Short Communications

Studies on Lignin

XV *. Nitrobenzene Oxidation of Lignin-Resorcinol Condensation Products, Methylated with Diazomethane

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In Part VI[1] it was shown that when spruce lignin or lignin sulphonic acids are heated with resorcinol in acid solution, the yield of vanillin obtained on subsequent oxidation with nitrobenzene and alkali is reduced, the decrease varying with the degree of sulphonation and the time of heating with resorcinol.

However, the yield of vanillin could not be reduced to less than about 35 % of the yield obtained from fresh spruce wood even on prolonged heating at pH 0.5. This behaviour may be explained in a number of ways [2], the most reasonable being that, owing to the instability of the resorcinol nuclei under the oxidation conditions, part of those vanillin-yielding elements which are attached to such nuclei still yield vanillin.

The latter explanation is supported by the fact that suitable model compounds containing resorcinol nuclei also give 30—35 % of the "theoretical" yield of vanillin and that resorcinol itself is completely destroyed under the standard oxidation conditions [3].

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* Part XIV. *Svensk Papperstidn.* In the press.

It was then desirable to study lignin-phenol condensation products containing more stable phenolic nuclei. Two ways have been tried; substitution of resorcinol for another phenol (2-naphthol) and methylation of the lignin-resorcinol condensation products with diazomethane.

The former method gave results comparable to those obtained with resorcinol. Thus the compound I, obtained from vanillyl alcohol and 2-naphthol, gave 36 % of the theoretical yield of vanillin and the product obtained by heating spruce wood with 2-naphthol at pH 0.5 (12 hours, 135°) gave 38 % of the "normal" yield obtained from spruce wood on nitrobenzene oxidation.
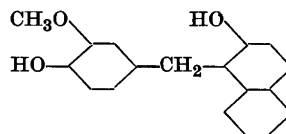
I

In order to obtain information about the behaviour of methylated phenolic nuclei under the standard oxidation conditions, a number of model compounds, obtained from vanillyl alcohol, were studied (*cf.* experimental part). On the basis of the analytical results and known analogies, these compounds were considered to have structures II—IV.

On oxidation with nitrobenzene and alkali, the compounds gave the following yields of vanillin (in per cent of the "theoretical" yield): II 5.6; III 6.6; IV 0. When resorcinol dimethyl ether was subjected to the same treatment, at least

CH3O—⟨⟩—HO CH3O—⟨⟩—OCH3
—CH—
R'
R
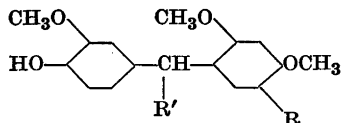
II R = H; R' = H
III R = OCH₃; R' = H
IV R = OCH₃; R' = C₆H₂(OCH₃)₃ (2,4,5)
(Szeki [4])

80 % of the material was recovered unchanged.

As a consequence of these results, various methylated lignin-resorcinol condensation products were subjected to nitrobenzene-alkali oxidation. The yields of vanillin are given in in Table 1, as compared with the yields obtained from methylated lignin preparations not heated with resorcinol and acid. The methylations were made with diazomethane in dioxan and repeated until a constant methoxyl content was obtained. In the methylations, no loss of material was observed, and thus the yields of vanillin and veratric acid

are calculated on the basis of the methoxyl content of the material before methylation. The yields of vanillin are also given in per cent of the "normal" yield obtained from spruce wood (30.5 %).

It is evident that the methylation causes a decrease in the yield of vanillin by up to 30 %, compared with the corresponding figures for unmethylated lignin-resorcinol condensation products [1]. However, methylation of untreated spruce wood causes a decrease in the yield of vanillin by 15—20 %, probably caused by the methylation of free phenolic hydroxyl groups in the vanillin-yielding elements, as shown by the occurrence of veratric acid among the oxidation products.

The figure 15—20 % conforms very well with the total content of phenolic hydroxyl groups in lignin [5,6], indicating that these groups are fairly evenly distributed among vanillin-yielding and non-vanillin-yielding elements in lignin. It is therefore reasonable to assume that most of the decrease in the yield of vanillin resulting on methyl-

Table 1. Yields of vanillin and veratric acid from lignin preparations, methylated with diazomethane.

Material	Heating with resorcinol		S/OCH₃ prior to methylation	OCH₃ after methylation	Veratric acid %	Vanillin %	
	Time, h	pH				based on OCH₃ in unmethylated material	based on "normal" yield
Extracted	0	—		8.6	1.1	25.7	84.3
	6	1.4		12.9	—	9.1	29.8
spruce	12	1.4		13.4	—	7.1	23.4
	6	0.5		15.6	0.5	4.8	15.7
wood	12	0.5		16.6	0.3	1.7	5.6
"Low sulphonated lignin"	0	—	0.34	15.4	1.5	24.1	79.0
	12	1.4	—	12.3	—	9.3	30.5
	12	0.5	0.33	14.6	—	3.8	12.4
"Further sulphonated lignin"	0	—	0.62	14.8	—	25.0	82.0
	12	0.5	0.59	13.0	—	18.4	60.3

ation of the condensation products is caused by stabilization of resorcinol nuclei attached to vanillin-yielding elements, and not simply by methylation of phenolic hydroxyl groups in such elements.

In Part VI [1] it was shown that "low sulphonated lignin" a preparation obtained by sulphonation of spruce wood at pH 5.3, gives only slightly higher yields of vanillin than wood, after reaction with resorcinol. On the other hand, lignin sulphonic acids of higher degrees of sulphonation give appreciably higher yields, approaching those from untreated wood. These results were explained by assuming that the sulphonic acid groups introduced at a fairly high pH, such as pH 5.3 (sulphonation of groups A [7]), are mainly located in non-vanillin-yielding elements, while a large proportion of the rest of the sulphonatable groups (groups B [7]) belong to vanillin-yielding elements. The sulphonation of the latter groups would then prevent the introduction of resorcinol nuclei into a large number of the vanillin-yielding elements.

This hypothesis is strongly supported by the above results, spruce wood and "low sulphonated lignin" giving only small yields of vanillin after reaction with resorcinol and methylation — yields comparable to those obtained from the corresponding model compounds referred to above.

In other words, practically all the vanillin-yielding elements contain, at the α-position, groups reactive towards resorcinol (and other phenols) in acid solution, and most of these groups seem to be of the B type.

EXPERIMENTAL

1-(4-Hydroxy-3-methoxybenzyl)-2-naphthol (I). 2-Naphthol (5 g) was dissolved in 25% ethanol (50 ml) and conc. hydrochloric acid (2 ml) added. To the boiling solution, vanillyl alcohol (2 g), dissolved in ethanol (10 ml), was added and the mixture boiled for one minute. After a few seconds an oil precipitated. On cooling, crystals were obtained (1.2 g, 33%).

Recrystallization from 50% ethanol gave colourless plates of m.p. 166—166.5°. (Found OCH_3 11.0; $C_{17}H_{13}O_2OCH_3$ requires OCH_3 11.1.)

4-Hydroxy-3',4',5'-trimethoxydiphenylmethane (II). To a boiling solution of resorcinol dimethyl ether (9 g) in ethanol (75 ml) and conc. hydrochloric acid (2 ml), vanillyl alcohol (3 g), dissolved in ethanol (20 ml), was added dropwise during a period of ca. 15 minutes. Then the mixture was boiled for 30 minutes, water added and the mixture extracted with ether. The ethereal solution was dried over sodium sulphate, the ether distilled off, and the residue distilled *in vacuo*. First, the excess resorcinol dimethyl ether went over (95—102°) and then at 236—238° (12 mm) a product distilled (2.5 g, 47%) which crystallized on cooling and scratching. The product was recrystallized from benzene-light petroleum. Colourless prisms of m.p. 72.5—73.5°. (Found OCH_3 33.8; $C_{13}H_9(OCH_3)_3$ requires OCH_3 33.9.)

The above compound was reacted with benzoyl chloride in anhydrous pyridine, yielding a *benzoate* melting at 109—110°, after recrystallization from acetic acid. (Found OCH_3 24.3; $C_{20}H_{13}O_2(OCH_3)_3$ requires OCH_3 24.6.)

4-Hydroxy - 3,2',4',5' - tetramethoxydiphenylmethane (III). Hydroxyhydroquinone trimethyl ether (3 g) and vanillyl alcohol (1 g) were reacted as described above. The ether extract was distilled *in vacuo*, yielding the excess hydroxyhydroquinone trimethyl ether as a yellow oil. The distillation residue crystallized on trituration with benzene (1 g, 51%). Recrystallization from light petroleum yielded colourless, coarse prisms of m.p. 110—111°. (Found OCH_3 41.0; $C_{13}H_9(OCH_3)_4$ requires OCH_3 40.8.)

Methylation of lignin-resorcinol condensation products with diazomethane. The methylations were carried out using a dioxan suspension of the finely pulverized lignin material. The lignin sulphonic acids were employed in the form of their barium salts.

In a typical run the following procedure was used:

A product obtained on heating extracted spruce wood powder with resorcinol at pH 0.5 for 10 hours at 135° (10 g) was suspended in dioxan (75 ml). A solution of diazomethane (ca. 3 g) in dioxan (150 ml) was added and the mixture left overnight. Then the mixture was filtered and the solid residue washed with dioxan and acetone. The procedure was repeated until a constant methoxyl content was obtained, as illustrated in Table 2.

In general 3 to 4 methylations were required.

Table 2. Variation of methoxyl content with number of methylations.

Material	Weight, g	OCH₃, %
Unmethylated material	10.0	4.1
After 1st methylation	10.0	10.7
» 2nd »	9.9	15.4
» 3rd »	9.7	16.8
» 4th »	9.7	16.6

Fig. 1. The solubility of decanediol in sodium oleate solutions at 20° C.

The nitrobenzene oxidations and the estimations of vanillin and veratric acid were carried out as described in previous communications [8,9].

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A new Solubilization Effect

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When hydrocarbons are solubilized by aqueous association colloid solutions the conductance is very little altered. When the solubilized substance is a polar compound such as a long-chain primary alcohol or fatty acid, a decrease in the con-
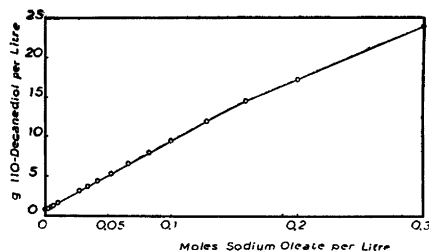
ductance is frequently noted. The solubilization of the glycol, 1,10-decanediol, however, leads to a marked increase in the conductance. This latter phenomenon has not been described previously.

One of us has shown that sodium oleate solutions are able to solubilize fairly large amounts of 1,10-decanediol [1] and the saturation capacity of oleate was preliminarily estimated at about 66 g diol per mole oleate at 20° C. We have now conducted a more detailed study of the solubilization of decanediol. The solubility values were determined with a Zeiss-Löwe interferometer for liquids. The solubility in pure water and in salt solutions of low ionic strength is only 720—730 mg per liter at 20° C and 1 400 mg per liter at 40° C. These values are lower than those previously used and hence the amounts solubilized are actually greater. Fig. 1 shows the relation between the solubility of the diol at 20° C and the oleate concentration. Decanediol does not seem to be solubilized by oleate solutions below 0.0015 M. The increase in the solubility of decanediol is linear over a fairly wide oleate concentration range up to about 0.17 M. In this range the saturation capacity of the micellar oleate is 82 g decanediol per mole oleate, *i.e.* 0.5 mole decanediol per mole oleate.

As already mentioned, the solubilized decanediol brings about a marked increase in the conductance of the oleate

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