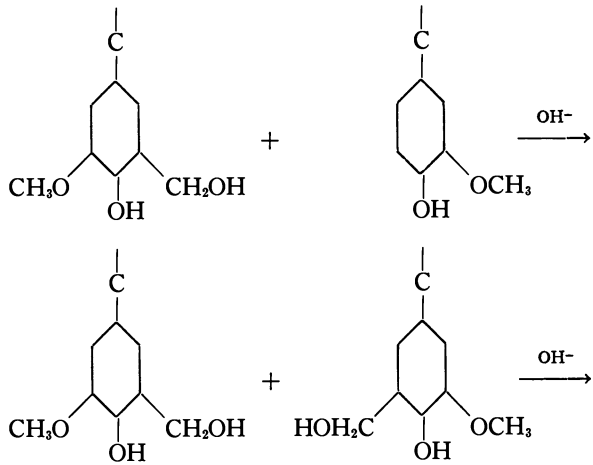
Table IV. Reactions of CH_2O

Condensation with Lignin → Lederer-Manasse
Condensation with Lignin → Tollens

Cannizzaro Reaction

Self-condensation: $HOCH_2—(CH_2OH)_n—CHO$

Reactions of



The main phase of reaction of pine kraft lignin with formaldehyde proceeds at almost constant pH (Figure 3). The extent of Cannizzaro reaction is insignificant since it can be estimated from the formic acid content. The formation of phenol alcohols (as determined by $FeCl_3$-color reaction) reached its peak after 2 hours, and the stability is rather high even after a day.

Figure 4 shows the curves for the reaction of corresponding lignin derivative which had been reduced previously with sodium borohydride. The curve of total CH_2O consumption (determined by NH_2OH, HCl) almost completely coincides with that of the formation of phenol alcohols. The slight overshooting is caused by Cannizzaro reaction; self-condensation was insignificant. The difference in formaldehyde consumption between these two experiments can be attributed to ketol formation in the side chains of lignin. The amount of phenol alcohol and ketol derived through these experiments (Table III) agrees excellently with the values obtained by other methods.

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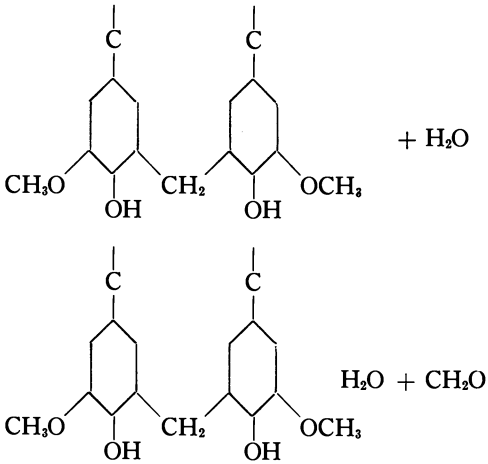
(Lignin–CH_2O–Alkali System)

Reaction

Reaction

Phenol Alcohols



The acidity of kraft lignin is decreased by $NaBH_4$ reduction. Less sodium hydroxide (0.07 mole NaOH per C_6-C_3 less) was needed to bring the solution of the reduced lignin to the same alkalinity (pH 10.9) than was needed for untreated kraft lignin.

In the latter preparation, about 0.05 α-CO groups per C_6-C_3 were found in phenolic units (*26*). It is known that the phenolic hydroxyl in acetovanillone or in similar phenolic ketones is quite acidic (*21*) (pK = 8); reducing these ketones would decrease the acidity to the usual level of phenols (pK = 10, or still higher in sterically hindered phenols). This observation is a further indication that our present concept concerning the presence of α-CO groups in kraft lignin (*24*) is right.

Hydroxymethylated lignin, when subjected to thermal cure, becomes insoluble in alkali. If we compare the DTA curves (*9*) of kraft lignin and methylol kraft lignin (Figure 5) we observe that in the latter a highly exothermic reaction started around 125°C., the material became stabilized over 190°C., and did not melt. Untreated kraft lignin is quite stable only

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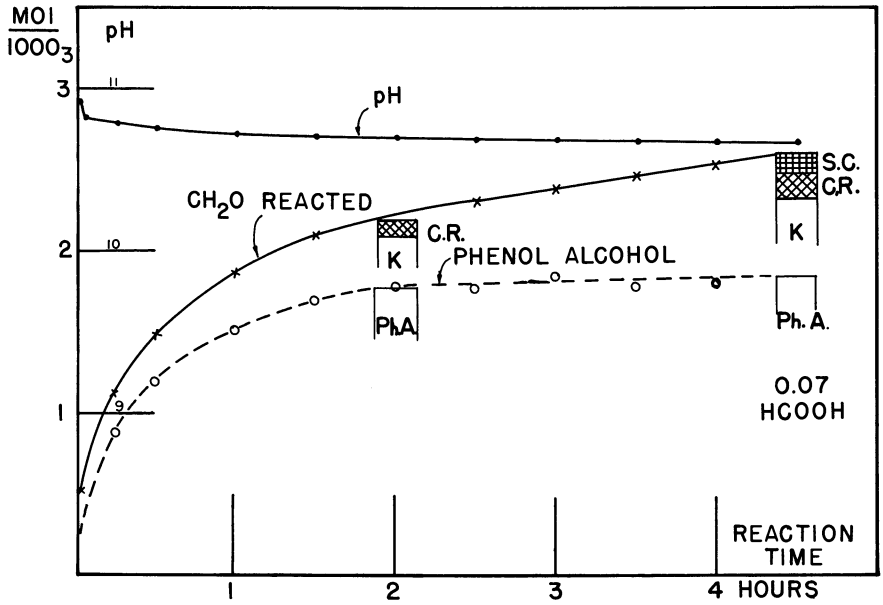

Figure 3. Formaldehyde-kraft lignin reaction

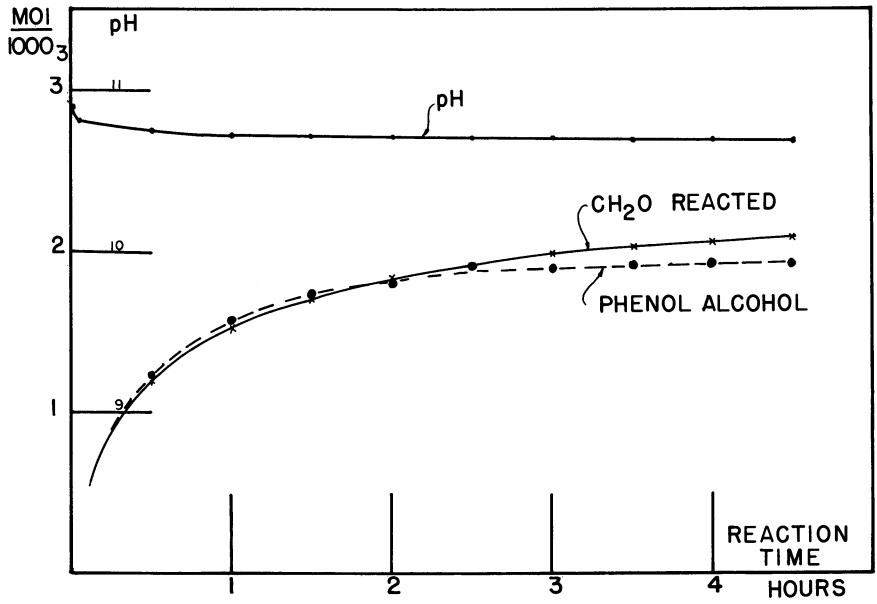

Figure 4. Formaldehyde reaction with $NaBH_4$-reduced kraft lignin

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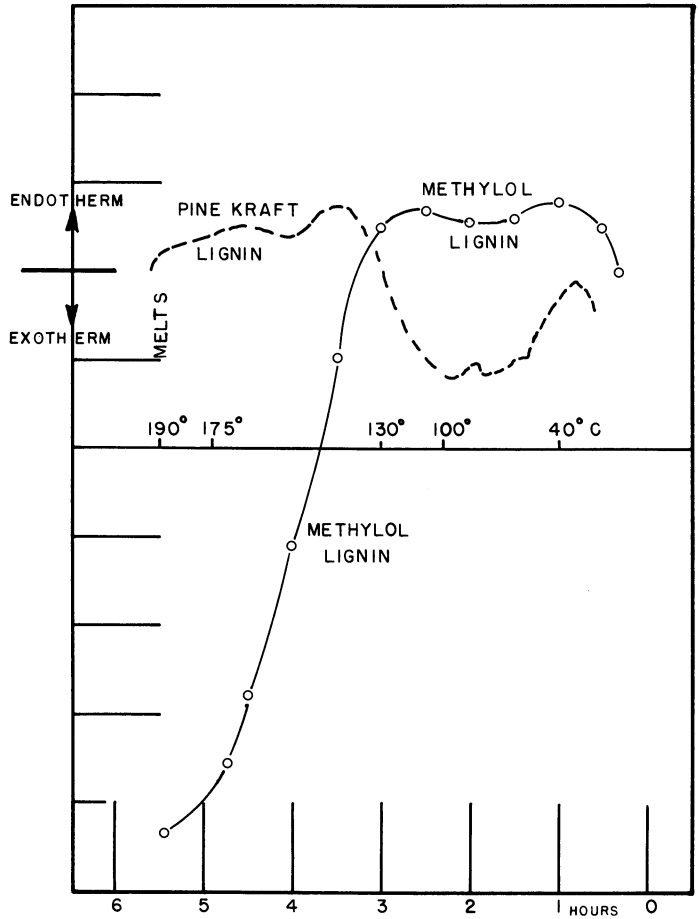

Figure 5. DTA curves of pine kraft lignin and its methylol derivative

up to 190°C. where it starts to soften. The endotherm change around 110°C. indicates a probable loss of water, adsorbed or structural. The thermal cure of methylol lignin is a further proof of the presence of phenol alcohol structures.

The reaction of lignin with formaldehyde is of practical interest not only for the potential use of lignin as reactive extender in phenol-formaldehyde resins but also for wood pulping.

It was observed early that formaldehyde is liberated from wood or lignin on distillation with mineral acids.

Freudenberg (*14*, *15*, *16*, *17*) studied the formation of formaldehyde from lignins under acidic and alkaline conditions and suggested that ω-hydroxymethyl groups may be the source of formaldehyde. Kratzl (*24*)

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pointed out that arylglycerol β-aryl ether structures might be the ones involved in supplying CH_2O at alkaline hydrolysis. Recent studies of Adler, Gierer, and their respective co-workers supplied further information about the possible mechanism of CH_2O formation in alkaline cook from phenylcoumaran structures (*7*, *12*, *19*), and from guaiacylglycerol β-aryl ether-types of lignin structure (*3*, *20*) (Table V).

Ekman (*11*) recently detected formaldehyde as a cleavage product in the alkaline hydrolysis at 100°C. of pine- and birchwood meal, though in lesser amounts than earlier reported for isolated lignins. He advanced a hypothesis that formaldehyde forms phenol alcohols in lignin during the cook, and these groups react with each other to form diphenylmethane structures. He suggests that the lignin condensation is at least partly an

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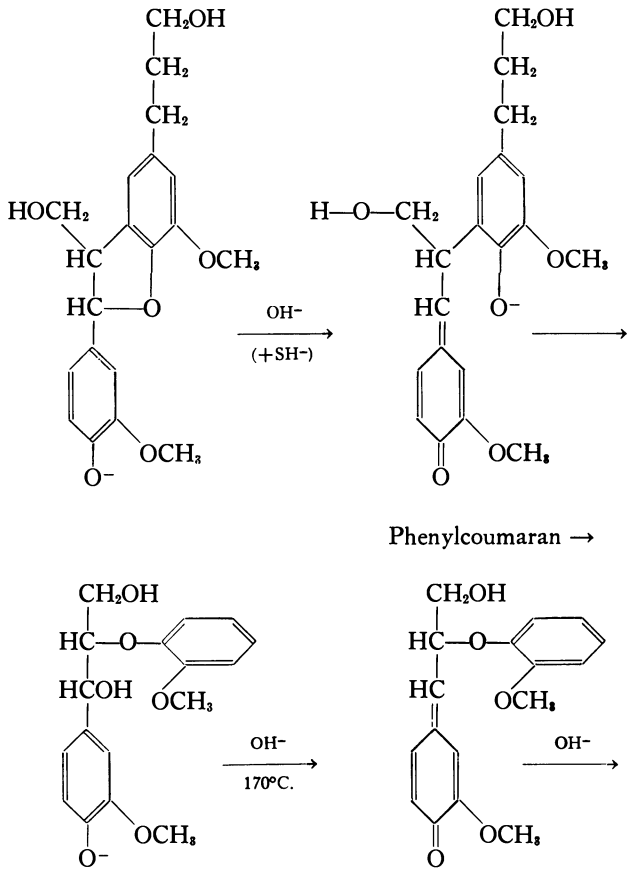
Table V. CH_2O Formation



effect of the reactions of liberated formaldehyde. Our experiments confirm that this possibility exists at least for the conditions of his hydrolysis experiments at 100°C. We have not yet demonstrated, however, that our results can be extrapolated to the much higher temperature (over 170°C.) of alkaline pulping where the self-condensation and Cannizzaro reactions of formaldehyde may be very significant.

Experimental

Condensation of Lignins with Formaldehyde. A sample of 10 grams of kraft lignin (45 meq. of OCH_3) was dissolved in 50 ml. of 1*N* sodium hydroxide, and commercial (35%) formalin was added, containing 120 mmoles of CH_2O. The solution was set aside at room temperature for

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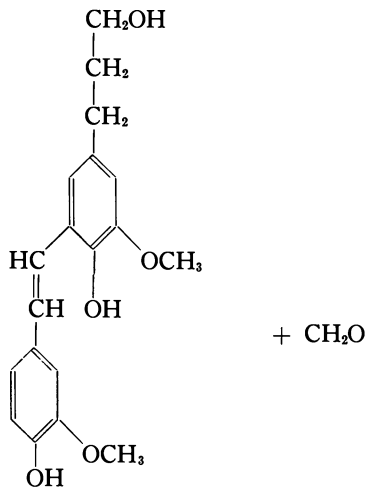
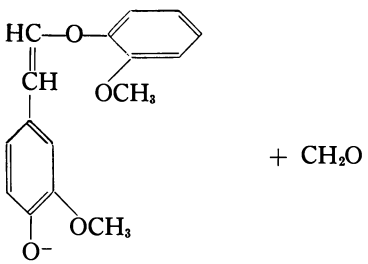


Stilbene



Enol ether

3 days, or at 70°C. for 20 hours. The reaction mixture was then acidified with dilute acetic acid to pH about 4. The resulting precipitate was centrifuged off, resuspended three times with water in the centrifuge tube, centrifuged, and finally dried over P_2O_5 and NaOH in vacuum desiccator. The yield was almost 100%. The solvent for diazomethane methylated lignin was a dioxane-water (2:3) mixture.

Reaction of Model Compounds with Formaldehyde. The model compounds were dissolved in dioxane; aqueous alkali and 35% formalin were added, and the reaction mixtures were kept 3–5 days at room temperature. The reaction mixture was carefully neutralized with dilute hydrochloric acid to pH = 4 to 5, and the larger part of the solvent was removed in a rotating film evaporator. The residue was then suspended in water, extracted with chloroform, the extracts were washed with water, dilute sodium bicarbonate, and again with water, and finally dried over anhydrous sodium sulfate. The solvent was evaporated and crystallization of the residue was attempted usually from a mixture of ether and petroleum ether, or ethyl acetate-petroleum ether.

Optimum conditions (Table VI) for ring-hydroxymethylation of 1 mole phenol: 2 moles of CH_2O, 1 mole of NaOH, 0.8–1*N* NaOH concentration, 3 to 4 days at room temperature; for Tollens reaction (1 mole of model ketone): 8 moles of CH_2O, 2 moles of NaOH, 2*N* NaOH concentration, 5 days at room temperature.

Table VI. Yield, Melting Point, and Analytical

Starting Model	*Product*	*Yield %*	*M.p. C°.*
I	R = CH_2OH	85	60
II	R = CH_2OH	75	48–52 ($\frac{1}{2}$ H_2O)
IV	R_1 = R_2 = CH_2OH	5	142
V	R = CH_2OH	50 (remainder, unreacted V)	145
VI	R = CH_2OH	10 (remainder, unreacted VI)	95

Hydroxyl Group Determination. The procedure described below is a modification of the acetylation method of Verley and Bölsing (*35*) and of the amended version of Freudenberg and Schlüter (*18*).

The acetylation reagent was a freshly prepared equimolar mixture of acetic anhydride (10.2 grams) and anhydrous pyridine (7.9 grams). The titration was carried out potentiometrically (glass electrode). In the

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macro method (100–200 mg. sample) 0.25*N*, in the semimicro method (15–20 mg. sample) 0.025*N* aqueous sodium hydroxide was used.

The sample and the acetylation mixture (about 1 ml. in the macro method, and about 0.1 ml. in the semimicro method) were, as rapidly as possible, weighed into a test tube, which in its upper part was drawn out until the narrowest part was just wide enough for a spatula to be introduced; the tube was sealed by oxygen flame and kept in a water bath at 50°C. for 24 hours. After cooling to room temperature, the top of the tube was cut off, and the reaction mixture, after dilution with about 2 ml. of acetone, was poured into a 100-ml. Erlenmeyer flask containing 50 ml. of water. The tube (including the top) was washed with two 4-ml. portions of acetone, and finally 10 ml. of water were added, rinsing the walls of the Erlenmeyer flask. The lignin precipitated out in finely dispersed form. Titration was carried on to pH 9, as rapidly as possible. At least four determinations were made for each sample, and a similar number of blank determinations were carried out. The mean deviation was about ±2% (rel.).

For checking the possible influence of COOH groups in kraft lignin, 8 samples were acetylated according to the macro procedure. In four of these samples the OH values were determined as usual: 11.1; 10.7; 11.1; 10.7; mean 10.9% OH. The four remaining samples, after acetylation, were transferred into centrifuge tubes containing distilled water; the lignin solids obtained were centrifuged off and washed 4 times with distilled water. The combined solution and wash water (about 150 ml.) were titrated potentiometrically. The OH content was found only slightly higher, mean 11.2%. Since some acetic acid loss was inevitable which would result in higher OH values, the results indicated that the COOH content of kraft lignin does not disturb this determination if the lignin is present in the form of a precipitate at the titration and the acetone content

Data of Hydroxymethylated Model Compounds

		Elemental Analysis	
Composition		*Calcd.*	*Found*
$C_{11}H_{16}O_3$	C	67.32	67.18
(196.25)	H	8.22	8.13
	OCH_3	15.82	15.71
$C_{18}H_{22}O_6$	C	64.66	64.24
(334.35)	H	6.63	6.85
(water-free)	OCH_3	18.55	18.55
$C_{12}H_{16}O_5$	C	59.99	60.04
(240.25)	H	6.71	6.93
	OCH_3	12.92	13.74
$C_{18}H_{20}O_6$	C	65.05	65.25
(332.34)	H	6.07	6.13
	OCH_3	18.67	18.49
$C_{19}H_{22}O_6$	C	65.88	65.88
(346.34)	H	6.41	6.27
	OCH_3	26.88	26.75

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of the titration mixture is not too high. It is important that the lignin sample completely dissolve in the acetylation mixture.

Acknowledgment

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11

Oxidation of Alkali Lignin

Studies on Oxidation in Alkaline Solution

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Alkali lignin was prepared from a commercial, concentrated, skimmed black liquor from the kraft pulping of mixed southern pines. Preliminary oxidation experiments, including alkaline cupric oxide oxidations at atmospheric and superatmospheric pressures, alkali fusions alone and in the presence of peroxides, sodium borate perhydrate, monopersulfate compounds, and sodium sulfide, and similar reactions under pressure gave various phenolic compounds, but in all cases the yields of ether-soluble compounds were relatively low, and much of the original lignin was undegraded. When alkaline solutions of lignin at 170°–180°C. were subjected to gaseous oxygen in 200 p.s.i.g. increments until 600 p.s.i.g. oxygen had been added, about 80% of the lignin decomposed. Fractionating the products yielded oxalic acid and phthalic acid as two of the chief oxidation products.

Between 1940 and 1960, in connection with our continuing studies on the oxidation of lignosulfonates, alkali lignins were subjected to various processes for producing guaiacyl compounds such as vanillin, vanillic acid, etc. In many instances the alkali lignin gave oxidation products similar both in kind and in quantity to those obtained under analogous conditions from lignosulfonates. This demonstrated amenability of alkali lignin to oxidation reactions together with an expressed interest in lignin utilization by many alkaline pulp producers led us in 1961 to initiate an industry-wide, group-sponsored research program on oxidizing alkali lignin to monomole-

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Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

cular organic chemicals. Our studies included vanillin and other guaiacyl derivatives as well as ether-insoluble, water-soluble oxidation products. This paper describes some of the results obtained from this experimental program between 1961 and 1963.

Alkali lignin was prepared in the laboratory from a commercial, concentrated, skimmed black liquor from the conventional kraft pulping of mixed southern pines. The liquor obtained was diluted to approximately 20% solids and acidified with dilute sulfuric acid. The resulting precipitated lignin was separated and washed thoroughly with water to give our alkali lignin starting material.

A preliminary experiment on the alkaline cupric oxide oxidation of this alkali lignin under conditions previously used to evaluate coniferous lignosulfonates (*11*) indicated that the same phenolic compounds found in lignosulfonate oxidations were found in the alkali lignin oxidation in essentially the same relative proportions. However, the actual yield of total identifiable products was less for this particular alkali lignin than for some lignosulfonates examined in the past, and more lignin was recovered unchanged. The ether-insoluble, water-soluble portion of the oxidation products was fractionated and examined by chromatography. Results indicated that several compounds were present in substantial amounts, but no previously identified or suspected components were noted in this preliminary experiment.

Other preliminary experiments on alkali lignin included oxidations by barium peroxide and alkali (*5*, *6*), alkali fusion, and alkali fusions in the presence of calcium peroxide, sodium borate perhydrate, and monopersulfate compound. Ether extractives and water extractives were examined, but in all cases too many of the oxidation products obtained were new and unidentifiable, and it was impossible to evaluate the experiments adequately with the available techniques. Vanillic acid appeared to be the chief oxidation product under conditions which did not demethylate further or destroy the aromatic nature of the oxidation products. Some oxidation conditions yielded *p*-hydroxybenzyl moieties as products, and some gave no trace of these products whatever. More detailed studies of the ether-insoluble, water-soluble components of the several oxidation mixtures were postponed until adequate procedures were developed for analytical isolation and identification.

Alkali lignin was fused with caustic in the presence of sodium sulfide (*1*, *2*) a number of times. Several compounds such as protocatechuic, vanillic, *p*-hydroxybenzoic, and oxalic acids were obtained, but the degradation of the alkali lignin was relatively low. Alkali fusion in nonaqueous systems (*4*, *20*) also gave only small amounts of desirable products, and most of the starting lignin was recovered undegraded.

Alkali lignin was oxidized with alkaline cupric oxide at atmospheric and superatmospheric pressure after first "etching" the lignin with alumi-

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num (in alkaline solution), with sodium borohydride, and with hydrogen peroxide. Results indicated that these "etching" reagents did not change the refractory nature of this alkali lignin toward the cupric oxide-alkali system.

In a final attempt to degrade essentially completely this alkali lignin, it was oxidized in alkaline solution with excess gaseous oxygen but at relatively low pressures. At 170°–180°C. gaseous oxygen was added in increments of 200 p.s.i.g. until a total of 600 p.s.i.g. oxygen had been added. Under these conditions about 80% of the lignin decomposed to water and ether-soluble products. Reaction mixtures were processed in two ways. Some were acidified with sulfuric acid and extracted exhaustively with ether. Others were passed through cation-exchange columns and then extracted with ether. The cation-exchange columns were then eluted with ethanol to give ethanolic solutions. All extracts were evaluated by paper chromatography in several developing solvents and with several spray reagents. Vanillin, vanillic acid, acetovanillone, and a trace of *p*-hydroxybenzoic acid were identified in the ether extracts along with many unidentified spots which gave acid reactions with indicator spray reagents but not with diazo reagents. The ethanol eluates and ether extracts were essentially similar in their paper chromatographic evaluations.

A sample of mixed ether and ethanol extracts representing 36% of the original lignin used for their isolation underwent countercurrent distribution in a Craig machine between the two phases of a 1:1:2 chloroform-ethyl acetate-water system. The two chief fractions of this distribution were diethyl phthalate and oxalic acid along with smaller amounts of the other compounds noted. The ethyl phthalate was formed by transesterification of phthalic acid with ethyl acetate during the countercurrent distribution and subsequent concentrations of fractions. The yield of diethyl phthalate corresponded with a phthalic acid yield of 34% on the basis of the mixed ether and ethanol extractives or 9.5% on the basis of the original alkali lignin. Similarly, the yield of oxalic acid amounted to approximately 40% on the basis of the mixed ether and ethanol extractives or 11% on the basis of the original alkali lignin.

While these last studies were in progress, Grangaard (*3*), noted that lignin preparations, including softwood kraft lignin, can be degraded almost completely in a relatively short time by oxygen in alkaline solution, provided the pressure of the oxygen added to the autoclave is at least as great as the pressure of the system owing to vapor pressure alone. In other words, the ratio $P_{O_2}/P_{v.p.}$ must be 1 or greater. Furthermore, the amount of oxygen added over a period of time appeared to be of little consequence compared with the original pressure of the oxygen. Grangaard also noted that 80% of the reaction products comprised a mixture of oxalic, formic, and acetic acids. Many other acids were identified but only in minute amounts.

Our continued interest in the complete degradation of the alkali lignin led us to investigate Grangaard's original high oxygen pressure procedure. These studies together with studies on the development of gas chromatographic techniques for evaluating lignin oxidation mixtures will be the subject of future papers.

Experimental

Starting Material. A drum of concentrated, mixed, southern pine kraft black liquor was kindly supplied by the Canton, N. C. mill of the Champion Paper and Fibre Co. Analytical data for the liquor indicated 49.7% total solids and a methoxyl content of the oven-dried solids of 5.54%. The pH of the liquor as received was 12.3. (All melting points are uncorrected. Infrared absorption spectra were determined by Mr. Lowell Sell of The Institute of Paper Chemistry Analytical Group.)

A sample of concentrated liquor weighing 1006 grams and containing 500 grams of solids and 27.7 grams of methoxyl was stirred with 1500 ml. of water to make a solution containing approximately 20% solids. The solution was acidified slowly with dilute sulfuric acid to pH 2 while maintaining the temperature at approximately 20°C. throughout the acidification. As the solution became acid, a heavy brown precipitate separated. The resulting mixture was centrifuged, and the centrifuged solids were washed by stirring with water and recentrifuging. The solid was resuspended in 2 liters of distilled water, stirred for 1 hour, and allowed to settle. The settled solids were centrifuged, washed once as before, and dried in a current of air. The alkali lignin thus obtained amounted to 167 grams on the oven-dry basis, and the oven-dry solids contained 13.0% methoxyl.

This experiment was repeated several times. All of the individual air-dried lignin preparations were powdered, screened, and mixed to yield a composite alkali lignin sample containing 90.5% solids, and these solids contained 13.4% methoxyl. The composite lignin sample represented 31.5% of the solids of the original kraft black liquor used in its preparation, and the methoxyl of the lignin represented 80.5% of the methoxyl of this original liquor. This composite lignin sample was used as a starting material in the experiments reported here.

Preliminary Oxidation with Cupric Oxide and Alkali. This first oxidation study under conditions used previously for evaluating lignosulfonate solutions (*11*) used the fractionation procedure developed recently for analyzing spent pulping liquors (*15*, *16*). This procedure was used with little change for most of the oxidation experiments here.

A mixture of 83 grams of alkali lignin (containing 75 grams of oven-dry solids and 10 grams of methoxyl), 150 grams of sodium hydroxide, 400 grams of hydrated copper oxide, and 1500 ml. of water was stirred and heated in a 1-gallon stainless steel autoclave at 170°C. for 2 hours. When the reaction mixture was cool, it was filtered, and the precipitate of cupric and cuprous oxides was washed with water. The combined filtrate and washings were acidified to pH 2 with dilute sulfuric acid and extracted exhaustively with ether in an air-agitated continuous extractor (*9*). The ether extract was dried and evaporated in a rotating evaporator to give

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19.8 grams of ether extractives containing 14.8% methoxyl. The ether extractives represented 26.4% of the starting solids, and the methoxyl of these extractives represented 29.3% of the starting methoxyl.

The aqueous raffinate was evaporated slightly under reduced pressure to remove ether, and then it was centrifuged. The centrifuged solids were washed with water, filtered, and dried. This insoluble material amounted to 60.8% of the starting lignin, and the methoxyl represented 51.1% of the starting methoxyl.

The clear aqueous centrifugate containing water-soluble, ether-insoluble components was fractionated by ion exchange into "neutral," "weak acid," and "strong acid" fractions as detailed previously (*15*, *16*).

The ether extractives were analyzed qualitatively and quantitatively by paper chromatography and spectrophotometry as described in detail previously (*13*, *17*, *18*). Vanillin, *p*-hydroxybenzaldehyde, acetovanillone, and vanillic acid were identified in this fraction. Quantitative evaluation indicated that these known compounds comprised 54% of the weight of the ether extractives and accounted for 69% of the methoxyl of these same extractives.

The water-soluble fractions were examined by paper chromatography in various solvent systems and by thin-layer chromatography in several systems. Spots were located by examination under ultraviolet light and by spraying with diazotized *p*-nitroaniline, 4-(4-dimethylamino-1-naphthylazo)-3-methoxybenzene sulfonic acid indicator (*21*), Mäule, permanganate-periodate, ferric chloride, modified silver (*19*), and silver nitrate-ammonia (*7*, *8*) reagents. Of all the spray reagents used, only the indicator and silver nitrate-ammonia reagents indicated spots. These two reagents indicated many acid spots, none of which was recognized from previous oxidation studies except oxalic acid. Further studies on isolating and identifying these many acids were postponed until adequate procedures could be developed.

Oxidation with Barium Dioxide and Alkali. The alkali lignin was boiled in alkaline solution with an excess of barium dioxide and a little cupric hydroxide under conditions reported to give high yields of vanillic acid (*5*, *6*). Analysis indicated only 13.8% ether extractives and the following yields on the basis of the original alkali lignin: 2.8% vanillic acid, 0.4% *p*-hydroxybenzoic acid, 0.1% vanillin, 0.2% acetovanillone, and a trace of *p*-hydroxybenzaldehyde.

Alkali Fusion. Several alkali fusions were performed in an attempt to convert the alkali lignin into low molecular weight compounds that could be identified in this exploratory part of the program.

FUSION WITH ALKALI ALONE. Alkali lignin was first fused with potassium hydroxide at 180°–190°C. under standard conditions used previously for converting vanillin to vanillic acid (*10*) and syringaldehyde to syringic acid (*14*). Under these conditions, protocatechuic and vanillic acids were the chief oxidation products, but over 70% of the lignin was recovered as a lignin-like polymeric product. Longer fusion times helped

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somewhat but always yielded less than half of the lignin as degraded products.

Fusion with Alkali and Other Agents. Calcium peroxide was added portionwise to the fusion mixture at 180°C. but did not change materially the nature of the yields or reaction products. It should be noted that, in these fusions, total recovery of solids was quite low owing to large conversion of organic matter to carbon dioxide.

Other fusions were made under the same conditions but with the addition of sodium borate perhydrate (duPont Perdox containing 15.5% minimum available oxygen) and monopersulfate compound (duPont Oxone containing 4.5% available oxygen). Again, no marked change over the standard fusions was noted.

Fusion with Alkali and Sodium Sulfide. Following the success of Enkvist and co-workers (*1*) in degrading kraft black liquor with sodium sulfide at high temperatures and pressures, our alkali lignin was fused with potassium hydroxide in the presence of sodium sulfide. A mixture of 65 grams of 85% potassium hydroxide and 65 grams of sodium sulfide nonahydrate in a tall form 500-ml. stainless steel beaker was heated to 200°C. with mechanical stirring. A total of 10 grams of alkali lignin were added over a period of 10 minutes while maintaining the temperature at 200°–210°C. The mixture was stirred an additional 15 minutes at 200°–210°C. and allowed to cool with stirring. The cooled mixture was diluted with water and passed through a column of Amberlite IR-120 cation-exchange resin. The column was washed with water, and the combined column effluent and washings were extracted with ether to give an extract containing only 4% of the original lignin. Major components were vanillic and protocatechuic acids. The cation-exchange column was eluted with ethanol to give 94% of recovered lignin. Similar fusion at 225°–230°C. gave somewhat better degradation, but recovery of lignin-like products approached 90%.

Fusion with Alkali and Cupric Oxide. Cupric oxide oxidation was also tried under fusion conditions. Preliminary experiments under the standard conditions at 180°–190°C. indicated too little degradation. Accordingly, alkali lignin was added to a mixture of 56 grams of potassium hydroxide, 7 ml. of water, and 19.5 grams of hydrated cupric oxide at 225°C., and the temperature was maintained at 225°–230°C. for 15 minutes after all the lignin was added. The reaction mixture was processed as before with cation-exchange resin to give 21% ether extractives, 46% aqueous raffinate from the ether extraction, and only 21% ethanol wash. Qualitative paper chromatography indicated that the ether extract contained oxalic acid, protocatechuic acid, and a little *p*-hydroxybenzoic acid; the aqueous raffinate contained mostly oxalic acid and unidentified materials; the ethanol wash contained protocatechuic, *p*-hydroxybenzoic, and vanillic acids along with unchanged lignin. Similar experiments using more cupric hydrate did not result in more complete reaction.

The same mixtures of reactants were diluted with water and heated in a stainless steel bomb at 225°–230°C. for the same length of time, but results were not as good as under the fusion conditions. No conditions gave results worth pursuing.

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FUSION WITH ALKALI AND CUPRIC OXIDE IN NONAQUEOUS SOLVENTS. Alkali lignin was fused with potassium hydroxide and cupric oxide in methanol under conditions suggested by Tiemann (*20*) and in *n*-amyl alcohol as suggested by Klages (*4*). These procedures were very effective in earlier model compound studies in our laboratories (*12*). Ether extracts obtained were less than those from corresponding experiments in aqueous solution, and qualitative compositions were essentially the same. In the case of the amyl alcohol experiments, artifacts with the cupric oxide were obtained. Again, experiments were conducted under more dilute conditions in a bomb under superatmospheric conditions, but results were no better.

Alkaline Cupric Oxide Oxidation after Preliminary "Etching". In an attempt to modify the refractory nature of this alkali lignin toward alkaline cupric oxide oxidation, the lignin was treated by several "etching" procedures before oxidation. These etching procedures consisted of treatment in alkaline solution with agents which might break chemical bonds or change reactivity by chemical oxidation or reduction. The etching reagents were aluminum foil in alkaline solution, sodium borohydride, and hydrogen peroxide. After etching, the reaction mixtures were treated with more alkali and cupric oxide at both atmospheric and superatmospheric pressure, but the results were not encouraging. Reaction products were essentially those found in similar experiments without previous etching.

Oxidation of Alkali Lignin with Oxygen in Alkaline Solution. Alkali lignin was oxidized with oxygen. A solution of alkali lignin in 10% sodium hydroxide was placed in a stainless steel high pressure model B3C Parr 455-ml. hydrogenation bomb. The bomb, heated by an electrically heated rocker, was equipped with a temperature well and a gage block carrying an accurate pressure gage and a line to a tank of oxygen, arranged so that oxygen could be added to the rocking mixture during the reaction. Temperatures were determined by a thermocouple and pyrometer.

GENERAL OXIDATION PROCEDURE. For this series we chose a ratio of sodium hydroxide to alkali lignin as 8:1, assuming the unit molecular weight of lignin as 180. A mixture of 11.3 grams of alkali lignin (containing 1.5 grams of methoxyl), 20 grams of sodium hydroxide, and 200 ml. of water was placed in the stainless steel bomb; the bomb was sealed with the gage block and placed in the rocker assembly. Rocking began, and the temperature was raised gradually to approximately 170°C. in 50 minutes. At this point the gage pressure was noted, and oxygen was introduced to raise the gage pressure 200 p.s.i.g. The temperature was maintained between 170° and 180°C. while the bomb was rocking. After another hour had passed, the gage pressure was noted, and oxygen was introduced to raise the gage pressure 200 p.s.i.g. The process was repeated after another hour. In all, 600 p.s.i.g. of oxygen at 170°C. were added to the reaction mixture. After approximately 3 hours at 170°C. the heater was turned off, and the bomb and its contents were allowed to cool with rocking. After 2 hours, the rocker was stopped, and the reaction mixture cooled to room temperature overnight. Pressure was relieved, and the bomb was opened.

Table I. Representative Schedule for Oxidizing Alkali Lignin with Gaseous Oxygen

Elapsed Time, min.	*Temperature, °C.*	*Gage Pressure, p.s.i.g.*
0	25	0
20	123	50
50	168	118
50[a]	168	318
85	178	195
100	177	160
100[a]	177	360
120	176	260
150	172	190
165	169	162
165[a]	169	362
235[b]	170	235
300	119	85
360[c]	83	55
1440	25	40

[a] Oxygen (200 p.s.i.g.) added at this point.
[b] Heater turned off at this point.
[c] Rocker turned off at this point.

A representative schedule for gaseous oxygen oxidation of alkali lignin is shown in Table I.

Processing of First Oxidation Mixture. The contents of the bomb and washings from the experiment of Table I were diluted to 1500 ml. and passed through a column of Amberlite IR-120 cation-exchange resin. A great amount of gas (carbon dioxide) evolution took place on the column. The resin was washed with water and allowed to drain as dry as possible. The effluent and washings were concentrated to 800 ml. and extracted exhaustively with ether to yield an ether extract containing 21.4% of the original solids and 18.8% of the original methoxyl. The aqueous raffinate was concentrated somewhat under reduced pressure to remove ether and then filtered to yield 17.2% of brown solid containing 6.6% of the original methoxyl. The clear aqueous filtrate was concentrated to give a solution containing 22.8% of the original solids but only an insignificant amount of the methoxyl. The drained column of Amberlite IR-120 resin was backwashed with just enough water to cover the resin bed and to classify it. The column was then washed with 3 liters of absolute ethanol and allowed to drain. The ethanol eluate was concentrated to give a solution containing 19.6% of the original solids and 20% of the original methoxyl. In this experiment, the total recovery of solids was over 80%, and the methoxyl recovery was 45%.

Qualitative paper chromatography of the ether extractives indicated vanillin, vanillic acid, acetovanillone, and a trace of *p*-hydroxybenzoic acid along with many unidentified spots giving reactions with the indicator spray reagent. The ethanol extract gave most of the same spots. The water solution gave spots for oxalic acid and for several unidentified acids.

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OTHER GASEOUS OXYGEN OXIDATIONS. Other, almost identical oxidations were performed in the same manner at 160°–170°C. and at 170°–180°C. for longer reaction times. Five experiments in all were made. Qualitative paper chromatography indicated very little difference between the individual experiments. However, quantitative differences were noted for the several isolated fractions.

EVALUATION OF ETHER EXTRACTIVES OF GASEOUS OXYGEN OXIDATIONS. Oxidizing alkali lignin with gaseous oxygen under the conditions of these experiments gave a good yield of ether-soluble materials containing several well-known products and a few unidentified ones. In addition, we found that the ethanol extracts contained essentially the same components as the ether extracts. Most of the recovered methoxyl appeared to be in these two fractions. Accordingly, a mixture of ether and ethanol extracts from the five experiments in this series was used as a starting material for further fractionation and evaluation. The solids of this combined fraction represented 36% of the weight of the original lignin used.

CRAIG-MACHINE SEPARATION OF COMBINED FRACTION. A sample of the combined extractives containing 19 grams of solids and 1.8 grams of methoxyl was evaporated to dryness in a vacuum-rotating evaporator. The residue was dissolved in the lower phase of the 1:1:2 chloroform-ethyl acetate-water system. The resulting solution was placed in the first seven tubes of a 100-tube 40 ml./40 ml. automatic Craig countercurrent distribution machine and distributed between the two phases of the same chloroform-ethyl acetate-water system at 20°C. After 103 transfers the distribution was monitored by paper chromatography on every fifth tube. On the basis of this qualitative chromatography, the tubes were combined in the fractions noted in Table II. These fractions were concentrated to dryness in a rotating evaporator under reduced pressure below 40°C. and residual products were weighed.

Table II. Craig-Machine Fractionation of Combined Extractives

Fraction	*Tubes*	*Yield, grams*
A	0–10	8.0
B	11–19	2.7
C	20–35	1.4
D	36–55	3.5
E	56–70	5.2
F	71–84	0.9
G	85–92	1.2
H	93–99	4.2
I	Overflow	1.3
		28.4

The apparent discrepancy between the yield of recovered fractions and the amount of starting sample is explained by the difference in solids' determination. The solids in the combined starting sample were determined by oven-drying the individual samples. The yields of the individual

fractions in Table II were determined by weighing residues after low pressure evaporation below 40°C. In addition, further work on these fractions (Table II) indicated that transesterification occurred to a certain extent during the Craig-machine processing, resulting in the partial production of ethyl esters from acids originally present in the combined fraction. All fractions were investigated individually.

Fractions A and B. Both of these fractions were mixtures comprising essentially vanillin and acetovanillone with a number of phenolic impurities in exceedingly small amounts.

Fraction C. This fraction was impure vanillic acid containing a little *p*-hydroxybenzoic acid and several unidentified materials as impurities.

Fraction D. After removing the nonaqueous solvents from this fraction, a thin, light yellow oil separated. The yield in Table II is the weight of this oil. Infrared spectral analysis indicated a fatty alcohol ester of phthalic acid.

A 2.0-gram sample of the oil was boiled with 50 ml. of *N* sodium hydroxide for 4 hours under reflux, and then the mixture was distilled to yield 20 ml. of distillate. Ethanol was identified in the distillate by gas chromatography. The alkaline aqueous residue was acidified with dilute sulfuric acid and extracted with ether. The ether was evaporated to yield a solid mass, which was recrystallized from water to yield colorless crystals, melting at 199°–201°C. and not depressing the melting point of a mixture with authentic *o*-phthalic acid. An infrated spectrum of this compound was identical with that of authentic *o*-phthalic acid.

The aqueous layer left after removing the yellow oil was hydrolyzed with alkali in the same manner. Paper chromatography of the hydrolyzate indicated vanillic and *p*-hydroxybenzoic acids as well as a major spot for phthalic acid. Again ethanol was noted in the neutral distillate.

Fraction E. This fraction was processed exactly as fraction D, and essentially the same results were obtained, except that fraction E contained a small but not significant amount of oxalic acid.

Fractions F and G. Paper chromatography indicated that these two fractions are substantially identical and consist almost entirely of oxalic acid with traces of other acids as impurities.

Fractions H and I. Paper chromatography indicated that these two fractions were identical except for a few minor spots. The combined fractions were purified by cellulose column chromatography with the upper layer of 4:1:5 *n*-butanol-ethanol-water as the developer. Over 95% of the combined fraction was recovered as pure oxalic acid.

Discussion of Results

In most of the oxidation experiments either *p*-hydroxybenzaldehyde or *p*-hydroxybenzoic acid was isolated or indicated in appreciable amounts. Thus, the *p*-hydroxybenzyl moiety must be present in significant amounts

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in the lignin or extractives of one or more of the species of pinewood used for the kraft pulping operation yielding the black liquor of this study.

All experiments employing reactions previously used on lignosulfonate materials appeared to give yields of guaiacyl oxidation products in lesser amounts than did the lignosulfonate materials. Therefore, we paid more attention to the nonguaiacyl portion of the oxidation products in continuing experiments. However, adequate procedures were not available for evaluating the nonguaiacyl components, and reaction mixtures have been stored until such procedures are developed.

The discovery of diethyl phthalate in the Craig-machine fractionation of the combined ether and ethanol extractives of the low pressure oxygen oxidations indicated that phthalic acid was present in the original oxidation mixture. The phthalic acid was converted to the diethyl ester by transesterification with ethyl acetate during the 103 transfers of the countercurrent distribution. Furthermore, ethyl esters of vanillic, *p*-hydroxybenzoic, and oxalic acids were found during this Craig-machine run. It is entirely possible that many other unknown acids were esterified in the same manner and were not revealed by the indicator spray reagent. Such esterification would explain the high yield of recovered products from the Craig-machine run of Table II.

Note that the high yield of phthalic acid was obtained from a mixture of extractives resulting from five different oxidation experiments. It is likely that some of these experiments gave much higher yields of phthalic acid than others. Therefore, the possible yield of phthalic acid from this alkali lignin is probably much higher than the 12.3% found in this combined sample.

The discovery of phthalic acid as a major oxidation product of kraft alkali lignin is important not only because it opens up a possible large-scale source of phthalic acid, but because it demonstrates that under the proper conditions, chemicals not ordinarily expected from lignin can be produced from this raw material. Thus, we expect that soon other completely unexpected chemicals will be found in lignin reaction mixture.

In addition, the discovery of phthalic acid as a major oxidation product is theoretically important with respect to the linkages in alkali lignin obtained from kraft black liquor and, therefore, to the mechanism of the kraft cook.

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12

Formation and Degradation of Biphenyl Structures During Alkaline Oxidation of Phenols with Oxygen

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The primary step in oxidizing monohydric phenols alkylated para to the phenolic hydroxyl group in aqueous alkali is the formation of resonance-stabilized free phenoxyl radicals. Their mesomeric nature is demonstrated by coupling at two carbon atoms to diphenols—the predominant step in such oxidative degradations. Oxidation of creosol (2-methoxy-4-methylphenol) (I) dissolved in 0.2N NaOH (1 mole equivalent alkali) at 70°C. yields about 60% 6,6'-bicreosol (2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl-1,1') (II), and minor amounts of dark colored, high molecular condensation products. The ESR spectra of the latter indicate the presence of "caged free radical structures." Oxidizing 6,6'-bicreosol yields 2-hydroxy-3-methoxy-5-methylbenzoic acid (V), acetone, methanol, and carbon dioxide. The oxidizability of monohydric phenols in terms of "critical oxidation potentials" was lower than that of the corresponding dihydroxybiphenyls.

Oxidations of lignin in alkaline media, representing the most important degradation reactions, are both theoretically and technically important. In technical processes oxygen (as air) is used as the oxidizing agent. In the vanillin process, for instance, temperatures between 180°–200°C. and rather short reaction periods are used (*35*).

Much milder conditions are used in bleaching procedures using oxygen (*9*, *11*, *23*, *24*, *25*, *26*, *31*, *32*). In general, temperatures around 100°C.,

In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

oxygen pressure from 5–7 atm., and reaction periods around 1 hour have been used.

Mild oxidation of kraft lignin dissolved in 1–2*N* NaOH at 70°C. was studied by Raff and Tomlinson (*29*) some years ago. By using this process, they observed remarkable changes in the solubilities of the oxidized products in organic solvents (e.g., decrease in acetone solubility) and changes in flow properties. These and other findings indicate that condensation occurs between lignin molecules (*1*, *17*, *22*).

Oxygenation Experiments

Our studies were concerned with the reactions occurring during mild oxidation. This paper deals with model experiments on one of the possible reaction sequences—namely, the formation of biphenyl structures and oxidative degradation. Numerous oxidation experiments with suitable lignin models were performed, and during these studies we determined the rate of oxygen consumption by the compounds dissolved in 0.2*N* NaOH at 70°C. A detailed description of our method is given under Experimental.

In general, differences were observed regarding oxygen uptake in the initial phase of oxidation between the models of the syringyl, guaiacyl, and catechol series. Pronounced differences could be observed, however, in presence of higher amounts of alkali (1–2*N* NaOH, 5–10 mole equivalents alkali per mole substance) (Figure 1).

Despite the numerous, complex oxidation mechanisms occurring during lignin oxygenation, kraft lignin fractions from various origins (angiosperm, gymnosperm, and partially demethylated gymnopserm lignin) exhibit initial oxygen uptake features similar to those observed in oxidizing models of the various types of basic building units (Figure 2). We found that the oxygen absorption depends greatly on the ratio of substance to alkali. Of great importance was the state of solution and the contact between oxygen and the material to be oxidized. Therefore, the mixtures were stirred magnetically with the same speed.

Applying such mild conditions we further observed fission reactions of ether bonds (alkyl aryl ethers—e.g. $ArOCH_3$) and —C—C—linkages by isolating fair amounts of methanol and carbon dioxide.

Creosol (2-methoxy-4-methylphenol) (I), for instance, yields 14.5% methanol and 15% carbon dioxide on a mole basis. Besides these degradation products, up to 60% of the crystalline *o*,*o*′-dihydroxybiphenyl derivative (6,6′-bicreosol—i.e., 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-dimethylbiphenyl-1,1′) (II) and small amounts of a higher molecular humic-like compound could be isolated.

Dihydroeugenol (2-methoxy-4-*n*-propylphenol) (III), a homologous guaiacyl model, shows practically the same behavior.

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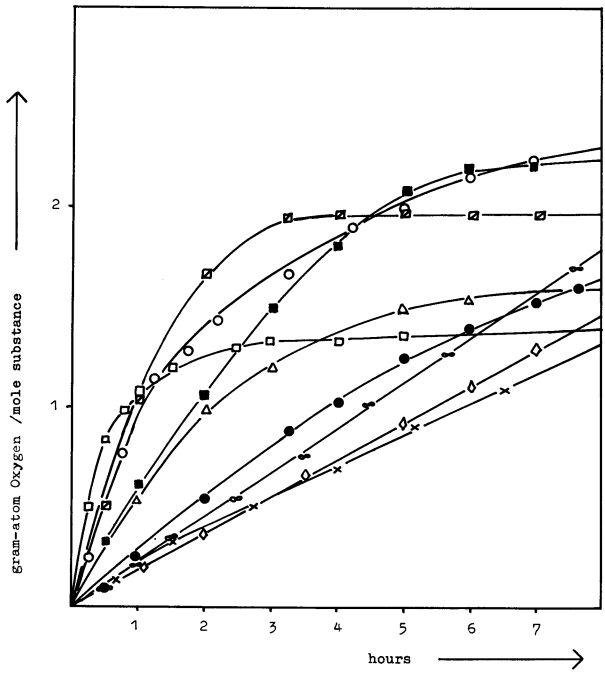

Figure 1. Oxidation of lignin model substances in aqueous alkali (0.2N NaOH); 1 mole equivalent of alkali, 70°C.

○—*Catechol*
□—*4-Methylcatechol*
×—*Guaiacol*
∞—*Creosol (I)*
◊—*6,6'-Bicreosol (II)*
△—*4-n-Propylguaiacol (III)*
●—*Vanillin*
■—*Pyrogallol-1,3-dimethyl ether (IX)*
⧄—*5-Methylpyrogallol-1,3-dimethyl ether*

The biphenyls are obviously formed by oxidative radical coupling in the sense of phenol dehydrogenation. The high molecular humic-like compound was investigated by electron spin resonance (ESR) using a Varian model V–4500 (Figure 3). These authors have shown that kraft lignins exhibit a pronounced single-line signal indicating the absence of free radicals with distinct structures. This particular signal is ascribed to macroradicals or free radical centers, stabilized or trapped in the three-dimensional network (*14*). Compared with the kraft lignin preparation, the ESR spectra of the "creosol polymer" show distinct differences. Besides the characteristic single line, a number of signals could be detected. These signals might be ascribed to free radicals with defined structures or to hydrogen interaction. As long as free phenolic hydroxyl groups are present, hydrogen interaction is possible. Both the formation of the biphenyl compound and the characteristic ESR spectra of the high

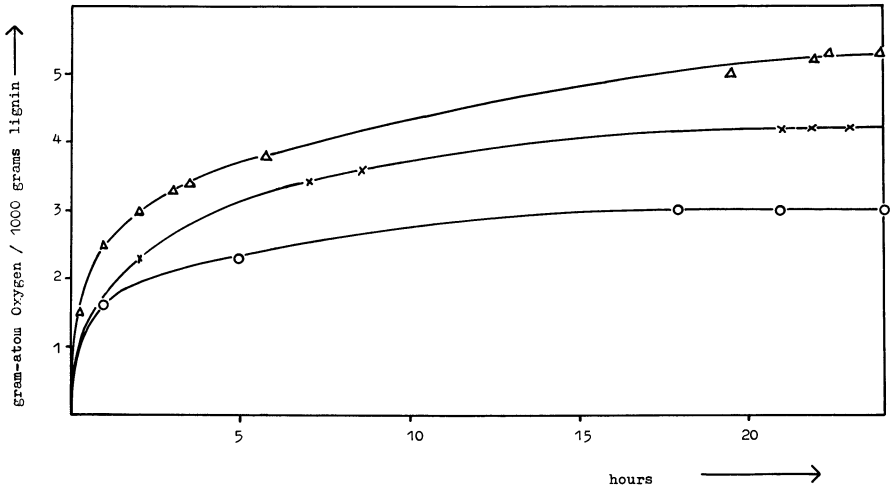

Figure 2. Oxidation of kraft lignin fractions in dilute aqueous alkali (dissolved in 0.2N NaOH); 2 mole equivalents alkali (based on MW 1000) 70°C.

O—*Pine kraft lignin*
×—*Hardwood kraft lignin*
△—*Partially demethylated pine kraft lignin*

molecular oxidation product show clearly the importance of radical reactions during oxidation.

Oxidative Coupling to Diphenols

The initial reaction step in phenol oxidation generally is the electrophilic attack by oxygen acting as biradical. Alkylated monohydric phenols, dissolved in aqueous alkali, react by losing one electron from the corresponding phenolate anion to give a resonance-stabilized free phenoxyl radical [Figure 4, (Ia)–(Ie)]. A one-electron transfer from a location of high electron density to the oxygen molecule occurs. Thus, the peroxy radical formed may then react either with a phenolate anion or with a resonance-stabilized phenoxyl radical [(Ia)–(Ie)] to peroxy compounds; these then rearrange to hydroxy derivatives. The total amount of active oxygen (peroxy compounds) could be determined iodometrically.

In further stages the resonance-stabilized free phenoxyl radical undergoes several reactions—e.g., formation of semiquinones and dimerization by coupling at locations with high degree of unpaired electron localization either at oxygen or at carbon atoms, while alkyl substituents can be lost at some late stage of the oxidation process. Further reactions between free radicals and atmospheric oxygen should also be considered. In general, a great variety of complex reactions might occur in phenol oxidation.

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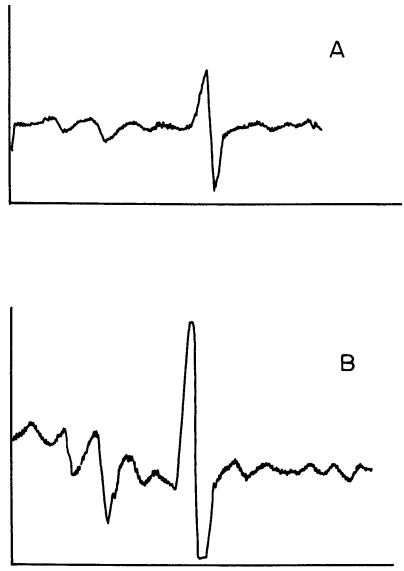
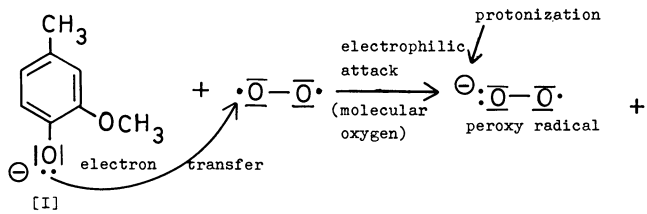


Figure 3. Electron spin resonance spectra of the high molecular fraction of creosol oxidation product

(A) Sample weight: 0.0096 gram in quartz tube; gain: 500; modulation: 500.
(B) Conditions as above; gain: 1000; modulation: 1000.



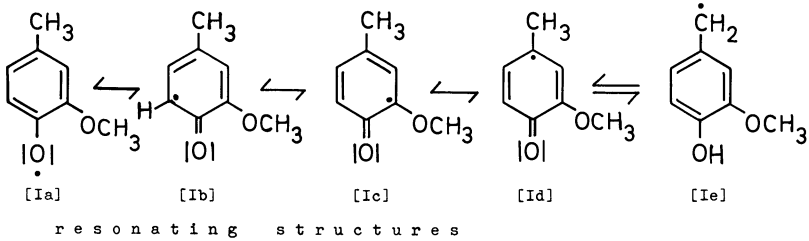


Figure 4. Formation of resonance-stabilized free phenoxyl radicals of creosol (I) by oxidation in aqueous alkali

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As a typical example of coupling reactions the oxidation of *p*-cresol (VII) to Pummerer's ketone (VIII) is presented in Figure 5, showing the mesomeric nature of the phenoxyl radical. According to Barton *et al.* (*2*) the ketone is formed by coupling at one *o*-carbon atom and at one *p*-carbon atom and subsequent formation of an ether linkage.

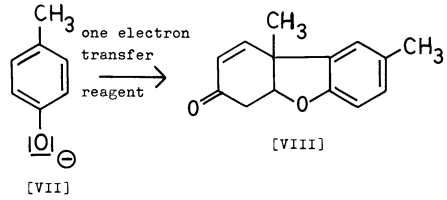

Figure 5. Formation of "Pummerer's ketone" (VIII) from p-*cresol (VII)*

Compounds with free para positions and blocked ortho positions couple at the *p*-carbon atoms. Pyrogallol-1,3-dimethyl ether (IX) gives the stable "coerulignone" (X) in excellent yields (Figure 6).

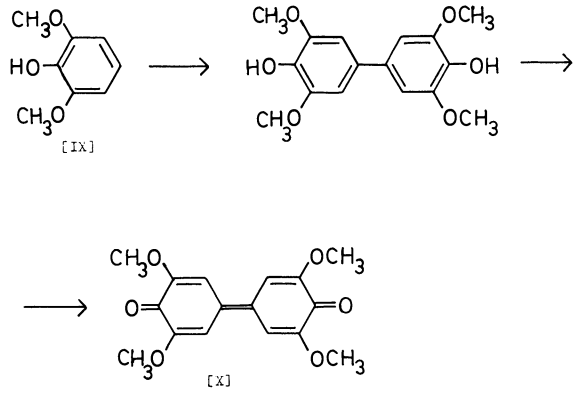

Figure 6. Formation of "coerulignone" (X) from pyrogallol-1,3-dimethyl ether (IX)

Compounds with blocked para and ortho positions, like 5-methyl-pyrogallol-1,3-dimethyl ether, serving as models for condensed lignin units tend to form a mesomeric structure with a high degree of unpaired electron localization at the methyl group para to the phenolic hydroxyl group, forming the corresponding diphenylethane or diphenylmethane derivatives (*30*). Such dimerizations could be accomplished by merely oxidizing in weak alkaline solution at room temperature.

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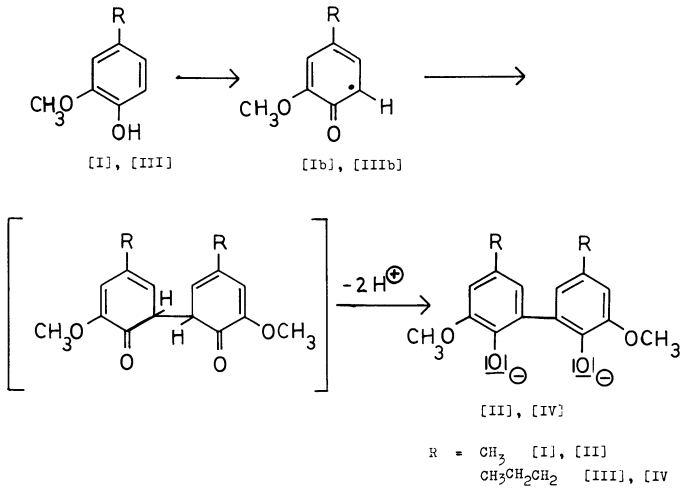

Figure 7. Dimerization (o-carbon–o-carbon coupling) of p-alkylated guaiacol derivatives

However, our discussion will be restricted to oxidation of simple alkylated monohydric phenols (2-methoxy-4-alkylphenols), serving as models for noncondensed lignin units. In creosol (I) one ortho position and the para position is blocked, and coupling occurs at the *o*-carbon atom under the conditions used. Other coupling mechanisms could not be detected (Figure 7).

o-Carbon–*o*-carbon coupling might, of course, also be considered in the case of lignin oxidation. Because there is no accurate method for determining biphenyl structures in lignins, the extent of such couplings could not be estimated.

Degradation of Diphenols

Our findings lead us to assume that the oxidative degradation of guaiacyl compounds with saturated side chains in the 4-position (para to the hydroxyl group) is proceeding via *o,o'*-coupling. Dimerization is then followed by ring fission reactions.

The oxidation of guaiacyl derivatives with α-keto or α-hydroxy groups in the side chain, on the other hand, follow a completely different pattern. The degradation of these compounds obviously proceeds via some kind of Dakin reaction (*15*). The concept of dimerization and subsequent degradation of the dimers has been envisaged also by Grangaard (*10*), who oxidized lignin and lignin models under more severe conditions (150°–200°C., 20% NaOH, 50 atm. oxygen, 5–10 minutes).

Therefore, to gain more information on the degradation mechanism of *o,o'*-dihydroxybiphenyls, 6,6'-bicreosol (II) was oxidized following our

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standard conditions (10 mmoles dissolved in 50 ml. 0.2*N* NaOH corresponding to 2 mole equivalents alkali per mole 6,6′-bicreosol, 70°C). In the past, further reaction stages during diphenol oxidations (e.g., *o,o′*-dihydroxybiphenyls) have received practically no consideration.

Isolation of Degradation Products

After a reaction period of 25 hours (total oxygen consumption 3.2 gram atoms oxygen per mole starting material), we were able to isolate (besides 60% unreacted starting material) carbon dioxide, methanol, acetone, and 2-hydroxy-3-methoxy-5-methylbenzoic acid (V) in rather fair amounts (Table I) as degradation products. Formaldehyde could not be detected. Oxidation of the homologous 4,4′-di-*n*-propyl-6,6′-biguaiacol (IV) yielded (besides carbon dioxide and methanol) *n*-propyl methyl ketone and 2-hydroxy-3-methoxy-5-*n*-propylbenzoic acid (VI) in comparable amounts. The fragmentation of the dimer (II) and (IV) is illustrated in Figure 8.

Table I. Yields of Degradation Products after Oxidizing 6,6′ Bicreosol (II)[a]

Degradation Products	*Yield, Moles*	
	Per Mole of Starting Material	*Per Mole of Reacted Material*
CO_2	0.31	0.80
Methanol	0.47	1.20
Acetone	0.05	0.12
Acid (V)	0.05	0.12

[a] Reaction conditions: 0.2*N* aqueous NaOH (2 mole equivalents alkali), 70°C., reaction period of 25 hours. Oxygen consumption: 3.2 gram-atoms oxygen per mole starting material, approximately 8.0 gram-atoms oxygen per mole reacted material.

The fate of C-2′, C-3′, and C-4′ as well as the exact origin of carbon dioxide is still unknown. Isolation of inactive carbon dioxide from the reaction mixture after oxidizing 4-*n*-propylguaiacol (III), labelled in the α-position of the side chain (adjacent to the aromatic nucleus), shows clearly that the α-C atom can not be considered as possible source of carbon dioxide. Furthermore, it seems to be formed from the aromatic nucleus via ring opening and decarboxylation reactions.

pH-Changes of the Reaction Mixture and Oxygen Consumption

Regarding the yield of formed methanol (*see* Table I) the results indicate that part of the second aromatic nuclei of the biphenyls has also been

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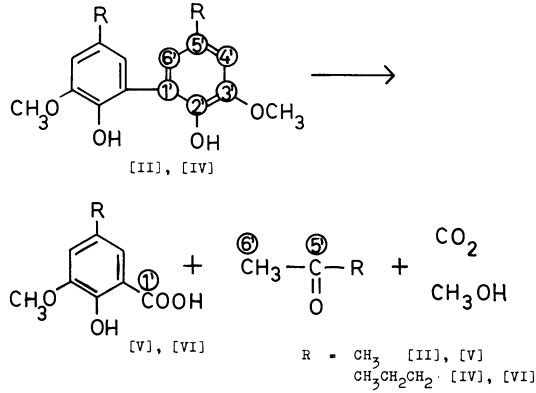

Figure 8. Fragmentation of o,o′-dihydroxybiphenyls (0.2N aqueous alkali); 2 mole equivalents NaOH, 70°C. O_2.

attacked. This has been shown by experiments carried out under more drastic conditions (adding more alkali after the first oxidation phase). The pH curve and the oxygen consumption for this particular experiment are shown in Figure 9. After a reaction period of 58.5 hours, the total oxygen uptake amounted to 7.6 gram-atoms oxygen per mole of reacted 6,6′-bicreosol. In the case of the complete degradation of 1 mole of the diphenol to 1 mole of the acid (V), methanol, acetone, and 3 moles of carbon dioxide (assuming that the products originating from the C atoms C-2′, C-3′, and C-4′ are oxidized to the highest possible stage of oxidation), the calculated theoretical oxygen demand amounts to 7.0 gram-atoms oxygen per mole reacted substance. Since, however, a higher oxygen consumption was observed, some of the oxidants must have been used to oxidize the second aromatic nucleus of the diphenol.

Oxygen uptake and pH changes in an oxidation experiment under standard conditions are presented in Figure 10. The pH curve corresponds to a titration curve. This may be explained by a change from a phenolate buffer to a carboxylate (sodium bicarbonate) buffer system. A similarly shaped curve was obtained by titrating the original alkaline solution of 6,6′-bicreosol with salicylic acid (*see* Figure 10). The characteristic break in the pH-curve was observed when 1 mole equivalent of salicylic acid was added per mole of diphenol, dissolved in 0.2*N* NaOH (amount of NaOH corresponding to 2 mole equivalents alkali).

As mentioned above, almost 60% of unreacted starting material could be recovered after a reaction period of 25 hours. The characteristic break in the pH curve was observed after a reaction period of about 9 hours. This means that at this early stage part (less than 40%) of the starting material has been oxidized to acidic compounds like carboxylic acids and

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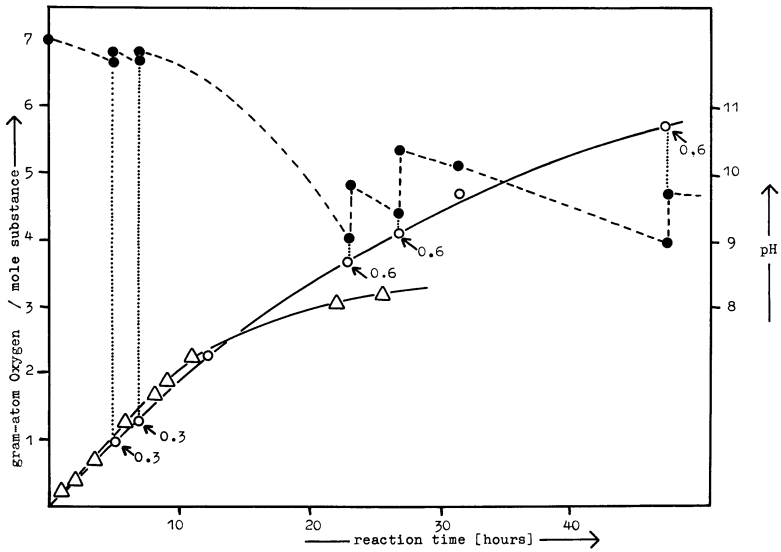

Figure 9. Oxygen uptake and pH change on oxidizing 6,6′-bicreosol (II); (0.2N NaOH); 2 mole equivalents alkali, 70°C.

△—*Oxygen absorption without addition of alkali*
○—*Oxygen absorption when alkali is added*
●—*pH curve*
↖ *0.3* *or* ↖ *0.6* *equivalents NaOH (0.6N aqueous NaOH) added per mole starting material*

carbon dioxide (via ring opening reactions), which neutralized the alkali of the reaction mixture. These findings clearly demonstrate that the secondary reaction steps (oxidative degradations) are proceeding faster than the primary step.

The oxidation rate decreased with the pH of the reaction mixture. Because of the continuous loss of free alkali of the reaction mixture, unreacted 6,6′-bicreosol precipitated, and the reaction with oxygen finally ceased. The oxygen uptake in further stages of the reaction might be ascribed to further oxidative degradations of already attacked molecules. The break in the pH curve was observed as soon as 1.7 gram-atoms oxygen per mole of starting material were consumed. This again indicates that further degradation of already oxidized molecules must have occurred to a remarkable extent at an early phase of oxidation. Assuming that within the first 9 hours (break of the pH curve) about 30% of the starting amount has been oxidized and that formation of 2 equivalents (based on reacted substances) of acidic compounds via ring opening (carbon dioxide, carboxylic acids) would not require more than 2–3 gram-atoms of oxygen per mole diphenol, a theoretical oxygen demand to reach this particular stage (break in pH curve) of 0.6–0.9 gram-atom oxygen per mole starting mate-

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rial was calculated. The experimental value amounted, however, to 1.7 gram-atoms oxygen per mole.

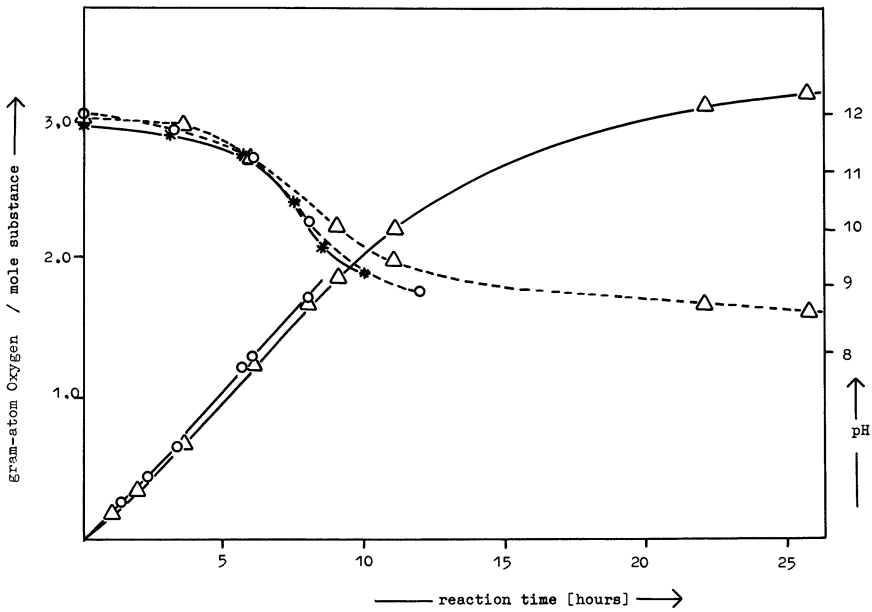

Figure 10. Oxygen uptake and pH change during oxidation of 6,6'-bicreosol (II); 0.2N NaOH; 2 mole equivalents alkali, 70°C.

○—, △— *Oxygen uptake (parallel runs)*

○- -, △- - *pH curves (parallel runs)*

∗—*This curve represents the titration curve obtained by titrating the sodium salt of 6,6'-bicreosol (II) with salicylic acid.*

Proposed Degradation Mechanisms

We assume that degradation of diphenols is also initiated by radical reactions like dimerization. The primary step in this case also seems to be a one-electron transfer from the diphenol giving a resonance-stabilized free monoradical as shown in Figure 11.

Principally, two polarized phenoxide anion groups (positions of high electron density) are available for the one-electron transfer reaction. Statistically, however, it seems improbable that both of the phenoxide anion groups are attacked at the same moment. One can assume that as soon as one of the phenoxide anions is attacked, the corresponding nucleus will be degraded by a sequence of rather fast oxidation reactions. Unfortunately, detailed information on these steps is not known.

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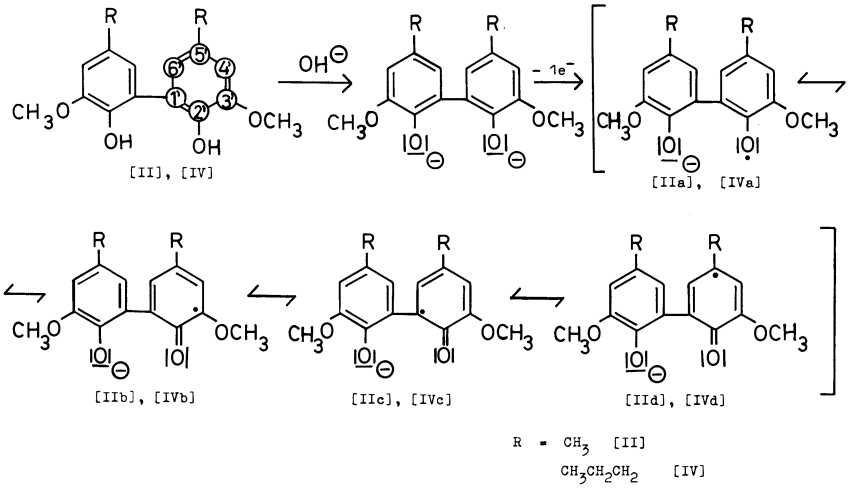

Figure 11. Formation of diphenol monoradicals

Therefore, we are in a position only to discuss various reaction pathways which might proceed perhaps even simultaneously. Possible degradation pathways via peroxy compounds are given in Figure 12.

Demethylation. Introduction of a peroxy group at C-3′ (oxidation of IIb) seems to represent one of several possible preceding steps for demethylation, formation of *o*-quinones, and finally oxidative ring opening between C-2′ and C-3′.

Formation of Benzal-Acetone Structures. Formation of a peroxy group at C-5′ (oxidation of structure IId) leads to ring opening between C-4′ and C-5′ and to formation of benzal acetone structures, which are assumed to be the possible source of the obtained degradation products (acetone and acid V, respectively, *n*-propyl methyl ketone and acid VI).

The formed peroxy compounds might rearrange to the corresponding hydroxy compounds. Direct hydroxylation by a hydroxyl radical (formed by decomposition of peroxy radicals) should also be considered. Hydroxylation at C-4′ would result in formation of a polyphenol quite sensitive towards oxygenation which would be further degraded via oxidation to quinonoid structures and ring-opening reactions. Unstable *o*-diphenoquinones (XI, XII) as intermediates might also be discussed (Figure 13).

The problems concerning the location of ring openings during oxidation in alkaline media have not been solved yet. By assuming ring opening between C-2′ and C-3′ similar to the fission of 3,5-di-*tert*-butylcatechol, 4,6-di-*tert*-butylpyrogallol (*34*) and 4,6-di-*tert*-butylguaiacol (*16*), dibasic acid formation is taken into consideration (Figure 14). However, it seems

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uncertain that these types of acids (XIII, XIV or XV, XVI) are further degraded under the given conditions to the corresponding substituted benzal acetones (XVII, XVIII) capable of yielding substituted salicylic aldehyde (XIX, XX) by alkaline hydrolysis.

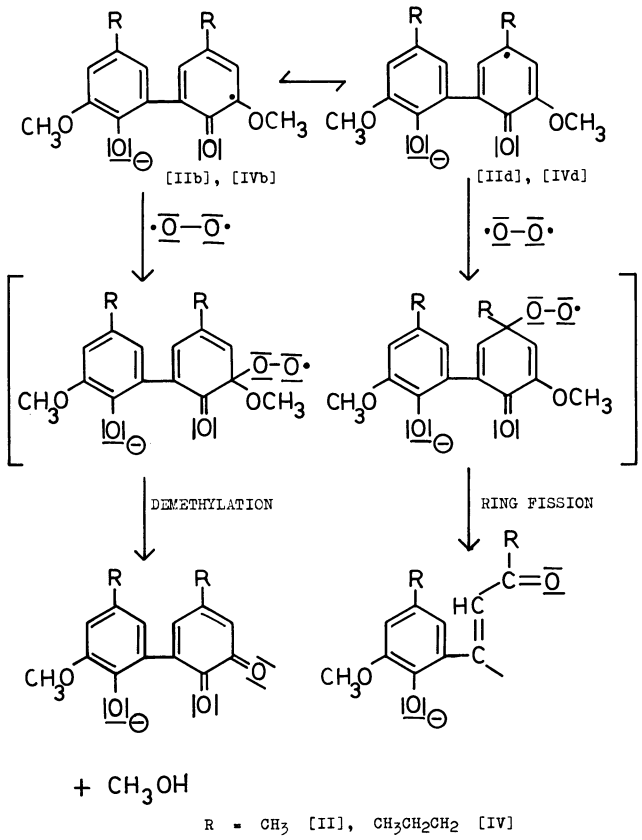

Figure 12. Possible degradation pathways
Demethylation and formation of benzelacetone structures.

In order to gain some information on the degradation mechanisms, experiments with substances assumed to represent essential intermediates were undertaken. 2-Hydroxy-3-methoxy-5-methylbenzal acetone (XVII) is considered to play a dominant role in the proposed degradation mechanism when 6,6′-bicreosol is oxidized in alkaline solution although it could not be detected among the degradation products. The benzal acetone (XVII) was oxidized and underwent alkaline hydrolysis under our standard conditions. Alkaline hydrolysis in nitrogen atmosphere yielded rather small amounts of acetone (about 10% of theoretical amount). Oxidation yielded

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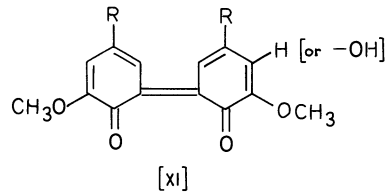
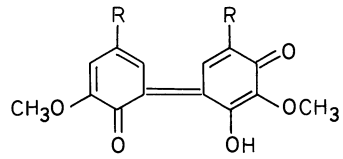


[XI]



[XII]

Figure 13. Possible o-diphencquinone intermediates (XI), (XII)

even smaller amounts (about 2%) of acetone and the corresponding salicylic acid (V).

Benzal acetones, in general, are readily oxidized by alkaline peroxide solution via epoxides (*see* XXI, XXII in Figure 14) which might even be isolated in some cases when mild conditions are used. Under more drastic conditions, however, the oxidation proceeds to the corresponding benzoic acids. Since active oxygen compounds (peroxides) are formed when 6,6′-bicreosol is oxidized, the proposed benzal acetone intermediate (XVII) seems to be oxidatively split into the corresponding salicylic acid (V) and acetone.

Alkaline hydrolysis of benzal acetone structures to the corresponding aldehyde (XIX) and acetone and subsequent oxidation of the aldehyde (XIX) to the corresponding benzoic acid (V) do not seem to represent an actual degradation stage since oxidizing the aldehyde (XIX) under our mild standard conditions yielded only traces of the corresponding benzoic acid (V). The aldehyde (XIX) was rapidly decomposed via Dakin reaction to formic acid and 3-methoxy-5-methyl-*o*-benzoquinone, which is immediately degraded to phenolic humic compounds.

The "Critical Oxidation Potentials" (C.O.P.)

We found that when phenols (or lignins) are oxidized in alkaline media the initial step is a one-electron abstraction from the phenolic hydroxyl group forming a phenoxyl radical. We discovered an electrochemical method which allows us to determine roughly the free enthalpy of this particular reaction (phenol → phenoxyl radical). This method has been

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developed by Fieser (*5*) for determining redox potentials of unstable systems (phenols and amines). He further introduced a concept of the so-called Critical Oxidation Potential (C.O.P.) which can be taken as an inverse measure of the ease of electron release from the phenoxyl oxygen (the lower the C.O.P., the greater the ease of electron release). The C.O.P. is determined by an indirect method and is defined as the potential of some oxidizing solutions (e.g., complex metal cyanides) which will cause a certain small amount of phenol to become oxidized in 5 minutes when equivalent amounts of the sample (phenol) and oxidizing agent are used.

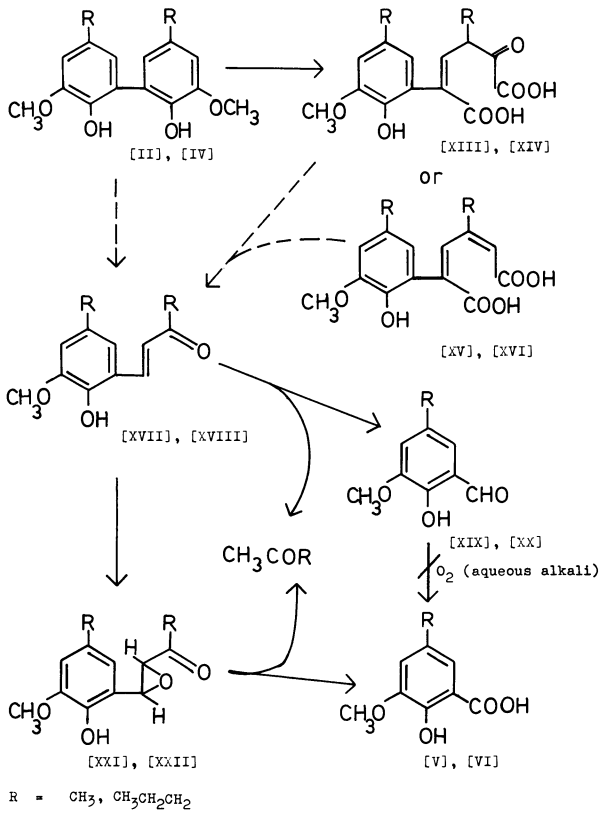

Figure 14. Proposed degradation pathways (Oxygenation, 0.2N NaOH (2 mole equivalents alkali), 70°C).

The C.O.P. of a compound depends strongly on the electronic effects of substituents on *o*- and *p*-positions and is linearly related to its normal redox potential. Using a modified procedure we determined the C.O.P. of several lignin models and lignins and found that a relationship exists between C.O.P. and initial oxidation rate. The oxidizability of monohydric

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phenols may, therefore, be expressed in terms of Critical Oxidation Potentials (Table II).

The *p,p'*-dihydroxy-, as well as, the *o,o'*-dihydroxybiphenyls exhibit lower C.O.P. values than the corresponding monomers. The decrease of only 40 mv. owing to *o,o'*-coupling is probably caused by the formation of hydrogen bonds between the phenolic hydroxyl groups hindering free rotation of the nuclei. In this case both nuclei are out of plane; therefore, only part of the resonating energy of the one aromatic ring is affecting the electron release from the other.

The *p,p'*-dimer of 6-methylguaiacol (3,3'-dimethoxy-4,4'-dihydroxy-5,5'-dimethylbiphenyl-1,1') exhibits the lowest C.O.P., and we found that this compound is even oxidized when exposed to the atmosphere (decrease of 80 mv.). The benzoic acid derivative (V), on the other hand, had the highest C.O.P. (caused by the electron attracting —COOH group in the *o*-position) indicating its stability towards oxidation.

These findings show that by dimerization to diphenol, structures are being formed which are less stable towards oxidation (radical one-electron transfer reactions), explaining dimerization by radical coupling during oxidative degradation from the energetic point of view.

Table II also lists the C.O.P. value of coniferyl alcohol, the basic lignin building stone of coniferous lignins. The low value indicates the rather

Table II. "Critical Oxidation Potentials" (C.O.P.) of Model Compounds[a]

Substance	*COP Mv.*	*ΔMv.*	*Kcal./Mole*	*Reference System*
Creosol (I)	180			Fe
		−40	0.92	
6,6'-Bicreosol (II) (*12*)	140			Fe
		+225	5.30	
2-Hydroxy-3-Methoxy-5-methyl-benzoic acid (V) (*36*)	365			Mo
6-Methylguaiacol (*18*)	160			Fe
		−80	1.84	
p,p'-Dimer of 6-methylguaiacol (3,3'-dimethoxy-4,4'-dihydroxy-5,5'-dimethylbiphenyl-1,1') (*20*)	80			Fe
Coniferyl alcohol[b] (*8*)	165			Fe

[a] Reference system: complex metal cyanides, 20 ml. of a 0.03*M* aqueous solution and 200 ml. 15*N* Sørensen buffer containing organic solvents (for detailed description *see* Experimental), apparent pH: 7.45. Electrodes: combined platinum electrode with Ag/AgCl in saturated KCl as reference electrode. Reaction temperature: 20°C. Abbreviations: Reference systems named as oxidants—Fe, potassium ferricyanide; Mo, potassium molybdicyanide. Mv.—millivolts.

[b] The apparent pH of the buffer was 6.5. The value for C.O.P. is assumed to be lowered by about 30–40 mv. when the C.O.P. determination is performed at apparent pH 7.45.

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low energy required for forming the corresponding resonance-stabilized free phenoxy radical, which is of interest in connection with the biosynthesis of lignins via dimers to oligomers as shown by Freudenberg's extensive studies (*7*).

This type of radical-like mechanism, however, is not strictly limited to the biosynthesis of this natural compound. According to Flaig (*6*) the biological degradation and oxidation of lignin (humification) to CO_2 is also initiated by radical reactions similar to the process we propose here. Carbon dioxide thus forms a cycle, starting from its assimilation by the green plants to its liberation by soil microorganisms.

Experimental

Synthesis of Model and Degradation Compounds. *6,6'*-BICREOSOL (*II*) (2,2'-DIHYDROXY-3,3'-DIMETHOXY-5,5'-DIMETHYLBIPHENYL-1,1'). Dehydrogenation of creosol (I) by potassium ferricyanide (*12*), m.p., 132°–134°C.

4-n-PROPYLGUAIACOL (*III*) ([1-(4-HYDROXY-3-METHOXYPHENYL) PROPANE]. Hydrogenation of eugenol (*27*), b.p., 128°–130°C./13 mm. Hg, $n_D^{24} = 1.5204$.

4,4'-DI-*n*-PROPYL-*6,6'*-BIGUAIACOL (*IV*) (2,2'-DIHYDROXY-3,3'-DIMETHOXY-5,5'-DI-*n*-PROPYLBIPHENYL-1,1'). Dehydrogenation of 4-*n*-propylguaiacol (III) by peroxidase and dilute hydrogen peroxide (*28*); m.p., 150°–152°C (ethanol).

2-HYDROXY-*3*-METHOXY-*5*-METHYLBENZOIC ACID (*V*). (*36*) m.p., 195°–196°C. (benzene).

2-HYDROXY-*3*-METHOXY-*5-n*-PROPYLBENZOIC ACID (*VI*). Hydrogenation of methyl-(2-hydroxy-3-methoxy-5-allyl) benzoate (*4*) and subsequent saponification; m.p., 119°–120.5°C. (benzene–*n*-hexane), yield = 80%. Elemental analysis: calculated: C, 62.85%; H, 6.72%; found: C, 62.64%; H, 6.80%.

2-HYDROXY-*3*-METHOXY-*5*-METHYLBENZAL ACETONE (*XVII*). According to the procedure reported for preparing 2-hydroxy-3-methoxybenzal acetone (*13*); m.p., 109°–110°C. (benzene–*n*-hexane), yield 66%. Elemental analysis: calculated: C, 69.88%; H, 6.84%; found: C, 70.03%; H, 6.79%.

2-HYDROXY-*3*-METHOXY-*5*-METHYLBENZALDEHYDE (*XIX*) (*21*). m.p., 75°–77°C.

Oxidation Procedure: (Standard Conditions). MONOMERIC PHENOLIC MODEL COMPOUNDS. 10 mmoles were dissolved in 50 ml. 0.2*N* NaOH (analytical grade, free of CO_2), corresponding to 1 mole equivalent alkali per mole phenol.

DIPHENOLS. 10 mmoles were dissolved in 100 ml. 0.2*N* NaOH, corresponding to 2 mole equivalents alkali per mole diphenol.

KRAFT LIGNIN FRACTIONS. 5 grams were dissolved in 50 ml. 0.2*N* NaOH, corresponding to 2 mole equivalents alkali per 1000 grams lignin.

The reaction mixture was stirred magnetically. In comparative studies the same constant stirring speed was adjusted. The oxygen absorption was determined volumetrically. The volume of gas absorbed under experimental conditions was converted to the volume at normal con-

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ditions (0°C., 760 mm. Hg). The oxygen was purified by passing through an absorption tube filled with soda lime and through a gas washing bottle containing 30% aqueous NaOH. The reaction temperature was kept at 70°C.

Isolation and Quantitative Determination of Degradation Products of 6,6′ Bicreosol (II). The reaction mixture was filtered to remove unreacted 6,6′-bicreosol, which precipitated during oxidation because of the decreasing pH of the solution. Further amounts of unreacted starting material could be isolated by continuously extracting the bicarbonate alkaline filtrate with ether after determining acetone.

Acetone. The alkaline filtrate was distilled under reduced pressure (approx. 150 mm. Hg). About a third of the original volume of the filtrate was collected as distillate in a receiver containing 150 ml. of a solution of 2,4-dinitrophenylhydrazine (prepared by dissolving 2.5grams 2, 4-dinitrophenylhydrazine in 50 ml. conc. H_2SO_4 and diluting to 1000 ml. with distilled water). The crude hydrazone was tested by paper chromatography using *n*-heptane saturated with methanol as developer. 2,4-Dinitrophenylhydrazone of formaldehyde could not be detected. The crude product was recrystallized from dilute ethanol and identified by mixed melting point with an original sample of acetone-2,4-dinitrophenylhydrazone.

2-Hydroxy-*3*-methoxy-*5*-methylbenzoic Acid (V). The residual alkaline solution was adjusted to pH 7.5–8, by adding dilute sulfuric acid, and extracted with ether in a continuous extractor for 48 hours. The phenolic fraction thus obtained contained mainly unreacted 6,6′-bicreosol and traces of an unknown phenolic compound (detected by thin layer chromatography on silica gel, developer was benzene: glacial acetic acid: water 4:2:1, R_f = 0.18). The extracted aqueous phase was acidified with dilute sulfuric acid to pH 1 and again extracted with ether for 48 hours. The ether phase was dried over anhydrous Na_2SO_4, and on removing the solvent a semisolid tarry residue remained. To remove water-soluble tarry materials, the residue was treated with warm water, filtered, and finally subjected to fractional high vacuum distillation in a "lying tube" (*3*) at 0.001 mm. Hg. The product, subliming within 120°–160°C., was recrystallized from benzene (m.p., 195°–196°C.) and identified by infra-red spectra, elemental analysis, and mixed melting point with an authentic sample prepared according to Wende (*36*). The yield of the benzoic acid (V) listed in Table I represents a lower limit. Elemental analysis: calculated: C, 59.34%; H, 5.49%; OCH_3, 17.03%; found C, 58.89%; H, 5.47%; OCH_3, 16.99%.

Methanol and Carbon Dioxide. Isolation and quantitative determination of these degradation products could be accomplished by analyzing the reaction mixture obtained from a separate oxidation experiment under "standard conditions." A sample of 5 mmoles of 6,6′-bicreosol was dissolved in 50 ml. 0.2*N* aqueous NaOH corresponding to 2 mole equivalents alkali.

Methanol. After oxidation, the alkaline reaction mixture was distilled under oxygen-free nitrogen under reduced pressure (approx. 150 mm. Hg). The receiver was cooled to −15° to −10°C. using a cooling mixture (ethanol-dry ice). The distillate was analyzed by vapor phase chromatography following a procedure developed by Machata (*19*) for quantitatively determining blood alcohol.

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Together with 0.1 ml. of a 1% aqueous solution of acetone (internal standard), 0.5 ml. of the distillate (dilute aqueous solution of methanol) was placed into a 20-ml. flask and closed with a tight rubber cap. The flask was then kept in a drying chamber for 15 minutes at 60°C. An injection needle tempered at the same temperature was pierced through the rubber cap, and 1 ml. of the vapor phase was sampled and injected into the gas chromatograph.

Compared with the method of injecting dilute aqueous solutions, this technique resulted in sharper peaks and shorter retention times.

Conditions Used. Apparatus: Perkin-Elmer Fractometer F 6/4 HF. Column: column "K" Perkin-Elmer; length, 2 meters; internal diameter, 4.65 mm.; stationary phase, polyethylene glycol (MW = 1500) (15%) on kieselguhr Celite 545 (60–100 mesh). Carrier gas: nitrogen, flow rate = 70 ml./min.; flow splitting 1 (FID): 6.5 (outlet); inlet pressure 0.8 atm. Detector: flame ionization (FID); flow rate, hydrogen: 24 ml./min.; air 200 ml./min. Temperatures: injection port heater, 140°C.; column, 80°C.; outlet, 120°C. Recorder: Siemens Kompensograph; speed, 1 cm./min., range, 2.5 mv.

CARBON DIOXIDE. The carbon dioxide formed by oxidation was determined by acidifying the residual alkaline reaction mixture with 6*N* HCl following the procedure and using the apparatus described by Schmid and Schmid (*33*).

4,4′-Di-*n*-propyl-6,6′-biguaiacol (IV) was oxidized under the same "standard conditions." The degradation products were isolated and determined quantitatively by practically the same procedures as mentioned above. The isolated 2-hydroxy-3-methoxy-5-*n*-propylbenzoic acid (VI) recrystallized from benzene–*n*-hexane (m.p., 119°–120.5°C.), was identified by elemental analysis and by mixed melting point with an authentic sample. Elemental analysis: calculated: C, 62.85%; H, 6.72%; found: C, 62.64%; H, 6.80%.

"Critical Oxidation Potentials" (C.O.P.) of Model Compounds. BUFFER SYSTEM. A volume of 1 liter of *N*/7.5 Sørensen buffer (pH 6.5) was diluted with 150 ml. water, 800 ml. acetone (purified by distillation over potassium permanganate), and 50 ml. methyl cellosolve (MCS). The apparent pH of the system was 7.45.

STANDARD REFERENCE SYSTEM. A volume of 20 ml. 0.03*M* aqueous solution of complex metal cyanides was added to 200 ml. of the described *N*/15 Sørensen buffer system (apparent pH 7.45).

SOLUTION OF MODEL COMPOUNDS. The samples (in amounts equimolar to the oxidant of the reference system) were dissolved in 2 ml. MCS and diluted with 25 ml. of the above-mentioned buffer system.

ELECTRODES. Combined platinum electrode with Ag/AgCl in saturated KCl as reference system.

APPARATUS. pH-meter, type E-396 Metrohm. For determination, the procedure reported by Fieser (*5*) was followed.

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Oxidative Degradation of Wood III

A Comparison of Products by Alkaline Nitrobenzene, Molecular Oxygen, and Nitric Acid Oxidations

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Gas-liquid chromatography of reaction liquors from alkaline nitrobenzene, molecular oxygen, and nitric acid oxidations of wood indicated the presence of a larger number of products than previously noted. A sequential methylation technique allowed us to analyze phenolic compounds such as vanillin, syringaldehyde, and p-hydroxybenzaldehyde as the methyl ethers and carboxy-containing compounds as the methyl esters or methyl ether esters. Acidic materials ranging from low molecular weight acids, such as formic and acetic to polycarboxybenzenes, were found in all reactions. Similarities in qualitative composition of reaction liquors were noted among all the oxidations. The occurrence in every reaction of at least two or more members of the group of di-, tri-, tetra-, and hexacarboxybenzenes may be significant in studying lignin chemistry.

For several years wood oxidation has been investigated at the University of California Forest Products Laboratory (*4*). At the same time, development of analytical techniques suitable for determining the various oxidation products has been emphasized. This report compares the oxidation products of wood using three different oxidants.

The oxidative procedures involve alkaline nitrobenzene, nitric acid, and molecular oxygen under acidic, neutral, and mildly alkaline conditions. Dilute nitric acid solutions were used under the conditions of the nitric acid pulping process. The analytical procedures which have been developed include gas-liquid chromatography (GLC) for quantitative analy-

In Lignin Structure and Reactions; Marton, J.;
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sis of low molecular weight acids and a sequential methylation technique in conjunction with GLC to determine semiquantitatively phenolics as their methyl ethers and carboxylic acids as their methyl esters. Many compounds have been resolved, and some of them have been identified by the use of GLC techniques.

Lignocellulose or isolated lignin has been oxidized, using various reagents, and many different oxidation products have been reported. To compare previous work with our results, Tables I and II present a survey of oxidation products reported in the literature in which the oxidants we studied—namely, nitrobenzene, oxygen, and nitric acid—were used. The review has been limited to these oxidants but includes certain products from related oxidations such as hydrogen peroxide or ozone, or from nitrating nitric acid solutions. The products isolated from the different oxida-

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Table I. Literature Citations of Nitrobenzene, Alkaline Oxygen,

Oxidation Products	*Alkaline Nitrobenzene*	
	Wood	*Deriv.*
Acetic acid	(*14*)	(*14*)
Butyric acid	—	—
Cellopentaose	—	—
Cellotetraose	—	—
Cellotriose	—	—
Citraconic acid	—	—
Dihydroxybutyric acid	—	—
Formaldehyde	—	—
Formic acid	—	—
Fumaric acid	(*32*)	—
Glycolaldehyde	—	—
Glycolic acid	—	—
β-Hydroxyglutaric acid	—	—
Isosaccharinic acid	—	—
Itaconic acid	—	—
Lactic acid	—	—
Maleic acid	—	—
Malic acid	—	—
Malonic acid	—	—
Oxalic acid	(*14*)	(*14*)
Succinic acid	—	—
Tartaric acid	—	—
Tartronic acid	—	—
Tricarballylic acid	—	—

[a] Numbers in parentheses refer to literature cited.
[b] Alkaline peroxide used as the oxidant.
[c] On jute.
[d] Ozone used as the oxidant.

tions are classified as to the nature of the starting material—i.e., either wood or products derived from wood. The latter include spent pulping liquors, isolated lignins, regenerated cellulose, decayed wood, and other similar materials. As noted in the tables, certain citations pertain to products from nonwoody lignocellulosic materials such as bagasse. The references are generally early, but not necessarily the first citations pertaining to a particular product.

Table I shows that aliphatic products in reaction liquors from both alkaline nitrobenzene and nitric acid oxidations have been largely neglected. The oligosaccharides listed were isolated from reaction of regenerated cellulose with oxygen under alkaline conditions. Table II lists references to the aromatic products isolated from the same three types of oxidations.

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Aliphatic Products of Alkaline and Nitric Acid Oxidations[a]

Alkaline Oxygen		*Nitric Acid*	
Wood	*Deriv.*	*Wood*	*Deriv.*
(*18*)	(*43*)	(*10*[c])	(*22*)
—	—	(*42*)	—
—	(*34*)	—	—
—	(*34*)	—	—
—	(*34*)	—	—
—	(*17*)	—	—
—	—	(*24*)	—
(*45*[b])	(*26*)	—	—
(*18*)	(*43*)	(*1*)	—
(*18*)	(*11, 13*)	—	—
(*45*[b], *46*[b])	—	—	—
—	(*39*[b], *40*[b])	—	—
—	(*39*[b], *40*[b])	—	—
—	—	(*24*)	—
—	(*16*)	—	—
—	(*16*)	—	—
—	(*17*)	—	—
—	(*16*)	—	—
—	(*16*)	—	—
(*25*[d], *45*[b])	(*43*)	(*10*[c])	(*25*[d])
(*18*)	(*43*)	—	(*25*[d])
(*45*[b])	(*15*)	—	—
—	(*39*[b], *40*[b])	—	—
—	(*39*[b], *40*[b])	—	—

Table II. Literature Citations of Nitrobenzene, Alkaline Oxygen,

Oxidation Products	*Alkaline Nitrobenzene*	
	Wood	*Deriv.*
Acetosyringone	(*48*)	(*3*)
Acetovanillone	(*32*)	(*31*)
Benzoic acid	—	—
5-Carboxyvanillic acid	—	—
5-Carboxyvanillin	(*14*)	(*14*)
Dehydrodivanillic acid	(*32*)	(*31*)
Dehydrodivanillin	(*32*)	(*37*)
3,4-Dimethoxy-5-nitrobenzoic acid	—	—
3,5-Dinitroguaiacol	—	—
4,6-Dinitroguaiacol	—	—
3,5-Dinitro-4-hydroxybenzaldehyde	—	—
2,3-Dinitrophenol	—	—
5-Formylvanillic acid	(*32*)	(*31*)
5-Formylvanillin	(*32*)	(*37*)
Guaiacol	(*14*)	(*14*)
Hemimellitic acid	—	—
p-Hydroxybenzaldehyde	(*8, 9*)	(*27, 36*)
p-Hydroxybenzoic acid	(*32*)	—
Isohemipinic acid	—	—
Isophthalic acid	—	—
Mellitic acid	—	—
4-Methoxy-3-nitrobenzoic acid	—	—
3-Nitro-4-hydroxybenzaldehyde	—	—
3-Nitro-4-hydroxybenzoic acid	—	—
Nitrophenols	—	—
Pentacarboxybenzene	—	—
Phthalic acid	—	—
Prehnitic acid	—	—
Protocatechuic acid	—	—
Pyromellitic acid	—	—
Syringaldehyde	(*8, 9*)	(*7*)
Syringic acid	(*32*)	(*31*)
Trimellitic acid	—	—
Vanillic acid	(*14*)	(*14*)
Vanillin	(*14*)	(*44*)
Veratric acid	—	—

[a] Numbers in parentheses refer to literature cited.
[b] On rice straw.
[c] On bagasse.
[d] Alkaline peroxide used as the oxidant.
[e] Individual nitro compounds not specified.

Aromatic aldehydes and ketones have been extensively reported from alkaline nitrobenzene oxidations but not from oxygen or nitric acid oxidations. A number of nitrophenols and nitrated aromatic acids have been

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Aromatic Products of Alkaline and Nitric Acid Oxidations[a]

Alkaline Oxygen		*Nitric Acid*	
Wood	*Deriv.*	*Wood*	*Deriv.*
—	—	—	—
—	—	—	—
—	(*11*, *13*)	—	—
—	(*39*[d], *40*[d])	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	(*20*[b])	—
—	—	—	(*6*)
—	—	(*19*)	—
—	—	(*21*[c])	—
—	—	—	(*41*)
—	—	—	—
—	—	—	—
—	—	—	—
—	(*11*, *13*)	—	—
—	—	—	—
—	(*38*)	—	—
—	(*39*[d], *40*[d])	—	—
—	(*11*, *13*)	—	—
—	(*11*, *13*)	—	(*5*, *23*)
—	—	(*20*[b])	—
—	—	(*21*[c], *47*)	—
—	—	(*21*[c])	—
—	—	—	(*5*[e])
(*12*)	(*12*)	—	—
—	(*11*, *13*)	—	—
—	(*11*, *13*)	—	—
(*45*[d])	—	—	—
(*18*)	(*11*, *13*)	—	—
—	—	—	—
—	—	—	—
—	(*11*, *13*)	—	—
(*45*[d])	—	—	—
(*30*)	(*28*, *29*)	(*42*)	—
—	(*39*[d], *40*[d])	—	—

reported from nitric acid reactions, but these have been obtained primarily under nitrating conditions using concentrated acid. Benzenepolycarboxylic acids have been reported almost exclusively as products of alkaline oxygen oxidation. Aromatic acids with guaiacyl or syringyl structures have been isolated largely from alkaline nitrobenzene reactions.

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The current study indicates a broader spectrum of products from each of these oxidations than previously reported. The nature of these products will be discussed in some detail below.

Experimental

Oxidation Reactions. Description of the reaction conditions, procedures, and details of the analytical techniques used in this study have been reported elsewhere (*2*, *35*) and are summarized here.

In all reactions, wood of white fir (*Abies concolor*) has been used. For the alkaline nitrobenzene reactions, extractive-free −20+40 mesh heartwood sawdust containing 28.0% Klason lignin was used. Sequential extraction of the original sawdust with alcohol-benzene, 95% ethanol, and hot water gave extractives amounting to 4.9, 0.5, and 1.2%, respectively. In the other oxidation reactions, nominal $\frac{5}{8}$-in. wood chips, commonly used in pulping procedures, were employed. The mixed sapwood-heartwood chips contained 26.5% Klason lignin and sequential extractives of 3.3, 0.5, and 3.2%, respectively.

Alkaline Nitrobenzene. Conditions of alkaline nitrobenzene oxidation of wood or lignin reported by Leopold (*33*) have been used throughout this work. The standard conditions used include:

Reaction temperature, °C.	180
Time, hours	2
Time-to-temperature, minutes	8.5
Wood:nitrobenzene:NaOH (8%)	1:1.25:10.4
Wood charge, grams (OD)	15.4

The components of the reaction mixture were charged to a stainless steel reaction vessel of 300-ml. capacity, which was then placed in an oil bath preheated to 184°C. This reaction vessel was rotated at 42 r.p.m. by a positive gear drive mechanism. Under the conditions used, the temperature of the oil bath dropped to 180 ± 2°C. in 8.5 minutes and was maintained at this temperature throughout the reaction. Immediately following the period at temperature, the reaction was quenched by submerging the vessel in cold water. After cooling, the contents of the reaction vessel were filtered, and the solids were washed with dilute sodium hydroxide and ether. The resulting liquids were transferred to a liquid-liquid extractor and extracted with ether to remove neutral materials. The extracted liquor was then analyzed for oxidation products by techniques outlined later.

Nitric Acid. Reactions of wood chips with nitric acid were carried out using a procedure described previously (*4*). The chips (2000 grams, OD) were charged to the jacketed digester along with a 7.5% HNO_3 solution (6666 grams). The liquor was circulated through an external circulation system and sprayed onto the chips. The liquor temperature was raised from room temperature to 80°C. over a 1-hour period and maintained at 80°C. for another hour. At the end of the reaction period, the vessel and contents were rapidly cooled to near room temperature, the spent acid was drained from the vessel, and the chips were washed with water. The washed chips were then extracted with ammonium hydroxide at 80°C.

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and again washed with three portions of water. All the ammoniacal solutions were normally combined to form a composite basic extract. The spent acid, acidic washes, and composite basic extract were each retained at 40°F. until analyzed for oxidation products.

Molecular Oxygen. The molecular oxygen reactions were carried out using a procedure similar to that described for the nitric acid reaction. An aqueous solution buffered with sodium phosphate salts to give a pH of either 3, 7, or 9.5 was continually sprayed over the chip charge (2000 grams, OD) in a 1.5-cu. ft. experimental digester by means of an external liquor circulation system. A partial pressure of oxygen of approximately 100 p.s.i.a. was maintained throughout the 4-hour reaction period at 150°C. At the end of the reaction period, the liquor and reacted chips were cooled, and the spent liquor was drained off. The fiber residue was then washed twice with water, and the spent liquor and combined washes were analyzed separately for oxidation products.

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Methods of Analysis

The methods outlined here deal with methylation and other techniques used to prepare samples of oxidation products for GLC analysis. Aliphatic acids have been determined either as free acids or methyl esters. Aromatics have been determined as methyl ethers of phenolics, methyl esters of carboxylic acids, or methyl ether esters of phenolic acids.

Low Molecular Weight Acids. Aliquots of aqueous solutions of products from oxidation reactions, prepared as described, were processed by (1) forming sodium salts by adding sodium carbonate or sodium bicarbonate solutions, (2) evaporating to dryness or to near dryness, and (3) either releasing the free acids into *p*-dioxane solvent by adding sulfuric acid or esterifying with methanol-HCl. Aliquots of the resulting solutions were injected directly to the gas chromatograph.

Formic and acetic acids were determined as the free acids because of high volatility of the methyl acetate and methyl formate and resultant handling losses. Analysis was accomplished with a stationary phase of FFAP (a Carbowax 20M derivative made by Wilkens Instrument and Research, Inc.) on a relatively inert fluorocarbon support. Conditions include:

A 3-ft. × ¼-in. stainless steel column (0.21 in. i.d.) packed with 10% FFAP on Teflon-6, 40/60 mesh.

Oven temperature, 140°C.

Helium flow rate, 50 ml./min.

An Aerograph A90P gas chromatograph with thermal conductivity detector.

For the other low molecular weight acids the dried salts were refluxed in methanol-HCl to form the methyl esters. Conditions for GLC of the esters include:

A 6-ft. × ⅛-in. stainless steel column (0.085 in. i.d.) packed with 15% Carbowax 20M on Chromosorb W, AW, DMCS, 100/120 mesh.

A nonlinear temperature increase from 50 to 130°C. over an 18-minute period followed by isothermal operation.

Nitrogen flow rate, 20 ml./min.

An Aerograph A600B gas chromatograph with flame ionization detector.

Methyl esters were identified by comparison with authentic compounds on both the Carbowax 20M column and a XE-60 (a General Electric cyanosilicone gum) column. Some of the earlier identifications were made with a Carbowax 20M + H_3PO_4 column and confirmed on 1,2,3-tris(2-cyanoethoxy) propane. Also, some of the analyses of free acids were run on a Carbowax 20M-TPA(terephthalic acid terminated) column rather than the FFAP. Quantitative analysis of free acids and methyl esters was carried out using internal standards. Acetophenone was used with the acids, and veratrole was used with the methyl esters. Formic acid in the nitrobenzene and nitric acid liquors was analyzed quantitatively by direct calibration.

Sequential Methylation Technique. A sequential methylation-extraction technique has been devised primarily to separate phenolics from aromatic and aliphatic acids. The procedure, outlined below, allows quantitative conversion of phenolic hydroxyls to methyl ethers in one step and esterification of carboxyl groups in another.

Aliquots of the aqueous oxidation products, prepared as described previously for each reaction, were methylated by continuously adding dimethyl sulfate and 50% sodium hydroxide over a 40-minute period at a reaction temperature of 80°C. The pH of the reaction mixture was carefully maintained at 11 ± 0.5, and the reaction chamber was continually purged with nitrogen. At the end of the reaction period, excess dimethyl sulfate was destroyed by adding ammonium hydroxide. The mixture was cooled, transferred to a liquid-liquid extractor, and continuously extracted with ether for 36 hours. The ether extract was brought to volume and divided into aliquots which were refrigerated until used. A given aliquot was reduced in volume under a stream of nitrogen and analyzed directly by GLC.

The aqueous phase from the previous step, after extracting methyl ethers of phenolics, was acidified to a pH of 1–2 with sulfuric acid, and the free acids were extracted continuously with ether by the procedure previously noted. The ether extract was brought to volume and divided into aliquots for analysis. The methyl esters of the acids were formed by distilling an excess of diazomethane into an ether aliquot containing the free acids plus 10% methanol. When esterification was completed (approximately 20 min.), the ether solution was purged with nitrogen to remove excess diazomethane and was reduced in volume. This solution was analyzed immediately by GLC.

Ether solutions of the methyl ethers and of the methyl esters were analyzed under identical chromatographic conditions which include:

A 6-ft. × ⅛-in. stainless steel column (0.055-in. id.) packed with 10% QF-1 (Dow Corning fluorosilicone fluid) on Chromosorb W, AW, DMCS, 100/120 mesh.

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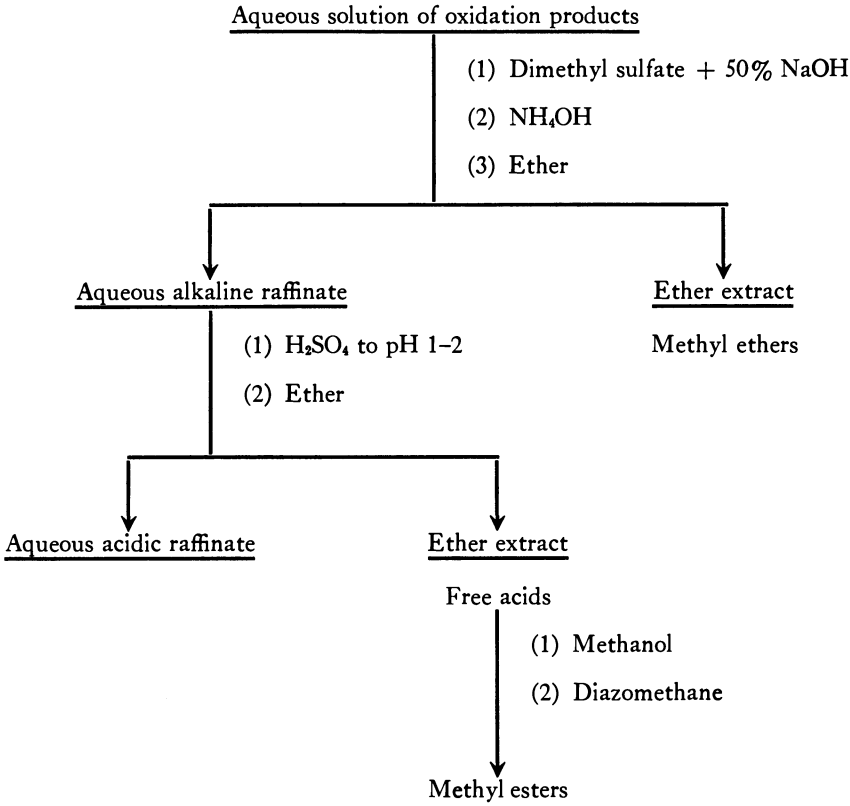

A linear temperature program at 8°C./min. from 65°C. to an isothermal limit at 250°C.

Nitrogen and hydrogen flow rates, 40 ml./min.

An Aerograph 204 dual column gas chromatograph with compensating flame ionization detectors to minimize baseline drift because of column bleed during temperature programming.

The methylated oxidation products were identified (as for low molecular weight acids) by comparing retention times with those of authentic compounds and by noting enhancement of peak size when known materials were chromatographed with unknown mixtures. Unequivocal identification remains to be obtained by isolating compounds present in peaks and determining their structures by IR spectroscopy and other appropriate techniques. Quantities of oxidation products have been estimated using a peak height-weight relationship. Certain components were selected as reference compounds, and their solutions at different concentrations were chromatographed. The weights required to give peaks of a given scale deflection were noted. This same detector response pattern was assumed to apply to components with retention times similar to the retention time of the reference compound. Quantitative analysis of greater accuracy will eventually require calibration of detector response for each identified oxidation product.

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Results and Discussion

Low Molecular Weight Acids. The method devised for analyzing free fatty acids will resolve C_1 to C_5 acids as shown in Figure 1, except for formic and propionic acids which are poorly resolved under the conditions used. Propionic acid, however, has been shown to be absent in all mixtures of oxidation products, and thus it presents no problem in this study. Acetophenone, shown in the chromatogram, was a convenient and reliable internal standard for this technique. Detection by thermal conductivity was selected because the flame ionization detector is insensitive to formic acid and, as noted, the high volatility of methyl formate and acetate precludes their quantitative determination by reasonably simple esterification procedures.

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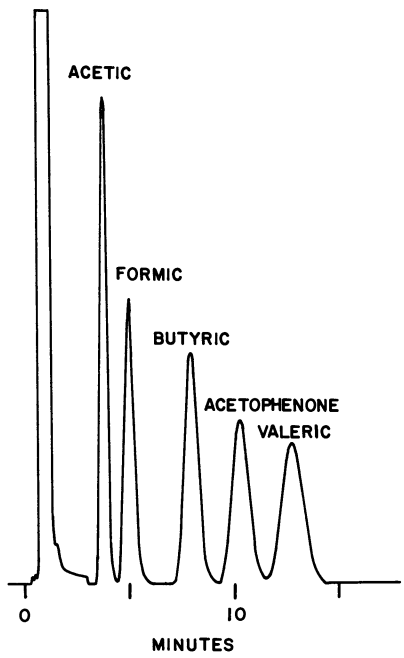

Figure 1. Chromatogram of a synthetic mixture of low molecular weight free acid standards. Acetophenone present as an internal standard.

The formation of methyl esters on an essentially quantitative basis by refluxing in methanol-HCl has been described previously (*35*). The method of chromatography as outlined is useful in isolating low molecular weight methyl esters whose retentions times are less than or similar to that of the internal standard, veratrole. A chromatogram of the methyl esters

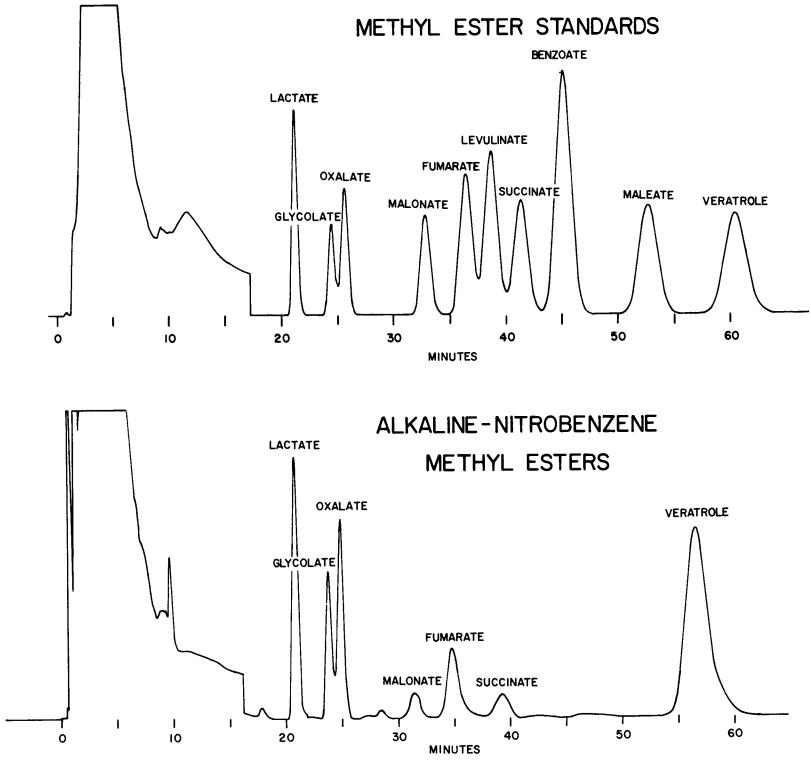

Figure 2. Chromatograms of low molecular weight methyl ester mixtures Veratrole present as an internal standard.

of authentic acids is shown in Figure 2, as methyl ester standards. These acids are mostly, but not exclusively, aliphatic, as noted by the inclusion of benzoic acid with these standards.

Results from analyzing the various aqueous solutions of oxidation products by the techniques described for the low molecular weight acids are summarized in Table III. The values included for each oxidation are totals of contributions from the various effluents analyzed. For example, the yields under nitric acid represent both spent acid and basic extract components, and the oxygen values are totals of spent liquor and combined washes. In general, the major product obtained in the oxidations was formic acid. Next in yield were the C_2 acids—acetic, glycolic, and oxalic, then the C_3 acids—lactic and malonic, and then the C_4 acids. The highest yields of acids were produced under alkaline conditions, intermediate amounts under neutral conditions, and the lowest amounts under acidic conditions. The acids reported in Table III tend to fall into three characteristic groups: acetic and succinic acids, which appear to be produced in greatest amounts by molecular oxygen oxidations and in least amount by alkaline nitrobenzene oxidations; formic, lactic, and glycolic acids, which

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Table III. Yields of Low Molecular Weight Acids Isolated in Oxidizing White Fir Wood[a]

Acid	*Alkaline Nitrobenzene*	*Oxygen*			*Nitric Acid*
		Alkaline	*Neutral*	*Acidic*	
	Grams/100 grams solubilized wood				
Acetic	1.5	8.2	9.1	6.2	4.7
Formic	20.0	26.0	12.5	11.4	7.8
Lactic	4.3	3.4	0.4	0.1	<0.1
Glycolic	10.6	8.1	1.4	2.3	2.6
Oxalic	9.6	5.2	4.4	1.8	9.3
Malonic	0.5	0.4	<0.1	trace	0.4
Fumaric	0.6	0.4	0.3	trace	trace
Succinic	0.5	1.4	2.1	1.4	0.8
Levulinic	—	—	—	—	0.6
Maleic	trace	0.9	1.0	0.1	trace
Benzoic	trace	—	—	—	0.1
Total	47.6	54.0	31.3	23.3	26.4
Lignin, % of solubilized wood	31.3	22.6	23.1	12.4	50.6[b]

[a] Yields based on quantitative procedure described in text.
[b] Much of this lignin was extracted in a second stage.

appear to be produced in greatest amounts under alkaline conditions and in least amounts under acidic conditions; oxalic acid and the combined yields of fumaric-maleic acids which appear to be highest in alkaline nitrobenzene and nitric acid oxidations and progressively lower in alkaline to acidic oxygen oxidations. Lignin and carbohydrates are solubilized in the alkaline nitrobenzene reactions to approximately the same percentages in which they are present in wood; lignin is preferentially solubilized in the nitric acid reaction; carbohydrates are preferentially solubilized in oxygen oxidations. Based on these preliminary data, it appears that the group of acids characterized by formic acid may be derived predominantly from carbohydrates of wood, and the group of acids characterized by oxalic acid, may be predominantly derived from lignin.

In the literature cited for wood oxidation only acetic and fumaric acids have been reported for alkaline nitrobenzene; only formic, acetic, and oxalic acids for nitric acid; glycolic, lactic, and malonic acids have not been previously reported for alkaline oxygen. In addition to these compounds minor peaks have been obtained on various chromatograms; these have not yet been identified.

Sequential Methylation Techniques

This technique allows one to convert phenolic and alcoholic hydroxy-substituted compounds present in the various oxidation mixtures directly

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to their readily extractable corresponding methyl ethers. Accompanying carboxy-substituted compounds are simultaneously converted to their salts. After quantitatively extracting the methyl ethers, these carboxy-substituted compounds are isolated as methyl esters by acidifying the salts, extracting with ether, and directly esterifying the ether extract.

The conditions of GLC for the methyl ether and methyl ester fractions have been selected to allow analysis of a wide range of molecular weights with a resultant loss of complete resolution of closely related compounds. In addition, identification of individual compounds in the various fractions has been directed exclusively to aromatic components. Results pertaining to methyl ethers are discussed first, followed by those for methyl esters.

A chromatogram illustrating the separation of a number of authentic methyl ethers is presented in Figure 3. The particular methyl ethers shown were selected on the assumption that the corresponding phenols may be present in the oxidation products of protolignin in wood or lignin-containing products derived from wood.

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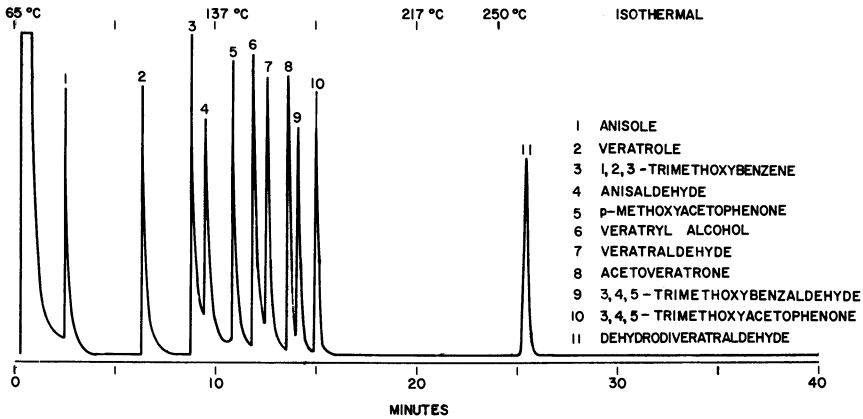

Figure 3. Chromatogram of a synthetic methyl ether mixture

In the methyl ether fraction of the alkaline nitrobenzene reaction, illustrated in Figure 4, methyl ethers of six of the eight phenols, not containing carboxyl groups, which have been reported in the literature (Table II), have been identified. These compounds, in order of elution as their methyl ethers are: guaiacol, vanillin, acetovanillone, syringaldehyde, acetosyringone, and dehydrodivanillin. Of the two remaining compounds the methyl ether of 5-formylvanillin is probably one of the two prominent peaks eluting from 1 to 2 minutes after 3,4,5-trimethoxyacetophenone. Qualitative identification of this product has not been completed. *p*-Hydroxybenzaldehyde may be present in a trace amount.

Of the four compounds—guaiacol, vanillin, syringaldehyde, and acetosyringone—found in the methyl ether fraction of the alkaline oxygen reac-

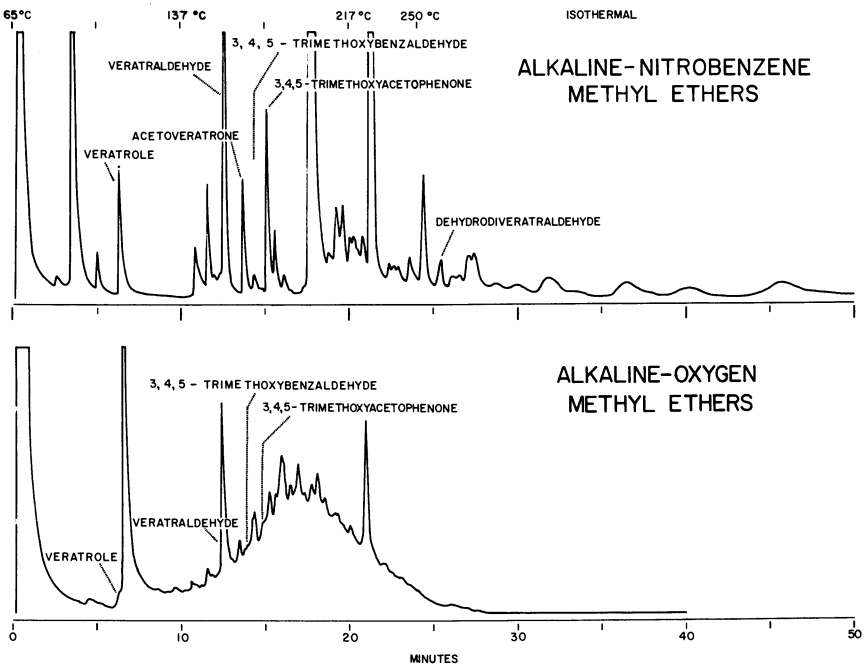

Figure 4. Chromatograms of methyl ethers from alkaline nitrobenzene and alkaline oxygen oxidation liquors

tion (Figure 4), only vanillin had been previously reported (Table II). The chromatogram of this reaction is characterized by a large background peak upon which many smaller peaks appear to be superimposed. This feature has only been found in the case of the alkaline oxygen methyl ether fraction. Although the presence of this background peak can not yet be explained, one possibility is that an "envelope" is formed because a great many closely related compounds eluting in this region are not completely resolved.

The compounds identified in the chromatograms of the neutral and acidic oxygen reactions, shown in Figure 5, are of particular interest—i.e., the methyl ethers of *p*-hydroxybenzaldehyde, vanillin, and acetosyringone. No reports have been found in the literature concerning oxygen oxidations under acidic conditions or products of neutral oxygen oxidations; hence, no entries were made for these reactions in Tables I and II. The presence of the three methyl ethers noted relates oxygen oxidations under these conditions to the others reported herein. Of further note is the absence of *p*-hydroxybenzaldehyde in either reaction carried out under alkaline conditions (Figure 4).

In the methyl ether fractions of the spent acid and basic extract from the nitric acid reaction, illustrated in Figure 6, the methyl ethers of

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p-hydroxybenzaldehyde, vanillin, acetovanillone, syringaldehyde, acetosyringone, and dehydrodivanillin have been identified. Guaiacol may also be present, but it could not be resolved from the large peak eluting at approximately 6 minutes in both chromatograms. Similarly, dehydrodiveratraldehyde could not be detected with certainty in the basic extract owing to the presence of other compounds in that area of the chromatogram. The nitro- and dinitro-substituted phenols reported in the literature (Table II), if present in either methyl ether fraction of the nitric acid reaction, could not be identified by the methylation chromatographic technique. Under the conditions used to form the methyl ethers, these compounds tend to form preferentially quinoid-type compounds characterized by their low volatility or thermal instability; this precludes GLC

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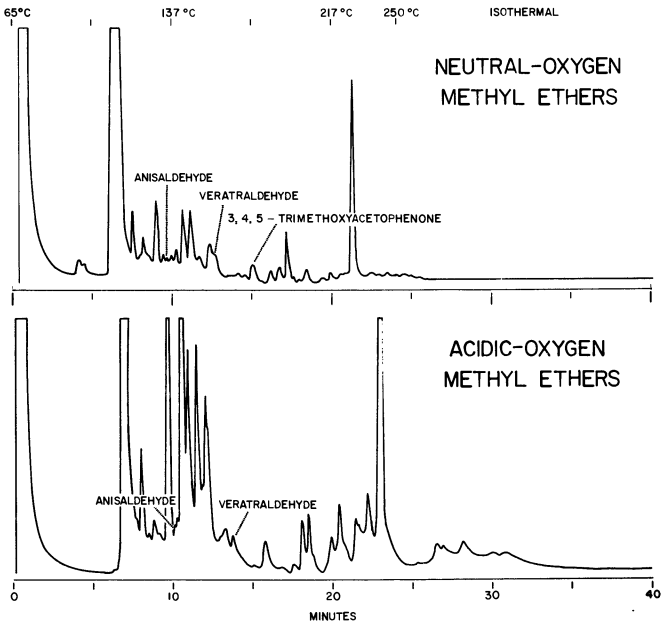

Figure 5. Chromatograms of methyl ethers from neutral oxygen and acidic oxygen oxidation liquors

analysis. Of further note is the relatively large size of peaks eluting before veratraldehyde in the spent acid methyl ether fraction as compared with the same regions in the basic extract fraction. This difference may be attributed to a greater proportion of low molecular weight, water-soluble substances in the spent acid and water washes and a larger percentage of less soluble, higher molecular weight material that is extracted with ammonium hydroxide as described in processing the products of nitric acid oxidations. The secondary and major peaks at approximately 2.5 and 3.5

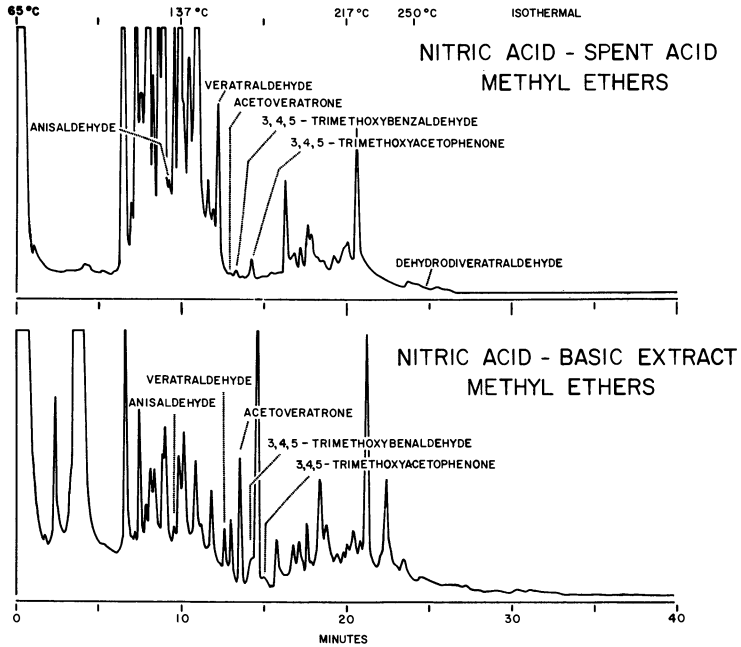

Figure 6. Chromatograms of methyl ethers from nitric acid oxidation liquors. Spent acid—the spent reaction liquor. Basic extract—an ammonium hydroxide extract of the nitric acid-reacted wood chips.

minutes, respectively, in the chromatogram of the basic extract probably can be attributed to products of hydrolysis or other reactions occurring during this extraction.

Results of the semiquantitative determinations of compounds present in the various methyl ether fractions are presented in Table IV. Where possible, the identities of compounds appearing as peaks in the chromatograms have been given together with their retention times relative to veratraldehyde. When the identity of a peak was unknown, only relative retention time was given. Relative rather than absolute retention times were used to minimize the effect of variations in temperature programming and condition of the column throughout its use. An unidentified peak, occurring at a given relative retention time and having a peak height of less than 0.3 of full-scale deflection in all of the chromatograms in which it appears, was not included in Table IV. As previously noted for low molecular weight acids, the quantities reported for each oxidation reaction are summations of the amounts found in the various effluents analyzed. Total yield of methyl ethers, considered here on a soluble wood basis, was low in all oxidations. Alkaline nitrobenzene oxidation had the largest yield, and the yields were noticeably lower for the other oxidations. In addition, 50–70% of the total yields in the alkaline nitrobenzene and acidic and neu-

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tral oxygen oxidations could be attributed to two or three unidentified peaks. The identified methyl ethers conversely, accounted for less than 20% of the total yields in all of the oxidations. The total yields of the alkaline oxygen and nitric acid oxidations appeared to be a summation of small amounts of several identified and unidentified peaks.

The array of products formed in the different oxidations, analyzed as their methyl ethers, tends to fall into two groups; those obtained under alkaline conditions and those obtained under acidic (including neutral) conditions. In alkaline oxidations very few products were formed that had relative retention times less than 0.923, but many products were present in this range in acidic oxidations. Thus, the array of oxidation products from alkaline oxygen oxidation is very similar to that from alkaline nitrobenzene and very different from that of acidic and neutral oxygen oxidations. The arrays of oxidation products from the latter reactions are very similar to that of nitric acid although fewer products were isolated. Furthermore, products having relative retention times of 0.923 or higher, with one exception, are present in greater quantities in the alkaline oxidations than in the acidic oxidations.

The methyl ether esters and methyl esters, hereafter referred to as methyl esters, isolated in the sequential methylation technique have been analyzed by the same methods used for methyl ethers. The same gas chromatographic conditions as used for methyl ethers results in the separation of synthetic esters shown in Figure 7. Under these conditions neither the methyl esters of the positional isomers of the di-, tri-, and tetracarboxybenzenes nor the methyl ester of pentacarboxybenzene and the methyl ether ester of dehydrodivanillic acid could be resolved. The position of methyl benzoate (t_r = 6 min.) in this chromatogram compared with that in the chromatogram of low molecular weight methyl esters (t_r = 45 min., Figure 2) indicates the relationship between these two chromatographic techniques. The chromatogram in Figure 2, in effect, expands the early portion of the analysis shown in Figure 7.

The methyl ester fraction of the alkaline nitrobenzene reaction, shown in Figure 8, contained, in addition to the expected methyl ether esters of *p*-hydroxybenzoic, vanillic, and syringic acids (Table II), the methyl esters of the di-, tri-, tetra-, and hexacarboxybenzenes. The individual esters of polycarboxybenzene isomers could not be resolved, as previously noted. Dehydrodivanillic acid or pentacarboxybenzene or both are present as an unmarked, secondary peak at approximately 25 minutes. Other acids reported in the literature—5-formylvanillic acid and 5-carboxyvanillin—may be present, but qualitative identification has not been completed.

Similarly, the methyl ester fraction of the alkaline oxygen reaction contained the methyl esters of benzoic acid, the di-, tri-, and tetracarboxybenzenes, and the methyl ether ester of vanillic acid. The methyl ether ester of syringic acid was also found. With regard to other acids reported

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Table IV. Yields of Methyl Ethers

Compound	*Relative Retention Time*[b]	*Alkaline Nitrobenzene*
Veratrole	0.277	0.80
	0.508	0.12
	0.532	—
	0.587	—
	0.648	—
	0.672	—
	0.703	—
	0.716	—
Anisaldehyde	0.760	—
	0.768	—
	0.797	—
	0.840	—
	0.877	—
	0.923	0.12
Veratraldehyde	1.000	0.32
Acetoveratrone	1.085	0.14
3,4,5-Trimethoxybenzaldehyde	1.138	0.03
3,4,5-Trimethoxyacetophenone	1.200	0.18
	1.238	0.08
	1.392	>1.60
	1.532	0.08
	1.554	0.08
	1.609	0.04
	1.677	0.80
	1.931	0.13
Dehydrodiveratraldehyde	2.000	0.06
Total		4.58

[a] Yields based on semiquantitative procedure described in text.
[b] Relative to veratraldehyde; t_r = 12.6 min.

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from this reaction (Table II), mellitic and pentacarboxybenzene were not present, and qualitative identification has not yet been undertaken for isohemipinic and protocatechuic.

More compounds have been identified in the neutral oxygen methyl ester fraction, shown in Figure 9, than in either the alkaline or acidic oxygen reactions. In addition to the products found in the alkaline oxygen reaction, the methyl ether ester of *p*-hydroxybenzoic acid and the methyl ester of mellitic acid are present. The acidic oxygen methyl ester fraction, also shown in Figure 9, qualitatively resembles the alkaline oxygen reaction. All the acids found in this latter reaction, except benzoic, are found in this fraction. The methyl ether ester of dehydrodivanillic acid or the methyl

Isolated in Oxidizing White Fir Wood[a]

Oxygen			*Nitric Acid*
Alkaline	*Neutral*	*Acidic*	
Grams/100 grams solubilized wood			
—	—	—	>0.49
<0.04	—	—	—
0.34	1.64	1.22	0.33
—	0.04	0.08	0.01
—	<0.03	0.04	0.10
—	—	—	0.08
—	—	—	0.04
—	0.04	0.23	0.07
—	<0.03	0.03	0.01
—	<0.03	0.30	0.05
—	<0.03	0.23	0.08
—	0.04	0.23	0.05
—	0.04	0.14	0.05
—	<0.03	—	0.03
0.17	<0.03	0.03	0.02
<0.04	—	—	0.02
<0.04	<0.03	—	<0.01
<0.04	<0.03	—	<0.01
0.04	—	<0.03	0.01
<0.04	—	—	0.01
—	—	—	<0.01
<0.04	<0.03	0.04	<0.01
<0.04	—	0.06	0.06
0.14	0.16	0.06	0.03
—	—	<0.03	<0.01
—	—	—	<0.01
0.97	2.23	2.75	1.60

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ester of pentacarboxybenzene or both are also present as the small, unmarked peak at 25 minutes in the acidic oxygen chromatogram. As previously noted in discussing methyl ethers, no literature has been found reporting products of the neutral and acidic reactions.

In the methyl ester fraction of the spent acid from the nitric acid reaction (Figure 10), the methyl ether esters of *p*-hydroxybenzoic, vanillic, and syringic acids and the methyl esters of benzoic acid and the di- and tricarboxybenzenes have been found. These compounds are also present in the chromatogram of the basic extract, as are the methyl esters of the tetracarboxybenzenes and mellitic acid. In addition, dehydrodivanillic acid or pentacarboxybenzene or both are present in both chromatograms

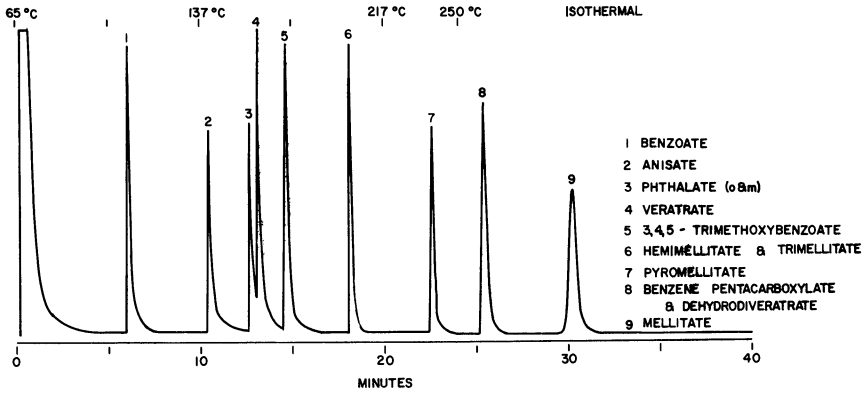

Figure 7. Chromatogram of a synthetic mixture of methyl ether esters and methyl esters

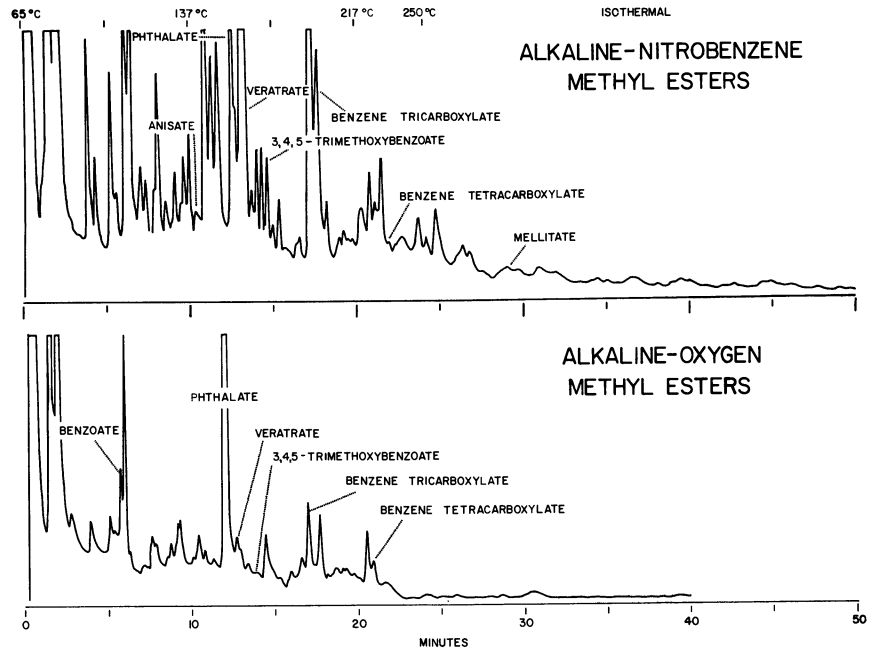

Figure 8. Chromatograms of methyl ether esters and methyl esters from alkaline nitrobenzene and alkaline oxygen oxidation liquors

as an unmarked peak at approximately 25 minutes. As mentioned for the methyl ether fraction of the nitric acid reaction, nitro-substituted compounds reported in the literature (Table II) can not be detected by this technique.

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Results of the previously described semiquantitative method of analysis, applied to methyl esters, are reported in Table V. Yields of products eluting before methyl benzoate have not been included in this table since these should be included in the results presented in Table III. Total yield of methyl esters was largest in the neutral oxygen oxidation, slightly lower under alkaline oxygen oxidation, and substantially lower in acidic oxygen, nitric acid, and alkaline nitrobenzene oxidations. The differences in yields may be attributed in a large part to three major peaks: phthalate, a component at a relative retention time of 0.490, and benzoate.

The peak attributed to phthalate represents the largest single contribution to yield under four conditions of oxidation with yields ranging from 7.3 to 0.48% based on solubilized wood. On the basis of total methyl esters, the phthalate peak amounts to 47, 35, 33, 32, and 8% of the alkaline oxygen, acidic oxygen, neutral oxygen, nitric acid, and alkaline nitrobenzene oxidations products, respectively. The unidentified peak at relative retention time, 0.490, represented the next largest component with 15, 20, 27, 12, and 12%, respectively. Benzoate in the neutral and alkaline oxygen oxidations is present as 1.97 and 0.45% of the solubilized wood which represents 10 and 3% of the methyl ester yields, respectively. Veratrate, present in all oxidation products, is present in substantial

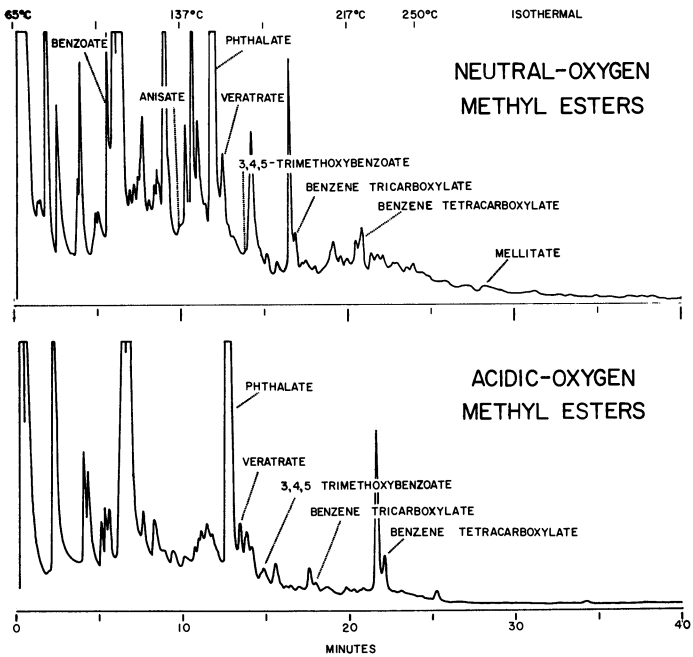

Figure 9. Chromatograms of methyl ether esters and methyl esters from neutral oxygen and acidic oxygen oxidation liquors

amounts only in the nitric acid and the alkaline nitrobenzene reactions comprising 15 and 10% of the methyl ester fractions.

The ratio of vanillin to vanillic acid and the yields of these two products, expressed as percentages of wood lignin, are the most significant data available to judge the severity of an alkaline nitrobenzene oxidation of a coniferous wood. The yields of vanillin and vanillic acid reported in Tables IV and V as methyl ether and methyl ether ester are only approximately 8 and 50%, respectively, of amounts that might be expected based on previous work. The ratio of vanillin to vanillic acid has been found to be 8: 1 whereas in the reaction reported here it is 1: 2. Furthermore, Leopold (*32*) reported vanillin: vanillic acid: oxalic acid as 6: 1: 2 whereas

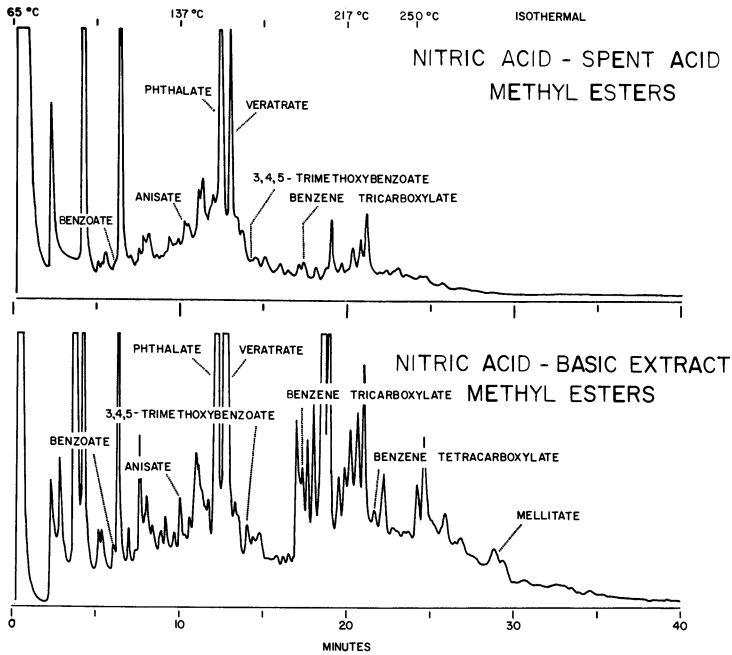

Figure 10. Chromatograms of methyl ether esters and methyl esters from nitric acid oxidation liquors
Spent acid—the spent reaction liquor. Basic extract—an ammonium hydroxide extract of the nitric acid-reacted wood chips.

in results reported here these ratios are 1: 2: 31. These data indicate that some reaction condition or conditions were unusually severe although parameters were apparently controlled to give more normal results. The results described for the alkaline nitrobenzene oxidation, therefore, are for relatively severe reaction conditions.

The presence of syringic acid as the methyl ether ester under all conditions of oxidation and of syringaldehyde and acetosyringone as the methyl

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ethers under all conditions of oxidation, except acidic oxygen is significant with respect to the degradation of the protolignin. Largest amounts of syringic acid, syringaldehyde, and acetosyringone, 0.10, 0.03, and 0.17 gram respectively, based on 100 grams of solubilized wood were obtained in the alkaline nitrobenzene oxidation. The yield of syringyl derivatives, 0.27 gram based on 100 grams of original wood or 0.95% based on the Klason lignin analysis of the original wood, is of the magnitude that would be expected by alkaline nitrobenzene oxidation of a coniferous wood. Similarly, the low yields of the *p*-hydroxybenzyl derivatives—methyl anisate, and anisaldehyde—where detected, are in the amounts expected. Thus, the presence of only small amounts of the syringyl and *p*-hydroxybenzyl derivatives on the chromatograms is essentially typical of yields of these products as reported in the literature for degradations of coniferous woods.

The occurrence of polycarboxybenzenes had been reported previously only as the products of alkaline oxygen oxidation (Table II). The high yields of dicarboxybenzenes (phthalic acid isomers), and the presence of tri- and tetracarboxybenzenes in the products of all oxidations, and hexacarboxybenzene in alkaline nitrobenzene, neutral oxygen, and nitric acid oxidations has been considered particularly significant in terms of lignin structure, but on the basis of present information and the possibility of secondary condensations, any conclusions would be premature. Yields of the polycarboxybenzenes decreased as the number of carboxyl groups increased. Although not determined, the distribution of the isomers of the di-, tri-, and tetracarboxybenzenes could also be significant.

The arrays of products from the various methyl ester fractions do not show the distinctive grouping noted for the methyl ethers. In contrast to the methyl ethers, the alkaline oxidations produced many acidic products having methyl esters with relative retention times less than 0.931. Methyl esters from alkaline nitrobenzene and nitric acid oxidations, present in more than trace amounts, were distributed more widely than esters from the oxygen reactions. In the latter instance most products with a relative retention time greater than 1.000 were present in small amounts.

Many unidentified peaks are present in all chromatograms of the various methyl ether and methyl ester fractions. Certain peaks may be attributed to the presence of partially or fully methylated carbohydrates or their derivatives. Based upon predicted retention times, considerations of molecular weight, and polarity of such compounds, and preliminary investigations of model compounds, it seems highly improbable that all of the unidentified compounds are derived from carbohydrates. Hence, identification of other compounds in these chromatograms can be pertinent not only to a more precise description of products formed in the various reactions but also to basic information concerning lignin chemistry.

A summary of yields of solubilized products is presented in Table VI. Identified aliphatic acids account for the largest percentage of products in

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Table V. Yields of Methyl Ether Esters and

Compound	*Relative Retention Time*[b]	*Alkaline Nitrobenzene*
Benzoate	0.470	—
	0.490	0.60
	0.496	—
	0.571	0.10
	0.599	0.24
	0.625	0.06
	0.720	<0.05
	0.735	0.12
	0.762	—
	0.769	0.12
Anisate	0.788	0.05
	0.807	—
	0.832	0.26
	0.842	—
	0.860	0.26
	0.931	0.26
Phthalate	0.955	0.48
Veratrate	1.000	0.60
	1.030	0.06
	1.050	0.12
	1.091	0.12
3,4,5-Trimethoxybenzoate	1.114	0.12
	1.136	0.05
	1.317	0.60
Benzene tricarboxylate	1.338	0.24
	1.373	—
	1.385	0.06
	1.431	0.05
	1.455	<0.05
	1.469	<0.05
	1.560	0.06
	1.600	0.10
	1.631	0.12
Benzene tetracarboxylate	1.659	<0.05
	1.922[c]	0.06
Mellitate	2.250	<0.05
Total		5.16

[a] Yields based on a semiquantitative procedure described in text.
[b] Relative to methyl veratrate; t_r = 13.1 min.

any category. These low molecular weight acids are primarily the C_1 to C_4 acids, as previously noted. The possible sources of the aliphatic acids have been discussed, and some components have been attributed primarily

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Methyl Esters Isolated in Oxidizing White Fir Wood[a]

Oxygen			*Nitric*
Alkaline	*Neutral*	*Acidic*	*Acid*
Grams/100 grams solubilized wood			
0.45	1.97	—	<0.05
2.27	5.26	1.60	0.82
0.68	—	1.83	—
0.18	0.13	0.12	<0.05
0.18	0.13	—	0.18
0.18	0.33	0.17	0.12
0.18	0.66	—	0.12
0.45	—	—	0.05
0.45	—	<0.05	—
—	—	0.05	0.07
—	<0.13	—	0.12
—	0.49	0.05	—
0.23	—	0.09	0.05
0.18	0.77	0.12	—
<0.18	0.49	0.05	0.28
—	—	—	—
7.27	>6.57	2.75	2.14
<0.18	0.33	0.12	0.97
<0.18	<0.13	0.12	0.12
<0.18	<0.13	0.05	0.12
—	—	—	<0.02
<0.18	<0.13	<0.05	<0.05
—	0.49	<0.05	<0.05
<0.18	0.66	<0.05	<0.05
0.45	<0.13	<0.05	0.10
<0.18	<0.13	—	—
0.36	<0.13	<0.05	0.07
—	<0.13	—	0.24
<0.18	—	—	0.12
<0.18	—	<0.05	0.18
—	<0.13	<0.05	—
—	—	—	0.17
0.23	<0.13	0.28	0.24
<0.18	<0.13	0.06	<0.02
—	—	<0.05	0.05
—	<0.13	—	<0.02
15.54	19.73	7.91	6.64

[c] Dehydrodiveratrate and/or benzene pentacarboxylate.

to lignin and others primarily to carbohydrates. The methyl ethers are present in comparatively small amounts and, based on the products identified, are primarily degradation products of lignin. Even in the alkaline

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nitrobenzene oxidation where large amounts of vanillin and other aromatic compounds are expected, yields of methyl ethers were low. Methyl ester yields are consistently larger than methyl ether yields and in the neutral and alkaline oxygen oxidations, are significantly higher than in the other reactions. Their combined yields are of particular interest since they represent the amount of material derived from lignin which still contains the aromatic nucleus.

Table VI. Summary of Yields of Solubilized Products

	Alkaline Nitrobenzene	*Oxygen*			*Nitric Acid*
		Alkaline	*Neutral*	*Acidic*	
	Grams/100 grams solubilized wood				
Aliphatic acids	47.6	53.1	31.3	23.3	26.3
Methyl ethers[a]	4.6	1.0	2.2	2.8	1.6
Methyl ether esters[a]	6.2	15.5	19.7	7.9	6.6
Total	58.4	69.6	53.2	34.0	34.5
CO_2 + CO	—	47.0	24.1	43.2	32.6
Lignin	31.3	22.6	23.1	12.4	50.6
	Grams/100 grams (OD) wood				
Solubilized wood	83.4	63.1	38.3	38.2	30.7

[a] Calculated as the methylated products owing to high content of unidentified components.

The variation among yields of products reflects the differences in the selectivity of oxidizing agents and the extent of reaction. The amount of CO_2 and CO indicates the severity of the reaction and the loss of organic substance. Lignin has been expressed on the basis of the weight dissolved per 100 grams of wood solubilized. Accordingly, the difference between 100 and the lignin value is the amount of carbohydrate solubilized. In the oxygen reactions carbohydrate was preferentially attacked, and under alkaline conditions was converted to large amounts of CO_2 and CO. The low value for solubilized lignin in the acidic oxygen reaction is partially caused by the absence of an alkaline wash of the reacted wood. The high lignin value for the nitric acid reaction together with the amount of solubilized wood indicates the most selective attack on lignin of the oxidations studied. In the nitrobenzene oxidation most of the wood was solubilized, and lignin removal was only slightly preferential.

Conclusions

One of the most important observations in this study is that gas-liquid chromatography is well suited for analyzing complex mixtures such as those obtained from the reactions of wood or related materials. Its use in this

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study allowed us to resolve a greater number of compounds than has previously been reported for the oxidations studied. Some of the compounds have not been noted before when using wood as the starting material.

A qualitative similarity in the products obtained was observed between all the oxidations studied. Although there were variations in quantitative amounts, many chromatographic peaks from a given fraction appeared in all or some of the different oxidations. The similarities were noted in each of the three fractions; low molecular weight acids, methyl ethers, and methyl esters.

Many compounds were identified in the oxidation liquors, but many still remain unidentified. On a weight basis, the identified products represent up to 50% of the total yields. Most of the low molecular weight acids have been identified.

Acidic materials, either as low molecular weight acids or methyl esters, represent the greater proportion, and materials isolated as methyl ethers represent a smaller proportion of the products formed.

The occurrence of polycarboxybenzenes in all oxidation reactions is of interest in studying lignin structure. These results do not indicate whether the basic structures were originally present in lignin or result from condensation. However, further improvement of the GLC technique to resolve all 11 polycarboxylic acids is desirable to determine which of the various isomers normally appear in the oxidations.

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Hydrogenation of Lignin by the Noguchi Process

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One of the most intensively studied routes for preparing simple chemicals from lignin has been hydrogenolysis in the presence of catalysts. By 1952 the Noguchi Institute of Japan had discovered a superior catalyst for converting lignin into substantial amounts of monophenols. This process was studied by the Crown Zellerbach Corp., and the effects of temperature, pasting oil composition, agitation, catalyst differences, lignin preparation, hydrogen pressure, and other variables were analyzed. We concluded that at present the monophenol yield was not high enough to give a suitable return. Future work to improve the yield and lower lignin preparation costs could make the production of chemicals from lignin an attractive economic venture.

During the past several decades, many routes have been proposed and investigated for converting lignin into more useful, lower molecular weight organic chemicals. Particular emphasis has been on lignins which are obtained as the by-products of chemical wood pulping processes. For various reasons, but mainly adverse economic considerations, this large source of potentially useful chemicals has not been developed extensively. One factor which contributes heavily to the adverse economic picture for chemicals from lignin is the fact that most of the chemical utilization schemes result in low yields of complex mixtures which are difficult to separate into pure components. Another factor is that the lignin is almost always obtained as a dilute aqueous solution, and chemical use requires that it be separated from a large quantity of water—a difficult and costly step.

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Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

These factors are also important in the two commercial processes which are being used presently to produce simple, low molecular weight chemicals from lignin. By now it is well known that most of the commercial vanillin used in flavoring and perfumery is obtained by oxidizing lignin sulfonates in sulfite-spent liquors. In this process, a fairly complex mixture of products is obtained, but the value of vanillin is high enough to justify the expense associated with its separation and purification. The other commercial process is preparing dimethyl sulfide from kraft black liquor. In this process, the lignin is not completely separated from the water of the black liquor but is heated as a 40–50% aqueous solution with some added sulfur in an autoclave. The dimethyl sulfide product is obtained in low yield, but in a relatively pure state, by flashing the black liquor down without having to evaporate any substantial amount of water. The yield of chemicals by either of the two commercial chemical degradative processes is quite low, and the major part of the lignin is not used by either scheme.

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Of all the proposals for converting lignin into chemicals, probably hydrogenation has been given the most attention. The techniques of hydroreforming and hydrocracking, which have been so successful in petroleum technology, have encouraged many investigators to study the hydrogenation (actually hydrogenolysis) of lignin in the hope that a substantial portion of the lignin macromolecule could be broken down into simple chemicals. The references given below are by no means a complete survey of the field but indicate only the historical development of lignin hydrogenation. The very first hydrogenation experiments were carried out using noncatalytic methods. Doree and Hall (*5*) treated lignin sulfonic acid with zinc in both dilute acetic and hydrochloric acid until hydrogen sulfide formation ceased. Analysis showed that some of the sulfur had been lost, but little or no lignin degradation occurred under these mild conditions. Willstatter and Kalb (*17*) treated hydrochloric acid spruce lignins with red phosphorus and hydriodic acid in various ways. This drastic treatment resulted in a yield of 60–80% of a complex mixture of hydrocarbons. Neither of these procedures showed much promise for making commercially useful materials.

Much more interesting results have been obtained by the techniques of catalytic hydrogenation, and many investigators have been working in this field. Lindblad (*16*) was the first to try to convert lignin into useful oils by catalytic hydrogenation of wood. He used many different catalysts such as nickel and cobalt hydroxides, nickel, zinc, copper, and manganese sulfides, zinc chloride, cupric hydroxide, and molybdic acid. He also treated wood with ferric hydroxide, then suspended it in sulfite-spent liquor, and hydrogenated this suspension. Ferrous sulfide was formed, and he claimed that this catalyzed the hydrogenation. At 350°C. heavy oils containing saturated hydrocarbons were obtained.

The hydrogenation of isolated lignins containing no sulfur was studied by Harris *et al.* (*9*, *10*) and Adkins *et al.* (*1*). A methanol lignin was hydrogenated in dioxane solution using a copper chromite catalyst at 260°C. for about 15 hours. Among the lower boiling products were substituted cyclohexyl alcohols. Higher boiling products of unknown structure were also obtained. Hydrogenation of soda lignin in dioxane, using a copper chromite catalyst for 12 hours at 250°–290°C., gave only small amounts of substituted cyclohexyl alcohols. The main products were polycyclic hydrocarbons of high boiling points.

Hibbert *et al.* (*2*, *3*, *4*) reported similar results on both isolated lignins and lignin in wood to obtain information on lignin structure. Lautsch (*12*, *13*) and Lautsch and Freudenberg (*14*) worked extensively on lignin obtained both by wood saccharification and from pulping operations. They wished not only to study lignin structure but also to try to produce useful chemicals such as phenols. Working in alkaline media, they hydrogenated the lignin in aqueous solution or suspensions using various catalysts including nickel, copper, copper-chromium-magnesium oxides, and metal sulfides. Quite complex mixtures of products including phenols, substituted phenols, and hydrogenated phenols were obtained.

By operating without catalysts but using caustic and alcohol for generating hydrogen in the autoclave, Lautsch and Piazolo (*15*) were able to obtain liquid products from lignin and lignin sulfonic acid. The products were obtained as extremely complex mixtures with little commercial value.

Lignin hydrogenation has continued to the present with many investigators studying a wide variety of catalysts and conditions (*6*, *7*, *8*, *11*). Both regular hydrogenation catalysts, such as copper chromite and Raney nickel, and sulfur resistant catalyst, such as molybdenum sulfide, thiomolybdates, and thiotungstates, have been used. Many investigators have used ether solubility of the hydrogenation products as the criterion of success, without properly considering the nature or separability of individual compounds of the product mixtures. Since ether solubility is characteristic of many materials of relatively high molecular weight, it does not necessarily follow that useful, low molecular weight materials will be found if the hydrogenation mixture can be solubilized in ether.

Noguchi Process

Based on experience obtained by hydrogenating coal during World War II, the Noguchi Institute of Japan began to study lignin liquefaction. By 1952 they had discovered a superior catalyst which converted a substantial portion of the lignin into relatively few monophenols and substantially suppressed additional hydrogenation of the phenols. This catalyst was improved some years later and, based on these two catalysts,

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a process was developed, and a pilot plant for producing monophenols was built.

The process consisted of the following steps. Sulfite-spent liquor was desulfonated by a two-stage treatment with calcium hydroxide and sulfur dioxide to give a low ash content desugared, desulfonated lignin sulfonate. The desulfonated lignin was treated with a pasting oil, generally phenol, to provide a reaction medium in which the lignin could dissolve during the hydrogenation reaction. The improved catalyst was added in amounts ranging from 1 to 10% of the lignin, and the mixture was placed in an autoclave and heated with continuous agitation to 370°–430°C. for periods of up to 4 hours in the presence of hydrogen with an initial pressure of at least 100 atm.

When the reaction was complete (claimed to be as short a time as one-half hour in some cases), the reaction mixture was removed from the autoclave, and solids were removed by filtering. The liquid product was then distilled. A yield of about 44% of monophenols based on the lignin was obtained with an additional 20–24% of heavy oils, suitable for use as recycling pasting oils. The rest of the lignin was lost as light oil, gas, and water. The monophenol fraction was composed of phenol, *o*-cresol, *p*-cresol, *p*-ethylphenol and *p*-propylphenol.

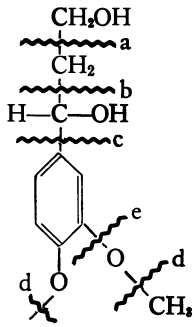
The new catalyst was claimed to have many of the ideal properties of a lignin hydrogenation catalyst. It was:

(1) Not deactivated by sulfur.

(2) Cheap enough to be expendable.

(3) Active enough to give a high liquefaction yield but not active enough to reduce phenolic materials extensively to neutral alcohols and hydrocarbons.

It was postulated that the reaction occurs by the following steps which are illustrated below. The illustration is a greatly idealized representation of an aromatic ring of the lignin polymer.



(1) The ether linkage (d) splits first. This provides products without methoxyl groups.

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(2) As long as the benzene nucleus remains unsaturated, side chains are split at (a), (b), or (c) into various free radicals, which are immediately hydrogenated to give methanol, ethanol, and various phenolic derivatives.

(3) Splitting also occurs at (e), the ether bond of the methoxyl group, to give monophenols.

(4) The Noguchi catalyst aids in splitting these bonds and stabilizing the radicals formed, but it does not promote the hydrogenation of the aromatic nuclei. This was considered as the reason for the production of a relatively small total number of separable simple compounds.

Crown Zellerbach Work on the Noguchi Process

Early in 1961, as a result of the excellent work reported by the Noguchi Institute, the Crown Zellerbach Corp. obtained an option on their process, subject to laboratory evaluation of process conditions and economics. Much effort has been expended both at the Chemical Products Division of Crown Zellerbach and at the Noguchi Institute on evaluating the process and in attempting to improve it and make it economically competitive with production of phenols from coal and petroleum.

Although many improvements in operation conditions were made so that capital costs could be lowered considerably, the process was not able to show a profitable economic picture for the United States market. A number of reasons contributing to this lack of profitability are:

(1) The monophenol products could not be obtained in as high a yield as originally estimated.

(2) Originally, we believed that the cresol fraction would be obtained as pure *p*-cresol which has considerable value. We found that *m*-cresol is always formed with *p*-cresol. The mixture of the two isomers is very difficult to separate and, without the separation, has a relatively low economic value.

(3) The use of phenol as the reaction pasting oil was recommended, but we found that phenol entered into the reaction, and part of it appeared in the product as substituted phenols, and part was lost as gas, light oil, etc.; hence it could not be completely recovered. Other pasting oils, such as stabilized high boiling cuts from the lignin hydrogenation, had to be used, and these are not as good solvents for the reaction as phenol.

(4) An important factor concerning the unprofitability is that in the past several years monophenol prices have steadily and drastically declined so that the potential return from the process has steadily decreased.

Despite the economic picture, the Noguchi hydrogenation process remains the best process for liquifying lignin that has yet appeared. We were routinely able to obtain over a 55% yield of distillable products, based on the net organic content of the starting material, and in several cases the yields were over 65%. The drawback to high liquefaction is that more

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than half is in the form of light oils, neutral oils, and high boiling fractions of little value. The average yield of monophenols was about 21–23% based on the net organic content of the lignin. These monophenols consisted mostly of phenol, *o*-cresol, *m*, *p*-cresol, *o*-ethylphenol, *m*, *p*-ethylphenol, *o*-propylphenol, *m*, *p*-propylphenol and 2,4-xylenol. Small amounts of 2,6-xylenol were also present. Compared with other hydrogenation processes, the phenolic products were remarkably simple and few in number.

A most important economic factor is the cost of lignin preparation. The original procedure we used, the two-stage desulfonation and de-ashing with lime and sulfur dioxide, gave a lignin which was relatively easy to hydrogenate, but its cost of something under 3 cents per pound was far too high for a product yield of 21% monophenols. The lignin raw material cost would exceed 10 cents per pound of monophenols. By a one-step lime desulfonation process, the lignin cost was reduced to less than 1½ cents per pound. This lignin hydrogenated nearly as well as the two-stage lignin, but its raw material cost was only about one-half the two-stage lignin. Further reductions in the cost of preparing the lignin could not be obtained, but if this were possible, the economic picture even with no increased monophenol yield would be greatly improved.

We found that the most important operating condition for the hydrogenation reaction was agitation. For many experiments, we were not able to achieve adequate liquefaction in the Magne Dash autoclave. When the shaft was lengthened and the agitation improved, the results were much better. By changing the shape of the impeller of the Magne Drive autoclave, we were able to obtain good liquefaction in only 15 minutes as compared with 2 hours before the change.

All of the hydrogenation work at Crown Zellerbach was conducted in two high pressure, high temperature autoclaves obtained from Autoclave Engineers, Inc., Erie, Pa. One of the autoclaves of 2-liter capacity was agitated by a Magne Dash type of stirrer, and the other of 1-gallon capacity was stirred by means of a Magne Drive assembly with a special impeller blade.

At the start of the hydrogenation study, detailed instructions from the Noguchi Institute were obtained and followed. Lignin was prepared by treating sulfite-spent liquor with lime to produce a precipitate of basic calcium ligninsulfonate. This was filtered, washed, and autoclaved at 190°–200°C. for 1 hour to desulfonate it. The mixture was then treated with sulfur dioxide to a pH of 2 and filtered. This treatment dissolved calcium as the bisulfite and gave a lignin product with only 2–3% ash. The lignin was obtained in 40% yield, based on the spent-liquor solids.

The hydrogenation procedure consisted of adding the lignin to phenol in a ratio of 1 part lignin to 3 parts phenol. After adding the catalyst (10% based on lignin), the mixture was placed in the 2-liter Magne Dash

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autoclave and heated to the reaction temperature with agitation throughout the heating period. In the first few hydrogenation runs the mixture was held at temperature for 2 hours, cooled, fresh catalyst and hydrogen added, reheated and held at temperature for 2 more hours. We soon learned there was no advantage to the two-stage reaction, and we held the reaction for 4 hours without interruption. Later we determined that 2 hours gave just about the same results as 4 hours, and most runs were made using 2 hours at temperature. In a few of these early runs, the oil obtained from distillation of liquefied lignin boiling above 260°C. was used as the pasting oil instead of phenol.

After the autoclave was cooled, the contents were transferred to a round-bottomed flask equipped with a Claisen-type distillation head. In the early runs, the crude oils were filtered to remove catalyst and other solids. The filtration was slow and difficult. We soon found that the filtration step was not necessary, and the solids were left in the oil. Distillation of the crude oil at atmospheric pressure gave water and light oils. The pressure was then reduced to about 15 mm., and everything that would distill was collected. The distillate was then fractionally distilled at atmospheric pressure through a 30-in. Vigreaux column and, at first, four fractions were collected:

(1) b.p. up to 170°C., light ends and neutrals.
(2) b.p. 170°–240°C., monophenol fraction.
(3) b.p. 240°–260°C., catechol fraction.
(4) b.p. 260°C., lignin tar or pasting oil fraction.

The monophenol fraction was extracted with 10% sodium hydroxide to separate it into phenolics and neutral oils. The neutral oils were found to be about 20% of the monophenols fraction. After removing the neutral oils, individual phenols were identified by gas chromatography using the retention times on three separate columns, (1) 25% Celanese ester #9 on Chromosorb W, (2) 25% diethylene glycol succinate on Chromosorb W, and (3) 20% silicone SE-30 on Chromosorb W. Quantitative estimates were made using the celanese ester column.

The apparent yields of monophenol ranged from 15% at 370°C. to 44% at 430°C. Neither the phenol nor the "green" lignin tar used for pasting oil could be completely recovered, and losses of 20–30% of the pasting oil were noted. Large, pitchy, nondistillable residues were obtained. In addition to the monophenols previously determined by the Noguchi Institute, we confirmed the presence of *o*-ethylphenol, *o*-*n*-propylphenol, 2,4-xylenol and 2,6-xylenol.

Several experiments were run to determine the stability of phenol and other pure compounds to hydrogenation conditions. When phenol was hydrogenated alone, it was recovered largely unchanged, but in the presence of lignin, some of it was always lost. When phenol was hydrogenated along with guaiacol in place of lignin, many of the same mono-

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phenols were obtained that were formed from lignin. This suggests an alternate path for monophenol formation in addition to the mechanism suggested by the Noguchi workers involving cracking of side chains.

It became obvious that part of the high yield of monophenols, obtained when phenol was used as the pasting oil, came from alkylating part of the phenol. Thus, we decided to use lignin tar (the fraction boiling above 240°C. of the liquefied lignin) as the pasting oil. Since this material also gave monophenols, when hydrogenated alone, the yields obtained by using the "green" lignin tar were also suspiciously high. To get around this, the Noguchi Institute suggested that the "green" tar should be hydrogenated several times to stabilize it and form a pasting oil that would not give many additional monophenols on further hydrogenation. This concept was adopted and used for subsequent hydrogenations. The pasting oils studied are summarized in Table I.

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Table I. Pasting Oils Used at Various Times

Pasting Oil	*Remarks*
Phenol	Could not be recovered; gave too high yields.
"Green" lignin tar	Could not be recovered; gave too high yields.
Diphenyl ether	Poor lignin solvent; could not be completely recovered.
Anthracene oil	Satisfactory, but gave no advantage.
Toluene	Poor lignin solvent.
"Stabilized" lignin tar	Good solvent for lignin; easily completely recovered.

The use of stabilized lignin tar by Noguchi resulted in their obtaining much lower yields (22–25%) of monophenols than they had previously reported. We had trouble in obtaining these yields and recovering 100% of the stabilized pasting oil from each run. The trouble was traced to poor agitation in our reactor. When the Magne Dash shaft was lengthened so that it cleared the bottom of the reactor by less than ¼ inch, our results quickly agreed with those reported by the Japanese. Paste oil recoveries in excess of 100% and monophenol yields of 21–23%, based on net organic content of the lignin, were obtained.

A study of the *p*-cresol fraction of the monophenol cut revealed that *m*-cresol was formed in amounts exceeding 25% of the cresol fraction. With increasing temperatures, more *m*-cresol was formed. The conventional Raschig analysis for *m*-cresol in the presence of *p*-cresol, which consists of treating the cresol fraction with fuming nitric acid to destroy *p*-cresol and form trinitro-*m*-cresol, was used at first. This proved to be a time-consuming step and was supplanted by a meta-para analysis based on infrared (IR) spectra. The *p*-cresol peak from the gas chromatograph was collected by cooling the effluent gases from the chromatograph in a dry ice-acetone mixture. This cut was then dissolved in carbon disulfide, and the IR curve was run in a 3 mm. sodium chloride cell. Absorbance peaks at

9.1, 12.2, and 12.4 μ were used for *p*-cresol and 10.8, 12.8, and 13.0 μ for *m*-cresol. From calibration curves for the pure compounds, the relative amounts of meta and para isomers were then calculated. This method compared very well with the gravimetric determination by the Raschig method.

After learning that we could achieve the same results as the Japanese by using stabilized lignin tar as the pasting oil, we made a number of miscellaneous hydrogenation runs. The results of some of these are shown in Table II.

Based on our best laboratory data, an economic evaluation of the process showed that it would not be profitable. Earlier studies had shown the opposite. These were based on two optimistic assumptions which were not borne out experimentally: (1) that a suitable lignin for hydrogenation could be obtained from spent liquor by a simple autoclaving step, and (2) that the yield of monophenols would be about 40% based on the lignin. Thus, in the economic study, using a more expensive lignin raw material from which lower monophenol yields could be obtained resulted in a poor economic picture.

Since the cost study of the process using a two-stage desulfonated, de-ashed lignin showed that this lignin was too expensive, we decided to use a less costly lignin starting material. We decided to use either a concentrated, desugared sulfite-spent liquor or the dried solids from such a liquor.

Using the same autoclave as before with similar catalyst levels, several experiments were made using a 37% SWL (sulfite waste liquor) concentrate with no pasting liquid except water and the concentrate with no pasting oil but with sodium hydroxide. These runs gave yields of distillable oil of 25–35% of the lignin. Adding sodium hydroxide did not improve this yield, and monophenol yields were low. We then tried to use such lignin concentrates along with various amounts of stabilized lignin tar as pasting oils. The monophenol yields in these runs were not high, but paste oil recoveries were good. This method looked encouraging except for the presence of much water, which not only made the working pressures high but would also be expensive to heat to the high temperature necessary for the hydrogenation reaction.

To eliminate the high pressure resulting from the excessive water, we studied the use of dried SWL solids in several experiments. It was never possible completely to recover pasting oil when the dried solids were used. At 380°C. the paste oil was nearly recovered, but the monophenol yield was low. At 428°C., the paste oil recovery was lower, and the monophenol yield was higher. In one experiment the dried solids were extracted with liquid ammonia so that carbohydrate material would be removed from the calcium lignin sulfonate. Approximately 10% of the solids were removed

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Table II. Miscellaneous Hydrogenations

Run No.[a]	*Lignin Used*	*Initial H_2 Pressure, p.s.i.g.*	*Reaction Temp., °C*	*Amount Catalyst, %*
110	De-ashed desulfonated	0 H_2 2000 N_2	405	7.5
111	Dried, desugared SWL	2000	405	7.5
114	De-ashed desulfonated	4600	350	0

[a] Run 110 showed that hydrogen is essential for obtaining good liquefaction. Run 111 proved that dried SWL solids were much inferior to desulfonated lignin. Run 114 showed that xylenol and high H_2 pressure, but no catalyst, were not satisfactory. Part of the monophenol yield came from alkylating and dealkylating the xylenol.

by ammonia. The monophenol yield was somewhat improved, but liquefaction and paste oil recovery were not.

Since we were not able to use dried solids, we again turned to a 55% concentrate of desugared, calcium base-spent liquor, which we called CZ 5–62L. Experiments with increased initial pressures of hydrogen gave good yields of distillable oils along with good pasting oil recoveries and low pitch residues. One experiment clearly showed the necessity of the catalyst. In this run, CZ 5–62L was treated with paste oil and hydrogen but no catalyst. A large gas loss at the autoclave was noted, the pasting oil recovery was low, and the net recovery of distillable oil was actually negative. No organic pitch residue was left. Apparently, in the absence of the catalyst, a great deal of the lignin and paste oil were converted to gas and water. In one further experiment along these lines, CZ 5–62L was treated with paste oil and a high initial pressure of 4000 p.s.i.g. The pressure in the autoclave reached nearly 12,000 p.s.i.g. The liquefaction was good, and the paste oil was nearly recovered. The monophenol yield was somewhat lower than when catalyst and lower pressure were used.

To help us determine why the dry lignin solids gave poorer results than the concentrate, dried solids were reconstituted in water to 55% solids and then hydrogenated in the same way as the CZ 5–62L. The results were poorer, and the pasting oil was not recovered in contrast to the runs with the regular concentrate. This indicated that drying adversely affects the lignin and may cause condensation and cross-linking of the lignin polymer.

During our study of the hydrogenation of dried, spent liquor and spent liquor concentrates, a new autoclave was obtained. To determine the effect of hydrogenation where there was no chance of any contamination of the reactor walls by catalyst, three runs were made with our standard desulfonated lignin in this autoclave. Phenol was used as pasting oil. The autoclave was pressured with hydrogen, but no catalyst was used. These runs gave the regular monophenols, but they also showed large gas losses with negative or low net yields of distillable oil.

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with Various Conditions

Pasting Oil Used	*Monophenol Yield Based on Net Organic, %*	*Pasting Oil Recovery of Added Pasting Oil, %*	*Pitch Residue Based on Net Organic in Lignin, %*
Stabilized	8.5	60	74
Stabilized	10.0	93	32
2,6-xylenol	24.0	81	36

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We studied some sulfur-resistant catalysts, previously known in the literature, to compare them with the Noguchi catalyst. Ferrous sulfide and cupric sulfide were prepared by precipitation from salts by sodium sulfide. This catalyst was not as good as the Noguchi catalyst and gave many more neutral oils in the monophenol cut. The liquefaction was also lower. Other catalysts based on ferrous sulfide with addition of the sulfides of Co, Ni, Zn, Mo, Mn, Cd, V, Ce, Ag, Pb, Bi, Sb, and Hg were also less effective than the Noguchi catalyst. On the possibility that, instead of hydrogen gas, a substance that could readily donate hydrogen in the reaction could be used, a run was made with crude sulfate turpentine as the hydrogen source. Much solid was produced, and only a small amount of monophenols was formed.

Several experiments were run to determine the suitability of various lignins for hydrogenation. Precipitated kraft lignin at first appeared to give very high yields of monophenols, but later experiments did not confirm this. Instead, low monophenols with good paste oil recoveries were obtained with kraft lignin. Wood flour was run to see if a native lignin would be suitable. Only a 13% yield of monophenols formed from the lignin. Much water, gas, and light oil were obtained.

The possible use of pasting oils other than stabilized lignin tar was studied, and we learned a considerable amount about the stability of some of the monophenol products of the hydrogenation. We concluded that meta and para isomers are more stable than ortho isomers and should be the favored configuration as the result of repeated hydrogenations. The results of some of these experiments are shown in Table III.

Neutral oils, obtained by extracting the monophenol cut with caustic, were tried as paste oil. These gave monophenols and must have contained phenyl ethers which cleaved upon hydrogenation.

As the result of many experiments, we concluded that a 55% concentrate of desugared, spent liquor was the best lignin starting material, based on cheapness and paste oil recovery. We also concluded that light oils (containing many hydrocarbons, etc. such as cyclohexane and benzene),

neutral oil from the caustic scrubbing of the monophenol cut and the higher alkylphenols (boiling above 205°C.) should be recycled, and eventually they would make up the major part of the paste oil. To test this idea, we made three series of simulated continuous runs in the autoclave. These three series all used CZ 5–62L lignin but variable amounts of catalyst. The run that gave the best results used 7% Noguchi catalyst, 1600 p.s.i.g. initial hydrogen pressure, 428°C. reaction temperature initially but later lowered to 405°C., and 2 hours hold time. The light oils, neutral oils, and 205°–240°C. phenols were recycled as paste oil, and during each cycle some lignin tar (above 240°C.) was removed and saved. We were not able to continue the runs long enough to reach a steady state, but from the data obtained we estimated that eventually no lignin tar boiling above 240°C. would be recycled, and the paste oil would consist of about 50% light oil, 10% neutral oil from the monophenol cut, and 40% of the 204°–240°C. monophenols. All of the lignin tar boiling above 240°C. formed during each cycle would be hydrogenated separately to give additional monophenols.

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Table III. Stability of Various

Run No.	*Phenol*	*H_2 Pressure, p.s.i.g.*	*Catalyst Amount, %*
161	*o*-Cresol	2000	3.2
180	*p*-Cresol	2000	3.2
176	*p*-Ethylphenol	2000	7.0
203	50-50 *p*-Cresol, *m*-Cresol	2000	3.2

A paste oil of the estimated composition was made up and used in hydrogenation. The total salable monophenols (b.p., 180°–205°C.) yield from this was found to be 8.5%, and a stabilized lignin tar yield from the second hydrogenator was 19% of the net organic of the lignin. In addition to the yield data, we fractionally distilled the combined monophenol cuts from the continuous runs. The *m*-,*p*-cresol peak from the gas chromatograph was analyzed by IR spectroscopy and found to be 45% *m*-cresol and 55% *p*-cresol, which meant that no pure *p*-cresol could be obtained by fractional crystallization of the meta, para mixture. From the fractional distillation we found we could obtain most of the monophenols indicated in the gas chromatographic analysis.

Based on the above-described continuous runs, an economic feasibility study was again made. Although the lignin concentrate was the cheapest possible lignin starting material to use, the presence of water made the reaction pressures very high, and this resulted in excessively high capital and operating costs; again the process showed a net loss.

Our many experiments and cost studies showed that either the yield of monophenols had to be markedly increased or the capital and operating costs had to be greatly reduced. We did not see any obvious way to in-

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crease the monophenol yield, so we concentrated on reducing the costs. We did, however, consider the possibility of controlling the formation of *m*-cresol and thereby increasing the yield of valuable *p*-cresol.

In order to keep the operating pressure down, we decided it would not be possible to use the cheapest lignin, CZ 5–62L, with all of its water content. The original desulfonated lignin, prepared according to the Noguchi directions, was too expensive for consideration. A one-step reaction, which was a modification of their lignin preparation, was tried and eventually produced a desulfonated material which was considerably cheaper than the Noguchi-prepared lignin. The modification consisted of a one-step heating of the desugared, spent liquor with lime at 200°C. in an autoclave, followed by de-ashing with sulfur dioxide. This process has only one filtration instead of the two in the Japanese process. The lignin yield from spent liquor is also larger. Depending on the lime used, we were able to prepare desulfonated lignins which cost less than 1½ cents per pound as compared with nearly double this for the two-step desulfonated product.

Monophenols to Hydrogenation

Temperature, °C.	*Phenol Recovery, %*	*Yield of Other Phenols, %*	*Light Oils Formed, %*
428	60	14.2	9.0
428	93.5	0.9	3.4
428	93	1.0	3.3
428	92	1.0	1.8

Most of our later work was done using this cheapest desulfonated lignin. We did find that a desugared, spray-dried spent liquor worked better than spent-liquor solids dried by merely heating in an oven. The spray-dried product was used for occasional experiments.

Several hydrogenations were made using our best previously determined conditions to see if the cheaper, one-step desulfonated lignin was as good as the more expensive, two-step material. The results were nearly comparable. Thus, we succeeded in materially lowering the lignin costs.

Many runs were made to study the effect of lower hydrogen pressures. The first method was to start with a low hydrogen pressure, heat to about 370°C., and hold at this temperature for a short time. Then the temperature was increased to reaction temperature with small additions of hydrogen so that the maximum pressure did not exceed 2500 p.s.i.g. The results were just about as good as when more hydrogen was used at first and then heated directly to higher final pressures. Several variations of this procedure were also studied. In one variation, the one-step desulfonated lignin was treated with pasting oil. Regular Noguchi catalyst was added, and the regular pressure (1200 p.s.i.g.) for hydrogen was applied. The reactor was heated to 300°C. and held for 1 hour. It was then heated to

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428°C. and held 2 hours. This gave a maximum pressure of only 2500 p.s.i.g. The results were not good, and apparently conditions were not vigorous enough since the pitch residue was high and the monophenol yield was low. Still another variation was tried. The lignin, pasting oil, and catalyst were placed in the autoclave which was charged with only 100 p.s.i.g. of hydrogen, and the temperature was raised to about 360°C. and held for ½ hour. Then, in various experiments, hydrogen was admitted so that the maximum pressures after heating to 428°C. were 1500, 2000, 2500, and 5000 p.s.i.g. The lower pressure did not give satisfactory liquefaction. The run at 2500 p.s.i.g. was satisfactory from the standpoint of liquefaction, but the monophenol yield was down somewhat. We observed no advantage in operating at 5000 p.s.i.g. Thus, we concluded that 2500 p.s.i.g. as a working pressure should serve just as well as 4000 p.s.i.g. or even higher, and this pressure was adopted as the maximum working pressure. Subsequent experiments justified this choice, and we also found that no waiting period at 350°–370°C. was necessary, but that heat-up directly to the reaction temperature with a relatively low initial hydrogen pressure and then adding hydrogen to maintain 2500 p.s.i.g. worked very well. Thus, we attained another objective in cost lowering since the design operating pressure could be lowered considerably from what was previously necessary.

Several experiments were run to determine the mechanism of formation of *m*-cresol in the *p*-cresol fraction. We determined that using phenol as the pasting oil resulted in the formation of almost pure *p*-cresol. The ratio was 3 meta to 97 para. When a pasting oil of 75% phenol plus 25% stabilized lignin tar was used, the same ratio was obtained. A paste oil composed of 25% phenol and 75% stabilized lignin tar, gave a ratio of 14 meta to 86 para. These experiments were run using spray-dried spent liquor solids and high pressures. The results are shown graphically in Figure 1.

When one-step desulfonated lignin and low pressure were used with a paste oil of 13% phenol and 87% lignin tar, the meta-para ratio was only 12:88.

Other experiments to control *m*-cresol formation were run. Guaiacol and eugenol were hydrogenated, and the meta-para ratios of the resulting cresol fractions were approximately 45:55. From these experiments, we postulated that during the hydrogenation methyl ions or radicals are formed, and when a ready methyl-acceptor such as phenol is present in sufficient amount, the methyl groups are directed to the ortho or para positions. Since we previously determined that para-substituted phenols are the more stable configuration during hydrogenation, it follows that *p*-cresol would be preferentially formed. Thus, the ortho-para directing influence of the pasting oil should determine the meta-para ratio. This was confirmed by using toluene, a relatively weak ortho-para director and

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aniline, a stronger ortho-para director but not as strong as phenol. Toluene gave a ratio of 30 meta to 70 para, and aniline gave a ratio of 20 meta to 80 para. The results are summarized in Table IV.

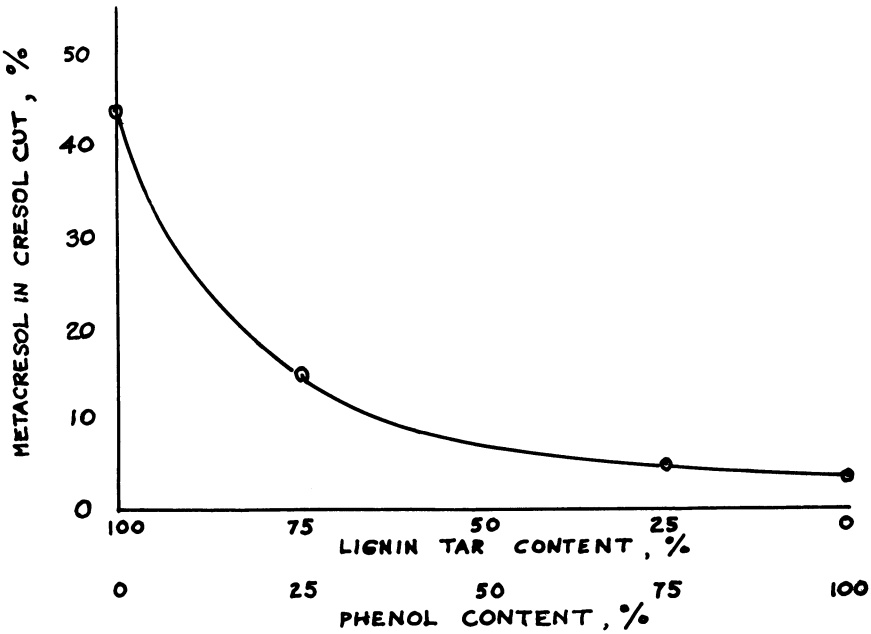

Figure 1. Effect of phenol in pasting oil

As the result of these experiments, using 12–15% phenol (this amount could usually be completely recovered or else the makeup was small) in the pasting oil was adopted as a standard procedure. One experiment using sodium phenoxide as the strongest ortho-para directing substance, was not successful owing to the condensation of the phenoxide with lignin.

Besides investigating the lignin starting material, lower pressures, and *m*- to *p*-cresol ratios, many miscellaneous experiments were run to try to find new catalysts and new methods of operation. The possibility of hydrogenation combined with dimethyl sulfide formation was examined. Sodium sulfide was added to desugared, spent liquor and to a kraft black liquor concentrate. No additional dimethyl sulfide was produced in either case. On the chance that the vanillin process might produce a partially degraded lignin which would be more readily hydrogenated, a run was made on such a lignin. There was no evidence that vanillin preparation aided the breakdown of the lignin. Elemental boron was tried as a catalyst but had little, if any catalytic activity. A cobalt-activated molybdenum sulfide catalyst gave good liquefaction but a high amount of neutrals and

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Table IV. Ratios of *m*- to *p*-Cresol

Run No.	*Lignin Used*	*Catalyst Amount, %*	*Temperature, °C.*
289	De-ashed desulfonated	14	428
309	CaSWL	7	405
313	CaSWL	7	405
345	De-ashed desulfonated	7	428
308	None	7	405
318	None	7	405
287	CaSWL concentrate	7	405
325	CaSWL	7	405
329	CaSWL	7	405

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unidentified material in the monophenol cut. A chelated iron catalyst, "Cataban," was a poor catalyst as was the iron salt of phenol.

Three series of simulated continuous runs, similar to those used on spent liquor concentrate, were set up. The first was designed to use the cheapest, desulfonated lignin, low pressure, and a paste oil with some phenol to help control the *m*-cresol formation. The results were fairly good especially when stirring in the autoclave was started as early in the run as possible. There was, however, a considerable amount of pitch residue, indicating incomplete reaction. Another series utilized the same lignin and pasting oil, but the temperature was raised to 438°C., and the hydrogen pressure was raised to 3000 p.s.i.g. Poor monophenol yields and liquefactions were obtained, and this series was terminated early. A third series utilized a one-step desulfonated lignin which was more expensive than the cheapest lignin since more lime was used in the desulfonating step. Again, good liquefactions were obtained, but the results were not much better than with the cheapest lignin.

During these simulated continuous runs, the heat-up curves during the hydrogenation were followed closely, and the curves exhibited exotherms and endotherms generally occurring at about the same temperature. Several runs were made to determine the reason for the breaks in the heating curve. In two runs the reaction was heated through the endotherm (at about 370°C.) and allowed to run through the exotherm, which was complete at about 420°C. The reaction coasted to 428°C., was terminated, and the autoclave contents analyzed. The reaction was incomplete as shown by low monophenols and a low net yield of distillable oil, but the recovery of much paste oil showed that lignin tar formation is the initial lignin reaction, and it occurs at relatively low temperatures. The reaction was repeated with phenol as the solvent. The same endo-

with Various Pasting Oils

H_2 Pressure, p.s.i.g.	*Pasting Oil*	*m- to p-Cresol Ratio*
1600	Phenol	3:97
1600	Three parts phenol One part stabilized lignin tar	3:97
1600	Three parts stabilized lignin tar One part phenol	14:86
1000	Six parts stabilized lignin tar One part phenol	12:88
1600	Guaiacol alone	46:54
1600	Eugenol alone	43:57
1600	Stabilized lignin tar	44:56
1600	Two parts stabilized lignin tar One part toluene	30:70
1600	Aniline	20:80

therms and exotherms were obtained, and the reaction also appeared to be incomplete. In a following run, phenol alone was used, and no breaks in the heating curve were observed. Certainly, lignin must be present to obtain the endotherms and exotherms, and they may be caused by sudden solution of lignin in the pasting oil causing the endotherm, which is then followed by a rapid reaction owing to the fact that lignin is in solution.

During the study of the endotherms and exotherms, we observed that the design of the impeller on the shaft of the Magne Drive autoclave did not allow the catalyst to mix well with the autoclave contents. Bars were added to the impeller blades, and the blades were bent so they exerted a scooping action on the bottom of the autoclave. Two standard hydrogenation runs with desulfonated lignin showed that this aided the yields very much. Monophenols were increased and so were liquefaction and paste oil recovery. These runs were made at 2 hours, and since the reaction had obviously been improved, we decided to study shorter reaction times. A run at 1 hour gave nearly as good a yield as a run at 2 hours. A ½ hour also gave good results. A run at 15 minutes gave good liquefaction and paste oil recovery, but the monophenol yield was reduced. We decided to use a short reaction time but with a maximum temperature higher than the 428°C. (used in previous runs). Runs at 450°C. with a 5-minute reaction time and a 15-minute reaction time were made. The 5-minute time appeared to be too short, and liquefaction fell off. To determine the top temperature, a run of 475°C. was made. This was too high, and the net yield of distillable oil fell off, and paste oil recovery was not quite 100%. We therefore chose 450°C. and 15 minutes as our preferred operating conditions.

The short reaction times were chosen using a lignin to paste oil ratio of 1 to 1.3. We tried an experiment increasing this ratio to 1 to 2. This

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aided the hydrogenation, probably by giving the lignin a better chance to dissolve during the progress of the reaction. Almost the same results were obtained in 5 minutes at 450°C. with this lignin to paste oil ratio as with 15 minutes at 450°C. with the lower ratio. Using more hydrogen and catalyst did not result in bettering the results significantly.

Since the reaction appeared to proceed better with the short time, high temperature conditions, using phenol as the total paste oil was again tried. We were still not able to recover all the phenol. We concluded that a relatively small amount of phenol can be recovered by what is made from the lignin, but when phenol is the total paste oil, the amount decomposed is too large to be made up from the lignin.

All the previous hydrogenations were conducted by the method suggested by the Noguchi Institute. This consisted of distilling the reaction mixture at atmospheric pressure to remove water and light oil, followed by a tedious and difficult distillation at reduced pressure to recover monophenols and lignin tar pasting oil. It was always difficult to distill high boiling lignin tar from the nonvolatile residue, and since the temperature became high near the end of the distillation, much decomposition and gas loss occurred. A new method of work-up was tried. This consisted of filtering or centrifuging insoluble material in the crude oil from the autoclave and then removing the water and light ends at atmospheric pressure. The monophenols were then recovered by a relatively low temperature, reduced pressure distillation. The pasting oil containing dissolved, unreacted pitch was recovered and used again as pasting oil so the pitch had another chance to be hydrogenated without being subjected to the high temperatures of a distillation.

A series of runs was made using this work-up. The procedure was satisfactory and gave an average monophenol yield exceeding 20%. An excess of pasting oil was always recovered, and the recycled oil appeared to survive many cycles before it had to be distilled to remove high boilers or pitch.

Another modification of this work-up was tried. This consisted of using only 3% catalyst and no filtration of the reaction mixture. The catalyst was recycled along with undistilled pasting oil and pitch with a make-up of 1% catalyst every recycle. The runs using this procedure gave good monophenol yields (average 21.7%) and oil recovery exceeding 100%. The solids did build up, so that by the third cycle the reaction mixture had to be filtered. Thus, it appeared that we could use this method of operation and use a filtration step every second cycle, making the catalyst usage 2% per cycle.

One bad feature of the short-time, high temperature reaction was the fact that phenol did not control the meta-para ratio nearly as well as at lower temperatures. At the lower temperatures, the pasting oil of 87 parts lignin tar and 13 parts phenol gave a meta-para ratio of about 15 to 85.

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At the higher temperatures, the ratio was 35 to 65. We concluded that the reason for this was that at lower temperatures, not far from the critical temperature of phenol, the concentration of phenol in the pasting oil was relatively high. At higher temperatures, well above the critical temperature of phenol, the phenol concentration in the pasting oil was low, and *m*-cresol and *p*-cresol were formed in a random manner, and the ratio was considerably increased. A run made at high temperature, but with double the amount of phenol, reduced the meta to para ratio from 35 to 65 to 29 to 71, indicating that the concentration of phenol in the liquid phase was increased but not by very much. Another factor resulting from the short-time, high temperature heating was that neutrals from the monophenol cut were largely hydrocarbons and contained little or no oxygen. This contrasted with the neutrals obtained at lower temperatures, which contained oxygen and probably alkylphenyl ethers.

Based on our work resulting in reduced operating costs owing to cheaper lignin, lower pressure, shorter reaction time, and improved work-up, the following is a distribution of the products expected from hydrogenation. The monophenol cut, obtained in an average yield of 30% based on the net organic content of the desulfonated lignin, should be fractionally distilled to recover the phenol used in the pasting oil. The remaining monophenols are then extracted with 10% sodium hydroxide to separate them from neutrals, which are about 30% of the monophenol cut. Thus, the monophenol yield is about 21% of the net organic lignin content and the neutrals yield is about 9%.

A typical analysis of the monophenol cut from the vacuum distillation is listed below. This is from 200 parts net organic in the lignin.

Monophenol cut	122 parts
Neutrals	18
Monophenols	104
Phenol	68 [a]
o-Cresol	8
m,*p*-Cresol	12
o-Ethylphenol	2
p-Ethylphenol	6.5
p-Propylphenol	4
2,4-Xylenol	2.5
Unidentified phenols	1
Total	104 parts

[a] 6 parts in excess of added phenol.

Thus, a monophenol yield of about 21% can be obtained with phenol, *o*-cresol and *m*,*p*-cresol being 13% of the net organic. This yield could be increased somewhat by hydrogenating the excess paste oil which is saved out of each cycle.

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The following is a materials breakdown of all the products that can be obtained from 200 parts of net organic.

Gas	35 parts	17.5%
Water	55	27.5
Light oils	10	5.0
Monophenols	42	21.0
Neutrals	18	9.0
Excess paste oil (b.p., 240°C.)	40	20.0

An economic evaluation of the above process, which incorporated all of the described cost saving features, still showed that the process would not be profitable. The substantially reduced costs were offset by a decrease in the value of products owing to:

(1) A decrease in total solids to the reactor.
(2) Lower yield of *p*-cresol available.
(3) A general softening of phenol and cresol prices.

A great deal of effort was expended on the process without resulting in an economically feasible monophenol production for the United States. This does not mean that the Noguchi hydrogenation process is not a significant advance in our attempts to produce useful low molecular weight chemicals from lignin wastes. In all experiments comparing their catalyst with previously known catalysts, better liquefactions with considerably greater specificity in the number of products were obtained.

If, by means of catalyst improvements which are not obvious at the present time, the monophenol yield could be improved by, say 50%, the process should become profitable. Another area of improvement lies in reducing lignin preparation costs still further. This is for the future, however. At present, the Noguchi process is the best hydrogenation procedure which has yet been developed for converting lignin into chemicals.

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Hydrogenolysis of Lignin

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The structural features of Alnus rubra lignin, isolated by mild hydrogenolysis over Raney nickel, have been examined primarily by nuclear magnetic resonance (NMR) spectroscopy techniques. The total lignin isolated using acidic catalysis is estimated to contain 34% syringyl units, 23% condensed guaiacyl units, and 43% guaiacyl units. A high molecular weight fraction (of this hydrol lignin) is estimated to contain 15% syringyl units, 51% condensed guaiacyl units, and 34% guaiacyl units. Identified monomeric products contain more than 99% C_6C_3 structures. The lignin isolated using basic catalysis apparently underwent some aromatic ring reduction and extensive side-chain degradation. NMR and gas chromatography techniques are discussed.

Nuclear magnetic resonance spectroscopy was used to determine structural features in lignin and lignin fractions isolated from the hardwood *Alnus rubra* by mild catalytic hydrogenolysis.

NMR spectroscopy enables one to obtain both qualitative and quantitative information concerning the various protons present in the lignin molecule, and often this information is unique and cannot be obtained readily by any other means. Ludwig, Nist, and McCarthy (*4*) determined the structural features of several acetylated conifer lignin preparations and were able to obtain a detailed picture of these preparations, including estimations of aromatic, methoxyl, and benzylic protons as well as other types of protons. Using NMR spectroscopy in connection with classical elemental and functional group analysis, they were able to estimate that the degree of condensation of the aromatic rings in acetylated Björkman spruce lignin was about 45%. Bland and Sternhell (*1*, *2*) studied methanol lignins from both conifer and deciduous species and obtained similar data;

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Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

with respect to degree of condensation they arrived at a figure of about 70% condensed aromatic units for *E. regnans* methanol lignin.

Experimental

Preparation. The lignin was isolated from red alder (*Alnus rubra*) by hydrogenating extracted wood meal over Raney nickel for a 4–8-hour period using 500 p.s.i.g. initial hydrogen pressure. Two solvent systems were used; 1:1 dioxane-water and 3% sodium hydroxide. The former system becomes acidic during the reaction, and the product is referred to here as hydrol lignin A; the latter is basic and is referred to as hydrol lignin B. The yields based on Klason lignin were 40–60% in case A and 70–95% in case B.

Hydrol lignin A was crudely fractionated by repeatedly precipitating a chloroform solution into ether; this yielded a low molecular weight ether-soluble fraction (65%) and a high molecular weight ether-insoluble fraction (35%).

The several lignin preparations were acetylated by standing 48 hours in an acetic anhydride-pyridine mixture, pouring onto crushed ice, and recovering the acetylated product.

Model compounds used in this study were obtained from commercial sources or were prepared by standard methods.

Elemental analysis was carried out by Micro-Tech Laboratories, Skokie, Ill., and methoxyl determinations were performed by the Georgia Pacific Co., Bellingham, Wash.

Procedures. Spectra were obtained on a Varian A-60 NMR spectrometer. Lignin samples and model compounds were analyzed as 16% solutions in deuterochloroform solvent using a tetramethylsilane internal standard.

Gas chromatography analysis was done on a Perkin-Elmer model 800 unit using dual $\frac{1}{8}'' \times 6'$ columns packed with silanized Chromasorb W (product of Johns-Manville) coated with 5% neopentylglycolsebecate and ½% phosphoric acid. The column temperature was programmed from 100° to 240° C. at 8°/min. during analysis.

Results and Discussion

Lignin isolated by mild catalytic hydrogenolysis was selected for this study to overcome solubility and NMR peak-broadening problems usually associated with polymeric materials. The hydrol lignin and its acetylated derivative are readily soluble in chloroform-*d*, and the lignin is degraded to a mixture of materials of lower molecular weight than the original lignin.

Chemical Shift Values for Hydrol Lignins. Lignins isolated by hydrogenolysis contain structural features not present initially, and it was necessary to determine the values for chemical shifts for the new types of protons. This was done using δ values from the literature (*1*, *2*, *5*); from spectra of model compounds prepared in this study of the guaiacyl and syringyl type, substituted with C_1, C_2, and C_3 hydrocarbon side chains,

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Table I. Ranges of δ Values for Protons in Compounds Related to Hydrol Lignin

Type of Proton	*Ranges of Chemical Shifts*
Aromatic	7.3–6.28
Guaiacyl	7.3–6.73
Condensed guaiacyl	6.73–6.48
Syringyl	6.48–6.28
Aliphatic-Substituted	6.28–3.50
Acetylated benzylic	6.28–5.74
α, β, γ	5.74–3.50
γ-CH_2OH	3.80–3.50
γ-CH_2OAc	4.28–3.97
Methoxyl	4.00–3.72
Acetoxyl	2.42–1.88
Aromatic	2.42–2.20
Aliphatic	2.20–1.88
Aliphatic hydrocarbon	2.80–0.78
α to Phenyl	2.80–2.34
β to Phenyl	2.12–1.03
β-Methylene to CH_2OH	2.12–1.66
β-Methylene	2.00–1.30
β-Methyl	1.37–1.03
γ-Methyl	1.18–0.78
Hydroxyl	4.40–3.60 (?)

C_2 and C_3 primary alcohol side chains; guaiacyl type models substituted in the C_6 position with reduced carbon side chains and acetylated derivatives of these models; from spectra of the several hydrol lignin preparations.

Ranges of values of chemical shifts useful in interpreting NMR spectra of hydrol lignins are summarized in Table I. These values differ from those assigned by Ludwig principally in the region where highly shielded aliphatic protons appear—i.e., the α, β, and γ protons giving chemical shift values in the δ range of 2.80–0.78 p.p.m. Table I is self-explanatory in this respect.

The protons in guaiacyl and syringyl types of aromatic substitution patterns exhibit distinct differences in NMR spectra. In the guaiacyl case, the aromatic nucleus contains three protons and is described as an AB_2 system. The NMR spectrum from this kind of system is a complex summation of nine lines depending on the spin-spin coupling (*7*). In guaiacyl compounds usually four lines are observed, and these appear in spectra of unacetylated model compounds in the δ range of 6.53–6.96 p.p.m. The syringyl nucleus contains two identical protons which produce a singlet in the δ range of 6.3–6.5 p.p.m. A guaiacyl nucleus substituted with a reduced carbon atom in the C_6 position usually produces a singlet in the δ range of 6.48–6.62 p.p.m. These δ values are somewhat sensitive to

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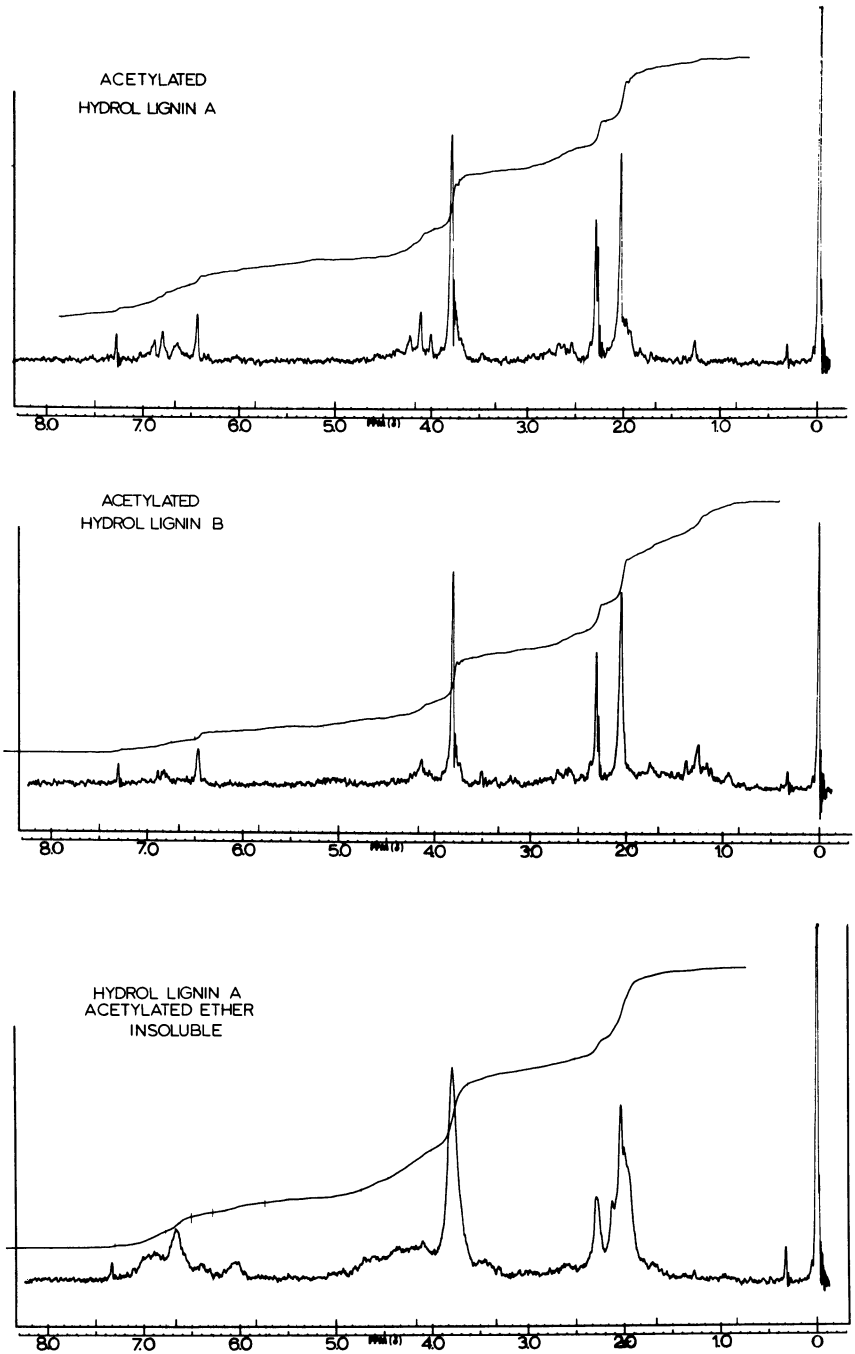

Figure 1. NMR spectra of acetylated hydrol lignins

the nature of substituents—i.e. on the hydroxyl group and the state of oxidation of the α-carbon atom in the side chain. The ranges cited are for reduced side chains and are not generally applicable to other models or lignin preparations. Taking into account peak-broadening effects and minor shifts caused by acetylation, δ ranges have been assigned for each type of nuclei; these are enumerated in Table I. The δ division line between guaiacyl and condensed guaiacyl shifts from 6.73 to 6.62 p.p.m. in unacetylated samples. NMR spectra on fractionated lignins indicated that it was necessary to use acetylated preparations for quantitative determinations owing to poor spectra from the unacetylated, higher molecular weight fractions.

NMR Spectra and Chromatography Data. NMR spectra of acetylated hydrol lignins are shown in Figure 1. Using the δ values in Table I, the distribution of types of protons in these hydrol lignins and lignin fractions has been estimated, and these values along with comparable values from acetylated Björkman spruce and western hemlock dioxane acidolysis lignins are summarized in Table II.

A second analytical tool used in this study was temperature-programmed gas chromatography. The application of this method to lignin chemistry was reviewed recently (*3*), and the monomeric hydrogenolysis products were analyzed satisfactorily using polyester columns. Chromatograms of hydrol lignin A and B are shown in Figure 2, identified compounds are indicated on the figure, and retention time and quantitative data are summarized in Table III. In general, cyclohexyl derivatives are eluted in the 3–6-minute period, followed by guaiacyl and syringyl hydrocarbons,

Table II. Distribution of Types Estimated from

Type of Proton δ Range	*Acetylated Lignins (Ludwig & McCarthy)*	
	Björkman Spruce	*Dioxane Acidolysis W. Hemlock*
Aromatic 7.3–6.28	18.6	17.2
Acetylated Benzylic 6.28–5.74	4.8	5.5
Methoxyl 4.00–3.72	20.2	20.7
Acetoxyl 2.42–1.88	29.5	28.0
Total Aliphatic	26.9	28.6
Total	100	100

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then by guaiacyl and syringyl alcohols. Some of the unidentified peaks in the 15–18-minute region are neutral compounds.

Proton Distribution. In hydrol lignin A the aromatic protons account for 15% of the total, and this seems to be a reasonable value for a hardwood lignin preparation of this type. The total aliphatic protons account for 42%—a substantial increase over the 27–30% observed for the Björkman lignin and indicative of appreciable side-chain hydrogenolysis. The NMR spectra in Figure 1 for hydrol lignin A show absorbtion of the typical α, β, and γ side-chain protons; NMR spectra of unacetylated samples show this absorbtion somewhat more clearly. Gas chromatography data suggests that no side-chain degradation has occurred with this preparation. Over 99% of the identified compounds are of the C_6C_3 type, and there is no evidence that cyclohexyl derivatives are among the monomeric products.

NMR spectroscopy is used in lignin studies to estimate the degree of condensation of a given lignin preparation. This may be done by calculating a C_9 formula from classical elemental and fractional group analysis; then from NMR spectra one can determine the percent of total protons which are aromatic, allowing one to estimate the number of aromatic protons per C_9 unit. For a guaiacyl lignin, the difference from three protons per C_9 unit represents the degree of condensation. For a hardwood lignin, the proportion of syringyl units must be taken into account.

The C_9 formula for acetylated hydrol lignin A has been determined as $C_9H_{7.9}O_{2.5}(OCH_3)_{1.3}Ac_{1.3}$. The total protons per C_9 unit is 15.8; the aromatic proton per C_9 unit is 2.37. This suggests a total of syringyl plus condensed guaiacyl units of 63% in this lignin preparation. From

of Protons in Hydrol Lignins NMR Data

Alnus rubra

Hydrol Lignin A Acetylated	*Hydrol Lignin B Acetylated*	*Ether Insoluble A Acetylated*
15	8	12
—	—	3.6
19	17	20
24	26	28
42	50	37
100	101	100.6

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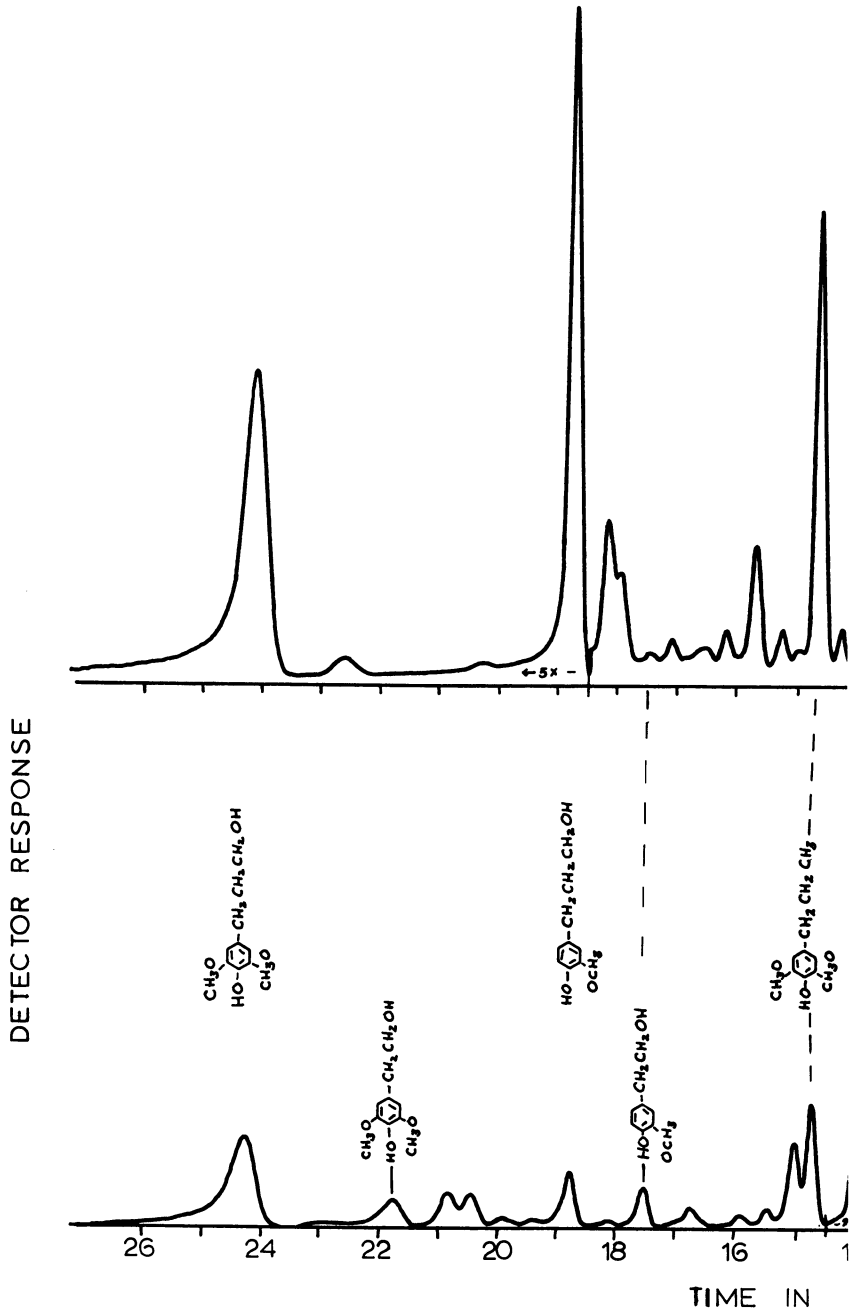
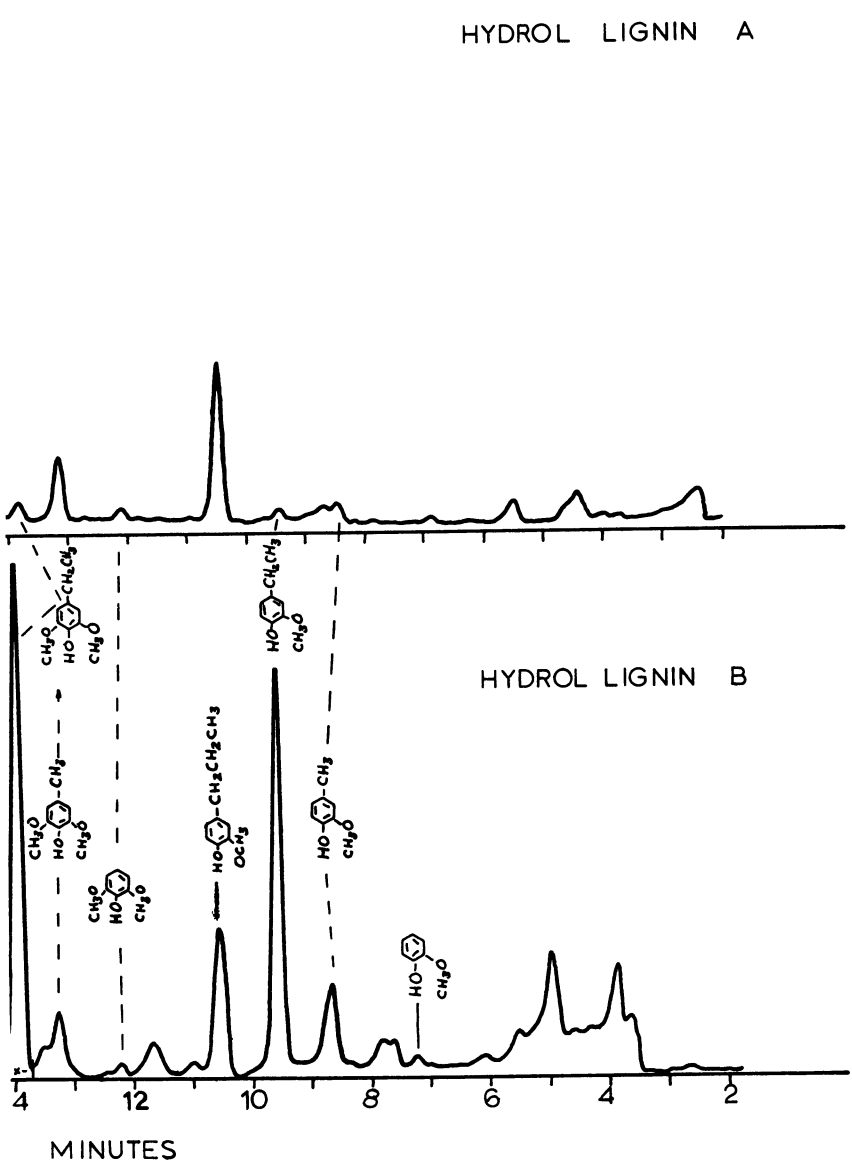


Figure 2. Chromatograms of



hydrol lignins A and B

Table III. Analysis of Monomeric Degradation Products Estimated from Gas Chromatography Data

Compound	*Retention Time, min.*	*Acid-Catalyzed Hydrol Lignin*	*Base-Catalyzed Hydrol Lignin*
G—H	7.2	0	0.5
G—CH_3	8.4	0.3	3.9
G—/	9.4	0.1	17.3
G—⌐	10.4	1.8	7.4
Sy—H	12.0	0.1	0.4
Sy—CH_3	13.1	0.6	2.8
Sy—/	13.8	0.2	42.7
Sy—⌐	14.6	4.5	5.5
G—/—CH_2OH	17.5	0.1	2.0
G—⌐—CH_2OH	18.7	43.6	3.5
Sy—/—CH_2OH	21.8		2.4
Sy—⌐—CH_2OH	24.0	49.1	11.8
Totals		100.4	100.2

	Percentages of C_6C_3 and C_6C_2		*Ratio of Syringyl to Guaiacyl*	
	A	*B*	*A*	*B*
C_6C_3	99	28	1.17	1.90
C_6C_2	0.4	64		
Other	0.6	8		

the methoxyl content it may be estimated that the lignin preparation contains about 30% syringyl and 70% guaiacyl units relative to the total number of aromatic rings. Assuming that only guaiacyl units are involved in condensation reactions, one may estimate that the lignin contains condensed guaiacyl units up to 33% of the total number of units—i.e., about 30% syringyl, 37% uncondensed guaiacyl, and 33% condensed guaiacyl units.

Using the assigned δ ranges, the number of each type of aromatic unit may be estimated from the relative number of protons in the aromatic region of the NMR spectra alone. This has been done for several acetylated preparations, and the results are summarized in Table IV. The total number of condensed guaiacyl plus syringyl units is estimated at

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57% for the hydrol lignin A, which is in reasonable agreement with the 63% arrived at from other data. Extending the subdivision of the aromatic region further, one may divide the condensed guaiacyl units and the syringyl units according to the assigned δ ranges and estimate that the hydrol lignin A contains 34% syringyl units, 23% condensed guaiacyl units, and 43% uncondensed guaiacyl units. The agreement between these various estimates as shown in Table IV is only moderate, and these estimates must be considered with caution. In addition to polymer and certain structural effects on the δ values, a possible source of error involves condensation in the C_5 position. This has not been considered as yet, and as pointed out by Sarkanen, appears to occur in acidic systems and particularly with syringyl nuclei (*6*).

Hydrol lignin B shows only 8% aromatic protons. The aliphatic proton content is 50%, substantially greater than that found with the hydrol lignin A. Most of the increase in aliphatic protons is in the δ region 1.0–3.0 p.p.m. where alicyclic structures exhibit absorption, and this indicates that appreciable aromatic ring reduction has taken place or that reduced carbohydrate fragments are present. The gas chromatogram of hydrol lignin B in Figure 2 also indicates the presence of cyclohexyl units (3½–6 minutes and 15–18 minutes). Because of the presence of alicyclic units in the preparation, little further work was done on the hydrol lignin B in this study.

From the aromatic region, the hydrol lignin B was estimated to contain 48% syringyl, 22% condensed guaiacyl nuclei, and 30% uncondensed guaiacyl nuclei. The changes in syringyl ratios between hydrol lignin A and B indicate that the guaiacyl nuclei were probably more readily lost via reduction to nonaromatic compounds.

Ether-insoluble hydrol lignin A, following acetylation, gave a satisfactory spectra which in overall appearance is nearly identical to that obtained by Ludwig from a typical acetylated conifer acidolysis lignin (*4*). This fraction contains about 12% aromatic protons. The decrease from the 15% in the total hydrol lignin A preparation in this case is probably caused by greater condensation. The most striking feature in the spectra is the dominant condensed guaiacyl proton absorption in the 6.5–6.75

Table IV. Estimations of Types of Aromatic Units from NMR Data—% of Total Aromatic

Lignin Preparation	*Hydrol A Acetylated*	*Hydrol A Ether Insoluble Acetylated*	*Hydrol B Acetylated*
Type of aromatic unit			
Syringyl	34 (30)[a]	15	48
Condensed	23 (33)	51	22
Guaiacyl	43 (37)	34	30

[a] Estimated from elemental analysis.

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p.p.m. region. The relative abundance of aromatic units was estimated to be 15% syringyl, 51% condensed guaiacyl, and 34% uncondensed guaiacyl. In addition there is a clear and strong absorption in the range 5.74–6.28 (p.p.m.) which is characteristic of a proton on an acetylated benzylic carbon atom. It is surprising to find this type of proton since benzylic alcohols are very readily reduced. Strong absorption also exists in the region 4.0–5.74; Ludwig has shown this absorption is caused by α, β, and γ protons in the important dimeric units of the pinoresinol, phenylcoumaran, and β-aryl ether type. The ratio of aliphatic to aryl hydroxyl groups is estimated to be 3:1 in this lignin fraction and is about 2:1 in the total hydrol lignin A, suggesting that there are fewer phenolic hydroxyl groups in the insoluble fraction as would be expected in a less degraded lignin. This lignin fraction is not typical of the reduced and degraded fragments characterized by dihydroconiferyl alcohol and dihydrosinapyl alcohol, and possibly it represents the 40% unrecovered Klason lignin remaining in the wood. While differentiation between guaiacyl and condensed guaiacyl units based solely on NMR data must be used with caution, the syringyl content of the lignin is reliably determined from the aromatic region, and this higher molecular weight fraction is definitely an undegraded and possibly highly condensed guaiacyl type of lignin.

The ether-soluble fraction from hydrol lignin A was analyzed by NMR spectra and by gas chromatography. The NMR spectra is nearly identical with that of dihydroconiferyl alcohol and dihydrosinapyl alcohol, which were shown to be present in large amounts by gas chromatography.

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Summary

(1) The structure of hydrol lignin has been examined by NMR spectroscopy. Tables of δ values for types of protons found in hydrol lignin have been established, and δ values for various types of aromatic ring substitution patterns have been clarified.

(3) The relative amounts of uncondensed guaiacyl, condensed guaiacyl, and syringyl nuclei in hydrol lignin preparations have been estimated at 43%, 23%, and 34% respectively for an acid-catalyzed product and 30%, 22%, and 48% for a base-catalyzed product.

(3) Ether-insoluble hydrol lignin from the acid-catalyzed product seems to be a highly condensed guaiacyl type of preparation which has not been severely degraded during the isolation process.

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Hydrogenation of Lignin Using Nickel and Palladium Catalysts

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A comparative study has been made of the nature of the products obtained by the catalytic hydrogenation of spruce-wood meal using Raney nickel and palladium-charcoal catalysts. The effect has been studied of an initial "neutral," acid, or alkaline medium on the nature of phenolic derivatives obtained by such hydrogenations. The results and those obtained by a similar treatment of model substances suggest an initial release of arylpropyl units, some of which then undergo secondary degradation. A model for the lignin substance has been proposed which consists of a "core" fraction to which are attached less condensed side-chain fragments. This latter portion may represent the more accessible lignin and maybe the origin of the several lignin degradation products obtained by each of several well-known methods.

The catalytic hydrogenation and hydrogenolysis of lignin has contributed significantly to a fuller understanding of the chemical nature of this substance. This paper reviews the more significant contributions that have been made, presents some recent results involving the comparison of Raney nickel and palladium-charcoal as hydrogenation catalysts for lignin and lignin model substances, and discusses the significance and limitations of this technique with respect to lignin structure.

Before 1938, although several reports had appeared dealing with lignin hydrogenation, no important conclusions regarding lignin structure had been formulated. Details of these researches may be found in "The Chemistry of Lignin" (*8*). Beginning in 1938 a series of valuable papers from various laboratories appeared. Harris, D'Ianni, and Adkins (*13*) hydrogenated aspen methanol lignin in dioxane over copper chromite for

In Lignin Structure and Reactions; Marton, J.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1966.

18 hours at 250°–260°C. and *ca.* 400 atm. (maximum) hydrogen. From the reaction mixture, 4-*n*-propylcyclohexanol, 2-hydroxy-4-*n*-propylcyclohexanol, and 1-(4-hydroxycyclohexyl)propanol-3 were isolated in a yield representing about 40% of the lignin.

Harris *et al.* (*15*) carried out similar hydrogenations in aqueous and 1% alkaline media over Raney nickel for 6–10 hours at 225°–250°C. and 1500–2500 p.s.i.g. hydrogen pressure; the products were identical with those found in dioxane. In 1941 lignin from soda black liquors was hydrogenated over copper chromite in dioxane at 250°–300°C., and colorless saturated products were obtained (*1*). Cyclohexane and four alkylcyclohexanes were detected, but the major part of the lignin was converted to alcohols and glycols related to polycyclic hydrocarbons of 20–70 (or more) carbon atoms.

Freudenberg *et al.* (*12*), in studying spruce waste liquors, found that temperatures as low as 250°C. were sufficient for reduction. At this temperature a moderately active copper-nickel catalyst gave a 50% yield of almost purely phenolic compounds, 30% of which were monocyclic phenols, but a highly active nickel catalyst gave 40% of ring-reduced components, 30% of which were cyclohexanols. This report constituted the first real proof for the lignin origin of the alkylcyclohexanols obtained earlier. In the same year, Cooke *et al.* (*10*) hydrogenated maple ethanolysis lignin under conditions similar to Harris' (*15*) and obtained similar cyclohexylpropyl derivatives but in a yield representing only about 14% of the total maple lignin.

In 1949 Harris *et al.* (*14*) reported the results of two large scale hydrogenations of a commercial lignin, "Meadol." They used copper chromite and stannous iodide as catalysts at 325° and 400°C., respectively, and isolated a phenolic fraction representing 8.0 and 10.2% of the products respectively. Higher boiling phenols constituted the large part of this fraction, but substantial amounts of guaiacol, 4-methyl-, 4-ethyl-, and 4-*n*-propylguaiacol were found.

A new and important phase was begun by Brewer *et al.* (*9*) who hydrogenated maplewood meal over Raney nickel catalyst in 50% aqueous ethanol for 4 hours at 165°–170°C. and 3000 p.s.i.g. hydrogen pressure. Under these conditions the lignin degradation products retained this aromatic character, and the new compounds, 4-*n*-propylsyringol, dihydroconiferyl alcohol, and dihydrosinapyl alcohol, were isolated and characterized. At the same time, Pepper and Hibbert (*19*) studied a similar hydrogenation of maplewood using alkaline (3%) aqueous dioxane (1:1). All the isolated products that were identified were of a phenylethanoid structure and included 4-ethylguaiacol, 4-ethylsyringol, and 4-(2-hydroxyethyl)syringol. In both cases rehydrogenation of the unidentified fractions over copper chromite at 250°C. gave rise to small amounts of the cyclohexyl derivatives that had been obtained previously.

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In further work on aspenwood Pepper and Hagerman (*18*) studied the effect of reaction conditions on isolating lignin from aspenwood as reflected in the amount of lignin products isolated as a chloroform-soluble fraction. Suitable conditions were established for removing most of the lignin. These consisted of using Raney nickel catalyst, a dioxane-water (1:1) medium, an initial hydrogen pressure of 500 p.s.i.g., a reaction time of 5 hours at a temperature of 175°–180°C. These conditions have served as the bases of those used in all subsequent hydrogenation studies in these laboratories.

A significant observation was reported (*6*) in 1958. From the products of the alkaline hydrogenation of maplewood, Arlt *et al.* isolated two new products, dihydrosinapyl alcohol and 4-(2-hydroxyethyl)syringol, along with previously reported phenolics.

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More recently, workers (*11*, *16*, *17*) have reported their results on the hydrogenation (over copper chromite catalyst at 240°–260°C.) of milled wood lignins from birch and oak and from white pine and blue spruce. Using gas-liquid chromatography for the first time to separate and identify the products gave significant data regarding the nature and relative abundance of the lignin derivatives. The compounds so identified were 4-methyl-, 4-ethyl-, 4-*n*-propylguaiacol and dihydroconiferyl alcohol from the pine and spruce lignins along with 4-methyl, 4-ethyl, 4-*n*-propylsyringol and dihydrosinapyl alcohol from the birch and oak lignins. For blue spruce the total yields of these products represented 19.9% of the lignin that was hydrogenated; for white pine, 17.7%; for birch, 21.2%, and for oak, 16.7%.

In 1963 Pepper and Steck (*20*) studied the effect of time and temperature on the hydrogenation of aspen lignin. Pre-extracted aspen sapwood meal was hydrogenated using a dioxane-water (1:1) medium, Raney nickel catalyst, and an initial hydrogen pressure of 500 p.s.i.g. At a fixed time of 5 hours the temperature was varied from 150° to 220°C., and later at a fixed temperature of 195°C. the time was varied from 0 to 24 hours. The highest yields of identified phenolic products were obtained at 195°C. for 5 hours. The reaction products were analyzed by gas-liquid chromatography. The same eight compounds reported by Coscia *et al.* (*11*) were identified along with guaiacol and syringol in a total yield representing 52.2% of the original Klason lignin of the aspenwood meal. (After these results were published, many unsuccessful attempts were made to duplicate the yields of the identified products that were published in this paper (*20*). The relative abundance of the products is confirmed, but the total yield based on the original Klason lignin of aspenwood consistently averages 26%. The authors can offer no satisfactory explanation of this variation in yields but recommend that the lower yield be recognized as the correct yield.)

Evaluation of Past Research

The foregoing outline indicates the nature of the contributions that catalytic hydrogenation has made to lignin chemistry. Some of the more significant observations are listed as follows.

Earlier research involving reaction conditions that led to only cyclohexyl derivatives has been followed by the ability to isolate and characterize relatively high yields of phenolic lignin degradation products under much milder conditions. This gives direct supporting evidence for the essentially aromatic nature of lignin.

Although in many of the reports lignin products of either a cyclohexyl or phenyl nucleus with one, two, or no carbon side chains attached have been reported, the greater abundance (under nonalkaline conditions) of the propyl side chain must be regarded as evidence for the essentially C_6-C-C-C nature of a unit of the lignin substance.

The isolation of either cyclohexylpropanol or arylpropanol derivatives presents strong evidence for the presence of oxygen attached to the γ-carbon atom of the side chain. The high yields of such products suggest further that the $—CH_2OH$ function arises by hydrogenolysis of an ether linkage rather than some other function such as an aldehyde, ester, acid, or acetal whose presence is not easily detectable in the original lignin.

The isolation of arylethanol derivatives under alkaline conditions of hydrogenation must be considered as evidence for the original presence of a carbon-oxygen linkage at the β-carbon of the side chain, and this linkage may have been most likely also in the form of an ether group.

Under alkaline conditions isolating lignin degradation products which are essentially of a phenylethyl rather than a phenylpropyl nature is structurally important and requires a lignin structure by which the γ-carbon may be removed as a result of a β-γ carbon-carbon cleavage reaction, either by direct alkaline hydrolysis or alkali-catalyzed hydrogenolysis.

Gas-liquid chromatography showed that much greater significance could be given to the quantitative aspects of these studies. Compounds whose yields are small and which were undetected using thermal distillation could now be isolated and characterized, and their relative abundance could be determined.

Experimental Results

Encouraged by the success of the hydrogenolysis of aspenwood meal this approach to lignin study was continued in these laboratories. Special attention was given to the effect of adding acid or base and to the use of palladium-charcoal as a catalyst on the products of hydrogenation of both aspen- and sprucewood meals.

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Table I reports the results of studying the effect of initial pH on the hydrogenolyses of aspenwood meal. The "neutral" conditions refer to those reported earlier (*20*), in which a dioxane-water (1:1) medium was used. To make an initially alkaline medium, sodium hydroxide was added so that the resulting medium was 3% in alkali. To make the initially acidic medium, hydrochloric acid was added so that the solution was 0.03% in hydrogen chloride. The details of hydrogenation and isolation of the products were the same as reported earlier (*20*).

Table I. Effect of pH on Hydrogenolysis Products of Aspen Lignin[a]

Compound	*Abundance as Mole % of Total Chromatographables*			
			0.03% HCl	
	"Neutral"	*3% NaOH*	*1 hour*	*5 hours*
Guaiacol	3.4	1.8		
4-Methylguaiacol		1.9		
4-Ethylguaiacol	2.3	19.5		
4-(2-Hydroxyethyl)guaiacol		trace		
4-*n*-Propylguaiacol	0.8	5.1	9.3	9.1
Dihydroconiferyl alcohol	25.0	1.4	23.87	22.9
Total	31.5	29.7	33.0	32.0
Syringol	0.9	trace		
4-Methylsyringol	4.0	6.2		
4-Ethylsyringol	7.5	36.5		
4-(2-Hydroxyethyl)syringol		16.0		
4-*n*-Propylsyringol	2.7	2.3	35.8	48.2
Dihydrosinapyl alcohol	53.4	6.6	31.2	19.8
Total	68.5	67.6	67.0	68.0
Unidentified compound		*ca.* 1.7		
Ratio: $\frac{\text{syringyl compounds}}{\text{guaiacyl compounds}}$	2.2	2.3	2.0	2.1

[a] Solvent-extracted wood meal (50 grams), dioxane-water (1:1) (400 ml.), Raney nickel (10 grams), initial hydrogen pressure (500 p.s.i.g.), time 5 hours. In each case the total yield of products represented approximately 26% of the original Klason lignin.

As a result of these studies, the following comments may be made. The initial pH of the reaction medium does not appear to affect markedly the total amount of lignin degradation products that may be isolated, but it is significant regarding the nature of these products. These results suggest that the initial reaction is one whereby propylphenolic fragments are released from the lignin substance, and that by a secondary reaction which depends on the reaction conditions, these may be further converted to the secondary products as shown. The effect of the alkali is again the most striking and requires an original lignin structure by which β-γ carbon-carbon bond cleavage occurs easily, in some cases with retention

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of a β-oxygen as the ethanol derivative and in others with loss of the oxygen to yield the saturated ethyl side-chain product. It may be significant to note that retention of this β-oxygen is much more pronounced in the lignin with the syringyl-type nucleus.

From the experiments in an initially acid medium it is apparent that the acid-catalyzed reaction is more rapid than the others and that secondary degradation into smaller units does not occur to any extent. The high yields of the propanol derivatives support the earlier conclusions that such units may indeed be joined through a γ-oxygen ether linkage.

The constancy of the ratio of about 2 of compounds having a syringyl nucleus to those having a guaiacyl nucleus may be particularly significant. Under these conditions of extremes in pH at the elevated temperature, it seems unlikely that deviation from a possible initial 1:1 ratio of these nuclei, which could arise by condensation at the reactive 5-position ortho to the phenolic hydroxyl of the guaiacyl nucleus, would indeed be so constant. The relative abundance of these two types of nuclei in the readily degradable part of aspen lignin may be close to the 2:1 ratio indicated by these results.

These results together with those reported earlier suggest that the hydrogenolysis process consists of two consecutive steps: (1) in which part of the lignin is separated from the body of the structure and from any carbohydrate to which it may be joined, and (2) whereby this part, now mainly in the form of smaller fragments, is stabilized by a reductive process.

To determine if a different hydrogenation catalyst would give rise to a different spectrum of products, we used palladium-charcoal instead of Raney nickel. For simplicity of product analysis, these comparative studies were made using pre-extracted sprucewood meal instead of aspen, in which case very little if any product with a syringyl nucleus would be obtained. The general procedure of hydrogenolysis was the same as used earlier for aspen, except that for the quantitative analyses of the chromatographable lignin degradation products an internal standard, *m*-methanesulfonanisidide, was added to the chloroform-soluble fraction prior to gas chromatography. In the earlier work (*20*) dioxane was used as the internal standard.

Table II records the experimental data obtained from a series of runs to determine the optimum conditions for using palladium-charcoal catalyst.

The most significant conclusion that may be drawn from these results is that palladium-charcoal exhibits similar catalytic properties as does Raney nickel if used under similar conditions. The same types of lignin hydrogenolysis products are obtained, and as before the major fraction under "neutral" conditions is the phenylpropanol derivative, dihydroconiferyl alcohol. With a minimum temperature *ca.* 150°C. required for any reaction to occur and an optimum temperature *ca.* 195°C. for maxi-

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Table II. Hydrogenation of Sprucewood Meal over Palladium Charcoal[a]

	Run 1	*Run 2*	*Run 3*	*Run 4*	*Run 5*
Wood meal, grams	50	25	20	10	10
Pd-C, grams	2	1.5	1	1	1
Dioxane-water (1:1), ml.	400	200	300	150	150[b]
Temperature, °C.	195	150	195	230	195
Time at temperature, hrs.	5	5	10	5	5
Residual pulp, %	52	81	48	16	83
$CHCl_3$-soluble fraction (% of Klason lignin)	77	15	78	93	37
Chromatographable Products (% of Klason lignin)					
Guaiacol	0.3	0.1	0.3	—	—
4-Methylguaiacol	0.2	0.03	0.2	0.5	—
4-Ethylguaiacol	—	—	0.2	0.3	—
4-*n*-Propylguaiacol	1.2	0.2	1.2	1.2	—
Dihydroconiferyl alcohol	13.5	4.1	15.3	12.5	3.5
Total	15.2	4.4	17.2	14.5	3.7

[a] Initial hydrogen pressure, 500 p.s.i.g.
[b] Dioxane only.

mum recovery of identifiable products, palladium-charcoal showed similar temperature effects to those reported for Raney nickel.

In light of the interesting results in Table I on the effect of pH on aspen lignin hydrogenolysis products, we investigated the effect of a similar pH change on the products of spruce hydrogenolysis products using Raney nickel and palladium-charcoal as catalysts.

Table III shows the results of such a study. The variation in the nature of the lignin degradation products with initial pH follows the same general pattern as observed using aspenwood—i.e., an increased percentage of the phenylpropane over the phenylpropanol derivative in acid medium and the almost sole production of phenylethane products under alkaline conditions. The total yield of identified products, based on original Klason lignin, is significantly less than that for aspen (Table I).

The results of these studies indicate that a definite amount of the lignin fraction of either aspen or spruce may be removed from the original lignin substance and degraded into smaller units which are chemically stabilized under the reducing conditions of the isolation process.

All these data support the concept of preferential liberation of the phenylpropanoid units, followed by the secondary degradation involving carbon-carbon bond cleavage to the other identified compounds.

Therefore, we decided to subject pure model compounds to some of the conditions of hydrogenolysis in the experiments using wood meals. Table IV shows the results of this study.

In interpreting these results it must be realized that any direct comparison with the results from the wood meal experiments is unsatisfactory. In the latter case, these monomeric compounds are released slowly over the 5-hour reaction time, and therefore are not subject to the identical reaction conditions. However it is clear that the variety of hydrogenolysis products from the wood meals may indeed result from a secondary reaction on those liberated early in the experiment. Knowing that the lignin substance probably has structural features which release C_6-C-C-C units initially and which are so oxygenated that subsequent hydrogenolysis gives the types of products isolated, some further studies were made on other model substances, which may be more closely related to the lignin. These were chosen because of their previous use and study as lignin models. The compounds were 1-(3-methoxy-4-benzoyloxyphenyl)-2-methoxyphenoxy)-3-hydroxypropanone (*4*, *3*); 1-(3,4-dimethoxyphenoxy)-2-(2-methoxyphenoxy)-3-hydroxypropanone (*4*); 1-guaiacylglycerol (*2*, *5*); 3-hydroxypropioguaiacone (*7*). Each of these compounds was hydrogenated for 5 hours at 195°C., in dioxane-water (1:1) under 900 p.s.i.g. hydrogen pressure using twice the sample weight of Raney nickel, in neutral or 3% alkaline solution. The products were studied by gas-liquid chromatography as reported earlier.

Table III. Hydrogenolysis of Sprucewood Meal[a]

Compound	*Abundance of Chromatographable Products*[b, c]					
	Neutral		*Acidic*[d]		*Alkaline*[e]	
	RaNi	*Pd-C*	*RaNi*	*Pd-C*	*RaNi*	*Pd-C*
Guaiacol	<1	<1	<1	<1	<1	<1
4-Methylguaiacol	<1	<1	<1	<1	<1	<1
4-Ethylguaiacol	<1	≪1	<1	<1	9.4	7.2
4-(2-Hydroxylethyl)-guaiacol	—	—	—	—	<1	<1
4-*n*-Propylguaiacol	≪1	1.2	5.1	3.2	≪1	≪1
Dihydroconiferyl alcohol	2.4	13.5	7.2	5.8	<1	<1
Unknown A	7.1	—	—	—		
B	1	—	—	—		
C	—	—	2.4	1.5		
Minimum total	9.5	14.7	14.7	10.5	9.4	7.2
Residual pulp, %	64	52	0	0	18	0
Klason lignin in $CHCl_3$-soluble fraction, %	59	77	120	128	94	113

[a] Solvent-extracted wood meal (10 grams), dioxane-water (1:1) (150 ml.), RaNi (10 grams) or Pd-C (10%) (1 gram), 5 hours at 195°C., initial hydrogen pressure 500 p.s.i.g.
[b] Reported as % of original Klason lignin.
[c] Chromatographed using a 6-ft., 10% Apiezon N on Fluoropak column, 198°C., helium rate 70 ml./min., using *m*-methanesulfonanisidide as an internal standard.
[d] Medium contains HCl (0.5%).
[e] Medium contains NaOH (3%).

Table IV. Hydrogenolysis of Reference Compounds[a]

Reference Compound	*Weight*	*Recovered Products*	*Weight % of total Chromatographables*
Dihydroconiferyl alcohol	0.5	Dihydroconiferyl alcohol	72
		4-*n*-Propylguaiacol	28
Dihydroconiferyl alcohol	0.74[b]	Dihydroconiferyl alcohol	100
Dihydrosinapyl alcohol	0.80	Dihydrosinapyl alcohol	85
		4-*n*-Propylsyringol	3
		4-Ethylsyringol	4
		Dihydroconiferyl alcohol	8
Dihydrosinapyl alcohol	0.5[c]	Dihydrosinapyl alcohol	73
		4-*n*-Propylsyringol	21
		Dihydroconiferyl alcohol	6
4-*n*-Propylsyringol	1.0	4-*n*-Propylsyringol	98
		4-*n*-Propylguaiacol	2
4-(2-Hydroxyethyl)guaiacol	[b]	4-(2-Hydroxyethyl)guaiacol	34
		4-Ethylguaiacol	66

[a] All hydrogenations were performed at 195°C. for 5.0 hours, in 100 ml. dioxane-water (1:1), Raney nickel catalyst equal to sample weight, initial hydrogen pressure 500 p.s.i.g.
[b] 3.0% NaOH added to the solvent.
[c] 0.03% HCl added to the solvent.

In each case, the products were very complex mixtures, the recoveries varied widely, and ring reduction occurred in some cases. All the monomeric products that have been obtained from lignin were found here, and similar to lignin, the yields from alkaline reactions were always greater than from the "neutral" runs. This may result from an added polymerization in the latter medium, which at the elevated temperatures is undoubtedly acidic owing to the phenols present. Loss of the terminal carbon of the three carbon side chain was a notable feature, occurring to a somewhat greater extent in alkaline than in neutral mixtures. The complexity of the products did not allow us to recognize any unique mechanism of hydrogenolysis. It may be important to realize that the nature of the products obtained by hydrogenation of the wood meal, was less complex. This may mean a less complex oxygenated pattern in the original lignin material.

General Summary

Undoubtedly, using catalytic hydrogenation and/or hydrogenolysis has contributed significantly to the fuller understanding of lignin chemistry. Appreciable percentages of the lignin, by weight, have been identified as phenolic degradation products. It is important to realize that the percentage so released and identified is always greater from angiospermic species (hardwood) than from gymnospermic species (softwood).

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It is highly probable that since a similar ratio is found regarding the identifiable products (phenolic aldehydes and ketones) obtained by the alkaline oxidation of these species, that the same readily releasable fraction of the original lignin is involved in each case.

The similar spectrum of products isolated under similar conditions of reaction from hard and softwoods indicates a basic similarity in the structural features of the releasable fragment of each species. The liberation, as the major product, of either dihydroconiferyl alcohol or dihydroconiferyl alcohol plus dihydrosinapyl alcohol (depending on the wood species) indicates that a fairly accessible portion of the lignin substance is of a polyphenylpropanoid structure. The other, more highly fragmented products are most likely secondary reaction products derived from the initially liberated phenylpropanoid compounds. As such they should not be considered as unique units of lignin structure.

Under the initially "neutral" conditions of hydrogenation, the production of the phenylpropanols as the major products represents a stabilized form of the initially released units. Loss of oxygen from the α- and β-positions by a hydrogenolysis reaction may well have occurred. The results of the studies, using initially alkaline conditions whereby phenylethanoid products result, help support the belief that alkali facilitates the β-γ carbon-carbon cleavage and that oxygen originally was associated with the β-carbon atom.

All these data appear consistent with a model for a lignin substance which consists of a core structure to which are attached the more readily accessible side-chain units. These units constitute the fragment of the lignin that is readily degraded and released as low molecular weight identified products by any of the well-studied procedures such as hydrogenolysis, oxidation, ethanolysis, sodium-liquid ammonia, etc. The greater yield of such products obtained by any of these methods, from the hardwood than from the softwood lignins, reflects the greater degree of complexity of the core fragment of the softwood lignins. This complexity may be associated with the greater ease of condensation of the guaiacyl nucleus as a result of the free reactive position ortho to the phenolic hydroxyl group. It is not inconceivable that the well-recognized lignin-carbohydrate bond exists with attachment to the lignin through this side-chain portion. The initial cleavage of this bond and removal of the carbohydrate substance facilitates subsequent release of the phenypropanoid units by rendering them more accessible to attack by the various degrading reagents.

We wish therefore to suggest that since all studies of lignin degradation have accounted for no more than about 50% and 25% of the initial lignin content of hardwoods and softwoods, respectively, that only the accessible side-chain portion of the lignin has been involved in such degradations. Indeed, little may be known about the chemical nature of the rest of the lignin substance in each case. Therefore it seems advisable to con-

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centrate on this residual "core" fraction, which is readily available as the non-chromatographable fractions obtained, for example, from the hydrogenolysis and oxidation of wood meals or isolated lignins.

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The Structure of Dimers from the Alkaline Hydrogenation of Lignin

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Experimental problems occur in isolating lignin dimers from alkaline hydrogenation pulping of both softwoods and hardwoods. The structures of dimeric compounds isolated have the following carbon skeletons: diphenylmethane; 1,2-diphenylethane; 3,3'-diethylbiphenyl, and 1-phenyl-2-(3-ethyldiphenyl)-ethane. Mechanisms for their probable origin from lignin structural units are proposed. Nuclear magnetic resonance (NMR) spectra of a number of hydrogenated monomers and dimers can be used to prove structures of the products.

The alkaline hydrogenation of wood (*3*, *4*, *5*, *6*, *7*, *21*, *22*, *25*, *26*) has been studied as a pioneering pulping and lignin utilization research and as a method of degradation for structure determinations. It is also a useful technique for investigating the mechanism of lignin degradation in alkali. It is believed that alkaline pulping methods degrade lignin into relatively small reactive molecular fragments, which repolymerize or condense to form the complex products that are isolated as kraft or soda lignin. Simultaneous hydrogenation tends to prevent repolymerization and allows one to isolate hardwood lignin almost entirely as an ether-soluble product containing stabilized monomeric fragments in rather substantial yields. Pepper and Hibbert (*22*) have shown that at least one-fourth of the lignin of sugar maplewood appears as three phenylethane derivatives of the guaiacyl and syringyl series. Quite comparable hydrogenations in the neutral or (actually) weakly acidic range, in contrast, give a higher molecular weight lignin, containing the corresponding phenylpropane derivatives usually in lower yields (*8*). A primary alkali-induced cleavage reaction must, therefore, occur between the β- and γ-carbons of the aliphatic side chains under alkaline pulping conditions. Previous studies from this

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laboratory have also shown that small quantities of 3-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanol and 3-(4-hydroxy-3-methoxyphenyl)-1-propanol are formed (*3*), and this result has been confirmed in this study by vapor phase chromatography. In addition, we have evidence of small amounts (of the order of 1%) of 4-methylguaiacol and of 2,6-dimethoxy-4-methylphenol. However, the corresponding *n*-propyl derivatives can be present only in trace quantities. A mixture of catechol and pyrogallol derivatives has been shown to be present and presumably formed by demethylation (*5*). Traces of *p*-hydroxybenzoic, vanillic, syringic, guaiacylacetic, guaiacylpropionic acids, and a compound called syringylpropionic acid [β-(3,5-dimethoxy-4-hydroxyphenyl)-propionic acid] were also identified (*5*). Although these compounds add little to our knowledge of lignin structure, the identified monomeric product mixture in its entirety probably amounts to 35–45% of the lignin.

We now wish to report our results on isolating lignin-derived dimers by alkaline hydrogenation and to propose mechanisms for their formation. In addition, we will present some information on the (NMR) spectra of these and related compounds; this technique has been useful for analyzing the structure of lignin degradation products and related synthetic materials.

A standard alkaline hydrogenation pulping of extractive-free sugar maplewood gave 75–80% yields of chloroform-soluble lignin; by modifying the procedure suitably, 40% yields of chloroform–ethanol-soluble lignin were obtained from Norway sprucewood. These products contain a spectrum of individual chemical species and molecular sizes and are difficult to separate. The Norway spruce lignin not only is obtained in lower yield but also contains higher molecular weight species which are best removed by precipitation in ether. The percent of acids, neutrals, and high molecular weight ether-insoluble material in maple lignin was so low that we did not separate these fractions in order to avoid mechanical losses.

Distillation from a brush-type molecular still separated the isolated lignins into three fractions containing alkyl-substituted monomeric phenols in the most volatile fraction, a mixture of monomeric phenolic alcohols and alkyl-substituted dimeric phenols in the intermediate fraction, and nonvolatiles which presumably contained dimeric phenolic alcohols and higher molecular weight material. Unfortunately, separation of monomeric alcohols and alkyl-sbustituted dimers was not complete, and this greatly hampered separation of the alkyl-substituted dimers in later chromatographic separations.

The dimer-rich fractions were adsorbed on 30 parts of Woelm alumina, activity grade IV (i.e., alumina containing 10% water) and eluted first with mixtures of chloroform and cyclohexane and on a second pass with benzene and cyclohexane. Occasionally, acetone-cyclohexane mixtures were used for better separation of alcohols and dimers and nylon powder chromatography for ultimate purification. Even at a 30:1 (alumina: lignin) weight

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ratio, the elution of a particular compound depended on the material it was associated with. Thus, it was necessary to analyze each separate chromatographic separation by gas chromatography and to repeat the separations again and again on combined fractions in order to isolate material which was pure enough to crystallize. Typically, at least six peaks were observed in the dimer range on gas chromatography of maple lignin, but usually they were only observed together in mother liquors from the removal of major components. Five or more dimers were also observed to be present in lignin from Norway sprucewood by vapor phase chromatography.

NMR positions were determined on 11 synthetic model compounds and dimers for comparison, and the data are recorded in Table I. The chemical shift positions of the protons are given in τ values, and the multiplicity follows in parentheses.

Usually the aromatic protons of guaiacyl nuclei produce complex multiplets in the region 3.0–3.5τ, and syringyl aromatic hydrogens are upfield around 3.5–3.65τ. Guaiacyl, biphenyl, and other unsymmetrically substituted rings have quite characteristic patterns whose major peaks only are indicated in parentheses in Table I; the theoretical multiplicities will be higher.

The chemical shift position of aliphatic hydrogen on the 11 compounds is determined largely by the deshielding influence of the aromatic ring or rings, and methylenes at a specific distance from one or two aromatic rings have nearly identical chemical shifts (Table II). The position of methyl groups is about 0.3-0.4τ units higher than the corresponding methylene group. In 1-acetoxy-2-methoxy-4,6-dimethylbenzene there are two methyl groups and two aromatic hydrogens in slightly different environments, and it is of some interest that the α-methyl protons form a single peak while there is evidence of only slight coupling between the aromatic protons. Apparently the differences in structure are insufficient to produce significantly different chemical shifts. Coupling in ethyl and propyl side chains produces the usual triplet and quartet patterns and two triplets and single sextet patterns characteristic of these isolated groupings; these are centered on the chemical shift positions listed above.

Bisyringyl [1,2-(4,4′-dihydroxy-3,3′,5,5′-tetramethoxydiphenyl)ethane (I)] and bivanillyl [1,2-(4,4′-dihydroxy-3,3′-dimethoxydiphenyl)ethane (II)] were unequivocally identified from maplewood by mixture melting points, diacetate derivatives, and comparative infrared and ultraviolet spectroscopy with authentic samples kindly supplied by I. A. Pearl. The two crystalline compounds are among the most important components of the dimer mixture. Bisyringyl (I) accounts for perhaps 1% and bivanillyl 0.5% of hydrogenated maple lignin. Bivanillyl (II) was also the most readily crystallized dimer from Norway spruce. Immediately preceding these two compounds on our vapor phase chromatograms of maple lignin

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Table I. Proton Magnetic

Compound as Acetate	*Ring*
4-Methyl-2-methoxyphenol	3.0–3.45(4)[a]
4-Ethyl-2-methoxyphenol	3.0–3.5(4)
4-Propyl-2-methoxyphenol	3.0–3.5(4)
4,6-Dimethyl-2-methoxyphenol	3.45(1)
4,4′-Dihydroxy-3,3′-dimethoxydiphenylmethane	3.0–3.4(4)
4,4′-Dihydroxy-3,3′,5-trimethoxydiphenylmethane	3.0–3.4(4) 3.55(1)
4,4′-Dihydroxy-3,3′,5,5′-tetramethoxydiphenylmethane	3.50(1)
4,4′-Dihydroxy-3,3′-dimethoxybibenzyl	3.0–3.4(4)
4,4′-Dihydroxy-3,3′,5,5′-tetramethoxybibenzyl	3.65(1)
2,2′-Dihydroxy-5,5′-dimethyl-3,3′-dimethoxybiphenyl	3.25(2)
5,5′-Diethyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl	3.24(2)

[a] τ-values listed. Aromatic multiplets have more complex structures than (4,6-dimethyl-2- methoxyphenol) has at least two additional minor peaks at 3.29

are two unknown compounds. That preceding bivanillyl has a retention time identical with 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane (III) and presumably is this compound. Similarly, the compound preceding bisyringyl has the same retention time as 4,4′-dihydroxy-3,3′,5,5′-tetramethoxydiphenylmethane (IV) and a crude melting point of 104°C. (m.p. lit., 113°–114°C.) (*19*), but attempts to form the diacetate resulted in loss of the compound.

Another dimer was isolated from both sugar maple and Norway spruce and obtained in pure form by chromatography on a nylon powder column. The individual melting points and mixture melting point of the substance obtained from the two woods were 77°–78°C. The compound acetylated

Table II. Aralkyl Proton Positions

Methylene Protons (τ-Values)

α,α[a]	α,β[a]	α	β
6.10	7.12	7.42	8.40
6.10	7.16	7.48	
6.10		7.35[b]	

Methyl Protons (τ-Values)

α	β	γ
7.75	8.82	9.10
7.81, 7.81	8.75	
7.65[b]		

[a] α or β to two aromatic rings.
[b] From 5,5′ substituted diphenyls.

Resonance Positions

		Side Chain Protons		
OCH_3	*Acetate*	*Alpha*	*Beta*	*Gamma*
6.35	7.82	7.75		
6.35	7.82	7.42(4)	8.82(3)	
6.32	7.82	7.48(3)	8.40(6)	9.10(3)
6.35	7.90	7.81		
6.25	7.72	6.10		
6.23	7.70	6.10		
6.24	7.70	6.10		
6.25	7.72	7.12		
6.25	7.70	7.16		
6.20	7.90	7.65		
6.20	7.90	7.35(4)	8.75(3)	

indicated with additional shoulders on the main peaks. The fourth compound and 3.19τ.

had a melting point of 80°–81°C. The carbon, hydrogen, and methoxyl analyses and molecular weight agreed precisely with the values for a dimethoxylated compound of formula $C_{18}H_{22}O_4$. The aromatic region of the NMR spectrum contained a diffuse series of peaks equivalent to five protons. The methoxyl protons gave two overlapping peaks at 6.20 and 6.24τ equivalent to six protons, and there were two overlapping acetate peaks (six protons) at 7.68 and 7.72τ. Apparently, substitution on the two rings differed slightly. A singlet at 7.20τ containing slightly more than four protons overlapped a multiplet at 7.41 containing slightly less than two protons. A triplet at 8.80τ (three protons) corresponded to the β-methyl of an ethyl side chain. The obscured two proton multiplet at 7.41 corresponded in chemical shift to the expected α-methylene protons and was presumably therefore a quartet. The four essentially identical protons at 7.20τ correspond to a bibenzyl bridge. The 26 protons of the spectrum would be expected of an ethyl-substituted bibenzyl in the guaiacol series. We assume that substitution is in the 4- and 6-positions of one guaiacol nucleus, and probably this compound is 2,4′-dihydroxy-3,3′-dimethoxy-5-ethylbibenzyl (V). We assume that the methylene carbons of the ethylene bridge are sufficiently identical to appear as a single peak since the two α-methyl groups in 4,6-dimethyl-2-methoxyphenol were similarly indistinguishable.

A fourth compound obtained from maple as a pure crystalline compound had a molecular weight, carbon, hydrogen, and methoxyl analysis characteristic of a diphenylmethane with four methoxyl and two hydroxyl groups. The NMR spectrum of the acetate also had a peak at 6.10τ equivalent to two protons and presumably caused by the methylene bridge,

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a six-proton acetate peak at 7.69τ, and two methoxyl peaks at 6.22 and 6.30, each containing six protons. The two distinct methoxyl peaks require unsymmetrical substitution, and the melting points of the free phenol and its acetate were different from those of 4,4′-dihydroxy-3,3′,5,5′-tetramethoxydiphenylmethane. We assume, therefore, that this substance is an unsymmetrically substituted isomer (VI).

A third dimer was obtained from Norway sprucewood in somewhat impure condition (m.p., 117°–127°C.). However, its vapor phase retention time and ultraviolet spectrum (*23*) were identical with those of authentic 5,5′-diethyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl (VII), m.p. = 143°C. (*9*). Furthermore, the NMR spectrum and melting point of its purified diacetate were identical with those of the synthetic compound. The corresponding 5,5′-di-*n*-propyl derivative has already been isolated from neutral hydrogenation of softwood lignin in our laboratory (*18*).

In summary, we have isolated and identified two dimeric compounds from the alkaline hydrogenation of sugar maplewood lignin—namely, 1,2-(4,4′-dihydroxy-3,3′,5,5′-tetramethoxydiphenyl)-ethane (I); 1,2-(4,4′-dihydroxy-3,3′-dimethoxydiphenyl)-ethane (II); we have demonstrated the presence of compounds which are probably the following: the two analogous diphenylmethanes (III and IV); an unsymmetrically substituted diphenylmethane of the syringyl series (VI); and 2,4′-dihydroxy-3,3′-dimethoxy-5-ethylbibenzyl (V). From hydrogenation of Norway sprucewood, two dimeric compounds have been identified 1,2-(4,4′-dihydroxy-3,3′-dimethoxydiphenyl)-ethane (II) and 5,5′-diethyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl (VII), and evidence for the presence of compound (V) has also been presented.

In the course of the previous work we have prepared compounds for comparative purposes, one of which has been reported by Gierer. He and his co-workers (*15*) synthesized an unsymmetrical diphenylmethane by acid-catalyzed condensation of syringyl alcohol and 2-methoxy-4-methylphenol and assumed substitution in the 6-position of the guaiacol nucleus. We repeated this synthesis and prepared an isomeric material by base-catalyzed condensation of the same starting materials. Our interpretation of the modes of synthesis and the NMR spectra of the two compounds is that Gierer's compound most probably is 3′,4-dihydroxy-6′-methyl-3,4′,5-trimethoxydiphenylmethane and that the compound prepared under basic conditions is 2′,4-dihydroxy-5′-methyl-3,3′,5-trimethoxydiphenylmethane, the structure claimed by Gierer. We do not, however, have unequivocal structural evidence and our data are summarized under Experimental.

Mechanism of Formation

It appears justifiable to propose mechanisms for the formation of the monomeric and dimeric products of the alkaline hydrogenation of lignin.

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It seems clear from the products isolated that alkaline hydrogenation of lignin proceeds by way of relatively reactive but still stable intermediate compounds. These seem to be formed primarily by the action of the alkali on lignin, and they are stabilized by hydrogenation at a later stage in the reaction after they have become soluble and accessible to the catalyst. One can then assume that the monomeric products are formed from the same portion of the lignin that produces the 4-propylguaiacol and 2,6-dimethoxy-4-propylphenol on neutral hydrogenation and the ethanolysis monomers on ethanolysis. Substantial evidence indicates that this is primarily a β-guaiacyl ether of guaiacylglycerol and presumably the corresponding syringyl derivative, although closely related structures may also contribute. The reaction course on phenolic residues which appears most probable to us (Figure 1) involves ionization of the two most acidic

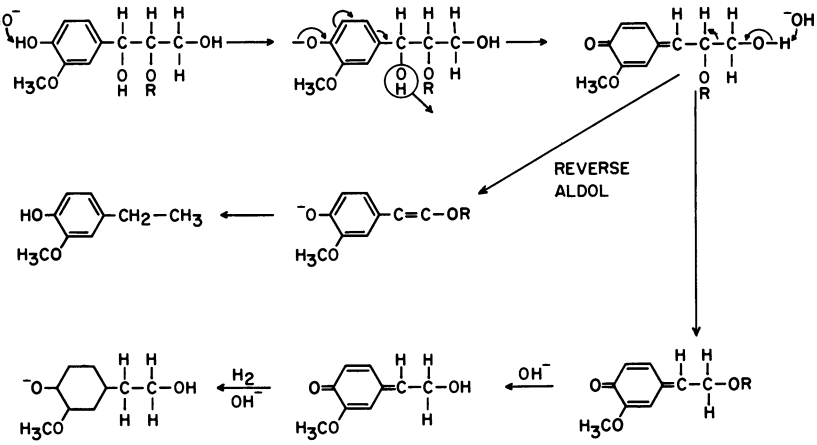

Figure 1. Preferred reaction course of guaiacylglycerol units

hydroxyl groups, quinonemethide formation, and typical elimination processes followed by hydrogenation. This follows the proposals of Gierer closely (*12*, *13*) and emphasizes the fact that β,γ-cleavage is a most significant process in alkaline degradation of lignin. Presumably, the cleavage of the aryl ether linkage must be primarily by hydrogenolysis rather than by alkaline cleavage from Gierer's results on models, and the hydrocarbon side chain is in fact the major product. If the phenolic hydroxyl group is blocked, the guaiacylglycerol moiety will undergo epoxide formation and β-aryl elimination according to Gierer (Figure 2). Ketonization on the α-position by an E-2 mechanism might be expected and could form a γ-hydroxypropioveratrone-type intermediate. The importance of this structure in alkaline pulping reactions has been emphasized by Enkvist, Ashorn, and Hästbacka (*10*). The substance would undergo a reverse

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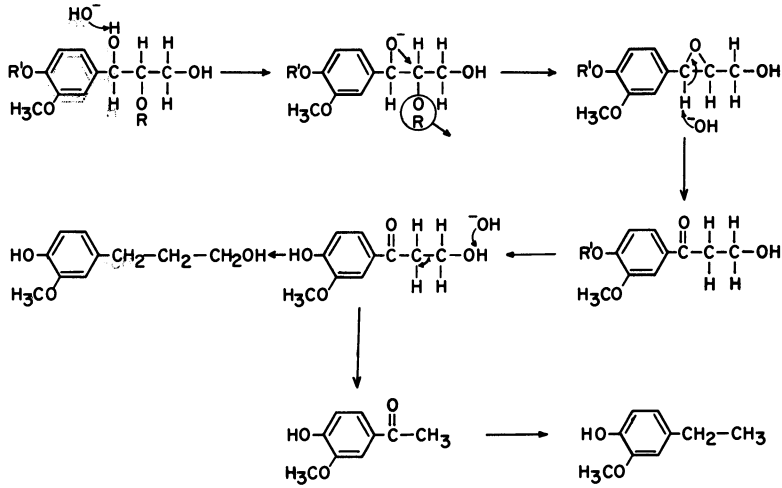

Figure 2. Preferred reaction course of veratrylglycerol units

aldol reaction, and according to these authors, ready *p*-ether saponification to give acetoguaiacone. It would, therefore, be an appropriate source of ethylguaiacol and also of small amounts of the corresponding γ-alcohols found in this product mixture. Some alternative functional group, perhaps an α-carbonyl, on the side chain may be preferred, however, since Gierer has found that veratrylglycerol is formed and stable under similar conditions (*14*). These two favored reaction courses (which must be considered partly schematic) do not lead to *n*-propyl hydrocarbon side chains, and in our experience only traces of these are formed under basic conditions.

If one attempts to propose similar reactions leading to products with side chains containing single carbons, the individual steps are less probable (as they should be) since only small amounts of such products are formed. Figure 3 indicates such a process beginning with primary proton abstraction and β-aryl ether elimination as an initial step. From the standpoint of the acidities of the hydrogen this would be less preferred than elimination of benzylic hydrogen, but steric factors can be significant in E-2 mechanisms, and elimination in this direction is possible. Formation of a terminal aldehyde seems to be required in order to permit a reverse aldol and elimination of vanillin. Reduction can lead to methylguaiacol via vanillyl alcohol or its corresponding quinonemethide. Simultaneous quinonemethide formation and elimination of the C_2–C_3 side chain might also be possible under extreme conditions, especially if no oxygenated functions were present on C_1.

The bibenzyls isolated in this work are closely related structurally to stilbenes and various products isolated by other workers (*10*, *16*, *20*, *24*) usually by alkali treatment of lignin or wood. Hägglund has suggested

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that the stilbene may be produced by the rapid coupling of quinonemethides derived from vanillyl alcohol while Pearl (*20*) has proposed that the α,α'-linkage may be present in lignin *in situ*. We are inclined to agree with Pearl's interpretation since Nimz (*11*) has now isolated, by mild hydrolysis, from lignin, a reasonable type of precursor, 1,2-bis-(3,5-dimethoxy-4-hydroxyphenyl)-propan-1,3-diol. Minor modification of Figure 1 would account for the formation of stilbenes or bibenzyls, and the reaction course appears more probable under our conditions than the formation and coupling of quinonemethides. Furthermore, we have not yet obtained the unsymmetrical bibenzyl from maplewood that would be expected from a coupling reaction.

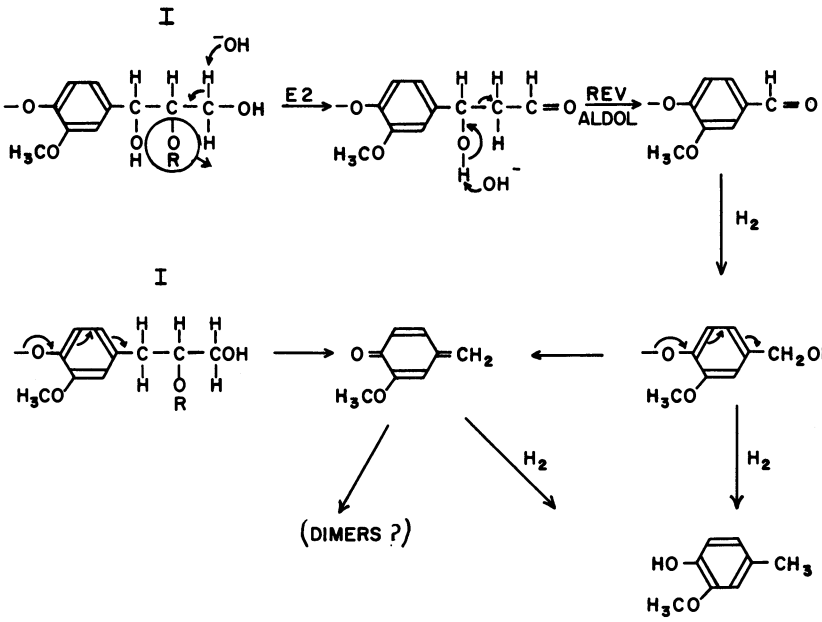

Figure 3. Less favored degradative processes

Pearl and Dickey (*20*) isolated 3,3′-dimethoxy-4,4′-dihydroxybenzophenone, an analog of the diphenylmethanes apparently present in our product mixture. They suggest that the ketone is a rearrangement product of vanillil. In our system the corresponding diphenylmethanes could also be produced by a coupling reaction of phenolic methylols or quinonemethides, and at present they cannot be considered proved structural elements native to lignin.

The isolation of 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-dialkylbiphenyls from both neutral (*18*) and alkaline hydrogenation supports Pew's proposal that the biphenyl structure is of considerable importance in lignin

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structure. The earlier isolation of analogous oxidation products of lignin was subject to the criticism that the products were perhaps artifacts (*17*). This now seems much less probable, and the oxidation states of the aliphatic carbons on the side chains of the biphenyl structures, are probably the same as that of guaiacylglycerol since the same kind of β,γ-cleavage reaction occurs in both cases.

The postulation that the structure of one dimer is 2,4′-dihydroxy-3,3′-dimethoxy-5-ethylbibenzyl is, of course, based on NMR data, on the proposal that phenylcoumarane structures are common in lignin [*see* (*1*)], and on evidence that they are cleaved to stilbenes by alkali (*14*) and eliminate γ-methylol units (*2*) as formaldehyde by mechanisms quite analogous to those above. Although there are some modest surprises in the structure of dimers isolated so far, it is gratifying how well these results fit into our long-standing concepts of lignin structure and reactions.

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Experimental

Preparing Hydrogenated Lignin. Sugar maplewood shavings (benzene-ethanol extracted, 22% Klason lignin, 400 grams) were intimately mixed with 50 grams of Raney nickel and 4 liters of 5% aqueous sodium hydroxide in a two-gallon stirred autoclave under 500–600 p.s.i.g. initial hydrogen pressure. Reaction occurred when the mixture was heated to 150°–160°C. over a 1-hour period and held at temperature for 3 hours. The mixture was cooled, the liquors separated from the well-cooked pulp, and acidified. Lignin was isolated by chloroform extraction and amounted to 75–80% of the Klason lignin. Higher temperatures resulted in lower yields of chloroform-soluble products from maplewood perhaps because of more demethylation. Norway spruce under comparable conditions was only slightly delignified, and a 3-hour cook at 170°–180°C. was necessary to obtain a 43% yield.

Fractionating Hydrogenated Lignin. A concentrated solution of lignin was placed in the delivery bulb of a brush-type molecular still with Teflon blades (Asco 2-inch Rotafilm model, Arthur F. Smith Co., Rochester, N.Y.). (Completely ether-soluble fractions of spruce lignin are preferable.) Solvent was stripped from the system and removed, and distillation was run at 250°C. and 0.5 mm. mercury pressure (maximum). The highest molecular weight material was nondistillable and amounted to 40–50% of the lignin. This was washed from the still with chloroform, dried, and stored for future research. The distillable fraction condensed partly on the water-cooled condensing surface and partly in the dry-ice trap. Redistillation of the former distillable fraction at 200°C. separated this product into 200°C. nondistillables called "dimer fraction," and two distillable fractions as above. The fraction distilling at 200°C. and condensing on the water-cooled surface was refractionated and collected as before. Final fraction yields from distillation of 400 grams of extracted maplewood at approximately 0.5 mm. were approximately as follows.

250°C. nondistillables	35 grams
200°C. nondistillables I	8 (syringyl dimers and alcohols primarily)
150°C. nondistillables II	3 (guaiacyl dimers and alcohols primarily)
150°C. distillable	8 (phenolic alcohols primarily)
dry-ice trap residues (all distillations)	16 (alkyl phenols primarily)
Total Yield	70 grams

Somewhat variable results were obtained with Norway spruce since optimum conditions were not used on all runs. However, the fractions of soluble lignin were roughly as above, although the yields of total soluble lignin were lower.

Column chromatography was carried out especially on fractions I and II above using Woelm alumina, activity grade 4 (10% water) in a 30:1 weight ratio. Five hundred ml. volumes of chloroform-cyclohexane mixtures were used to elute the product beginning with 10% chloroform and increasing by 10% in chloroform up to pure solvent. The fractions containing eluted lignin were analyzed by vapor phase chromatography, and like fractions were combined. These were rechromatographed in the same way using benzene-cyclohexane mixtures at a higher than 30:1 weight ratio (alumina:lignin). Acetone and cyclohexane were also used occasionally to separate alcohols and dimers. The gas chromatograph used was homemade with a maximum temperature of 260°C. and temperature stability of 1° above 180°C. Copper or aluminum tubing (¼") of various lengths was used for columns. Our standard conditions for analyzing the dimers were a 2-foot column packed with 20% silicone rubber on firebrick, a helium flow rate of 60 ml./min., and a temperature of 260°C.

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Table III. Nuclear Magnetic Resonance Spectra[a]

Compound	*No. H*	*Type*	*Chemical Shift*	*Multiplicity*
Diacetate of A	2	Aromatic	3.21	2
(Acid catalysis)	2	Aromatic	3.61	1
	2	Methylene	6.16	1
	3	Methoxyl	6.24	1
	6	Methoxyl	6.30	1
	6	Acetate	7.77	1
	3	α-Methyl	7.71	1
Diacetate of B	1	Aromatic	3.35	1
(Base catalysis)	1	Aromatic	3.42	1
	2	Aromatic	3.56	1
	2	Methylene	Under methoxyl	
	3	Methoxyl	6.24	1
	6	Methoxyl	6.28	1
	6	Acetate	7.71	1
	3	α-Methyl	7.78	1

[a] An analysis of these spectra can be found in the Ph.D. thesis of Paul E. Parker, available from University Microfilms.

Condensation of 4-Methyl-2-methoxyphenol and Syringyl Alcohol. Repeating Gierer's condensation of the title compounds by acid catalysis (*15*) gave us compound A of m.p. 121°–122°C. presumably identical with their product. A diacetate (m.p. 135°–136°C.) was prepared by conventional methods for NMR analysis (Table III).

A solution of 5 grams of syringyl alcohol, 5 grams of zinc chloride, and 10 grams of 4-methyl-2-methoxyphenol in 300 ml. of 5% sodium hydroxide was refluxed for 24 hours. After cooling, it was acidified with dilute hydrochloric acid, and the products were extracted with chloroform. The chloroform-soluble products were chromatographed on alumina to give crystals melting at 106°–108°C. and a small amount of 4,4′-dihydroxy-3,3′,5,5′-tetramethoxydiphenylmethane. The yield of the desired product (B) was about 3 grams, and the amount of the symmetrical diphenylmethane was about 1 gram. The desired product was acetylated in the usual manner to give crystals melting at 138°–139°C.

Analysis: Calculated for: $C_{17}H_{20}O_5$; C, 67.11%; H, 6.58%; OCH_3, 30.58%. Found: C, 67.20%; H, 6.63%; OCH_3, 30.27%.

Analysis: Calculated for the diacetate: C, 64.95%; H, 6.21%; OCH_3, 23.97%. Found: C, 64.70%; H, 6.18%; OCH_3, 23.97%.

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