

SHORT COMMUNICATIONS

Chlorination of Guaiacol Relating to Bleaching Mechanism of Pulp

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To make clear the mechanism of chlorination of lignin by an aqueous chlorine solution, chlorination of lignin and model compounds¹⁾ have been investigated since some years ago.

In advance of the investigation of the behavior of complex lignin-like models against aqueous chlorine solution, guaiacol was investigated first. Because, it is expected that this simple case will show the fundamental principle of the chlorination reaction of the benzene nucleus.

As quite recently C. Dence and K. Sarkanen²⁾ have reported similar investigations, the results obtained in our laboratory till now are summarized and reported briefly as follows.

A homogenous aqueous solution of guaiacol (128 g. guaiacol in 7 l. of water) was treated 7.5 l. of aqueous chlorine solution (molar ratio 1:1) for about 1/2 hr. at 0°C. A small amount of sodium sulphite solution was added to destroy the excess of remaining chlorine or

hypochlorous acid if any, and the pH of the solution was adjusted to nine with sodium hydroxide. Sodium borohydride was added in order to reduce the quinoidal structure to pyrocatechol structure to prevent the polymerization of quinoidal structure if any. Then, the solution was acidified, resinous products separated (I), and the whole was extracted continuously with chloroform (II) followed, by ether (III).

I and II were distilled in vacuo into four fractions respectively, each fraction was examined gas chromatographically, and the fractions containing similar components were combined.

From the five fractions thus obtained the following compounds were separated and identified.

1) Guaiacol: The compound was separated as 3, 5-dinitrobenzoate, m. p. 137~139°C, which was not depressed on admixture with the authentic sample. (Found: OCH₃, 10.25. Calcd. for C₁₄H₁₀O₇N₂: OCH₃, 9.75%.)

2) 5-Chloroguaiacol*: The compound was separated as 3, 5-dinitrobenzoate, m. p. 170~171.5°C, which was not depressed on admixture with the authentic sample. (Found: C, 47.71; H, 3.20; Cl, 10.08; OCH₃, 8.77. Calcd. for C₁₄H₉O₇N₂Cl: C, 47.68; H, 2.55; Cl, 10.07; OCH₃, 8.79%.)

3) 4, 5-Dichloroguaiacol: White needles, m. p. 71~73°C, which was not depressed on

1) K. Sato, K. Ebisawa and H. Mikawa, *J. Chem. Soc. Japan, Ind. Chem. Sec (Kogyo Kagaku Zasshi)*, **61**, 1090 (1958).

2) C. Dence and K. Sarkanen, *Tappi*, **43**, No. 1, 83 (1960).

* Named according to Beilstein's Handbook.

admixture with the authentic sample. (Found: C, 43.68; H, 3.29; Cl, 36.65. Calcd. for $C_7H_6O_2Cl_2$: C, 43.55; H, 3.13; Cl, 36.74%.)

4) Trichloroguaiacol: Pale yellow needles, melting at 103~106°C. (Found: C, 37.58; H, 2.41; OCH_3 , 13.91. Calcd. for $C_7H_5O_2Cl_3$: C, 36.94; H, 2.21; OCH_3 , 13.62%.) The positions of chlorine atoms are not settled as yet.

5) 3,3'-Dimethoxy-4,4'-dihydroxydiphenyl: White prisms, melting at 166~167°C. (Found: C, 67.71; H, 5.73; OCH_3 , 25.75; Cl, 0.00. Calcd. for $C_{12}H_8O_2(OCH_3)_2$: C, 68.28; H, 5.73; OCH_3 , 25.21%). Diacetyl derivative, melting at 200.5~202°C. (Found: C, 65.35; H, 5.95; mol. wt. (Rast), 336. Calcd. for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49%; mol. wt., 330.32). Dimethyl derivative (biveratrol), melting at 132~133°C. (Found: C, 69.85; H, 6.72; mol. wt. (Rast), 273. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61%; mol. wt., 274.30).

Melting points of the diphenyl and its two derivatives agree well with the values reported in literatures^{3,4}. The diphenyl has one phenolic hydroxyl group per methoxyl group, according to the so-called $\Delta\epsilon$ -method of Aulin-Erdtman⁵.

From the fraction III the following compounds were separated and identified.

1) Pyrocatechol: White prisms, melting at 103.5~104.5°C, undepressed on admixture with the authentic sample. (Found: C, 65.33; H, 5.54. Calcd. for $C_6H_6O_2$: C, 65.44; H, 5.49%.)

2) 3-Chloropyrocatechol: The compound was isolated as mono carboxymethyl ether, melting at 122~123.5°C, undepressed on admixture with the authentic sample of 3-chlorocatechol monocarboxymethyl ether. (Found: C, 47.70; H, 3.71; Cl, 17.71. Calcd. for $C_8H_7O_4Cl$: C, 47.43; H, 3.46; Cl, 17.52%). The position of the carboxymethyl group of the mono-ether is not determined. Diether was not prepared, as it was found to be difficult to etherify both hydroxyl groups of 3-chloropyrocatechol by an usual method.

Results so far obtained on the effects of aqueous chlorine water on the guaiacol nucleus are summarized as follows:

1) Methoxyl group is demethylated to give methanol in high yield¹.

2) Isolation of pyrocatechol suggests that demethylation can occur without introduction of any chlorine atoms into the nucleus.

3) One to three chlorine atoms are introduced without cleavage of methoxyl groups.

4) It seems therefore to be probable that chlorination of the nucleus and the demethylation of methoxyl group are independent reactions.

5) Guaiacol dimerizes by dehydrogenation. Details of this work will be published later.

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3) F. Fichter and W. Dietrich, *Helv. Chim. Acta*, **7**, 131 (1924).

4) S. Tamura, K. Okuma, Y. Miyao and N. Haramaki, *J. Agr. Chem. Soc. Japan (Nippon Nogei-Kagaku Kaishi)*, **27**, 877 (1953).

5) Aulin-Erdtman, *Svensk Papperstidn*, **55**, 745 (1952).