Table 5. The reductions of the body weight of pupae of the common housefly in percent through the pupal period.

<table>
<thead>
<tr>
<th>Days after pupation</th>
<th>Control</th>
<th>Abnormal*</th>
<th>Abnormal**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>97.2</td>
<td>95.4</td>
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<tr>
<td></td>
<td>97.2</td>
<td>96.2</td>
<td>93.0</td>
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<td>96.2</td>
<td>95.4</td>
<td>90.7</td>
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</tr>
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<td>90.7</td>
<td>66.5</td>
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<td>90.7</td>
<td>80.7</td>
<td>57.8</td>
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<td></td>
<td>80.7</td>
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<td>66.5</td>
<td>57.8</td>
<td>47.8</td>
</tr>
</tbody>
</table>

* Adult emerged  ** Died in pupal period

The reductions of the body weight and pupation rate become low when third instar larvae were exposed to water or insecticide. Early pupated individuals have more heavy body weight and higher percentage of emergence of adult than the late pupated individuals.

Résumé

In this paper, the writer analyzed the several ecological problems when the larvae of the common housefly, Musca domestica vicina, were reared for the biological assay of insecticide. The results are as follows:

1. The total weight of the breeding medium decreases with elapse of day. With the increase of the larval density the rate of this reduction increases exponentially.

2. At the low larval density the percentages of pupation and emergence become low, and at the high density the larval period elongates and the small pupae appear.

3. The reduction of the pupal body weight and the low percentage of emergence of adult are observed when the third instar larvae were dipped in water or insecticide. Early pupated individuals have more heavy body weight and higher percentage of emergence of adult than the late pupated individuals.

4. During the pupal period, the pupal body weight decreases gradually with the elapse of day, but at the second day after pupation and the day before emergence this reductions are remarkable.


22. Dialkyl β-Dichlorovinyl Phosphate 及びその α-Methoxy 誘導体と Sodium p-Nitrophenoxide との反応について 有機誘導体化学的研究 第3報 永江進・柳原靖夫・小島基一（東亜農業株式会社薬剤研究所）33. 7. 5 受理

Dialkyl β-dichlorovinyl phosphate (IV, DDVP 又はその diethyl 体) 及びその α-methoxy 誘導体 (V) に就て β- 位の Cl を p-nitrophenoxy 基で置換した場合、果して殺虫効果の増強が認められたか否か検討した結果、次の結果が得られた。

* Part II: Botyu-Kagaku 23, 89 (1958)
** Kozu, Odawara, Kanagawa-ken.
Spiess and Spiess reports that dialkyl chloro-carbalkoxy-(p-nitrophenoxy)-methyl phosphonates (X) useful as insecticides, were obtained by the treatment of dialkyl carbalkoxy-dichloromethyl phosphonates (VI) with sodium p-nitrophenoxide (VII). They prepared VI by the normal Arbuzov reaction of trialkyl phosphites (I) with alkyl trichloroacetates (III). Other workers also prepared a series of VI, which were reported to be excellent insecticides with systemic activities.

Being interested in the enhancement of insecticidal activity of VI by introducing p-nitrophen oxy group, we have studied in details on the above reactions and obtained quite different results from those mentioned in the literatures.

This paper deals with the unexpected results of the reaction of dialkyl β-dichlorovinyl phosphates (IV) or their α-methoxy derivatives (V) with VII.

As mentioned above, many workers reported that VI was obtained by treating I with III according to the ordinary Arbuzov reaction. But Kharasch et al. found that this reaction gave dialkyl α-alkoxy-β-dichlorovinyl phosphates (V). They prepared diethyl α-ethoxy-β-dichlorovinyl phosphate (R=H in V) from triethyl phosphite and ethyl trichloroacetate. They confirmed the vinyl structure of V (R=H in V)
by infrared absorption data and behavior against acidic hydrolysis.

Similar reaction took place when I was treated with chloral (II) yielding dialkyl β-dichlorovinyl phosphates (IV). Dimethyl ester of IV (IVa) is an excellent systemic insecticide known as the name of DDVP, which was also obtained by the treatment of dimethyl α-hydroxy-β-trichloroethyl phosphonite (Dipterex) with alkali.

It is reasonable that V has high insecticidal effectiveness because of its very similar structure of IV, or dimethyl 1-carbomethoxy-2-propen-2-yl phosphate (Phosdrin, XIII, R=R'=CH₃) as shown in Fig. 2. In Fig. 2, phosphorus atoms of IV, V, XIII and dialkyl p-nitrophenyl phosphates (XI) have considerable electropositivity. Relation of biological properties to electronic effect of phosphorus atom has already been discussed by Fukuto, and similar relation was reported by us in the case of azophenyl phosphates.

Shown in Fig. 2, XIII or XI has a group with strong electromeric effect such as carbonyl or nitro conjugated to the double bond linkage. Hence, the phosphorus of XI or XIII seems to have a considerably high electropositivity. Perhaps this is the main reason why XI or XIII has high effectiveness against insects.

On the contrary, IV or V has only two chlorines in β-position, which cause less electropositivity of phosphorus than that of XI or XIII, owing to the inductomeric effect of chlorine. Moreover, alkoxy group of + inductomeric effect in α-position of V will lessen the electropositivity of phosphorus. From these points of view, IV or V, especially the latter, will be less effective to some extent against insects than XI or XIII.

Reaction of IV or V with VII will afford dialkyl β-chloro-β-(p-nitrophenoxy)-vinyl phosphates (VIII) or their α-alkoxy derivatives (IX) respectively. Therefore, it seemed to us that the compounds obtained by Spiess and Spiess were IX instead of X as shown in Fig. 1.

At first we tried to prepare IX according to the description in the literature. Reaction product (XIV) obtained by the treatment of diethyl α-methoxy-P-trichloroethyl phosphate (Vb, R=CH₃, R'=CH₃ in V) with VII was purified by the column chromatography or high vacuum distillation. XIV purified by chromatography (fraction A, in Fig. 8) had no chlorine. Fraction B of XIV by distillation also had no chlorine. These results showed that IX or X was not obtained. Fraction A by distillation had about 5% of chlorine owing to the contaminated Vb. Therefore clean-cut separation was done more easily by chromatography than by distillation. Elemental analyses, ultra-violet spectrum and other physical properties such as specific density and refractive index of purified XIV were compared with those of authentic sample of diethyl p-nitrophenylphosphate (para-axon, XIb, R=C₂H₅ in XI) yielding well agreed results.

Reaction of dimethyl ester of V (Va, R=R'=CH₃) with VII gave dimethyl homolog of XI (XIIa, R=CH₃) similarly.

We have continued our investigation on the reaction of IV with VII. Reaction product (XV) of diethyl β-dichlorovinyl phosphohate (IVb, R=C₂H₅ in IV) with VII was purified by repeated distillations. Data of ultra-violet and infrared spectra and paper chromatography of purified XV were very similar to those of XI (Figs. 5, 6, 7, and 8). However, it had a small content of
chlorine (from 2 to 6%), which was too high to be considered as experimental error.

Purified XV (fraction B) showed characteristic absorption at $1645 \text{ cm}^{-1}$ corresponding to double bond linkage ($\text{C} \equiv \text{C}$). This suggested that vinyl compound (starting IVb) still remained to some extent. Therefore it seemed that the purified XV by chromatography or distillation was XIb contaminated with a small amount of the starting material, IVb. Calculating the remained IVb in XV (fraction B) from the content of chlorine, IVb amounted to about 20%. Results of elemental analyses of C, H and N agreed with those of the mixture of 20% of IVb and 80% of XIb.

The same result was obtained when IVa was treated with VII. Distillation of reaction product yielded the mixture of 20% of IVa and 80% of XIa.

One of us (K. K) and his associate also determined the content of IV and XI by bioassay and enzymatic method, and obtained the same result mentioned above.

The experimental results showed that ordinarily repeated distillations or chromatography failed to separate XI from IV.

Optimum condition was tried to be found out by the following experiments. In these experiments, content of XI in the crude product, from which main part of unreacted IV was removed at reduced pressure, was determined directly by Averell and Norris' method. VII was used in either thoroughly dried salt or hydrate with 2 moles of water, and benzene or alcohol was used as a solvent. Result is shown in Table 1. Reaction in benzene generally gave better result than in alcohol, but there was no significant difference between dried and hydrated VII.

Havig obtained XIb instead of expected VIIb (R=CH$_3$) by the treatment of IVb with VII, we have tried to prepare VIIb by another method. IVb was treated with silver $p$-nitrophenoxide instead of sodium salt. Two fractions (A and B of XVI) were obtained by repeated distillations. From the result of paper chromatography, it was proved that the reaction also gave unreacted IVb (fraction A) and XIb (fraction B) as shown in Fig. 8.

In Fig. 8, the results of paper chromatography are summarized. Fractions B of XV and XVI gave almost the same $R_f$ values with that of XIb and also gave yellow spots by spraying potassium hydroxide owing to the presence of $p$-nitrophenoxy group. On the contrary, fractions A of XV and XVI gave the same $R_f$ values with IVb and gave no spot by spraying alkali.

This is the strong evidence that fractions A of XV and XVI were IVb and fractions B of them were XIb. However it was failed to detect contaminated IVb in fractions B (about 20%) because of its low sensibility to Hanes-Ischerwood reagent.

The authentic sample of XI was prepared by the ordinary method. Diethyl ester (XIb) was obtained in a high yield by the method reported by Fletcher et al. Treatment of VII with diethyl chlorophosphate (XIIIb, R=CH$_3$ in XIII) gave unsatisfactory result. On the contrary, dimethyl ester (XIa) was prepared in satisfactory yield by the treatment of VII with dimethyl chlorophosphate (XIIIa, R=CH$_3$ in XIII). XIa was obtained in poor yield by Fletcher’s method. In another run, it was tried to prepare XIa by the nitration of dimethyl phenyl phosphate. But the over-all yield from phenol or XIIIa was poor.

The formation of XI by the treatment of IV or V with VII will be explained as shown in Fig. 3.

\[
\text{(RO)}_2\text{P-OCH=CCl}_2 \rightarrow \text{(RO)}_2\text{P-O-} \overset{\text{Na}^+}{\text{[O=}} \text{C} \equiv \text{C} \text{]} \rightarrow \text{NaCl} + \text{[-C=O]}\text{ or C-C-} \text{]} \quad \text{decomposition}
\]

\[
\text{NaCl} + \text{[-C=O]} \quad \text{polymerization}
\]

\[
\text{resinous matters}
\]
\(p\)-Nitropenoxy group of VII reacts as nucleophilic reagent to the site of electropositively charged phosphorus, and the replacement of \(\beta\)-dichloro-vinyl or its \(\alpha\)-alkoxy substituted group by \(p\)-nitrophenoxy group occurs. Eliminated (\(\alpha\)-alkoxy-) \(\beta\)-dichlorovinyl groups will be further hydrolysed in alkaline medium to ethylenic or \(\alpha\), \(\beta\)-dicarbonyl compounds which will polymerize to unknown materials. But in the present study, resinous matters obtained as by-product are not yet examined in details.

**Experimental**

Column chromatography. The reaction products in the following experiments were purified by either high vacuum distillation or column chromatography. Pure Xlb was separated from products containing Xlb chromatographically with aluminum oxide. But satisfactory results were not obtained in the case of Xla. Owing to the alkalinity of reagent used, Xla was hydrolysed during elution only giving free \(p\)-nitrophenol and changing color of \(\text{Al}_2\text{O}_3\) from white to yellow, which suggested the formation of sodium \(p\):nitrophenoxide on the surface of \(\text{Al}_2\text{O}_3\). Therefore silica gel treated with dilute hydrochloric acid, was used to purify the products containing Xla. Aluminum oxide (Standardisiert nach Brockman) and silica gel for chromatographic separation from Merck were used in this experiment.

Partition paper chromatography. Paper chromatography was used as an analytical tool. Ascending development in normal or reversed phase was employed. Toyo Filter Paper No. 50 or No. 51 was used. Solvent systems employed are as follows, and \(R_t\) values in each system are given in \(R_t\) (No. 50 paper) or \(R_t'\) (No. 51 paper).

(a) Normal phase, chloroform-ethanol-water (10:10:6, upper layer). (b) Normal phase, acetic acid-\(n\)-butanol-water (1:4:5, upper layer). (c) Reversed phase, stationary phase: silicone oil (Silicone KF-54 from Shinetsu Chem. Co.), solvent: chloroform-ethanol-water (10:10:6). (d) Reversed phase, stationary phase: soy bean oil, solvent: 95% ethanol\(^{10}\). Thus, for example, \(R_t'\) shows the \(R_t\) value obtained by solvent system c and No. 51 paper. Paper was dipped into 5% ethereal solution of stationary phase, and dried in the air.

Organophosphorus compounds were detected by spraying Hanes-Ischerwood reagent\(^{19}\) and ultraviolet irradiation. Compounds containing \(p\)-nitrophenoxy group were detected by spraying 5% alcoholic potassium hydroxide\(^{16}\). No. 51 paper was more suitable than No. 50 for separation of Xlb from IVb, and system c gave the most satisfactory result in general.

Sodium \(p\)-nitrophenoxy (VII). Anhydrous VII was prepared by heating hydrated VII with 2 moles of water at \(110^\circ\)\(\text{C}\).

Preparation of methyl trichloroacetate (IIIA, \(R = \text{CH}_3\) in III). IIIa was prepared by the esterification of trichloroacetic acid with absolute methanol using conc. sulfuric acid as catalyst instead of hydrogen chloride\(^{16}\). \(b_p\) 70—71° (in 80—94% yield).

Preparation of dialkyl \(\beta\)-dichlorovinyl phosphates (IV). IV was prepared by the treatment of trialkyl phosphite with chloral. Dimethyl ester (IVA): \(b_p\) 84°, \(n_p^2\) 1.4554, \(d_p^2\) 1.4223. Anal. Calcd. for \(\text{C}_4\text{H}_4\text{Cl}_2\text{O}_4\text{P}\): C, 21.73; H, 3.19; Cl, 32.08; P, 14.03. Found: C, 21.52; H, 3.19; Cl, 32.10; P, 14.30. \(R_t\) 0.72, 0.94. I. R. is given in Fig. 6 (A). Diethyl ester (IVb): \(b_p\) 100°, \(n_p^2\) 1.4498, \(d_p^2\) 1.2973. Anal. Calcd. for \(\text{C}_6\text{H}_8\text{Cl}_2\text{O}_4\text{P}\): C, 28.93; H, 4.45; Cl, 28.47; P, 12.45. Found: C, 29.18; H, 4.41; Cl, 29.06; P, 12.35. U. V.: in Fig. 5 (C). I. R.: in Fig. 6 (B). \(R_t\) 0.47; \(R_t'\) 0.53; Rtd' 0.69.

Preparation of dialkyl \(\alpha\)-methoxy-\(\beta\)-dichlorovinyl phosphate (V). V was prepared from I and IIIa similarly as reported by Kharasch et al\(^{14}\). Dimethyl ester (Va): \(b_p\) 102—3° (in 28% yield). Anal. Calcd. for \(\text{C}_6\text{H}_6\text{Cl}_2\text{O}_4\text{P}\): Cl, 28.53. Diethyl ester (Vb): \(b_p\) 117—121° (in 58—61% yield). Anal. Calcd. for \(\text{C}_7\text{H}_12\text{Cl}_2\text{O}_4\text{P}\) Cl, 25.41. Found: Cl, 25.51. U. V.: in Fig. 5 (A). I. R.: in Fig. 6 (C).

Preparation of dialkyl \(p\)-nitrophenyl phosphates (XI) Dimethyl ester (Xla). (a) Dimethyl chlorophosphate (XIIa, 144.5 g, 1 mole) was added dropwise into the suspension of thoroughly dried and finely pulverized VII (161 g, 1 mole) in benzene (800 cc) under external cooling. After adding XIIa, the mixture was stirred at reflux for 4 hrs. Red
volatile components were removed by heating on the boiling water bath at 0.1 mm Hg. Viscous oil (XIV, 89 g) was obtained. A part (5 g) of XIV was purified by column chromatography as shown in Fig. 4.

Fig. 4. Column chromatogram of XIV.

Three fractions were obtained.

Fraction A: Colorless oil, 2.9 g (80.5% yield of XIb based on XIb found P, 11.26; Cl, 4.79) (bp 0.1-2144.7°, in ca. 34% yield of XIb; nD 1.4936, d4° 1.2839, Re0.84). Anal. Calcd. for C10H14NO3P: C, 38.87; H, 4.95; N, 5.03. Found: C, 38.5; H, 4.96; N, 5.05. I.R. : in Fig. 7 (D).

Fraction C: 0.7 g. Two fractions were obtained, one of which was a mixture of unreacted Vb (ca. 20%) and XIb (ca. 80%), 6.4 g (bp 0.1-2148.5°, in 33% yield of XIb; nD 1.5035, d4° 1.2839, Re0.84). Found: P, 11.06; Cl, 4.79. I.R. : in Fig. 7 (E).

Reaction of Vb with VII. Vb (65 g) was added dropwise into the suspension of dried VII (37.5 g) in ethanol (200 cc). After adding Vb, the mixture was stirred at reflux for 4 hrs. After cooling to the room temperature, reaction mixture was filtered to remove sodium chloride. The filtrate was concentrated in vacuo to remove ethanol. Any
Fig. 5. Ultra-violet spectra.
A: Diethyl α-methoxy-β-dichlorovinyl phosphate (Vb).
B: Diethyl p-nitrophenyl phosphate (XIIb) and fraction A of XIV.
C: Diethyl β-dichlorovinyl phosphate (IVb).
D: Fraction B of XVII.
E: Fraction B of XV.
Optical densities were observed at the concentration of 25% of substance per ml. of 95% ethanol in silica cell of 10mm width.

Fig. 6. Infrared spectra.
A: Dimethyl β-dichlorovinyl phosphate (IVa).
B: Diethyl β-dichlorovinyl phosphate (IVb).
C: Diethyl α-methoxy-β-dichlorovinyl phosphate (Vb). (Pure liquid, instrument: Koken Model D 301.)

Fig. 7. Infrared spectra.
D: Dimethyl p-nitrophenyl phosphate (XIIa).
E: Diethyl p-nitrophenyl phosphate (XIIb).
F: Fraction B of XVII.
G: Fraction B of XV.
(Pure liquid, instruments: Koken Model D 301 for D and E, Perkin Elmer Model 112 for F and G).

was purified chromatographically with silica gel giving XIIa (2.8 g, in 56% yield of XIIa, nD 1.4905, dD 1.3895, found P, 12.60; N, 5.65; Cl, 0).

Reaction of IVb with VII. IVb (24.7 g) was treated similarly as Vb with VII (16.1 g) in benzene. Reaction mixture was decanted to separate benzene layer from tarry matters, which were discarded. Crude product (XV) obtained from benzene layer, was distilled repeatedly in vacuo.

Fraction A: Unreacted Vb, 7.1 g (b.p. 96-98 71-5°C, 35% of starting Vb, nD 1.4514, dD 1.2961, Rf 0.55, Rf' 0.59, Rf' 0.89, found C, 30.00; H, 4.76; Cl, 28.49; N, 0.71; mol. wt. 226).
Fraction B: The mixture of IVb (ca. 20%) and
Fig. 8. Partition paper chromatograms.

- a: Diethyl p-nitrophenyl phosphate (XIIb).
- b: Diethyl p-dichlorovinyl phosphate (IVb).
- c: Fraction A of XV.
- d: Fraction B of XV.
- e: Fraction A of XVI.
- f: Fraction B of XVI.

A, B and C were sprayed with Hansiscerwood reagent, and radiated with UV lamp. A', B' and C' were sprayed with 5% alcoholic potassium hydroxide.

- A and A': System d and No. 51 paper.
- B': System c and No. 50 paper.
- C and C': System c and No. 51 paper.

**XIIb** (ca. 80%), 3.1 g (bp 80°-82°, in 11% yield of XIIb, n\(D\) 1.4912, d\(D\) 1.2820, RfC 0.63, RfC' 0.71, Rfd' 0.90, found C, 41.74; H, 5.02; CI, 5.83; N, 4.07, mol wt. 275). U.V.: in Fig. 5 (E). I.R.: in Fig. 7 (G).

In another run, XV was purified chromatographically on Al\(_2\)O\(_3\) yielding XIIb of ca. 93% purity (found C, 42.57; H, 5.06; Cl, 2.07).

Reaction of IVb with silver p-nitrophenoxide.

IVb (12.5 g) was treated with silver p-nitrophenoxide (3.7 g) prepared by double decomposition between VII and silver nitrate similarly as described in the reaction of IVa with VII. Crude product (XVII) was twice distilled in vacuo.

**XIIb** (ca. 93%) recovered 3.7 g (bp 68°-82°, 33% recovery of starting IVb, n\(D\) 1.4528, d\(D\) 1.4223, RfC 0.71, RfC' 0.96, found C, 35.93; H, 3.71; Cl, 13.17). U.V.: in Fig. 5 (D). I.R.: in Fig. 7 (F).

**Table 1**

<table>
<thead>
<tr>
<th>Mols. of IV and VII used</th>
<th>IV used</th>
<th>Form of VII</th>
<th>Solvent</th>
<th>Yield of crude product (A) g</th>
<th>Content of XI in A %</th>
<th>Total yield of XI from IV %</th>
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<td>0.05</td>
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<td>3.3</td>
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</table>

The result is given in Table 1.
Summary

(1) Dialkyl α-methoxy-β-dichlorovinyl phosphates (V) were prepared by the treatment of trialkyl phosphites with methyl trichloroacetate. Their vinyl structures were confirmed from infrared absorption data.

(2) V was treated with sodium p-nitrophenoxide (VII) in order to prepare 1-(p-nitrophenoxy) derivatives of V (IX). But the reaction gave only unexpected dialkyl p-nitrophenyl phosphates (XI) instead of IX or dialkyl chloro-p-nitrophenoxy-carbomethoxy-methyl phosphonate (X, R' = CH₃) which was reported in the earlier literature.

(3) Reaction of dialkyl β-dichlorovinyl phosphates (IV) with VII also gave XI. However, in this case, it was very difficult to remove starting IV contaminated in XI.

(4) The formation of XI in the above reactions (Summary 2 and 3) was confirmed from the data of ultraviolet and infrared spectra, partition paper chromatography and physical properties such as specific density and refractive index.

(5) Reaction of IV with silver p-nitrophenoxide failed also to give IX. It gave XI similarly as VII did.

(6) The yield of XI from V and VII was 56% (in dimethyl ester) or 80% (in diethyl ester) respectively. Reaction of IV with VII gave poorer yield than V, namely 11-12% in dimethyl and diethyl esters.

(7) Optimum condition was tried to be found out in the reaction of IV with VII. Reactions in benzene gave better result (from 20 to 28% yield of XI) than those in alcohol (from 3 to 11% yield of XI). Dried or hydrated VII gave no significant difference to the yield of XI.

Acknowledgement

We wish to express our thanks to Ph. Dr. Kizo Hiratsuka, Head of this Institute, for his kind encouragement and guidance throughout this work.

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Literature Cited