

STUDIES ON LIGNIN HYDROLYSIS PRODUCTS AND THEIR
RELATIONS TO LIGNIN STRUCTURES

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TO LIGNIN STRUCTURES

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This thesis is based on the following papers, which will
be referred to by Roman numerals I-XIV:

- I. Knut Lundquist, Isolation of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone from Lignin.
Acta Chem. Scand. 16 (1962) 2303.
- II. Knut Lundquist, On the Separation of Lignin Degradation
Products. Acta Chem. Scand. 18 (1964) 1316.
- III. Knut Lundquist and Gerhard E. Miksche, Nachweis eines
neuen Verknüpfungsprinzips von Guajacylpropaneinheiten
im Fichtenlignin. Tetrahedron Letters 1965 2131.
- IV. Knut Lundquist and Kenneth Hedlund, Acid Degradation
of Lignin. I. The Formation of Ketones of the Guaiacyl-
propane Series. Acta Chem. Scand. 21 (1967) 1750.
- V. Knut Lundquist, Gerhard E. Miksche, Lennart Ericsson
and Lissela Berndtson, Über das Vorkommen von Glycer-
aldehyd-2-arylätherstrukturen im Lignin.
Tetrahedron Letters 1967 4587.

- VI. Knut Lundquist, Acid Degradation of Lignin. II. Separation and Identification of Low Molecular Weight Phenols. Acta Chem. Scand. 24 (1970) 889.
- VII. Knut Lundquist and Lennart Ericsson, Acid Degradation of Lignin. III. Formation of Formaldehyde. Acta Chem. Scand. 24 (1970) 3681.
- VIII. Knut Lundquist and T. Kent Kirk, Acid Degradation of Lignin. IV. Analysis of Lignin Acidolysis Products by Gas Chromatography, Using Trimethylsilyl Derivatives. Acta Chem. Scand. 25 (1971) 889.
- IX. Knut Lundquist and Kenneth Hedlund, Acid Degradation of Lignin. V. Degradation Products Related to the Phenylcoumaran Type of Structure. Acta Chem. Scand. 25 (1971) 2199.
- X. Knut Lundquist and Lennart Ericsson, Acid Degradation of Lignin. VI. Formation of Methanol. Acta Chem. Scand. 25 (1971) 756.
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- XII. Knut Lundquist and Rolf Lundgren, Acid Degradation of Lignin. VII. The Cleavage of Ether Bonds. Acta Chem. Scand. 26 (1972) 2005.
- XIII. Lennart Hemrã and Knut Lundquist, Acidolytic Formation of Methanol from Quinones and Quinonoid Compounds Related to Lignin. Acta Chem. Scand. 27 (1973) 365.
- XIV. Knut Lundquist, Acid Degradation of Lignin. VIII. Low Molecular Weight Phenols from Acidolysis of Birch Lignin. Acta Chem. Scand. In press.

A. Introduction

Studies on low molecular weight solvolysis products have been of paramount importance for the elucidation of the structure of lignin, as well as other naturally occurring polymers. Knowledge about lignin solvolysis products* also provides information about the reactions of lignin on solvolytic treatments. Furthermore, examinations of solvolysis products can be used for the characterization of lignin preparations. The above mentioned aspects are the primary concern in the present studies of hydrolysis products, but knowledge about solvolysis products from lignin is also of interest in numerous other connections, e.g. biological degradation, environmental pollution, and utilization of lignin.

In the present work the formation of low molecular weight products on hydrolysis of Björkman lignin from spruce⁸ (Picea abies) (in some experiments pretreated by reduction with borohydride) and birch⁹ (Betula verrucosa) has been studied. The major part of the work deals with products formed on acid degradation (compounds 1-36). (Compounds 35 and 36 obviously originate from carbohydrate impurities in the Björkman lignin preparations, see Parts XII and XIV. The formation of 33 and 34 has also been studied with spruce wood and lignin carbohydrate complex from spruce¹⁰ as starting material.)

* The literature concerning lignin solvolysis products has been reviewed up until 1969.¹⁻⁴ More recent work of interest in connection with these studies is described in Refs. 5-7.

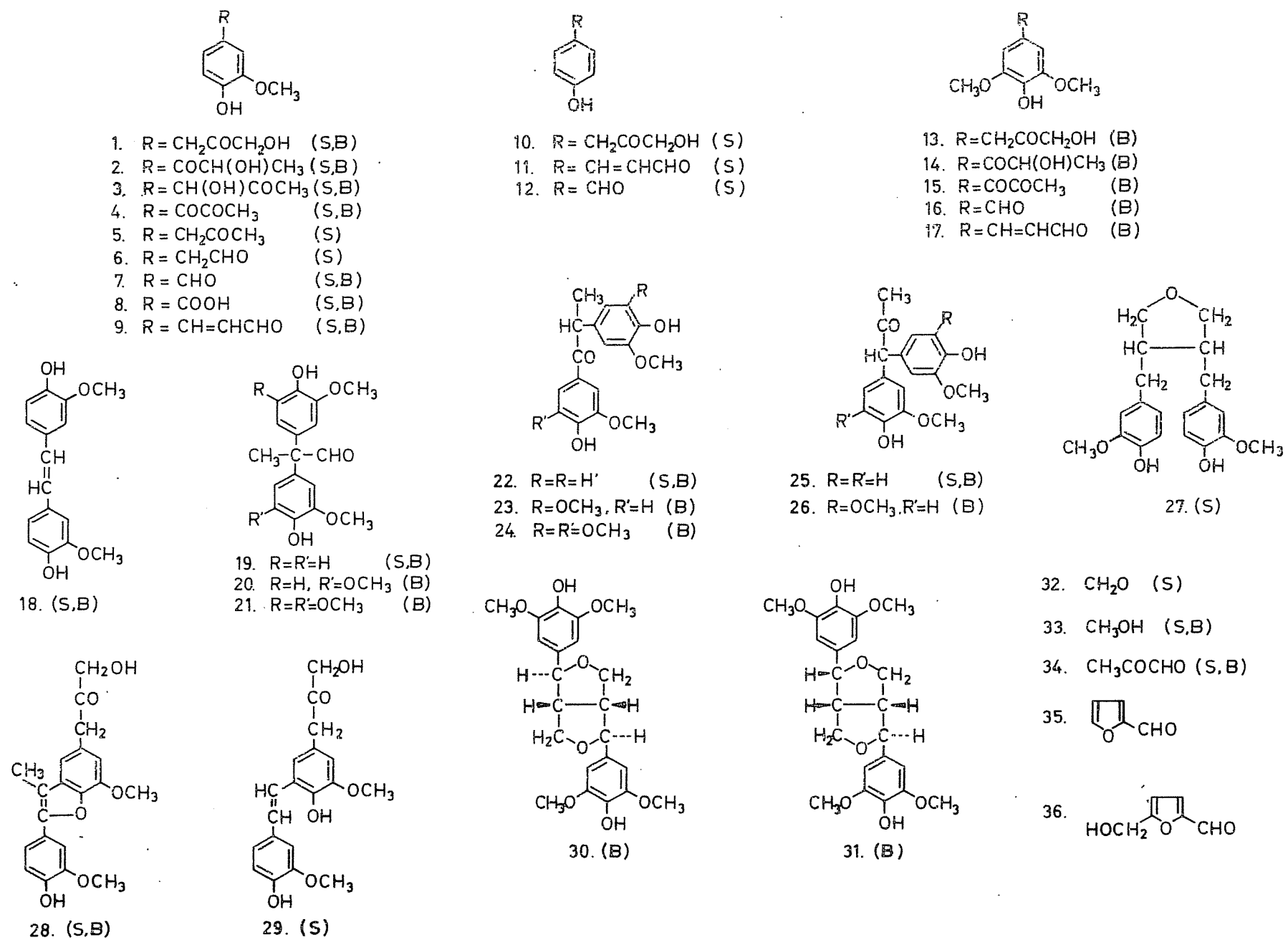


Fig. 1. Products obtained on acidolysis of Björkman lignin from spruce (S) and birch (B).

Compounds formed on alkaline hydrolysis ("soda cooking") have also been studied. Here only the formation of a few of these products will be treated, namely compounds 37-40.^{11,12} The formation of these products on alkaline hydrolysis is of interest for the elucidation of the relations of products formed on acid degradation to specific lignin structures and for structural questions associated therewith.

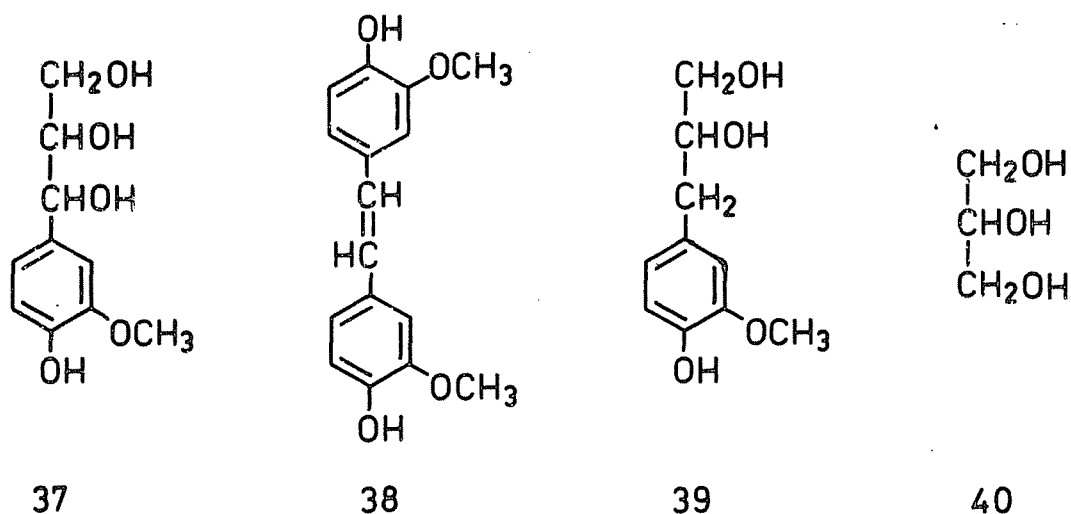


Fig. 2. Some products obtained on "soda cooking" (1:5 M NaOH, 170°, 4h) of Björkman lignin from spruce (38=18).

In the acid degradation procedure Björkman lignin has been subjected to acidolysis by refluxing with 0.2 M hydrogen chloride in dioxan-water (9:1) (in most experiments for 4h). For simplicity, the term acidolysis is used specifically for this treatment in the following. The conditions were chosen on the basis of analytical acidolysis work¹³ with consideration being taken of uniformity and high yield of products. Furthermore, experiences from earlier acidolysis studies concerning the arylglycerol- β -aryl ether¹³ and the phenyl-coumaran¹⁴ systems could be expected to be helpful in the task of relating products obtained to specific lignin structures.

The use of Björkman lignin instead of wood makes it possible to work in a homogeneous system (dioxan containing a small percentage of water is an excellent solvent for Björkman lignin). This makes comparisons with model experiments more reliable. Possible interaction with carbohydrate products (e.g. compounds 35 and 36, see Part XIV) is also essentially eliminated. However, the use of Björkman lignin raises the question as to whether this material is representative for lignin in situ. This has been discussed by Lai and Sarkanen¹⁵ recently. Their main reservation is that Björkman lignin, in all likelihood, originates from the middle lamella region and thus can not be expected to be representative for cell wall lignin. However, it has recently been demonstrated that Björkman lignin at least in several respects is an adequate representative for lignin in situ.¹⁶

Among other solvolytic degradations applied to lignin, "ethanolysis" (refluxing with hydrogen chloride in ethanol) resembles rather closely acidolysis. "Ethanolysis" was introduced by Hibbert and co-workers¹⁷ and has been used frequently by other workers. The most interesting similarity between acidolysis and "ethanolysis" is, in this connection, the analogy in the formation of so-called Hibbert ketones (compounds 2, 3, 4, 5 and analogues of types 41 and 43; in case of "ethanolysis" ketols are obtained as ethyl ethers). Concerning the analogy in the formation of "Hibbert ketones" of the guaiacyl type (42) from spruce lignin, see Part IV. Acidolysis and "ethanolysis" will not be compared in detail here. However, it is noteworthy that dioxan-water is a better solvent for lignin than ethanol and that this fact favors acidolysis.

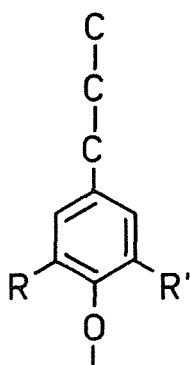
As shown by Adler and co-workers,^{18,13} the "Hibbert ketones" originate from arylglycerol- β -aryl ether structure (A, Fig. 3). This relationship has been further elucidated in the present work.^{I,IV, XII} Cleavage of the β -aryl ether bond in structures of type A (which is involved in the formation of "Hibbert ketones") and to some extent other types of ether bonds are primarily responsible for the degradation of lignin on acidolysis.^{XII}

It should be pointed out that about one half of the acidolysis products have been encountered in other solvolytic degradations of lignin. However, in most of these cases the relation to specific lignin structures has been clarified or further elucidated in the present studies.

At an early stage of the work it became apparent that it was necessary to develop more suitable separation methods than those previously used for the separation of lignin degradation products. Gel filtration was found to be useful for the separation of low molecular weight fractions as well as for demonstrating the depolymerization of the lignin. The behaviour of lignin model compounds on gel filtration was studied separately.^{XI} By the use of a combination of gel filtration and chromatography on silica gel columns, it was possible for the first time to isolate a solvolysis product containing two phenylpropane units.^{II} Later the combination of gel filtration and gas chromatography using trimethylsilyl derivatives was introduced as a more convenient method for the examination of lignin acidolysis products.^{VIII}

B. Relation of degradation products found to lignin structures

Concomitantly with the studies of the formation of low molecular weight products from lignin, experiments with model compounds have been made. Based on these studies and other observations it has been possible to relate with high probability almost all the products to specific lignin structures. The results are summarized in the figures below. The phenylpropane units in lignin are of types 41, 42, and 43. For



- 41 R=R'=H
 42 R=H, R'=OCH₃
 43 R=R'=OCH₃

simplicity, units of the guaiacyl type (42) have been used in the examples shown below. This type of units also strongly dominates in spruce lignin, which has been investigated most thoroughly. Thus the formation of products obtained with units of types 41 and 43 (see Fig. 1) is not shown in the figures. However, as far as it is known, these products are formed in the same way as the corresponding guaiacyl compounds. Most lignin structures shown are connected to the lignin with aryl ether linkages (denoted O-, in some cases O- alternatively can be a hydroxy group). When the formation of degradation products involves more than one step, such ethers are depicted to be hydrolyzed in the first step in the figures. This is,

of course, not always the case in reality. Products detected in lignin degradation mixtures are framed in the figures. Some results from attempts to obtain degradation products which provide evidence for hypothetical lignin structures are also presented in the figures.

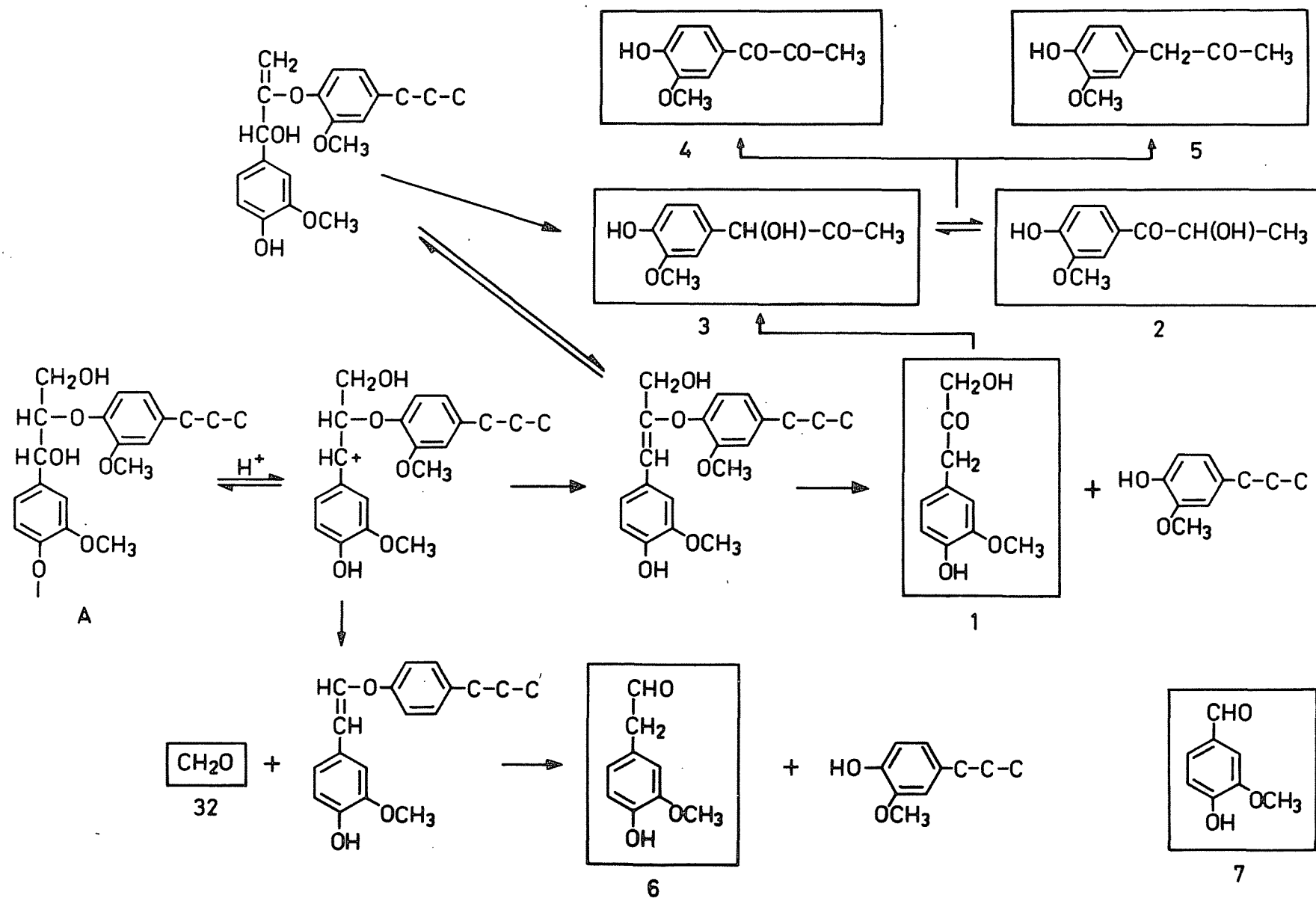


Fig. 3. (commented on next page)

Fig. 3. Formation of products from arylglycerol- β -aryl ether structures (A).^{IV,VI,VII,XIII,XIV} Compounds which originate from such structures dominate quantitatively among the low molecular weight acidolysis products. (Guaiacylglycerol (37) present in "soda cooking" mixtures from spruce lignin may originate from sequences of units attached to each other by β -ether bonds.¹¹)

Note to Fig. 3. The arylglycerol- β -aryl ether structure (A) is considered to be the most important lignin structure.⁴ Studies of the formation of ketol side chains of the type present in compound 1 on acidolysis of spruce lignin and model compounds suggest that 25-30 % of the units in spruce lignin are linked to adjacent units by β -ether bonds.^{13b,19} On the basis of less direct evidence, several authors suggest a higher frequency for this type of structure (see, e.g., Ref. 16). An explanation for the comparatively low value obtained in analytical acidolysis studies may be that condensation reactions preventing the formation of ketol side chains occur to a greater extent in experiments with lignin than in experiments with model compounds.

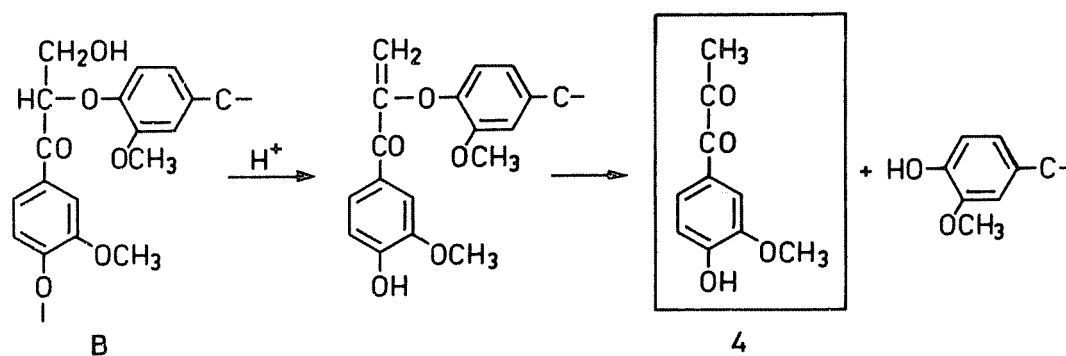


Fig. 4. Formation of diketone 4 from ketol ethers of type B.^{XIII,XIV}

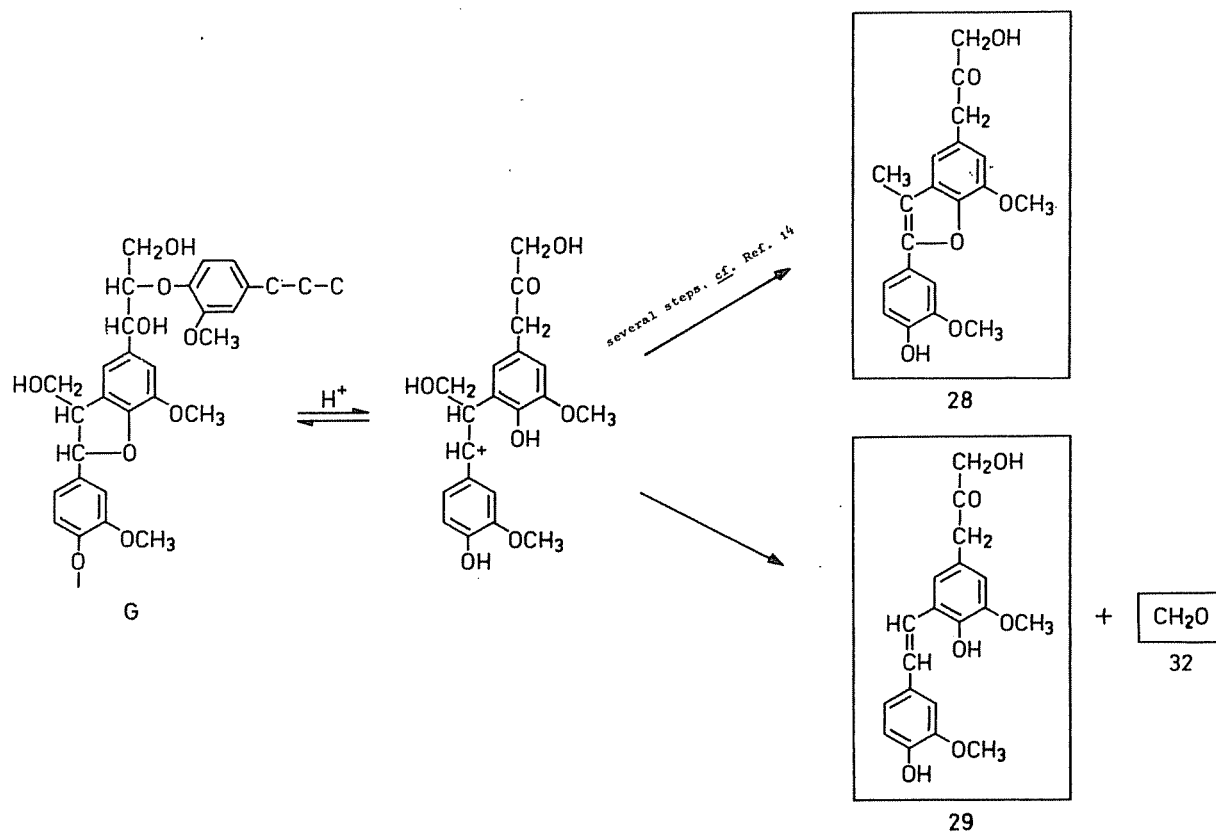


Fig. 9. Formation of degradation products from lignin structures of type G^{VII, IX} (concerning the formation of the ketol side chain, see Fig. 3).

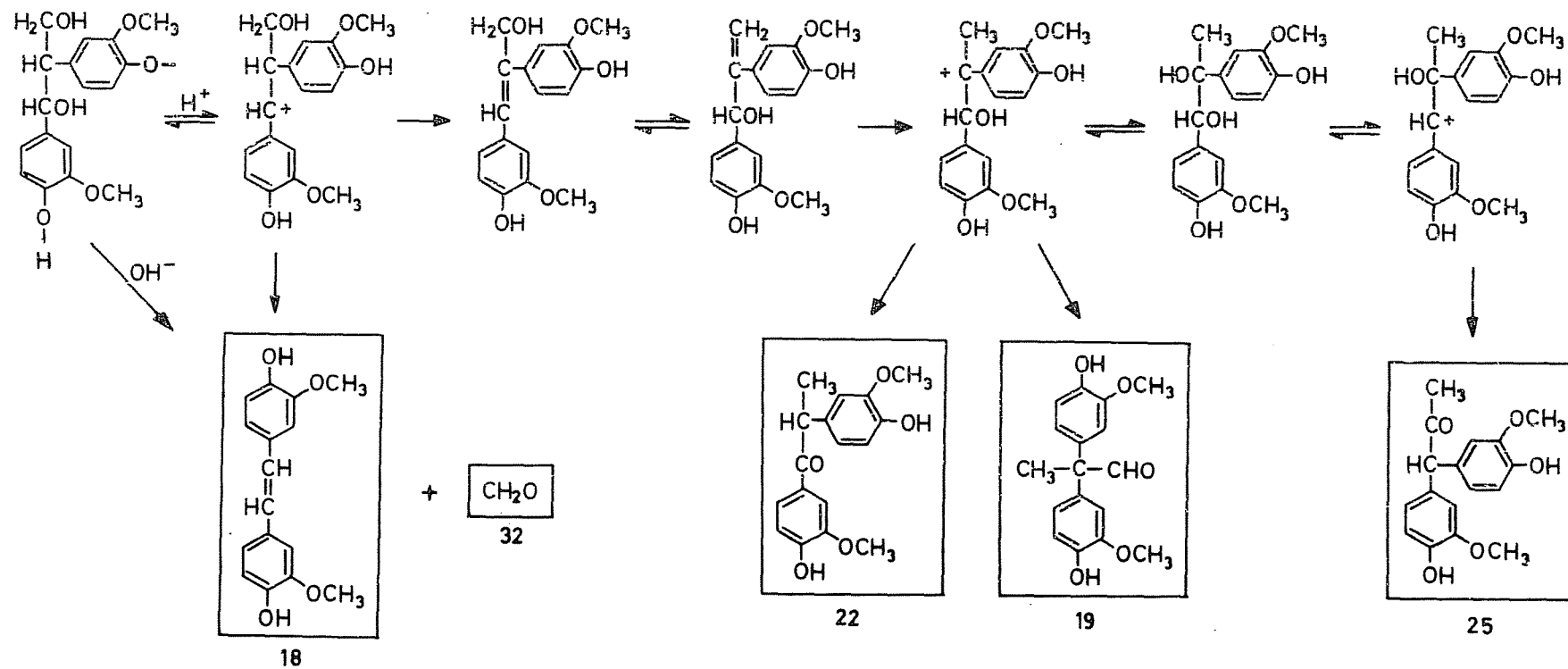


Fig.10. Formation of products from 1,2-diaryl-1,3-propanediol structures (H).^{III,VI,VII,XIV, 11}

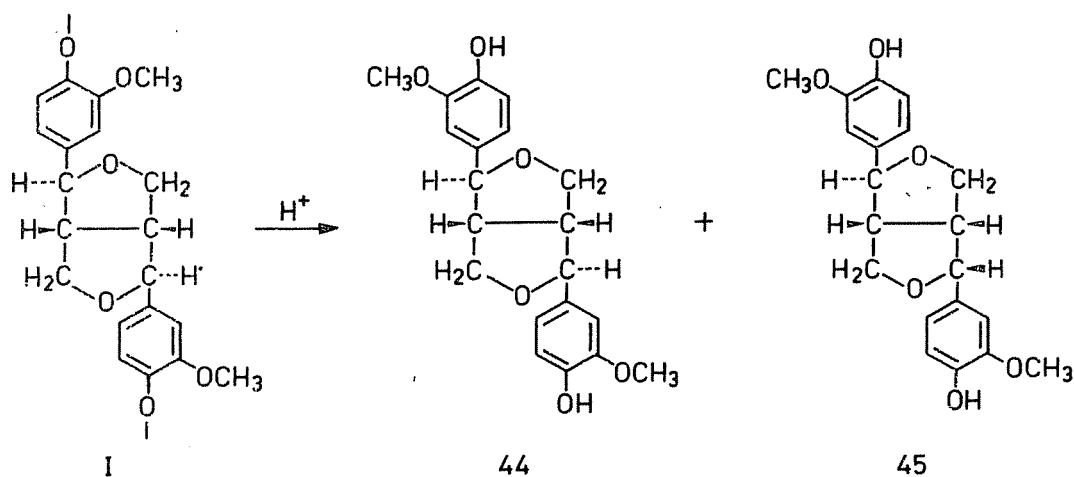


Fig. 11. According to model studies, structures of type I should give (+)-pinoresinol (44) and (+)-epipinoresinol (45) on acidolysis. These products were not formed in detectable amounts on acidolysis of spruce lignin.^{VI} However, the corresponding syringyl analogues, compounds 30 and 31, have been obtained from birch lignin.^{XIV} The structural significance of the results concerning this type structure has been discussed in Parts VI, IX, and XIV.

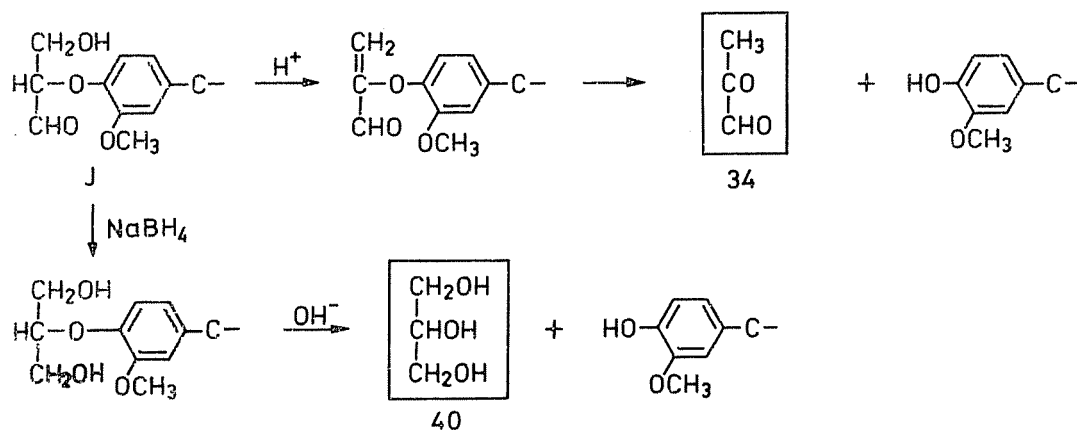


Fig. 12. Formation of products from glycerol-2-aryl ether structures (J). Support for the enol ether intermediate in the acidolytic degradation^{V, VII} has been obtained from the fact that a model compound of this type gave 34 rapidly on acidolysis.¹² The formation of glycerol¹² (40) on "soda cooking" of sodium borohydride treated spruce lignin is attributed to the presence of structures of type J in lignin (for the reactions involved in the formation of the glycerol, see Refs. 20 and 21).

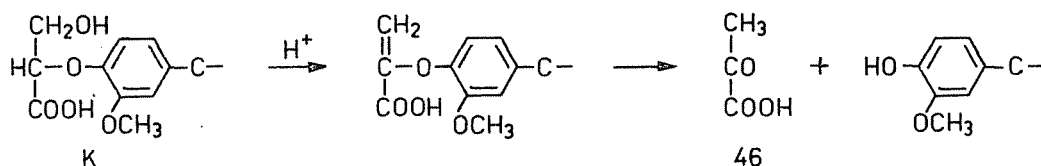


Fig. 13. Minor amounts of structures of type K may be present in lignin (probably with an esterified carboxylic group).²² Experiments with model compounds suggest that such ethers are stable during acidolysis.²³ No pyruvic acid (46) was formed on acidolysis of spruce lignin.²³ In additional experiments with model compounds it was found that some pyruvic acid (46) was formed on acidolysis at elevated temperature.²³

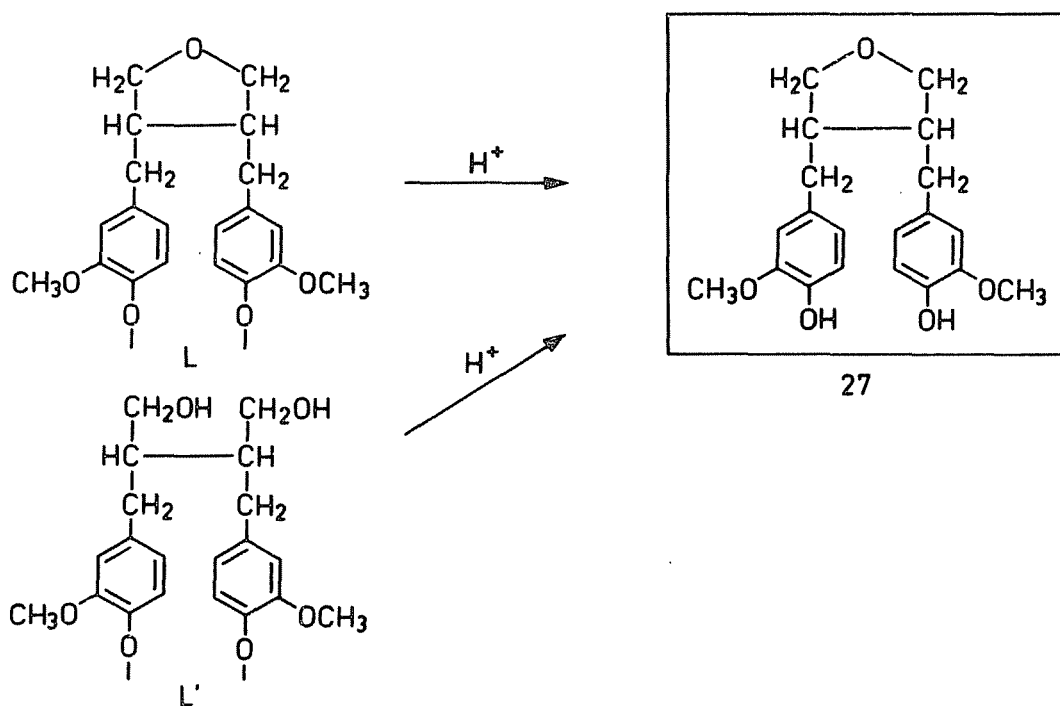


Fig. 14. (\pm)Divanillyltetrahydrofuran (27) formed on acidolysis of spruce lignin^{VI} may originate from structures of type L and L'. Concerning the occurrence of such structures in lignin, see also Refs. 24 and 25.

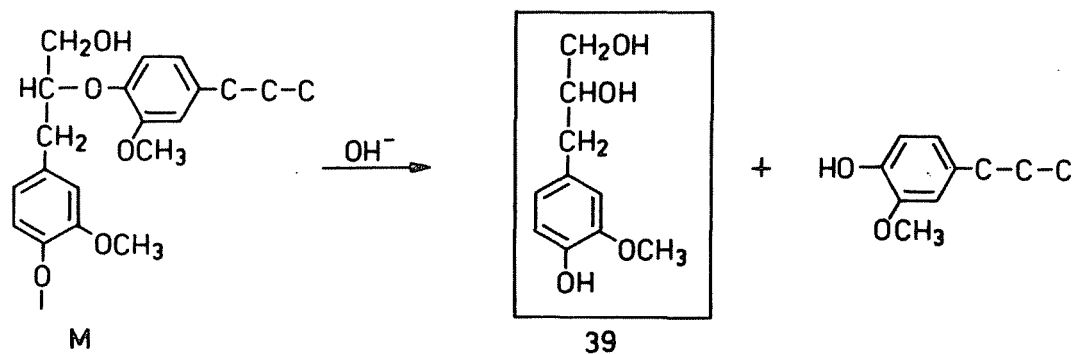


Fig. 15. Minute amounts of compound 39 are formed on "soda cooking" of spruce lignin.¹¹ This may be interpreted to indicate the occurrence of structures of type M in lignin (cf. Ref. 21) (the possible occurrence of structures of types L and L', carrying a methylene group in the benzyl position, provides some justification for such an assumption). However, there are other plausible reaction routes for the formation of compound 39 under the drastic conditions of "soda cooking".

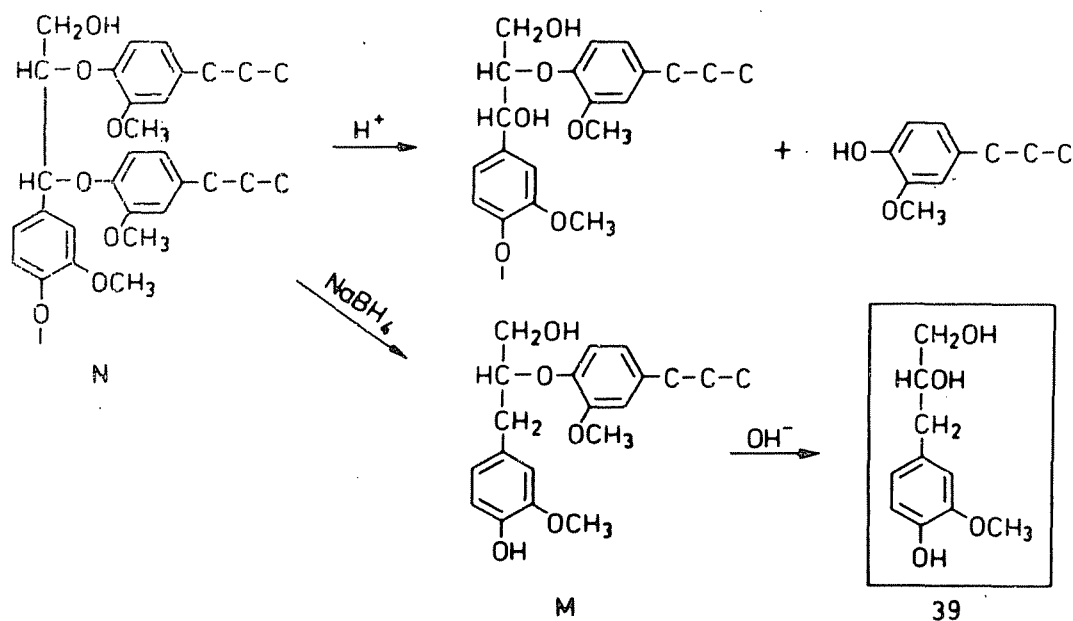


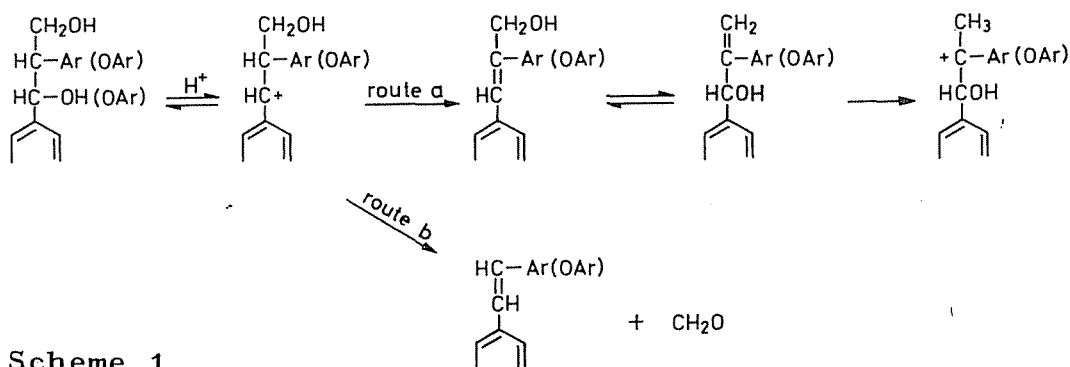
Fig. 16. Benzyl aryl ether structures of type N are cleaved on relatively mild acidic treatment²⁶ and are therefore expected to be cleaved rapidly on acidolysis. On treatment with borohydride in alkaline solution, structures of type N with free phenolic groups should give structures of type M, which give compound 39 on "soda cooking" (see Fig. 15). In accord with the expectation, borohydride treated lignin gave more of compound 39 than nontreated lignin. This provides additional proof for the occurrence of such benzyl ether structures in lignin; earlier evidence is based on the increase in phenolic groups on alkaline treatment.^{27,28}

C. Reactions of lignin on acidolysis

Reactions of lignin on acidolysis are exemplified in the preceding section. The degradation on acidolysis is essentially due to cleavage of ether bonds, mainly the β -aryl ether bonds in structures of type A. This has been discussed in Part XII.

Some initial reactions, such as isomerization of benzyl alcohols and hydrolysis of benzyl aryl ethers, are not reflected in the structure of the degradation products. Selective cleavage of the latter type of ethers gives only small amounts of low molecular weight products (see Part VI). According to studies with the acidolysis reagent at 50° on model compounds, such reactions proceed via a symmetric intermediate (benzylium ion, and in case of phenolic units, quinone methide intermediates also are conceivable).²⁶ A bimolecular pathway has also been suggested for this type of reactions.²⁹

The most important reactions leading to degradation products on acidolysis can be formulated via an initial formation of a benzylium ion. The above mentioned studies with the acidolysis reagent at 50° provides some support for the assumption that benzylium ions are actually present in the lignin acidolysis mixture. Reaction steps which, according to the formulations in Section B are common to different lignin structures giving degradation products via benzylium ions are shown in Scheme 1.

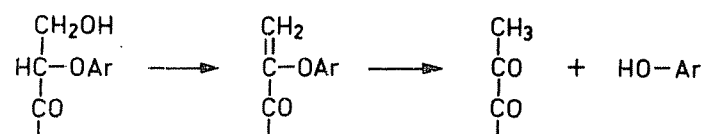


Scheme 1

The benzylium ion can either expell a proton (route a) or protonated formaldehyde (route b); in both cases, unsaturated products are formed. Products formed via route a include the stilbenes detected in lignin acidolysis mixtures. In other cases the unsaturated products are intermediates which react directly or after rearrangement react to form degradation products. The results obtained show that route a dominates while route b proceeds to a small extent only. Comparatively large amounts of formaldehyde are obtained from lignin³⁰ on distillation with 28 % sulphuric acid which suggests that route b plays a more important role under these conditions. Scheme 1 include reactions of lignin structures A, G, and H (Figs. 3, 9, and 10).

It is very likely that benzylium ions also are intermediates in condensation reactions. This and other types of condensation reactions have been discussed to some extent in Parts VI and XIV. Condensation reactions decrease the yield of low molecular weight degradation products.

Scheme 2 shows reaction steps common to reactions shown in Figs. 4, 12, and 13. These reactions are of minor importance for the formation of degradation products on acidolysis (the reaction shown in Fig. 13 occurs only on acidolysis at elevated temperature).

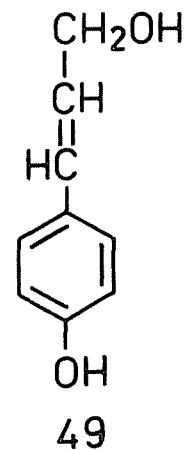
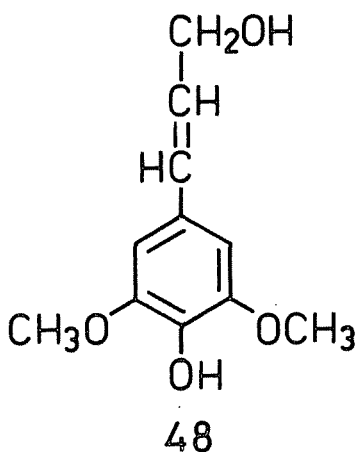
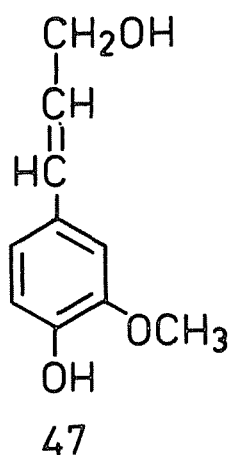


Scheme 2

The reactions involved in the formation of methanol from quinones and quinonoid units have been discussed to some extent in Part XIII. Concerning reactions shown in Figs. 11 and 14, see Parts VI and XIV. The reactions involved in the interconversions of ketones 1-5 have been discussed in Part IV.

D. Results concerning the structure of lignin

The present state of lignin chemistry permits a definition of lignins. As formulated by Sarkanen and Ludwig,⁴ lignins are polymeric natural products arising from an enzyme-initiated dehydrogenative polymerization of three primary precursors: trans-coniferyl (47), trans-sinapyl (48), and trans-p-coumaryl (49) alcohols. Thus far, with the



exception of the formation of acidolysis product 27 (Fig. 14) - in which the units have a lower degree of oxidation than in coniferyl alcohol, all the results obtained in this study are compatible with this definition. Most of the hydrolysis products obtained have been related to specific lignin structures with confidence. From the structural point of view, this implies that structural proof for the occurrence

of a series of lignin structures has been obtained. The arguments for the presence of different lignin structures appear in Parts I - XIV and some additional points are mentioned in Section B and will therefore not be repeated here.

Studies on solvolysis products provide the most direct evidence for different structural elements in lignin. Such structural lignin work for several reasons had succeeded only to a limited extent at the time these studies were undertaken. However, during the course of the present work progress in this area has proceeded rapidly (for a recent review, see Ref. 31). In hydrolysis studies by Nimz³² (percolation of wood meal with water at 100°) and more recently Sakakibara and co-workers⁷ (heating of wood meal with dioxan-water (1:1) at 180°) products were obtained which clearly demonstrate different types of connections between phenylpropane units. However, the formation of some of the products (those with glycerol side chains) has not been clarified and unexpected reactions also occur (formation of coniferaldehyde and phenylcoumarans from structures of type A, see Ref. 31). This complicates the interpretation of the results to some extent.

Acidolysis gives comparatively high yields of degradation products. In addition to qualitative conclusions, it is therefore possible to make some quantitative estimations.

Most other studies of solvolysis products have been made with wood as starting material. The present studies with isolated lignin therefore, in addition to providing new results, in some respects complement other studies.

Acknowledgements

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