The Alkylation of Lignin with Alcoholic
Hydrochloric Acid

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Brauns' "native lignin" from spruce was shown to contain 0.12 CO groups per methoxyl. By reduction with sodium borohydride a practically carbonyl-free preparation was obtained. The original as well as the reduced lignin were subjected to treatment with 0.5 % methanolic hydrochloric acid either during 48 hours at room temperature or during 2.5 hours under reflux. Extensive methylation took place in each case, the ratio OCH_3 introduced/OCH_3 orig. present ranging from 0.41 to 0.52.

From these results it is concluded that the methylation is not due to acetal formation. The most probable explanation is the etherification of benzyl alcohol groups and the re-etherification of benzyl ether groups present in "native lignin".

In 1893, Klason[1] made the observation that some lignin was brought into solution when spruce wood was heated with ethanol containing a small amount of hydrogen chloride. This reaction has been studied more closely by Holmberg[2,3], who found that the formation of the "ethanol lignin" involves the uptake of approximately 0.5 ethoxyl groups for every methoxyl present in the lignin. Several alcohol lignins have been prepared from wood by using alcohols other than ethanol, and in all cases alkylation of the lignin was demonstrated[4,5]. Similarly, "native lignin", isolated according to Brauns' method, i. e., a lignin fraction which is extracted from wood by ethanol at room temperature and which amounts to a few per cent of the total lignin, is methylated when heated with methanolic hydrochloric acid[6].

This alkylation of lignin has been interpreted mainly in two ways. Holmberg and Runius[2] assumed that lignin contains carbonyl groups partly involved in an acetal-like linkage between lignin and carbohydrates. Heating with alcoholic hydrochloric acid was then believed to bring about an acetalization (1) of free carbonyl groups or a re-acetalization (2) of bound carbonyl groups.

(1) $\quad >C=O$

(2) $\quad >C\Big\langle{}^{OR_1}_{OR_2}$
$\qquad\qquad \xrightarrow[\text{H}^+]{\text{ROH}} \quad >C\Big\langle{}^{OR}_{OR}$
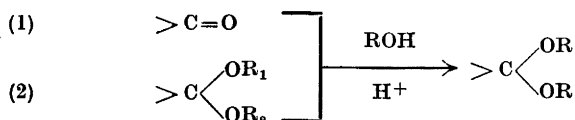
This view, which was shared by several other authors, seemed to find support in the fact that the alkoxyl groups were removed when the alcohol lignin was treated with strong acids [7].

An alternative explanation was suggested by Holmberg [8] in 1935. On the basis of experiments with model substances, such as α-phenyl ethyl alcohol and benzhydrol, he assumed the presence in lignin of exceedingly reactive alcoholic hydroxyl or ether groups, viz., benzyl alcohol or benzyl ether groupings. The alkylation reaction was then considered as an etherification of benzyl alcohol groups (3) or a re-etherification of benzyl ether groups (4), or both.
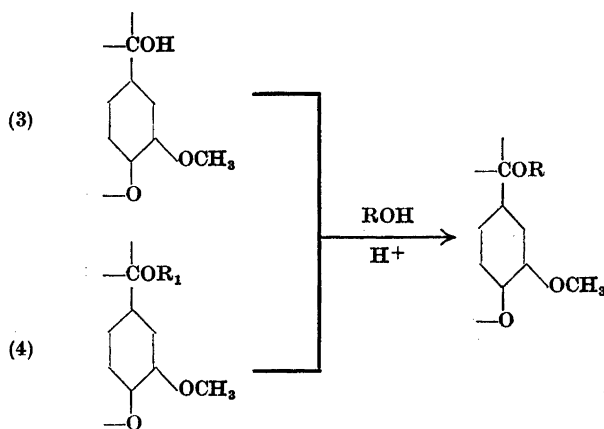
The same types of groups were assumed to be responsible for other typical lignin reactions such as the sulphonation with sulphite solutions and the formation of lignothioglycolic acids.

Concerning the two last-mentioned reactions, and especially the sulphonation, Holmberg's benzyl alcohol and benzyl ether hypothesis has been supported by a vast amount of experimental work (cf. Lindgren [9]).

The alkylation of lignin, however, has been comparatively little studied and, until recently, has been interpreted in the sense of Holmberg's older theory. Thus, Brauns expressed the view that the methylation, which takes place when isolated "native lignin" is heated with methanolic hydrochloric acid, is probably due to the acetalization of carbonyl groups [6, 10]. It is known, however, that p-hydroxybenzyl alcohols are readily etherified by alcoholic hydrochloric acid, and also that corresponding benzyl alkyl ethers are re-etherified under very mild conditions [11]. With this fact in mind it was attempted to find conclusive evidence for the mechanism of the alkylation reaction.

The lignin material used in the present work was „native lignin" isolated according to Brauns [6] from spruce (Picea excelsa). The preparation contained 14.67 % OCH_3. By potentiometric titration of the hydrochloric acid which was liberated when the lignin was treated with hydroxylamine hydrochloride, the preparation was found to contain 1 CO group per 8.3 OCH_3 groups ($CO/OCH_3 = 0.12$). Since "native lignin" contains roughly one coniferyl aldehyde group per forty methoxyl groups [12], about every tenth guaiacyl

propane monomer thus carries a carbonyl group not belonging to a coniferyl aldehyde structure.

On treatment of the "native lignin" with sodium borohydride in aqueous ethanol, a reduced "native lignin" with a methoxyl content of 15.19 % was obtained, in which only traces of carbonyl groups (about 3 % of the amount originally present) could be detected (see Fig. 4). The presence of carbonyl groups in the original preparation and their elimination on sodium borohydride reduction was also demonstrated by infrared absorption measurements *. Whereas the original "native lignin" shows a definite band in the C=O region (about 1 660 cm⁻¹), only a slight inflection is observed at this position in the absorption curve of the reduced lignin (Fig. 1, a and b).
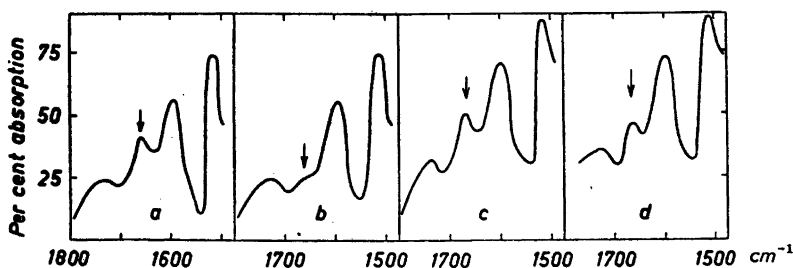

Fig. 1. Infrared absorption curves. a. "Native lignin". b. "Native lignin", reduced with sodium borohydride. c. "Native lignin", methylated with 0.5 % CH₃OH—HCl (48 h, room temp.). d. "Native lignin", methylated with 0.5 % CH₃OH—HCl (2.5 h, reflux). The arrows mark the position of the C=O absorption.

Fig. 2 shows the ultraviolet absorption curves of the original and the reduced "native lignins". The reduced product gives a considerably lower absorption in the range above 300 mμ compared with the original preparation. The decrease must be partly due to the reduction of coniferyl aldehyde residues, which cause a comparatively high extinction in this wavelength range [13], yielding coniferyl alcohol groups. This is also indicated by the fact that the reduced product does not give the colour reaction with phloroglucinol and hydrochloric acid, in contrast with the original preparation [14]. Further, the nearly white colour of the reduced product suggests that quinoid groupings have been eliminated.

The original as well as the reduced lignin were subjected to methylation with methanol containing 0.5 % hydrogen chloride, i. e., the reagent used by Brauns [6] in the methylation of "native lignin" from black spruce (Picea mariana). In Brauns' experiments the reaction mixture was heated under reflux for 2.5 hours. It was found, however, that treatment at room temperature during 48 hours was sufficient to produce extensive methylation, and therefore the experiments were carried out both at room temperature (48 hours) and under reflux (2.5 hours).

* The authors are indebted to Dr. K. Almin for kindly carrying out the infrared measurements.
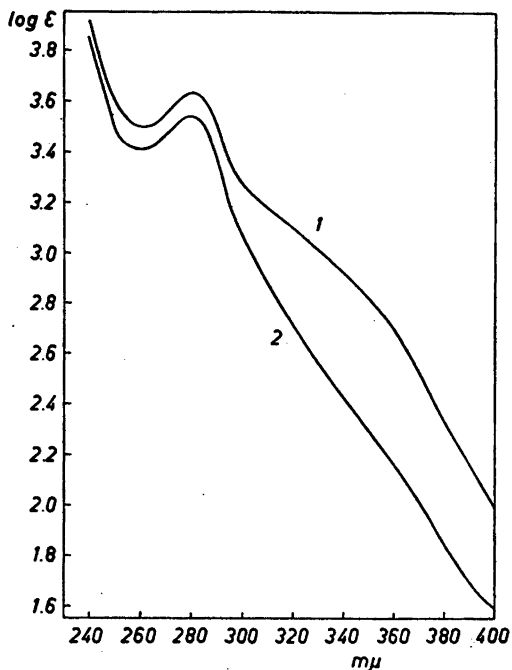
Fig. 2. Ultraviolet absorption curves. Curve 1: "Native lignin". Curve 2: "Native lignin", reduced with sodium borohydride. Based on methoxyl concentration. Solvent: 96 % ethanol.

The ultraviolet absorption curves of the resulting methylated products (Fig. 3) do not reveal any distinct structural changes due to the methylation when compared with the absorption of the corresponding starting materials (Fig. 2).

The analytical findings are summarized in Table 1. From the increase in the methoxyl content after methylation at room temperature, it can be calculated that the original "native lignin" acquired 0.47 new OCH_3 groups for

Table 1.

Lignin preparation	Before methylation % OCH_3	After methylation at room temp., 48 h		After methylation at reflux, 2.5 h	
		% OCH_3	$\dfrac{OCH_3 \text{ introd.}}{OCH_3 \text{ orig.pres.}}$	% OCH_3	$\dfrac{OCH_3 \text{ introd.}}{OCH_3 \text{ orig.pres.}}$
"Native lignin"	14.67	20.49	0.47	21.09	0.52
Reduced "native lignin"	15.19	20.46	0.41 [0.47]	21.02	0.46 [0.51]

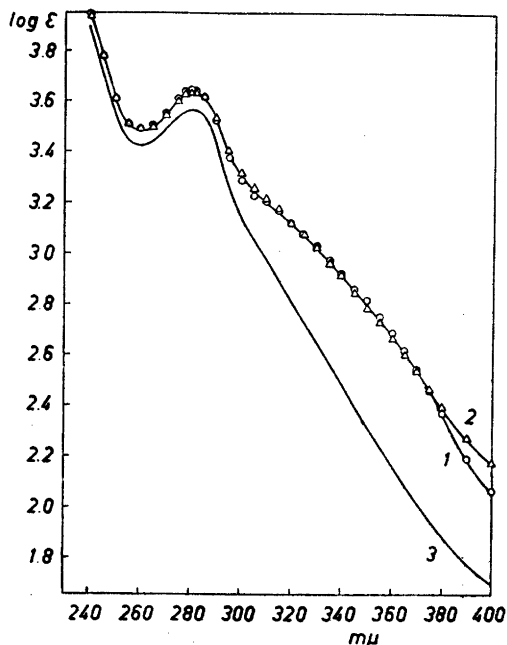*Fig. 3. Ultraviolet absorption curves. Curve 1: "Native lignin", methylated with 0.5 % CH₃OH−HCl (48 h, room temp.). Curve 2: "Native lignin", methylated with 0.5 % CH₃OH−HCl (2.5 h, reflux). Curve 3: Sodium borohydride-reduced "native lignin", methylated with 0.5 % CH₃OH−HCl (2.5 h, reflux). All curves based on concentration of OCH₃ present in unmethylated starting material. Solvent: 96 % ethanol.*

every OCH_3 originally present. The corresponding value, 0.52, obtained when the reaction was performed under reflux, is in good agreement with the result reported by Brauns [6] in the case of black spruce "native lignin".

The most important finding shown in Table 1 is that the reduced lignin preparation behaves similarly to the original lignin. The methoxyl values of the methylated reduced preparations are practically identical with those of the methylated non-reduced lignins.

Due to the fact that the methoxyl value of the reduced lignin (15.19 %) is slightly higher than that of the original lignin (14.67 %), the ratio OCH_3 introduced/OCH_3 orig. present becomes somewhat lower in the first case than in the latter one. One might assume that the comparatively high methoxyl value of the reduced lignin is caused by an etherification of some highly reactive hydroxyl groups by the ethanol used as a solvent in the sodium borohydride reduction and also present during the recovery of the reduced product. Unintentional temporary acidification after completed reduction (cf. experimental part) might be sufficient to bring about such slight ethylation. If this assumption is accepted, the alkylation values given in brackets are obtained. These "corrected values" are nearly identical with those obtained in the methylation of the non-reduced lignin.

But even if no consideration is taken of such a correction, it is obvious that methylation takes place to a very similar extent irrespective of the presence or

absence of carbonyl groups in the lignin material. Hence, the methylation cannot be due to acetal formation.

This conclusion is further supported by the fact that the carbonyl band of the infrared absorption curve of "native lignin" does not disappear on methylation (see Fig. 1, c and d) *. Obviously, the carbonyl groups present in spruce "native lignin" do not form stable acetals. If there is any acetalization during the interaction of the methanolic hydrochloric acid, the acetals or ketals formed must be hydrolyzed again during the isolation of the methylated product. It may also be noted that the carbonyl groups present in the original "native lignin" (0.12 CO/OCH_3), if completely acetalized, could give rise to at most 0.24 OCH_3 introduced per OCH_3 orig. present, whereas the figures actually obtained are 0.47 and 0.52.

The question now arises which types of groups are responsible for the methylation.

It was found that the methoxyl content (20.1 % OCH_3) of a methylated product obtained by treatment of "native lignin" at room temperature for 24 hours with 0.5 % methanolic hydrochloric acid, remained practically unchanged in 0.1 N aqueous sodium hydroxide (48 hours, room temperature), the recovered product containing 19.8 % OCH_3. This result shows that the introduced methoxyl groups are not present as ester groups. It is in agreement with the alkali stability of the methoxyl and ethoxyl groups in methanol and ethanol lignins from spruce wood as reported by Hibbert and Brauns [7], and by Holmberg and Runius [2].

Since acetalization and ester formation can be excluded, the alkylation must be due to the reaction of hydroxyl groups in the lignin. There are three possible types of such groups which are sufficiently reactive to undergo alkylation with alcoholic hydrochloric acid.

One type to be considered is the a-ketol structure, the hydroxyl group of which is known to be etherified by alcoholic hydrochloric acid [16]. It is also known by the work of Hibbert [17] that monomeric a-ketol ethers are formed if wood or isolated lignin is heated for 48—72 hours with ethanolic hydrochloric acid. The appearance of side-chains with an a-ketol structure with subsequent etherification of its hydroxyl group during the treatment of native lignin with methanolic hydrochloric acid might therefore be considered possible. In this case, the alkylation of lignin would be expected to be accompanied by the formation of keto groups. By means of the hydroxylamine hydrochloride method it was found, however, that sodium borohydride-reduced and subsequently methylated "native lignin" (methylation during 2.5 hours under reflux) was practically free of carbonyl groups. Hence, the methoxyl groups introduced into the lignin are not present as a-ketol ether groupings.

Some years ago, Erdtman [18] suggested the presence of cyclic hemiacetal structures (I) in lignin. The open hydroxyl group (OR_1, $R_1 = H$) or an alkyl derivative of it ($-OR_1$) would be the site of the typical lignin reactions such as sulphonation and alkylation with alcoholic hydrochloric acid. Sulphonation

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* The opposite observation has been reported by Jones [15], who states that the absorption band in the spectrum of black spruce „native lignin" at 1 663 cm⁻¹ is no longer found in the spectrum of the CH_3OH—HCl methylated lignin. The reason for this discrepancy is obscure.

$$C-C \qquad OCH_3$$
$$R_1O-C-O$$
$$OCH_3$$
$$-O$$

I
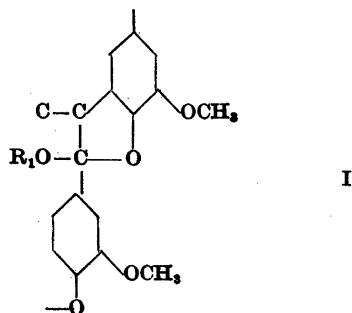
studies with a model substance [18] containing a structure not very closely related to I constitute the only experimental support hitherto available, and further model experiments would be highly desirable. Although, at present, the possibility of structures like I being responsible for the alkylation and other reactions of lignin cannot be excluded, it appears that its further discussion must be postponed until more experimental material has been collected.

The benzyl alcohol and benzyl ether concept of lignin structure seems to provide an excellent basis for the explanation of the alkylation with alcoholic hydrochloric acid. In addition, the results reported in the present paper strongly support this concept. The following structures, a—d, previously suggested to be present in lignin of coniferous wood mainly as a result of sulphonation studies (cf. Ref. [9]), can undergo alkylation in the benzyl position:

CHOH	CHOR$_1$	CHOH	CHOR$_1$
OCH$_3$	OCH$_3$	OCH$_3$	OCH$_3$
OH	OH	OR$_2$	OR$_2$
a	b	c	d
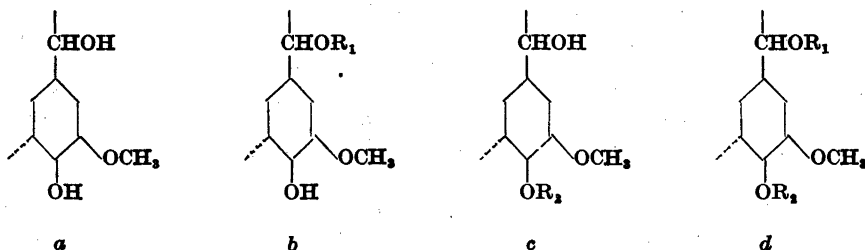
The p-hydroxybenzyl alcohol structure a and the p-alkoxybenzyl alcohol structure c will be alkylated by etherification, whereas the p-hydroxybenzyl (alkyl) ether structure b and the p-alkoxybenzyl (alkyl) ether structure d will react by re-etherification.

Direct experimental evidence for the occurrence in lignin of the phenolic structures a and b has recently been provided. Thus, the ''quinone methide reaction'' of ''native lignin'', briefly reported by Adler and Gierer [19], is probably due to the presence of one or both of these structures, and the ,,indophenol reaction'' of wood and isolated ''native lignin'', which has been described by Gierer [20], has to be ascribed to structure a.

The extent of methylation (about 0.5 OCH_3 introduced $/OCH_3$ orig. present) indicates that the methylatable structures a—d constitute together about

50 % of the guaiacyl propane monomers of spruce "native lignin". This, of course, is true only if not more than one OCH_3 is introduced into each of the methylatable monomers. According to Gierer [20] structure a occurs in 12—14 % of the monomers.

If the carbonyl groups in "native lignin" (0.12 CO per OCH_3), apart from those belonging to coniferylaldehyde residues (about 0.025 per OCH_3), were keto groups in the α-position of the side-chain, i. e., adjacent to the aromatic nucleus, sodium borohydride reduction of the lignin would be expected to produce about 0.1 new methylatable aryl carbinol group of the types represented by structures a and c. However, the methylation values of the reduced lignin are not higher than those of the original preparation. This seems to indicate that the carbonyl groups are mainly not in the α-position of the side-chains. In agreement herewith, Gierer [20] arrived at the conclusion that phenolic units with α-keto groups seem not to be present in "native lignin", since the amount of groups a, estimated by the „indophenol reaction", was not increased after reduction of the lignin with sodium borohydride.*

It can be expected that the four structures a—d will differ in their reactivity towards alcoholic hydrochloric acid. In fact, model experiments, which are still under progress [21], have shown that p-hydroxybenzyl alcohols (type a) react faster than p-alkoxybenzyl alcohols (type c), and, in addition, there are certain differences in reactivity between free benzyl alcohols (a, c) and benzyl ethers (b, d). Furthermore, sharp dissimilarities have been found in the behaviour of different benzyl ethers. Whereas ethers, in which R_1 (in formulae b and d) is an open alkyl residue, are readily re-etherified, cyclic ethers such as dehydro-diisoeugenol and pinoresinol are more or less resistant to methanolic hydrochloric acid under the conditions used in the present investigation. Finally, it has been found that the course of the alkylation of aryl propane derivatives containing the structures a—d is greatly dependent upon the chemical nature of the substituents present at the β- and γ-positions of the propane side-chain. Thus, a closer examination of the alkylation of lignin, in comparison with the behaviour of appropriate model substances, seems to offer a new means of elucidating the principles of lignin structure. In this connection, the finding that alkylation takes place under very mild conditions is of considerable interest.

EXPERIMENTAL

Reduction of "native lignin" with sodium borohydride. The procedure has already been described in a preceding paper by Gierer [20]. In the present case, the reduction was carried on for two days at room temperature, and the alkaline reaction mixture neutralized with hydrochloric acid.

Estimation of carbonyl groups. Brauns' "native lignin" [6] from spruce wood meal or the sodium borohydride-reduced product (100 mg) was dissolved in 25 ml 96 % ethanol. The pH of the solution was adjusted to 3.5 by the addition of dilute aqueous hydrochloric acid. A solution of 0.17 g $NH_2OH\cdot HCl$ in 10 ml ethanol, likewise adjusted to pH 3.5, was added. A stream of nitrogen was bubbled through the mixture, which after certain

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* *Note added in proof:* In a recent publication a similar result was reported by G. Aulin-Erdtman [*Svensk Papperstidn.* **57** (1954) 745], who found by spectrophotometric measurements on different lignin preparations that the sum of α-keto groups and C−C double bonds conjugated with the aromatic ring can not be greater than 0.01−0.02 per OCH_3.
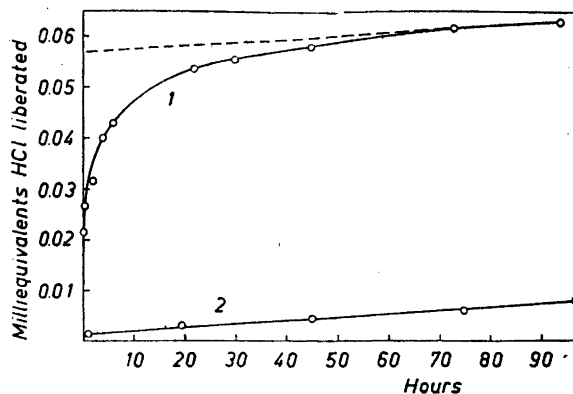
Fig. 4. *Estimation of carbonyl groups. Curve 1: "Native lignin". Curve 2: Sodium borohydride-reduced "native lignin".*

time intervals was titrated with 0.0099 N NaOH to pH 3.5 (glass electrode). The consumption of sodium hydroxide is shown in Fig. 4. The slow liberation of hydrochloric acid indicated by the nearly linear slope of the right part of the curves is caused by some oxidative decomposition of hydroxylamine, due to incomplete exclusion of air. The true consumption of sodium hydroxide due to oxime formation was found by extrapolation to time zero.

"Native lignin" (curve 1): 100 mg lignin with 14.67 % OCH_3, *i.e.*, 0.47 mequ. OCH_3, consumed 0.057 mequ. NaOH, corresponding to 0.057 mequ. CO. $CO/OCH_3 = 0.12$.

The reduced lignin (15.19 % OCH_3) consumed about 0.002 mequ. NaOH (curve 2). $CO/OCH_3 = 0.004$.

Methylation with 0.5 % methanolic hydrochloric acid. The procedure was similar to that already reported by Gierer [20]. The lignin preparation (200 mg) was dissolved in 4 ml absolute methanol, and 1 ml methanol containing 0.25 g hydrogen chloride was added. The mixture was either allowed to stand at room temperature for 48 hours or refluxed for 2.5 hours, then neutralized with a few drops of 2 N Na_2CO_3 solution and evaporated *in vacuo* to dryness. The residue was dissolved in 2 ml absolute methanol-acetone mixture (1 : 1), filtered, and washed with a few ml of the same solvent. The solution was poured into 60 ml of water. The precipitate, after standing overnight, was collected on a glass filter, washed thoroughly with water and dried *in vacuo* over phosphorus pentoxide. The yield of this product was about 60 %. It was dissolved in dioxan and re-precipitated in ethyl ether [5]. Yield about 50 % of the original lignin.

The calculation of the ratio OCH_3 introduced/OCH_3 orig. present may be illustrated by the following example:

Methylation of "native lignin" in boiling $CH_3OH-HCl$, 2.5 hours. "Native lignin", 14.67 % OCH_3; methylated product, 21.09 % OCH_3.

If methylation is assumed to involve the etherification of hydroxyl groups, the increase in weight is $CH_2 = 14$ for every introduced methoxyl group. If it is assumed to involve the re-etherification of ether bridges, the corresponding increase is $CH_3OH = 32$. The mean value of 23 has been adopted for the present calculation.

The two equations

$$\frac{31.034 \cdot 100}{x} = 14.67,$$

and

$$\frac{(1 + y) \cdot 31.034 \cdot 100}{x + y \cdot 23} = 21.09$$

give x (= the weight of one OCH_3 equivalent in "native lignin") = 211.5, and y (= OCH_3 introduced/OCH_3 orig. present) = 0.52.

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