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Abstract

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Preparation from Hydrolysis Lignin of Quinone Nitro Polycarboxylic Acids–Stimulators of Plant Growth

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According to the views of Bach, Palladin, and Szent-Györgyi, quinones [1] are catalysts of oxidation-reduction reactions, which probably proceed according to the scheme:

$$[\text{quinone}] \underset{\frac{1}{2}O_2}{\overset{H_2}{\rightleftharpoons}} [\text{hydroquinone}] \quad \text{or} \quad [\text{quinone}] \underset{\frac{1}{2}O_2}{\overset{H_2}{\rightleftharpoons}} [\text{hydroquinone}]$$

The principal structural units of lignin substances of plant tissue [2] are phenylpropane monomers, in particular derivatives of pyrocatechol [3]. Thus, lignin may be an unlimited source for obtaining quinone substances.

As a result of the hydrolysis of wood and plant wastes, carried out at 180–190° in dilute solutions of sulfuric acid, lignin undergoes irreversible condensation reactions, which lead to the appearance of new carbon substituents in the aromatic guaiacyl nuclei of lignin and to the formation of secondary aromatic structures [4]. As is known, the introduction of bulky substituents into guaiacol considerably stabilizes it. This makes it possible, upon oxidation of di-tert-butylguaiacol, to obtain comparatively stable quinone substances [5].

It was shown earlier that oxidative cleavage of low-molecular lignin models also passes through a quinone stage [6–8]. However, from natural or technical lignins it has so far not been possible to obtain stable quinone products. To obtain stable quinone substances we proceeded from samples of lignin maximally condensed in an acid medium. The structural units of such lignin have, in addition to the side propyl chain in the first position of the ring, carbon substituents in the fifth and sixth positions [9]. In accordance with the theory of oxidative-hydrolytic cleavage of carbon–carbon bonds in molecules of organic compounds [10], cleavage of such bonds in hydrolysis lignin necessarily requires the combined action of oxidative and hydrolytic effects.

We developed and applied a method of fractional, stepwise oxidation and hydrolysis of condensed lignin with nitric acid in an aqueous medium at 100°. The

Fig. 1. Curve of potentiometric titration of quinone acids

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gradual introduction of the oxidizing agent into the reaction mixture minimized the decomposition of the quinone acids formed and allowed the process to be carried out with small expenditures of oxidant.

Various types of technical–

···of technical lignins that have undergone prolonged condensation treatment. We present the procedure for oxidizing factory lignin of cottonseed hulls, obtained after pentosan-hexosan hydrolysis (duration of acid treatment of the lignin, 14–16 h). Lignin (lignin content by König 85–90%, OCH_3 4.7–5%) in an amount of 500 g and 5 liters of water were charged into a stainless-steel reactor equipped with a cooling coil, reflux condenser, stirrer, and electrical heating device. The suspension of lignin in water was heated to 100°. With the stirrer operating, nitric acid (1.35) in an amount of 0.75 kg (calculated as monohydrate) was gradually introduced into the mixture over 6 h, while hot air was simultaneously fed into the lower part of the reactor. The reaction proceeds vigorously, with evolution of gaseous products, and in some cases requires cooling. After completion of the reaction, the solution, which contained only traces of nitric acid, was filtered from the insoluble residue and neutralized with calcium carbonate to pH 2.8–3. The precipitated calcium oxalate was filtered off; then the filtrate was acidified with sulfuric acid to pH 1, gypsum was separated, the solution was saturated with sodium sulfate and extracted with chloroform to remove a small amount of nitrophenols.

Fig. 1. Curve of potentiometric titration of quinone acids

To isolate the quinone acids, the solution was then extracted with methyl ethyl ketone. The extract was dried with sodium sulfate. After removal of most of the solvent in vacuo, the thick syrup was poured into dry petroleum ether. The dark-red oil that separated was removed from the ether and dried in a vacuum dryer at 40° and in a vacuum desiccator over alkali, and then over phosphorus anhydride for one week. The yield was up to 30% of the weight of the lignin.

The brick-red, very hygroscopic powder obtained dissolved well in water and in polar organic solvents. For the study of its properties, the fraction used was that which dissolved on heating in dioxane. The product was potentiometrically titrated in aqueous solution as a strong acid (Fig. 1). Molecular weight (cryoscopically in dioxane), 286. Gram-equivalent, 132. The content of carboxyl groups in the molecule is approximately 2. Elemental composition (%): C 45.1, H 3.74, O 45.84, N 5.32.

The acids possess strong oxidizing properties and already in the cold liberate iodine from a solution of potassium iodide in acetic acid. The content of oxidizing groups, determined by Shemyakin' s method ([11]), varied within the range 6.5–

Fig. 2. IR spectra: a —quinone acids, CaF_2 prism; —silver salt of quinone acids, CaF_2 prism; —quinone acids, NaCl prism

Figure 2: Fig. 2. IR spectra: a —quinone acids, CaF_2 prism; —silver salt of quinone acids, CaF_2 prism; —quinone acids, NaCl prism

8.5%. The oxidation-reduction potential is 0.41, which suggests the presence of quinone groups in the product obtained.

To establish the quinone structure of the acids, an IR spectrum was recorded on an IKS-12 instrument with a CaF_2 prism. The samples were pressed in KBr.

In the initial acid sample (Fig. 2a) there are 5 absorption bands:

a) 1725 and 1737 cm^{-1} are assigned to stretching vibrations of C=O bonds included in carboxyl groups, since absorption at these frequencies disappears upon neutralization of the acids (see the spectrum of the silver salt, Fig. 2b);

b) 1650 and 1660 cm^{-1} (Fig. 2b) are assigned to absorption of the C=O bonds of quinones, since these bands remain after neutralization and in frequency correspond to absorption in the case where two quinone carbonyls are located in one ring ([12]);

c) 1707 cm^{-1} (Fig. 2b) are assigned to absorption of carbonyl-containing

impurities characteristic of the products of transformation and alteration of unstable quinones (12).

In the spectrum taken with a NaCl prism (Fig. 2), along with other bands, absorption at 1520 cm^{-1} is observed. This band is assigned to vibrations of an aromatic nitro group.

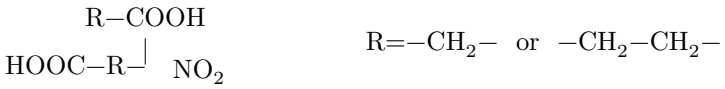
Of special interest is the absorption at frequencies of 1650 and 1660 cm^{-1}, since it is assigned to quinone groups located in the ortho position. Evidence for this was given by Moller (5) and Otting (12) in the spectra of a number of ortho-quinones.

After reduction of the quinone acids with potassium iodide in acetic-acid solution and titration of the liberated iodine with thiosulfate, extraction with ether made it possible to isolate a partially crystalline product (phenolic acids) possessing strong reducing properties. In air, the phenolic acids are readily oxidized and, on slight heating, precipitate metallic silver from an ammoniacal $AgNO_3$ solution. We were unable to obtain the acetyl and phenazine derivative, which may be explained by steric difficulties (5).

Fig. 2. IR spectra: *a* —quinone acids, CaF_2 prism; —silver salt of quinone acids, CaF_2 prism; —quinone acids, NaCl prism

Investigation by paper chromatography (7) showed that the product obtained is a mixture of 5-6 closely related substances.

On the basis of a comparison of the found and calculated data (elemental composition, molecular weight, gram-equivalent, IR spectra), it is suggested that the products obtained by us may be assigned to the class of quinone nitropolycarboxylic acids (QNPCA). For the main product, the following probable structural formula may be proposed:



(quinone ring with NO_2, O, and O substituents)

The position of the nitro group and the nature of the side chains are shown conventionally and are currently being clarified.

The QNPCA obtained are nontoxic, stable during storage, and have successfully passed tests as effective plant-growth stimulators. Aqueous solutions of the ammonium salts of the acids are used for pre-sowing seed treatment and for foliar treatment of plants at the early vegetation stage. At an acid consumption of 3 to 5 kg/ha, it is possible to increase the yield of a number of vegetable crops, cotton, and maize by 20–30%.

The availability of the raw material and the simplicity of the technology for obtaining new inexpensive plant growth stimulants predetermine the possibility of their broad introduction into agriculture.

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