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Pesticides Combined with Polymeric Substances

Part II. Synthesis of Thiolignin-(dialkyl phosphorothioate)

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By treating thiolignin with sodium hydride in *N,N*-dimethylformamide, thiolignin *O*-sodio derivative was obtained. The derivative was combined with dialkyl phosphorochloridothioate to afford thiolignin-(dialkyl phosphorothioate).

INTRODUCTION

It is well known that the manufacture and use of some efficient pesticides for pest controls have been placed under a ban, because of their pollution to human and environment. Therefore, persistent pesticides are undesirable. There are, however, pesticides of which short lives tend to be ineffective.

In these points the development of pesticidal chemicals, which are toxic to insects and diseases of plant but relatively less toxic to mammals, moreover, which are not source of the environmental pollution, will be more required for the direct control of pests.

Allan (1969) and Allan *et al.* (1971) have suggested that if pesticides are chemically combined with polymer substance such as sawdust, bark, cellulose, lignin, protein materials and tannin etc., their useful lives will be prolonged. Because the pesticides-wood waste combinations decompose gradually in the soil and the active pesticide is continuously released over a long period of time. That is, this chemical combination makes pesticides inactive until the linkage is broken, thus ensuring slow release of pesticides. They have demonstrated by use of, what is called, controlled-release pesticides as a combined herbicide-polymer.

Goryaev *et al.* (1971) have reported that dry distillation product of hydrolyzed lignin can be used as insecticides against *Aphididae* (aphids) and *Brevicoryne brassicae* (aphid), and that this preparation is not toxic to human and warm-blooded animals and it has no harmful effects on plants. Prior to the present report, it has already been discussed about some of other general advantages (Lee and Maekawa, 1974). Thus, we have also continued to study the synthesis of organophosphorus thiolignin derivatives.

Studies on phosphorylation of lignins have already been attempted by following researchers to obtain substance with pesticidal properties. In 1966, lignin phosphites and phosphinites (Nifant'ev and Fursenko, 1966) were produced by treating lignin with esters or amides of acids of trivalent phosphorus at 110-

150° C in the presence of catalysts such as metallic sodium or sodium alcoholate. O-Methyl-O-ethyl-O-lignothiophosphate (lignothiophos) was prepared by treating O-methyl-O-ethyl chlorothiophosphate with nitrolignin derived from cotton seed hulls (Pershina *et al.*, 1966). Later on, O,O-diethyl-O-nitrolignothiophosphate was prepared by reactions of nitrolignin with O,O-diethyl chlorothiophosphate at 92-95°C in the presence of sodium hydroxide and pyridine, and this compound was a quite powerful insecticide (Tronov *et al.*, 1966).

Recently, Polishchuk and Pershina (1972) have shown that a phosphorylated lignin was prepared by reaction of chlorolignin with tributyl phosphite by Arbuzov's rearrangement, and that this compound had bactericidal and insecticidal properties. Pershina *et al.* (1969) have reported that the reaction of lignin with phosphorus oxychloride in carbon tetrachloride gave a product with weak insecticidal properties, while by the reaction with thiophosphoryl chloride, a highly insecticidal product was obtained from nitrochlorolignin.

More recently, Vasil'eva and Pershina (1973) have described that phosphorylated lignins obtained from the reaction of dimethyl hydrogen phosphite with lignin model compounds containing a carbonyl group and alkyl-aryl ether bond had weak pesticidal activity.

As described above, most of these phosphorylations of lignins have been carried out by reactions of chlorolignin or of nitrolignin with organophosphorus compounds at higher temperatures. The present paper deals with the synthesis of thiolignin-(dialkyl phosphorothioate) through a quite different route.

EXPERIMENTAL

Materials

Thiolignin powder was supplied by Toukai Pulp Co. Ltd. This sample was dried overnight at 110°C and used as a starting material. The physical and chemical properties of thiolignin used are shown in Table 1.

Preparation of thiolignin-(dialkyl phosphorothioate)

Thiolignin (1 g) was placed in a four necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel with a calcium chloride tube. Then, 30 ml of *N,N*-dimethylformamide was added. The mixture was treated with 0.6 g of 50% sodium hydride dispersed in mineral oil and stirred in an atmosphere of dry nitrogen for 1 hr, under cooling to maintain the temperature below 10°C. To the mixture was added dialkyl phosphorochloridothioate (2 g) slowly. After 3.5 hrs, the mixture was poured into ice-water under stirring, and a solid product separated was filtered and sequentially washed with methanol and *n*-hexane or petroleum ether, and dried in air, then *in vacuo*.

Analytical procedure

The synthesized compounds were chromatographed on thin layer plate of silicagel using a mixture of methyl cellosolve and acetone (1: 2, v/v) as a developing solvent. The chromatographic plates were sprayed with 0.5% palladium chloride (in 1 N hydrochloric acid), or placed in iodine vapor.

Infrared spectra were measured with a Shimadzu IR-27 G infrared spectro-

Table 1. Physical and chemical properties of thiolignin.*

Physical	Appearance	brown powder
	Water content	5 %
	Apparent density (density, g/ml)	0.45
	pH	over 3.0**
Chemical	Inorganic impurity	below 0.5 %
	Degree of purity	over 95%
	Methoxyl group	13.5 %
	Sulfur	below 2.0 %
	Functional group	Mole per (C ₆ -C ₃) unit
	Phenolic OH	0.4
	Alcoholic OH	0.7
	Carboxyl	0.16
Solubility	Water	insoluble
	Acid	insoluble
	Alkali	soluble

* Data of Toukai Pulp Company.

** Value was measured in 25% suspended solution.

photometer. Potassium bromide pellet technique was used; the conc. was 1-1.5 mg substance in 250 mg oven-dried potassium bromide. Ultraviolet spectra were measured with a Shimadzu UV-200 double beam spectrophotometer. The procedure was carried out according to the method of Sarkanen *et al.* (1967). Thus, thiolignin and its derivatives (3.2 g) were dissolved in methyl cellosolve (3 ml) and diluted with 95 % ethanol to 10 ml respectively. Several 2 ml of these solutions was transferred carefully into two 10 ml volumetric flasks. One of them was then diluted with 95 % ethanol to 10 ml, and a spectrum was measured. To the other flask, 1 N sodium hydroxide solution (1 ml) was added and the solution was diluted to 10 ml with distilled water.

Determination of phosphate in thiolignin derivatives was carried out by slightly modified Allen's method (Lee and Maekawa, 1974).

RESULTS AND DISCUSSION

The amount of lignin in dried woody stem of ordinary tree is about 20-30% (Higuchi, 1970). Thiolignin was isolated from kraft pulp and wood according to Björkman (1956) and from black liquor by acidification (Hartler and Norrström, 1969). It has been presumed that thiolignin from kraft pulp is a polymer electrolyte with complex structure and its molecular weight is about 11,000 (wt. average) or about 60 phenylpropane units.

Thiolignin powder is deep brown and bright. The chromophoric groups in lignin are generally quinoid structure, double bond and carbonyl group conjugated with the aromatic ring and catechol structures binding with metals (Hartler

and Norrström, 1969 ; Meshitsuka and Nakano, 1973). The color of organophosphorus thioglignin derivatives changed to light yellow and brown. This fact may be due to disappearance of some chromophoric groups by combining with organophosphorus compounds.

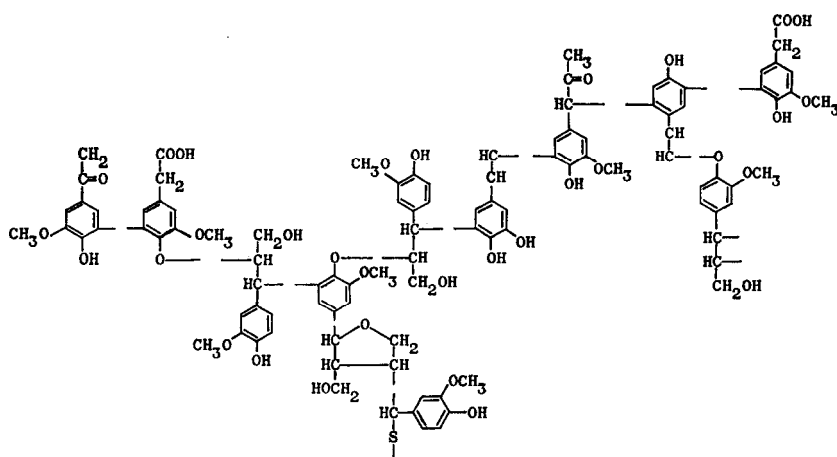


Fig. 1. Tentative structural features in a segment of pine kraft lignin molecule (Marton, 1964).

A tentative constitutional scheme of pine kraft lignin molecule proposed by Marton (1964) is mainly based on a similar type of structural presentation of native lignin (Fig. 1). He estimated that about two-thirds of the C₆—C₃ units carried free phenolic OH group in position 4, and the rest was probably etherified with carbon atom of another unit, and that kraft lignin might contain one sulfur atom in about every 12 units.

Freudenberg et al. (1961) established that almost half of units in spruce native lignin was condensed in their 5-position. Adler and Lundquist (1961) suggested that the free 5-position was evenly distributed in the etherified portion (2/3 parts) and phenolic one (1/3 parts) of MWL (milled wood lignin). Mikawa et al. (1956) reported that only about one third of the phenolic unit of kraft lignin had a free S-position, and that the solubility of thioglignin in alkali was ascribable to its carboxyl groups and phenolic hydroxyl groups.

The analytical data of thioglignin and its derivatives are given in Table 2. The analytical data of the thioglignin are quite similar to those of pine kraft lignin. The amount of the methoxyl and sulfur in pine kraft lignin was 14.04 and 1.56 % respectively (Marton, 1964), while those of the lignin obtained from a spruce (*Picea abies*) sulfate pulp showed 14.4 and 0.8 % respectively (Nilsson-Idner and Norrström, 1974).

IR-spectra of thioglignin and its derivatives showed the presence of absorption bands as shown in Fig. 2. The main feature of IR-spectrum of thioglignin sample is also similar in many respects to that of MWL and kraft pine lignin.

It is known that carbonyl groups conjugated with aromatic ring absorb at

Table 2. Elemental analysis of thiolignin and its derivatives.

	C	H	P	Ash (%)
Pine kraft lignin*	65.87	5.82	—	0.96
Thiolignin powder	66.10	5.90		0.75
Thiolignin-O- $\overset{\text{S}}{\underset{\text{P}}{\text{OEt}}}_2$	54.06	6.15	5.9	—
Thiolignin-O- $\overset{\text{S}}{\underset{\text{P}}{\text{OMe}}}_2$	50.84	5.40	7.7	—

* Data of Marton (1964).

1665 cm^{-1} , and that the content of conjugated carbonyl groups is lower in lignin from sulfate or bisulfite pulps than in lignin from wood (Norrström, 1970).

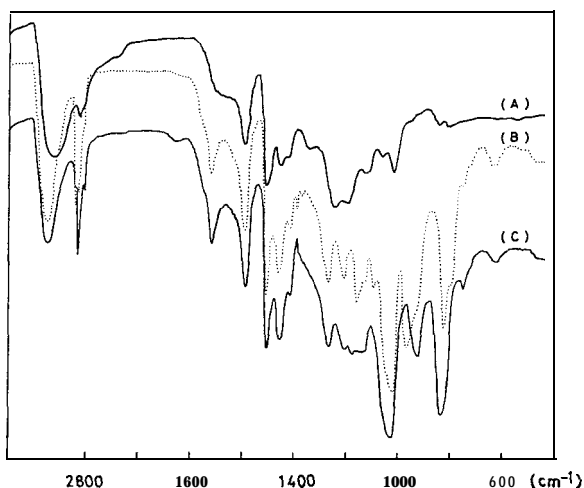


Fig. 2. IR spectra of organophosphorus thiolignin derivatives (KBr). (A): Thiolignin ; (B) : Thiolignin-O-P(S)(OEt)₂ ; (C) : Thiolignin-O-P(S)(OMe)₂.

As illustrated in Fig. 2, IR absorption characteristic to carboxyl or ester groups of thiolignin showed a weak band at 1720 cm^{-1} , but thiolignin-(dialkyl phosphorothioate) showed a strong band. Absorption bands in the region 1600-1400 cm^{-1} are typical as aromatic skeletal vibration, and those of 1400-1000 cm^{-1} are characteristic of guaiacyl and syringyl groups. while those of 1380-1340 and 1250-1150 cm^{-1} are showing the presence of hydroxyl group (Sarkanen et al., 1967).

In general, following assignments of absorption bands were made ; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3400, 3300 (OH stretching) ; 2950, 2920 (CH stretching) ; 1590, 1510 (aromatic ring C=C double bond) ; 1460, 1420 (CH deformation of methyl and methylene groups) ; 1390, 1370 (ring stretching with phenolic OH bending character) ; 1270

(CO aromatic methoxyl group ; guaiacyl type) ; 1210 (aromatic phenol ; ArOR) ; 1080 (CO aliphatic ether secondary hydroxyl) ; 1170, 1040, 1030 (CH in-plane deformation) ; 850, 810 (CH out-of-plane deformation ; aromatic).

IR-spectra of thiolignin-(dialkyl phosphorothioate) showed the presence of both absorption band characteristic of thiolignin and dialkyl phosphorothioate group. The assignments of following absorption bands were made ; IR ν_{\max}^{KBr} cm^{-1} : 1030-1020 (P-O-C alkyl) ; 970 (C-C) ; 840-820 (P(-O-)₂) ; 630 (P=S).

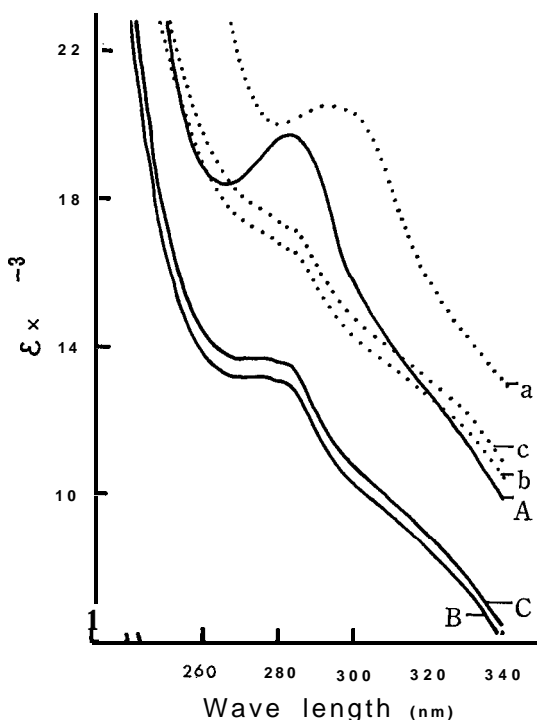


Fig. 3. UV spectra of organophosphorus thiolignin derivatives. A, Thiolignin in EtOH ; Methyl cellosolve; B, Thiolignin-O-P(S)(OEt)₂ in EtOH : Methyl cellosolve ; C, Thiolignin-O-P(S)(OMe)₂ in EtOH : Methyl cellosolve ; a, Thiolignin in 1 N NaOH ; b, Thiolignin-O-P(OEt)₂ in 1 N NaOH ; c, Thiolignin-O-P(S)(OMe)₂ 1 NaOH.

It is known that ultraviolet spectra of lignins isolated from bisulfite pulp and spent liquor have a marked maximum at 280 nm (Norrstrbm, 1970). Doub and Vandebelt (1947) have demonstrated that UV absorption spectra of mono- and disubstituted benzene derivatives could be represented as a regular progression resulting from the displacement of the absorption of benzene. These band displacements, including the effect of ionization of the substituent groups, can be interpreted on the basis of the electronic interaction between substituent groups and benzene ring. They reported the effects of alkali and strong sulfuric acid on the ultraviolet absorption spectrum of lignin. Thus they proposed a method to recognize the absorption due to phenylpropane units substituted with certain ionizable groups from that of the remaining lignin units.

UV absorption band (280 nm) of thioglignin preparation was shifted in 1 N sodium hydroxide solution to approximately 290 nm, but the spectrum of thioglignin-(dialkyl phosphorothioate) was not shifted (Fig. 3). The bathochromic shift of the characteristic absorption of lignin in alkaline solution was due to the ionization of phenolic hydroxyl groups (Aulin-Erdtman, 1953 ; Goldschmid, 1954).

Thus, it can be supposed that phosphorylation of thioglignin is related to both phenolic and aliphatic OH groups. This result is in accord with that of Galochkin et al. (1971), though they conducted the reaction of lignin with *O,O*-dimethyl chlorothiophosphate in alkaline medium.

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REFERENCES

- Adler, E. and K. Lundquist 1961 Estimation of "uncondensed" phenolic units in spruce lignin. *Acta. Chem. Scand.*, **15** : 223-224
- Allan, G. G. 1969 Pesticides (herbicidal) having a slow release action and prolonged life. *Chem. Abst.*, **71**: 100731 y
- Allan, G. G., C. S. Chopra, A. N. Neogi and R. M. Wilkins 1971 Controlled-release pesticides part II. The synthesis of herbicide-forest solid waste combinations. *Tappi*, **54**: 1293-1294
- Allan, G. G., C. S. Chopra, A. N. Neogi and R. M. Wilkins 1971 Design and synthesis of controlled release pesticide-polymer combinations. *Nature*, **234** : 349-351
- Aulin-Erdtman, G. 1953 Spectrographic contributions to lignin chemistry. III. Investigations on model compounds. *Sv. Papperstidn.*, **56** : 91-101
- Björkman, A. 1956 Studies on finely divided wood. part I. Extraction of lignin with neutral solvents. *Sv. Papperstidn.*, **59** : 477-485
- Doub, L. and J. M. Vandenbelt 1947 The ultraviolet absorption spectra of simple unsaturated compounds. I. Mono and p-disubstituted benzene derivatives. *J. Amer. Chem. Soc.*, **69** : 2714-2723
- Doub, L. and J. M. Vandenbelt 1949 II. m-and o-disubstituted benzene derivatives. *ibid.*, **71** : 2414-2420
- Freudenberg, K., V. Jovanovic und F. Topfmeier 1961 Versuche mit deuteriertem Coniferylalkohol zur Bestimmung der Substitution am C-Atom 5 der Coniferyleinheit des Lignins. *Chem. Ber.*, **94** : 3227-3238
- Galochkin, A. I., A. Pershina, Yu. S. Pilipchuk and V. I. Shufledovich 1971 Phosphorylated lignins. II. Reaction of lignins with *O,O*-dimethyl chlorothiophosphate. *Chem. Abst.*, **74** : 55388 r
- Goldschmid, O. 1954 Determination of phenolic hydroxyl content of lignin preparations by ultraviolet spectrophotometry. *Anal. Chem.*, **26** : 1421-1423
- Goryaev, M. I., L. I. Tret'yakov, M. G. Puyachev, M. G., A. N. Popov and G. P. Kornilova 1971 Use of a product of the dry distillation of hydrolyzed lignin as an insecticide. *Chem. Abst.*, **75** : 4568 n
- Hartler, N. and H. Nörrström 1969 Light-absorbing properties of pulp and pulp components. III. Kraft pulp. *Tappi*, **52** : 1712-1715
- Higuchi, T. 1971 Formation and biological degradation of lignins. *Adv. Enzymol.*, **34** : 207-

283

- Lee, C. S. and K. Maekawa 1974 Synthesis of cellulose-6-(diethyl phosphorothioate). *J. Fac. Agr., Kyushu Univ.* **19** : 1-9
- Marton, J. 1964 On the structure of kraft lignin. *Tappi*, **47**: 713-719
- Meshitsuka, G. and J. Nakano 1973 Effect of metal ion on color of lignosulfonate and thiolignin. *Tappi*, **56** : 105-108
- Mikawa, H., K. Sato and C. Takasaki 1956 Studies on the cooking mechanism of wood. XV. Mannich reaction on lignin model compounds and the estimation of the amount of the simple guaiacyl nucleus in thiolignin. *Bull. Chem. Soc., Japan*, **29** : 259-265
- Nifant'ev, E. E. and I.V. Fursenko 1966 Lignin phosphites and phosphinites. *Chem. Abst.*, **65**: 10794
- Nilsson-Iddner, K. and H. Norrström 1974 Absorption bands in electronic spectra of lignins. part VII. Lignins from a semichemical spruce sulphate pulp. Sv. *Papperstidn.*, **77**: 99-101
- Norrstrom, H. 1970 Spectra of lignins from pulp and spent liquor. Sv. *Papperstidn.*, **73** : 619-630
- Pershina, L. A., A. I. Galochkin and G. G. Lykhina 1969 Phosphorylation of lignins by phosphoric acid chlorides. *Chem. Abst.*, **71** : 14329 s
- Pershina, L. A., A. I. Galochkin, V. P. Zhuchkov and V. V. Vagin 1966 An *O*-methyl-*O*-ethyl-0-lignothiophosphate (lignothiophos). *Chem. Abst.*, **65** : 913
- Polishchuk, N. P. and L. A. Pershina 1972 Phosphorylation of lignin. III. Reaction of chlorolignin with tributylphosphite. *Chem. Abst.*, **77**: 36619 n
- Sarkanen, K. V., H. M. Chang and B. Ericsson 1967 Species variation in lignins. I. Infrared spectra of guaiacyl and syringyl models. *Tappi*, **50** : 572-575
- Sarkanen, K. V., H. M. Chang and G. G. Allan 1967 Species variation in lignins. II. Conifer lignins. *Tappi*, **50** : 583-587
- Tronov, B. V., L. A. Pershina and A. A. Kovalenok 1966 Optimum conditions for synthesis of 0,0-diethyl-0-nitrolignothiophosphate. *Chem. Abst.*, **65** : 13942
- Vasil'eva, V. P. and L. A. Pershina 1973 Phosphorylated lignins. IV. Reaction of dimethyl hydrogen phosphite with lignin model compounds containing a carbonyl group and an alkyl-aryl ether bond. *Chem. Abst.*, **79**: 106257 k