10th International Symposium on Wood and Pulping Chemistry

Main Symposium, Yokohama, Japan
June 7-10, 1999

10th Biennial

ISWPC

Main Symposium

STRUCTURAL ANALYSIS OF LIGNIN AND LIGNIN DEGRADATION PRODUCTS

K. Lundquist and S. Li*
Department of Forest Products and Chemical Engineering and *Department of Organic Chemistry, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

ABSTRACT
Lignins (and lignin degradation products) can be analysed *in situ* or as isolated samples. Drawbacks and advantages of the two approaches are discussed. The importance of reagent specificity and the relevance of some structural features of lignins (the network structure and co-polymerization during the biosynthesis) in connection with the analysis of lignins is illustrated. Selected topics in lignin analysis (Milled wood lignin, Lignin stereochemistry and Structure and stereochemistry of lignin degradation products) are surveyed.

INTRODUCTION
Analysis of lignins (and lignin degradation products) is a difficult task and there are many pitfalls. This presentation does not cover the whole field (for comprehensive reviews, see refs. 1 and 2). Selected topics in lignin analysis (Milled wood lignin, Lignin stereochemistry and Structure and stereochemistry of lignin degradation products) are surveyed. Other more general considerations that are of relevance to lignin analysis are also discussed.

SOME GENERAL CONSIDERATIONS

Analysis of lignin *in situ* compared to analysis of isolated lignin samples
Lignins (and lignin degradation products) are analysed *in situ* or as isolated samples. It should be kept in mind that an isolated lignin sample is in principle not chemically but operationally defined, *i.e.* it is defined by the starting material and the operations applied to it in order to obtain the sample. This implies that lignin samples isolated from botanically and morphologically equivalent wood samples using different methods may have different properties (such as number of phenolic groups and molecular-weight distribution). It also means that other materials than lignins may be present in the samples and that the possibility that chemical modifications have occurred during the isolation procedures has to be considered. As a very obvious example of problems related to studies of isolated lignin samples, it could be mentioned that proteins and tannins both give rise to so-called Klason lignin. Some of the drawbacks faced in connection with the use of isolated lignin samples can be avoided by studying the lignin *in situ*. However, other constituents in the wood (or pulp) may interfere in this case. The biological microstructure is another complication when lignins are studied in wood or pulps. Furthermore, wood and pulps are insoluble in unchanged form and this excludes the use of several of the most powerful analytical techniques. In many *in situ* studies of lignins, scientists have used property-based lignin definitions *(e.g.* materials exhibiting particular color reactions or materials giving UV absorption at specific wavelengths). This is adequate in some contexts but may in other cases lead to erroneous results. In most cases characterization of lignin requires studies of lignins *in situ* as well as of isolated lignin samples.

Network structure
The lignin (protolignin) structure is often described as a "three-dimentional network." This is in principle true but the extent of cross-linking is in all probability low. In any linear polymer the number of interconnections per molecule (α) in a molecule consisting of n units is (n-l)/n. This is true even if the molecule is branched (Fig. 1). In a linear or branched polymer a cannot exceed 1. A greater α is obtained if the molecule contains rings of units (Fig. 1). A description of the structure of a lignin in terms of the occurrence of different types of linkages is incomplete unless the a value (or corresponding

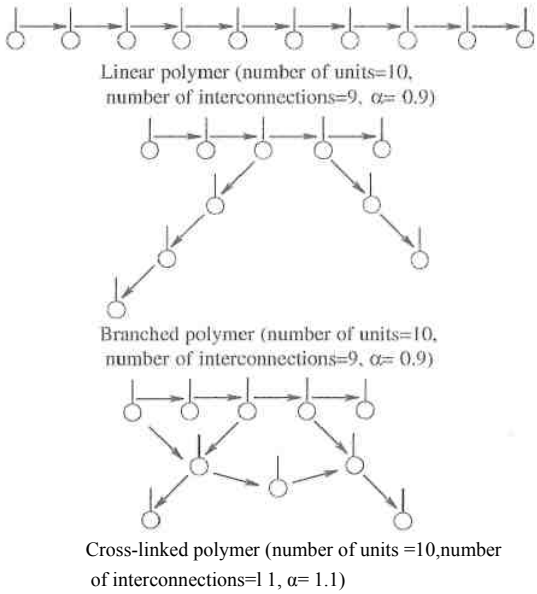
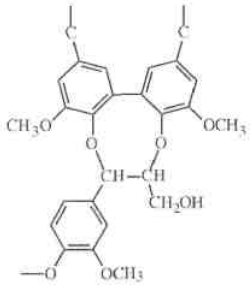


Fig. 1. Number of interconnections/ number of units (α) in different types of polymers.

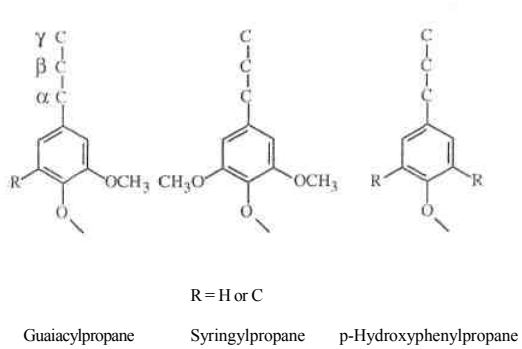
information) is given. Available lignin data (in particular the number of "non-condensed" units, the number of benzyl alcohol groups, the number of phenolic groups and the number of end groups) suggest that the number of rings is small. It has recently been demonstrated that "mini-rings" of the dibenzodioxocine type (1) are present in lignins (3). This lowers the probability for the formation of other types of rings, *i.e.* cross-linking leading to a network.



1

Co-polymerization

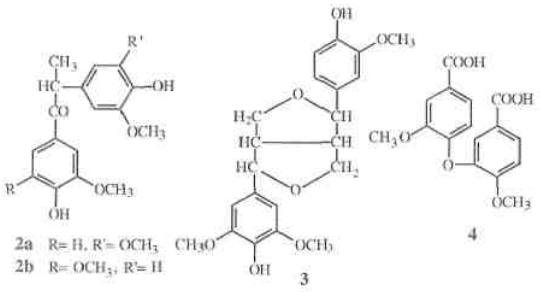
The primary building blocks in lignins are guaiacylpropane, syringylpropane and *p*-hydroxyphenylpropane units (Fig. 2). It is evident from studies of lignin degradation products *[e.g.* the isolation of **2** (4), **3** (5) and **4** (6)] that cross-coupling of the different types of phenylpropane units occurs in connection with the oxidative phenol coupling involved in the biosynthesis of lignins. However, the yields of cross-coupling products are comparatively low suggesting that cross-coupling is not a favored reaction. The oxidation potential required for the oxidation of different types of phenols is of importance for the extent of cross-coupling (7). The proportions of different types of units with free phenolic group is also of interest in this context (8-10). It seems that the lignin structure is heterogeneous with respect to the distribution of different types of phenylpropane units (11). It is



R = H or C

Guaiacylpropane Syringylpropane p-Hydroxyphenylpropane

Fig. 2. The primary building blocks in lignins.



2a R= H, R'= OCH_3
2b R= OCH_3, R'= H

3 4

noteworthy that low molecular weight fractions of lignins are heterogenous in this respect even if the distribution of units is completely random. Table 1 shows some results from calculations of the statistical distribution of units in hypothetical lignins consisting of equal amounts of guaiacylpropane and syringylpropane units.

Table 1. Statistical distribution of units in molecules of different size in a lignin sample consisting of equal amounts of syringylpropane units and guaiacylpropane units

Number of units	≈MW	Fraction containing ≥70% syringyl units
10	2000	17%
20	4000	5.8%
30	6000	2.1%
50	10000	0.003%
100	20000	≈0

Reagent specificity

A variety of functional groups are present in lignins (and in lignin products in pulps and pulping liquors). As a consequence of this there is a considerable risk of side reactions when chemical reagents are used in lignin analysis. The occurrence of side reactions is sometimes overlooked. Treatment with acetic anhydride/base is an appropriate method for the acetylation of lignin. Although the specificity of this derivatization method is satisfactory in many cases, it should be kept in mind that the esterification may be incomplete and that side reactions may occur (Fig. 3). Reduction with sodium borohydride is of great value in connection with studies of the carbonyl groups in lignins (1, 12, 13). However, specificity is a problem in this case too. Borohydride reduces not only ketones and aldehydes but also esters and lactones under certain conditions. Non-cyclic benzyl aryl ethers are reduced by borohydride (14). Reduction of cinnamaldehydes results in a partial hydrogenation of the double bond (15). On reduction of lignin under alkaline conditions, there may be a consumption of

borohydride due to reduction of formaldehyde liberated from the lignin in alkali-catalysed reactions.

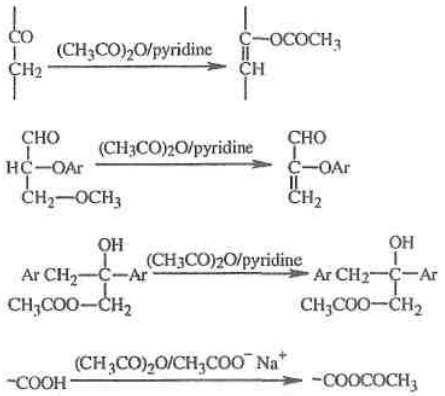


Fig. 3. Reactions with acetic anhydride/ base.

MILLED WOOD LIGNIN

Milled wood lignin (MWL) (1, 16) is the most commonly used reference substance in lignin studies. It seems that MWL prepared according to the standard procedure is fairly representative of the lignin in the wood examined (1). Short milling times results in low lignin yields and lignin from certain morphological regions may be overrepresented in the samples obtained (17). The milling causes chemical changes in the lignin but to what extent this occurs is largely unknown. It is notable that compounds formed on milling of spruce wood according to Björkman (18) (Fig. 4) are of the types expected to form on the basis of milling experiments with lignin model compounds of the arylglycerol β-aryl ether type(19).

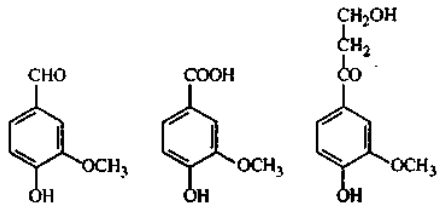


Fig. 4. Compounds detected (ref. 18) in products obtained on milling of preextracted spruce wood according to Björkman (ref. 16).

Small amounts of carbohydrates are present in milled wood lignins. The carbohydrates are in all probability linked to the lignin by covalent bonds. Xylans present in MWL's are removed on borohydride reduction or mild alkaline treatment (20). This can be very well illustrated by NMR spectral examinations (Fig. 5). The xylan present in MWL's may be attached to the lignin by ester Linkages.

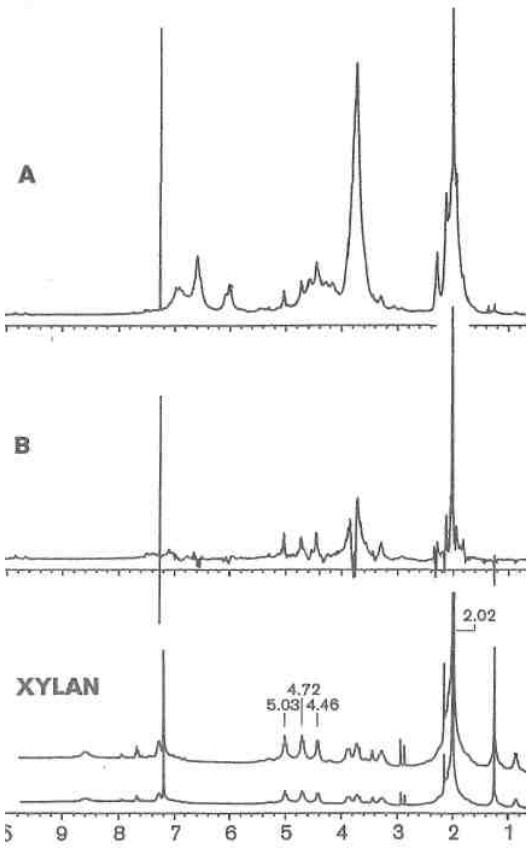


Fig. 5. ^{1}H NMR spectrum of MWL from birch (acetate) (Spectrum A) and a difference spectrum (Spectrum B) obtained by subtraction of the spectrum of borohydride reduced MWL from birch (acetate) from Spectrum A. A spectrum of acetylated xylan is included in the figure. It is evident from a comparison of the xylan spectrum with Spectrum B that borohydride reduction results in a removal of xylan from MWL from birch.

To study the homogeneity of MWL's we have recently examined low molecular weight (MW) and high molecular weight (MW) MWL fractions (obtained by gel permeation chromatography) of MWL's isolated from spruce wood and birch wood (21). The studies (thioacidolysis, ^{1}H NMR spectrometry) showed that the samples were rather homogeneous. As expected the number of end groups was comparatively large in the low molecular weight fractions. It is evident from ^{1}H NMR spectra of the

spruce lignin fractions that the number of phenolic groups is larger in the low MW fraction than in the high MW fraction (Fig. 6). The carbohydrate content is higher in birch MWL (≈2%) than in spruce MWL (≈0.3%). It was found that the carbohydrate content in the high MW birch lignin fraction (4.1%) was higher than in the low MW fraction birch lignin fraction (1.3%). The carbohydrate contents of the low MW and high MW spruce lignin fractions did not differ significantly.

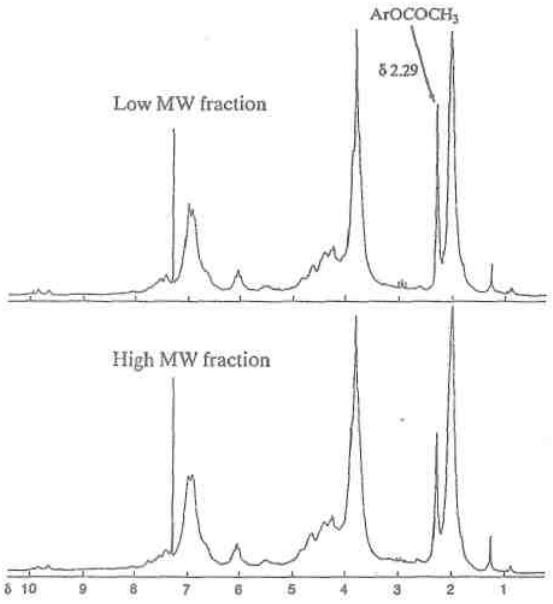
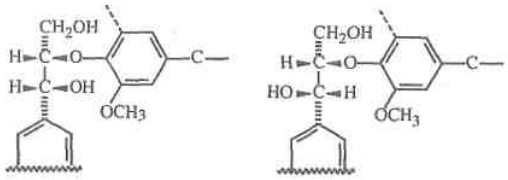


Fig. 6. ^{1}H NMR spectra of the acetate derivatives of a low MW fraction and a high MW fraction of spruce lignin.

LIGNIN STEREOCHEMISTRY

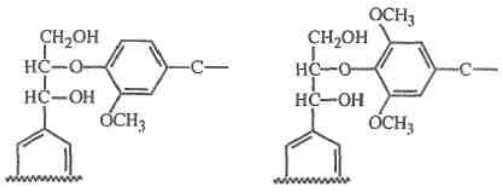
It is in general assumed that lignins are optically inactive and that the structural elements in lignins are "racemic." The correctness of this assumption has now and then been questioned. Proof of the occurrence of the "racemic" forms of structural elements of the β-β type in lignins has been presented (22). It has been demonstrated in recent ozonation studies of lignins that the racemic forms of threonic acid and erythronic acid are produced (23). These acids originate from the β-O-4 type of structures and the yields are rather high. It follows that structures of the β-O-4 type in lignins are "racemic" and that different structural elements in lignins other than those of the β-β and β-O-4 types probably also are present in their "racemic" forms.

It is important to recognize that the occurrence of "racemic" structural elements in lignins by no means excludes an uneven distribution of different diastereomeric forms. The distribution of *erythro* (**5**) and *threo* (**6**) forms of arylglyceryl β-aryl ethers has been studied by a variety of methods (24-28). The results concur in the respect that they suggest about equal amounts of the diastereomeric forms in softwood lignins and that *erythro* forms (**5**) are predominant in hardwood lignins.



erythro **5** *threo* **6**

Guaiacylpropane units (Fig. 2) are prevalent in softwood lignins. Acid-catalysed equilibration of lignin models of the arylglycerol β-guaiacyl ether type (**7**) gave reaction mixtures consisting of about equal amounts of the *erythro* and *threo* forms (29, 30), *i.e.* the distribution of diastereomers in the equilibrium mixtures is similar to that found in softwood lignins. It cannot be concluded from this that an equilibration has occurred, since equal amounts of the diastereomeric forms are obtained on the addition of water to model quinone rnethides under suitable conditions (29). The *erythro/threo* ratio in equilibrium mixtures of arylglycerol β-syringyl ethers (**8**) was 55:45 (29). Hardwood lignins are composed of about equal amounts guaiacylpropane and syringylpropane units (Fig. 2) and some 60-70 % of the arylglycerol β-aryl ethers in such lignins have the *erythro* configuration (**5**). It is evident from the equilibration experiments with model compounds that the distribution of β-ether diastereomers in hardwood lignins does *not* correspond to the equilibrium mixture. Recent 2D NMR studies of a hardwood lignin (31) illustrate in a very clear way that the predominance of *erythro* forms (**5**) is due to the



7 **8**

presence of large amounts of *erythro* forms of arylglycerol β-syringyl ethers (Fig. 7). The *erythro* β-syringyl ether/*threo* β-syringyl ether ratio was

estimated to be about 3. This ratio is in accordance with results from *in vitro* studies of the stereochemistry of the addition of water to quinone methides (29).

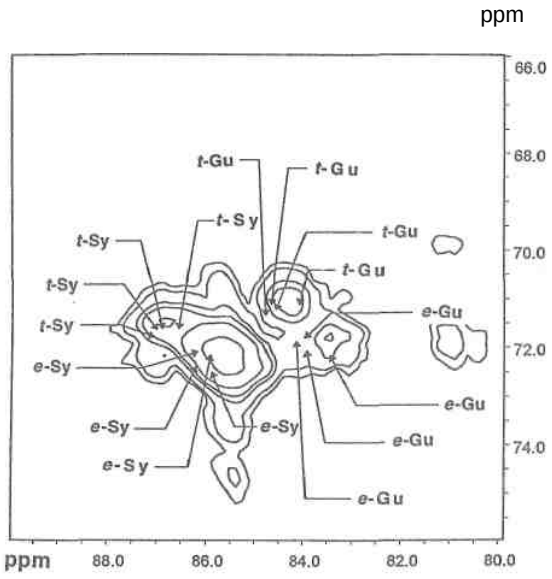
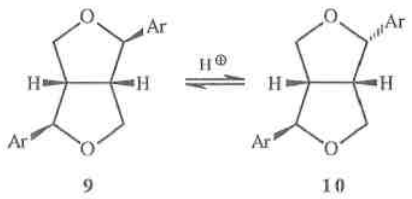


Fig. 7. Cα/Cβ cross-peaks attributed to different types arylglycerol β-aryl ethers in a hardwood lignin spectrum obtained using the ^{13}C-^{13}C 2D INADEQUATE experiment. The position of peaks corresponding to Cα/Cβ cross-peaks of a variety of model compounds are indicated in the figure *[erythro* β-syringyl ethers (*e*-Sy), *threo* β-syringyl ethers (*t*-Sy), *erythro* β-guaiacyl ethers (*e*-Gu) and *threo* β-guaiacyl ethers (*t*-Gu)].

Acidolytic treatment of pinoresinol (or syringaresinol) (**9**) results in an equilibrium mixture consisting of about equal amounts of the starting material and its *epi* form (**10**) (Fig. 8). Pinoresinol (or syringaresinol) structures are the predominating type of β-β structures in lignins and enzymic oxidation *(in vitro)* of coniferyl alcohol (or sinapyl alcohol) almost solely produces pinoresinol (or syringaresinol) as far as β-β linked products are concerned. Studies on the occurrence of different types of β-β structures in lignins (and the distribution of their diastereomeric form) have been reviewed (32).

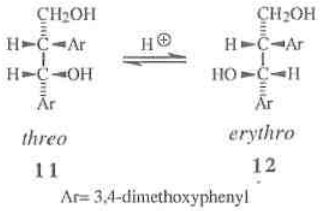
The diastereomeric forms **(11** and **12**) of a model representative of β-l structures, l,2-bis(3,4-dimethoxyphenyl-l,3-propanediol, gave on prolonged treatment (≈7 days) with 0.2 M HC1 in dioxane-water (1:1) at room temperature an equilibrium mixture (Fig. 9) in which there is a slight excess of the *threo* form *(erythro* form*/threo* form ratio 44:56). In spite



Al- 4-hydioxy-3-methoxyphenyl or 4-hydioxy-3,5-dimetrioxyphenyI

Fig. 8. Acid-catalysed isomerization of pinoresinol (or syringaresinol).

of the mild reaction conditions some conversion to 3,3',4,4'-tetramethoxystilbene occurred (yield ≈2-3%) (33). The distribution of diastereomeric forms of β-l structures in softwood lignin samples has been studied by NMR spectroscopic methods (28, 34). The studies indicate that there are somewhat larger amounts of *threo* forms than *erythro* forms. As judged from the experiments with model compounds **11** and **12** it is conceivable that the distribution of diastereomers of β-l structures in lignin agrees with that in the equilibrium mixture. Results from ozonation studies are compatible with the presence of both *erythro* and *threo* forms of β-l structures in lignins (35).

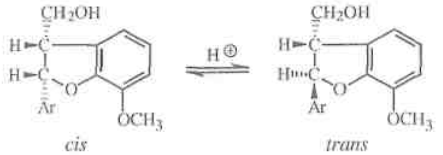


Ar= 3,4-dimethoxyphenyl

Fig. 9. Acid-catalysed equilibration of stereoisomeric forms of a model compound representative of β-l structures in lignins.

Acidolysis of β-5 models **13**/**14** showed that only a few percent of the *cis* form (**13**) (36) were present in the equilibrium mixture (Fig. 10) (37). The half-life period of **13** on refluxing with 0.1 M HBr in dioxane-water (9:1) was about 30 min. Phenylcoumarans formed by oxidative phenol coupling have the *trans* configuration at the furan ring [no *cis* isomer is present in oxidation products of isoeugenol (38), attempts to detect *cis*-dehydrodiconiferyl alcohol in the reaction mixture obtained on oxidation of coniferyl alcohol failed (39)]. The ^{1}H NMR spectrum of the acetate of **13** exhibits a signal at δ 5.87 (36). No signal can be discerned at this position in spectra of lignin acetates. Such spectra clearly reveal the presence of *trans* phenylcoumaran structures (40). It can be concluded that the number of *cis* phenylcoumaran structures in

lignins is negligible compared to the number of *trans* phenylcoumaran structures. Ozonation studies show that *trans* forms of β-5 structures predominate in lignins (35).

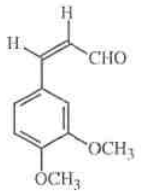


13 14

Ar= 3,4-dimethoxyphenyl

Fig. 10. Acid-catalysed equilibration of stereoisomeric forms of a model compound representative of β-5 structures in lignins.

Signals at ≈δ 9.6 in ^{1}H NMR spectra of lignin acetates can be attributed to the formyl group in *trans* forms of cinnamaldehyde end groups. The formyl proton signal of a model compound (**15**) representative of *cis* forms of such end groups is located at δ 10.02 (**15**). There is no signal at this position in the lignin spectra and, consequently, *cis* forms of cinnamaldehyde end groups are not present in detectable amounts in lignins.



15

To summarize, the distribution of stereoisomers in lignins is in accordance with the hypothesis that lignins are produced by oxidative polymerization *(via* radicals) of *p*-hydroxycinnamyl alcohols. The distribution of diastereomers agrees fairly well with that expected from oxidation experiments with *p*-hydroxycinnamyl alcohols *in vitro* and deviates in some cases from that corresponding to equilibrium mixtures.

STRUCTURE AND STEREOCHEMISTRY OF LIGNIN DEGRADATION PRODUCTS

The discussion in this section covers not only low molecular weight lignin degradation products but also structural elements in lignin in pulping liquors and in lignin in pulps.

Interconversion of diastereomers of the lignin structures discussed in the preceding section may occur during pulping *(e.g.* thermomechanical pulping). The proportion of *epi* forms of β-β structures in the lignin in steam-hydrolysed aspen wood is for instance rather large and this can be explained by acid-catalysed isomerization (41). *cis*-Forms of cinnamaldehyde end groups may be present in high yield pulps exposed to light due to isomerization. Acid treatment of *trans* phenylcoumarans results in an isomerization and a few percent of the *cis* isomer are formed (37). This suggests that small amounts of *cis* phenylcoumaran structures may be present in certain types of processed wood materials. Changes of the proportions of diastereomers can also be due to differences in reactivity (see, *e.g.*, ref. 42). From an analytical point of view it is important to recognize that spectral changes of the lignin component observed during pulping reactions may be due to variations of the proportions of stereoisomers.

During pulping structural elements in protolignin undergo chemical transformations leading to new types of structures. Many pulping (and bleaching) processes result in dramatic changes of the structure of the lignin component (Fig. 11) and analytical methods used for the elucidation of the structure of MWL's are not always applicable for the structural elucidation of lignin-derived materials in pulping products.

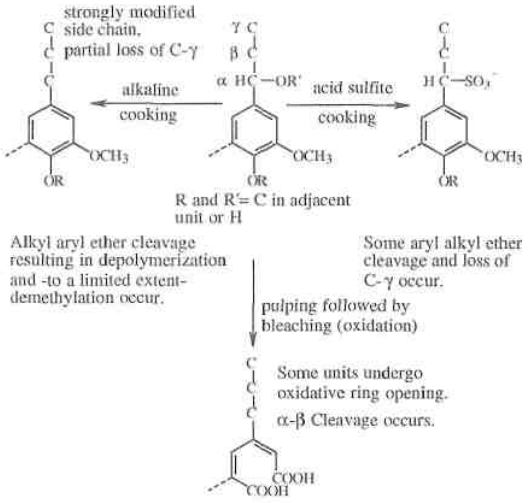


Fig. 11. Examples of lignin reactions during pulping and bleaching.

Both alkaline and acid treatments of β-1 and β-5 structures results in the formation of stilbenes. Under acid conditions the yields of stilbenes is strongly dependent on the nature of the catalyst. HBr (and to a lesser extent HC1) catalyses the formation of a series

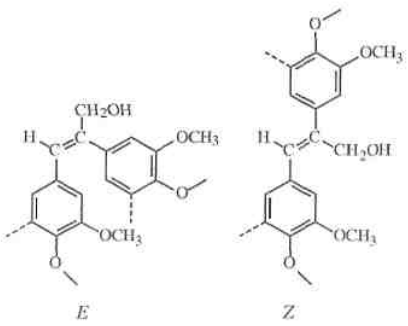


Fig. 12. Stereoisomers of intermediates of the 2,3-diaryl-2-propen-l-ol type.

of carbonyl compounds from β-1 structures and the formation of phenylcoumarones from β-5 structures (4, 37, 43). Both *(E)* and (*Z*) forms of 2,3-diaryl-2-propen-1-ols (Fig. 12) are intermediates in the acid-catalysed formation of carbonyl compounds from β-1 structures (37). It seems that stilbenes formed from β-1 structures invariably have the (*E*)-configuration. β-5 Structures primarily give rise to (*E*)-stilbenes but small amounts of the (*Z*)-isomers are present in the reaction mixtures (37). We have recently subjected a series of stilbenes, derived from β-5 model compounds or produced from β-5 structures in lignin during alkaline pulping, to examinations by X-ray crystallography and spectral methods (NMR, UV and fluorescence spectroscopy) (44-46). It was found that stereoisomers of stilbenes of this type are very prone to undergo photochemical interconversions. Stilbene **16** [(*Z*)-form] on exposure to daylight in chloroform solution was converted to almost pure (*E*)-stilbene (Fig. 13). Exposure of acetylated stilbene **16** [(*Z*)-form or (*E*)-form] to daylight resulted in a mixture of

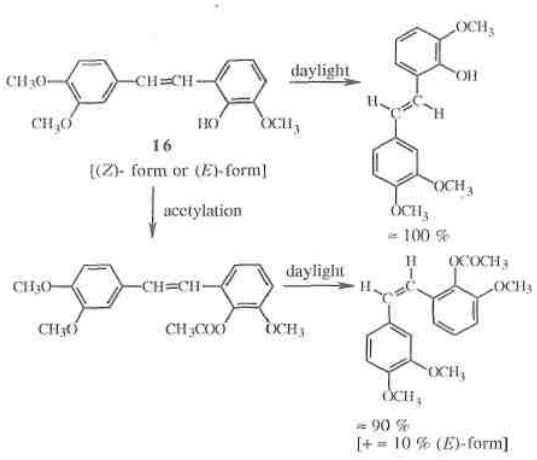
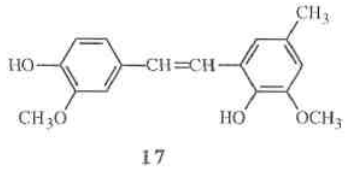


Fig. 13. Photochemical conversions of stilbene 16 and its acetate on exposure to daylight.

stereoisomers in which the (*Z*)-form dominated (≈90 %*)* (Fig. 13). Stilbene **17** behaved in a similar way. Preliminary experiments suggest that (*E*)-forms of acetates of stilbenes derived from β-1 structures also undergo a partial conversion to (*Z*)-forms on exposure to daylight. It is obvious that the observations are of interest in connection with spectral analysis of lignins from alkaline cookings.



Enol ethers of type **18** are formed on soda cooking of arylglycerol β-aryl ethers (Fig. 14) (47). Acid degradation of such structural elements proceeds to some extent *via* enol ethers of type **18** (Fig. 14) (48). Stereoselective synthesis of stereoisomers of model compounds representative enol ethers of type **18** (**19-21**) was accomplished by decarboxylation of **22, 23** and **24** (49). The steric assignments of the starting materials have been verified by X-ray crystallography (50).

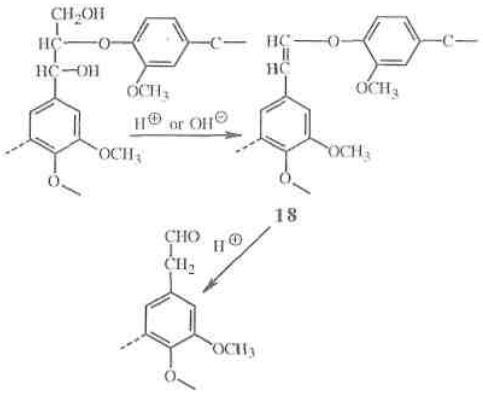
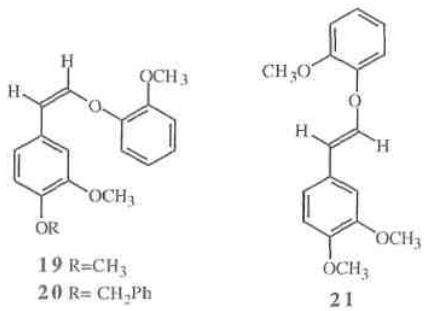
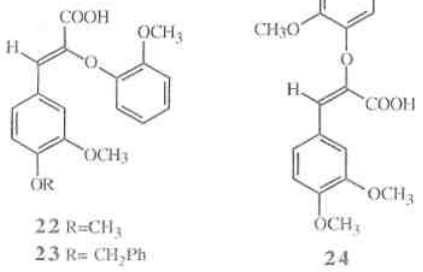


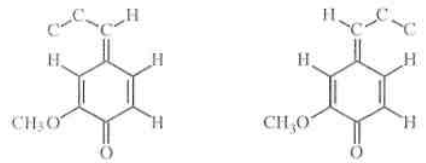
Fig. 14. Formation of enol ethers of type 18 on alkaline treatment of arylglycerol β-aryl ethers and on acid treatment leading to a degradation of such structures.





22 R=CH_3
23 R= CH_2Ph
24

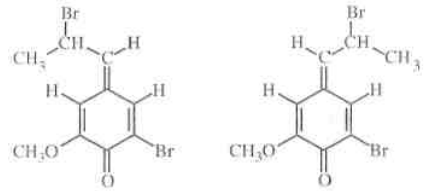
It is questionable if quinone methides can be regarded as "lignin degradation products." However, quinone methides are key intermediates in several pulping reactions leading to degradation products. Quinone methides of type **25** exist in two isomeric forms *(syn* and *anti,* Fig. 15) (51). It has been shown that the two isomeric forms differ in reactivity (51). We have recently examined a crystalline quinone methide, **26**, by X-ray crystallography (52). NMR examinations of solutions of this quinone methide showed the presence of two isomers *("syn",* **26**; *"anti",* **27**) and indicated that after several hours at room temperature an equilibrium is set up *("syn"/"anti",*≈1.8:1).



syn *anti*

25

Fig. 15. Stereoisomers of quinone methides.



"syn" *"anti"*

26 27

Demethylation leading to catechol structures occurs to a greater or lesser extent during pulping processes. It is noteworthy that demethylation not only can be a result of a direct substitution of methyl groups but also can proceed *via* dienone intermediates (Fig. 16). Oxidation of catechol structures gives rise to *o*-quinoid groups. Such groups can be analysed by ^{31}P NMR (10)

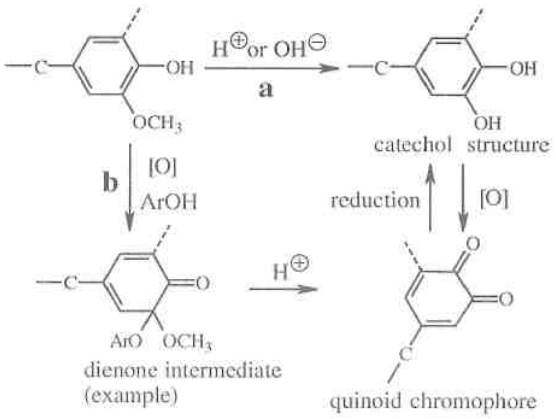


Fig. 16. Demethylation by substitution reactions (reaction route a) and demethylation *via* dienone intermediates (reaction route b).

REFERENCES

1. Methods in lignin chemistry. Eds. S.Y. Lin. and C.W. Dence. Springer-Verlag, Berlin-Heidelberg 1992.
2. Analytical methods in wood chemistry, pulping and papermaking. Eds. E. Sjöström and R. Alen. Springer-Verlag, Berlin-Heidelberg 1999.
3. P. Karhunen, P. Rummakko, A. Pajunen and G. Brunow. J. Chem. Soc., Perkin Trans. 1, 2303-2308, 1996.
4. S. Li, K. Lundquist and G. Stenhagen. Holzforschung, 50, 253-257, 1996.
5. S. Omori and A. Sakakibara. 1974. Mokuzai Gakkaishi, 20, 388-395, 1974.
6. M. Erickson, S. Larsson and G.E. Miksche. Acta Chem. Scand., 27, 1673-1678, 1973.
7. K. Syrjänen and G. Brunow. J. Chem. Soc, Perkin Trans. 1, 3425-3429, 1998.
8. C. Lapierre and C. Rolando. Holzforschung, 42, 1-4, 1988; C. Lapierre, B. Monties and C. Rolando. Holzforschung, 42, 409-411, 1988.
9. S. Li and K. Lundquist. Nord. Pulp Pap. Res. L, 9, 191-195, 1994.
10. D. Argyropoulos. Res. Chem. Intermed., 21, 373-395, 1995.
11. N. Terashima, K. Fukushima, L-F. He and K. Takabe. In: Forage Cell Wall Structure and Digestibility. Eds. H.G. Jung, D. R. Buxton, R.D. Hatfield and J. Ralph. American Society of Agronomy, Madison, WI 53711, USA, 1993, pp. 247-270.
12. E. Adler. Wood Sci. Technol., 11, 169-218, 1977.

13. K. Lundquist and T. Olsson. Acta Chem. Scand., Ser. B, 31, 788-792, 1977.
14. K. Freudenberg. Angew. Chem., 76, 349, 1964; B. Johansson and G.E. Miksche. Acta Chem. Scand., 26, 289-308, 1972.
15. S. Li and K. Lundquist. Acta Chem. Scand., 49, 64-67, 1995.
16. A. Björkman. Sven. Papperstidn., 59, 477-485, 1956.
17. Z.Z. Lee, G. Meshitsuka, N.S. Cho and J. Nakano. Mokuzai Gakkaishi, 27, 671-677, 1981.
18. K. Lundquist, B. Ohlsson and R. Simonson. Sven. Papperstidn., 80, 143-144, 1977.
19. D.-Y. Lee and M. Sumimoto. Holzforschung, 44, 347-350, 1990; K. Itoh, M. Sumimoto and H. Tanaka. J. Wood Chem. Technol., 15, 395-411, 1995.
20. K. Lundquist, R. Simonson and K. Tingsvik. Nord. Pulp Pap. Res. J., 5, 107-113, 1990; K. Lundquist, R. Simonson and K. Tingsvik. Nord. Pulp Pap. Res. J., 5, 199, 1990.
21. C. Lapierre and K. Lundquist. To be published.
22. K. Ogiyama and T. Kondo. Tetrahedron Lett., 2083-2088, 1966; Erratum, Tetrahedron Lett., 3144, 1967.
23. Y. Matsumoto, T. Akiyama, A. Ishizu, K. Lundquist and G. Meshitsuka. To be published.
24. K. Lundquist. Acta Chem Scand., Ser. B, 34, 21-26, 1980; M. Hauteville, K. Lundquist and S. von Unge. Acta Chem. Scand., Ser. B, 40, 31-35, 1986.
25. H.H. Nimz, U. Tschirner, M. Stähle, R. Lehmann and M. Schlosser. J. Wood Chem. Technol, 4, 265-284, 1984.
26. Y. Matsumoto, A. Ishizu and J. Nakano. Holzforschung, 40 (Suppl.), 81-85, 1986.
27. B. Saake, D.S. Argyropoulos, O. Beinhoff and O. Faix. Phytochemistry, 43, 499-507, 1996.
28. R.M. Ede and J. Ralph. Magn. Reson. Chem., 34, 261-268, 1996.
29. G. Brunow, O. Karlsson, K. Lundquist, and J. Sipilä. Wood Sci. Technol., 27, 281-286, 1993.
30. K. Lundquist and S. Li. 1997. In: Recent Res. Devel. in Agricultural & Food Chem. Ed. S.G Pandalai, Trivandrum, India, Vol. 1, 1997, pp. 15-27.
31. M. Bardet, D. Robert, K. Lundquist and S. von Unge. Magn. Reson. Chem., 36, 597-600, 1998.
32. K. Lundquist and R. Stomberg. Holzforschung, 42, 375-384, 1988.
33. K. Lundquist and S. Li. Acidolytic lignin reactions. Extended abstracts, "Fifth European Workshop on Lignocellulosics and Pulp", August 30-September 2, 1998, Aveiro, Portugal, pp. 491-494.
34. R.M. Ede, J. Ralph, K.M. Torr and B.S.W. Dawson. Holzforschung, 50, 161-164, 1996.
35. N. Habu, Y. Matsumoto, A. Ishizu and J. Nakano. Holzforschung, 44, 67-71, 1990.
36. S. Li, T. Iliefski, K. Lundquist and A.F.A. Wallis. Phytochemistry, 46, 929-934, 1997!
37. S. Li and K. Lundquist. Holzforschung, 53, 39-42, 1999.
38. K.V. Sarkanen and A.F.A. Wallis. Chem. Commun., 298-299, 1969.
39. S. Li and K. Lundquist. Unpublished results.
40. K. Lundquist. Nord. Pulp Pap. Res. L, 7, 4-8, 16, 1992.
41. M. Bardet, D.R. Robert and K. Lundquist. Sven. Papperstidn., 88, R61-67, 1985.
42. H. Taneda, N. Habu and J. Nakano. Holzforschung, 43, 187-190, 1989; L. Jönsson, O. Karlsson, K. Lundquist and P.O. Nyman. FEBS Lett., 276, 45-48, 1990; Z.-H. Wu, M. Matsuoka, D.-Y. Lee and M. Sumimoto. Mokuzai Gakkaishi, 37, 164-171, 1991; T. Tokimatsu, S. Miyata, S.-H. Ahn, T. Umezawa, T. Hattori and M. Shimada. Mokuzai Gakkaishi, 42, 173-179, 1996.
43. S. Li, O. Karlsson, K. Lundquist and R. Stomberg. Acta Chem. Scand., 51, 431-437, 1997.
44. S. Li, K. Lundquist and R. Stomberg. Acta Cryst, C52, 3118-3121, 1996; R. Stomberg, S. Li, K. Lundquist and B. Albinsson. Acta Cryst, C54, 1929-1934, 1998.
45. B. Albinsson, S. Li, K. Lundquist and R. Stomberg. J. Mol. Struct. In press.
46. S. Li, K. Lundquist and R. Stomberg. Acta Cryst., C. In press.
47. J. Gierer. Sven. Papperstidn., 73, 571-596, 1970.
48. O. Karlsson, K. Lundquist, S. Meuller and K. Westlid. Acta Chem. Scand., Ser. B, 42, 48-51, 1988.
49. G. Brunow and K. Lundquist. Acta Chem. Scand., Ser. B, 38, 323-325, 1984.
50. R. Stomberg and K. Lundquist. Z. Kristallogr., 209, 835-836, 1994; Unpublished results.
51. R.M. Ede, L. Main and J. Ralph. J. Wood Chem. Technol., 10, 101-110, 1990.
52. S. Li, K. Lundquist, N. Soubbotin and R. Stomberg. Acta Cryst., C51, 2366-2369, 1995.