

PHOSPHORYLATION OF TECHNICAL LIGNINS

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A method for phosphorylation of technical lignins and their derivatives by the action of thiophosphoryl chloride on air-dried sodium lignates over 5–30 min with vigorous stirring and simultaneous grinding in a solvent-free vibrating reactor at 20–80°C followed by alkali-metal alkoxides with vigorous stirring and simultaneous grinding for 10–40 min at the same temperature and a 1:1 mole ratio of phosphorylating reagents calculated per mole of lignin OH groups was developed.

Keywords: phosphorylation, technical lignins, lignothiophos, sodium lignates, thiophosphoryl chloride, vibrational grinding, alkali-metal alkoxides.

Phosphorylation of lignins is a promising method for preparing organophosphorus sorbents and fertilizers and pesticides based on them. Esters of lignins and *O,O*-dialkylthiophosphoric acids are most interesting. Technical lignins and their derivatives containing electron-accepting groups ($-\text{NO}_2$; $-\text{NO}_2$ and $-\text{Cl}$; $-\text{CN}$, etc.) that are recommended for application as insecticides are used for preparation of the esters as the principal active ingredients of Lignothiophos [1].

Methods were developed for preparing esters of *O,O*-dialkylthiophosphoric acid and lignin derivatives in which a functional lignin derivative was dissolved in aqueous base solution or the air-dried sodium salt of a functional lignin derivative was suspended in an organic solvent and then mixed with a catalyst and *O,O*-dialkylthiophosphoric acid chloride. The final product was isolated from the reaction mixture by acidification and rinsing with a large amount of H_2O [2, 3]. Shen carried out phosphorylation of aminochlorolignin obtained with lignin from alkaline sulfates to produce preparations exhibiting elevated fungicidal activity and containing up to 4.2% P [4]. The main drawbacks of these methods are the length of the process (up to 2.5 h), the elevated process temperature (60–80°C), and the need to use and regenerate organic solvents.

A method is known for the phosphorylation of lignin and its derivatives by *O*-methyl-*O*-ethylchlorothiophosphate that results in the production of lignothiophos [5]. Air-dried sodium or potassium lignates are treated with *O,O*-dialkylthiophosphoric acid chloride by a solvent-free mechanical chemical method in order to produce it.

A drawback of this method is the fact that the reaction uses *O,O*-dialkylthiophosphoric acid chloride, the preparation of which consumes considerable time and material resources, uses metallic sodium and organic solvents, and takes up to 8 h [6].

The goal of the present work was to develop a method for phosphorylation of lignins [7] through successive treatment of air-dried sodium or potassium lignates first with thiophosphoryl chloride and then with alkali-metal alkoxides by a solvent-free mechanical chemical method.

The following starting lignins were studied: H_2SO_4 acid-hydrolyzed (I), H_2SO_4 acid-hydrolyzed nitro (II), H_2SO_4 acid-hydrolyzed chloro (III), H_2SO_4 acid-hydrolyzed chloronitro (IV).

The first synthesis step was production of lignothiophosphoric acid dichlorides. For this, a weighed portion of air-dried sodium lignate was treated with an amount of thiophosphoryl chloride calculated for the hydroxyl content in the starting lignin (1 mol per mol of lignin OH groups). The resulting product was analyzed for Cl and S content (Table 1).

Thus, intermediates for the synthesis of *O,O*-diethyl esters of lignothiophosphoric acids containing up to 7.5% bound S and up to 19.2% Cl were obtained. The lignin derivatives containing electron-accepting substituents ($-\text{Cl}$ and $-\text{NO}_2$ groups) were the most reactive. Larger amounts of S and Cl were introduced into lignins with a larger amount of OH groups (nitro and chloronitro derivatives) (Table 1).

†Deceased.

TABLE 1. Composition of Lignothiophosphoric Acid Dichlorides (40°C, Synthesis Time 30 min)

Starting lignin	Starting reagent, g		Starting lignin, %		Reaction product, %	
	sodium lignate	PSCl ₃	OH	Cl	S	Cl
I	50.0	26.0	5.2	–	3.2	5.8
II	19.6	13.5	6.9	–	7.5	14.2
III	17.3	9.2	5.3	21.7	3.0	19.2
IV	50.8	30.0	6.1	11.0	6.6	18.5

TABLE 2. Effect of Synthesis Conditions on Properties of Ethyl Esters of Lignothiophosphoric Acids (40°C, Synthesis Time 30 min)

Starting lignin	Starting reagent,* g	Starting lignin, %		Reaction product, %		
	C ₂ H ₅ ONa	Cl	S	Cl	S	Insecticidal activity, min (paralysis/death)
I	2.3	–	0.9	–	3.0	Inactive
II	5.7	–	0.7	–	6.9	15/30
III	7.7	21.7	0.6	19.5	3.0	30/45
IV	7.0	17.5	0.5	11.2	7.1	5/10

*The amount of lignothiophosphoric acid dichloride in all starting lignins was 20 g.

TABLE 3. Effect of Synthesis Time on Properties of Lignothiophos (1:1:1 OH-PSCl₃-C₂H₅ONa Mole Ratio, Synthesis Temperature 40°C)

Time, min	Amount of sodium nitrolignate, g	S content, %	Time, min	Amount of sodium nitrolignate, g	S content, %
5	20.0	5.0	20	20.0	7.2
10	40.0	5.5	30	20.0	7.5
15	20.0	6.8	40	10.0	7.3

The effect of the nature of the lignin preparation and the amount of sodium ethoxide on the properties of the resulting ethyl esters of lignothiophosphoric acids was studied (Table 2).

The effect of the synthesis temperature on the properties of lignothiophos (synthesis time 30 min, 1:1:1 OH:PSCl₃:C₂H₅ONa mole ratio, amount of sodium nitrolignate 20 g) was studied. The content of bound S increased smoothly with increased synthesis temperature. Thus, the S content was 7.2% at 20°C; 7.8%, 40 and 60°C; and 8.1%, 80°C. All resulting preparations exhibited insecticidal activity.

The synthesis time affected the properties of *O,O*-diethyl-*O*-nitrolignothiophosphate (lignothiophos) as follows. Increasing the time of mechanical chemical synthesis from 5 to 40 min at 40°C and various amounts of sodium nitrolignate (1:1:1 OH:PSCl₃:C₂H₅ONa mole ratio) increased the content of bound S in the resulting products from 5.0 to 7.3%. All resulting preparations exhibited insecticidal activity (Table 3).

Increasing the amount of thiophosphoryl chloride from 1.1 to 2.0 mol per mole of lignin OH groups increased smoothly the amount of bound S from 7.0 to 7.8%. All resulting preparations exhibited insecticidal activity (Table 4).

Increasing the amount of sodium ethoxide from 1.1 to 2.0 mol per mol of lignin OH groups caused a smooth increase in the amount of bound S from 7.0 to 7.9%. All resulting preparations exhibited insecticidal activity (Table 4).

Thus, the optimum conditions for preparing lignothiophos were treatment of air-dried thiophosphoryl chloride lignates with vigorous stirring and grinding in a solvent-free vibrational reactor for 5–30 min at 20–80°C and treatment of the resulting products with alkali-metal alkoxides with vigorous stirring and simultaneous grinding for 10–40 min at the same temperature with a 1:1 mole ratio of phosphorylating reagents and lignin OH groups.

The resulting products had high insecticidal activity and could be used as insecticides.

TABLE 4. Effect of Amount of PSCl_3 and $\text{C}_2\text{H}_5\text{ONa}$ on Properties of Lignothiophos (40°C, Synthesis Time 30 min, Amount of Sodium Lignate 10.0 g)

OH- PSCl_3 - $\text{C}_2\text{H}_5\text{ONa}$ mole ratio		S content, %	
PSCl_3	$\text{C}_2\text{H}_5\text{ONa}$	PSCl_3	$\text{C}_2\text{H}_5\text{ONa}$
1:1.1:1	1:1:1.1	7.0	7.0
1:1.2:1	1:1:1.2	7.5	7.2
1:1.3:1	1:1:1.3	7.5	7.5
1:1.5:1	1:1:1.5	7.7	7.5
1:2.0:1	1:1:2.0	7.8	7.9

EXPERIMENTAL

The starting material was air-dried H_2SO_4 acid-hydrolyzed lignin (Krasnoyarsk Hydrolysis Plant) with ash content 7.5%. The functional composition of the lignin was OCH_3 (13.2%), OH_{tot} (5.2%), and COOH (0.8%).

Preparation of Chlorolignin. A weighed portion of lignin (10 g) was suspended in CCl_4 (100 mL) in a three-necked quartz flask (250 mL) equipped with a stirrer and reflux condenser. Dry Cl_2 was passed through the lignin suspension in CCl_4 for 5 h with continuous illumination by UV light. The temperature in the reaction flask was thermostatted at 70°C ($\pm 1^\circ\text{C}$). After the indicated time, the reaction mixture was cooled. The precipitate was filtered off, rinsed with CCl_4 until neutral, and dried *in vacuo*. The yield of chlorolignin was 120%; content of bound Cl, 21.7%.

Nitrolignin was prepared by nitration of H_2SO_4 acid-hydrolyzed lignin with HNO_3 (12%) as before [8]. Chloronitrolignin was prepared by chlorination of nitrolignin in CCl_4 by the method given above. The yields of nitro- and chloronitrolignin were 117 and 120%, respectively.

Preparation of Lignothiophosphoric Acid Dichloride. A weighed portion of sodium lignate and an amount of thiophosphoryl chloride calculated from the content of OH groups in the starting lignin preparation (1 mol per mol of lignin OH groups) were stirred vigorously with simultaneous grinding in a vibrational reactor for 5–30 min at 20–100°C. After the indicated time, the reaction mixture was transferred onto a glass filter and rinsed with icewater to remove NaCl. The dried product was analyzed for Cl and S content by the Schoeniger method [9].

Preparation of *O,O*-Diethyl-*O*-nitrolignothiophosphate (Lignothiophos). A weighed portion of air-dried lignothiophosphoric acid dichloride prepared in examples 1-6 was treated in small portions with an alcohol solution of the calculated amount of sodium ethoxide (1 mol per mol of lignin OH groups) and stirred vigorously with simultaneous grinding in a vibrational reactor for 30 min at 40°C. After the indicated time, the reaction mixture was transferred onto a glass filter and rinsed with icewater to remove NaCl. The dried product was analyzed for Cl and S content by the Schoeniger method [9].

The insecticidal activity of the Lignothiophos preparations was determined according to Methodical Instructions [10] from the lifespan of 20 flies of the species *Musca domestica* in a closed 1-L vessel with lignothiophos (1 g) placed in it at room temperature.

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