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Studies on Pyrethroidal Compounds* Part III Photostability of Pyrethroidal Compounds
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15. ピレスロイド系化合物の研究 第3報 ピレスロイドの光安定性 安部八洲男, 津田小亮, 藤田義雄 (住友化学工業株式会社 農薬事業部研究部, 宝塚市高司4丁目2ノ1) 47. 6. 21 受理

合成ピレスロイド4種および天然ピレスリン類6種の光安定性について調査し、次のことを明らかにした。

1. 合成ピレスロイドは天然ピレスリン類に比べて一般に安定である。2. Resmethrin が最も安定であり、Tetramethrin と Furamethrin がそれに次ぐ。Allethrin はやや不安定である。3. 天然ピレスリン類6成分の中では Pyrethrin I と II が極端に不安定である。4. Cinerin I と II は Pyrethrin I と II より安定であり、Jasmolin I と II は、それぞれ Cinerin I と II 及び Pyrethrin I と II の中間くらいの安定性である。5. 第一菊酸エステルは第二菊酸エステルより光に対して不安定である。更にピレスロイドの紫外吸収極大波長と安定性との関係について述べた。

B. H. T. 及び種々の芳香族アミンのアレスリンに対する光安定化効果を調査し、N, N'-Diphenyl-p-phenylenediamine が最も効果が強いことを明らかにした。蚊取線香中ではアレスリンは、光の影響は小さいことがわかった。

更に天然ピレスリン類の中で Pyrethrin I 及び II のみが特異的に不安定な原因について考察した。

Introduction

In spite of their relatively high cost as compared with other insecticides, the current increase in demand for insecticides which do not leave

toxic residue in plants or animal foodstuffs for human consumption has resulted in renewed attention to pyrethroidal insecticides. Pyrethroids

* The previous paper, *Botyu-Kagaku*, 37, 48 (1972).

are nonpersistent insecticide compounds partly as the result of their instability on exposure to air and sunlight or ultraviolet light. Thus, it is important to consider the photostability of pyrethroids to predict conditions for their use and the possibility of retarding the photodecomposition.

There have been some studies of the stability and stabilization of pyrethrins in light¹⁻¹¹. Tattersfield and Martin found that ground flower heads and pyrethrum-impregnated talcs lost their biological activity when irradiated with either sunlight or tungsten light¹¹. The addition of hydroquinone and tannic acid slowed down the rate of photodegradation. Blackith showed that benzene-azo- β -naphthol (BABN) partially protected pyrethrins from photodecomposition². He showed that pyrethrins were less stable than allethrin when exposed to ultraviolet light and BABN had less effect as a protectant with allethrin than with pyrethrins³. Phipers and Wood showed that piperonyl butoxide stabilized the pyrethrins when a solution was irradiated with ultraviolet light⁶. Donaldson and Stevenson reported, however, that stabilization of pyrethrins by piperonyl butoxide was not demonstrated⁶. Jones found that para-aminoazobenzene (PAAB) protected primarily cinerin II and pyrethrin II and also that Sudan IV, *p*-methoxyazobenzene and Spirit Red had similar stabilizing properties to PAAB⁷. Brown and his coworkers showed under irradiation with a tungsten lamp that pyrethrin I and cinerin I degraded before pyrethrin II and cinerin II, and that the cinerins were more stable than the pyrethrins¹⁰.

This paper reports the photostability of representative synthetic pyrethroids in comparison with that of natural pyrethrins (pyrethrum extract as a mixture of six active esters), and deals the photostability of allethrin in mosquito coils used as a practical formulation and the protective effect of some chemicals on allethrin. It discusses also the relation of UV absorption spectrum to photodecomposition of pyrethroids and the alteration of natural pyrethrins.

Materials and Methods

Chemicals

Four synthetic pyrethroids were manufactured by Sumitomo Chemical Co., Ltd. Their purities or physical constants are shown in Table 1. Pyrethrins were from Dainippon Jotyugiku Co., Ltd. A preparation of it was purified in this laboratory as follows.

Purification of pyrethrins; Pyrethrins were extracted by shaking with nitromethane from pyrethrum extract. Its nitromethane extract was treated with activated charcoal and evaporated to yield a pyrethrins concentrate¹²⁻¹⁴.

Phenylamines were technical grade from chemical manufactures.

Preparation of films

A 5ml quantity of acetone, containing 500mg of pyrethroid alone or with indicated weight of an additive, was evaporated at 25°C to form a film on the inner surface (38.5cm²) of a Petri dish.

Irradiation conditions

The method of Chen and Casida was applied with a modification¹⁵. The films were irradiated

Table 1. Pyrethroidal compounds.

Allethrin	allethronyl chrysanthemate. technical grade (Pynamin®*, purity 83.3%).
Tetramethrin	N-(3,4,5,6-tetrahydrophthalimido)methyl chrysanthemate. technical grade (Neo-Pynamin®*) was recrystallized from <i>n</i> -hexane (mp 74.5-77.5°C).
Resmethrin	5-benzyl-3-furylmethyl chrysanthemate. technical grade (Chryson®*) was recrystallized from methanol (mp 56-58°C).
Furamethrin	5-propargyl-2-furylmethyl chrysanthemate. technical grade (Pynamin-D®*, purity 84.6%).
Pyrethrins	purified and concentrated pyrethrum extract. (purity 55.7%; cinerin I 14.7%, jasmolin I 5.1%, pyrethrin I 12.1%, cinerin II 9.6%, jasmolin II 4.2%, pyrethrin II 10.0%).

* Registered trade name by Sumitomo Chemical Co., Ltd.

at a distance of 70cm below a 500-watt incandescent lamp* (Xenolight UXL-500D, Ushio Electric Co., Japan) for several hours. During the test period, the surface temperature of the samples was 25-30°C and the illumination intensity was 7000-7800 lux. Same prepared films, which were covered with cardboards, were also tested at the same time in darkness as controls.

Volatilization

Five ml of acetone solution containing 1g of pyrethroid was evaporated at 25°C to form a thin coating on the inner surface (38.5cm²) of a Petri dish (ca. 40g).

Weight of the Petri dish holding pyrethroid coating was measured before and after irradiation of 24 or 48 hr.

Gas chromatographic analysis

Residues on a Petri dish after irradiation were sampled and the recoveries of active ingredient were determined by gas chromatography in the way as instructed in the literatures^{12,16-19}.

Results and Discussion

Relative rates of volatilization on irradiated condition

Changes of weight in exposed pyrethroids are given in Table 2. The test was conducted in duplicates.

Four synthetic pyrethroids in light increased by 0.5-1.3% in weight, but pyrethrins decreased by 2.2-4.4% both in light and in darkness. Synthetic pyrethroids underwent some photoreactions to give oxidized products, which were larger molecule and less volatile than original pyrethroids. It may be considered that the increase of weight in four irradiated pyrethroids depended on the formation of these heavier oxidized products. Heavy oxidized products were probably made in pyrethrins by the photoreaction. However the components (44.3%) besides insecticidal pyrethrins in the concentrated preparation of pyrethrins used were possibly volatile, resulting in the loss of weight.

If some pyrethroids were volatile, they could vapourize even in darkness because of the upper opened. Each of the four synthetic pyrethroids

* JIS Z8902; The lamp makes very similar light to sunlight.

however suffered little loss of weight both in light and in darkness. This table suggests that pyrethroids used were of low volatility under the irradiated condition of this experiment.

Photostability of ten pyrethroids

1. Rates of loss by photodecomposition

There are three possibilities of loss from films on irradiated condition;

$$\text{Total loss} = \text{photodecomposition} +$$

$$\text{thermodecomposition} + \text{volatilization.}$$

In order to determine the rate of photodecomposition, this test had two controls; one was a film in darkness which was placed beside irradiated film and covered with boardcard to interrupt light. This film in darkness was kept completely at the same temperature as that of irradiated film. The other control was the measurement of the weight of a Petri dish, which held pyrethroid coating, before and after irradiation (Table 2). Volatilization was found to be almost little in pyrethroids used.

Table 2. Change of weight in exposed pyrethroids.*¹

Pyrethroids	Rate* ² of change	
	Light	Darkness
Allethrin	+0.57%	-0.06%
Tetramethrin	+1.26	-0.08
Resmethrin	+1.3	-0.1
Furamethrin	+0.96	-0.92
Pyrethrins	-4.4	-2.2

* 1; Exposed time: 48 hours.

* 2; Average of duplicates.

(+): increase.

(-): decrease.

Recovery of pyrethrins for up to 48 hours both in light and in darkness is shown in Fig.1-6. In Fig.5, 6, a film of pyrethrins as a mixture of six active esters was used and each ester was analyzed separately after exposure. There was little loss in the recovery of pyrethroids when held for up to 48 hours in the dark as a film. It is evident that pyrethroids undergo little thermodecomposition during irradiation.

In general synthetic pyrethroids were more stable than natural pyrethrins. Especially resmethrin showed recovery at 90.4% after 24 hours and was the most stable of the used pyrethroids

against light (Fig.3). Tetramethrin and furamethrin had loss of about 18-29% after 24 hours and were almost as good (Fig.2, 4). Allethrin was slightly less stable than these three compounds and decomposed at 40.5% after 24 hours (Fig.1). The pyrethrins were the most labile of

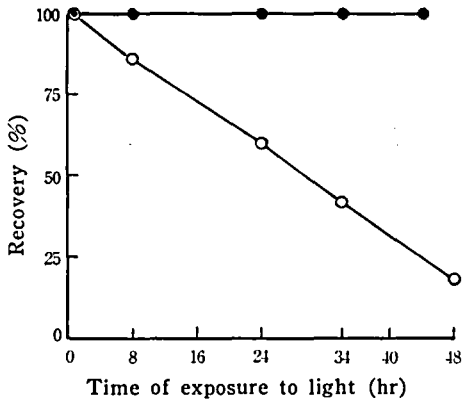


Fig. 1. Rate of loss by photodecomposition of allethrin.

Recovery of allethrin in darkness (●) and in irradiated condition (○).

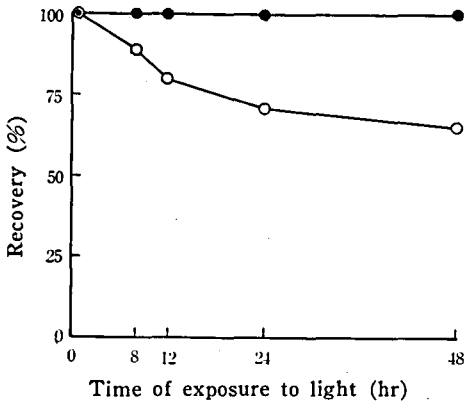


Fig. 2. Rate of loss by photodecomposition of tetramethrin.

Recovery in darkness (●) and in light (○).

pyrethroids used. Six esters of pyrethrins varied greatly in stability. Pyrethrin I and pyrethrin II, which are known the most important and toxic to insect in the six esters of pyrethrins, were the most unstable, reaching no recovery after 16 hours (Fig.5,6)²⁰⁻²⁶. This fact must affect largely stability and persistence of toxicity of whole

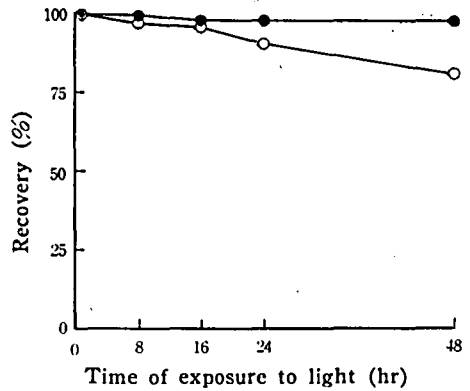


Fig. 3. Rate of loss by photodecomposition of resmethrin. Recovery in darkness (●) and in light (○).

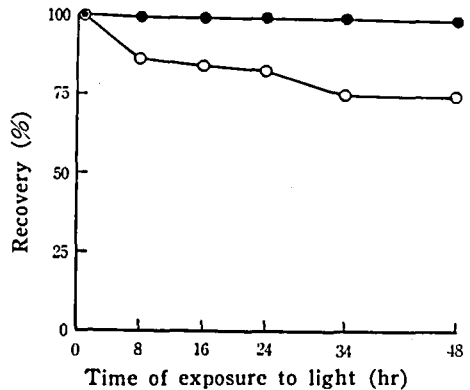


Fig. 4. Rate of loss by photodecomposition of furamethrin. Recovery in darkness (●) and in light (○).

pyrethrins. Cinerin I and cinerin II were more stable than pyrethrin I and pyrethrin II to light. This result is consistent with the view in sunlight by Head *et al*¹¹. Pyrethrin I, jasmolin I, and cinerin I were less stable than the corresponding pyrethrin II, jasmolin II and cinerin II to light. This finding is not in accord with the data of Webley on the content in mosquito coils and their smoke. He reported that pyrethrins I were recovered in better yield than pyrethrins II from smoke of mosquito coils²⁷. This is probably due to the difference in stability of pyrethrins between to light and to heat. The photostability of jasmolin I and jasmolin II were intermediate be-

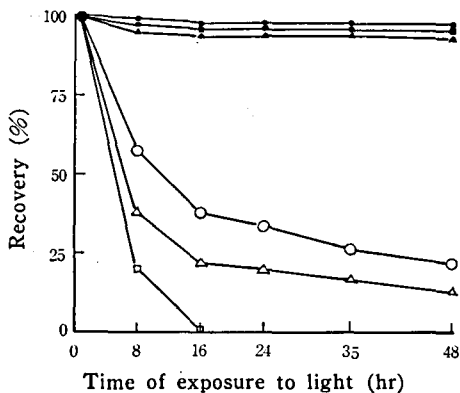


Fig. 5. Rates of loss by photodecomposition of pyrethrins I.

Recovery of cinerin I (●), jasmolin I (▲) and pyrethrin I (■) in darkness, and cinerin I (○), jasmolin I (△) and pyrethrin I (□) in irradiated condition.

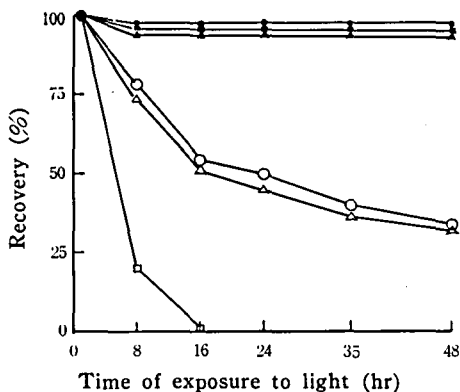


Fig. 6. Rates of loss by photodecomposition of pyrethrins II.

Recovery of cinerin II (●), jasmolin II (▲) and pyrethrin II (■) in darkness, and cinerin II (○), jasmolin II (△) and pyrethrin II (□) in irradiated condition.

tween cinerin I and pyrethrin I, and between cinerin II and pyrethrin II, respectively.

2. Relation of UV absorption spectrum to photodecomposition of pyrethroids.

Relation of UV absorption spectrum to photodecomposition of pyrethroids used is shown in Fig.7. Rates of loss (D_{24}) of pyrethroids after 24 hours were plotted as ordinate and the wave length (λ_{max}) at absorption maxima in ethanol

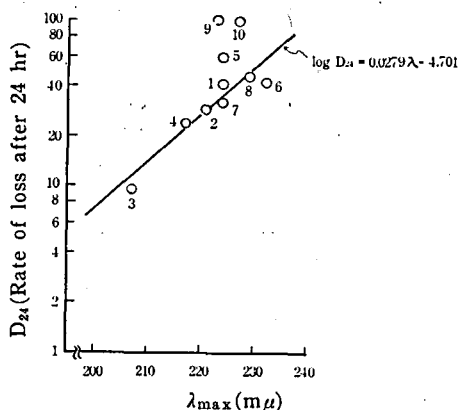


Fig. 7. Relation of UV absorption spectrum to photodecomposition of pyrethroids.

- 1; Allethrin
- 2; Tetramethrin
- 3; Resmethrin
- 4; Furamethrin
- 5; Cinerin I
- 6; Cinerin II
- 7; Jasmolin I
- 8; Jasmolin II
- 9; Pyrethrin I
- 10; Pyrethrin II

solution as abscissa. Fig.7 shows linearity and that the larger λ_{max} a pyrethroid exhibits, the more unstable it is to light. The straight line gave a equation.

$$\log D_{24} = 0.0317\lambda - 5.463$$

$$(r = 0.731)$$

where r denotes correlation coefficient. Pyrethrin I and pyrethrin II placed extraordinarily apart from the line, suggesting that they had other rate-determining stage in the photodecomposition. A line excepting pyrethrin I and pyrethrin II gave another equation with the variance (r^2) of 78%.

$$\log D_{24} = 0.0279\lambda - 4.701$$

$$(r = 0.882)$$

The results must, however, be interpreted with caution as the data obtained in high intensity of sunlight might not be wholly applicable to these results obtained by artificial light.

Stabilizing effect on pyrethroids

1. The effect of dibutylhydroxytoluene

Photodecomposition of pyrethroids is known to be mainly oxidative reaction^{4,10}. Therefore, several antioxidant were evaluated for the protective effect to the photodecomposition of pyrethroids. Dibutylhydroxytoluene (B.H.T.), which is widely used as an antioxidant additive for

foods and medicines, demonstrated some stabilizing effect on allethrin and tetramethrin, but not on furamethrin (Table 3).

Table 3. The effect of B. H. T. on recoveries of synthetic pyrethroids in light.

Pyrethroids	Recovery (%) ^{*1}	
	no B. H. T.	plus B. H. T. ^{*2}
Allethrin	59.5	71.1
Tetramethrin	71.0	87.0
Resmethrin	90.4	92.2
Furamethrin	76.0	73.2

*1; Recovery rate of pyrethroids after 24 hours exposure.

*2; Dibutylhydroxytoluene (B. H. T.) was mixed at one wt%.

2. The protective effect of aromatic amines

Protective effect of various aromatic amine on allethrin is shown in Table 4. An aromatic amine was mixed at one wt% with allethrin. Table 4 contains also the results of allethrin without addition of any aromatic amine both in light and in darkness as blanks.

When any aromatic amine was not mixed with allethrin preparation, about 70% of allethrin was decomposed after 48 hours exposure. N-Phenyl-N'-isopropyl-*p*-phenylenediamine and N,N'-diphenyl-*p*-phenylenediamine showed the best protective effect on allethrin: the recovery of allethrin increased up to more than 70% by the addition of one of these compounds. On the other hand, recovery with N,N'-di- β -naphthyl-*p*-phenylenediamine gave the almost same value as that of blank in light, indicating that it has no

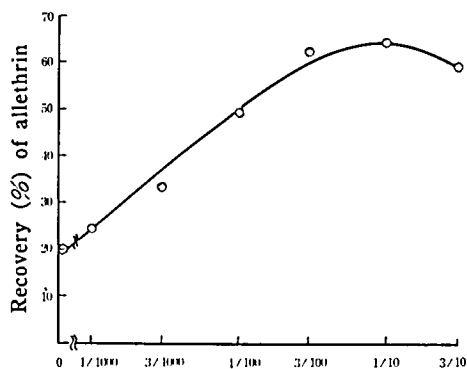
protective effect on allethrin against photodecomposition.

The relationship between chemical structure of aromatic amines and protective effect showed that phenylamines were more capable of stabilization than naphthylamines, and that among the phenylamines cyclic amines were less capable than linear amines. α -Naphthylamines among the naphthylamines were a little less capable than β -naphthylamines.

3. Action of N,N'-diphenyl-*p*-phenylenediamine as a stabilizer

The protective effect of N,N'-diphenyl-*p*-phenylenediamine (hereafter referred to as DPPD) was further studied in more detail at its various levels.

As shown in Fig. 8, recovery-molar ratio curve



Molar ratio of N,N'-diphenyl-*p*-phenylenediamine applied to allethrin applied.

Fig. 8. Effect of varying the molar ratio of N,N'-diphenyl-*p*-phenylenediamine to allethrin on the recovery of allethrin film exposed to light for 48 hrs.

Table 4. The protective effect of aromatic amines on allethrin in light.

Aromatic amines ^{*1}	Recovery of allethrin (%) ^{*2}
N-Phenyl-N'-isopropyl- <i>p</i> -phenylenediamine	76.0
N,N'-Diphenyl- <i>p</i> -phenylenediamine	73.6
Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline	66.2
6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline	61.6
Phenyl- β -naphthylamine	57.0
Phenyl- α -naphthylamine	54.4
N,N'-Di- β -naphthyl- <i>p</i> -phenylenediamine	30.7
Blank (light)	30.6
Blank (dark)	99.5

*1; An aromatic amine was mixed at one wt% with allethrin.

*2; Recovery rate of allethrin after 48 hours exposure.

has a maximum and stabilizing effect of DPPD decreased at the higher DPPD levels studied. It may be considered that DPPD yielded certain products by photodecomposition and the products reduced the stabilizing effect at the higher DPPD levels. There was a maximum in the region of 6/100 and 1/10 molar ratio, in other words the stabilizing effect of DPPD was the largest when DPPD was added at 5.2-8.6 wt% to allethrin.¹¹

Photostability of allethrin in mosquito coils as a practical formulation

Table 5 shows photostability of allethrin in

Table 5. Photostability of allethrin in mosquito coils.

Day	Content of allethrin (%)	
	Light	Darkness
0	0.37	0.37
1	0.35	
2	0.35	
3	0.34	
4	0.33	
5	0.32	0.34
7	0.31	
10	0.29	0.33

mosquito coils for 10 days on exposure to light. Allethrin in mosquito coils decreased linearly with days and approximately 22% of allethrin was lost after 10 days. In practice, however, the loss by photodecomposition might be about 10% for 10 days because about 11% of allethrin were lost even in darkness. About 82% of allethrin in film were reduced on exposure to light for two days (Fig. 1), while in coil 5.5% of allethrin was reduced. It can be considered that there is little effect by light on allethrin in coils.

It is possible that some loss of allethrin in darkness may be owing partially to the higher temperature of irradiated surface (30-45°C), and to some thermodecomposition catalyzed by coil basic components such as tabu powder.

Photodecomposition of natural pyrethrins

Three esters of chrysanthemic acid (pyrethrin I, jasmolin I and cinerin I) were less stable against light than corresponding esters of pyrethric acid (pyrethrin II, jasmolin II and cinerin II) in natural pyrethrins. This fact may probably result from the more susceptibility of the oxidative photodecomposition of acid moiety^{11,19}.

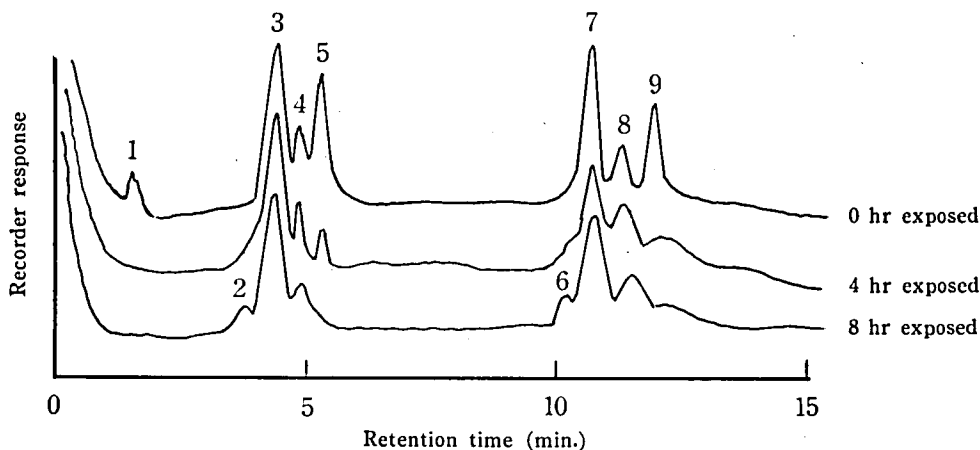


Fig. 9. Gas-chromatograms of pyrethrins exposed to light for various hours. Peak assignment: 1, 2, 6; unknown, 3; cinerin I, 4; jasmolin I, 5; pyrethrin I, 7; cinerin II, 8; jasmolin II, 9; pyrethrin II.

Operating condition: Yanagimoto GCG-550F (FID detector) was used. Stainless steel column packed 5%-Silicone XE-60 on acid washed 60-80 mesh Chromosorb W. Temperatures programming 200-240°C at 4°C/min. Injection temperature 200°C, detector temperature 230°C. Carrier gas nitrogen-flow rate 22.5ml/min.

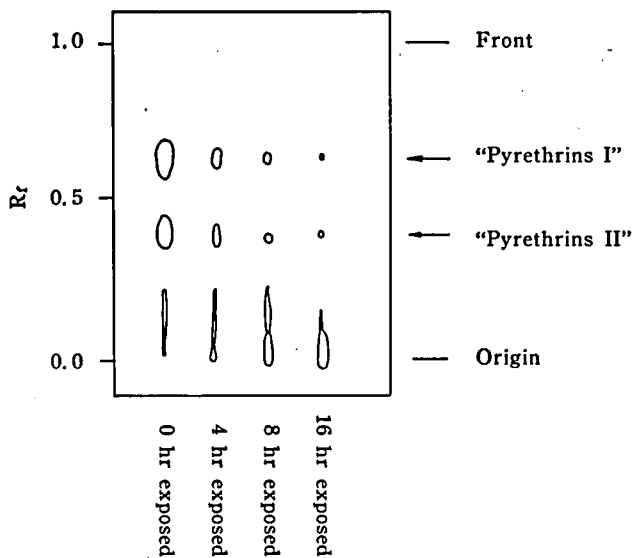


Fig. 10. Thin-layer chromatogram of pyrethrins exposed to light for various hours.

TLC plate: Silica Gel HF₂₅₄ (Merck).

Solvent system: n-hexane: ethyl acetate (3:1, v/v).

Detector: UV light.

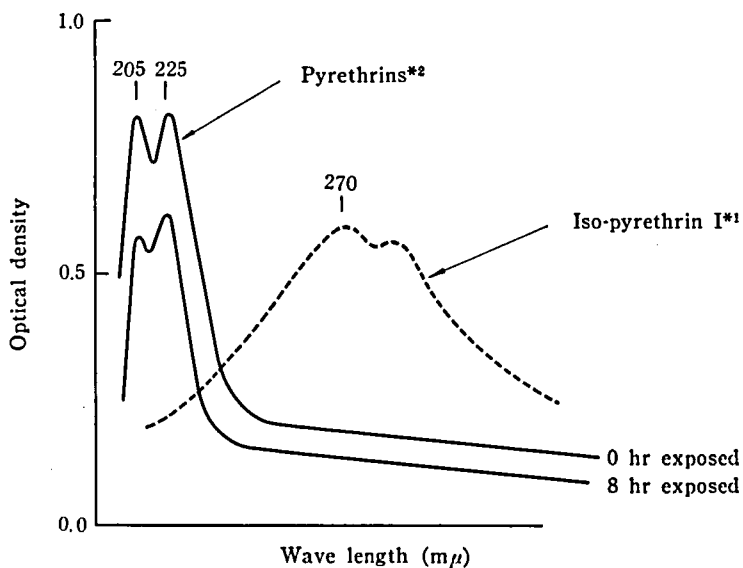


Fig. 11. Decrease in absorption intensity of pyrethrins exposed to light.

UV spectra were made from ethanol solution with a Hitachi 124 spectrometer.

*1; N. C. Brown *et al.* (1957), 270 m μ (ϵ =ca. 20,000).

*2; Y. Abe *et al.* (1971), ca. 225 m μ (ϵ =ca. 30,000).

Pyrethrin I and pyrethrin II were the most unstable to light in active six components of pyrethrins (Fig. 5, 6). In the gas-chromatograms of pyrethrins on exposure to light, peak responses of pyrethrin I and pyrethrin II (peaks 5 and 9 respectively) decreased rapidly and new peaks (peaks 2 and 6) appeared at the front of cinerin I and cinerin II (Fig. 9). Decomposition products were more polar than original compounds as shown on thin-layer chromatogram (Fig. 10). The unstability of pyrethrin I and pyrethrin II to light is considered to arise from a conjugated diene in side chain of cyclopentenolone in view of a structural difference from other components.

It has been reported that pyrethrin I and pyrethrin II were readily isomerized by heat to the corresponding isopyrethrin I and isopyrethrin II^{28,29}, through the transformation of cis-diene side chain to a cyclic transition state³⁰. However, an optical density at 225m μ decreased in UV absorption spectrum of photodecomposition products, but no increase at 270m μ , which is characteristic absorption of isopyrethrins, was observed (Fig. 11)³¹. This result indicates that unstability of pyrethrin I and pyrethrin II to light can not be explained on the basis of isomerization to isopyrethrins. Pyrethrin was suggested to form dimer or polymer by intermolecular combinations in cyclopentenolone side chain⁹. The polarity of decomposition products, however, suggests that the alteration on the chrysanthemate moiety, which is influenced by the nature of the alcohol moiety, and the oxidative degradation on the alcohol moiety (particularly on the conjugated diene portion) should be taken into account together with other decomposition reactions¹⁹.

Acknowledgement The authors wish to express their thanks to Associate Prof. Dr. M. Eto in Kyushu University for his helpful suggestion in the preparation of this manuscript and Mr. N. Muramoto for his continuing interest and encouragement. They also would like to express their acknowledgement to Sumitomo Chemical Co., Ltd. for permission to publish this work.

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The Fundamental Research to the Application of Systemic Insecticides. (IV) Residues and Half-life of Vamidothion in Spinach. Takeo ISHIGURO (Aburahi Laboratories, Shionogi & Co. Shiga Pref.) Ichiro TOYODA (Fourth Laboratory, Basic Research Division, Aichi Agricultural Research Center, Yazako, Nagakute, Aichi) Tetsuo SAITO (Laboratory of Applied Entomology and Nematology, Faculty of Agriculture, Nagoya University, Nagoya) Received July 10, 1972. *Botyu-Kagaku*, 37, 111, 1972. (with English Summary 115).

16. 浸透殺虫剤の施用法に関する基礎的研究 IV. ホウレンソウにおける vamidothion の残留とその半減期について 石黒丈雄 (塩野義製薬株式会社, 油日ラボラトリーズ) 豊田一郎 (愛知県総合農業試験場 基礎研究部) 斎藤哲夫 (名古屋大学農学部 害虫学教室) 47. 7. 10 受理

¹⁴C-標識 vamidothion を用いてホウレンソウにおける残留とその半減期を求めた。

生育の盛んな時期のホウレンソウに茎葉散布し、主として、作物の肥大生長による薬物の濃度の減少についてしらべた。

クロロフォルムおよび水可溶物は散布後日数の経過によって次第に低下した。しかし、この残留量の低下は作物の肥大生長が最も強く影響を与えていると思われる。

クロロフォルム可溶物 (殺虫有効成分) の半減期は最少自乗法により直線回帰式より求め、ほぼ 11.9 日であり、同様に可溶性物質 (クロロフォルム可溶性物質および水溶性物質) のそれは 20.2 日であった。

そして、作物体中の分解消失と肥大生長による希釈の相乗効果として示される実際上の残留半減期は 5.4 日であった。

緒 論

有機合成農薬は病害虫に対する強力な防除効果を発揮し、農産物の増産と安定生産のため、農薬を散布する作物の範囲が拡大すると共にその使用量も急速に増大した。

しかし、有機塩素系殺虫剤や金属腐蝕剤のように化学的に安定であり、しかも持続性の高い化合物を使用し続けると農産物はもとより、土壌、水、大気などの環境中に残留し、自然生態系の汚染をひきおこし、食物連鎖によって人間の健康にも有害であることが次第に認識されてきている。

そのため、使用される農薬は作物の保護の面より見れば安定性の高いことが望ましいが、残留性の面からは早く分解し、消失することが必要である。

しかし、作物体上の農薬残留の経時的変化を規制する要因は極めて多岐にわたり、化合物の種類、施用法、植物の種類やその生育状態、更に、光線や気温など外的因子が相互に関連し合い極めて複雑な様相を示す。

化合物のうちには、一般に、茎葉散布後、付着した場所にとどまったままであるものと植物体中に浸透移行するものがあり、前者は揮散による消失や紫外線

による光分解を受けて消失するものが多い。後者は植物組織内にとり込まれ、植物体内の酵素系により代謝分解をうける。

この外にも、生育の盛んな作物では、相対的なものであるが、肥大生長によって体内の薬物濃度の希釈も考えられる。

Gunther and Blinn (1956) は植物体における農薬の残留について詳細に調べ、種々の殺虫剤の作物体の残留は施用された殺虫剤の半減期 half life time を求めることによって予想できる。即ち、薬剤施用後、揮散、希釈、分解などの多くの要因によって作物体から消失し、最初の残留の半までになるに要する時間を求めることによって農薬残留可能性の指標となると述べている。

以上のような観点より、浸透殺虫剤である vamidothion の残留性を明らかにする意味からも、ホウレンソウに ¹⁴C-標識 vamidothion を葉面散布し、生物学の半減期を求めた。

実験材料および方法

供試した ¹⁴C-vamidothion は石黒ら (1970)⁹⁾ が用いたと同じ ¹⁴CH₃OH から合成した 40% 乳剤であり、