PHOSPHORYLATION OF LIGNINS

I. PHOSPHORYLATION OF PIPERIDINOMETHYLATED DIOXANE LIGNIN FROM COTTONSEED HUSKS

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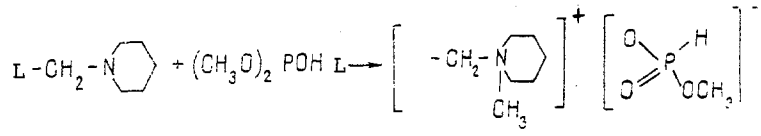
The phosphorylation of piperidinomethylated dioxane lignin has been studied. It has been shown that the reaction takes place with the formation of quaternary ammonium phosphates, while the transesterification of dimethyl phosphite with an aliphatic hydroxy group of the lignin is also possible.

The introduction of phosphorus into the lignin molecule is of great interest, since it results in the formation of products possessing pesticidal, ion-exchange, and fire-resistance properties [1]. The aminomethylation of phenol by dimethyl phosphites has been described [2]. The reaction of phosphites with tertiary amines leads to the corresponding quaternary ammonium compounds [3]. The formation of quaternary compounds takes place analogously on the interaction of phosphoric acid esters with piperidine.

The production of aminomethylated dioxane lignins been reported previously [4]. In order to study the reaction and find ways of using the phosphorus-containing products obtained, we have investigated the interaction of the piperidinomethylated dioxane lignin from cottonseed hulls (PDLA) with dimethyl phosphite.

The phosphorylation of piperidinomethylated lignin took place by the following scheme [2] at room temperature with a quantitative yield of product:



The product obtained was a brown powder readily soluble in water, which confirmed the formation of quaternary ammonium compounds. The amount of chemically bound phosphorus was 5.95%. The initial dioxane lignin and the phosphorylated lignin obtained were analyzed for their elementary and functional compositions, and their semiempirical formulas were deduced from the results obtained.

I. Dioxane lignin

$$C_9H_{6,30}O_{1,78}(OCH_3)_{0,81}(OH_{phe})_{0,60}(OH_{al})_{0,86}(O_{CO})_{0,43}(OOH_{COOH})_{0,02}$$

II. Piperidinomethylated dioxane lignin

$$C_9H_{5,20}O_{2,38}(OCH_3)_{0,54}(OH_{phe})_{0,48}(OH_{al})_{0,68}(O_{CO})_{0,31}(OOH_{COOH})_{0,01}N_{0,7}$$

III. Phosphorylated PDLA

$$C_9H_{4,80}O_{4,50}(OCH_3)_{0,23}(OH_{phe})_{0,45}(OH_{al})_{0,12}(O_{CO})_{0,3}(OOH_{COOH})_{0,12}N_{0,5}P_{0,42}$$

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A comparison of the semiempirical formulas of the lignins shows that 0.42 of a unit of phosphorus per phenylpropane structural unit had entered the lignin macromolecule. The amount of aliphatic hydroxy and methoxy groups had diminished, while the amount of phenolic hydroxy and carbonyl groups had remained unchanged.

In the IR spectrum of the phosphorylation product, absorption bands were observed at 1460 cm^{-1}, showing the presence of a –N–C– bond, while the intensity of the bands in the 3300-3500 cm^{-1} region due to the stretching vibrations of hydroxy groups had decreased. There were absorption bands at 1160 cm^{-1}, corresponding to a P–O–CH_3 bond, at 2380-2450 cm^{-1} of a P–H bond, and at 1230 cm^{-1} of the stretching vibrations of P=O bonds. The absorption band at 1720 cm^{-1} of β-carbonyl groups had remained unchanged.

It was established on the basis of the IR spectrum and functional analysis that the phosphorylation of piperidinomethylated DLA takes place with the formation of quaternary ammonium phosphites, while the transesterification by DMP of the aliphatic hydroxy groups of the lignin is also possible.

EXPERIMENTAL

IR absorption spectra were taken on a UR-20 instrument.

Carbonyl groups were determined by the oximation method, total hydroxyls by acetylation, and phenolic hydroxyls by the chemosorption method [7].

Dimethyl phosphite was obtained by the phosphorylation of methanol with phosphorus trichloride [5], dioxane lignin by Pepper's method [6], and piperidinomethylated lignin by Khaskin's method [3].

Phosphorylation of PDLA. PDLA suspended in 50 ml of dioxane was charged into a round-bottomed flask, and dimethyl phosphite was added in a ratio of lignin to dimethyl phosphite of 1:2.5. The reaction was continued at room temperature for 72 h. After its end, the excess solvents were distilled off, and the residue was dissolved in 40 ml of water and was precipitated in acetone.

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