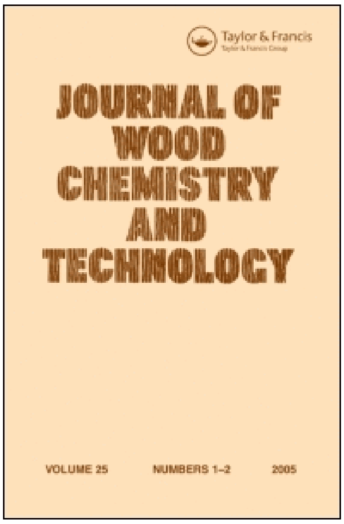

**Journal of Wood Chemistry and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# The Modification of Lignin at Positions 2 and 6 of the Phenylpropanoid Nuclei. IV. The Reactivity of *Meta* Hydroxymethyl Groups

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**To cite this Article** van der Klashorst, Gerrit H. and Jackson, Siobhan A.(1989) 'The Modification of Lignin at Positions 2 and 6 of the Phenylpropanoid Nuclei. IV. The Reactivity of *Meta* Hydroxymethyl Groups', Journal of Wood Chemistry and Technology, 9: 1, 17 — 34
**To link to this Article: DOI:** 10.1080/02773818908050283
**URL:** http://dx.doi.org/10.1080/02773818908050283

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 9(1), 17-34 (1989)

# THE MODIFICATION OF LIGNIN AT POSITIONS 2 and 6 OF THE PHENYLPROPANOID NUCLEI - PART IV: THE REACTIVITY OF META HYDROXYMETHYL GROUPS

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## ABSTRACT

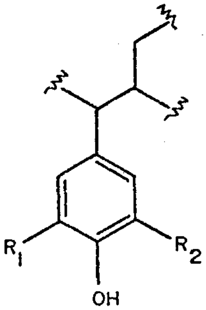
Lignin model compounds hydroxymethylated at the 2 and 6 positions reacted with phenol or resorcinol to afford methylene linked products. Optimum conditions for the reactions were established.

## INTRODUCTION

Ever since the start of chemical pulping, which currently produces large quantities of underutilized by-product lignin, the development of uses for this material has received widespread attention. Although various uses have been developed, the lignin produced by alkali pulping in particular, is hardly used commercially. The major reason for this is most probably the low number of reactive sites on the by-product lignin which can be utilized for modification. This is particularly the case for the use of alkali lignins (or lignosulphonates) in phenol formaldehyde resins. By-product lignin is usually fairly condensed and does not contain a high number of unsubstituted

5-positions on phenolic $C_9$ units to contribute in crosslinking reactions with formaldehyde. Industrial by-product lignins therefore cannot be used to subtitute large proportions of phenol formaldehyde adhesives. This constraint can be overcome in various manners, such as demethylation[1] of the methoxy groups or the use of selected high molecular mass lignin fragments obtained from ultrafiltration[2]. The 2- and 6-positions of the demethylated lignin nuclei (Fig. 1) can undergo classical alkali catalysed substitution reactions and hence impart the required reactivity to the demethylated lignin. On the other hand, the high molecular mass fragments can be expected to contain about the same number of reactive sites per $C_9$ as the small lignin fragments[2]. Owing to their size, the larger fragments contain more reactive sites per fragment and hence contribute more to the crosslinking of the final resin. These methods, however, possess some drawbacks such as cost or the utilization only of a part of the lignin source.

Recently it was shown that the 2- and 6-positions of the lignin nuclei can be used for modification without demethylation and with the aromatic hydroxy group either etherified or free (i.e. phenolic)[3]. Each of these positions are available in a high ratio of about one per $C_9$. The 2- and 6-positions are situated <u>meta</u> to the aromatic hydroxy group of the lignin phenylpropanoid unit and are considered unreactive for classical electrophilic displacement reactions. Nevertheless, model compounds were used to show that these positions can in fact be utilized for controlled polymerization[3] and hydroxymethylation[4] with formaldehyde. These reactions were also successfully evaluated on lignin obtained from three different industrial origins[5]. In this paper the reactivity of the <u>meta</u> hydroxymethyl groups is investigated in view of the potential application of these reactions for the preparation of cold and hot-cure wood adhesives. The approach used is the controlled addition of phenol or resorcinol on the



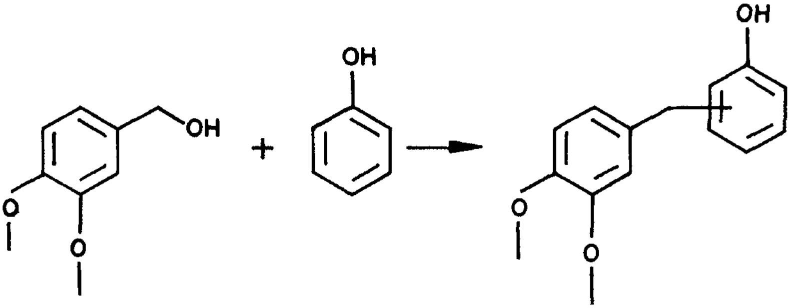
($R_1$,$R_2$ = H/$OCH_3$/ ⌇)
( ⌇ = possible linkage to other phenylpropanoid units)

FIGURE 1: Lignin phenylpropanoid units

meta positions. The addition of phenols to lignin has previously been shown to result in the increase in reactivity of the lignin[6]. The introduction at the meta positions which are available in much larger quantities than the positions previously used for the introduction of phenyl clearly gives more potential to this avenue.

## DISCUSSION

The reactivity of meta hydroxymethyl groups with phenol was firstly assessed with 3,4-dimethoxy benzyl alcohol (1) as model compound. The model was reacted with phenol in 50 % aqueous dioxane (Table 1). When the aqueous dioxane was prepared from water at pH 1,0 no reaction was observed between 1 and phenol (Table 1, entry 1). Even with a ten times excess of phenol to 1 no consumption of the benzyl alcohol (1) was detected by HPLC. The reaction was subsequently repeated with 1,1 N acid. Under the stronger acidic conditions, 90 % of 1 reacted with the phenol



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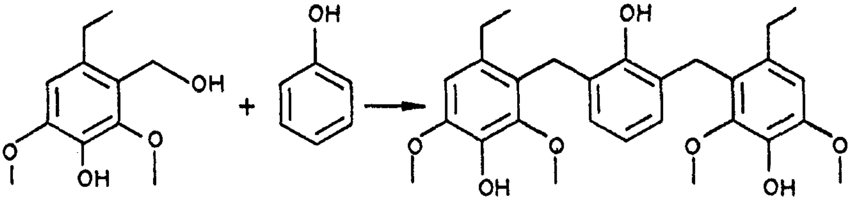


4 5 6

TABLE 1

Reaction of lignin model compounds with phenol in acid aqueous dioxane

| ENTRY | MODEL | $[H^+]$ | MOLE PHENOL/ MOLE MODEL | RESULTS |
|---|---|---|---|---|
| 1 | 1 | pH = 1,0 | 1:1 | No reaction |
| 2 | 1 | pH = 1,0 | 10:1 | No reaction |
| 3 | 1 | 1,1 N | 1:1 | Figure 2 |
| 4 | 4 | pH = 1,0 | 1:1 | Figure 3 |
| 5 | 4 | 1,1 N | 1:1 | Figure 4 |

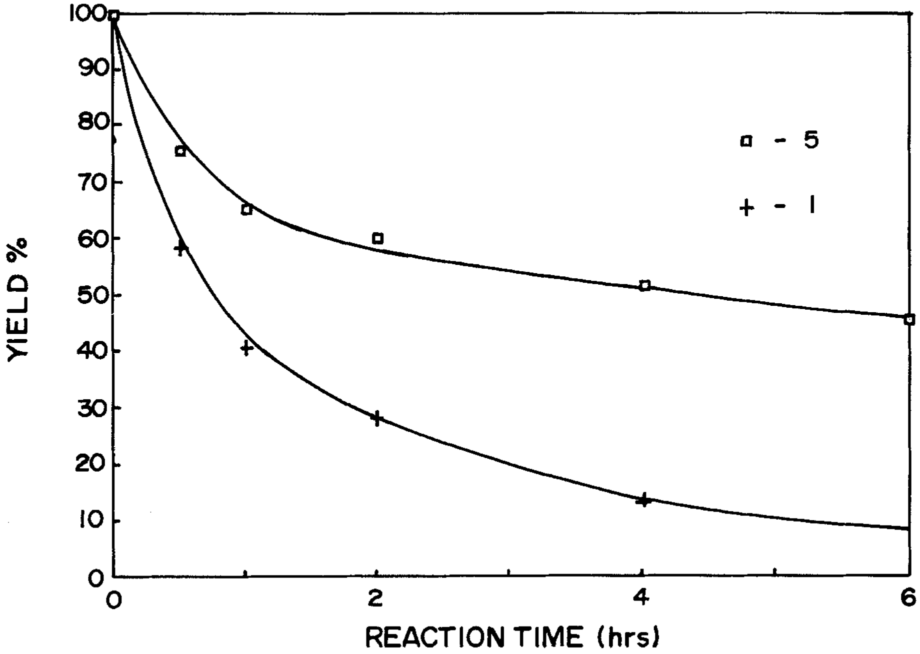


FIGURE 2 REACTION 1 WITH PHENOL (5) IN 50 % AQUEOUS DIOXANE AT 80 °C, 1,1 N HCl

in six hours (Figure 2). The HPLC results (Figure 2) showed that about 2 moles of 1 reacted per mole of phenol indicating that di- or tri-substitution of the phenol occurred.

The 3,4-dimethoxy benzyl alcohol (1) used in the above reactions does not contain an alkyl substituent on position 1 such as the phenylpropanoid units in alkali lignin (Fig. 1). Highly condensed alkali lignin can particularly be expected to contain a high degree of alkyl substituents without any α-oxy substituents[7]. A decrease in α-oxy functionalities is expected owing to condensation reactions during pulping. The more appropriate model compound 1-ethane3-hydroxy-2,4-dimethoxy benzyl

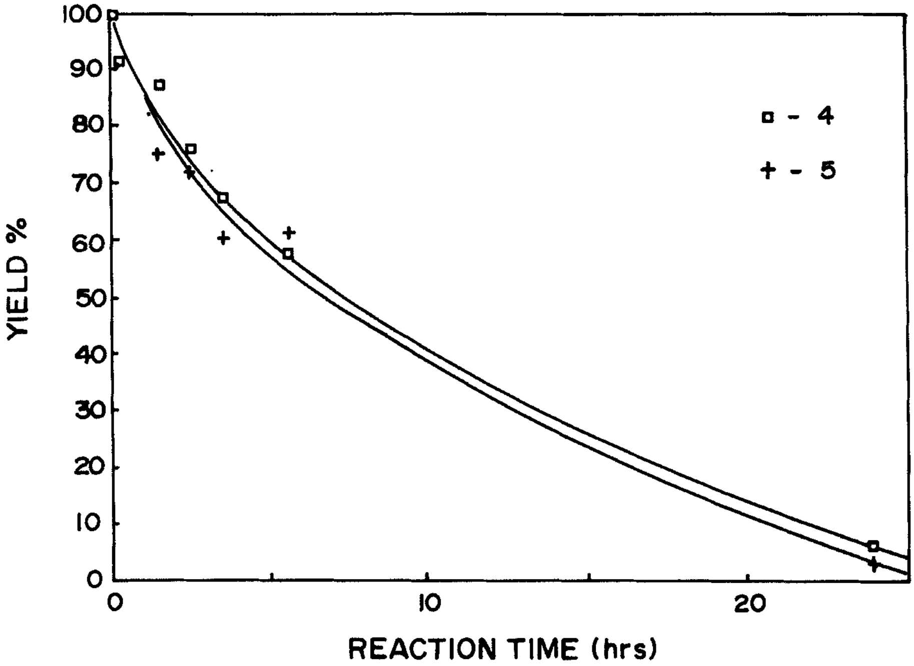


FIGURE 3 REACTION OF 4 WITH PHENOL (5) IN 50 % AQUEOUS DIOXANE AT 80 °C, pH = 1,0

alcohol (4) was subsequently used to study the reactivity of the *meta* benzyl alcohols.

Phenol (5) reacted with the alkyl substituted model (4) to consume about 50 % of the model in six hours at pH 1,0 and 80 °C (Fig. 3). The reaction was repeated with an acid concentration of 1,1 N resulting in the consumption of all 4 in about four hours reaction time. At the same time only 50 % of the phenol was consumed indicating that di-substitution of the phenol again occurred. The reaction was repeated for a reaction time of six hours to afford the tri-aryl product 6 in a yield of 51 % after separation by flash chromatography.

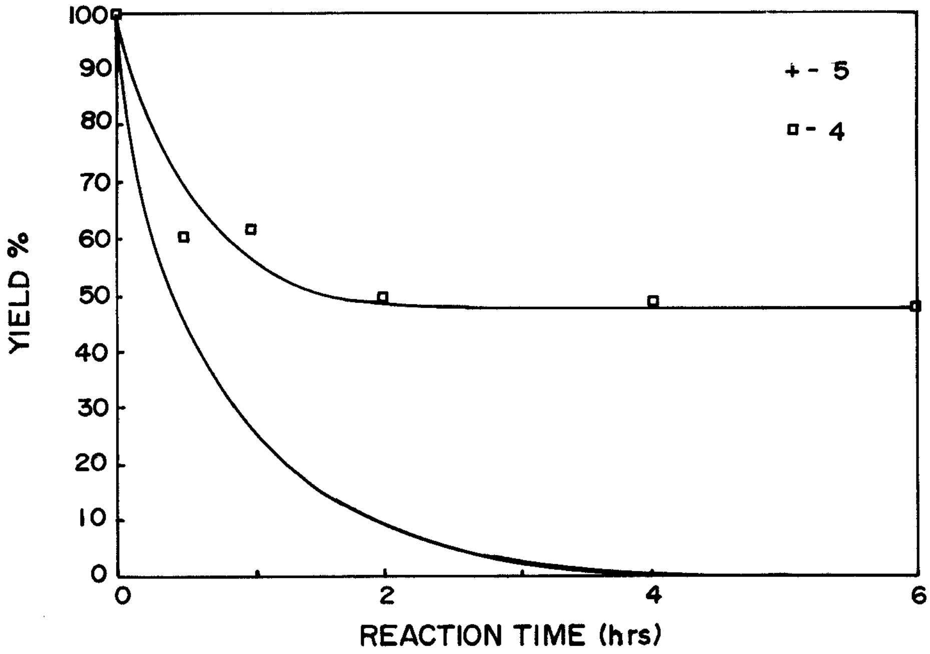


FIGURE 4 REACTION OF 4 WITH PHENOL (5) IN 50 % AQUEOUS DIOXANE AT 80 °C, 1,1 N HCl

The reaction of the 'meta hydroxymethyl' groups with resorcinol Was subsequently evaluated. Model 1 reacted with resorcinol at pH = 1,0 in 50 % aqueous dioxane (Figure 5). The reaction was slow and took about 24 hours to completion. When the acid concentration was increased to 1,1 N the reaction rate increased dramatically (Figure 6). The rate was even higher when an excess of resorcinol (10:1) was employed (Figure 7).

The reactions were subsequently repeated with the ethyl substituted model 4. In the presence of 0,22 N acid, 4 is consumed in less than two hours (Figure 8). The reaction was

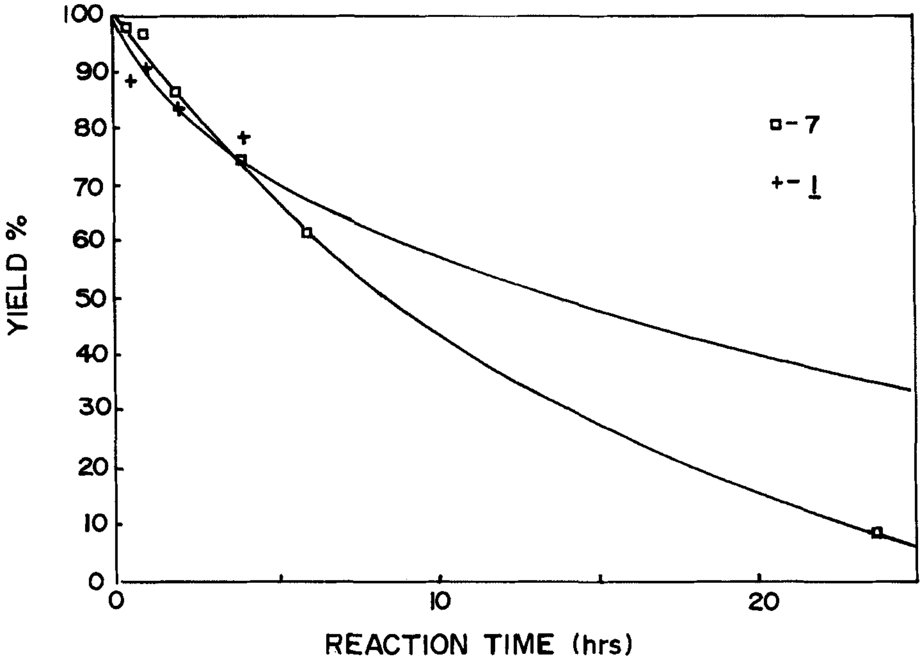


FIGURE 5 REACTION OF BENZYL ALCOHOL (1) WITH RESORCINOL (7) IN 50 % AQUEOUS DIOXANE AT 80 °C, pH = 1,0

repeated with an acid concentration of 1,1 N and the products separated by chromatography to afford 9 in a yield of 53 %.

The formation of methylene linkages was previously suggested to be in competition with protonolysis cleavage reactions[3]. This cleavage reaction may be useful for the derivation of condensed lignin to yield for example a resorcinol substituted lignin as explained by A below (Scheme 1). If uncontrolled, it may, however, lead to defunctionalization of the lignin as suggested by B.

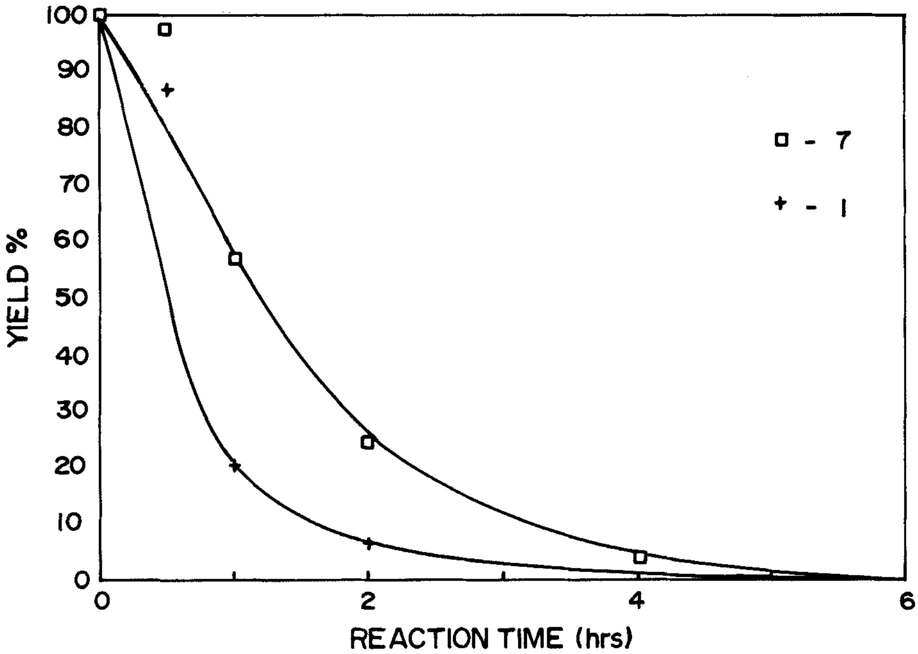


FIGURE 6 REACTION OF BENZYL ALCOHOL (1) WITH RESORCINOL (7) IN 50 % AQUEOUS DIOXANE AT 80 °C, 1,1 N HCl

The occurrence of the cleavage of the methylene linkages was subsequently assessed employing the dimer 10. The dimer was heated with a stoichiometric quantity of resorcinol to 80 °C in 90 % aqueous dioxane and 1,1 N hydrochloric acid. Tlc showed no change in the composition of the reaction mixture over a period of 12 hours.

The reaction was subsequently repeated with a much higher acid concentration of 2,2 N in 50 % aqueous dioxane similar to the conditions reported earlier to result in protonolysis of the methylene linkage[3]. The reaction was followed by tlc indicating

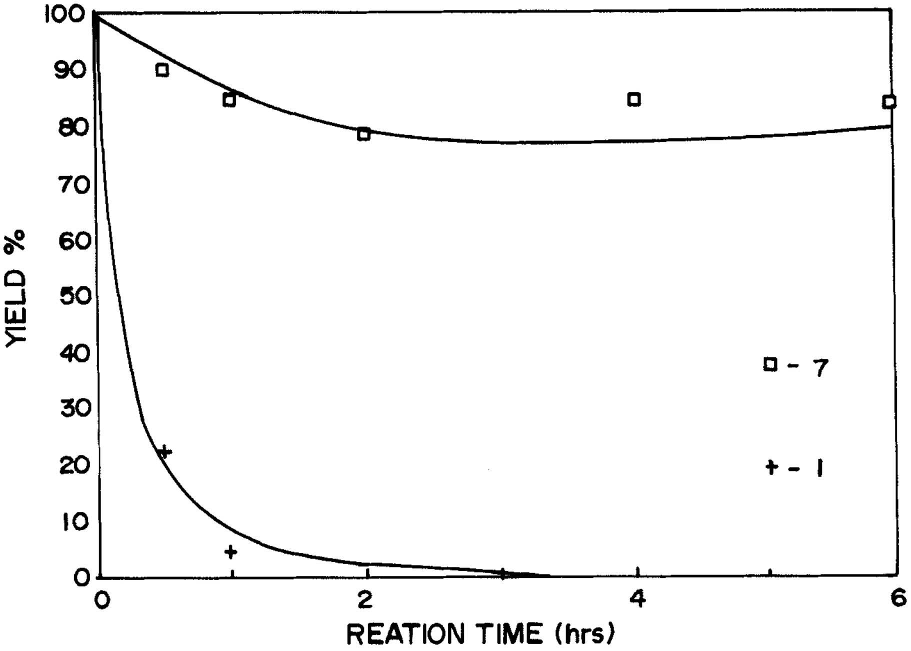
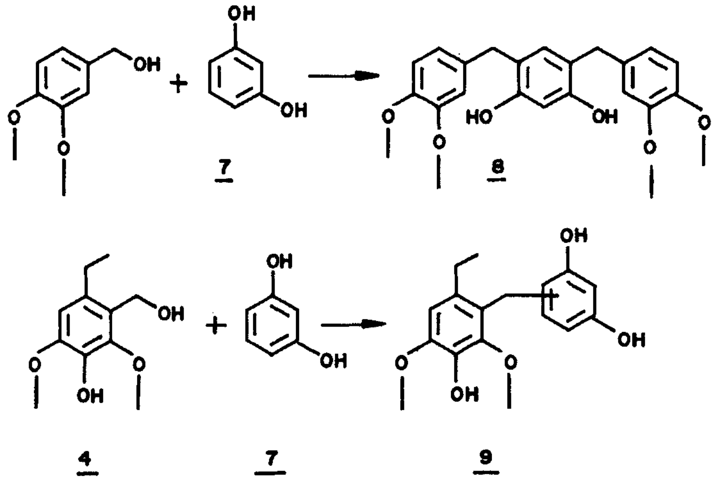


FIGURE 7 REACTION OF BENZYL ALCOHOL (1) WITH RESORCINOL (7) (10 MOLAR EXCESS) IN 50 % AQUEOUS DIOXANE AT 80 °C, 1,1 N HCl



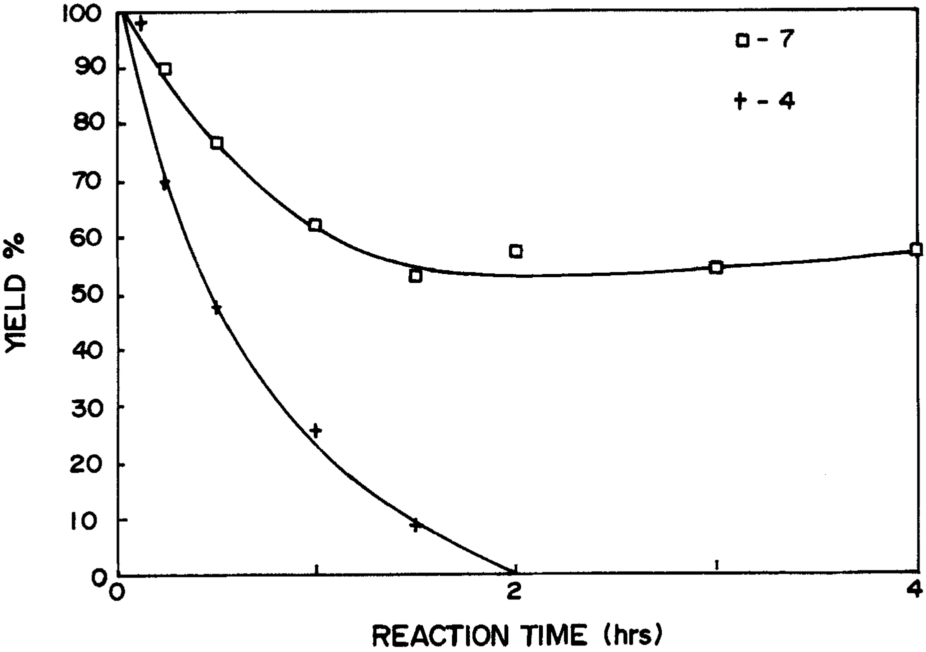


FIGURE 8 REACTION OF 4 WITH RESORCINOL (7) IN 50 % AQUEOUS DIOXANE AT 80 °C, 0,22 N HCl

TABLE 2

Reactions of model compounds with resorcinol

| ENTRY | MODEL | $[H^+]$ | MOLE PHENOL/ MOLE MODEL | RESULTS |
|---|---|---|---|---|
| 1 | 1 | pH = 1,0 | 1:1 | Fig. 5 |
| 2 | 1 | 1,10 N | 1:1 | Fig. 6 |
| 3 | 1 | 1,10 N | 10:1 | Fig. 7 |
| 4 | 4 | 0,22 N | 1:1 | Fig. 8 |
| 5 | 4 | 1,10 N | 1:1 | Fig. 9 |

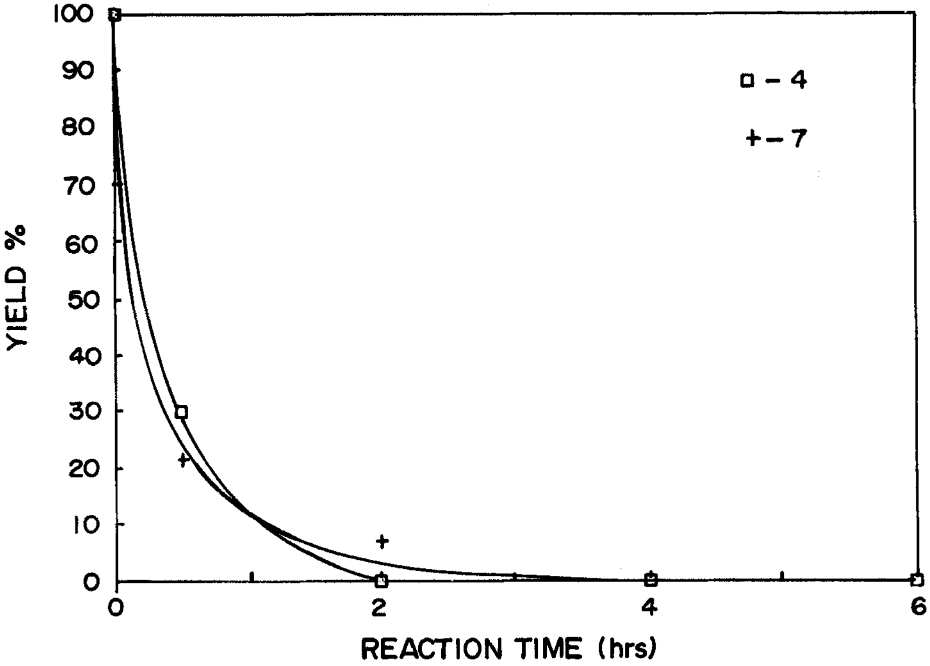
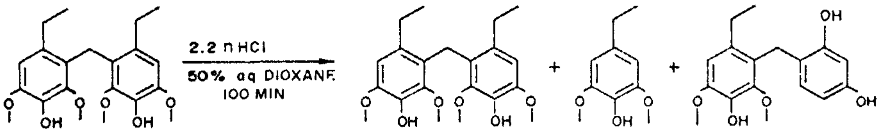
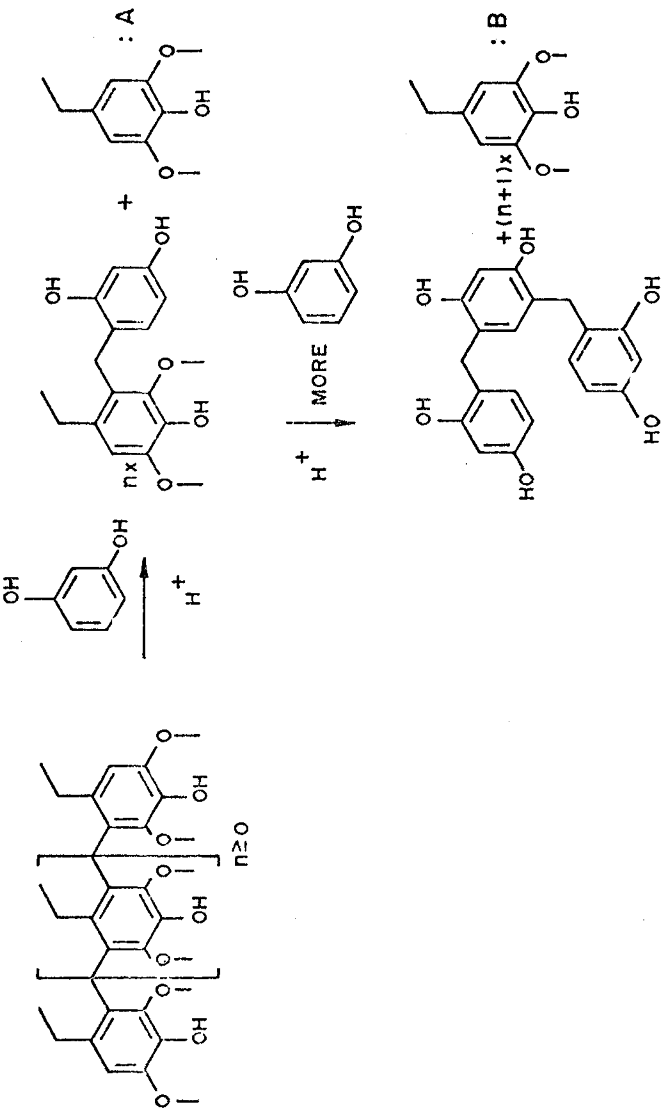


FIGURE 9 REACTION OF 4 WITH RESORCINOL (7) IN 50 % AQUEOUS DIOXANE AT 80 °C, 1,1 N HCl

the formation of inter alia the monomer 11. After 100 minutes, the reaction was stopped and the products separated to afford the dimer 10 in 14 % yield, 11 in 43 % yield and the resorcinol adduct 12 in 37 % yield.



10 10 11 12



SCHEME 1: Possible depolymerization of lignin due to protonolysis

## CONCLUSION

Hydroxymethyl groups situated on 2- and 6-positions of lignin model compounds are reactive 'handles' to introduce phenol or resorcinol into the lignin polymer. The reactions are fast and lead to the formation of methylene linkages between the model compound and phenol. These reactions of the meta hydroxymethyl groups hold tremendous potential for the utilization of lignin, in particular since the highly available 2- and 6-positions are utilized for these reactions, implying that most condensed lignin could be transformed by this reaction. Obvious avenues opened up by this reaction are the use of lignin in coldset and hot curing PF type adhesives.

## EXPERIMENTAL

Infrared (IR) spectra were recorded on a Perkin Elmer spectrophotometer (710 B) in chloroform. Proton NMR spectra were determined on a Varian 90 spectrometer in deuterochloroform with tetramethyl silane as internal standard. Mass spectra, including accurate mass determinations, were obtained on a Varia MAT-212 double focussing spectrometer with direct probe insertion, operated with an ionization potential of 70 eV. Qualitative thin layer chromatography was done on Merk (Kieselgel $60F_{254}$) plates and flash chromatography on Merk Kieselgel 60 (0,063 - 0,2 mm). High pressure liquid chromatography (HPLC) was done on a Knauer Lichrospher Si 100 column with ethylacetate/hexane as eluent at a pump rate of 4 ml/min. Detection was done at 280 nm.

### Preparation of the model compounds

The model compound 6-ethane-3-hydroxy-2,4-dimethoxy benzyl alcohol (4) was prepared by reacting 4-hydroxy-3,5-dimethoxy phenyl ethane (0,72 g) with formaldehyde (0,48 g) in 90 % aqueous dioxane (100 ml) and 0,4 N hydrochloric acid. The reaction was done at 80 °C for 6 hours. Flash chromatography with ethylacetate hexane 1:2 as eluent yielded 4 in an 86 % yield as before[4]. The 3,4-dimethoxybenzyl alcohol model (1) was purchased from Aldrich Chemicals.

## Reactions of the **1** and **4** with phenol and resorcinol

The model compounds (ca. 200 mg) were reacted in the solvent specified in Tables 1 and 2 (20 ml) with phenol or resorcinol in the molar ratio's specified. The reactions were done at 80 °C and samples taken at different intervals. The samples (2 g) were neutralized ($NaHCO_3$), diluted with chloroform (10 ml), dried ($MgSO_4$) and analysed by HPLC to observe consumption of the models and the phenol or resorcinol.

The reaction of 1 (0,500 g) with phenol (0,279 g) was repeated in 50 % aqueous dioxane and 1,1 N HCl at 80 °C for 6 hours. The crude product was flash chromatographed on 100 g silica with ethylacetate hexane 1:1 to afford pure (3,4-dimethoxyphenyl)methylphenol (3) in a yield of 22 %. After acetylation with $\upsilon_{max_s}$ ($CHCl_3$) 2900, 1720-1760, 1600, 1510, 1480-1420, 1390, 1170-1320; $\delta$ $CDCl_3$ 2,25 (s, 3H, $ArOCOC\underline{H}_3$), 3,85 (s, 6H, 2 x $OC\underline{H}_3$), 3,9 (s, 2H, $ArC\underline{H}_2Ar$), 6,65-7,2 (M, 7H, $Ar\underline{H}$). m/e 436($M^+$ 1 %) 435 (5), 434 (5), 421 (3), 398 (18), 397 (15), 270 (30), 151 (70), 138 (55), 43 (100 %).

3,4-Dimethoxybenzyl alcohol (1) (500 mg) was reacted with resorcinol (327 mg) in 50 % aqueous dioxane (100 ml) containing hydrochloric acid (32 %, 9 ml) at 80 °C for 24 hours. The crude product was flash chromatographed (100 g silica) with

ethylacetate/hexane (1:3) to yield pure 4,6-bis-[3,4-dimethoxyphenylmethyl]resorcinol (8) in a yield of 62 %. After acetylation (pyridine/aceticanhydride):
$\upsilon_{max}$ ($CHCl_3$) 2930, 2840, 1750, 1600, 1500, 1460, 1380, 1300-1150, 1080, 1030; $\delta$ $CDCl_3$ 2,20 (s, 6H, 2 x $ArOCOC\underline{H}_3$), 3,75-3,85 [Multiplet (mainly dublet), 14 H, 4 x $OC\underline{H}_3$ + 2 x $ArC\underline{H}_2Ar$] 6,55-6,90 (m, 8H, $Ar\underline{H}$).

The reaction of 4 with phenol and resorcinol was repeated in order to isolate the products formed. The reaction of 4 (0,08 g) with phenol (0,04 g) was repeated at 80 °C in 50 % aqueous dioxane and 1,1 N hydrochloric acid for 6 hours. The reaction mixture was diluted with water and extracted with chloroform (3 x 30 ml) to afford a crude product after drying ($MgSO_4$) which was flash chromatographed with ethylacetate/hexane 3:2 to afford 6 in a yield of 51 % $\upsilon_{max}$ 3600, 3400, 2870, 1600, 1470, 1200 $cm^{-1}$; $\delta$ ($CDCl_3$) 1,10 (t, 6H, J = 7,5 Hz, 2 x $CH_2C\underline{H}_3$), 2,55 (q, 6H, J = 7,5 Hz, 2 x $C\underline{H}_2CH_3$), 3,72 & 3,90 (singlets, 12H, 4 x $OC\underline{H}_3$), 3,95 (s, 4H, $ArC\underline{H}_2Ar$), 5,5 (br multiplet, 3H, $ArO\underline{H}$), 6,5-7,0 (m, 5H, $Ar\underline{H}$); m/e (70 °C) $M^+$(482 0,4 %), 378 (5 %), 289 (60 %), 195 (85 %).

Resorcinol and 4 was also reacted in 50 % aqueous dioxane and 1,1 N acid for two hours. Work-up and chromatography as before, afforded 9 in a yield of 52,6 %. After acetylation (aceticanhydride/ pyridine) $\upsilon_{max}$ 2880, 1760, 1600, 1480, 1330, 1150 $cm^{-1}$; $\delta$ $CDCl_3$ 1,1(t, 3H, J = 7,5 Hz, $-CH_2C\underline{H}_3$), 2,27 & 2,35 (s, 9H, 3 x $ArOCOC\underline{H}_3$), 2,5 (q, 2H, J = 7,5 Hz, $-C\underline{H}_2CH_3$) 3,6 (s, 2H, $ArC\underline{H}_2Ar$) 3,83, 3,87 (s's, 6H, 2 x $OC\underline{H}_3$), 6,5-6,9 (m, 4H, $Ar\underline{H}$); m/e(110 °C) $M^+$(304, 3 %), 303 (20), 193 (30), 181 (100 %), 166 (65), 122 (30) and 76 (40).

Cleavage of meta methylene linkages

The dimer bis-(6-ethyl-3-hydroxy-2,4-dimethoxyphenyl)-methane (10) was prepared by the reaction of 4-hydroxy-3,5-dimethoxyphenyl ethane (0,53 g) with formaldehyde (0,12 g) in 50 % aqueous dioxane and 2,2 N HCl at 80 °C for four hours. The crude product obtained after extraction ($CHCl_3$) was flash chromatographed (ethylacetate/hexane 1 : 2) to afford the dimer 10 as before[3].

The dimer (0,18 g) was reacted with resorcinol (0,05 g) in aqueous dioxane at 80 °C. When the reaction was done in 90 % aqueous dioxane and 1,1 N hydrochloric acid no new compounds were observed by tlc over a reaction period of twelve hours. When the reaction was repeated in 50 % aqueous dioxane and 2,2 N hydrochloric acid tlc indicated the formation of new products. After a reaction time of 1 hour 40 min, the reaction was neutralized ($NaHCO_3$), diluted ($H_2O$ 50 ml) and extracted with chloroform. The combined extracts were dried ($MgSO_4$), evaporated and subjected to flash chromatography (ethyl acetate hexane 1:2) to afford 4-hydroxy-3,5-dimethoxyphenyl ethane (11) in 43 % yield, unreacted dimer in 14 % yield and 12 in a 37 % yield.

## ACKNOWLEDGEMENT

This research was partly sponsored by the FOUNDATION for RESEARCH DEVELOPMENT of the CSIR which is gratefully acknowledged.

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