MODIFICATION OF LIGNIN BY PHOSPHORYLATION AND AMINATION

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The results of a study of the modification of lignin have shown that phosphorus-containing preparations based on lignin possess ion-exchange and bactericidal properties [1], and nitrogen-containing derivatives are biostimulators of plant growth [2].

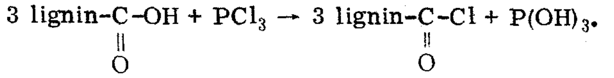
To obtain biologically active substances and modifiers (converters) of rust we have studied the changes in the functional groups taking place in the water-insoluble part hydrolysis ammoniated lignin (HAL) after phosphorylation with phosphorus trichloride followed by amination by nitrogen-containing heterocyclic compounds.

It is known [3] that the chemical activity of lignin rises after its activation by chlorination or by treatment with alkalis. Activation is accompanied by a change in the quantitative composition of the functional groups of the macromolecules: the amount of alcohol and carboxy groups rises. This is brought about particularly by oxidative ammonolysis [4], and therefore for syntheses we selected HAL, into the macromolecule of which it is possible to introduce considerably larger amounts of phosphorus and nitrogen, than into hydrolysis lignin (HL).

The phosphorylation of HL with various reagents has been studied fairly broadly [5, 6]. The interaction of HAL with PCl_3 takes place mainly in two directions:

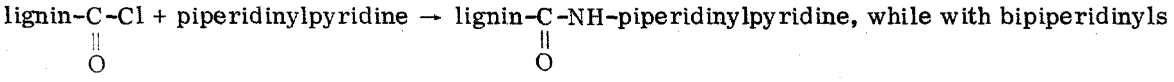
a) The formation of esters of phosphoric acid through the primary alcoholic and phenolic hydroxy groups: $3\ \text{lignin-OH} + PCl_3 \rightarrow P\text{-(lignin-O)}_3 + 3HCl$; and

b) the formation of carbonyl chlorides from carboxy groups:



$$3\ \text{lignin-}\underset{\overset{\|}{O}}{C}\text{-OH} + PCl_3 \rightarrow 3\ \text{lignin-}\underset{\overset{\|}{O}}{C}\text{-Cl} + P(OH)_3. \qquad (I)$$

The reaction of lignincarbonyl chloride (I) with piperidinylpiperidines apparently takes place in the following way:



$$\text{lignin-}\underset{\overset{\|}{O}}{C}\text{-Cl} + \text{piperidinylpyridine} \rightarrow \text{lignin-}\underset{\overset{\|}{O}}{C}\text{-NH-piperidinylpyridine, while with bipiperidinyls} \qquad (II)$$

the formation of mono and di derivatives of lignin is possible: $\text{lignin-}\underset{\overset{\|}{O}}{C}\text{-NH-bipiperidinyl (III)}$ and $\text{lignin-}\underset{\overset{\|}{O}}{C}\text{-NH-bipiperidinyl-NH-}\underset{\overset{\|}{O}}{C}\text{-lignin (IV)}$.

In actual fact, the elementary and functional analysis (Table 1) and also the IR spectra of phosphorylated hydrolysis ammoniated lignin (PHAL) and the products of its amination (am-PHAL) with anabasine, 4-(piperidin-4'-yl)-pyridine, and 4,4'-bipiperidinyl confirm these assumptions.

The IR spectra of PHAL convincingly show that the phosphorylation of HAL takes place at aliphatic and phenolic hydroxy groups. The absorption band in the region of the stretching vibrations of phenolic groups at 1220 cm^{-1} and the deformation vibrations at 1378 cm^{-1}, and also the bands at 1070 and 1030 cm^{-1} characteristic of C−O in secondary and primary alcohols, have almost disappeared. A new broad band has appeared in the

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TABLE 1

Compound	Elementary composition, %			Functional groups, %			
	N_{tot}	P	Cl	OH_{tot}	OH_{Phen}	COOH	OCH_3
HL	—	—	—	9,44	4,96	3,95	15,41
HAL	4,38	—	—	18,78	4,11	14,34	10,36
PHAL	3,12	4,62	12,70	3,62	3,20	2,40	3,12
Anabasine-PHAL	8,64	3,97	1,37	3,80	3,12	2,27	3,00
4-(Piperidin-4'-yl)pyridinyl-PHAL	9,21	3,90	1,12	3,74	3,17	2,30	3,10
4,4'-bipiperidinyl-PHAL*	11,40	3,37	0,97	3,12	3,00	2,15	2,96

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*Mixture of mono and di derivatives.

1280-1030 cm^{-1} region which combines the bands of $P-O-C_{alip}$(1050-990 cm^{-1}), $P-O-C_{arom}$(1240-1190 cm^{-1}), and $P=O$ (1300-1250 cm^{-1}), and there is also a $P-Cl$ band at 530 cm^{-1}. The band due to the $C-Cl$ bond in the carbonyl chloride grouping is shifted as a result of interaction of the bonds in the high-frequency direction – to 820 cm^{-1}. There is a weak band at 2935 cm^{-1}, and the band at 2850 cm^{-1} which characterizes the asymmetrical and symmetrical stretching vibrations of methylene groups, has completely disappeared. Consequently, the phosphorylation of HAL is accompanied by intensive demethylation.

A comparison of the amounts of hydroxy groups and carboxy groups in the HAL that have reacted with PCl_3 (81.0% and 83.5%, respectively) shows that the reaction leading to the formation of carbonyl chlorides takes place in preference to that leading to phosphate esters.

EXPERIMENTAL

The samples for analysis were washed with water to neutrality and dried to constant weight in a vacuum desiccator over P_2O_5. The IR spectra of the samples were recorded on a UR-10 spectrophotometer in the 3600-500 cm^{-1} region in tablets with KBr (5 mg of substance and 300 mg of KBr).

Methoxy groups were determined by a volumetric method of analysis [7], carboxy groups by the oximation method [8], and the total hydroxy groups by a modification of the method of acetylation in the presence of perchloric acid as catalyst [9]. For the quantitative analysis of the phenolic hydroxyls we used the method of potentiometric titration with potassium methanolate in a nonaqueous medium [10], and for the carboxy groups potentiometric titration.

The initial anabasine, 4-(piperidin-4'-yl)pyridine, and 4,4'-bipiperidinyl were obtained by known methods, and the resulting compounds were characterized by properties corresponding to those given in the literature [11, 12].

The ammoniated lignin was obtained on the equipment of the Zaporozh'e hydrolysis-yeast factory, using for this purpose the hydrolysis apparatus in which the hydrolysis of plant raw material is usually performed in order to obtain ethanol or protein fodder yeast. A 1 : 1 mixture of maize stumps and sunflower husks (8 tons) was subjected to percolation with sulfuric acid at 11 atm and 200-220°C. After the pressing out of the hydrolyzate, the HL remaining in the apparatus was washed with water until SO_4^{2+} had disappeared and was ammoniated with a 25% solution of ammonia (1000 liters) at 12 atm for 4 h. Then it was washed, pressed out, and dried. The properties of the HAL obtained are given in Table 1.

The reaction of the HAL (1 part by weight) with phosphorus trichloride was performed in dioxane (10 parts by weight) at 25-30°C (14-16 h) and the PHAL obtained (see Table 1), after being washed on the filter with chloroform, was subjected to amination. To the PHAL (1 part by weight) in chloroform (10 parts by weight) was added 0.2 parts by weight of an amine – anabasine, 4-(piperidin-4'-yl)pyridine, or 4,4'-bipiperidinyl – and the mixture was heated at 65-70°C for 6 h. The am-PHAL (see Table 1) was washed on the filter with hot water until the reaction for Cl^- was negative.

Preliminary trials of the am-PHAL for anticorrosion activity gave positive results. Thus, comparative results with HAL, which is the basic rust converter PRL-2 [13], showed that preparations based on phosphorylated ammoniated lignin are capable of readily forming salts with iron cations and that their ion-exchange capacity is 2.5 times greater than that of HAL, and, consequently, their anticorrosion activity is higher.

SUMMARY

On reaction with phosphorus trichloride, hydrolysis-ammoniated lignin forms products containing phosphate ester and carbonyl chloride groups.

Lignincarbonyl chloride reacts with anabasine, 4-(piperidin-4'-yl)pyridine and 4,4'-bipiperidinyl to form the corresponding amides of phosphorylated lignins.

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