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Pesticides Combined with Polymeric Substances Part I. Synthesis of Cellulose-6- (diethyl phosphorothioate)

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Phosphorylation of 1,2,3,4-tetra-*o*-acetyl- β -D-glucopyranose was carried out with diethyl phosphorochloridothioate. The product was separated by TLC, column chromatography, and was identified by elementary analysis, IR and NMR with 1,2,3,4-tetra-*o*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate).

On the one hand, cellulose-6-(diethyl phosphorothioate) was prepared by the reaction with sodium cellulose-6-(diethyl phosphorochloridothioate). By means of periodate oxidation, the phosphorylated position in anhydroglucose units of cellulose was deduced as C-6 position.

INTRODUCTION

It has been attempted to develop new pesticidal chemicals which can display its effect after decomposing. Its purposes are to prevent environmental pollution because of their low solubility, and to save working time. Therefore, the synthesis of cellulose derivatives with organophosphorus compounds was primarily undertaken.

Most of papers on phosphorylation of cellulose have been described to the purpose of obtaining flame resistant fabrics (Cooke, 1954 ; Hendrix and Drake, 1972 ; Marvel and Bluestein 1950 ; Petrov and Sopikova, 1967; Reid and Mazzeno, 1919 ; Tesoro *et al.*, 1968 ; Yuldashev *et al.*, 1973). Among others, phosphorylated cellulose materials obtained by Arbuzov's rearrangement from chlorocellulose were non-flammable and had some bactericidal properties (Yuldashev and Muratova, 1966).

Recently it has been reported that macromolecular compounds such as cellulose and lignin etc. might be used as pesticidal chemicals with favorable natures (Allan *et al.*, 1971).

This paper deals with the synthesis of cellulose-6-(diethyl phosphorothioate) and with the confirmation of the structure. As to the biological activity it will be reported elsewhere.

EXPERIMENTAL

Preparation of 0,0-diethyl phosphorochloridothioate

This substance was prepared according to the procedure of Fletcher and co-workers (1948).

1,2,3,4-Tetra-*O*-acetyl-6-*O*-triphenylmethyl- β -D-glucopyranose and 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose

These glucose derivatives were prepared from anhydrous *n*-glucose according to the description of Whistler and co-workers (1972).

1,2,3,4-Tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate)

In a three necked flask equipped with a mechanical stirrer, a thermometer and a dropping funnel with calcium chloride tube, 1,2,3,4-tetra-*O*-acetyl-6-*O*-triphenylmethyl- β -D-glucopyranose (1 g) dissolved in dry ether (15 ml) and pyridine (0.6 g) were placed. The mixture was cooled in an ice bath at 0°C with stirring. Then *O,O*-diethyl phosphorochloridothioate (1 g) was added slowly in portions over a period of one and a half hours at 0°C. The reaction mixture was allowed to stand overnight at room temperature, then filtered. The filtrate was evaporated to remove ether. Still remaining pyridine was removed by means of azeotropic distillation with toluene. The crude product thus obtained was yellow and viscous sirup. The column chromatography using silicic acid was adopted to purify the product,

Sodium cellulosate

Sodium cellulosate was prepared by the method of Schwenker and co-workers (1961), and others (Avny and Rebenfeld, 1968; Berni et al., 1970; Lobunetz and Dusenbury, 1961; Soignet et al., 1972).

Toyo cellulose powder (A) dried overnight at 110°C was used as a starting material.

Cellulose-6-(diethyl phosphorothioate)

In a four necked flask equipped with a mechanical stirrer, a thermometer, a reflux and a dropping funnel with calcium chloride tube, sodium cellulosate (1 g) was placed with dry benzene (20 ml) and pyridine (6 g). To the suspension, *O,O*-diethyl phosphorochloridothioate (2 ml) was added slowly. The mixture was refluxed with agitation for 4-6 hrs. After it was allowed to cool and filtered, the precipitate was treated with 5 % acetic acid and washed with water until neutral. Then, it was washed with ethanol and acetone, and dried *in vacuo*.

Analytical procedure

Determination of phosphate in cellulose derivatives was carried out by the Allen's method modified slightly.

Periodate oxidation was carried out according to the method of Müller and Friedberger (1902).

Infrared spectra were measured with a Shimadzu IR-27 G infrared spectrophotometer. Nuclear magnetic resonance spectrum was measured with a JNM-C60-H spectrometer in a deuteriochloroform solution with tetramethylsilane as internal standard.

Analysis of phosphate

In a 25 ml test tube, 0.1-0.5 mg of samples and 0.5 ml of 60 % perchloric acid were placed. Then, it was heated by means of an electric heater until the digesting mixture became colorless. The cooled digested solution was diluted with 0.5 ml of water, and then heated again on a water bath for 10 min. The

cooled contents of the tube was transferred into a 25 ml volumetric flask. Then, 1 ml of amidol reagent and 1 ml of 1.5 % ammonium molybdate were added in the order to the flask, and filled up with water. After 20 min, the absorbance at 700 nm was measured with a Hitachi photoelectric spectrophotometer. The amount of phosphorus was determined from a standard curve obtained using standard solutions of potassium dihydrogen phosphate.

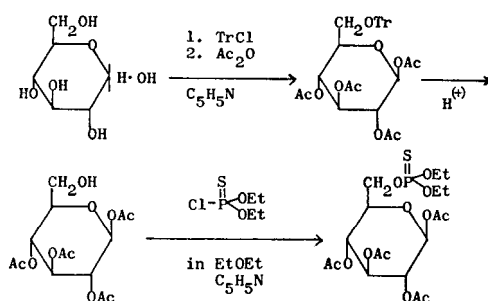
Periodate oxidation

Sample (0.1 mmole) was treated with 0.01 M NaIO_4 solution (100 ml) with stirring at 18°C in the dark. The oxidation was followed for several days by measuring the unconsumed periodate. Namely, in 5 ml aliquot of the reaction mixture, 10 ml of saturated sodium bicarbonate and 2 ml of 20 % potassium iodide solution were added, and the liberated iodine was estimated by the arsenometry using 0.01 N Na_3AsO_3 . Thus, the amount of periodate consumed after given period was determined.

RESULTS AND DISCUSSION

Anderson and Percival (1256) reported the synthesis of glucosamine 6-(dihydrogen phosphate) by phosphorylation of glucosamine with diphenyl phosphorochloridate. Recently Paulsen und Thiem (1973) prepared a series of phosphorus-containing carbohydrates by the reaction of glucopyranosyl halides with salts of dialkyl phosphate or with trialkyl phosphites.

In order to prepare glucopyranose-6-(diethyl phosphorothioate) from glucose, it is necessary to protect the secondary hydroxyl groups (Scheme 1).



Scheme 1. Synthesis of 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6- (diethyl phosphorothioate).

Preliminary experiments were therefore carried out to prepare 1,2,3,4-tetra-*O*-acetyl-6-*O*-triphenylmethyl- β -D-glucopyranose. After removal of the triphenyl methyl residue, phosphorylation of the intermediate was carried out with *O,O*-diethyl phosphorochloridothioate. The reaction mixture was stirred at first at 0°C for 1 hour then at room temperature for several hours. The progress of the reaction was pursued by TLC. TLC (silica gel) was carried out using a solvent system of *n*-hexane and ethyl acetate (1: 1, v/v). As spray reagents 0.5 % palladium chloride (in 1 N hydrochloric acid) or 50 % sulfuric acid solution (heating for 4 min at 105°C) were adopted. Glucose and its derivatives appeared as black spots by 50 % sulfuric acid solution, while phosphorothioate group appeared

as yellow and brown spots by palladium chloride solution as shown in Fig. 1.

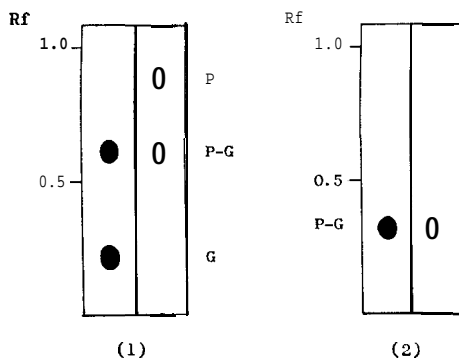


Fig. 1. Thin layer chromatogram of 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate) : (P-G), G : Acetylated glucose, P : ClP(S)(OEt)₂, TLC layers : Silica gel, Solvent (1) : n-Hexane/Ethyl acetate (1 : 1, v/v), Solvent (2) : n-Hexane/Ethyl acetate (2 : 1, v/v). Detecting agent : 50 % H₂SO₄ (●), PdCl₂ (○).

1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate) was isolated from the reaction mixture by a column chromatography based on preliminary TLC using of n-hexane and ethyl acetate (1: 1, v/v). Fractions having the same single component were combined, concentrated in a rotary evaporator and dried *in vacuo* over phosphorus pentoxide. IR spectrum of the compound obtained is shown in Fig. 2.

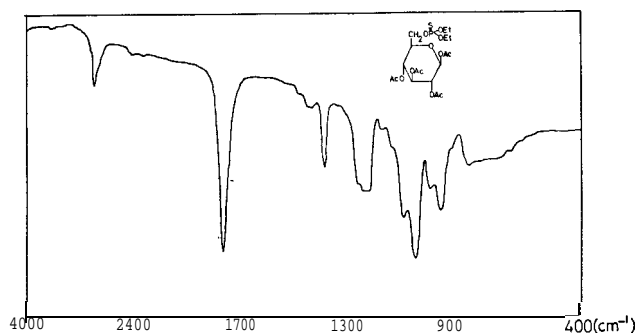


Fig. 2. Infrared spectrum of 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate). (CHCl₃)

The following assignments of absorption bands were made.

IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹ : 2975, 1440 and 1370 (-CH); 1760 (carbonyl group) ; 1030 (P-O-C alkyl); 660 (P=S).

The elementary analysis indicated the experimental formula of C₁₈H₂₉O₁₂PS. Anal. Calcd. for C₁₈H₂₉O₁₂PS·H₂O : C, 41.69; H, 5.88; P, 6.20 %.

Found: C, 41.81; H, 5.91; P, 6.40 %.

NMR spectrum of this substance is shown in Fig. 3. A detailed assignment

of the signals in the spectrum of 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate) in deuterochloroform solution is served as an illustration of the chemical shifts observed for protons. It is shown that the signals for the protons on carbon atom position of the D-glucopyranosyl ring are shifted chemically.

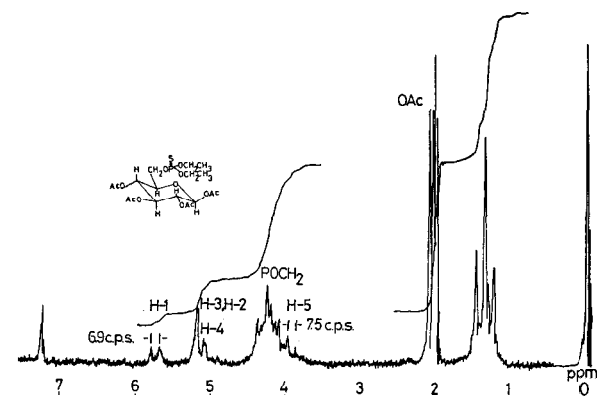


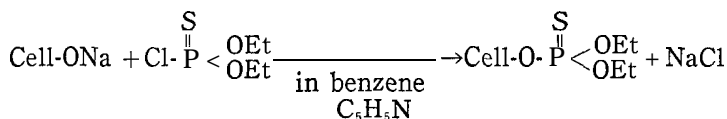
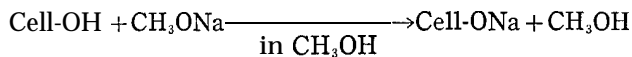
Fig. 3. Nuclear magnetic resonance spectrum of 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate). (CDCl_3)

NMR $\delta_{\text{Me}_4\text{Si}}^{\text{CDCl}_3}$ ppm: 1-H, 5.75 doublet; 2-H and 3-H, 5.19 triplet; 4-H, 5.09 triplet; 5-H, 3.98 multiplet; 6-H and $\text{P}(\text{OCH}_2)_2$, 4.25 multiplet; OAc, 2.05 quartet.

On the basis of these data, the compound was identified with 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose-6-(diethyl phosphorothioate).

Cellulose-6- (diethyl phosphorothioate)

In studies of the chemical modification of cellulose material, it is necessary to prepare alkali cellulose or sodium cellulosate as a reactive intermediate. The preparation of cellulose ester and ethers were reported by many researchers (Lobunez and Dusenbury, 1961; Schwenker *et al.*, 1961). They found that the presence of water in the cellulose impregnated with sodium hydroxide is inimical to reactions involving reagents sensitive to -OH group. Indeed, attempts for reaction of alkali cellulose with diethyl phosphorochloridothioate were unsuccessful. Thus, the following procedure was adopted for the preparation of cellulose having organophosphorus compound.



Yuldashev and co-workers (1966) reported the phosphorylation of modified cellulose preparations with phosphorylchlorides, and postulated that the presence

of primary OH group in cellulose preparations was very important for the phosphorylation. Schwenker and co-workers (1961) described that the degree of substitution found for the sodium celluloses ranged from 0.52 to 1.72, and that all three hydroxyl groups in anhydroglucose units of cellulose are available for monosubstitution by sodium.

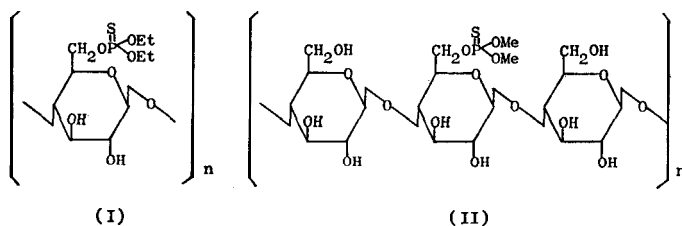
From the analytical data, it appears that cellulose diethyl phosphorothioate contains approximately one atom of phosphorus per anhydroglucose unit, and that cellulose dimethyl phosphorothioate contains one atom of phosphorus per every three anhydroglucose unit, as shown in Scheme 2.

Anal. Calcd. for Cell-O-h $\begin{matrix} \text{S} \\ \diagup \quad \diagdown \\ \text{OEt} \quad \text{OEt} \end{matrix}$ (I): C, 38.21; H, 6.05; P, 9.84; S+O, 45.90%.

Found: C, 32.09; H, 5.12; P, 7.90; S+O, 54.89 %.

Calcd. for Cell-O-P $\begin{matrix} \text{S} \\ \parallel \\ \text{O} \end{matrix}$ $\begin{matrix} \diagup \quad \diagdown \\ \text{OMe} \quad \text{OMe} \end{matrix}$ (II): C, 33.56; H, 5.24; P, 10.84; S+O, 50.36 %.

Found: C, 39.73; H, 5.64; P, 4.44; S+O, 50.19%.



Scheme 2. Supposed structures of phosphorothioated cellulose.

Champetier (1933) described the formation of a product containing one phosphate group per three glucose residues in cellulose. However, that compound could not be regarded as a true ester, because it decomposed rapidly in water. Reid and Mazzeno (1949) prepared cellulose phosphate corresponding to approximately 1 atom of phosphorus per 1.5 glucose units, by using phosphorus oxychloride and pyridine as the phosphorylating agent. Cooke (1954) reported that the phosphorus content of his preparation corresponded approximately to one phosphate group per every 4 anhydroglucose unit.

Infrared spectrum of cellulose-diethyl phosphorothioate preparation did not show sharp bands as shown in Fig. 4.

However, the following assignments of absorption bands were made.

IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3350, (-OH); 2870 and 1480, (-CH); 740, (P=S, weak).

Hendrix and Drake (1972) postulated that the secondary hydroxyl group of cellulose is much less reactive toward esterification than the primary hydroxyl group; therefore, it may be considered easily that the secondary hydroxyl group is not a major position for the binding reaction. This fact was actually demonstrated by the periodate oxidation procedure as shown in Fig. 5.

In the periodate oxidation of cellulose, it should be required 1 mole for cleavage of the bond between carbon atoms at 2 and 3 positions with formation of



Fig. 4. Infrared spectrum of cellulose-6-(diethyl phosphorothioate). (KBr)

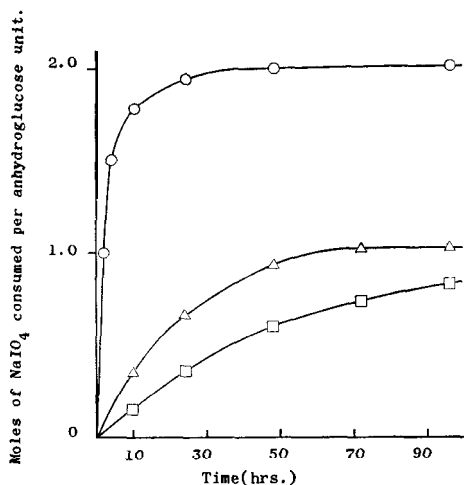


Fig. 5. Periodate oxidation of cellulose and cellulose derivative. \square — \square : Cellulose powder, \bigcirc — \bigcirc : Cellulose-6-(diethyl phosphorothioate), Δ — Δ : Phenyl salithion.

a dialdehyde (Jackson and Hudson, 1937; Rankin and Mehltritt, 1956). Theoretically, if any secondary hydroxyl groups in each anhydroglucose unit of cellulose were substituted, the consumption of periodate would be decreased corresponding to that extent.

The amount of periodate consumed for oxidation of cellulose derivatives was estimated at time intervals of 24 hrs for several days. It was found that the consumption of periodate corresponded to about 2 moles per anhydroglucose unit of cellulose-diethyl phosphorothioate. On the other hand, the consumption of periodate by phenyl salithion corresponded to about 1 mole. The latter fact might be ascribed to the conversion of the $P=S$ to $P=O$. On the whole, it was deduced that 1 mole of periodate was necessary for glycol-cleavage of cellulose derivative, and another 1 mole for oxidation of phosphorothioate group.

On the basis of above experiments, it can be supposed that phosphorylation of cellulose with dialkyl phosphorochloridothioate takes place at C-6 position of anhydroglucose units.

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