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Dehydrogenation of Phenols

II. Dehydrogenation Polymers from Guaiacol

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The dehydrogenation polymers which are obtained from guaiacol by treatment with silver oxide, potassium ferricyanide, sodium persulphate and an oxygen-laccase system have been examined. The first two reagents gave polymers in which the phenol units were linked together with ether bonds (Formula II) while the other two reagents produced polymers with carbon-carbon bonds (Formulae III and IV).

It was shown in an earlier paper [1] that 2,6-dimethylphenol on dehydrogenation with silver oxide is transformed mainly into a polymer * with ether linked phenol units (I). In connection with studies on lignin, which is probably formed by dehydrogenation of coniferyl alcohol by an oxygen-laccase system [2], it seemed to be of interest to examine the dehydrogenation of guaiacol also. Silver oxide, potassium ferricyanide, persulphate catalysed with ferro-ions, and oxygen-laccase were used as oxidation systems.

Silver oxide dehydrogenation

The dominant product obtained on treating a benzene solution of guaiacol with silver oxide was a polymeric material. 3,3'-Dimethoxy-4,4'-dihydroxydiphenyl was also isolated but the yield was low. This compound has previously been obtained in low yield from guaiacol by electrolytic oxidation [3].

The polymeric material was an amorphous, light-coloured powder with the formula $[C_6H_3O(OCH_3)]_n$, where n is higher than 6. Its structure was determined mainly by using spectrophotometric methods.

The NMR spectrum of the polymer showed no peak for aliphatic or olefinic hydrogen except that for the hydrogen in methoxyl groups. The aromatic structure of at least the greater part of the guaiacol nuclei had therefore not been destroyed during the oxidation. The UV spectra in neutral (Fig. 1) and alkaline solutions differed only slightly showing that the proportion of phenolic groups present was low [4].

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* See addendum p. 2096.

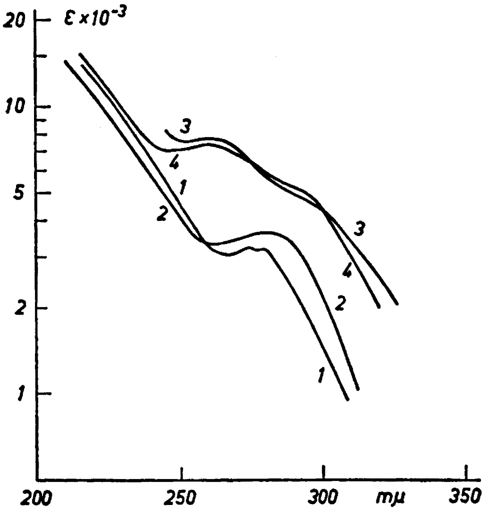
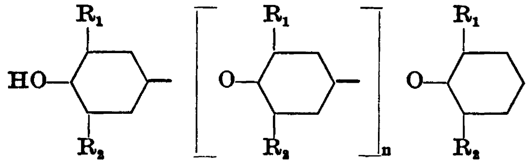


Fig. 1. UV spectra of guaiacol polymers. Oxidation reagents: 1) silver oxide, 2) potassium ferricyanide, 3) laccase plus oxygen, and 4) sodium persulphate plus ferro-ions. Solvent: ethanol. The ε values are calculated for one C_6-unit.

The IR spectrum of the polymer (Fig. 2) has no or, in some preparations, only weak carbonyl bands. Its hydroxyl content, determined by acetylation, was low. The two samples examined contained one hydroxyl group to 14 and to 5 C_6-units, respectively. The polymer contained no peroxide groups.

Most of its oxygen atoms must for these reasons be present in ether groups, and the polymer is therefore built up in the same way as the polymer from 2,6-dimethylphenol *i.e.* phenol units linked by ether bonds. Its formula is then (II).



I. $R_1 = R_2 = CH_3$
II. $R_1 = OCH_3, R_2 = H$

It has been assumed that the ether bond links the carbon atom of guaiacol which in almost all reactions has the greatest reactivity, *i.e.* that in the *para* position to the phenolic group. Even if an *ortho* carbon linkage seems less likely it cannot however at present be excluded.

The dimeric compound (II, n = 0) could not be isolated from the oxidation mixture even though a considerable amount of guaiacol was recovered. This may be explained as in the dimethylphenol oxidation [1] by a faster rate of oxidation for the dimer than for guaiacol.

When the silver oxide dehydrogenation was done in a mixture of dimethylformamide and methyl iodide, veratrol and the polymer (II) were obtained, indicating that the methylation competed better with the oxidation of guaiacol than with the oxidation of the dimer. This is a further proof of the easier oxidation of the dimer than of the guaiacol.

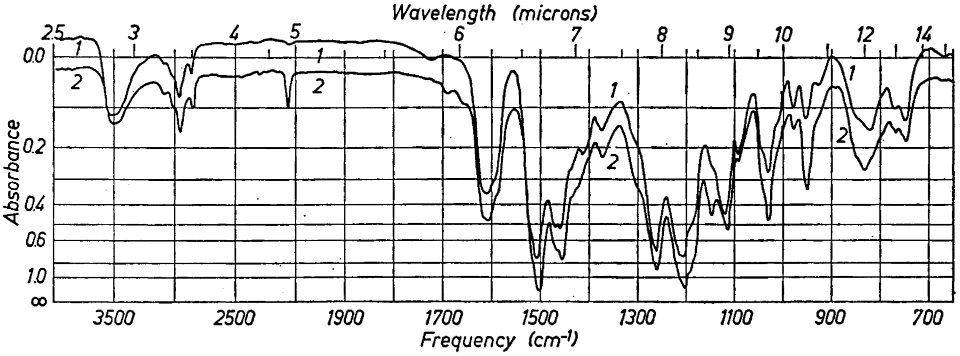


Fig. 2. IR spectra of guaiacol polymers. Oxidation reagents: 1) silver oxide, and 2) potassium ferricyanide. Potassium bromide disc.

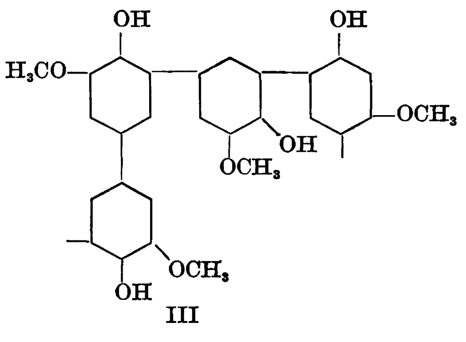
Potassium ferricyanide dehydrogenation

Potassium ferricyanide in alkaline solution transformed guaiacol into a grey amorphous product, the UV and IR spectra of which (Figs. 1 and 2) agreed so closely with those of the silver oxide polymer that they must be structurally similar.

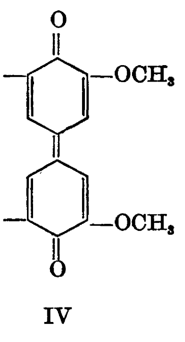
Laccase-oxygen dehydrogenation

Treatment of guaiacol with oxygen in the presence of laccase or peroxidase gives a bright red dehydrogenation polymer, which has been called "tetraguaiacoquinone" by Bertrand [5]. Booth and Saunders [6] in addition to "tetraguaiacoquinone" also obtained a very small amount of 2,2'-dihydroxy-3,3'-dimethoxy-diphenyl. Reductive acetylation of the polymer gave, also in a very low yield, the diacetate of 3,3'-dimethoxy-4,4'-dihydroxy-diphenyl. From this they concluded that "tetraguaiacoquinone" is a polymer of guaiacol units linked together with carbon-carbon bonds (III) and that the red colour is due to the oxidation of some units to diphenoquinone (IV) residues.

As the support for their assumption is rather indirect, a further examination was made of "tetraguaiacoquinone".



III



IV

Analyses of the polymer gave the formula

$$C_6H_{2.4}O_{0.32}^{\text{carbonyl}}\ (OH)_{0.7}\ (OCH_3)_{1.0}$$

which is consistent with the assumption that (III) should be the predominant structural element. After reduction with sodium borohydride, which removed the red colour, the polymer did not react with dibromoquinone-monochloroimide. Evidently the *para* positions in the polymer were substituted. On the other hand, *p*-diazobenzenesulphonic acid gave a red colour with the reduced polymer and thus at least a part of the *ortho* positions (possibly those belonging to the end groups) are free.

Further support for the structure (III) was given by UV spectra, as shown below. The bonds from a benzene nucleus in the polymer to the two proximal nuclei are in *meta* position to each other. The largest mesomeric system in the polymer consists therefore of only two nuclei and the UV maximum should therefore be at the same wavelength as that of the corresponding diphenyl (*cf.* Ref[7].). Two guaiacyl nuclei can be linked in either *o,o'*-, *p,p'*- or *o,p'*-positions to the phenol groups. The *ortho*-substituents decreased the extinction value of the diphenyl maximum as is evident from the fact that the diphenyl maximum has a higher extinction value for 3,3'-dimethoxy-4,4'-dihydroxy-diphenyl than for 3,3'-dimethoxy-2,2'-dihydroxy-diphenyl (Table 1) (*cf.* Ref.[8]). A polymer (III) would therefore be expected to have a UV maximum reminiscent of that of 3,3'-dimethoxy-4,4'-dihydroxy-diphenyl. In reality it was found that even if there are some differences between the spectrum of "tetraquinone" and that of the diphenyl they are certainly of the same type (Table 1).

The presence of the diphenoquinone structure (IV) was supported by the IR spectrum of the polymer. The carbonyl band was at 1 625 cm^{-1}, close to the aromatic 1 600 cm^{-1} band (Fig. 3). This frequency, which is unusually low for a carbonyl band, agrees with that of diphenoquinones (diphenoquinone [9] at 1 626 cm^{-1}, its 3,3', 5,5'-tetramethyl derivative at 1 633 cm^{-1}, and the 3,3',5,5'-tetramethoxy derivative at 1 628 cm^{-1}). The carbonyl peaks of benzoquinones are in the vicinity of 1 650^{-1} cm (benzoquinone [10] at 1 667 cm^{-1}). In the visible part of the polymer spectrum there is a maximum at 475 mμ which was evidently due to the diphenoquinone groups since they absorb in this region.

Persulphate oxidation

Erdtman [11] has pointed out that a polymer similar to "tetraguaiacoquinone" is formed when guaiacol is treated with sodium persulphate in acidic aqueous solution containing a small amount of ferrosulphate. The results of analyses on material prepared here indicated a formula

$$C_6H_{2.3}O_{0.40}^{\text{carbonyl}}\ (OH)_{1.0}(OCH_3)_{0.75}$$

(This formula agrees reasonably well with data by Erdtman and Johanson [12]).

The persulphate polymer differed in several respects from "tetraguaiacoquinone". The lower methoxyl value showed that some methoxyl had been eliminated during the persulphate oxidation and that a part of the aromatic

Table 1. UV data for "tetraguaiacoquinone", the persulphate polymer, and two related diphenyl derivatives.

Substance	Neutral solution [1]				Alkaline solution [2]	
	Diphenyl maximum		Benzene maximum			
	mμ	ε	mμ	ε	mμ	ε
"Tetraguaiacoquinone"	257	7 520	300*	3 600	298	5 250
Reduced ditto	261	7 750	300*	4 300		
Persulphate polymer	258	6 900	295*	4 300	298	8 350
Reduced ditto	261	7 350	295*	5 000		
3,3'-Dimethoxy-4,4'-dihydroxy-diphenyl	268	7 800	291	6 600	308	11 200
3,3'-Dimethoxy-2,2'-dihydroxy-diphenyl [3]	247	4 100	283	2 500	304	3 650

Extinction values (ε) calculated per C$_6$-unit for both polymers and diphenyls. The maxima marked with * were noticeable only as inflections in the absorption curves

[1] Solvent: ethanol.

[2] Solvent: 0.1 N ethanolic potassium hydroxide solution.

[3] Synthesised according to Ref.[6]

nuclei might have been destroyed. Even though the IR spectra of the two polymers were of the same aromatic type (Fig. 3) they show distinct dissimilarities. For instance the spectrum of the persulphate polymer showed no diphenoquinone band in the vicinity of 1 625 cm^{-1} but, on the other hand, it had an absorption peak at 1 645 cm,$^{-1}$ which might be due to benzoquinone groups. The visible light spectrum also indicated differences between the carbonyl groups of the two polymers, the persulphate polymer having a maximum at

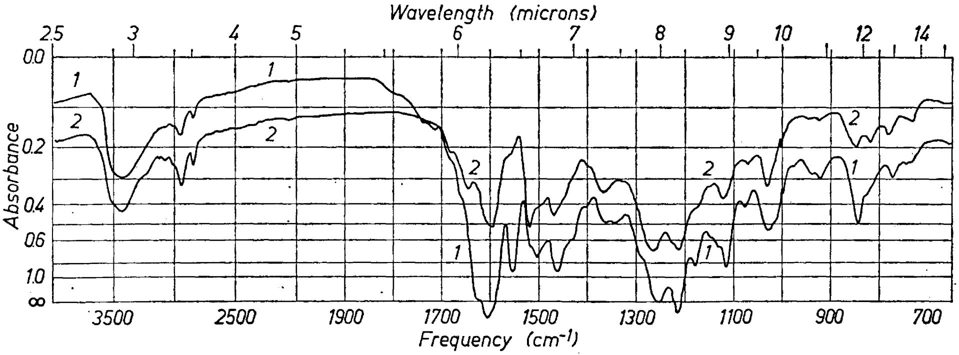


Fig. 3. IR spectra of guaiacol polymers. Oxidation reagents: 1) laccase plus oxygen, and 2) persulphate plus ferro-ions. Potassium bromide disc.

438 mμ, significantly different from the wavelength of that of "tetraguaiacoquinone" (475 mμ). It therefore seems probable that the greater part of the carbonyl groups in the persulphate polymer are benzoquinone groups formed by an Elbs persulphate reaction [13].

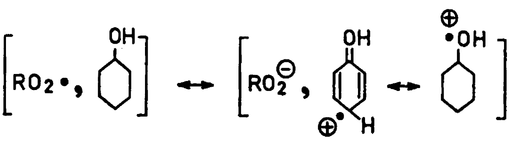
The UV spectra of the polymer (Table 1 and Fig. 1) closely resembled that of the "tetraquaiacoquinone". Furthermore the reduced persulphate polymer did not react with dibromo-quinone-monochloroimide and gave only a weak colour reaction with diazobenzene-sulphonic acid. Together with the general conformity of the IR spectra, these results indicated that the persulphate polymer contained a large proportion of the predominant structural elements in "tetraguaiacoquinone", *i.e.* (III).

DISCUSSION

It is apparent from these experiments that different types of dehydrogenation polymers are obtained from guaiacol depending on the type of oxidation reagent used. Polymers with ether-linked units are obtained when silver oxide and potassium ferricyanide are used while persulphate and the oxygen-laccase system link the units by carbon-carbon bonds.

The formation of both types of polymers can be explained according to the well known scheme for dehydrogenation of phenols (reviewed in Refs. [14,15]) in which the primary reaction products are considered to be phenoxyl radicals. These radicals may combine with each other or with phenol molecules. The formation of both oxygen bonds and carbon-carbon bonds can be accounted for by this process.

However, that the oxidation reagent should affect the manner of linking is not indicated in this simplified scheme; it might be explained in several ways. One alternative is that the radicals are never really free but form π-complexes with the oxidation reagents such as those assumed by Hammond and co-workers [16] to be the primary products obtained by reaction of peroxy radicals with phenols or amines (V).



V

EXPERIMENTAL

Oxidation of guaiacol with silver oxide in benzene solution. Isolation of the polymer. Guaiacol (15 g) dissolved in benzene (140 ml) was shaken with silver oxide (16 g) for 48 h. Undissolved material (15 g) was removed and the filtrate was shaken with 2 N sodium hydroxide solution, which dissolved a part of the product. The benzene solution was dried and evaporated. The residue was dissolved in chloroform, and light petroleum was added to the solution. The white precipitate obtained was collected (1.4 g, Preparation A).

The alkaline solution was acidified and the solution decanted from the sticky precipitate, which was washed with water and dissolved in dioxane. The dioxane solution was dried and evaporated. The residue (5.2 g) was precipitated from chloroform solution by addition of light petroleum, and the white precipitate obtained was collected (3.3 g, Preparation B).

The acidified aqueous solution was extracted with ether and the ether solution was combined with the chloroform-light petroleum filtrate. The combined solution was evaporated. The residue (10 g) yielded guaiacol (5 g) on distillation.

Examination of the polymeric preparations A and B. Analyses: Preparation A, found C 68.8; H 5.0; O 26.7; OCH_3 26.6; OH 1.1. Preparation B, found C 67.3, H 5.3, O 27.2, OCH_3 24.4, OH 2.7 peroxide [17] 0.0, molecular weight at least 750.

The hydroxyl content was determined by heating the preparations with acetic anhydride and pyridine for 3 h, precipitating the acetylated material by addition of water and determining the acetyl content of this material.

UV and IR spectra of the two preparations were the same. They are shown in Figs. 1 and 2, respectively.

NMR spectrum of preparation B in a benzene solution showed a peak at a shift of 3.7 p.p.m. relative to the benzene peak. The peak due to the hydrogen of the methoxyl group in guaiacol has a shift of 3.8 p.p.m.

Isolation of 3,3'-dimethoxy-4,4'-dihydroxy-diphenyl. Guaiacol (20 g) was treated with silver oxide (21 g) as described. The alkaline solution was acidified and extracted with benzene, which was then dried and evaporated. Distillation of the residue gave guaiacol (8.5 g) and a fraction, distilling at 0.3 mm Hg/160—180° (bath temperature). The latter partly crystallised and on recrystallisation from methanol gave a product (0.15 g), m.p. 153°, raised to 166—167° by further recrystallisation from methanol. (Found C 68.3; H 5.9. Calc. for $C_{14}H_{14}O_4$ (246): C 68.3; H 5.7.) UV data are given in Table 1. Its structure was determined by methylation to 3,3'4,4'-tetra-methoxy-diphenyl.

Methylation of 3,3'-dimethoxy-4,4'-dihydroxy-diphenyl. Dimethyl sulphate (1 ml) was added with vigorous agitation to a solution of the dimethoxy-dihydroxy-diphenyl (3.4 mg) in 3 N potassium hydroxide (1 ml). When the solution turned acidic 3 N potassium hydroxide (1 ml) was added. The treatment with dimethyl sulphate (1 ml) and 3 N potassium hydroxide (1 ml) was repeated once and then dimethyl sulphate (1 ml) and solid potassium hydroxide were added. The temperature was kept at about 80° during the whole methylation procedure. When all the dimethyl sulphate had reacted the crystals were removed from the solution and washed with water, m.p. 129—130°, undepressed by addition of 3,3'4,4'-tetramethoxy-diphenyl prepared by Ullman coupling of 3,4-dimethoxyphenyl iodide [18]. The IR spectrum of the methylation product was identical with that of the tetramethyl-diphenyl.

Oxidation of guaiacol with silver oxide in dimethylformamide-methyl iodide solution. Silver oxide (25 g) was added in portions during 1 h to a solution of guaiacol (10 g) in dimethylformamide (50 ml) and methyl iodide (30 ml). The mixture was then shaken for 17 h, undissolved material was removed and benzene was added to the filtrate. The precipitate obtained was removed and the benzene solution was extracted with 5 % sodium thiosulphate solution, then water, and dried. Light petroleum was added to the benzene solution. The white amorphous precipitate obtained was collected (3.2 g). (Found: C 68.9; H 5.0; O 25.6; OCH_3 27.1; OH 0.0.) IR and UV spectra were identical with those of the polymer preparations obtained by oxidations in benzene solution.

The light petroleum-benzene solution from the polymer precipitation was evaporated. The residue (2.2 g) distilled at 130° (bath temperature); the m.p. of the distillate, 22°, was undepressed by addition of veratrol. Its IR spectrum was identical with that of veratrol.

Oxidation of guaiacol with potassium ferricyanide. An aqueous solution of potassium ferricyanide (30 g in 100 ml) was added during 1 h to a solution of guaiacol (5 g) in 1 N sodium hydroxide solution (150 ml) which was strongly agitated (room temperature). The reaction mixture was agitated for a further 5 h and then extracted with chloroform. The chloroform solution was dried and evaporated. The residue (0.5 g) was reprecipitated from a chloroform solution by addition of light petroleum. Weight 0.3 g. (Found: C 66.2; H 5.3; O 25.1; OCH_3 22.8.)

The chloroform-extracted alkaline solution was acidified and extracted again with chloroform. The extract was dried and added to light petroleum. The precipitate obtained was collected (1.5 g). (Found: C 64.6; H 4.9; O 27.0.) UV and IR spectra are shown in Figs. 1 and 2, respectively.

Oxidation of guaiacol with sodium persulphate. The polymer was prepared as described by Erdtman [11]. (Found: C 65.4; H 4.4; O 28.4; OCH_3 18.2.)

The carbonyl group content was determined by sodium borohydride reduction according to Lindberg and Paju [19]. The reduction time was about half an hour. Found: 0.20 moles of hydrogen consumed per equivalent weight of 122. The UV and IR results are shown in Figs. 1 and 3 and in Table 1.

Reductive acetylation: A mixture of zinc powder (5 g), the polymer (2 g) and acetic anhydride-pyridine (10 ml, v/v) was heated on a boiling water bath for 1 h. Undissolved material was removed and water was added to the filtrate. The light brown precipitate obtained was collected and washed with water. Weight: 2.7 g. (Found: OCH_3 12.1, CH_3CO 26.3.) The formula given in the discussion was calculated on the assumption that the carbonyl groups are reduced to hydroxyl groups and then acetylated in this procedure.

"*Tetraguaiacoquinone*". A dialysed solution from a culture of *Polyporus versicolor* (3 ml) was added to guaiacol (1 g) dissolved in a 0.01 M acetic acid-sodium acetate buffer of pH 4.8 (80 ml). The solution was shaken for 24 h. The precipitate obtained was collected and washed with water. (This experiment was kindly performed by Dr. Gösta Fåhraeus and Mr. Hans Ljunggren). Weight 770 mg. (Found: C 67.8; H 4.9; O 25.8; OCH_3 25.4.) Carbonyl was determined as in the case of the persulphate polymer. Found: 0.16 moles of hydrogen consumed per equivalent weight of 122. Reductive acetylation was also carried out as with the persulphate polymer. (Found: OCH_3 18.7; CH_3CO 22.0.) UV and IR data are collected in Figs. 1 and 3 and in Table 1.

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Added in proof. This polymer recently been synthesised by two other methods (Hay, A. S. *et al. J. Am. Chem. Soc.* **81** (1959\ 6335, and Staffin, G. D. and Price, Ch. C. *ibid.* **82** (1960) 3632).

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