



CHALMERS

CPL

Chalmers Publication Library

Institutional Repository of
Chalmers University of Technology
<http://publications.lib.chalmers.se>

This is an author produced version of a paper published
in **Applied Polymer Symposia**.

Citation for the published paper:

Lundquist, Knut

Low-molecular weight lignin hydrolysis products

Applied Polymer Symposia, 1976, no 28, pp 1393-1407

Published with permission from: John Wiley & Sons, Inc.

www.onlinelibrary.wiley.com

LOW-MOLECULAR WEIGHT LIGNIN HYDROLYSIS PRODUCTS

KNUT LUNDQUIST

*Department of Organic Chemistry
Chalmers University of Technology and University of Göteborg
Fack, S-402 20 Göteborg, Sweden*

SYNOPSIS

Results from studies of the formation of low-molecular weight compounds on refluxing of lignins with 0.2 M hydrogen chloride in dioxane-water (9:1) are reviewed. With this review as a background the possibilities of producing low-molecular weight hydrolysis products from lignins are discussed. Acid-catalyzed degradation as well as general aspects are concerned.

The formation of low-molecular weight products from lignin during alkaline pulping (sulfate cooking and soda cooking) is also treated.

INTRODUCTION

Only low to moderate yields of low-molecular weight products are formed on hydrolytic treatments of lignins. Lignins differ in this respect from most other biopolymers, e.g., polysaccharides and proteins, which give high yields of low-molecular weight products on hydrolysis. In this paper the possibilities of producing low-molecular weight hydrolysis products from lignin are discussed. The introductory section consists mainly of a review of a series of studies (refs. [1-12]) of low-molecular weight degradation products obtained on refluxing of lignins with 0.2 M hydrogen chloride in dioxane-water (9:1); for simplicity, this particular treatment is called acidolysis* in the following. This review will serve as a background for a more general discussion of the hydrolytic degradation of lignins.

The degradation of lignin during acidolysis and the formation of low-molecular weight material are very well visualized in gel filtration experiments (Figs. 1 and 2). Peak F in Figure 2 is due to the presence of 2-furaldehyde, which is produced from minor amounts of xylan present in the birch lignin samples. The results with birch lignin also differ from those obtained with spruce lignin in that considerably more low-molecular weight products are produced from birch lignin.

* Treatment of lignin during these conditions was originally made in connection with analytical lignin studies [13] and the preparation [14] of lignin samples from plant materials.

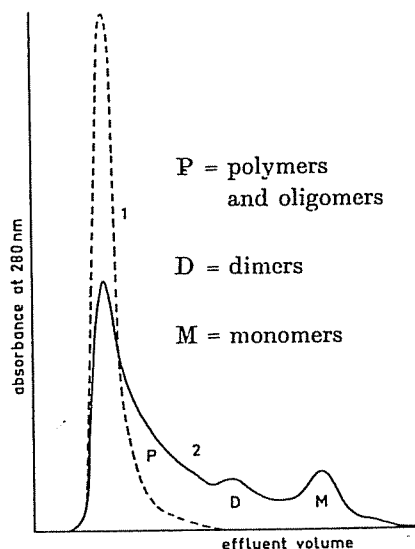


FIG. 1. Gel filtration of Björkman lignin from spruce (curve 1) and its reaction product obtained on 4 hr acidolysis (curve 2) on Sephadex G-25 with dioxane-water (1:1) as eluting solvent.

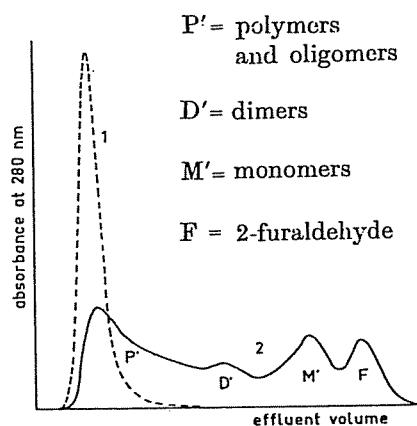
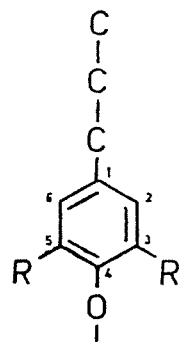


FIG. 2. Gel filtration of Björkman lignin from birch (curve 1) and its reaction product obtained on 4 hr acidolysis (curve 2) on Sephadex G-25 with dioxane-water (1:1) as eluting solvent.

In preparative experiments, the yield of low-molecular weight products (dimers and monomers) was 17% with spruce lignin and 30% with birch lignin [12]. These results can easily be related to differences in the structures of these two lignins. Spruce lignin consists almost entirely of units of the guaiacyl type, while birch lignin (a typical hardwood lignin) consists of nearly equal amounts of units of the guaiacyl and the syringyl types; both lignins contain small amounts of units of the p-hydroxyphenyl type (Fig. 3). In syringyl units the 3- and 5-positions are occupied by methoxyl groups and only a small percentage of the aromatic rings are therefore linked to adjacent units by acid-stable biphenyl and diaryl ether linkages. As a consequence of the presence of the many syringyl units, the frequency of hydrolyzable ether linkages is greater in birch lignin.

Studies of the low-molecular weight products formed on acidolysis of Björkman lignin from spruce and birch resulted in the identification of those individual components which are shown in Figure 4. The three types of units present in lignins (Fig. 3) are all represented in the compounds. On the basis of studies with model



p-hydroxyphenyl $R=R'=H$

guaiacyl $R=H, R'=OCH_3$

syringyl $R=R'=OCH_3$

FIG. 3. Structure for p-hydroxyphenyl, guaiacyl, and syringyl units.

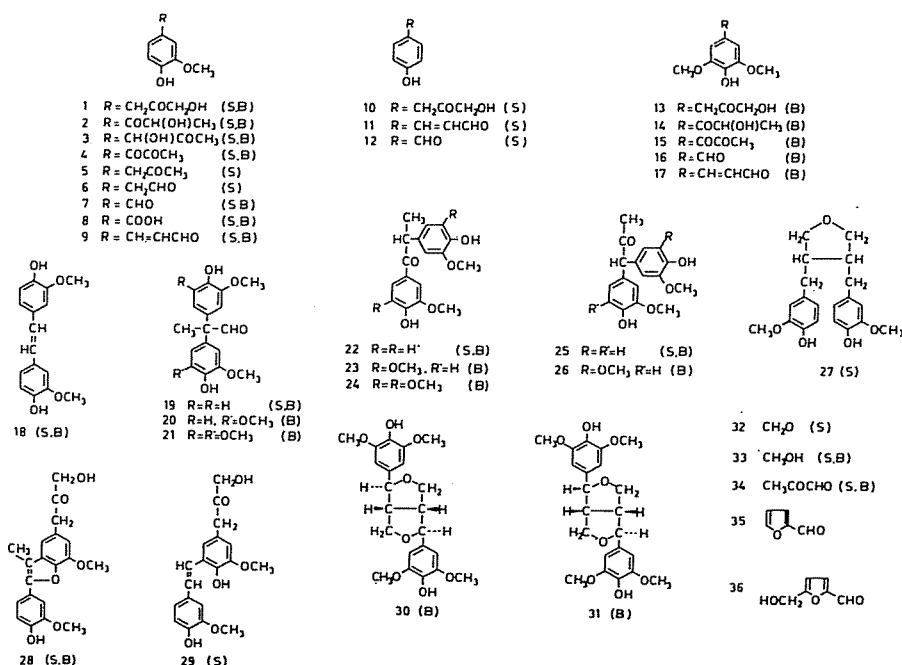


FIG. 4. Products obtained on acidolysis of Björkman lignin from spruce (S) and birch (B). See Refs. [4-7, 9, 12].

compounds and other observations it has been possible to relate almost all compounds to lignin structures. The furan derivatives (35) and (36) originate from minor amounts of carbohydrates present in the lignin preparations and are not further discussed. Figures 5-16 show the formation of acidolysis products from lignin structures A-L. Relevant references and, in some cases, remarks are appended to the figures. Only the guaiacyl type of units has been considered in these figures. However, so far as is known, degradation products composed of other types of units can be derived from lignin structures in an analogous way. Some results from studies of the alkaline degradation of lignins are included in the figures. Products detected in lignin hydrolysis mixtures are framed in the figures.

The degradation of lignin during acidolysis is mainly due to cleavage of ether

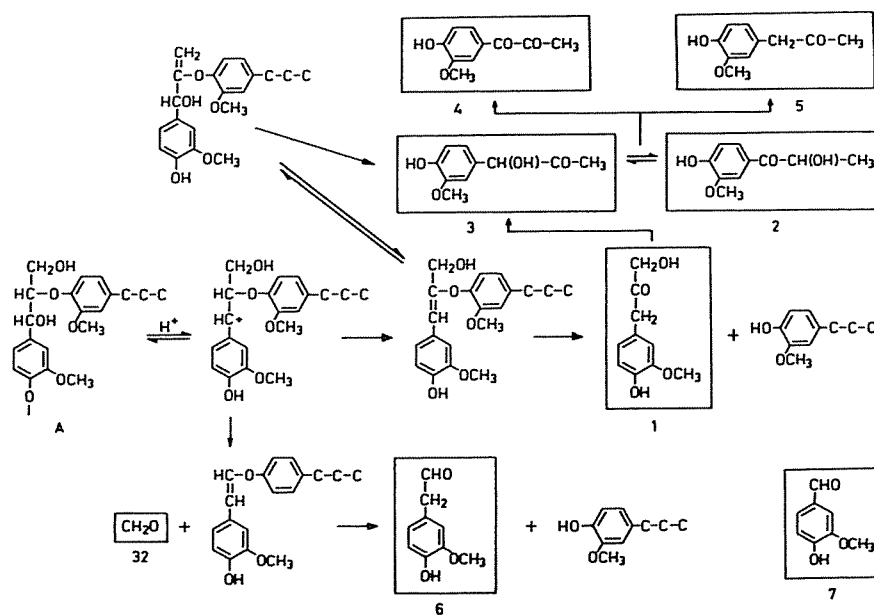


FIG. 5. See Refs. [3, 6, 10, 12].

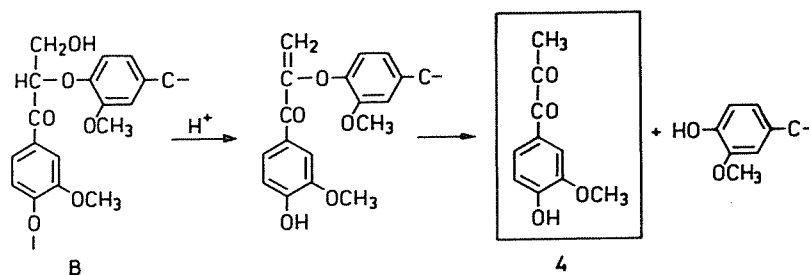


FIG. 6. See Refs. [10, 12].

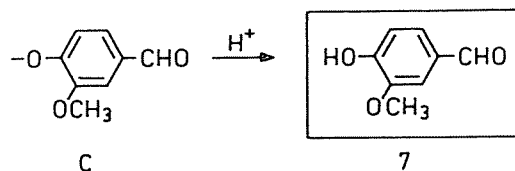


FIG. 7. See Refs. [5, 12].

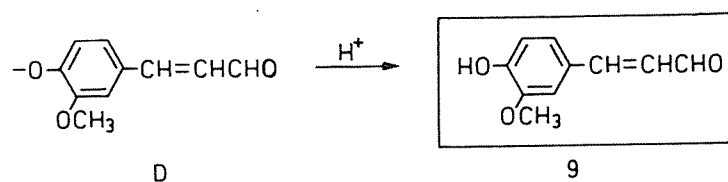


FIG. 8. See Refs. [5, 12].

bonds [10]. Most important is the cleavage of arylglycerol- β -aryl ethers (structural elements of type A, Fig. 5). In accordance with this fact, products resulting from cleavage of such ethers dominate quantitatively in the lignin acidolysis mixtures. The major monomeric product is ketol 1 which is obtained in 5% yield from spruce lignin. Birch lignin gives in addition to ketol 1 (yield 3%) the syringyl analogue of this compound (13) in 5% yield. During acidolysis, ketol 1 is

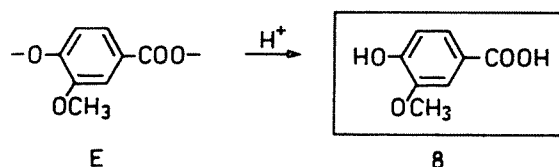


FIG. 9. See Refs. [5, 12].

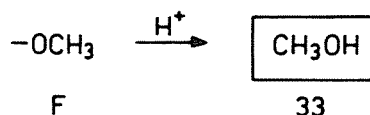
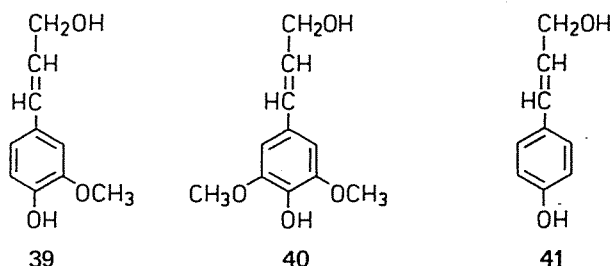


FIG. 10. See Refs. [9, 11].

slowly converted into other products (Fig. 5). Evidence for two other reaction routes for the cleavage of the β -ether bond in structures of type A has been obtained (Fig. 5). The quantitative importance of these two additional reaction routes is small.

SOME ASPECTS OF THE STRUCTURE OF LIGNIN

The present state of lignin chemistry permits a definition of lignins. As formulated by Sarkanen and Ludwig [18], lignins are polymeric natural products arising from an enzyme-initiated dehydrogenative polymerization of three primary precursors: trans-coniferyl (39), trans-sinapyl (40), and trans-coumaryl (41) alco-



hols. Most of the above mentioned hydrolysis products 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 results are consistent with the concept that during lignin biosynthesis oxidative dimerization of p-hydroxycinnamyl alcohols is very much suppressed in favor of reaction of p-hydroxycinnamyl alcohol radicals with radicals of phenolic units in the lignin molecule with a saturated side chain.

When estimating the possibilities of obtaining low-molecular weight hydrolysis products from lignin, the types and frequencies of the different structural elements, as well as more general structural aspects, are of interest. In any linear polymer the number of interconnections (interconnection is here defined as any arrangement keeping two units together and may thus comprise more than one bond) per unit (α) in a molecule consisting of n units is $(n - 1)/n$. This is true even if the molecule is branched (branching of the molecule is expected to occur during lignin biosynthesis [18-20]). Thus, in a linear or branched polymer α is below but close to 1. A greater α is obtained if the molecule contains rings of units which, if the

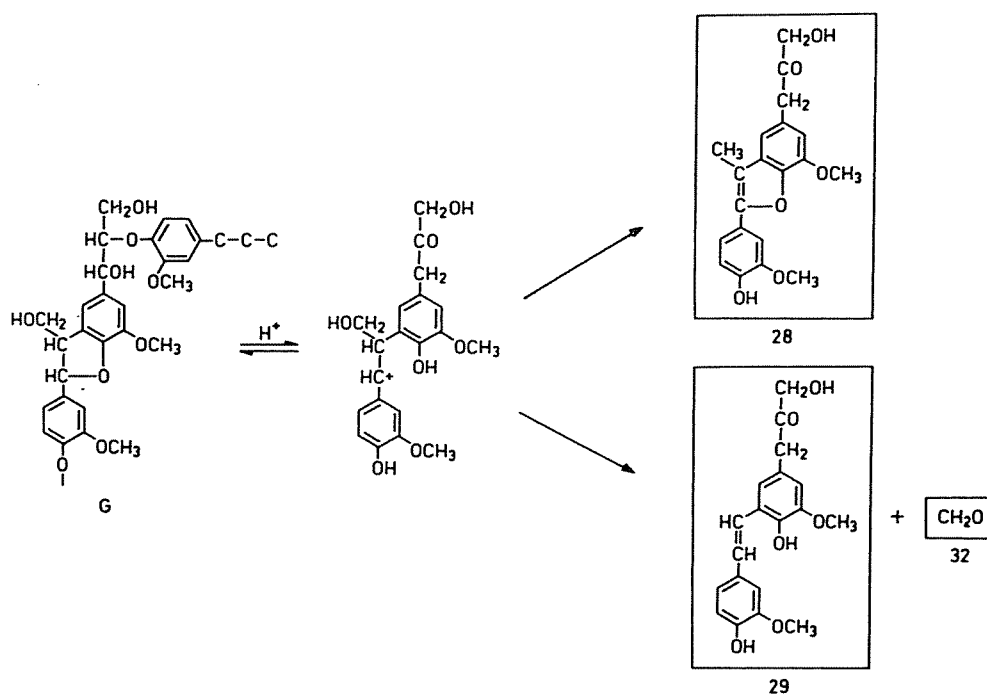


FIG. 11. See Refs. [6, 8].

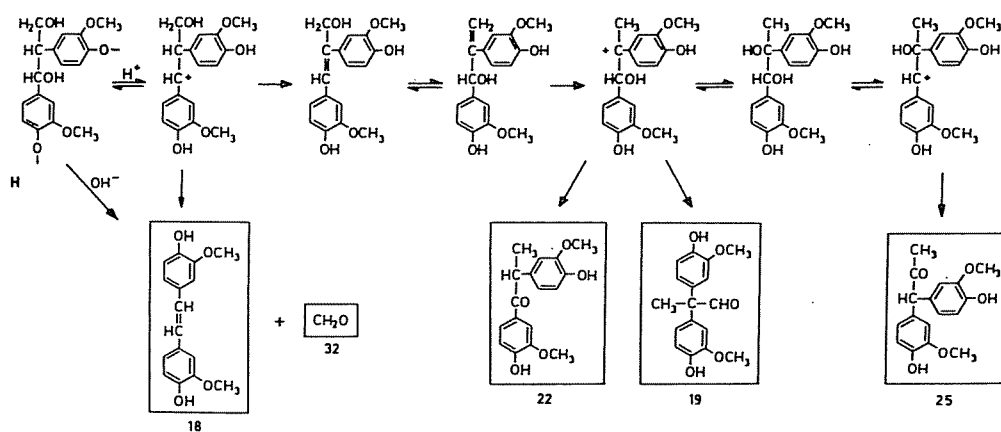


FIG. 12. See Refs. [2, 5, 6, 12].

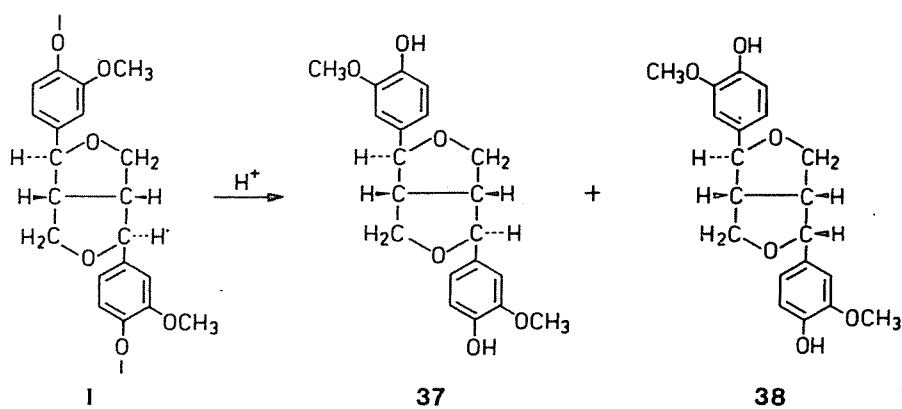


FIG. 13. Pinoresinol (37) and epipinoresinol (38) have not been detected in lignin acidolysis mixtures. The corresponding syringyl analogue compounds (30) and (31), have been obtained from birch lignin. See Refs. [5, 8, 12].

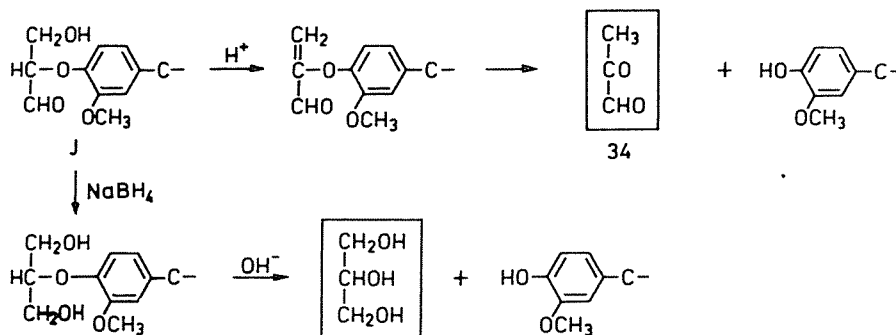


FIG. 14. See Refs. [4, 15].

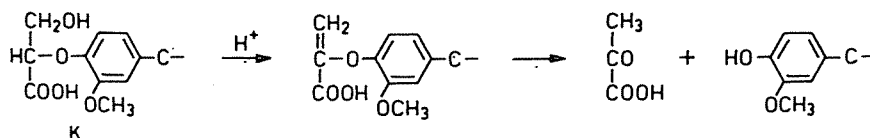
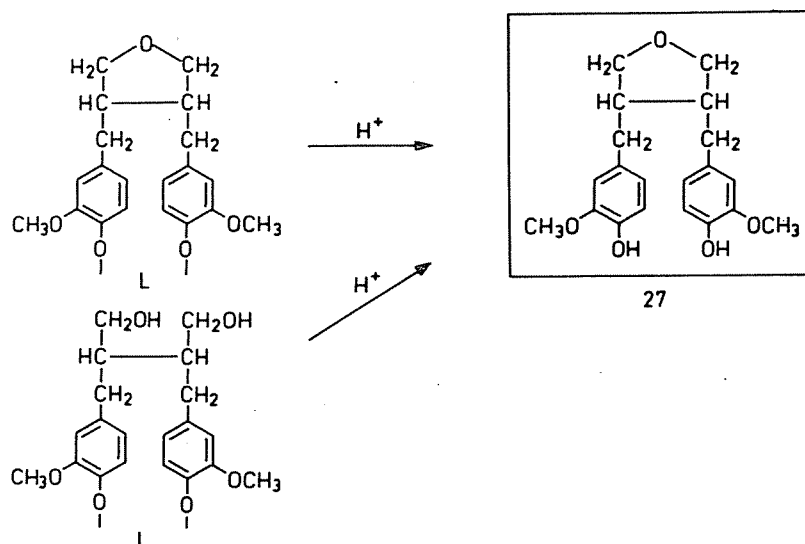
FIG. 15. Some attempts to detect pyruvic acid in lignin acidolysis mixtures, in order to obtain evidence for the hypothetical lignin structure *K*, are described in Ref. [15].

FIG. 16. See Ref. [5]. Concerning the origin of compound (27), see also Refs. [16] and [17].

frequency of the rings is big enough, results in a so-called network. Available lignin data suggests that the number of such rings is very small in lignin. An α -value as high as 1.1 seems highly unlikely. Presumably α is very close to unity. According to this view lignin should be regarded as a branched polymer rather than one having the network type of structure. Current opinions about the structure of spruce lignin suggest that less than one half of the interconnections are nonhydrolyzable (e.g., contain C-C bonds). Assuming a random distribution of these nonhydrolyzable linkages and keeping in mind the above considerations, one can conclude that it should be theoretically possible to obtain a fairly high yield of low-molecular weight products (monomers and dimers) on hydrolytic degradation of spruce lignin. An even higher yield should be possible with hardwood lignins, since the number of nonhydrolyzable bonds is lower in such lignins.

DEGRADATION REACTIONS

A variety of reactions leading to low-molecular weight degradation products are shown in Figures 5–16. However, only in Figures 5 and 6 are reactions shown which demonstrate the separation of phenylpropane units from each other (depolymerization). Undoubtedly the predominant depolymerization reaction is the cleavage of arylglycerol- β -aryl ether linkages (Fig. 5). The hydrolysis of noncyclic benzyl aryl ethers (structure M) should be fairly important for the depolymerization (Fig. 17). Hydrolysis of such ethers is not reflected in the structure of any low molecular weight degradation product. Some depolymerization may occur due to hydrolysis of quinol ethers [9, 11], quinone ketals (see Refs. [9] and [10]), and ester linkages (cf. Fig. 9). Liberation of small fragments [formaldehyde (Figs. 5, 11, and 12), methanol (Fig. 10), and pyruvaldehyde (Fig. 14)] also contributes to the degradation of the lignin. For a more detailed discussion of the degradation reactions see Refs. [10] and [11].

CONDENSATION AND POLYMERIZATION REACTIONS

During acidolysis reactions occur which counteract the degradation and cause an increase in molecular weight (condensation and polymerization reactions). Studies of the formation of formaldehyde from lignin during acidolysis suggest that the liberated formaldehyde is partly consumed in condensation reactions [6]. Possibly other types of carbonyl compounds present in acidolysis mixtures take part in condensation reactions, but hitherto no evidence for this has been obtained. Coniferyl alcohol polymerizes under acid conditions. Since lignin contains minor amounts of cinnamyl alcohol end groups, this reaction may be of some importance in the acidolysis of lignin. It is very tempting to assume that the benzyl alcohol groupings of the type present in structural elements of type A (Fig. 5) condense with aromatic rings during acidolysis. Figure 18 shows gel filtration results obtained with the 4h acidolysis mixture of model compound A (a p-hydroxybenzyl alcohol). The portion of the reaction mixture consisting of compounds with two or more aromatic rings (fractions 33–43) was 17% of the starting material, contained compound A (3%) and unidentified constituents (14%) which must include the condensation products. The major part of the reaction product (fractions 44–54) consisted of compounds formed on cleavage of the β -ether bond (guaiacol and ketols, see Fig. 20). The conclusion must be that the condensation of benzyl alcohol groups with aromatic rings is of minor importance in the acidolysis of this model compound. Examination of the 4h acidolysis mixture of compound A with a methylated phenolic group indicates that in this case condensation reactions are also suppressed (Fig. 20). However, even if the frequency of such condensation reactions is small they may have a considerable importance for the yield of low-molecular weight hydrolysis products from lignin. This is exemplified by the hypothetical lignin fragment shown in Figure 19 which contains a linkage formed by condensation of a benzyl alcohol group with an aromatic ring. The formation of this bond prevents units *r*, *s*, and *t* [because the formation of a benzylium ion (cf. Fig. 5) is prevented] from being liberated as monomers, and, moreover, liberation of unit *u* is delayed because cleavage of p-alkoxyaryl-glycerol- β -aryl ethers is comparatively slow (cf. Fig. 20).

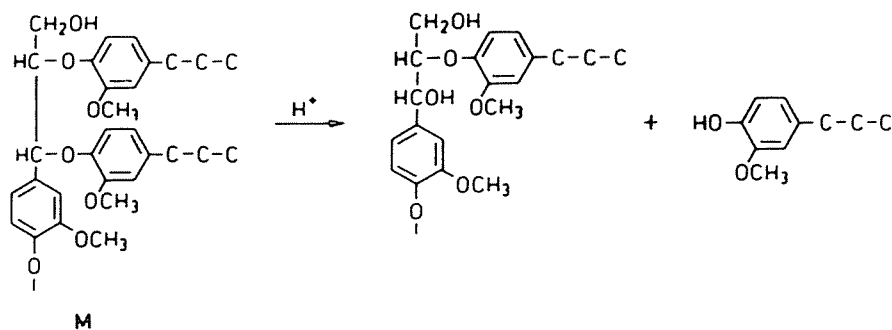
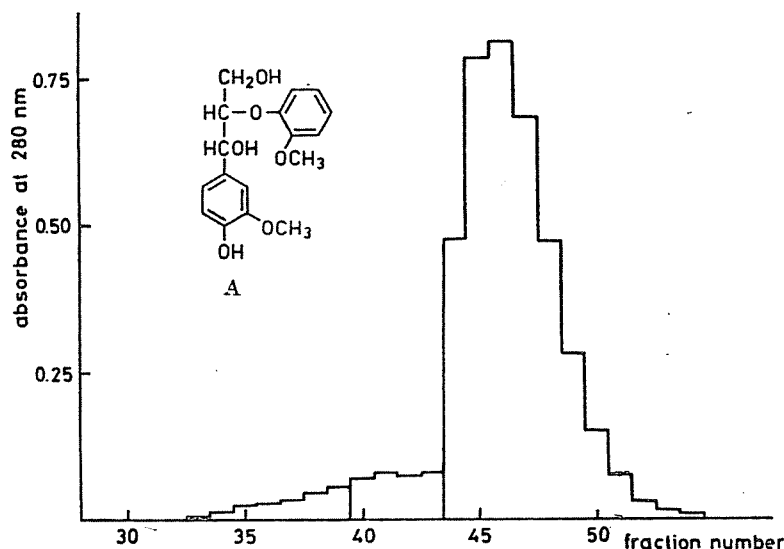


FIG. 17. Hydrolysis of noncyclic benzyl aryl ether.

FIG. 18. Gel filtration of the reaction product obtained on 4h acidolysis of compound *A* [Sephadex G-25, eluting solvent, dioxane-water (1:1)]. Residual starting material was found in fractions 40–43.

OPTIMIZATION OF THE YIELD OF KETOL 1—A DISCUSSION OF FACTORS INFLUENCING THE YIELD OF LIGNIN HYDROLYSIS PRODUCTS

Ketol 1 is the major monomeric product formed on acidolysis of spruce lignin (5% yield). The predominating monomers obtained from birch lignin are ketol 1 (3% yield) and its syringyl analog, ketol 13 (5% yield). Ketols 1 and 13 originate from structural elements of the arylglycerol- β -aryl ether type (Fig. 5). The following discussion mainly concerns spruce lignin. Figure 20 shows results from studies [10] of the composition of reaction mixtures obtained on 4h acidolysis of guaiacylglycerol- β -guaiacyl ether and the corresponding compound with a methylated phenol group. The total amount of identified compounds is high and about the same from both model compounds. Major components of the reaction products are guaiacol, ketols, and starting materials. The amounts of condensation products, included in "other products", are small. The main difference between the two model compounds is the rate of reaction. In addition to products shown in Figure 20, formaldehyde is formed in a few per cent yield [6]. The reaction routes by which the products are formed appear in Figure 5. No systematic studies have been made to compare the acidolytic degradation [defined as refluxing

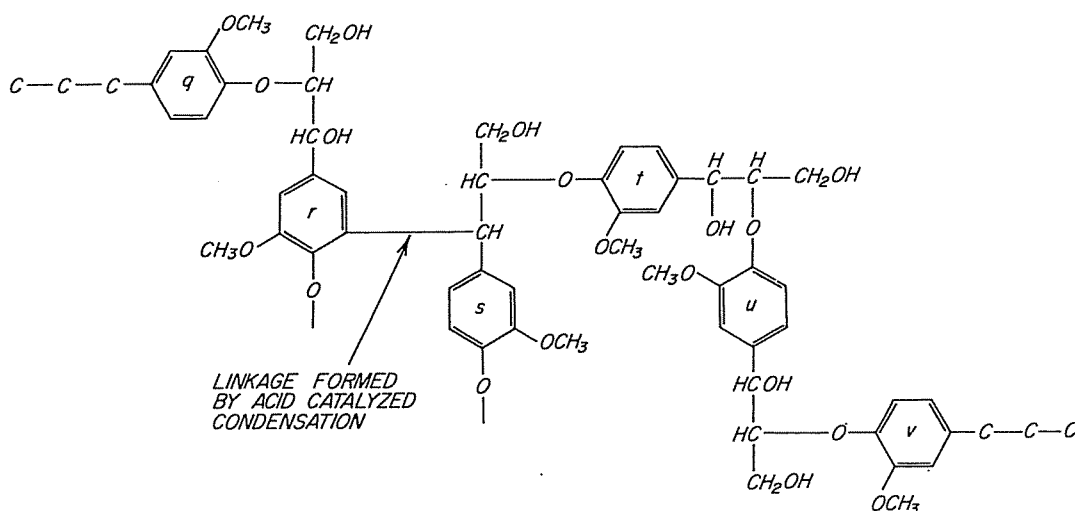


FIG. 19. Hypothetical lignin fragment which contains a linkage formed by acid catalyzed condensation.

	3%		42%
	53%		36%
	14%		5%
	72%		43%
Total yield of products:		96%	
Starting material, ketols, guaiacol:		82%	
Other products:		14%	

FIG. 20. Yields obtained on 4 hr acidolysis of β -ether models.

with 0.2 M hydrogen chloride in dioxane-water (9:1)] with other similar degradations (i.e. comparative studies of the influence of type and concentration of acid, medium, and temperature). Acidolysis at elevated temperature (120°C) does not seem to result in an increase of the yield of ketols from lignin [21].

The yield of ketol 1 on acidolysis of lignin for various periods of time has been studied to some extent. The maximum yield of ketol 1 is reached after treatment for a few hours [7]. Selection of reaction conditions which suppress the side reactions shown in Figure 5 should increase the yield of ketol 1. Experimental data

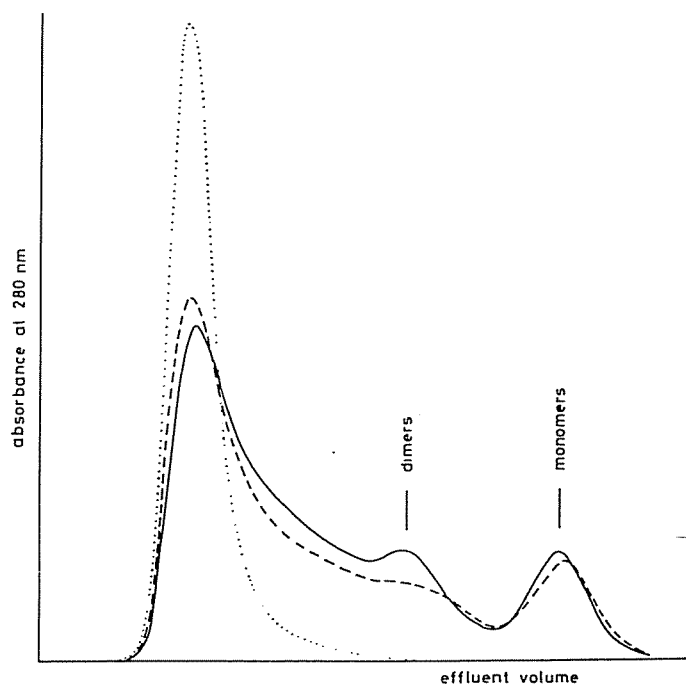


FIG. 21. Gel filtration [Sephadex G-25, eluent: dioxane-water (1:1)] of "milled wood lignin" from spruce (.....) and reaction mixtures obtained during sulfate cooking (—) and soda cooking (- - -) of this material.

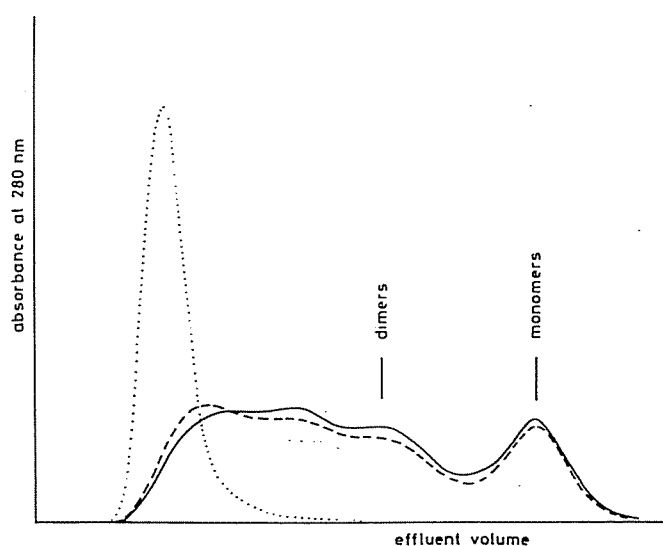


FIG. 22. Gel filtration [Sephadex G-25, eluent: dioxane-water (1:1)] of "milled wood lignin" from birch (.....) and reaction mixtures obtained during sulfate cooking (—) and soda cooking (- - -) of this material.

suggest that the amount of liberated formaldehyde is dependent upon reaction conditions. Thus, spruce lignin gives formaldehyde in 10% yield on distillation with 28% sulfuric acid [20], while acidolysis gives a yield of only 2–3% [6]. It is not known if the reaction route leading directly to ketol 2 as cleavage product (Fig. 5) can be suppressed. The yield of ketol 1 is diminished by conversion into other products. This can be counteracted by continuous or intermittent removal of the low-molecular weight products formed and possibly also by modifying the

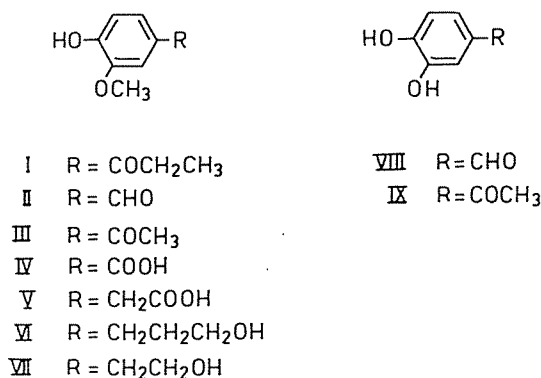


FIG. 23.

reaction conditions. The same methods can be used to neutralize the negative effects of condensation reactions. Such effects can also be diminished by performing the reaction in dilute solution (cf. the study of the formation of formaldehyde [6]).

Comparisons of the results of acidolysis of lignin (spruce) and model compounds suggest that the theoretical yield of ketol *I* is 10–15%. It is clear that the frequency of condensation reactions is low in the case of model compounds (Figs. 18 and 20), but that such reactions may have greater importance in the case of lignin (see discussion of Fig. 19). Therefore, the value obtained from acidolysis studies can be assumed to be fairly close to the lower limit. In fact, most information in the literature suggests that the theoretical value for the yield of ketol *I* is considerably higher. Here, as in many other cases, precise analytical lignin data are lacking.

COMPARISONS OF DIFFERENT HYDROLYTIC DEGRADATIONS OF LIGNIN

Among other solvolytic degradations applied to lignin, "ethanolysis" (refluxing with hydrogen chloride in ethanol) rather closely resembles acidolysis. "Ethanolysis" was introduced by Hibbert and co-workers [22], and has been used frequently by other investigators. A characteristic of acidolysis and "ethanolysis" is the formation of arylpropanones ("Hibbert ketones" and related compounds) in fairly high yields. Hitherto no other hydrolytic degradations have been performed which can produce such high yield of monomeric phenylpropane compounds. Arylpropanones of the actual types have frequently been encountered in wood hydrolyzates obtained by various methods (see Ref. [23]).

Many of the products detected in lignin acidolysis mixtures have been found in wood hydrolyzates obtained by other degradation methods (for a recent review, see Ref. [23]; other recent literature in this field is quoted in Refs. [10] and [12]). However, in most other studies the origin of the products has not been elucidated.

Sulfite pulping at low pH resembles acidolysis in the respect that vanillin, pyruvaldehyde, and formaldehyde are liberated from the lignin [24], but the introduction of sulfonic acid groups is, of course, the most important reaction [25, 26].

Wood hydrolyzate samples have often been obtained by hydrolysis at high temperatures [23]. It is questionable if the degradation which occurs during such conditions can be described merely as a hydrolysis. Thus, e.g. coniferyl alcohol

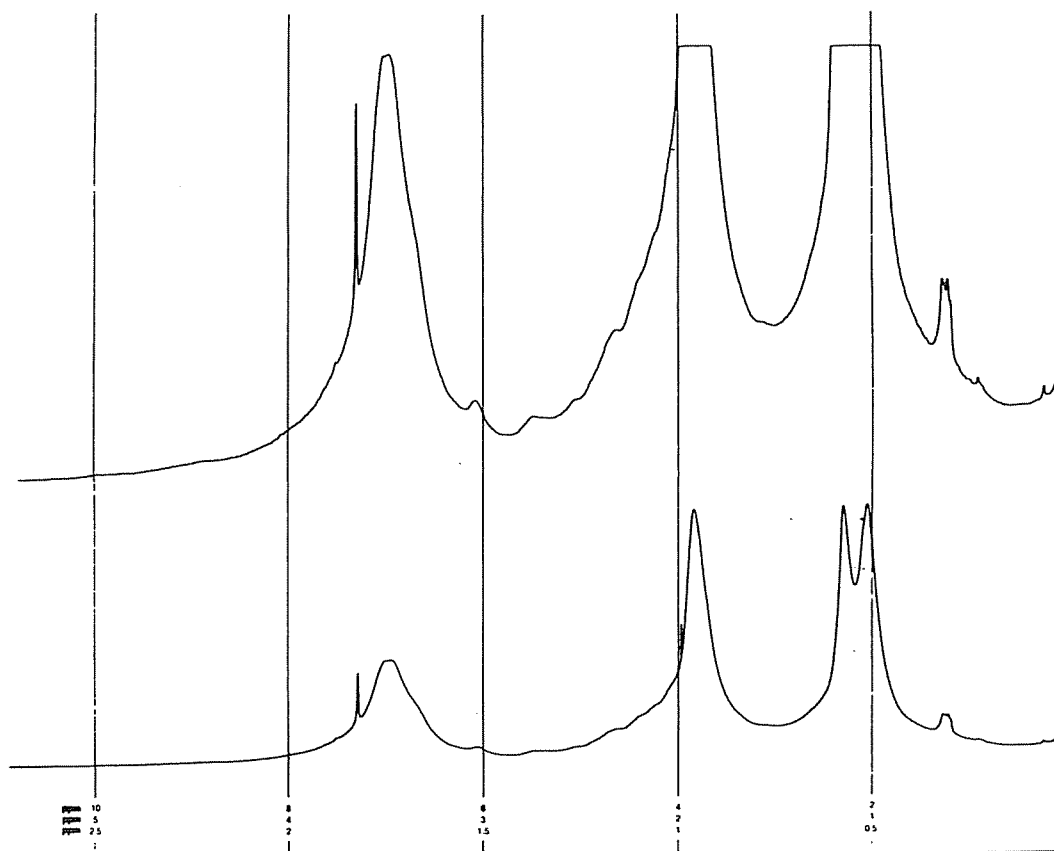


FIG. 24. NMR spectrum of acetylated Indulin AT. Solvent, chloroform-d.

obtained from wood by brief heating in dioxane-water (1:1) at 180°C has been shown to originate from structural elements of the guaiacylglycerol- β -aryl ether type (structure 7A in Fig. 5) [27]. It is clear that reactions other than hydrolysis—at least if this term is taken in a more narrow sense—must have been involved in the formation of coniferyl alcohol from structures of type 7A.

The technically most important hydrolytic treatments of lignins are involved in the alkaline pulping processes. It is clear that the reactions of lignin during alkaline pulping differ entirely from those occurring during acidolysis, although the structure of the resulting products sometimes show similarities. Alkaline as well as acid degradation, for example, results in the formation of stilbene [18] from structures of type 7H (Fig. 12). In the following section some results from studies [28] of products obtained on sulfate cooking and soda cooking of lignin are described. The origin of the low-molecular weight compounds formed during such digestions has so far been known only to a limited extent [28], but progress in this area has been made recently [29, 30].

DEGRADATION DURING SULFATE AND SODA COOKING

Gel filtration experiments demonstrate the formation of low-molecular weight materials from lignin during sulfate and soda cooking (Figs. 21 and 22). Birch lignin is degraded more extensively than spruce lignin. This can be explained in terms of structural differences between the two lignins. Due to the high specific

TABLE I

	Sulphate	Soda
Monomers	6.8%	5.8%
Dimers	11.0%	7.5%

absorbance at 280 nm of the low molecular weight fraction, the gel filtration curves overemphasize the amounts of such materials formed. This is demonstrated in preparative experiments made with spruce lignin (Table I). The preparative experiments corroborate that the amounts of low-molecular weight materials formed are somewhat greater on sulfate than on soda cooking (Table I).

Compounds detected in monomer fractions obtained on preparative gel filtration of cooking mixtures from spruce lignin are shown in Figure 23. The monomer fraction obtained on sulfate cooking differed mainly from the corresponding fraction obtained on soda cooking in that appreciable amounts of catechol compounds (*VIII* and *IX*) are present in fractions obtained on sulfate cooking. This is easily understood as being due to demethylation caused by strong nucleophiles (sulfide and hydrosulfide ions) present in the sulfate cooking liquor. The most prominent component is vanillin (about 2% of the lignin). Other quantitatively important products are acetovanillone (*III*) and vanillic acid (*IV*). Vanillin seems to be most attractive to extract as a useful product. It seems to be largely unknown how cooking conditions influence the yield of vanillin.

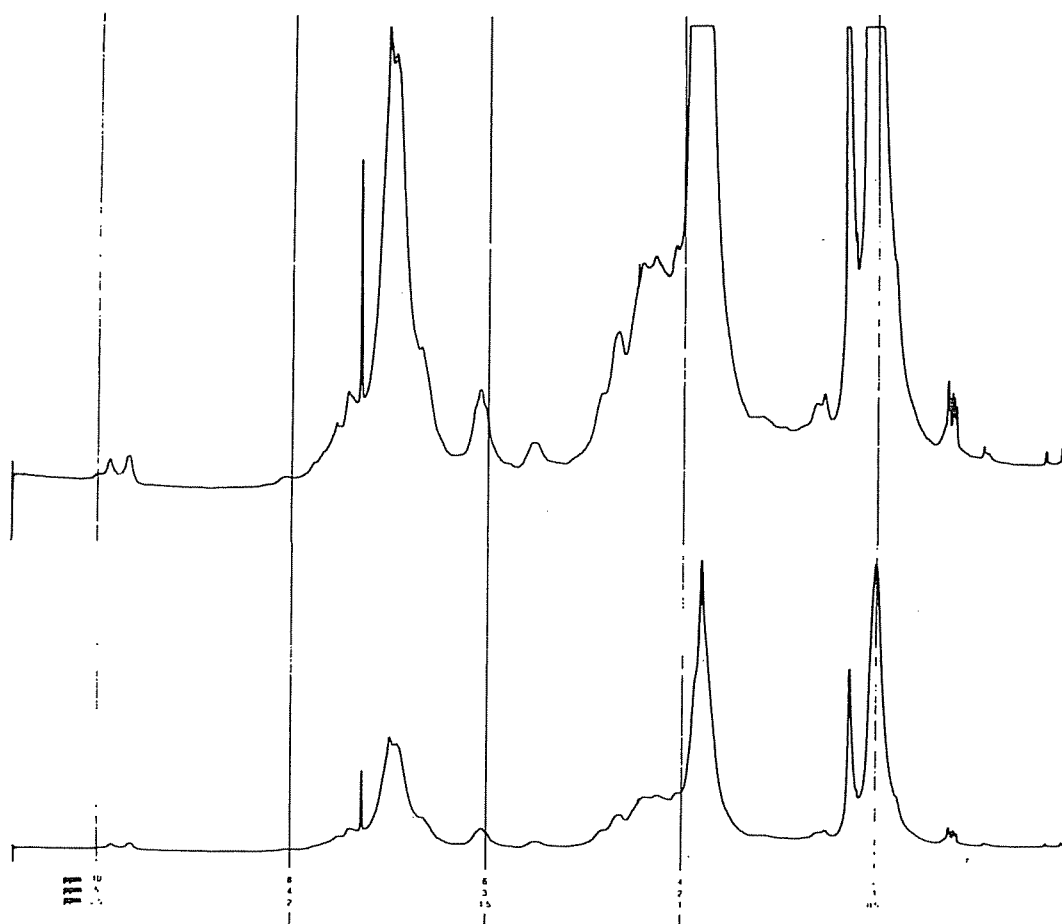


FIG. 25. NMR spectrum of acetylated Björkman lignin from spruce. Solvent, chloroform-d.

It is of interest to note in this connection that an NMR* spectrum (270 MHz instrument) of acetylated sulfate lignin (Indulin AT) (Fig. 24) did not give any signal indicating the presence of protons in aldehyde groups. In an NMR spectrum of acetylated milled wood lignin (Fig. 25), recorded under the same conditions, aldehyde protons are clearly visible. Signals at $\delta = 9.66$ (cinnamaldehydes) and $\delta = 9.86$ and 9.96 (other aldehydes) are attributed to protons in aldehyde groups (Fig. 25). From the NMR studies it can be concluded that the number of vanillin units is less than 1% of the units in the polymeric fraction of sulfate lignin, while isolated vanillin constitutes about one third of the monomer fraction. The reason for this discrepancy is not known. Diguaiacylstilbene (18) was a major component of the dimer fraction. It originates from structural elements of the 1,2-diaryl-1,3-propanediol type (Fig. 12). The present results are in good agreement with those obtained by Enkvist and co-workers [31] in their studies of the composition of black liquor from commercial cookings.

* NMR studies have been made in cooperation with T. Olsson, M. Sci.

REFERENCES

- [1] K. Lundquist, *Acta Chem. Scand.*, **18**, 1316 (1964).
- [2] K. Lundquist and G. E. Miksche, *Tetrahedron Lett.*, **1965**, 2131.
- [3] K. Lundquist and K. Hedlund, *Acta Chem. Scand.*, **21**, 1750 (1967).
- [4] K. Lundquist, G. E. Miksche, L. Ericsson, and L. Berndtson, *Tetrahedron Lett.*, **1967**, 4587.
- [5] K. Lundquist, *Acta Chem. Scand.*, **24**, 889 (1970).
- [6] K. Lundquist and L. Ericsson, *Acta Chem. Scand.*, **24**, 3681 (1970).
- [7] K. Lundquist and T. K. Kirk, *Acta Chem. Scand.*, **25**, 889 (1971).
- [8] K. Lundquist and K. Hedlund, *Acta Chem. Scand.*, **25**, 2199 (1971).
- [9] K. Lundquist and L. Ericsson, *Acta Chem. Scand.*, **25**, 756 (1971).
- [10] K. Lundquist and R. Lundgren, *Acta Chem. Scand.*, **26**, 2005 (1972).
- [11] L. Hemr  and K. Lundquist, *Acta Chem. Scand.*, **27**, 365 (1973).
- [12] K. Lundquist, *Acta Chem. Scand.*, **27**, 2597 (1973).
- [13] E. Adler, J. M. Pepper, and E. Eriksoo, *Ind. Eng. Chem.*, **49**, 1391 (1957); E. Adler, *Paperi Puu*, **43**, 634 (1961); E. Adler and K. Lundquist, *Acta Chem. Scand.*, **17**, 13 (1963).
- [14] J. M. Pepper, P. E. T. Baylis, and E. Adler, *Can. J. Chem.*, **37**, 1241 (1959); D. F. Arsenau and J. M. Pepper, *Pulp Paper Mag. Can.*, **66** (8), T415 (1965).
- [15] L. Berndtson, K. Hedlund, L. Hemr , and K. Lundquist, *Acta Chem. Scand.*, **B28**, 333 (1974).
- [16] H. Nimz and K. Das, *Chem. Ber.*, **104**, 2359 (1971).
- [17] M. Matsukura and A. Sakakibara, *Nippon Mokuzai Gakkaishi*, **17**, 263 (1971).
- [18] *Lignins*, K. V. Sarkanen and C. H. Ludwig, Eds., Wiley, New York, 1971.
- [19] J. M. Harkin, in *Oxidative Coupling of Phenols*, W. I. Taylor and A. R. Battersby, Eds., Marcel Dekker, New York, 1967, p. 243.
- [20] K. Freudenberg, in *Constitution and Biosynthesis of Lignin*, K. Freudenberg and A. C. Neish, Eds., Springer, Berlin, 1968, p. 45.
- [21] T. Higuchi, M. Tanahashi, and F. Nakatsubo, *Wood Res.*, **54**, 9 (1972).
- [22] H. E. Fischer and H. Hibbert, *J. Amer. Chem. Soc.*, **69**, 1208 (1947) and preceding work.
- [23] A. F. A. Wallis, in Ref. [18], p. 345.
- [24] K. Christofferson, *Sv. Papperstidn.*, **73**, 566 (1970).
- [25] G. Gellerstedt and J. Gierer, *Sv. Papperstidn.*, **74**, 117 (1971).
- [26] J. Gierer, *Sv. Papperstidn.*, **73**, 571 (1970).
- [27] A. Sakakibara, H. Takeyama, and N. Morohoshi, *Holzforschung*, **20**, 45 (1966).
- [28] K. Lundquist, *Sv. Papperstidn.*, **76**, 704 (1973).
- [29] J. Gierer, I. Petterson, L.-  Smedman, and I. Wennberg, *Acta Chem. Scand.*, **27**, 2083 (1973).
- [30] G. Brunow and G. E. Miksche, *Acta Chem. Scand.*, **B29**, 349 (1975).
- [31] T. Enkvist, *Paper and Timber*, **43**, 657 (1961).