ACTA CHEMICA SCANDINAVICA 4 (1950) 1365–1374

Veratryl Alcohol, Diveratryl Ether, and Veratryl-ethyl Ether as Lignin Models

BENGT O. LINDGREN

Department of Cellulose Technology and Wood Chemistry, Royal Institute of Technology, Stockholm, Sweden

Holmberg [1] showed that lignin behaves as α-phenethyl alcohol in its reactions with sulphite cooking acid, thioglycollic acid, and ethanolic hydrochloric acid. For that reason he considered that these lignin reactions may be due to benzyl alcohol groups, or because of the great reactivity of these alcohol groups, to benzyl ether groups in the lignin. He also considered that the lignin molecule may be bound in the wood by benzyl ether linkages to other lignin molecules or to carbohydrate molecules.

On the assumption that phenolic groups are formed during the sulphonation of lignin, Freudenberg [2] considered that the groups responsible for the sulphonation are benzyl-*aryl* ether and benzyl alcohol groups. Later Freudenberg, Lautsch, and Piazolo [3] showed, however, that no phenolic groups are formed during the sulphonation. For that reason they considered that the ether group may be a benzyl-*alkyl* one, as, for example, in pinoresinol.

Benzyl alcohols have recently been found to be suitable lignin models in many respects [4–6]. These alcohols are easily transformed into ethers (called to the author's attention by E. Adler). Hedén and Holmberg [7] showed that α-phenethyl alcohol is transformed into α-phenyl-ethan-sulphonic acid and di-(α-phenethyl) ether if an excess of the alcohol is heated with sulphite cooking acid. If *p*-methoxy-α-phenethyl alcohol [8] and veratryl alcohol (compare experimental part) are kept at room temperature for a few months they are partly transformed into the corresponding ethers.

It has been assumed that there are two groups in lignin responsible for its sulphonation [9, 10]. On the basis of the above-mentioned results and theories, the author has examined if the reactivity of veratryl alcohol and diveratryl ether run parallell to the reactivity of the lignin groups. For that reason

the earlier studies on the reactions of veratryl alcohol [4] have been improved and extended.

Reactions of veratryl alcohol and diveratryl ether with sulphite solutions

If veratryl alcohol is heated at 135° with a normal sulphite cooking acid it readily forms 3,4-dimethoxy-toluene-ω-sulphonic acid [4]. The sulphonation rate of the alcohol decreases with increasing pH (see Table 1. All pH values were measured at room temperature). The decrease in the rate can not be due to the formation of diveratryl ether, because the unsulphonated substance which was recovered after heating for 20 hours at pH 7 was, for the main part, veratryl alcohol.

Table 1 also shows that diveratryl ether readily forms 3,4-dimethoxy-toluene-ω-sulphonic acid with sulphite solutions of pH 1.4—2.5. At pH 3.7 to 5.9 the sulphonation rate rapidly decreases. Table 2 shows the amounts (in per cent of diveratryl ether employed) of the ether which were not recovered after heating with sulphite solutions of pH 3.7—5.9.

Table 1. The yields of 3,4-dimethoxy-toluene-ω-sulphonic acid from veratryl alcohol ("A") and diveratryl ether ("E") by heating at 135° with sulphite solutions of varying pH. pH determined at room temperature.

Time, hours	pH															
	1.4		1.9	2.5	3.7		4.2		5.0		5.9		7.0	8.7	11.0	
	A	E	E	E	A	E	A	E	A	E	A	E	A	A	A	E
½	96	94														
1	96	97														
3 ½			93	91	69	24	56	3		2	27	1				
10					91	65	83	30	60	6						
20					96	81	98	91	84	10	58	2	43	40	44	0

Table 2. The amounts of diveratryl ether hydrolyzed at 135° by sulphite solutions with varying pH. pH determined at room temperature.

Time, hours	pH				
	3.7	4.2	5.0	5.9	11.0
3 ½	42	15	2	1	
10	75	42	8		
20	94	97	13	2	0

Table 3. The yields of S-veratryl-thioglycollic acid from veratryl alcohol and diveratryl ether on heating at 100° for 4 hours with thioglycollic acid solutions of varying pH, and the amounts of diveratryl ether recovered.

pH	Thioglycollic acid derivative obtained from		Diveratryl ether recovered
	the alcohol	the ether	
0.8	86	84	0
1.4	86	78	0
2.0	80	65	4
3.0	57	0	80
4.0	47	0	96

To summarize, veratryl alcohol and diveratryl ether are readily sulphonated at pH 1.4—3.7. At pH 6 and higher the ether reacts scarcely at all. The alcohol is sulphonated even at pH 11 at an appreciable rate. (Vanillyl alcohol * is sulphonated much more rapidly than veratryl alcohol at higher pH[4].)

Reactions of veratryl alcohol and diveratryl ether with thioglycollic acid

The model substances were heated at 100° for 4 hours with thioglycollic acid-sodium thioglycollate solutions of varying hydrogen ion activity. Table 3 shows the yields of S-veratryl-thioglycollic acid and the amounts of diveratryl ether recovered. Both substances readily react at low pH (0.8—1.4). At higher pH (3.0—4.0) only the alcohol reacts. The yields of veratryl-thioglycollic acid formed are up to 15 per cent (absolute) higher than those recorded in the table for some of the acid was lost during its isolation.

These two points, sulphonation and reaction with thioglycollic acid, are to be discussed in forth-coming papers concerning the sulphonation of lignin at high pH, and the reaction of lignin with thioglycollic acid.

Reactions of veratryl alcohol and diveratryl ether with sulphite solutions containing β-naphthol

If vanillyl alcohol is heated with a normal sulphite cooking acid (pH 1.5—2) containing resorcinol, the condensation with the phenol predominates over the sulphonation [4]. At pH 4.5, however, the sulphonation predominates. The

* Added in proof. A lignane with *p*-hydroxybenzyl ether groups, pinoresinol, also reacts in this way (B. O. Lindgren, forthcoming paper).

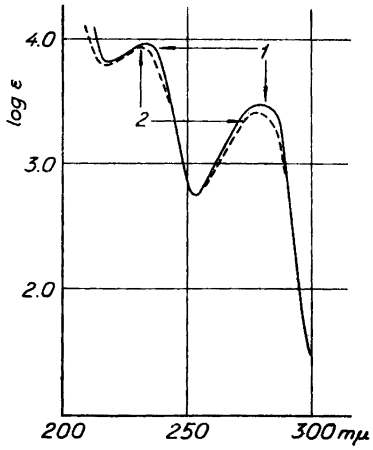

Fig. 1. Ultra-violet spectra.
1. *Diveratryl ether (in alcohol).*
2. *Sodium salt of 3,4-dimethoxy-toluene-ω-sulphonic acid (in water).*

poly-benzyl alcohols synthesized and examined by Erdtman and Leopold [5] also react in this way.

Because resorcinol is transformed into a sulphonic acid by long heating with sodium bisulphite solution [11], β-naphtol was used in the following experiments. This phenol does not react with sulphite solutions during the conditions used in these experiments (compare experimental part).

When veratryl alcohol was heated with sulphite solutions containing β-naphthol it was transformed partly into a condensation product with the phenol, and partly into the sulphonic acid. As β-naphthol has only one strongly reactive position (the α-position), it was postulated that the condensation product was formed from one molecule of the phenol and one molecule of the alcohol by loss of one molecule of water. The product was not further investigated. On this assumption Table 4 shows the yields of the condensation product from veratryl alcohol. It also shows the number of moles of naphthol (determined from the amounts of the phenol recovered) which reacted per mole of veratryl alcohol employed.

Table 4. Heating of veratryl alcohol with sulphite solutions containing β-naphtol.

	pH of the sulphite solution		
	1.4	2.8	5.4
The condensation product: weight, g	1.49	0.76	0.15
yield, %	85	43	8
Moles of β-naphtol reacted per mole of veratryl alcohol employed	0.92	0.51	0.09

Veratryl alcohol reacts similarly to the other benzyl alcohols which have been examined in this way. At low pH the condensation predominates, at higher pH the sulphonation.

At pH 2 diveratryl ether reacts as veratryl alcohol. At pH 5.3 the ether was recovered almost quantitatively (84 %) after heating for 24 hours. The rest of the ether was evidently sulphonated, as no condensation product was obtained.

Reactions of veratryl alcohol and diveratryl ether with ethanolic hydrochloric acid

Berg and Holmberg [12] have shown that α-phenethyl alcohol reacts with ethanolic hydrochloric acid with the formation of α-phenethyl-ethyl ether. They considered this as a model reaction for the introduction of ethoxyl groups into lignin when wood is treated with ethanolic hydrochloric acid.

Veratryl alcohol and diveratryl ether also yielded the corresponding ethyl ether when refluxed with ethanolic hydrochloric acid (0.1—0.55 N). During these reactions condensation products were also obtained: in the case of 1 N acid the model substances yielded 2,3,6,7-tetramethoxy-9,10-dihydro-anthracene. (This compound has been obtained by G. M. Robinson [13] by condensation of veratryl alcohol with acetic acid in the presence of hydrochloric acid.) As the complete delignification of wood by ethanolic hydrochloric acid has not yet been achieved, it is generally assumed that lignin, like the above-mentioned model substances, partly condenses during this treatment.

Treatments of veratryl alcohol and diveratryl ether with acetic anhydride and pyridine

The above-mentioned experiments show that diveratryl ether is easily hydrolyzed. To prove if dibenzyl ether linkages are split under the conditions employed in the acetylation of ligninsulphonic acids [14], diveratryl ether was treated in the same manner as these lignin preparates. The ether was recovered unchanged after the treatment. Veratryl alcohol was transformed into veratryl acetate under these conditions.

Reactions of veratryl-ethyl ether with thioglycollic acid and sulphite cooking acid

Berg and Holmberg [12] showed that ethanol lignin reacts with thioglycollic acid with a loss of ethoxyl groups. Veratryl-ethyl ether (like α-phenethyl-

ethyl ether [12]) is a good model substance for this reaction. It is easily transformed into veratryl-thioglycollic acid by thioglycollic acid and hydrochloric acid.

Erdtman and Pettersson [15] showed that ethoxylated low sulphonated ligninsulphonic acids obtained from wood according to the Kullgren process [16] can be sulphonated by normal sulphite cooking acid with loss of the ethoxyl groups. In the same way the ethoxyl group of veratryl-ethyl ether can easily be substituted for a sulphonic acid group.

EXPERIMENTAL *

The reduction of veratraldehyde by hydrogen and platinum

Veratraldehyde [17] (100 g) was reduced by hydrogen and platinum activated by iron according to the method used by Carothers and Adam [18] to synthesize several other benzyl alcohols. The oil obtained was distilled, veratryl alcohol being collected in the distillate at 157—160° (5 mm Hg) (75 g, yield 74 %).

The distillation residue crystallized on cooling. Repeated recrystallizations raised the m. p. of the product from 60—62° to 69—72° (8.3 g, yield 9 %). The product gave no m. p. depression with diveratryl ether, synthesized according to Method 1 described below.

The syntheses of diveratryl ether

1. Potassium (1.3 g) was pulverized in the usual manner in toluene (30 ml). Veratryl alcohol (5.8 g) dissolved in toluene (20 ml) was added. The mixture was refluxed for 1 hour. A further amount of veratryl alcohol (2 g) dissolved in toluene (10 ml) was added and the mixture refluxed for a further half hour. Veratryl chloride [19] (6.4 g) dissolved in toluene (25 ml) was then added and the mixture refluxed for 1 hour and then left over night at room temperature.

The potassium chloride was filtered off and the filtrate passed through a column (3 × 10.5 cm) containing aluminium oxide. The toluene was distilled off under vacuum. The residue crystallized (8.5 g). Recrystallization from methanol yielded a product with the m. p. 68—70° (7.2 g, yield 65 % calc. from the amount of veratryl chloride employed).

Repeated recrystallizations yielded a product with the m. p. 70—72.5°. The analyses agree with the compound being diveratryl ether.

$C_{18}H_{22}O_5$	Calc.	OCH_3	39.0	C	68.0	H	6.93
	Found	»	39.3	»	68.0	»	6.96

2. If veratryl alcohol was kept at room temperature a few months it was partly transformed into diveratryl ether (about 10 %).

3. See the reduction of veratraldehyde above.

* All m.p. uncorr. M.p. made on aluminium-block.

Reactions of veratryl alcohol and diveratryl ether with ethanolic hydrochloric acid

Veratryl alcohol (2 g) was heated with ethanolic hydrochloric acid (10 ml) of varying concentration (0.01, 0.1, 0.55, and 1 N) on a steam bath for 4 hours. The solution was neutralized with potassium hydroxide and evaporated in a vacuum. The residue was distilled. An oil with the boiling temperature 152—154° (20 mm Hg) and $n_D^{20} = 1.519$ was obtained. The analysis agrees with the compound being veratryl-ethyl ether.

$C_{11}H_{16}O_3$	Calc.	Alkoxyl	(calc. as OCH_3)	47.4
	Found	»	» » »	46.9

The yields of veratryl-ethyl ether were: 0.01 N acid 56 %, 0.1 N 58 %, 0.55 N 32 %, and 1 N 0 %.

During the heating with N acid a precipitate was observed. It was filtered off (m. p. 227°, yield 20 %). The product gave no m. p. depression with 2,3,6,7-tetramethoxy-9,10-dihydro-anthracene, synthesized from veratrol and formaldehyde [13].

Diveratryl ether was treated in the same way. The yields of veratryl-ethyl ether were: 0.1 N acid 49 %, 0.55 N 16 %, and 1 N 0 %.

With 1 N acid the anthracene derivative was obtained in a yield of 89 %.

Reactions of veratryl alcohol, diveratryl ether, and veratryl-ethyl ether with sulphite solutions

Diveratryl ether (0.6 g) was mixed with sulphite cooking acid (60 ml, 0.7 % NaOH and 5 % total SO_2) and heated in a rotating tube for 3 hours at 135°. After the heating all the ether was dissolved. The barium salt of the sulphonic acid was isolated by the method described before [4], its weight was 1.03 g (yield 91 %). The barium salt was transformed into the pyridinium salt [4], m. p. 144—146°. Equivalent weight; $C_{14}H_{17}NSO_5$; calc. 311, found 318.

Veratryl-ethyl ether, treated in the same way, gave the barium salt of the sulphonic acid in a yield of 91 %. The pyridinium salt melted at 144—146°. It gave no m. p. depression with the corresponding product from diveratryl ether.

Veratryl alcohol (0.1 g) was dissolved in a sulphite solution (10 ml, 5 % SO_2, varying amounts of sodium hydroxide) in a glass tube. The tube was rotated in a glycerol bath at 135°.

After the heating, the solution was extracted 3 times with ether (total 60 ml). The extract was dried over anhydrous sodium sulphate and evaporated. The residue was assumed to be veratryl alcohol. The residue obtained from the treatment at pH 7, was found to contain mainly the alcohol. This was shown by the fact that the oily residue was for the main part soluble in water, and by transforming the oil into veratryl-thioglycollic acid (see below).

The extracted water solution was diluted to a suitable degree and the absorption at 280 mμ was determined with a Beckman spectrophotometer. From the absorption (see the Figure) the amount of the sulphonic acid in the solution was calculated.

The yield of the sulphonic acid was determined by these two methods (Table 1).

Diveratryl ether was treated as veratryl alcohol above. The amount of diveratryl ether which did not react was determined by filtering off and weighing the ether. (Diveratryl ether is not soluble in water, in contrast to veratryl alcohol.) The yield of the sulphonic acid was determined according to the two methods mentioned above with the exception that the amount of recovered diveratryl ether was added to the amount of the residue from the ether extract to determine the amount of substance not transformed into the sulphonic acid.

The yield of the sulphonic acid is shown in Table 1, and the amount of diveratryl ether which had reacted, in Table 2.

Reactions of veratryl alcohol, diveratryl ether, and veratryl-ethyl ether with thioglycollic acid

Veratryl alcohol (0.5 g) was heated on a steam bath for 4 hours with a water solution (7.5 ml) of thioglycollic acid (2.5 g). The pH of the solution was adjusted to the desired value by hydrochloric acid or sodium hydroxide. After the heating the solution was extracted with ether. The extract was shaken with a solution of sodium bicarbonate. The bicarbonate solution was mixed with the extracted water solution. On acidifying the combined solutions (about 50 ml), a crystalline substance was obtained. (Some of the veratryl-thioglycollic acid obtained was lost, as the product is slightly soluble in water, 2 g/l). The m. p. was about 89—91° in the different experiments.

Recrystallizations from benzene yielded a product with m. p. 92—92.5°. The equivalent weight agrees with the compound being S-veratryl-thioglycollic acid.

$C_{11}H_{14}O_4S$	Calc.	Equivalent weight	242
	Found	» »	246.5

The yield of the thioglycollic acid derivative is shown in Table 3.

Diveratryl ether was treated in the same way. The yield of the thioglycollic acid derivative and the amount of diveratryl ether recovered are shown in Table 3.

Veratryl-ethyl ether was treated as above with a thioglycollic acid solution at pH 1.4. The yield of the thioglycollic acid derivative was 65 %.

Reactions of veratryl alcohol with sulphite solutions containing β-naphtol

Veratryl alcohol (1 g) and β-naphthol (1 g) were heated with a sulphite solution (50 ml, 5 % SO_2, pH 1.4) in a rotating tube for 20 hours at 135°.

After the heating, the solution was extracted with ether. The extract was dried over anhydrous sodium sulphate and the solvent evaporated. The weight of the residue was 1.70 g. The naphthol in the residue was removed by sublimation, its weight was 0.21 g. The residue from the sublimation (1.40 g) was considered to be a condensation product of the phenol and veratryl alcohol, but was not further investigated.

When β-naphthol was heated at 135° for 24 hours with sulphite solutions of pH 1.4 and 5.7, it was recovered almost quantitatively (87 resp. 93 %).

The Table 4 shows the yields of the condensation product at varying pH.

Treatment of veratryl alcohol and diveratryl ether with acetic anhydride and pyridine

Veratryl alcohol (2 g) was heated with a mixture of acetic anhydride (4 ml) and pyridine (36 ml) for 9 hours on a steam bath. The mixture was evaporated in a vacuum desiccator over sulphuric acid and sodium hydroxide. The residue was vacuum distilled. An oil with boiling point 170—172° (18 mm Hg) was obtained (1.8 g, yield 72 %, $n_D^{20} = 1.523$).

The analysis agrees with the compound being veratryl acetate.

$C_{11}H_{14}O_4$	Calc.	Ac	20.5
	Found	»	20.0

When diveratryl ether was treated in the same way, it was recovered quantitatively in an unchanged condition.

SUMMARY

1. The following new substances have been synthesized: diveratryl ether, veratryl-ethyl ether, veratryl acetate, and S-veratryl-thioglycollic acid.

2. The following lignin model reactions of veratryl alcohol and diveratryl ether have been examined:

a. with sulphite solutions at varying pH
b. with sulphite solutions containing β-naphtol
c. with ethanolic hydrochloric acid
d. with thioglycollic acid at varying pH.

3. The reactions of veratryl-ethyl ether with sulphite cooking acid and thioglycollic acid have been examined.

This work has been supported by a grant from Swedish Natural Science Research Council. I gratefully acknowledge the assistance of Miss Ulla Saedén.

REFERENCES

1. Holmberg, B. *Svensk Papperstidn.* **39** (1936) Special number 113.
2. Freudenberg, K. *Fortschritte der Chemie organischer Naturstoffe.* II Wien (1939) p. 14.
3. Freudenberg, K., Lautsch, W., and Piazolo, G. *Cellulosechemie* **22** (1944) 97.
4. Lindgren, B. O. *Acta Chem. Scand.* **3** (1949) 1011.
5. Erdtman, H., and Leopold, B. *Acta Chem. Scand.* **3** (1949) 1358.
6. Enkvist, T., and Moilanen, M. *Svensk Papperstidn.* **52** (1949) 183.
7. Hedén, S., and Holmberg, B. *Svensk Kem. Tid.* **48** (1936) 207.
8. Balfe, M. P., Evans, A., Kenyon, J., and Nandi, K. N. *J. Chem. Soc.* **1946** 803.
9. Hägglund, E., and Johnson, T. *Pappers- och Trävarutidskrift för Finland* **16** (1934) 282.

10. Erdtman, H. *Svensk Papperstidn.* **43** (1940) 255, *Research* **3** (1950) 63.
11. Fuchs, W., and Elsner, B. *Ber.* **53** (1920) 886.
12. Berg, G. A., and Holmberg, B. *Svensk Kem. Tid.* **47** (1935) 257.
13. Robinson, G. M. *J. Chem. Soc.* **107** (1915) 267.
14. Erdtman, H., Lindgren, B. O., and Pettersson, T. *Acta Chem. Scand.* **4** (1950) 228.
15. Erdtman, H., and Pettersson T. *Acta Chem. Scand.* **4** (1950) 971.
16. Kullgren, C. *Svensk Kem. Tid.* **44** (1932) 15.
17. Buck, J. S., Johnson, J. R., and Snyder, H. R. *Organic Syntheses* Coll. Vol. II (1943) p. 619.
18. Carothers, W. H., and Adams, R. *J. Am. Chem. Soc.* **46** (1924) 1680.
19. Freudenberg, K., Carrara, G., and Cohn, E. *Ann.* **446** (1926) 94.

Received September 6, 1950.