

Substituted Benzyl Alcohols as Lignin Models. II *

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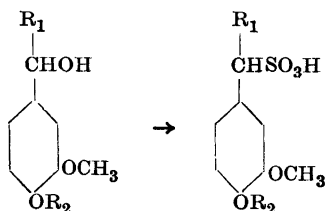
In the investigations of the nature of the reactive groups in lignin responsible for its sulphonation, different model substances play a great rôle. Holmberg¹ showed, in an important paper, that α -phenethyl alcohol reacts with bisulphite under the conditions of the technical sulphite cook: $C_6H_5 \cdot CH(OH) \cdot CH_3 \rightarrow C_6H_5 \cdot CH(SO_3H) \cdot CH_3$. This alcohol resembles lignin not only as regards sulphonation but also in other respects, *e. g.* reaction with thioglycolic acid² and with ethanolic hydrochloric acid³. For that reason Holmberg considered that a hydroxyl group, activated by a benzene ring in α -position, is of great importance, not only in the reactions of lignin mentioned above, but also in the condensation reactions of lignin. Wacek and Kratzl^{4a}, however, pointed out that the yield of sulphonic acid from α -phenylpropyl alcohol is low, and therefore consider these alcohols unsuitable as lignin models.

Setting out from Freudenberg's theory of the sulphonation of lignin, Richtzenhain⁵ examined the reactions of different benzyl ethers with sulphite cooking acid. The formation of sulphonic acids was far too slow to correspond to the sulphonation of lignin. Investigations, made not only on the benzyl ethers but also on substituted chalcones^{4b}, however, showed that substituents in the benzene ring have a great influence on the yield of sulphonic acids.

Results to be published by Erdtman, Lindgren and Pettersson⁶ show that the sulphonation of 'low sulphonated lignin sulphonic acids' is due to a substitution of hydroxyl groups of outstanding reactivity. For these reasons a series of alcohols which appear to be more lignin-like than α -phenethyl and α -phenylpropyl alcohols have been subjected to sulphite cooking. Vanillyl alcohol (I), veratryl alcohol (II), apocynol (III), and 3,4-dimethoxy- α -phenethyl alcohol (IV) were heated with normal sulphite cooking acids and were found

* Part I, preliminary communication. *Acta Chem. Scand.* 1 (1947) 779.

to react rapidly and quantitatively (compare Table 1) to yield the corresponding sulphonic acids (V—VIII). (A similar reaction is used for making cation exchange resins ⁷.)



	I	R ₁ = H	R ₂ = H		V	R ₁ = H	R ₂ = H
	II	R ₁ = H	R ₂ = CH ₃		VI	R ₁ = H	R ₂ = CH ₃
	III	R ₁ = CH ₃	R ₂ = H		VII	R ₁ = CH ₃	R ₂ = H
	IV	R ₁ = CH ₃	R ₂ = CH ₃		VIII	R ₁ = CH ₃	R ₂ = CH ₃

The model substances studied by other researchers are subject to two fundamental objections. They either react far too slowly with bisulphite or they contain groups (carbonyl groups or C=C-groups) which, obviously, do not occur in lignin, at least not to such a degree that they can be responsible for the sulphonation reaction. The alcohols (I—IV), however, are not subject to these objections.

It has been assumed that lignin contains two different, sulphitable groups ^{8,9}. The one group should be characterized by greater reactivity, such as easier sulphitability, greater condensation power etc. The great reactivity of the alcoholic hydroxyl group in vanillyl alcohol decreases considerably if the phenol group is methylated. Therefore, it has been examined by model tests whether these two groups in lignin could be benzyl alcohol groupings, in the one case activated by a free phenolic hydroxyl group in para position (model vanillyl alcohol), and in the other case by an alkyl ether group in the same position (model veratryl alcohol).

THE RELATION BETWEEN SULPHONATION AND CONDENSATION

Lignin shows a characteristic relation between sulphonation and condensation. It was therefore examined whether it was possible to imitate this relation with the model alcohols. Corey and Maas ¹⁰ showed that if dry wood powder is heated in nitrogen, or in toluene, at 130° for six hours, the wood can be delignified as easily as unheated wood by sulphite cooking. If the heating is accomplished in water, however, it is considerably more difficult to dissolve the lignin by sulphite cooking. In fact, the wood treated in this way had to be heated with sulphite cooking acid twice as long as untreated wood to

obtain the same degree of delignification. This may be explained in the following way: there are two sulphitable groups in lignin, group α and group β . When heated in water only group α condenses. None of the groups condense if wood is heated dry or in toluene.

Vanillyl alcohol behaves in the same way as group α , and veratryl alcohol like group β . Vanillyl alcohol did not polymerize when heated in a toluene solution or in air, and the alcohol was easily recovered in the form of crystals. In water vanillyl alcohol polymerized to a product which did not dissolve when heated with sulphite cooking acid. Veratryl alcohol did not polymerize even when heated with water.

HEATING OF LIGNIN AND MODEL SUBSTANCES WITH SULPHITE SOLUTIONS OF DIFFERENT pH

Hägglund and Johnson⁹ have investigated the sulphonation of wood using sulphite solutions of different acidities. It appeared that lignin is easily sulphonated by a sulphite solution of pH about 5 to a lignin sulphonic acid

Table 1. The yield of sulphonic acid at various cooking times and various acidities. The temperature was always 135°.

	5 % SO ₂					
	0.7 % NaOH pH = 1.5		4.5 % NaOH pH = 6.4		8.7 % NaOH pH = 11-12	
	Time hour	Yield %	Time hour	Yield %	Time hour	Yield %
Vanillyl alcohol	1/2	100	1/2 1	100 100	1/2 1	95 95 *
Veratryl alcohol	1/2 1 1/6	80 95	1 16 1/2	45 70	1 1/2 26	25 50
3,4-Dimethoxy-phenethyl alcohol	1/2 1	95 100	15	70	2 1/4 24	20 30

* 0.5 g of pyridinium salt of V isolated (65 % yield).

containing on the average one sulphur atom per three to four methoxyl groups. Further sulphonation is very difficult to bring about. That may also be explained by considering two sulphitable groups in lignin, only one of which can be easily sulphonated by sulphite solutions of a high pH. Therefore it was of interest to examine the sulphonation of the model alcohols with sulphite solutions of different acidities, (see Table 1).

From this table it can be seen that the rate of sulphonation of vanillyl alcohol was high even with sulphite solutions of high pH, but that the rate of sulphonation of veratryl alcohol and 3,4-dimethoxy- α -phenethyl alcohol was low at a high pH. (By cooking with a sulphur dioxide solution containing no sodium hydroxide, non-reproducible yields of sulphonic acid and polymerized alcohol were obtained.)

HEATING OF LIGNIN AND MODEL SUBSTANCES WITH SULPHITE SOLUTIONS IN THE PRESENCE OF A REACTIVE PHENOL

If wood is heated with technical sulphite cooking acid (pH = 1.5—2) in the presence of a reactive phenol (*e. g.* resorcinol or pinosylvin) the lignin reacts with the phenol to form an insoluble product^{8, 11}. If, however, lignin is heated with sodium bisulphite solution (pH = 4.5) in the presence of resorcinol, it is sulphonated to a certain degree and, afterwards, it can be dissolved by an ordinary sulphite cooking procedure (Graham's method). These observations were explained by assuming that there are two sulphitable groups in the lignin⁸: group A and group B, which have the following properties:

- Group A. 1) Is sulphonated easily with sulphite solution at pH 1.5—2 and at pH 4.5.
2) Reacts more quickly with phenols than with bisulphite at pH 1.5—2.
3) Reacts more quickly with bisulphite than with phenols at pH 4.5.
- Group B. 1) Is sulphonated easily with sulphite solution at pH 1.5—2.
2) Does not react at all or slowly with sulphite solution at pH 4.5.
3) Reacts more quickly with bisulphite than with phenols at pH 1.5—2.
4) Does not react at all or slowly with phenols at pH 4.5.

In model tests it appeared as if the vanillyl alcohol behaved like group A. By heating with a normal sulphite cooking acid (pH = 1.5—2) in the presence of resorcinol, an insoluble condensation product and a small amount of sulphonic

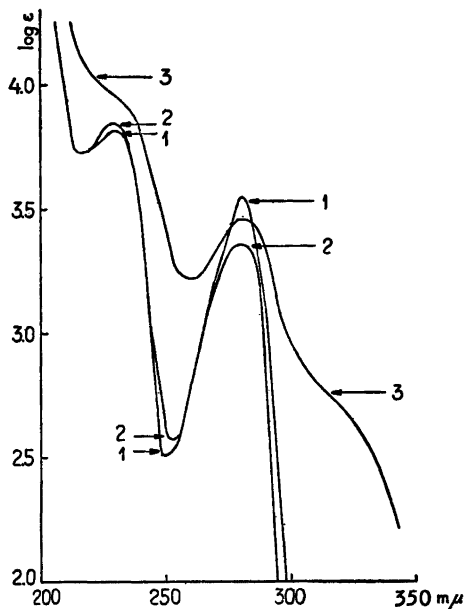


Fig. 1. Ultra-violet spectra.

1. Vanillyl alcohol (in ethyl alcohol).
2. Guaiacyl-methane sulphononic acid (in water).
3. Lignin sulphononic acid (in water)¹².

acid were obtained. When heated with sodium bisulphite solution (pH = 4.5), however, the vanillyl alcohol only yielded sulphononic acid.

On the other hand, veratryl alcohol did not behave like group B, as it condensed with resorcinol in normal sulphite cooking acid.

SAFROLE GLYCOL

It is necessary that the hydroxyl group be in the α -position to the benzene ring for reaction with bisulphite. When safrole glycol (3,4-methylenedioxy-1², 1³-dihydroxy-1-propyl-benzene) was heated with sulphite cooking acid it was recovered unchanged. The alcohol was recovered unchanged even after heating with ethanolic hydrochloric acid under such conditions when α -phenethyl alcohol reacts to form ethyl α -phenethyl ether. Thus in both these respects safrole glycol is not a suitable lignin model.

The ultra-violet spectra of vanillyl alcohol and guaiacyl-methane sulphononic acid (V) have been measured (Fig. 1). Like the spectrum of lignin, they show maxima at 230 and at 280 $m\mu$ but, they show no maximum at 320 $m\mu$.

During the course of these experiments it was observed that when sulphur dioxide was led into a water solution of any of the alcohols (I–IV) the solution turned yellow. The colour appeared even in ether or benzene solutions. The colour is evidently due to the formation of an addition product of sulphur dioxide and the alcohol. This addition product is very labile. When the sulphur dioxide was removed by leading nitrogen through the solution, the colour rapidly disappeared. Obviously this addition product has nothing to do with the sulphonation reaction, since the sulphonic acids (V–VIII) as well as even simple phenols produced this colour.

EXPERIMENTAL

Sulphite cooking of benzyl alcohols (I–IV)

1 g of alcohol (I–IV) was heated with 60 ml of sulphite cooking acid (1 % calcium oxide, 6–8 % total sulphur dioxide) for three hours at 135°. The alcohols were thereby completely dissolved. In order to remove free sulphur dioxide, nitrogen was passed through the solution until the smell of sulphur dioxide disappeared. The solutions were extracted with ether, and the extracts dried over sodium sulphate and evaporated. No residues were obtained. The solutions were passed through a column of cation exchange resin (Wofatit K) in the hydrogen state in order to exchange the cations for hydrogen ions. The acid solutions were neutralized by suspending barium carbonate in the solution, centrifuged, and evaporated to dryness. The crude barium salts of the sulphonic acids (V–VIII) crystallized when the residues were treated with ether or acetone. The barium salts were purified by

1) dissolving the products in aqueous methanol, filtering and precipitating the barium salts with ether (V, VI, VII)

2) re-crystallizing the product from 98 % alcohol (VIII).

The yield of crude products was quantitative.

Sulphonic acids (V–VIII) were characterized as pyridinium salts. (The benzylthio-uronium salts were too soluble in water and therefore unsuitable.) The barium sulphonates were dissolved in water, and the barium ions were exchanged for hydrogen ions by means

Pyridinium salts of	Melting point	Sulphur, %	
		Calc.	Found
Guaiacyl-methane sulphonic acid (V)	189–190°	10.8	10.6
Veratryl-methane sulphonic acid (VI)	149°	10.3	9.9
α -Guaiacyl-ethane sulphonic acid (VII)	164–164.5°	10.3	10.3
α -Veratryl-ethane sulphonic acid (VIII)	148°	9.8	9.9

of cation exchange resin. The solutions were neutralized with pyridine and evaporated in a vacuum to dryness. The pyridinium salts obtained were purified by

- 1) re-crystallizing from methanol (V)
- 2) re-crystallizing from pyridine (VI)
- 3) re-precipitating the methanol solution with ether (VII, VIII).

Heating of vanillyl alcohol in air, toluene and water

Vanillyl alcohol was heated in a drying oven for six hours at 130°. The alcohol melted to a brown oil. This oil was dissolved in hot benzene. On cooling the solution, vanillyl alcohol crystallized.

1 g of vanillyl alcohol was heated for six hours at 130° in a sealed tube with, in one case, 50 ml of toluene, and in the other, with 50 ml of water. In both cases the alcohol dissolved in the hot liquid. After two hours, polymerized vanillyl alcohol began to precipitate from the water solution. After six hours all vanillyl alcohol was precipitated. The polymerized vanillyl alcohol could not be dissolved by heating with sulphite cooking acid at 130° for three hours.

In toluene solution, however, the vanillyl alcohol was still unchanged even after six hours. On cooling the toluene solution, the vanillyl alcohol crystallized.

Veratryl phenylcarbamate

1 g of veratryl alcohol was mixed with 1 g of phenyl isocyanate and the mixture was heated for ten minutes on a steam bath. The phenylcarbamate was re-crystallized from benzene. M. p. 118°.

$C_{14}H_{11}O_2N(OCH_3)_2$	Calc.	N	4.9	OCH_3	21.6
	Found	»	4.7	»	21.5

Heating of veratryl alcohol in toluene and water

1 g of veratryl alcohol was heated with 20 ml of distilled water for six hours at 130°. 40 ml of sulphite cooking acid (1.1 % sodium hydroxide and 8.5 % sulphur dioxide) were added, and the solution was heated for five hours at 135°. The solution was extracted with ether; the extract contained 0.1 g of an oil.

The water solution was evaporated to dryness and the residue was extracted with hot alcohol. The alcohol extract contained 1.32 g of impure sodium salt of veratryl-methane sulphonic acid (OCH_3 : found 21.6 %, calc. 24.4 %). The product contained 78 % of the methoxyl groups of the veratryl alcohol employed in the experiment. It was recrystallized from alcohol. The product now contained 24.4 % OCH_3 .

0.5 g of veratryl alcohol was heated with 20 ml of toluene for 18 hours at 130°. 0.4 g of phenyl isocyanate was added and the carbamate was synthesized in the manner mentioned above. 0.6 g of a product m. p. 115.5° was obtained. After re-crystallization from benzene m. p. 118°. Mixed m. p. with veratryl phenylcarbamate 118°.

Heating of vanillyl alcohol with sulphite cooking acid and resorcinol

1 g of vanillyl alcohol was mixed in a tube with 0.71 g of resorcinol (1 mole resorcinol per mole vanillyl alcohol) and 50 ml of sulphite cooking acid (6.6 % sulphur dioxide, 1 % calcium oxide). The mixture was heated slowly to 100° (two hours) in a drying oven. Thereafter the tube was heated further for three quarters of an hour at 130° (this temperature schedule corresponds to that used by Erdtman⁸ his studies of the delignification of wood in presence of phenols). After being heated, the tube contained a clear yellow solution and a thick brown oil. On cooling, the solution became cloudy. Nitrogen was passed through the solution in order to remove most of the free sulphur dioxide. The solution was shaken repeatedly with ether. The brown oil which was formed during cooking was also dissolved in the ether. The extract was dried over sodium sulphate and evaporated. 1.6 g of an oil were obtained as a residue.

The cations of the aqueous solution were exchanged for hydrogen ions whereafter the solution was neutralized with barium hydroxide solution. The cloudy (barium sulphate) solution was evaporated in a vacuum to dryness. The residue was extracted with water, the water extract was centrifuged and evaporated to dryness on a water bath. Residue (impure barium salt of guaiacyl-methane sulphonic acid) 0.2 g (yield 12 %).

Heating of vanillyl alcohol with sodium bisulphite solution and resorcinol

1 g of vanillyl alcohol, 0.85 g of resorcinol and 50 ml of 15 % sodium bisulphite solution were heated slowly to 90° (two hours). The temperature was then rapidly increased to 130°, and the tube heated for an hour at that temperature. During the heating the vanillyl alcohol dissolved completely in the bisulphite solution. The solution was shaken with ether, and 0.74 g of resorcinol was obtained from the ether extract.

The sodium ions of the water solution were exchanged for hydrogen ions, nitrogen was passed through the solution until the smell of sulphur dioxide disappeared. The solution was evaporated in a vacuum, neutralized with barium hydroxide and filtered. Barium ions were exchanged for hydrogen ions and the solution was mixed with a few ml of pyridine and evaporated in a vacuum to dryness. The residue was a crystalline substance, which was dissolved in water, filtered, and evaporated on a water bath. The residue consisted of 1.1 g of crystals; m. p. 188°; undepressed by the pyridinium salt of guaiacylmethane sulphonic acid.

Heating of veratryl alcohol with sulphite cooking acid and resorcinol

1 g of veratryl alcohol and 2 g of resorcinol were dissolved in 60 ml of sulphite cooking acid (1 % calcium oxide, 5.1 % sulphur dioxide). The temperature of the solution was increased to 100° during two hours. The temperature was then increased to 120° during half an hour and to 130° during another 1 1/2 hours. During the heating an insoluble oil was formed. On cooling, it yielded crystals contaminated with oily impurities (0.79 g total). Carbon dioxide was passed into the filtrate and a white crystalline substance (0.50 g) was obtained. The latter was re-crystallized from benzene, and 0.1 g of a product was obtained, m. p. 153°. This product contained 25.5 % OCH₃. The compound formed from

one molecule of resorcinol and one molecule of veratryl alcohol by loss of one molecule of water would contain 23.8 % OCH_3 . The material was obviously an impure condensation product of these substances.

Heating of vanillyl alcohol, veratryl alcohol, and 3,4-dimethoxy- α -phenethyl alcohol with sulphite solutions of different pH (Table 1)

Mixtures of 0.5 g of veratryl, vanillyl, or 3,4-dimethoxy- α -phenethyl alcohol and 40 ml of a sulphite solution containing 0, 0.7, 4.5, or 8.7 % sodium hydroxide and 5 % total sulphur dioxide; (pH at room temperature 1.1, 1.5, 6.4, or 11–12 respectively) were heated in steel tubes by immersing the tubes in a glycerol bath at 135° for five minutes. The temperature of the sulphite solutions was raised to 135° in about three minutes. The tubes were then brought to rotate in a drying oven for different lengths of time at 135°.

After being heated, the sulphite solutions were extracted three times with ether. The ether extracts were washed with water and evaporated to dryness. The residues were considered to be unsulphonated alcohols. The yields of sulphonic acids were calculated from the weight of the residues.

By cooking with sulphite cooking acids containing no base (pH = 1.1) the alcohols were not recovered. Instead, amorphous condensates of the alcohols were obtained.

Experiments with safrole glycol

1 g of the alcohol was heated with 25 ml of sulphite cooking acid (1 % calcium oxide, 7 % sulphur dioxide) for five hours at 118° and thereafter for ten hours at 135°. After being heated, the cooking acid contained an oil from which crystals of safrole glycol (0.93 g) were obtained.

A solution of safrole glycol in ethanolic hydrochloric acid (2 % HCl) was refluxed for two and a half hours. The solution was poured into water when crystals of safrole glycol were obtained.

SUMMARY

Vanillyl alcohol, veratryl alcohol, apocynol, and 3,4-dimethoxy- α -phenethyl alcohol have been studied as lignin models in the following respects:

- a) sulphite cooking at different pH,
- b) sulphite cooking in the presence of resorcinol,
- c) polymerization reactions.

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Received June 17, 1949.