recovery for fortified milk samples, no azo compound (<0.8 ppb) was found. This is not surprising, since it has been shown that rumen fluid has a detoxification mechanism that not only destroys azo-forming systems but also destroys azo compounds already present (Katz et al., 1969).

Metabolites in Tissues. Over 90% of the radioactivity in fat was extractable with boiling hexane. Approximately 82% partitioned from hexane into acetonitrile. TLC, autoradiography, and GC/MS data confirmed the presence of intact dichloran, compound I (57.7%), and compound III (14%). The rest of the radioactivity was present as minor compounds dispersed among many fractions.

Approximately 80% of the radioactivity in kidney was extractable with chloroform–methanol (1:1) of which 15% was characterized as compound III by TLC and GC/MS, but no metabolites were found that correspond to compounds I, II, or XIII on the TLC plate even after sulfatase and glucuronidase hydrolysis. Only about 20% of the liver radioactivity was extractable with chloroform–methanol (1:1). TLC analysis of these extracts showed that 2.5% of the liver radioactivity was present as compound III. No metabolites were found corresponding to I, II, or XIII in the solvent extracts or after sulfatase and glucuronidase hydrolysis.

Radioactivity in the liver was separated into various protein fractions according to that reported by Krowke (1971), i.e., lipids as lipoproteins, 12.4%, glycoproteins as sulfurated glycosaminoglycans, 10.9%, and proteins, 33.9%. No radioactivity was found in the liver DNA fraction according to the phenol extraction procedure described by Irving and Veazcy (1968).

When the protein bound fraction in liver was hydrolyzed to the individual amino acids, only 19.6% was found in the aqueous phase, while the rest was found in the black polymeric residue resulting from the presence of carbohydrates.

CONCLUSION

The metabolism scheme (Figure 9) shows that the nitro group of dichloran was reduced and then acetylated in the ruminant goat as Van Alfen and Kosuge (1974, 1976) observed in soils and not by displacement of the nitro group by hydroxyl as Eberts (1967) and Mate et al. (1967) observed in rat urine. No azo compound (XV) was found in milk. The nucleophilic displacement of chlorine by a sulfhydryl group (methionine?) in IV was unexpected because of the ortho amine function. Since this displacement is unlikely under normal laboratory conditions, it may be enzyme mediated and probably involves a metal ion as a cofactor. Major metabolite IV may readily decompose to yield a methylthio-containing metabolite (VIII) that can be easily oxidized to V. The reaction of dichloran or metabolites with sulfhydryl groups appears to be a detoxification mechanism because of their polarity and rapid excretion in urine.

ACKNOWLEDGMENT

The technical help of Dr. R. E. Hornish, Dr. A. W. Neff, Dr. L. F. Krzeminski, Dr. L. Baczynskyj, P. A. Meulman, S. Mizsak, and R. J. Wnuk is acknowledged. The animal phase of this study was conducted by R. E. Gosline, C. J. Subacz, and T. Butine.

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Received for review April 26, 1982. Accepted August 18, 1982.

Fiber-Reactive Insect-Proofing Agents for Wool: Phosphorus Esters of 3-(Hydroxymethyl)-4-nitrophenol

Gary J. O'Loughlin

Organophosphorus esters of some substituted (hydroxymethyl)phenols were synthesized and screened for insecticidal activity against the keratin-digesting insects *Tineola bisselliella* and *Anthrenus flavipes*. Fiber-reactive groups were attached via the hydroxymethyl substituent of the more active compounds, and these were applied to wool from a dyebath. Fiber-reactive esters of *O*-ethyl *S*-*n*-propyl *O*-[3-(hydroxymethyl)-4-nitrophenyl] phosphorothionthiolate durably protected wool at an application rate of 1.5 mg/g of wool.

Recent work in this laboratory has shown that the usefulness of insecticidal organophosphorus esters for the protection of wool from insect damage is greatly enhanced by the presence of a 2-bromoacryloyl substituent in the molecule (Jones et al., 1982). This substituent is capable of covalently binding the insecticide to the wool so that the resistance of the treated wool to insect damage is rendered durable to washing, exposure to light, and dry cleaning.

Organophosphorus esters of nitrogen heterocyclic compounds have very good insecticidal activity (Jones, 1983a), but these compounds are readily hydrolyzed during dye-

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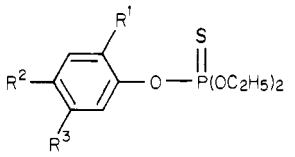
Table I. Insecticidal Activity of *O,O*-Diethyl Phosphorothioates of Substituted Phenols against Keratin-Digesting Insects



compd	R^1	R^2	R^3	application level, mg/g of wool, required to control feeding damage due to: *A. flavipes*	*T. bisselliella*
parathion	-H	$-NO_2$	-H	0.05	0.05
I	-H	$-NO_2$	$-CH_3$	0.05	0.05
II	-H	$-NO_2$	$-CH_2OH$	0.5	1.5
III	$-NO_2$	-H	$-CH_2OH$	>2	>2
IV	-Cl	-Cl	$-CH_2OH$	1.5	2
V	-H	$-SCH_3$	$-CH_2OH$	0.7	1.8
VI	-H	$-NO_2$	-CHO	0.1	1.0
VII	-H	$-NO_2$	-CH=NHOH	0.1	1.2

bath application, especially at lower pH values. It is thought that this hydrolysis of the phosphorus ester occurs by protonation of the nitrogen atom adjacent to the phosphorus ester bond.

This mechanism is not available to phosphorus esters of phenols and thus fiber-reactive derivatives of *O,O*-diethyl *O*-[4-(2-hydroxyethyl)thiophenyl] phosphorothioate possess a greater degree of hydrolytic stability in the dyebath (Jones, 1983b). However, these compounds have lower insecticidal activity.

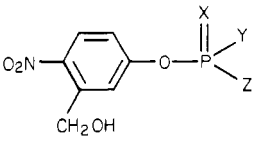
In general, the insecticidal activity of organophosphorus esters of substituted phenols is related to the electronegativity of the substituent. In this study, the insecticidal properties of phosphorus esters of substituted (hydroxyalkyl)phenols have been investigated in an attempt to obtain a suitable fiber-reactive insecticide for the industrial insect proofing of wool. Various phosphorus esters of 3-(hydroxymethyl)-4-nitro-, 3-(hydroxymethyl)-4-(thiomethyl)-, and 3-(hydroxymethyl)-4,6-dichlorophenol and some fiber-reactive derivatives have been prepared. Their insecticidal activity and hydrolytic stability have been determined.

EXPERIMENTAL SECTION

Preparation of Phosphorus Esters. The organophosphorus esters of substituted phenols and the fiber-reactive derivatives used in this study (Tables I–III) were prepared as described below. They were oils, unless otherwise stated, and were purified by liquid chromatography on a Waters Associates Preparative LC System 500 using silica gel as the adsorbent and mixtures of ethyl acetate and hexane as the mobile phase. All new compounds were fully characterized by satisfactory microanalysis, proton magnetic resonance spectrometry (Varian T-60A), and infrared spectrophotometry.

Preparation of Intermediate Phenols. *3-Formyl-4-nitrophenol* and *3-formyl-6-nitrophenol* were prepared by the nitration of 3-hydroxybenzaldehyde in benzene at 30 °C and separated by preparative liquid chromatography. *3-Formyl-4-nitrophenol* was recrystallized from water, mp 169–170 °C [Hornig (1952): mp 167–168 °C], and *3-formyl-6-nitrophenol* from toluene–hexane, mp 127–128 °C [Heilbron and Bunbury (1946, p 161): mp 128 °C]. The *oxime* of *3-formyl-4-nitrophenol* was obtained from

Table II. Insecticidal Activity of Phosphorus Esters of 3-(Hydroxymethyl)-4-nitrophenol against Keratin-Digesting Insects



compd	X	Y	Z	application level, mg/g of wool, required to control feeding damage due to: *A. flavipes*	*T. bisselliella*
II	-S	$-OC_2H_5$	$-OC_2H_5$	0.5	1.5
VIII	-S	$-OC_2H_5$	$-S$-*n*-C_3H_7	0.6	0.5
IX	-O	$-OC_2H_5$	$-OC_2H_5$	0.1	0.5
X	-O	$-OC_2H_5$	$-SCH_3$	1.5	>2
XI	-O	$-OC_2H_5$	$-SC_2H_5$	0.7	1.5
XII	-O	$-OC_2H_5$	$-S$-*n*-C_3H_7	0.6	0.7
XIII	-O	$-OC_2H_5$	$-S$-*n*-C_4H_9	0.8	1.3

Table III. Insecticidal Activity of Fiber-Reactive Derivatives

compd	R	application level, mg/g of wool, required to control feeding damage due to: *A. flavipes*	*T. bisselliella*
(A) *O,O*-Diethyl *O*-[3-(Hydroxymethyl)-4-nitrophenyl] Phosphorothioate			
II	-H	0.5	1.5
XIV	$-COCH_2Cl$	1.0	1.5
XV	$-COCBr=CH_2$	0.7	1.9
XVI	$-COCHClCH_2Cl$	0.5	1.5
XVII	$-CO(CH_2)_2SOCH=CH_2$	0.5	1.5
XVIII	$-CO(CH_2)_2SOCH_2CH_2Cl$	0.5	1.5
XIX	$-CONHCOCH_2Cl$	0.1	0.8
(B) *O*-Ethyl *S*-*n*-Propyl *O*-[3-(Hydroxymethyl)-4-nitrophenyl] Phosphorothionthiolate			
VIII	-H	0.6	0.5
XX	$-COCBr=CH_2$	0.5	1.0
XXI	$-CO(CH_2)_2SOCH=CH_2$	0.5	1.0
XXII	$-CO(CH_2)_2SOCH_2CH_2Cl$	0.5	1.0
XXIII	$-CONHCOCH_2Cl$	0.3	0.2

ethanol–water, mp 169–170 °C [Richter (1948): mp 172 °C].

3-(Hydroxymethyl)-4-nitrophenol. 3-Formyl-4-nitrophenol (10 g) in methanol (40 mL) was neutralized with dilute sodium hydroxide solution (ca. 30 mL of 2 M). To this solution, maintained at 25 °C, was added dropwise over 2 h a solution of sodium borohydride (3 g) in methanol (30 mL). Stirring was continued for 4 h during which time the sodium salt precipitated. The reaction mixture was diluted with water, acidified with dilute hydrochloric acid, and repeatedly extracted with diethyl ether. The dried ethereal layer was evaporated to yield *3-(hydroxy-*

methyl)-4-nitrophenol, mp 119–120 °C, from toluene: 78% [Heilbron and Bunbury (1946, p 163): mp 120.5 °C].

3-(Hydroxylmethyl)-6-nitrophenol was prepared from 3-formyl-6-nitrophenol by the above method, mp 98–99 °C, from toluene: 85% [Heilbron and Bunbury (1946, p 163): mp 97 °C).

3-(Hydroxymethyl)-4-(methylthio)phenol. Chlorine (6.1 g) was added slowly to a stirred solution of 3-(hydroxymethyl)phenol (10 g) and ammonium thiocyanate (12.9) in dry methanol (40 mL) while maintaining the temperature below 3 °C. Stirring was continued at this temperature for a further 30 min and then ammonia (1.4 g) was bubbled into the solution. The reaction solution was evaporated to half-volume and then poured into saturated sodium chloride solution (400 mL) and extracted with toluene. After standing 12 h the aqueous solution yielded *3-(hydroxymethyl)-4-(thiocyanato)phenol*: mp 123–124 °C; 68%. A solution of sodium methoxide (5.4 g) in dry methanol (60 mL) was added slowly with stirring to a solution of the above phenol (6 g) and methyl iodide (4.71 g) in dry methanol (50 mL), and the resulting solution was boiled under reflux for 2 h. The solution was concentrated to $^1/_3$ volume and poured into ice–hydrochloric acid. Extraction with diethyl ether gave *3-(hydroxymethyl)-4-(methylthio)phenol.*

2,4-Dichloro-5-(hydroxymethyl)phenol. 3-Hydroxybenzaldehyde was chlorinated in glacial acetic acid at 25 °C. On being cooled, 2,6-dichloro-3-hydroxybenzaldehyde separated. From the mother liquor was obtained 4,6-dichloro-3-hydroxybenzaldehyde, mp 127–128 °C [Hodgson and Beard (1926): mp 129 °C]. *2,4-Dichloro-5-(hydroxymethyl)phenol* was obtained from 4,6-dichloro-3-hydroxybenzaldehyde by sodium borohydride reduction as above.

Phosphorylation of Phenols. The following general method was used: To a solution of the appropriate phenol (0.05 mol), 4-(dimethylamino)pyridine (0.4 g), and either *O,O*-diethyl phosphorochloridothionate (9.5 g) or *O*-ethyl *S-n*-propyl phosphorochloridothionthiolate (Kishino et al., 1976) (11 g) in dry ethyl methyl ketone (70 mL) was added anhydrous postassium carbonate (9.66 g). The mixture was heated under reflux until the reaction was complete (usually 1–3 h) and filtered, and the solvent was removed under reduced pressure. The residue was dissolved in chloroform (50 mL), washed successively with 10% sodium hydroxide solution (2 × 30 mL) and water (2 × 30 mL), and dried over anhydrous sodium sulfate, and the chloroform was removed under reduced pressure to yield the phosphorothioate or phosphorothionothioate.

O-Ethyl *S*-alkyl *O*-[3-(hydroxymethyl)-4-nitrophenyl] phosphorothiolates were prepared from *O,O*-diethyl *O*-[3-(hydroxymethyl)-4-nitrophenyl] phosphorothioate by the action of an ethanolic potassium hydroxide–hydrogen sulfide solution (Beriger and Drabek, 1976) and subsequent alkylation with an alkyl halide.

Fiber-Reactive Precursors. *Chloroacetyl chloride* was obtained from BDH. *2,3-Dibromopropionyl chloride* and *2,3-dichloropropionyl chloride* were prepared by the method of Marvel et al. (1940): bp 93–96 °C, 25 mmHg (lit. bp 81–84 °C, 18 mmHg), and bp 64–67 °C, 24 mmHg (lit. bp 52–54 °C, 16 mmHg), respectively.

3-(2-Chloroethyl)sulfonylpropionyl chloride was prepared from 3-(2-chloroethyl)sulfonylpropionic acid (Badishe Aniline & Soda Fabrik A.G., 1964) with excess of thionyl chloride.

α-Chloroacetyl isocyanate was prepared by the method of Speziale and Smith (1973): bp 48–51 °C, 27 mmHg (lit. bp 68–70 °C, 70 mmHg).

Preparation of Fiber-Reactive Esters. All fiber-reactive esters were prepared by the following general method. To a solution of hydroxymethyl-substituted organophosphorus ester (0.01 mol) and the appropriate acid chloride (0.01 mol) in anhydrous toluene (60 mL) was added slowly with stirring a solution of triethylamine (1.01 g) or collidine (1.21 g) in anhydrous toluene (15 mL). The reaction solution was maintained at ambient temperature during the addition. The mixture was stirred for 22 h, filtered, and then extracted successively with dilute HCl (2 M, 3 × 20 mL), aqueous Na_2CO_3 (10%, 2 × 20 mL), and water (2 × 20 mL). For fiber-reactive precursors requiring the elimination of a hydrohalide, an extra equivalent of base was used.

Insect Testing. Insect-resist effectiveness was evaluated by assay with larvae of the common cloths moth (*Tineola bisselliella*, Hummel) and the furniture carpet beetle (*Anthrenus flavipes*, Le Conte) according to the fabric-weight-loss method as described in AATCC Standard Test Method 24-1977 (American Association of Textile Chemists and Colorists, 1979). By this standard, wool is considered resistant to insects if the feeding damage does not exceed 8 mg, provided that the feeding damage of an untreated control is 30 mg or more.

Treatment of Fabric To Determine Minimum Level Required To Inhibit Feeding Damage. Known amounts of insecticide were applied dropwise to wool fabric from an acetone solution. After the acetone had evaporated, these fabrics were bioassayed as above to determine the minimum level of the insecticide required.

Application of Fiber-Reactive Insecticide to Wool Fabric from an Aqueous Emulsion. The required amount of insecticide was dissolved in a solution of an ethoxylated nonylphenol containing 13 ethylene oxide units (Teric N13, ICI) (0.01 g) and calcium dodecylbenzenesulfonate (Alkanate CS, ICI) (0.01 g) in xylene (0.5 mL) and blended with water (49 mL) in a high-speed blender. This emulsion was applied to wool in an Ahiba Turbomat laboratory dyeing machine. The fabric package (25 g) was wet out and immersed in an aqueous solution (450 mL) of ammonium sulfate (1.0 g) and acetic acid (0.25 g) at 40 °C, and the liquor was circulated. The emulsified insecticide was then added and the temperature raised to 100 °C over 30 min and maintained at this level for 2 h. The treated fabric was removed, hydroextracted, and air-dried.

Wash-fastness. The fastness of the treatments to repeated washing in soap solutions was determined as described in AATCC Standard Test Method 28-1977 (American Association of Textile Chemists and Colorists, 1977). Oven drying (60 °C, 15 min) was included between wash cycles.

Light Exposure. Accelerated exposure to light was conducted in fan-ventilated boxes (Fincher et al., 1975) equipped with Phillips G-74 mercury–tungsten fluorescent lamps (500 W).

The samples were suspended vertically on aluminum plates 17 cm from the lamp. The black-panel temperature at the point of exposure was about 42 °C (Fincher and Rothery, 1976).

Analysis of Insecticide on Wool. *O,O*-Diethyl phosphorothioates on wool were converted to *O,O*-diethyl *S*-methyl phosphorothiolate and *O*-ethyl *S-n*-propyl phosphorothionthiolates on wool were converted to *O*-ethyl *S*-methyl *S-n*-propyl phosphorodithiolate by hydrolysis with strong alkali and methylation with dimethyl sulfate, and these derivatives were determined by gas chromatography as described by Jones (1983a).

Any insecticide that had not reacted with the fiber was removed by a 3-h Soxhlet extraction with an azeotropic mixture of benzene, methanol, and water (70:26:4). The amount of insecticide on the wool before and after Soxhlet extraction was determined.

RESULTS AND DISCUSSION

In an attempt to find organophosphorus esters with optimum biological activity and hydrolytic stability but containing an hydroxyalkyl substituent suitable for the attachment of a fiber-reactive group, several new phosphorus esters of substituted phenols were synthesized. These compounds were screened against two of the major textile pests, *A. flavipes* and *T. bisselliella* (Tables I and II).

It has been reported (Eto, 1974, p 156) that methyl substitution in the 3 position of the phenyl ring of phenyl phosphorothioates increased stability of the compounds toward hydrolysis and decreased mammalian toxicity without significant alteration to the insecticidal activity. Similarly, in this study, no change in insecticidal activity was observed when parathion was substituted in the 3 position with a methyl group (compound I, Table I). However, when this methyl group was replaced with a hydroxymethyl group, the insecticidal activity decreased by a factor of 10 against *A. flavipes* but by 30 against *T. bisselliella*. The 2-nitro isomer (compound III) was relatively inactive. Replacing the 4-nitro group with a methylthio group had little effect on the insecticidal activity whereas chloro substituents produced slightly poorer activity (compounds V and IV, respectively). When the hydroxymethyl group of compound II was replaced by an aldehydo group or its oxime (compounds VI and VII), the compounds showed enhanced activity toward *A. flavipes* but possessed similar activity against *T. bisselliella*.

When an ethoxy group of the *O,O*-diethyl phosphorothioate (II) was replaced by an *n*-propylthio group (compound VIII, Table II), a 3-fold increase in activity against *T. bisselliella* was observed, making this compound equally active against both insect species. The phosphate (compound IX) showed a further improvement in activity against *A. flavipes*, but in view of the poorer hydrolytic stability of phosphates compared to phosphorothioates or phosphorothionthiolates (Eto, 1974, p 58), this compound was not considered further. A series of phosphorothiolates of 3-(hydroxymethyl)-4-nitrophenol (compounds X–XIII) showed that optimum insecticidal activity occurred when the carbon chain length of the alkylthio radical was three (compound XII).

Several fiber-reactive derivatives were prepared by coupling a reactive precursor to the organophosphorus ester via the hydroxymethyl substituent (Table III). This ester linkage acts as the release mechanism to free the bound insecticide from the wool during insect digestion as discussed in an earlier paper (Jones et al., 1982). In general, these fiber-reactive derivatives displayed similar insecticidal activity to the parent compounds.

The insecticidal activity of these compounds was determined by applying them to the surface of wool from an acetone solution. Under these conditions it is interesting to note the enhanced insecticidal activity of the chloroacetyl carbamate derivatives (compounds XIX and XXIII).

Dyebath Application and Durability. Reaction between the fiber-reactive groups and the wool was brought about by dyebath application of the insecticides. The results of biological testing of fabrics thus treated and their durability testing to washing and light exposure are given in Table IV. To acquire adequate and durable resistance to insect attack these compounds had to be applied in the dyebath at 1.5–2 times the minimum level required to be present on the wool (as shown in Table III). Once these compounds had reacted with the fiber, the resistance to insect damage which they imparted was durable to washing and exposure to light (Table IV). In contrast, the parent hydroxymethyl compounds when applied at 3 times the minimum level required on the wool failed to pass the biological assay after minimal washing.

Table IV. Biological Testing of Some Fiber-Reactive Derivatives of the *O,O*-Diethyl Phosphorothioate and *O*-Ethyl *S*-*n*-Propyl Phosphorothionothiolate of 3-(Hydroxymethyl)-4-nitrophenol after Application in a Dyebath (at 100 °C)

compound	application level, mg/g of wool	feeding damage, mg, after application A[a]	feeding damage, mg, after application T[a]	feeding damage, mg, after 10 washes A	feeding damage, mg, after 10 washes T	light-fastness rating[b]
II	2.0	4	6	52	41	
XV	2.0	8	7	9	18	
XVII	2.0	3	7	6	12	7
XIX	2.0	4	6	8	14	6
VIII	1.5	1	2	45	12	
XX	1.5	1	3	4	6	6
XXI	1.5	2	4	3	6	7
XXIII	1.5	2	2	8	7	6

[a] A, *A. flavipes*; T, *T. bisselliella*. [b] Maximum British Standard Blue Scale rating corresponding to the light exposure above which the fabric failed the biological test (British Standards Institution, 1961).

Table V. Hydrolysis of Fiber-Reactive Derivatives of *O,O*-Diethyl *O*-[3-(Hydroxymethyl)-4-nitrophenyl] Phosphorothioate in the Dyebath[a]

compound	max deg of fixation with the wool, %	half-life, min, on the wool in the dyebath
XV	52	60
XVI	54	70
XVII	60	72
XVIII	58	63
XIX	41	37

[a] Insecticide as its emulsifiable concentrate was added to the dyebath at 40 °C. The temperature was then raised to 100 °C over 30 min and held for 90 min; pH 5.5.

Hydrolysis of the Fiber-Reactive Esters. Fabrics treated during dyeing were analyzed for residual insecticide after varying times in the dyebath. The fabrics were extracted with benzene–methanol–water azeotrope and reanalyzed to determine the degree of binding of intact insecticide to the wool (Table V). The maximum degree of fixation to the fiber was around 60% of the insecticide added to the dyebath at the beginning of the dyeing and occurred soon after the dyebath had reached 100 °C (Figure 1). In comparison, only 2% of the non-fiber-reactive insecticide (compound II) applied to the dyebath was found on the fabric after the fabric was extracted.

The amount of fixed insecticide on the wool steadily decreased by hydrolysis during the remainder of the time the dyebath was maintained at its operating temperature. This hydrolysis on the wool followed first-order kinetics, and the half-lives are listed in Table V.

The (chloroacetyl)carbamoyl derivative (compound XIX) was the least stable to hydrolysis and gave a lower level of fixation with the wool. Better levels of fixation were obtained with the other fiber-reactive groups used, but the hydrolytic stability of all of these compounds after reaction with the wool would result in severe losses of

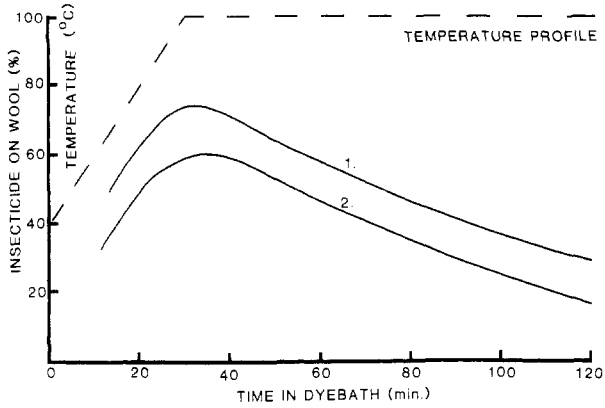


Figure 1. Application of compound XVII to wool fabric in a dyebath (1 mg/g of wool, pH 5.5). (1) Percentage of applied amount of insecticide on the wool. (2) Percentage of applied amount of insecticide on the wool after Soxhlet extraction.

insecticide during a protracted dyeing cycle.

So that the stability of phenyl phosphorus esters to hydrolysis could be increased, the electron-withdrawing effect of the phenyl substituents must be minimized (Fest and Schmidt, 1973), which generally is the opposite requirement for high insecticidal activity (Eto, 1974, pp 145–146). It is known that alkylthiophenyl phosphorus esters can be metabolically activated by oxidation of the sulfur atom to the corresponding sulfone or sulfoxide (Eto, 1974, p 164). This type of in vivo activation probably occurs in *T. bisselliella* and *A. flavipes* since the organophosphorus ester containing a 4-methylthio substituent (compound V, Table I) displayed similar activity to that of the 4-nitro analogue. The 4-methylthio substituent is an electro-releasing group and therefore would be expected to confer greater hydrolytic stability on the phosphorus ester. This was refelcted in the longer half-life on the wool of 137 min of the vinylsulfonylpropionic ester of compound V compared with 72 min for the corresponding 4-nitro derivative.

Organophosphorus compounds capable of in vivo activation will be the subject of subsequent papers from this laboratory.

CONCLUSION

Fiber-reactive derivatives of 4-substituted-3-(hydroxymethyl)phenyl phosphorus esters are useful and durable insect-proofing agents for controlling *T. bisselliella* and *A. flavipes* on wool textiles. With the electronegative nitro group as the 4 substituent, the half-lives of the insecticides when covalently bound to wool are around 70 min in a boiling dyebath (pH 5.5). The bonding to the fiber is rapid with maximum fixation occurring soon after the dyebath has reached its operating temperature.

The *S-n*-propyl phosphorothionthiolate compound is more active than the corresponding phosphorothiolate. The choice of the fiber-reactive group has little effect on the insecticidal activity but does influence the hydrolytic stability of the insecticide on the wool.

A dyebath application rate of 1.5 mg/g of wool of fiber-reactive O-ethyl *S-n*-propyl *O*-[3-(hydroxymethyl)-4-nitrophenyl] phosphorothionthiolate is adequate to durably protect wool from *A. flavipes* and *T. bisselliella.*

ACKNOWLEDGMENT

I thank P. F. Sceneay for excellent technical assistance.

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Received for review April 22, 1982. Accepted June 30, 1982.