SULFONATION OF SOME LIGNIN MODELS

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In the work of [1, 2] it was shown that the sulfonation of benzyl alcohols which are not substituted in the nucleus with bisulfite under the conditions of wood sulfite digestion takes place with difficulty. Thus, under these conditions phenylethylcarbinol (II) is converted to a sulfonated derivative only to the extent of 25%, and benzyl alcohol, phenylbenzylcarbinol, and benzoin are not sulfonated at all. Lignin model compounds which are substituted in the nucleus are considerably more reactive. Thus, p-hydroxybenzyl alcohol [3] is easily sulfonated even at pH 7.68 and a temperature of 100°. Vanillyl alcohol [4, 5] is sulfonated at pH 1.4, but at pH 7 and 135°, only 43% of a sulfonic acid was obtained after 20 h. Guaiacylmethylcarbinol (III) and its monomethyl ether (IV), among the other models, were sulfonated at pH 1.5 [5], but at pH 6.4 only 70% of the sulfonated derivative was formed after 15 h.

These experiments show that the rate of sulfonation of 3,4-dimethoxyphenlbenzyl alcohols is distinctly reduced when the pH is raised from 3.0 to 7.0. Work on sulfonation of guaiacyl- and veratrylglycerols [6, 7] shows the same thing. The first rapidly formed the sulfonic acid at all pH values, in high yield, but α -veratrylglycerol at pH 5.7 gave 70% sulfonic acid after 20 h.

The β -guaiacyl ether of α -veratrylglycerol was sulfonated in [8] at pH values of 1.5, 2.0, 3.0, 5.0, and 6.0, for various time periods. The sulfonation rate of this model is comparable with the rate of sulfonation of the B'-group in low-sulfonation lignin. Therefore, the authors of [8] consider this model similar to the B'-group in lignin. The low rate of sulfonation as compared with veratrylglycerol is explained by the presence of the bulky substituent in the neighborhood of the benzyl alcohol hydroxyl. The yields of sulfonated derivatives from the various arylcarbinols under the conditions of technical sulfite digestion are hardly quantitative, which is explained by the presence of competing processes of dehydration with formation of dimeric compounds under these conditions. These processes, which probably take place to some extent even in lignin during wood sulfite digestion, have still not been studied much.

We have previously reported on the sulfonation of three lignin model compounds: guaiacylethylcarbinol (VII), veratrylethylcarbinol (VIII), and isoeugenol (IX) [9]. All these compounds give 10-20% of the corresponding indane derivatives under the conditions of bisulfite digestion (pH 0.8-1.5), along with high yields of sulfonated derivatives. The carbonium ion formed as a result of splitting out the hydroxyl group under the influence of hydrogen ion reacts with the aromatic ring of another molecule, from which a proton is abstracted under the influence of substituents (OH or OCH₃) which polarize the ring.

 $\begin{array}{c} H \\ (H - - - Ar) - CH - CH - CH_{3} \\ Ar - CH - CH_{3} \\ H \end{array} \xrightarrow{H^{+}} Ar - CH - CH_{2} - CH_{3} \\ Ar - CH - CH_{3} \\ H \end{array}$

This condensation does not take place via the intermediate formation of isoeugenol or methylisoeugenol, respectively. In [10] it was observed still earlier that alkylphenylcarbinols and their analogs are converted into indane derivatives upon treatment with acids. Upon prolonged boiling with concentrated H_2SO_4 , dimethylphenylcarbinol (X) forms 1,1,3-trimethyl-3-phenylindane (XI) in 70% yield

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As an intermediate product there is formed an oxygen-containing compound, which goes over into the 1,1,3-trimethyl-3-phenylindane itself upon further treatment with H_2SO_4 . Consequently, the condensation of dimethylphenylcarbinol does not take place via intermediate formation of α -methylstyrene. A study by the same author [10] of the analogous self-condensation of other carbinols of the structure



to indane derivatives showed that such a condensation is possible only when R' is a CH_3 group. If R' = OC_2H_5 , the condensation does not take place; R" can be H, CH_3 , C_2H_5 (or possibly even larger alkyl groups), or C_6H_5 . The reaction takes place easiest of all in the case where R" is CH_3 . However, as has already been said above, according to our data compounds (VII) and (VIII) form indane derivatives under the conditions of sulfite digestion.

In the progress of this study, in the present work we have conducted the sulfonation of a number of other alkylcarbinols. Here, just as before, we were interested mainly in the presence and type of competing reactions.

Sulfite digestion of the models was carried out at pH 0.8, 1.5, 3.0, or 7.0, in sealed glass ampoules, with a liquor ratio of 1:20, at 135° for 3 h. Experimental results are shown in Table 1, from which it is evident that none of the substances investigated gave an indane derivative at any of the pH values we selected.

Phenylmethylcarbinol (I) and phenylethylcarbinol (II) show the dependence of sulfonate derivative formation on pH, although the yield of the latter compounds did not exceed 20% even at pH 0.8. The chloroform-extractable products were starting materials. No formation of dimers was detected. However, as was indicated above, under the severer conditions in [10], the corresponding indane derivative was obtained from (I). In spite of the presence of OH and OCH₃ substituents in the aromatic ring, guaiacyl- and veratrylmethylcarbinols, (III) and (IV), did not give indane derivatives, apparently because of the great

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Starting compound	Yield of sul- fonated prod- uct, %	Byproduct
Phenylmethylcarbinol Ar= C_6H_5 ; R = CH ₃ (I)	<20	Not formed
phenylethylcarbinol $Ar = C_8 H_5$; $R = C_2 H_5$ (II)	<20	32
Guaiacylmethylcarbinol $Ar = $ $OH; R = CH_3$ (III)	>90	Not isolated
OCH,		
Veratrylmethylcarbinol	>90	H
$Ar = \underbrace{-OCH_3}_{OCH_3} (IV)$	at pH 0.8	
p-Hydroxyphenylethylcarbinol Ar=OH; R=G_sH_6 (V)	<80	Corresponding sub- stituted dibenzy1 ether
Guaiacylguaiacoxymethylcarbinol Ar=OH; R=CH2-O (VI)	~40	Guiacol
OCH. OCH.		

TABLE 1. Sulfonation of Models of General Formula Ar -CH(OH) - R

ease of sulfonation of these models at the low pH values where dimerization could take place. At all pH guaiacylmethylcarbinol (III) rapidly and quantitatively formed the sulfonated derivative. Even in experiments where the reaction mixture was not stirred the amount of sulfonic acid exceeded 90% of theory. Veratrylmethylcarbinol (IV) is also easily sulfonated, and gives a sulfonated derivative quantitatively if the pH is 3 or less. At pH 7.0 (IV) essentially does not react with sulfite, and is recovered unchanged to the extent of 85-90%. p-Hydroxyphenylethylcarbinol (V) was of interest to us under the conditions of sulfite digestion because the elements of the p-hydroxyphenylpropane structure are present in rather large amounts in Siberian larch lignin. p-Hydroxybenzaldehyde and vanillin have been detected among the products from nitrobenzene oxidation of Siberian larch wood sawdust [11]. Methoxyl groups (0.9 per C_6H_3 structural element) have been found in lignin of this wood species, isolated by the mechanical grinding method [12]. Consequently, part of the elemental structural units of this lignin is not methylated.

Sulfonation of this model takes place easily at all pH; however, the yield of sulfonated derivative did not exceed 80%. In the experiments at pH 1.5 and 3.0, the yield of sulfonic acid was 50-60% of theory. The chloroform-extracted portion of the reaction mixture was a dark-colored, resinous product. Using thinlayer chromatography on KSK silica gel, two spots were detected in it, with $R_f = 0.713$ and 0.82. The substance with $R_f 0.713$ proved to be 1,1'-bis(p-hydroxphenylpropyl) ether (XII); the substance with $R_f = 0.82$ was not identified



In [13] a similar dehydration was observed for veratrylethylcarbinol when it was nitrated with 4 N HNO_3 in ether. The substituted dibenzyl ether was obtained along with nitration products. A small amount of 1,1'-bis(p-methoxyphenylethyl) ether was obtained as a by-product in the synthesis of p-methoxyphenly-methylcarbinol by the Grignard method in [14]. The authors of [2] observed the formation of di(benzohydryl) ether (XIII) under the conditions of sulfite digestion of benzohydrol, together with sulfonation of the latter, which took place to the extent of 41%



The β -guaiacyl ether of α -guaiacyl glycol (guaiacylguaiacoxymethylcarbinol) (VI) could be sulfonated only at pH 1.5. For reaction we took 2 g of material, having mp 129-130°, and after the digestion we isolated about 40% of the theoretically calculated amount of sulfonated derivative plus about 60% of the starting sample as resinous materials. The composition of the barium salt showed that replacement of the benzyl alcohol hydroxyl by a sulfonate group had occurred. Guaiacol was detected among the substances extractable with chloroform. Consequently, hydrolysis of the β -aryl-alkyl ether bond takes place as a side reaction under the conditions described. Our attempts to isolate other individual compounds from the condensation products in addition to guaiacol were unsuccessful. Cleavage of the β -alkyl-aryl bond to form guaiacol in an amount up to 10% of the starting sample was observed in [8] during sulfonation of α -veratrylglycerol β -guaiacyl ether. The yield of barium salt was approximately the same as in our work.

The formation of guaiacol from α -guaiacyl glycol β -guaiacyl ether when it is sulfonated in acid medium probably takes place analogously to the formation of guaiacol from α -guaiacylglycerol β -guaiacyl ether upon acidolysis (0.2 molar HCl in a 9:1 dioxane-water mixture, boiling for 4 h) [15]. Adler and his co-workers suggest the following scheme of acidolysis



Under the conditions indicated the yield of guaiacol was 74% of theory.

Apparently in our case sulfonation of the model takes place via a quinone methide as intermediate product, to form a stable sulfonated derivative, but because of the bulky substituent in the β -position the sulfonation is hindered, and therefore processes which lead to hydrolysis of the aryl-alkyl bond to form guaiacol and condensation products begin to play an important role. In a study of the behavior of polyaro-matic ethers during sulfonation at various pH at 135°, hydrolysis of β -aryl-alkyl bonds was not observed [16].

EXPERIMENTAL

Sulfite Digestion of Models. A 0.5-2.0 g sample of the starting carbinol, and an appropriate amount of digestion acid (liquid ratio: 1:20) having the necessary pH (0.8, 1.5, 3.0, or 7.0) were sealed in a glass ampoule. Digestion was continued for 3 h at 135°, with agitation. Isolation of the reaction products was carried out as previously described in [9].

 $\frac{Phenylmethylcarbinol (I). n_D^{20} \text{ values for the products isolated by chloroform extraction after digestion at pH 0.8-3.0 were 1.525-1.527; for the starting phenylmethylcarbinol, 1.525.$

<u>Phenylethylcarbinol (II)</u>. The product isolated by chloroform extraction after digestion at pH 1.5 had bp 97-99° (12 mm) and n_D^{21} 1.520; the starting phenylethylcarbinol has bp 98-99° (12 mm), n_D^{21} 1.520.

Guaiacylmethylcarbinol (III). The barium salt of the sulfonated derivative was analyzed. Found: C 38.10; H 4.30; S 12.03%. C₂₈H₂₂O₁₀S₂Ba. Calculated: C 36.06; H 3.69; S 10.69%.

<u>Veratrylmethylcarbinol (IV)</u>. The barium salt of the sulfonated derivative gave the following analysis. Found: C 38.37; H 4.78; S 11.27; OCH₃ 19.63%. C₂₀H₂₇O₁₀S₂Ba. Calculated: C 38.29; H 4.11; S 10.21; OCH₃ 19.8%.

<u>p-Hydroxyphenylethylcarbinol (V)</u>. Analysis of the barium salt of the sulfonated derivative. Found: S 10.37%. C₁₈H₂₂O₈S₂Ba. Calculated: S 10.69%.

<u> β -Guaiacyl Ether of α -Guaiacyl Glycol (Guaiacylguaiacoxymethylcarbinol) (VI)</u>. About 60% of the starting weight was extracted with chloroform. Guaiacol was detected chromatographically on paper (Whatman No. 1, or W. and R. Balston L.) (orange spot). The solvent system was benzene --petroleum ether (40-60°) --water (1:1:1); the developer was a 0.2% solution of 2,4-dinitrophenylhydrazine in 2 N HCl.

The syntheses of ethylphenylcarbinol, guaiacylmethylcarbinol, veratrylmethylcarbinol, and p-hydroxyphenylethylcarbinol were carried out by the Grignard method, from the appropriate aromatic aldehydes and alkylmagnesium halides. Purification of the products was effected by two or three recrystallizations or by distillation under vacuum.

<u>Ethylphenylcarbinol.</u> An oil, bp 98-99° (12 mm); n_D^{21} 1.52. Found: C 79.56; H 8.94%. C₉H₁₂O. Calculated: C 79.41; H 8.82%.

Guaiacylmethylcarbinol. Crystals, mp 100-101°. Found: C 64.65; H 7.50%. C₉H₁₂O₃. Calculated: C 64.28; H 7.14%.

<u>Veratrylmethylcarbinol.</u> Oil, bp 112° (1.5 mm). Found: C 65.33; H 7.83%. $C_{10}H_{14}O_3$. Calculated: C 65.93; H 7.69%.

<u>p-Hydroxyphenylethylcarbinol.</u> Crystals, mp 78.80°. Found: C 70.85; H 7.87%. C₉H₁₂O₂. Calculated: C 71.05; H 7.89%.

<u>Guaiacylguaiacoxymethylcarbinol</u>. Prepared by reduction of the benzyl ether of ω -guaiacoxyaceto-guaiacone [17] with hydrogen over Pd/BaSO₄ in methanol; it formed crystals which melted at 130-131°. Found: C 66.17; H 6.16%. C₁₆H₁₈O₅. Calculated: C 66.21; H 6.21%.

CONCLUSIONS

1. The sulfonation of some lignin model compounds has been performed: phenylmethylcarbinol, phenylethylcarbinol, guaiacylmethylcarbinol, veratrylmethylcarbinol, p-hydroxyphenylethylcarbinol, and guaiacylguaiacoxymethylcarbinol, under the conditions of acid bisulfite digestion. Models not substituted in the nucleus are sulfonated with difficulty even at pH 0.8, and are recovered to the extent of 80% in unchanged form. Arylalkylcarbinols with a guaiacyl structure in the aromatic nucleus are sulfonated easily at all pH; veratrylmethylcarbinol is not sulfonated at pH 7.0 and is recovered under these conditions almost entirely unchanged. Guaiacylguaiacoxymethylcarbinol was sulfonated at pH 1.5 and formed a sulfonated derivative in yield up to 40% of the theoretically possible.

2. Competing processes of acid condensation to form substances of a polymeric character take place along with sulfonation of lignin models which are substituted in the nucleus. In distinction from guaiacyland veratrylethylcarbinols, which form indane derivatives, in the case of p-hydroxyphenylethylcarbinol the formation of the corresponding dibenzyl ether was observed. Guaiacylguaiacoxymethylcarbinol forms guaiacol in a yield of about 1% of that theoretically possible, which indicates hydrolysis of the β -alkyl-aryl ether bond under the conditions of sulfite digestion.

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