DIFFERENT TYPES OF PHENOLIC UNITS IN LIGNINS

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The influence of cross-linking and branching on the number of interconnections between lignin units and the number of end groups (phenolic and non-phenolic) in the lignin molecules is discussed. Branching results in an increased number of end groups. It appears from an evaluation of the literature that *p*-hydroxyphenylpropane units are phenolic to a larger extent than guaiacylpropane units and that such units in turn are phenolic to a larger extent than syringylpropane units. It is proposed that this is related to the relative oxidation potentials of the lignin units. Guaiacylpropane units C-substituted in the 6-position are phenolic to a large extent. Alternative explanations for this are presented.

Keywords: Lignin; Phenolic units; End groups; Cross-linking

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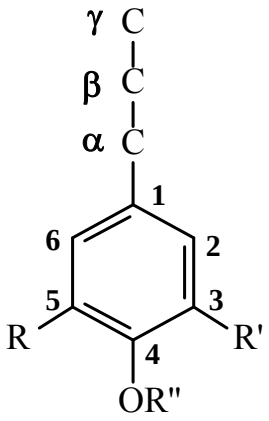
Lignins are polymers consisting of phenylpropane units in which the aromatic rings are substituted with one methoxyl group (guaiacylpropane units, **2**), with two methoxyl groups (syringylpropane units, **3**) or are lacking methoxyl substituents (*p*-hydroxyphenylpropane units, **1**) (Ralph *et al*. 2004). There are quite a few options for the linkages between these units (Ralph *et al*. 2004, 2007). The frequency of different structural elements in lignins has been discussed by Brunow and Lundquist (2010). The present analysis is directed to plant lignins, whereas technical lignins such as kraft lignin and lignosulphonates are not considered. The phenol content of lignins differs considerably. In general 10 to 30 percent of the units are phenolic (Brunow and Lundquist 2010). This presentation covers some general aspects regarding the nature of phenolic groups in lignins and a detailed discussion of the occurrence of certain types of phenolic units.



1a R=R'=R"= H
1b R=R'= H, R"= C
2a R= H, R'= OCH_3, R"= H
2b R= H, R'= OCH_3, R"= C
3a R=R'= OCH_3, R"= H
3b R=R'= OCH_3, R"= C

Branching and End Groups

Lignin units attached to adjacent units in ring positions 2, 3, 5, or 6 are in the following referred to as "condensed units," and consequently units lacking connection to other units in these positions are "uncondensed". Lignins consist of phenolic units of types **1a**, **2a** and **3a**, non-phenolic units of types (**1b**, **2b** and **3b**) and their "condensed" counterparts. "Condensed" phenolic units are normally not end groups. The lignin structure is often described as a "three-dimensional network". This is in principle true, but the extent of cross-linking is in all probability low. In any linear polymer consisting of n units the number of interconnections per unit (α) is (n-1)/n (Fig. 1, formula **a**; it should be noted that an interconnection may involve more than one bond). This is true even if the molecule is branched (Fig. 1, formula **b**). In a linear or branched polymer α cannot exceed 1 (Fig. 1, formulas **a** and **b**). A greater α is obtained if the molecule contains rings of units (Fig. 1, formulas **c**, **d**, and **e**).

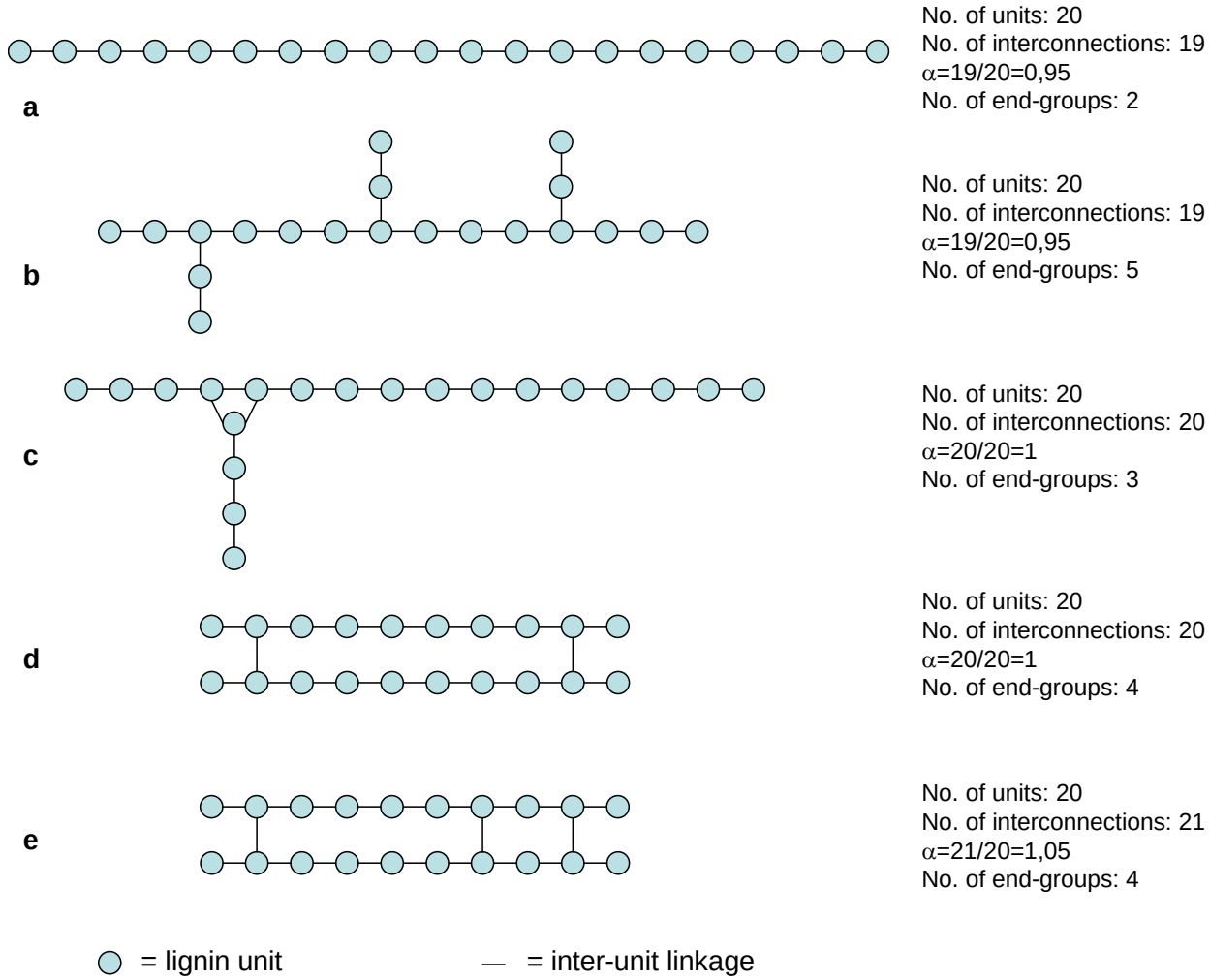


Fig. 1. Number of interconnections per lignin unit (α) and number of end groups in different types of lignin polymers

Available lignin data (Brunow and Lundquist 2010) suggest that the number of rings of units is small in lignins and that α is probably close to 1 (cf. Lundquist 1976; Lundquist and Li 1999). It has been demonstrated that "mini-rings" (see Fig. 1, formula **c**) of the dihydrodibenzodioxocin type are present in lignins (Ralph *et al*. 2004). This lowers the probability for the formation of other types of rings, *i.e.* cross-linking leading to a network (Fig. 1, formulas **d** and **e**).

Examples of branching are shown in Fig. 2: branching involving a dihydrodibenzodioxocin (cf. formula **c** in Fig. 1) and branching involving a diaryl ether. The structures in Fig. 2 are exemplified with guaiacylpropane units but, depending on the lignin type, also *p*-hydroxyphenylpropane and syringylpropane units are possible in some positions.

Branching of the lignin molecule results in an increased number of end groups (*here defined as lignin units connected to just one adjacent unit*). Figure 1 illustrates the connection between branching and the number of end groups.

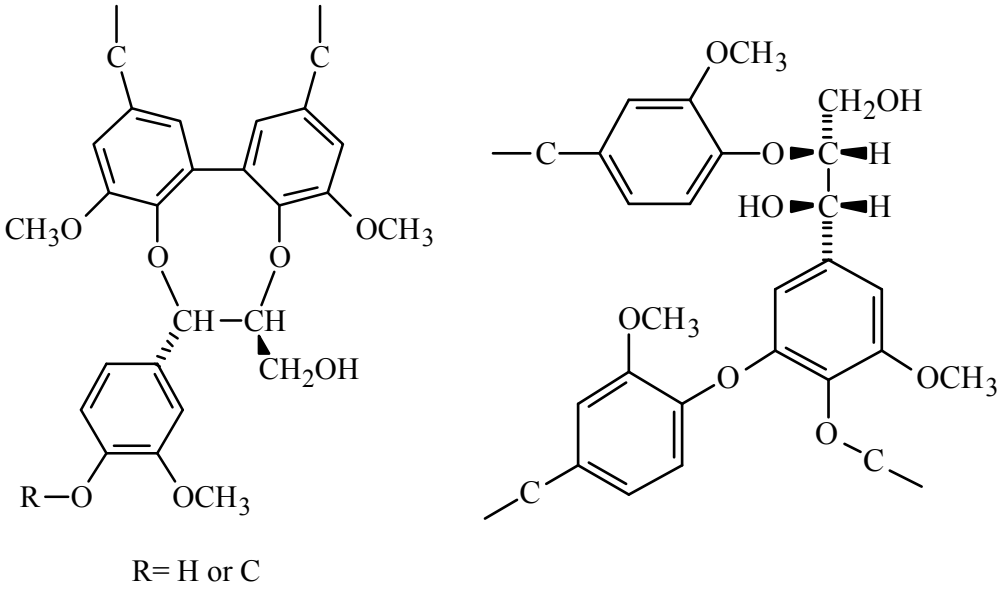


Fig. 2. Examples of branching of lignin molecules: dihydrodibenzodioxocin (left) and diaryl ether (right).

There are two main categories of end groups: units lacking side chain connection, and certain types of phenolic units (**1a**, **2a** and **3a** disregarding a few units (Brunow and Lundquist 2010) in which the side chain is linked to two units). An example of end groups lacking side chain connection is shown in Fig. 3 (for other examples see Brunow and Lundquist 2010). Examples of unit sequences with a phenolic end group are given by Langer *et al*. (2007) and Lundquist *et al*. (2009).

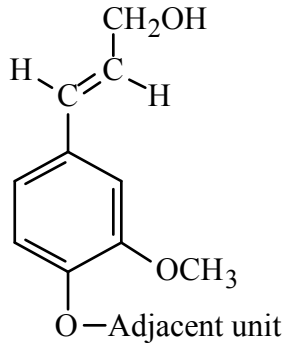
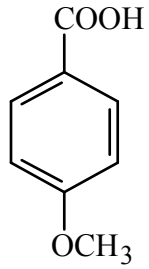


Fig. 3. An example of a non-phenolic end-group

Distribution of Certain Types of Phenolic Units

Permanganate oxidation of methylated spruce lignin before and after cleavage of ether groups gives about the same amount of anisic acid (**4**) (Erickson *et al*. 1973a).



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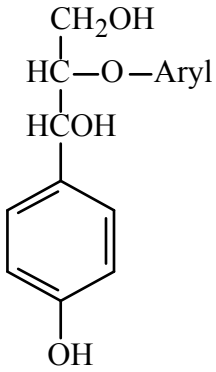
This suggests that "uncondensed" *p*-hydroxyphenylpropane units primarily exist with phenolic end groups (**1a**) in the lignin. "Uncondensed" guaiacyl units (**2**) and syringyl units (**3**) are to a large extent etherified (formulas **2b** and **3b**) (Larsson and Miksche 1971; Erickson *et al*. 1973a). Thioacidolysis studies show that "uncondensed" *p*-hydroxyphenylglycerol β-aryl ethers in pine compression wood are primarily phenolic (**5**) (Lapierre and Rolando 1988; Lapierre *et al*. 1988).



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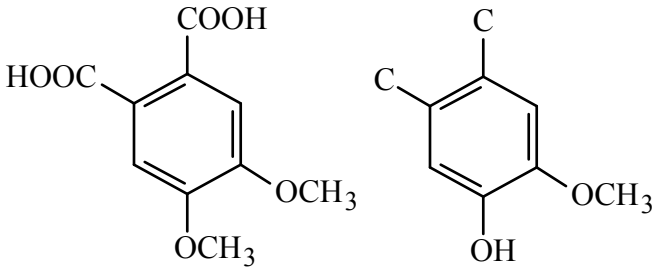
It could be anticipated that *p*-hydroxyphenylpropane units in lignins to a comparatively large extent are "condensed," since substitution in several ring positions is possible in such units. As judged from a number of studies, this is not the case (Larsson and Miksche 1969; Yamasaki *et al*. 1972; Erickson *et al*. 1973b,c). It seems that *p*-hydroxyphenylpropane units are phenolic to a larger extent than guaiacylpropane units and that such units in turn are phenolic to a larger extent than syringylpropane units (Larsson and Miksche 1971; Erickson *et al*. 1973a; Li and Lundquist 1994). This may reflect the relative ability of different types of phenolic groups to undergo oxidative phenol coupling during the biosynthesis of lignin. Of interest in this context is the oxidation potential of different types of phenolic units (cf. *e.g*. Kratzl *et al*. 1974; Wei *et al*. 2004; Sasaki *et al*. 2004). It has been proposed that the amount of *p*-hydroxyphenylpropane units (disregarding esterified *p*-coumaric acid) is comparatively large in grass lignins (Yamasaki and Higuchi 1971; Faix 1991). However, this is gainsaid in other studies (Higuchi and Kawamura 1966; Higuchi *et al*. 1972; Nakatsubo *et al*. 1972; Rolando *et al*. 1992).

Permanganate oxidation of methylated spruce lignin before and after cleavage of ether groups gives about the same amount of metahemipinic acid (**6**) (Erickson *et al*. 1973a). This implies that metahemipinic acid primarily originates from phenolic lignin structures (**7**). The amount of metahemipinic acid corresponds to a few percent of the lignin units (Lundquist and Brunow 2010).



6 **7**

A number of biosynthetic reaction routes which may provide an explanation of this have been presented in the literature (Lundquist and Miksche 1965; Freudenberg 1968; Larsson and Miksche 1971; Lundquist 1980; Ralph *et al*. 1998). One option for the formation of lignin structures giving rise to metahemipinic acid on permanganate oxidation involves rearrangement of cyclohexadienones (formed by radical coupling in the 4-position or formed in radical transfer reactions). An explanation of the phenolic character of the topical lignin structures would be that the rearrangements proceed during the later stages of lignin biosynthesis when oxidative phenol coupling has ceased. As an alternative explanation it has been suggested that 6-substitution is due to slow acid-catalysed condensation reactions during the "aging" of the lignin (Larsson and Miksche 1971).

CONCLUSIONS

1. Lignins are branched, but the extent of cross-linking is very limited.
2. Branching causes an increase of the number of phenolic and non-phenolic end groups.
3. Irregularities with respect of the distribution of phenolic units in lignins can be traced to factors influencing the biosynthetic pathways.

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