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Reference

1) Schrader, G.: German Patent; 1,011,416

(1955).

2) Malatesta, L. and F. Laverone: *Gaz. Chim. Italiana*, 8, 596 (1951).

3) Ping-Fang, Hu, Li Shou-Cheng and Cheng Wan-Yi: *Acta Chim. Sinica*, 22, 49 (1956).

4) Kabachnik, M. I. and T. A. Mastrykova: *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 121-5 (1953).

Thermal Decomposition of Bis-(*O, O*-dimethylthionophosphoryl)-disulfide. Kazuyuki MAEKAWA, Yoshihiro SHUTO, Eiji TANIGUCHI and Yasutaka MIYOSHI (Faculty of Agriculture, Kyushu University) Received November 8, 1973. *Botyu-Kagaku*, 39, 21, 1974.

6. Bis-(*O, O*-dimethylthionophosphoryl)-disulfide の熱分解 前川一之, 首藤義徳, 谷口栄二, 三好康之 (九州大学農学部) 48. 11. 8 受理

種々の有機燐農薬の重要な中間体である *O, O*-dimethylthiophosphoric acid は酸化還元電位 -0.302 volt で容易に酸化され, bis-(*O, O*-dimethylthionophosphoryl)-disulfide, (disulfide と略) を生成する。この disulfide は加熱によって比較的容易に分解される。Disulfide の示差熱分析では, 140°C 位から爆発的に発熱反応が始まることがわかった。この時発生するガスは, GC-MS分

析により調べた結果, CH_3SH , CH_3SCH_3 , $\text{CH}_3\text{-S-S-CH}_3$, $(\text{CH}_3\text{O})_2\text{-P}^{\text{O}}\text{-S-CH}_3$, $(\text{CH}_3\text{O})_2\text{-P}^{\text{S}}\text{-S-CH}_3$ などであった。この際の重量の減少は 39.1% であった。また disulfide は比較的低温でも変化することが観察された。即ち, 融点附近の温度に数時間保った後の IR では 1300 cm^{-1} に P=O の吸収があらわれ, NMR で δ 2.25 ppm に S-CH_3 の signal が見られること, およびその強度から, P-O-CH_3 から P-S-CH_3 への転移が推察された。

O, O-Dimethyldithiophosphoric acid, $(\text{MeO})_2\text{-P}^{\text{S}}\text{-SH}$, derived from methanol and P_2S_{10} , is an important intermediate of various organic phosphorus pesticides¹⁾. The pK' value of this acid is 1.55 (in 7% ethanolic solution)²⁾. Its redox potential has not been reported, but it is supposed to be considerably negative referred to hydrogen electrode. In fact, it is easily oxidized to convert to bis-(*O, O*-dimethylthionophosphoryl)-disulfide*. When the disulfide is heated with *p*-dioxene in the presence of hydroquinone, it converts to a pesticide analogous to Delnav³⁾. Some of bis-(*O, O*-dialkylthionophosphoryl)-disulfides have insecticidal activities⁴⁾.

However, chemical properties of the disulfide have not been sufficiently clarified⁵⁾. In particular, the thermal lability of this compound has not

* Abb. The disulfide: bis-(*O, O*-dimethylthionophosphoryl)-disulfide.

been investigated in detail. The present paper deals with an investigation of the thermal decomposition of this disulfide under the anhydrous condition.

Experimentals

1) Redox potential

The redox potential of a system of the disulfide and *O, O*-dimethyldithiophosphoric acid was measured by the polarographical method using 0.1 M, pH 7 phosphate buffer solution containing 25% methanol, 16% ethanol, and $(\text{MeO})_2\text{-P}^{\text{S}}\text{-SH}$ and $[(\text{MeO})_2\text{-P}^{\text{S}}\text{-S}]_2$ (in molar ratio of 1 : 1). Other experimental conditions are shown in Fig. 1.

From the results shown in Fig. 1, the redox potential (E_0) was calculated as $-0.304 \pm 0.005\text{V}$. vs. normal hydrogen electrode.

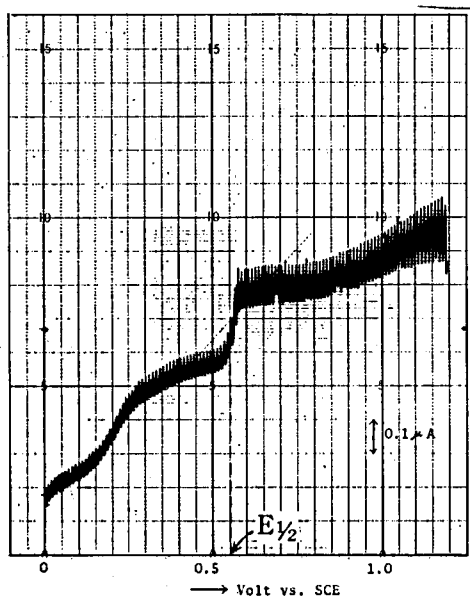


Fig. 1. Determination of the redox potential (E_0) of a system of the disulfide and *O,O*-dimethyldithiophosphoric acid by the polarography. Dumping $25\mu\text{F}$, Hg : 0.5mg/sec. Drop time=4.5 sec.

2) Differential thermal analysis

The analysis was carried out using a thermoflex-unit of Rigaku-Denki. The rate of the programming temperature was $5^\circ\text{C}/\text{min}$. Other conditions are shown in Fig.2. Fig.2 shows that as the temperature rose an endothermic reaction occurred at 61°C . An exothermic reaction started at about 140°C and reached the maximum at 174°C . At this point the weight loss was about 39%. Thus, the disulfide decomposed explosively at about 140°C and evolved a gaseous mixture.

3) Gas produced by the pyrolysis of the disulfide

The experiment was performed in order to clarify components of the gaseous mixture produced by the exothermic degradation reaction. Three grams of the disulfide was weighed into a bent, narrow-necked glass tube (about 10ml), then was gradually heated in an oil-bath. The evolved gas was trapped in a tube cooled by dry-ice and acetone. The trapped sample was examined by gas chromatography-mass spectrometry. The results are shown in Table 1 and

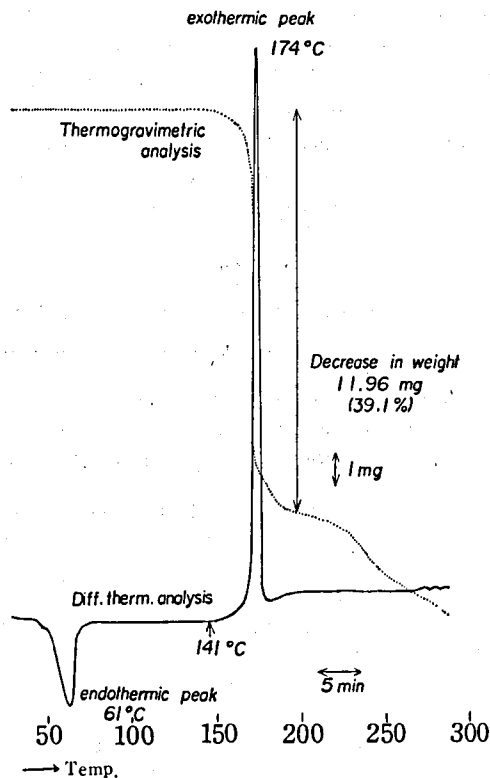


Fig. 2. Differential thermal analysis of the disulfide.

Sample wt.: 30.60mg, Std. Sample : Al, $\alpha\text{-Al}_2\text{O}_3$, Atmosphere : air, Thermocouples : platinel, Temp. Range : 20mV, Heating rate : $5^\circ\text{C}/\text{min}$, Range DTA : $\pm 500\mu\text{V}$, TG : 20mg.

Fig.3. The relative amounts of the products varied remarkably, depending on the conditions of the decomposition, but the components contained in the mixture were not changed. The identification of compounds isolated by gas chromatography was performed by comparison of mass spectra with authentic samples.

Mass spectra were determined at 75 eV on an JEOL OISG instrument with source temperature 230°C . As shown in Fig.3, $\text{CH}_3\text{-S-S-CH}_3$ (peak 2), $(\text{CH}_3\text{O})_2\overset{\text{O}}{\parallel}\text{P-S-CH}_3$ (peak 4) and $(\text{CH}_3\text{O})_2\overset{\text{S}}{\parallel}\text{P-S-CH}_3$ (peak 6) were identified. From the mass spectrum of the peak 1, $\text{CH}_3\text{-S-CH}_3$ (m/e 62) and $\text{CH}_3\text{-S}^+$ (m/e 47) were recognized (the peak 1 may be due to $\text{CH}_3\text{-S-CH}_3$ or $\text{CH}_3\text{-SH}$). Chemical

composition of peaks other than those mentioned here still remain to be investigated.

4) Mass spectrometry of the disulfide

From the spectrum of the disulfide, the fragmentation sequence can be presented as shown in

Table 1. Gas chromatogram* of decomposed disulfide.

Peak No.	Retention time (min.)	Relative amount (%)
1	1.4	5.7
2	2.2	13.0
3	3.7	1.0
4	5.1	16.0
5	10.6	1.8
6	12.9	26.9
7	16.7	6.4
8	20.1	0.8
9	24.3	5.2
10	25.9	6.0
11	33.3	1.0
12	38.2	0.6
13	41.8	0.1
14	53.3	15.5

* Gas chromatography was carried out under following conditions:

- Column 3m × 3mm, glass
- Packing 3% Silicon SE-30 on Chromosorb W-AW 60-80 mesh
- Oven temp. 70-120°C
- Carrier gas He, flow 15ml/min.
- Injection temp. 165°C
- Separator temp. 150°C
- Chart speed 10mm/min.

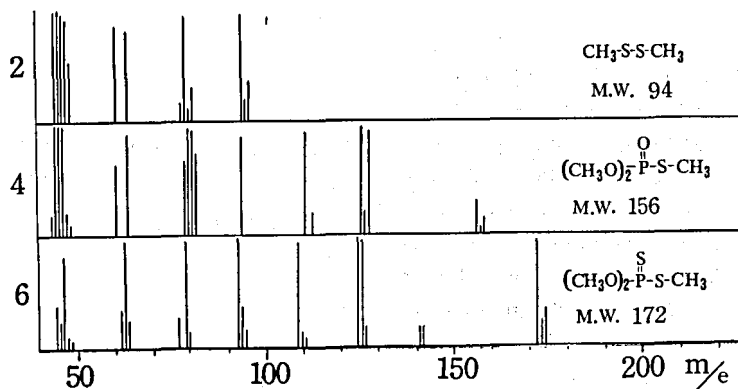


Fig. 3. Mass spectrometry of some peaks of the gas chromatogram. (Number refers to the peak of Table 1)
 Ionizing volt.: 75 eV, Accel. pot.: 3.5 KV, Trap curr.: 60μA,
 Sample temp.: 130°C, Chamber temp.: 230°C, Scan speed: 7min.

Fig. 4. Main processes were the α- and β-cleavages for the phosphorus atom, corresponding to

$\frac{S}{m/e\ 125\ (CH_3O)_2P^+}$, and $m/e\ 157\ (CH_3O)_2PS_2^+$ respectively. Then $m/e\ 157$ eliminated sulfur atoms to form the base ion peak $m/e\ 93\ (CH_3O)_2-P^+$, which was followed by further elimination to form $m/e\ 63\ CH_3O-PH$. The peak $m/e\ 125$ was decomposed into $m/e\ 79\ HO-P-OCH_3$, then $m/e\ 47\ PO$. These fragmentation patterns (shown by the gothic type in Fig. 4) seem to be reliable by the observation of metastable ions, shown in Table 2, and by referring to the literature^{6,7,9}.

5) The change of the disulfide at a relatively low temperature

After the disulfide sealed in a glass tube was maintained at 58°C for 5 to 10 hours, it was examined by means of TLC, IR, NMR and Mass spectrometry. The results obtained are as follows:

(a) TLC and column chromatography:—After being heated, the sample was applied to TLC (Silicagel HF 254). The suitable developing solvent was *n*-hexane : toluene = 4 : 1 and spots were visualized by UV-lamp or spraying 0.5% PdCl₂ in 1 N HCl. It was discernible from the TLC that the disulfide was decomposed by the mild heating into four main and a few minor compounds. R_f values of these four main products were 0.44 (α), 0.35 (β), 0.30 (γ) and 0.00 (δ), while that of the disulfide was 0.25.

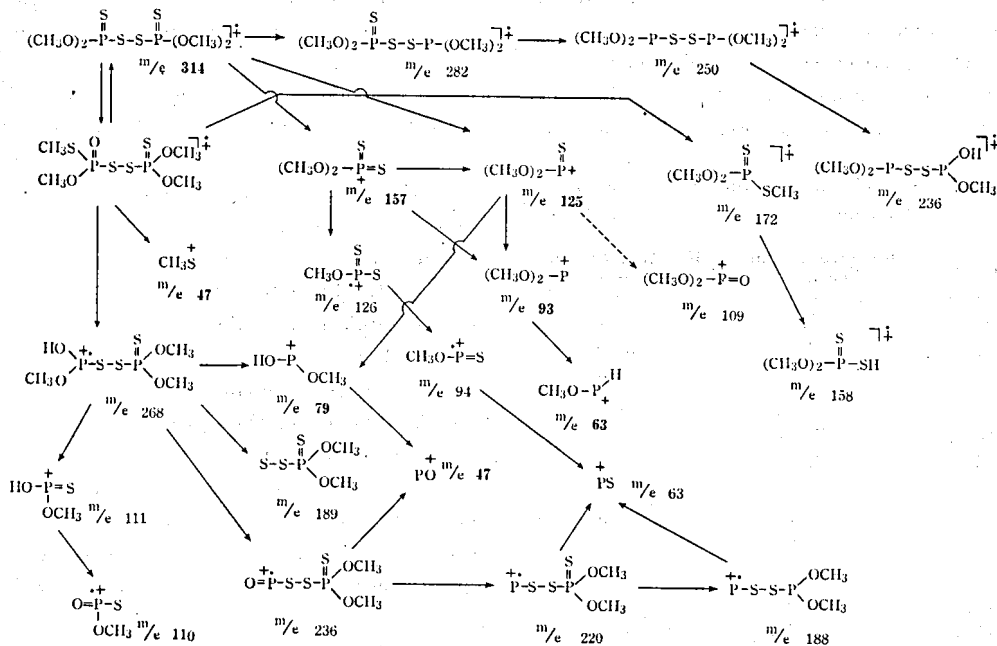
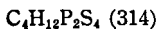


Fig. 4. Supposed fragmentation of the disulfide (Refer to the text as to m/e written by gothic type.)

In order to isolate the reaction products which were detected by TLC, the column chromatography in equivalent conditions to TLC was carried out (column: Silicagel, solvent: *n*-hexane-toluene =4-1). Among the separated fractions only γ -fraction was present in sufficient quantity to be scrutinized.

(b) Analysis of γ -fraction:



	C	H	P	S
Calcd.	15.28	3.82	19.74	40.76
Found	15.69	3.76	18.95	41.10

(c) IR, NMR and Mass spectra of the γ -fraction:

The absorption of P=O in the IR spectrum of γ -fraction appeared at 1300cm^{-1} ^{9,10}. There were some differences from the disulfide in absorptions observed at 2980, 2940, 1440 and 1165cm^{-1} (Fig. 5). NMR spectrum showed a signal due to S-CH₃ at δ 2.25 ppm

	Signal (δ ppm)	Assignment	N. B.
The disulfide	3.68 ¹¹⁾ , 3.93	P-O-CH ₃	coupling with P J=0.25
γ -fraction	3.68, 3.93 2.25 ¹²⁾	P-O-CH ₃ S-CH ₃	

Table 2. Metastable ions observed in mass spectrum of the disulfide.

Metastable ion (m/e)		Degradation passway assigned
Found	Calcd.	
199.0	$\frac{(250)^2}{314} = 199.04$	m/e 314 \rightarrow m/e 250
154.4	$\frac{(220)^2}{314} = 154.14$	m/e 314 \rightarrow m/e 220
112.6	$\frac{(188)^2}{314} = 112.56$	m/e 314 \rightarrow m/e 188
98.8	$\frac{(142)^2}{204} = 98.84$	m/e 204 \rightarrow m/e 142
55.1	$\frac{(93)^2}{157} = 55.09$	$(\text{CH}_3\text{O})_2\text{-P}=\overset{\text{S}}{\overset{+}{\text{P}}}$ $(\text{CH}_3\text{O})_2\text{-P}^+$ m/e 157 \rightarrow m/e 93
50.0	$\frac{(79)^2}{125} = 49.93$	$(\text{CH}_3\text{O})_2\text{-P}^+$ $\text{CH}_3\text{O-P-O}^+$ m/e 125 \rightarrow m/e 79
42.6	$\frac{(63)^2}{93} = 42.57$	$(\text{CH}_3\text{O})_2\text{-P}^+$ $\text{CH}_3\text{O-P-H}^+$ m/e 93 \rightarrow m/e 63

These results suggest that the γ -fraction is a compound where one methyl group of the disulfide migrated intramolecularly from O to S (Fig. 6, I).

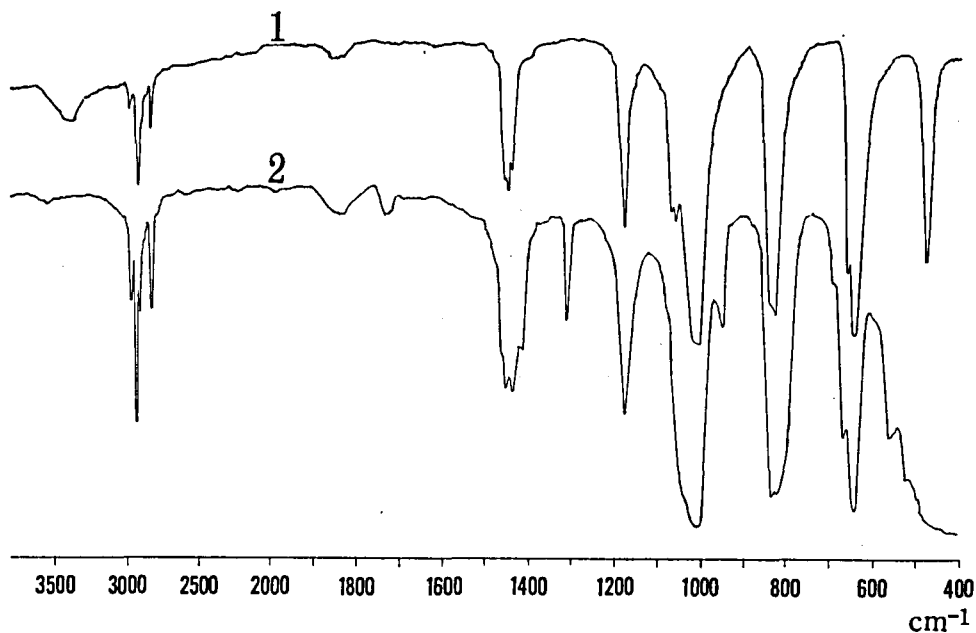


Fig. 5. IR-spectra of the disulfide (1) and the fraction isolated from the heated disulfide (2) (KBr)

The fragmentation of the mass spectra showed differences between the disulfide and the γ -fraction as shown in Table 3. On the spectrum of the γ -fraction, for example, the appearance of the peak of m/e 236 and the intensity of the peak of m/e 172 are characteristic.

Cooks and Gerrard¹³⁾ reported that the mass spectra of *O*-methyl-*O,O*-diphenyl-phosphorothioate and *S*-methyl-*O,O*-diphenyl-phosphorothiolate were characteristic in a relative intensity between the ion peaks corresponding to $M-CH_3$, $M-PhS$ and PhS : by electron impact the thiolate gave a predominant $M-CH_3$ ion along with less intensive ions of $M-PhS$ and PhS , while the latters were more intensive and the former less

intensive in the thioate. Furthermore, the occurrence of $PhSMe^{+}$ rather than $PhSPh^{+}$ in the thiolate served to distinguish it from the thioate although rearrangements between substituents in the phosphorothioate and phosphorothiolate gave rise to both ions.

In the mass spectra of bis-(*O,O*-dimethylthionophosphoryl)-disulfide and the heated sample, the splitting of the disulfide bond and/or the alpha-cleavage of the $-P(S)-S-$ are much predominant as even in the spectrum of the heat-isomerized disulfide the $M-CH_3$ ion is hardly observed; many ions were common in both spectra.

The ion peaks corresponding to (IV), (II) and

Table 3. Differences in fragmentation between the disulfide and the γ fraction isolated from the heated disulfide.**

m/e	47	63	79	93	125	157	172	188	220	236	250	314(M ⁺)	316
Disulfide	11.8	15.6	12.5	100	52.0	15.3		6.3	2.1		4.2	8.3	2.1
Heated Disulfide	12.5	9.3	8.3	100	21.3	3.3	3.4	2.5	1.3	0.4	1.8	8.2	2.1

The values of this table are shown in percentage to base ion peak m/e 93.

** Mass spectra were taken under following conditions:

Ionizing volt 75 eV Sample temp. 42°C Scan speed 3 min.

Ionizing curr. 200 A Chamber temp. 157°C Chart speed 0.8 cm/sec.

Accel. Voltage 6.1 KV

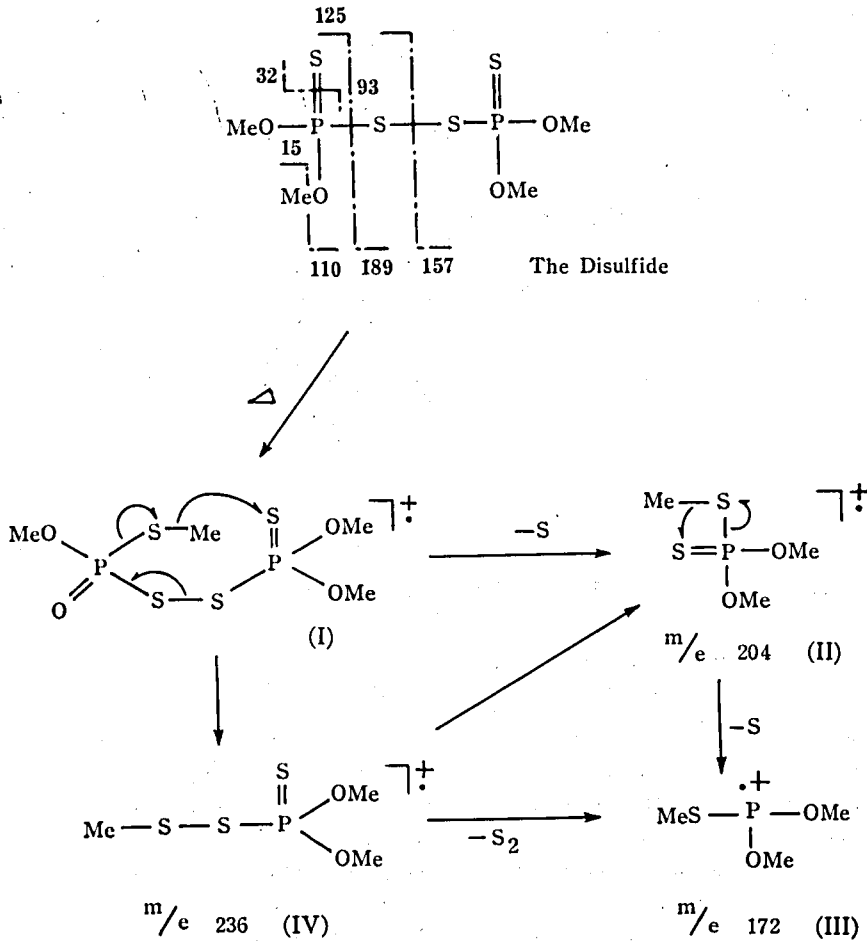


Fig. 6. Main fragmentation of the disulfide and supposed fragmentation mechanism of the heat-isomerized disulfide.

especially (III) in Fig. 6, however, are considerably more intense in the heat-isomerized disulfide, suggesting a molecular rearrangement of the phosphorothioate to a thiolate such as (I)¹⁰. The ions (II), (IV) and (III) may result from methyl migration in such ionized phosphorothiolate.

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References

- 1) Christman, L. J. (Amer. Cyanamid Co.), A. P. 1893018 (1928-33).
Malatesta, L.: *Gazz. Chim. Ital.*, 81, 596 (1951).
Malatesta, L. and R. Pizzotti: *Chem. Ind.* (Milan), 27, 6 (1945).
Wegler, R.: *Chemie der Pflanzenschutz- und Schädlingsbekämpfungsmittel*, i. Springer Verlag (1970), S. 281.
- 2) Kabachnik, M. I. *et al.*: *Zhur. Obshehei Khim.*, 31, 140 (1961); *Chem. Abst.*, 55, 22079a (1961).
- 3) Diveley, W. R. (Hercules Powder Co.), U. S. 2725327 (1955); *Chem. Abst.*, 50, 95973a (1956).
- 4) Zbirovský, M. and V. Ettel: *Sbornik vysoké*

- školy chem. -technol. v Praze*, 253 (1957);
Chem. Abst., 53, 60571 (1959).
 Pat. Brit., 847,655: *Chem. Abst.*, 55, 6775b
 (1961).
 Offen, Ger., 2,063,491: *Chem. Abst.*, 75,
 88103t (1971).
- 5) Kabachnik, M. I. and T. A. Mastryukova :
Izvest. Akad. Nauk S. S. S. R., Otdel. Khim.
Nauk, 1953, 121; *Chem. Abst.*, 48, 3244e (1954).
- 6) Biro, F. J.: *Residue Review*, 40, 4 (1971).
- 7) Damico, J. N.: *J. Assoc. Offic. Anal. Chem.*,
 49, 1027 (1966).
- 8) Gillis, R. G. and J. L. Occoclowitz: "The Mass
 Spectrometry of Phosphorus Compounds",
 Ed. by M. Halmann, *Anal. Chem. of Phos-*
phorus Compounds, 1972, p. 295.
- 9) Bellamy, L. J. and L. Beecher: *J. Chem. Soc.*,
 1952, 475.
- 10) Thomas, A.: *J. Applied. Chem.*, 1957, 198.
- 11) Fiat, D., M. Halmann, L. Kugel and J. Reuben:
J. Chem. Soc., 1962, 3837.
- 12) Bovey, F. A.: NMR data tables for org. com-
 pounds, vol.1 (1967), p. 46 and 128.
- 13) Cooks, R. G. and A. F. Gerrard: *J. Chem.*
Soc., 1968, B 1327.
- 14) Fest, C. and K.-J. Schmidt: The Chemistry
 of Organophosphorus Pesticides, Springer Ver-
 lag (Berlin, Heidelberg, New York), 1973,
 p. 37.

抄 録

幼若ホルモンの代謝阻害剤としての類縁体の作用
 Juvenile Hormone Analogs: A Possible Case
 of Mistaken Identity?

M. Slade and C. F. Wilkinson. *Science*, 181,
 672 (1973).

セクロピア蚕の幼若ホルモンの一つは, methyl-
trans, trans, cis-10, 11-epoxy-7-ethyl-3, 11-dime-
 thyltrideca-2, 6-dienoate (**JH**) である。その後,
JH 活性をもつものとして, piperonyl butoxide (1),
 piperonyl 6, 7-epoxy-3-ethyl-7-methyl-2-nonenyl
 ether (2), 10, 11-epoxy-*N*-ethyl-3, 7, 11-trimethyl-
 2, 6-dodecadienamide (3), isopropyl 11-methoxy-
 3, 7, 11-trimethyldodeca-2, 4-dienoate (4), ethyl 3,
 7, 11-trimethyldodeca-2, 4-dienoate (5), 2-propy-
 nylphenylphosphonate (6) などが知られている。

一方, スズメガ (*Manduca sexta*), ヤガ (*Prodenia*
eridania), バッタ (*Schistocerca vaga*), ニクバエ
(Sarcophaga bullata), セクロピア蚕 (*Hyalophora*
cecropia) において, **JH** は2つの経路を経て dihy-

droxy acid に代謝される。一つは, まず esterase
 が作用して, epoxy acid が生成し, 次いで epoxide
 hydrase が作用する系, 他はまず, epoxide hydrase
 が作用し, dihydroxy ester が生成し, 次いで esterase
 が作用する系である。

in vitro での実験の結果, 上記(1)~(6)の化合物は,
 本来のホルモン活性を示すというより, 昆虫に含まれ
 る, **JH** の代謝経路を阻害するように作用すると考え
 られる。

6令初期の *P. eridania* の中腸磨砕物から酵素液を
 調整し, その中へ, 2の位置を ¹⁴C でラベルした **JH**
 と上記化合物を加え一定時間培養後, TLC で分析し
 た。その結果, (1) (2) (3) を加えた場合は, epoxy
 acid に, (4) (5) (6) を加えた場合は dihydroxy
 ester に radio activity が見られた。しかも (1) (2)
 (3) については, epoxy acid の生成の割合が多いこ
 とから, (1) (2) (3) は epoxide hydrase の阻害剤と
 して, 強く作用していることがわかった。

(北村実彬)