Insecticidal Activity of a New Synthetic Pyrethroidal Compound, 3-Phenoxy Benzyl-(+)*cis*, *trans* Chrysanthemate (*d*-Phenothrin). Yoshitoshi OKUNO, Takashi YAMAGUCHI, and Yoshio FUJITA. (Research Department, Pesticides Division, Sumitomo Chemical Co., Ltd., Takarazuka, Hyogo, Japan) Received September 25, 1975. *Botyu-Kagaku*, 41, 42, 1976.

9. 新合成ピレスロイド・*d*-フェノトリンの殺虫特性

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新しいピレスロイド化合物たるフェノトリンの光学活性体である(+)シス・菊酸エステルと(+)トランス・菊酸エステルを混合して用いると，実用的に興味ある殺虫効果を示すことが明らかとなった．混合割合は，(+)シス・菊酸エステル：(+)トランス・菊酸エステルが，2：8，3：7のとき，好結果が得られた．特に2：8の殺虫効果が良好で，これを*d*-フェノトリンと称し，イエバエ，カ，ゴキブリ等の衛生害虫に対する殺虫効力を，ピレトリン，レスメトリンなどと，種々の施用法を用いて比較した．

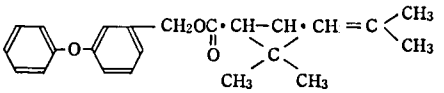
その結果，*d*-フェノトリンは，速効的なノックダウン効果でピレトリンに劣るが，致死効力は，著しくすぐれていることが明らかとなった．すなわち，*d*-フェノトリンのイエバエに対する致死効力は，その系統あるいは施用法によって異なるが，ピレトリンの8.5〜20倍に達し，チャバネゴキブリに対しても，ピレトリンよりもすぐれ，レスメトリン様の高い致死効力を持つピレスロイドといえる．

特に，イエバエ幼虫，アカイエカに対する致死効力では，レスメトリンに勝り，残留接触効果あるいは油剤の煙霧，蚊取線香のような，加熱条件下での使用で，安定した確実な効果を示すことが特徴として見出された．

Introduction

Since the chemical structures of the insecticidal principles of natural pyrethrins were elucidated by La Forge *et al.*[1], a number of studies on analogues of chrysanthemic acid esters have been conducted, and many insecticidal synthetic pyrethroids such as allethrin[2], tetramethrin[3], resmethrin[4], furamethrin[5], proparthrin[6] etc. were discovered. A synthetic pyrethroid consists of four isomers, (+)*cis*, (+)*trans*, (−)*cis* and (−)*trans*, originating from the chrysanthemic acid moiety, and the insecticidal activity of each isomer of several pyrethroids was reported by Gersdorff *et al.*[7,8], Elliott *et al.*[9], and Nishizawa[10], etc.

Phenothrin[11], which has the following structure, is a more recent addition to this group of synthetic pyrethroids.



3-phenoxybenzyl chrysanthemate

Fujimoto *et al.*[12] reported that this pyrethroid was more effective than pyrethrins against houseflies, and was more stable than resmethrin to irradiation. Miyamoto *et al.*[13] studied the insecticidal efficacy of each isomer of phenothrin and showed that the highest efficacy was exhibited by (+)*trans* followed by (+)*cis*, (−)*cis* and (−)*trans* in that order.

We evaluated the joint toxic action of (+)*trans* and (+)*cis* isomers of phenothrin to houseflies, and the most effective combination was found to be a mixture of 2 parts of (+)*cis* with 8 parts of (+)*trans* isomers. Hereafter, this combination will be referred to as *d*-phenothrin.

This paper presents the experimental results on the joint toxic action mentioned above, and also discusses the results of evaluations of *d*-phenothrin in comparison with resmethrin and natural pyrethrins, with respect to insecticidal efficacy and application methods.

Materials and Methods

I. Test Insects. The following stock colonies of houseflies, mosquitoes and cockroaches were reared in this laboratory at 27±1°C and at 60±

5% in relative humidity.

(1) Houseflies (*Musca domestica*)

Susceptible strain; Lab-em-7-em, NAIDM, CSMA or Sumitomo (hereinafter referred to as SK), diazinonresistant strain; 203d were used.

(2) Mosquitoes; susceptible strain of *Culex pipiens pallens* was used.

(3) Cockroaches; susceptible strain of *Blattella germanica* and *Periplaneta fuliginosa* were used.

II. Chemicals. The following chemicals were used in this study.

d-Phenothrin; 2 to 8 (*cis* to *trans*) mixuture of 3-phenoxybenzyl-(+)-chrysanthemate was prepared in this laboratory. The purity was 97.7%. Physical and chemical properties are presented in Table 1.

(±)*trans*-Phenothrin (98.6% pure), (±)*cis*-phenothrin (96.8% pure), (+)*trans*-phenothrin (98.7% pure), (+)*cis*-phenothrin (97.2% pure) were prepared in this laboratory.

Allethrin; technical grade (91% pure) of 2-allyl-3-methylcyclopent-2-ene-1-one-4-yl-chrysanthemate (Pynamin®, Sumitomo Chemical Co., Ltd.) was used.

(+)*trans*-Allethrin (90.9% pure) was prepared in this laboratory.

Resmethrin; technical grade (91.6% pure) of 5-benzyl-3-furylmethyl chrysanthemate (Chrysron®, Sumitomo Chemical Co., Ltd.) was used.

Tetramethrin; technical grade (93.3% pure) of *N*-(3, 4, 5, 6-tetrahydrophthalimido)-methyl chrysanthemate (Neo-Pynamin®, Sumitomo Chemical Co., Ltd.) was used.

Pyrethrins; 20.35% pyrethrin extract (Pyrethrin I 10.77%; Pyrethrin II 9.58%) supplied by Dainippon Jotyugiku Co., Ltd. (Cockthrin®).

III. Testing Methods.

(1) Topical application method

An appropriate amount of acetone solution of each chemical was applied topically with a microsyringe to test insects which had been temporarily paralysed with carbon dioxide as follows:

Housefly: a group of 3 to 5 days old 10 each male and female adults were used. Various concentrations of the test chemical in 0.5 μl of actone was applied to the dorsum prothorax of the insects.

Mosquito: a group of 2 to 3 days old 20 female adults were used. Various concentrations of the chemical in 0.3 μl of acetone was applied to the dorsum prothorax of the insects.

Cockroach: a group of 20 to 30 days old 10 each male and female adults were used. Various concentrations of the test chemical in 1.0 μl of acetone was applied to the dorsum thorax of insects.

Five to 10 replications were made and the mortality was recorded 24 hours (for Housefly, mosquito) and 72 hours (for cockroach) after application. The LD_{50} value was calibrated by the Finney's graphic method.

(2)* Campbell's turn table method[14]

(3)* Glass chamber method by oil spray

(4)* Aerosol test method[15] for flying insects

(5)* Immersion method for larva mosquitoes

The methods with *were described in the previous paper (Okuno *et al.*[16]).

(6) Direct spray method for cockroaches

Ten cockroaches were released into a plastic cup (9.5 cm in diameter and 4 cm in height) and covered with a 16-mesh nylon net, and then was placed beneath a glass cylinder 10cm in diameter and 37 cm in height. Half a m*l* of an oil formulation was sprayed into the glass cylinder through an atomizer at a pressure of 0.6kg/cm^2. Then, the glass cylinder was immediately coverd with a glass lid. Twenty minutes later, the cockroaches were transferred into a recovery container containing food and water, and kept for 72 hours to observe the mortality. Three replications were made. The LC_{50} was calibrated by the Finney's graphic method.

(7) Immersion method for larva houseflies

Emulsifiable concentrate containing 5% of test chemicals was diluted with water to various concentrations. Eight m*l* of emulsion was poured into a petridish (14 cm in diameter and 7 cm in height) containing 30 full-grown larva houseflies. Subsequently, the petridish was covered with a glass lid. After 24 hours, the mortality was recorded. Three replications were made, and the LC_{50} was calibrated by the Finney's graphic method.

(8) Thermal fogging method

(8-a) Peet Grady chamber method

Around 5.8 m*l* of an oil formulation containing the indicated amount of test chemicals was introduced into the Peet Grady chamber[15] by use of an electrical thermal fog generator ("Insect Fogger®" Model F-900, Burgess Vibrocrafters Inc.) and a group of 50 each male and female houseflies or 50 female mosquitoes were immediately released into the chamber. The number of the knocked down insects were counted at 5, 10 and 15 minutes after the discharge of the oil fog. Thereafter, the chamber was ventilated and the knocked down insects were collected into a recovery container within 5 minutes. After 24 hours, the mortality was recorded.

(8-b) Semi-field test method

The test insects which had been held in several containers were placed on the fixed position of a test room (28m³) as shown in Fig. 1. Around 56m*l* of an oil formulation containing the indicated amount of test chemicals was introduced into the test room by use of "Insect Fogger®" in the same manner as described for the method (8-a). The number of knocked down insects was counted 2 hours (for houseflies, mosquitoes) and 16 hours (for cockroaches) after the discharge of the oil fog. Thereafter, the room was ventilated and all the insects were transferred into a recovery container to observe the mortality 24 hours (for houseflies, mosquitoes) and 72 hours (for cock roaches) arfet discharge. The test room was air conditioned at 28°C.

(9) Contact activity test method for cockroaches

(9-a) Confined contact method

Emulsions prepared in the same manner as discribed for the method 7 were uniformly applied onto the surface of plywood panels (15×15 cm) with a microsyringe at a rate of 50m*l*/m² (1, 125m*l* per panel). The panels were tested at 2 hours, 1, 2, 3 and 4 weeks after treatment. During the test period the panels were kept in the room at 25°C and 50 to 60% in relative humidity. Experiments were conducted in triplicate using 30 cockroaches. The insects were confined to the treated surface of the panel for exposure for 24 hours. After the exposure time, they were transferred into recovery containers for mortality counts at 72 hours.

(9-b) Semi-field unconfined contact method

As shown in Fig. 2 (A), the shelters (filter paper) and foods (solid mouse food or sugar

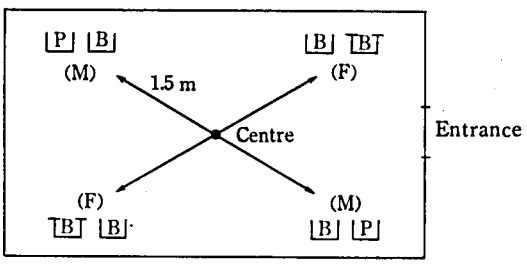


Fig. 1. The positions of the containers in the test room 2.7 × 4.3 m in area and 2.4 m in height

(M): mosquito cage[a] (30 cm diameter × 30 cm height) containing 25 adults

(F): housefly cage[a] (same as above) containing 50 adults

[B]: open dish (14 cm d. × 7cm h.) containing 10 *B. germanica* adults

[B̄]: 1/5 open dish[b] (same as above) containing 10 *B. germanica* adults

[P]: open dish (same as above) containing 10 *P. fuliginosa* adults

The mosquito or housefly cages were hung at 1.5 m above the floor and the petri dishes containing roaches placed on the floor.

[a] covered with a nylon-net (16 mesh)

[b] covered with a lid having a slit of 3×10 cm

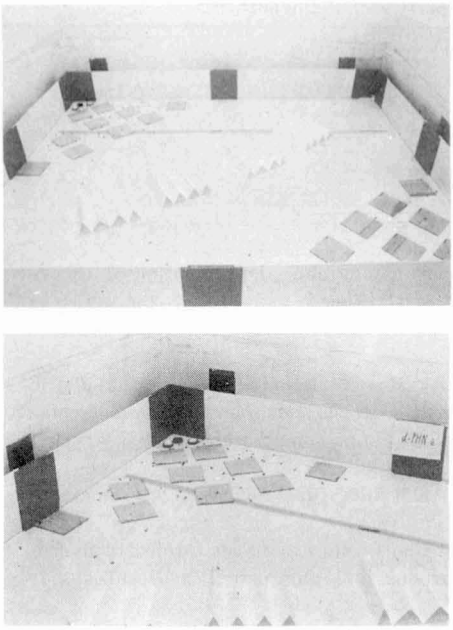


Fig. 2. A : View of the semi-field test area for cockroach contact method.
B : The positions of the shelters, foods and test plywood panels in the test area.

solution) were placed in the test area which were surrounded with plastic plates (5m² in area and 0.25 m in height) with the inside of the wall coated with butter. A group of around 100 cockroaches were released into the test area and were allowed to stand overnight for acclimatization. Next, 20 panels of the plywood treated with chemicals in the same manner as the above method (9-a) were placed in the test area as shown in Fig. 2 (B). The number of the knocked down and killed cockroaches were recorded at the indicated intervals for a week.

(10) Mosquito coil test methods

(10-a) Low concentration method

A group of 50 female mosquitoes were released into the Peet Grady chamber 5.8 m³ in volume, and electric fan (20cm in diameter) covered with 16-mesh nylon net which had been equipped in the chamber, was turned on. Subsequently, 0.8 gram of a test coil containing an indicated amount of active ingredient was fixed on a stand at the centre of the chamber bottom and ignited at the one end. The number of knocked down mosquitoes was counted at various time intervals for 2 hours. Five replications were made. The KT_{50} (50% knock down time) was calibrated by the Finney's graphic method.

(10-b) High concentration method

A group of 20 female mosquitoes were released into a glass chamber 0.34 m³ in volume. Subsequently, 1 gram of a test coil prepared by the above method (10-a) was fixed on a stand at the centre of the chamber bottom and ignited at the both ends. The number of knocked down mosquitoes was counted at various time intervals for 24 minutes to calculate KT_{50}. After the 24 minutes, the knocked down mosquitoes were collected and transferred into a recovery container to observe the mortality after 24 hours. Five replications were made. The KT_{50} was calibrated by the Finney's graphic method.

Results and Discussion

1. Joint toxic action between each isomer of phenothrin against houseflies

The test results of joint toxic action between (±)*cis* and (±)*trans* isomers, and between (+)*cis* and (+)*trans* isomers of phenothrin were presented in Tables 2 and 3, respectively. Table 2 showes that the co-toxicity coefficient values of (±)*cis* and (±)*trans* isomers of phenothrin are around 100 in any mixed ratio, and the joint toxic action of these isomers is evaluated to be "Similar action" according to Sun's index[19]. This tendency is the same as the case of allethrin as discribed by Gersdorff *et al.*[7,8]. On the other hand, co-toxicity coefficient values were 123 and 138, when (+)*cis* and (+)*trans* isomers were mixed in ratio of 3 to 7 and 2 to 8, respectively (Table 3), joint toxic action of these mixture is higher than "Similar action". These are very interesting results and it is taken that (−) isomers may play an unknown important role. On the foregoing results, the mixture of 2 parts of (+)*cis* with 8 parts of (+) *trans* isomers was found to be the most effective and this mixture was named *d*-phenothrin. In the next 2, insecticidal efficacy of *d*-phenothrin is discussed in comparison with those of resmethrin and pyrethrins, in terms of formulation and application method.

Table 1. Physical and chemical properties of *d*-Phenothrin.

Item	Outlines of properties
Empirical formula	$C_{23}H_{26}O_3$
Molecular weight	350
Appearance	colorless clear liquid
Specific gravity	d_{25}^{25} 1.016
Melting point	below −20°C
Viscosity	86.4 c.p. at 30°C
Vapor pressure	1.64 mm Hg at 200°C (Gas chromatographic determination[17]) lower than allethrin, resmethrin and pyrethrins I, and almost the same as tetramethrin.
Solubility	*in water*: 2 ppm at 30°C *in organic solvent*: miscible with almost all of aromatic or aliphatic hydrocarbons, chlorinated hydrocarbons and other organic solvents.
Stability	*under storage conditions*: stable at room temperature for 2 years and at 60°C for 3 monthes. *under irradiation*: more stable than allethrin, resmethrin, tetramethrin and pyrethrins. *in organic solvents*: stable in alcohols, esters, ketones, aromatic hydrocarbons, aliphatic hydrocarbons and chlorinated hydrocarbons at 40°C for 3 monthes. *in inorganic diluents*: stable in inorganic mineral diluents such as talc, bentonite and diatom-earch at 40°C for 3 monthes.

Table 2. The joint toxic action of (±) *cis* and (±) *trans* isomers of phenotrin to houseflies (Lab-em-7-em strain).

Mixed ratio (±) *cis* : (±) *trans*	LD_{50} (μg/fly)	Joint action Co-toxicity coefficient[a]
10 : 0	0.222	—
7 : 3	0.218	97
5 : 5	0.215	95
3 : 7	0.192	103
2 : 8	0.202	97
0 : 10	0.190	—

[a] Calculated by the formula of Sun *et al.* (1960)[19]

Table 3. The joint toxic action of (+) *cis* and (+) *trans* isomers of phenothrin to houseflies (Lab-em-7-em strain).

Mixed ratio (+) *cis* : (+) *trans*	LD_{50}[a] (μg/fly)	Joint action Co-toxicity coefficient[b]
10 : 0	0.125 (0.111-0.140)	—
7 : 3	0.097 (0.086-0.109)	109
5 : 5	0.083 (0.075-0.093)	116
3 : 7	0.072 (0.065-0.081)	123
2 : 8	0.061 (0.056-0.068)	138
0 : 10	0.078 (0.071-0.085)	—

[a] Calculated by the Bliss's method summarized in Botyu-Kagaku (1951)[18]
( ): Fiducial limit (Pr=0.05)

[b] Calculated by the formula of Sun *et al.* (1960)[19]

2. Insecticidal activities of *d*-phenothrin

2.1 Killing activity

Killing activity of *d*-phenothrin against adult houseflies, mosquitoes and cockroaches were evaluated by topical application, turn table and direct spray methods. Table 4 shows that the activities of *d*-phenothrin to houseflies are 10-20 times superior to that of pyrethrins and almost the same as that of resmethrin (11-35 times as potent as pyrethrins). Against cockroaches, *d*-phenothrin is slightly superior to pyrethrins and about equal to resmethrin. On the other hand, the activities of *d*-phenothrin and resmethrin against mosquitoes are 2.9 and 1.8 times as high as that of pyrethrins, respectively. Schechter *et al.*[20] and Haskins *et al.*[21] also noticed this point. According to the results, it can be summerized that the killing activity of *d*-phenothrin is almost the same as that of resmethrin against houseflies and cockroaches, and a slightly superior to it against mosquitoes.

2.2 Effect of synergists

Effects of synergists on killing activity of *d*-phenothrin against houseflies and cockroaches were evaluated by the same manner as described in 2.1. Among the synergists used, piperonyl botoxide was the most effective to enhance the activity of *d*-phenothrin and resmethrin, however the contribution of the synergist was not remarkably high compared with the case of pyrethrins (Table 5).

2.3 Larvicidal activity of emulsion formulations

The efficacy of emulsion formulation against larva houseflies and larva mosquitoes was evaluated by immersion method as shown in Table 6, the activity of *d*-phenothrin, resmethrin and pyrethrins decreased in that order. *d*-Phenothrin was 1.3 and 1.7 times as active as resmethrin against larva mosquitoes and larva houseflies, respectively. Buei[22] reported that the activity of *d*-phenothrin against larva mosquitoes was 1.8 times as high as that of resmethrin. The author suggested in his report that the relative activity might depend upon the differences of strain of test insects.

2.4 Efficacy of oil formulations by spraying and thermal fogging methods

The knock down effect of *d*-phenothrin against houseflies and mosquitoes was much inferior to that of pyrethrins (Table 7), in spite of higher killing effects of the former (Table 4). The combinations of a so-called killing agent and a so-called knock down agent are generally used in practical control of sanitary insects. Table 8 shows that the combinations of *d*-phenothrin and a knock down agent exhibited almost the same efficacy as the corresponding resmethrin formulae and pyrethrins formula as compared by spraying method. Therefore, it is recommended that *d*-phenothrin be used in combination with knock down agent such as tetramethrin and (+)*trans* allethrin in practical use. On the other hand, the thermal fogging of oil formulation is also a popular method for pest control. In this application method, the insecticides have to be thermo stable, because they are heated to 300 to 500°C. Tables 9 and 10 are the test results obtained by the thermal fogging method at around 300°C. They show that *d*-phenothrin formulae are as effective as resmethrin formula, DDVP plus fenitrothion formula, and pyrethrins formula except for lower killing effect of pyrethrins formula against houseflies.

2.5 Efficacy of aerosol formulations to houseflies and mosquitoes

Aerosl is the world wide formulation for housefhold insecticides, because of its easiness in handling. In this section, aerosol formulations containing several kinds of pyrethroids were subjected to efficacy tests against houseflies and mosquitoes. The results show that the efficacies of *d*-phenothrin were almost the same as those of resmethrin against several strains of houseflies and several species of mosquitoes, when they were used in combination with tetramethrin as a knock down agent (Tables 11 and 12). Table 12 also shows that these combinations exihibited almost the same effect as OTA (Official Test Aerosol of CSMA, USA). These results are obtained by using exclusively the oil based formulation. The insecticidal efficacy of the water based aerosol formulation of *d*-phenothrin will be published in our future report.

2.6 Residual contact activity against cockroaches

There are two application methods, direct spray and residual contact, to control crawling insects,

Table 4. Toxicity of *d*-Phenothrin to insects and mammals in comparison with other pyrethroids.

Insects and mammals		Toxicity		
		d-Phenothrin	Resmethrin	Pyrethrins
		Topical LD_{50} μg/fly		
Houseflies	SK strain	0.022 (10.1)	0.020 (11.2)	0.223 (1.0)
	CSMA strain	0.022 (16.8)	0.015 (24.6)	0.370 (1.0)
	Lab-em-7-em strain	0.050 (20.0)	0.028 (35.7)	1.0 (1.0)
	NAIDM strain	0.056 (15.9)	0.034 (26.2)	0.89 (1.0)
		Turn table LC_{50} mg/100 m*l*		
Houseflies	Lab-em-7-em strain	34.5 (8.7)	22.0 (13.6)	300 (1.0)
	NAIDM strain	20.2 (8.5)	16.5 (10.4)	172 (1.0)
		Topical LD_{50} μg/insect		
Mosquitoes (*C. pipiens*)		0.0075 (2.9)	0.0125 (1.8)	0.022 (1.0)
Cockroaches (*B. germanica*)		0.89 (1.3)	0.80 (1.4)	1.15 (1.0)
		Direct spray LC_{50} mg/100 m*l*		
Cockroaches (*B. germanica*)		66 (1.3)	80 (1.1)	88 (1.0)
		Oral LD_{50} mg/kg		
Mice		> 5000[a]	690[b]	370[b]
Rat		>10000[a]	>5000[b]	2160[b]
		>10000[a]	>5000[b]	1300[b]

( ): Relative toxicity (Pyrethrins = 1.0)

a) From previous study (Miyamoto *et al.*, 1973[13])

b) Read at the Conference on Human Health Effects of Newer Approaches to Insect Pest Control sponsared by National Institute of Environmental Health Sciences and Environmental Protection Agency (Junshi Miyamoto, Aug. 1975, North Carolina, USA)

Table 5. Effect of synergists on several pyrethraids.

Composition		Degree of synergism[e]			
Insecticide + Synergist (1 : 5)		Houseflies (Lab-7-em strain) Topical	Houseflies (Lab-7-em strain) Turn table	Roaches (*B. germanica*) Topical	Roaches (*B. germanica*) Direct spray
d-Phenothrin	PBO[a]	2.3	2.4	1.0	1.4
	Sulfoxide[b]	1.7	1.7	—	—
	I. B. T. A.[c]	1.1	1.3	—	—
	S-421[d]	1.2	1.2	—	—
Resmethrin	PBO	1.7	1.2[f]	1.0	1.7
	Sulfoxide	1.4	1.1[f]	—	—
Pyrethrins	PBO	10.9	4.4	2.1	2.8

a) α-[2-(2-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyltoluene

b) 1,2-methlenedioxy-4-[2-(octylsulfinyl)propyl]-benzene

c) Isobornylthiocyanoacetate

d) Octachlorodipropylether

e) Degree of Synergism = $\frac{LD_{50} \text{ or } LC_{50} \text{ insecticide alone}}{LD_{50} \text{ or } LC_{50} \text{ insecticide \& synergist}}$

f) SK strain: From previous study (Okuno *et al.*, 1969[16])

Table 6. Larvicidal activity of emulsion formulations against mosquitoes and houseflies by immersion method.

Insecticides	LC_{50} (ppm)	
	Mosquitoes (*C. pipiens*)	Houseflies (NAIDM strain)
d-Phenothrin	0.022 (2.8)	0.54 (3.4)
Resmethrin	0.028 (2.2)	0.91 (2.0)
Pyrethrins	0.061 (1.0)	1.85 (1.0)

( ): Relative efficacy (Pyrethrins=1.0)

Table 7. Knock down activity of oil formulations against houseflies and mosquitoes by glass chamber method.

Insecticides	Conc. (%)	KT_{50} (sec.)	
		Houseflies (Lab-em-7-em strain)	Mosquitoes (*C. pipiens*)
d-Phenothrin	0.5	345	319
Resmethrin	0.5	180	198
Pyrethrins	0.5	50	42

Table 8. Efficacy of oil formulation against houseflies and mosquitoes by glass chamber method.

Composition		KT_{50} (sec) - % Mortality at 24 hrs.			
Insecticides	Conc. (%)	Houseflies (Lab-em-7-em strain)		Mosquitoes (*C. pipiens*)	
d-Phenothrin Tetramethrin	0.075% 0.2	129	86	119	95
d-Phenothrin Tetramethrin	0.1 0.2	126	97	105	97
Resmethrin Tetramethrin	0.075 0.2	127	95	129	95
d-Phenothrin (+) *trans*-Allethrin	0.075 0.2	115	90	127	100
d-Phenothrin (+) *trans*-Allethrin	0.1 0.2	130	95	125	100
Resmethrin (+) *trans*-Allethrin	0.075 0.2	133	95	107	100
Pyrethrins P.B.O.	0.2 1.6	131	93	125	98

Table 9. Efficacy of oil formulations against houseflies and mosquitoes by thermal fogging method.

Composition	Dosage (ml/5.8m³)	% Knock down 5 min	10 min	15 min	(20 min)	% Mortality at 24 hrs.
		Houseflies (NAIDM strain)				
d-Phenothrin/Tetramethrin/PBO 0.025% 0.05% 0.2%	5.8	21	67	79	94	56
Resmethrin/Tetramethrin/PBO 0.025% 0.05% 0.2%	5.9	18	53	74	87	58
Resmethrin/(+) *trans*-Allethrin/PBO 0.025% 0.05% 0.2%	5.9	19	55	76	89	60
Pyrethrin/PBO 0.05% 0.4%	6.0	25	63	81	87	17
		Mosquitoes (*C. pipiens*)				
d-Phenothrin/Tetramethrin/PBO 0.025% 0.05% 0.2%	5.8	61	87	95	98	95
Resmethrin/Tetramethrin/PBO 0.025% 0.05% 0.2%	5.9	47	77	92	97	94
Resmethrin/(+) *trans*-Allethrin/PBO 0.025% 0.05% 0.2%	5.9	45	83	88	97	91
Pyrethrin/PBO 0.05% 0.4%	6.0	51	76	89	97	89

Table 10. Efficacy of oil formulations against insects by thermal fogging test method under semi-field conditions.

Composition[a]	% Knockdown —% Mortality Houseflies (NAIDM starin) cage	Mosquitoes (*C. pipiens*) cage	Cockroaches (*B. germanica*) open dish	1/5 open dish[d]	(*P. fulliginosa*) open dish
d-Phenothrin/Tetramethrin/PBO 0.1% 0.2% 0.75%	100 - 100	100 - 100	100 - 100	80 - 100	90 - 100
d-Phenothrin/Tetramethrin/PBO/S-421 0.1% 0.2% 0.3% 0.45%	100 - 100	100 - 100	100 - 100	70 - 100	100 - 100
Resmethrin/Tetramethrin/PBO 0.1% 0.2% 0.75%	100 - 100	100 - 100	100 - 100	60 - 100	80 - 85
DDVP[b]/Fenitrothion[c] 0.2% 0.5%	100 - 100	100 - 100	100 - 100	100 - 100	100 - 100

[a] Dosage: 56 ml/28 m³

[b] DDVP: O, O-dimethyl-O-(2, 2-dichlorovinyl) phosphate

[c] Fenitrothion: O, O-dimethyl-O-(3-methyl-4-nitrophenyl)-phosphorothioate

[d] This condition is a modification of roach harborage.

Table 11. Efficacy of oil based aerosol formulations against houseflies by CSMA method.

Composition		Dosage (g/1000ft³)	% Knockdown				% Mortality at 24 hrs.
			5 min.	10 min.	15 min.	(20 min.)	
				Lab-em-7-em strain			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.1	17	49	65	76	66
Resmethrin Tetramethrin	0.1% 0.2%	3.2	21	50	71	84	62
				203 d strain			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.0	17	44	60	69	60
Resmethrin Tetramethrin	0.1% 0.2%	3.0	17	41	56	62	60
				CSMA strain			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.2	25	58	73	79	89[a)]
Resmethrin Tetramethrin	0.1% 0.2%	3.1	22	59	73	81	92[a)]
Resmethrin (+) *trans*-Allethrin	0.1% 0.2%	3.0	26	56	68	78	85[a)]
Tetramethrin PBO	0.2% 1.0%	3.1	34	63	74	79	67[a)]
Pyrethrins PBO	0.2% 1.0%	3.2	24	59	75	79	86[a)]

[a)] Total mortality: After the end of the exposure period, knocked down and unknocked down houseflies were collected into a recovery container to observe the mortality 24 hours later.

Table 12. Efficacy[a] of oil based aerosol formulations againrt houseflies and mosquitoes by CSMA method.

Composition		Dosage (g/1000ft³)	% Knockdown			% Mortality at 24 hrs.
			5 min.	10 min.	15 min.	
			Houseflies (NAIDM strain)			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.2	28	48	89	89
Resmethrin Tetramethrin	0.1% 0.2%	3.1	30	55	97	97
OTA[b]		3.1	30	58	94	94
			Houseflies (F58W[c] strain)			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.2	29	46	85	85
Resmethrin Tetramethrin	0.1% 0.2%	3.0	27	48	90	90
OTA		3.1	30	51	91	91
			Mosquitoes (*Aedes aegypti*)			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.0	26	56	100	100
Resmethrin Tetramethrin	0.1% 0.2%	3.1	31	71	100	100
OTA		3.1	26	51	100	100
			Mosquitoes (*C. pipiens*)			
d-Phenothrin Tetramethrin	0.1% 0.2%	3.1	41	68	98	100
Resmethrin Tetramethrin	0.1% 0.2%	3.1	33	62	96	100
OTA		3.2	27	54	89	100

[a] Obtained at WARF Institute, INC., USA.
[b] Official test aerosol of CSMA (Pyrethrins 0.2%, PBO 1.6%)
[c] DDT-resistant strain

Table 13. Residual effect of emulsion formulations against German cockroaches by the confined contact method.

Insecticides[a]	% Mortality at indicated weeks				
	0	1	2	3	4
d-Phenothrin	100	100	100	90	55
Resmethrin	95	90	75	48	5
Pyrethrins	100	100	80	68	43

[a] Dosage: 250 mg active ingredient /m²

Table 14. Residual contact activity of emulsion formulations against German cockroaches by the semi field test method.

Insecticides[a)]	% Knockdown and mortality						
	3 hrs.	6 hrs.	1 days	2 days	3 days	5 days	7 days
d-Phenothrin	21	35	67	81	88	97	98
Resmethrin	3	7	72	81	84	84	88
Pyrethrins	20	37	44	47	50	53	57

[a)] Dosage: 625 mg active ingredient/20 panels/test plot ($5m^2$)

Table 15. Efficacy of mosquito coil formulations to mosquitoes.

Composition		Low conc. method (Peet grady chamber) KT_{50} (min.)	High conc. method (glass chamber) KT_{50} (min.) - % Mortaltity
d-Phenothrin Allethrin	0.05% 0.3%	15.0	9.5 - 55
d-Phenothrin Allethrin	0.1% 0.3%	9.5	9.3 - 83
Resmethrin Allethrin	0.05% 0.3%	19.0	9.5 - 58
Resmethrin Allethrin	0.1% 0.3%	10.0	9.2 - 70
d-Phenothrin	0.3%	40.0	17.1 - 63
	0.6%	24.0	15.2 - 90
Resmethrin	0.3%	29.0	14.3 - 80
	0.6%	20.5	11.6 - 100
Allethrin	0.3%	26.0	10.0 - 47
	0.6%	12.0	8.7 - 73
Pyrethrins	0.3	27.5	14.0 - 53

and oil, aerosol, dust and emulsion formulations are generally used for this purpose. In this section, the lasting period of residual activity against cockroaches were evaluated by using plywood panels treated with emulsion formulation. Cockroaches were confined to the plywood panels which had been kept for 1, 2, 3 and 4 weeks after treatment with the insecticide formulation. The mortalities were recorded as shown in Table 13. Residual activity of *d*-phenothrin lasted for the longest period, followed by pyrethrins. Resmethrin rapidly lost the residual activity. The residual contact activity of pyrethroids were also examined under a semi-field condition (Fig. 2), and the results were shown in Table 14 and Fig. 3. Under this condition, cockroaches could avoid the treated panels if they wanted to. The results show that *d*-phenothrin was the most effective, followed by resmethrin in residual activity. Pyrethrins showed almost the same activity as *d*-phenothrin at 3 and 6 hours, but it became the least active after 1 to 7th day. The reason why the efficacy of pyrethrins was lower than others after 1 day, in spite of its strong activity under confined conditions, has not been experimentally clarified, but it may be possible that biological properties of pyrethrins such as repellency and biodegradability might be different from the other pyrethroids tested.

2.7 Efficacy of coils to adult mosquitoes

Efficacy tests were conducted by using glass chamber (for high concentration) and Peet Grady chamber (for low concentration). The results are shown in Table 15. Although knock down effect of *d*-phenothrin or resmethrin was much inferior to that of pyrethrins or allethrin, the mixture of 0.3% allethrin with 0.05 to 0.1% *d*-phenothrin exhibited almost the same effect as 0.6% allethrin.

Summary

The joint toxic action of (±)*cis* and (±)*trans* isomers of phenothrin was identified as "Similar action" in any mixed ratio against houseflies, while that of 2 to 3 parts of (+) *cis* and 7 to 8 parts of (+)*trans* isomers gave high value than that for "Similar action" according to Sun's index.

The mixture of 2 parts of (+)*cis* with 8 parts of (+)*trans* isomers was the most effective and was named "*d*-phenothrin". *d*-Phenothrin is chemically stable under various conditions and has low mammalian toxicity in comparison with resmethrin and pyrethrins. The insecticidal activities of *d*-phenothrin against several kinds of sanitary insects such as houseflies, mosquitoes and cockroaches were examined. *d*-Phenothrin was inferior to pyrethrins in knock down effect, but 8.5 to 20 times superior to it in killing effect against houseflies, thus it was characterized as so-called "killing agent" like resmethrin. It is expected that *d*-phenothrin alone or together with a so-called "knock down agent", such as tetrame-

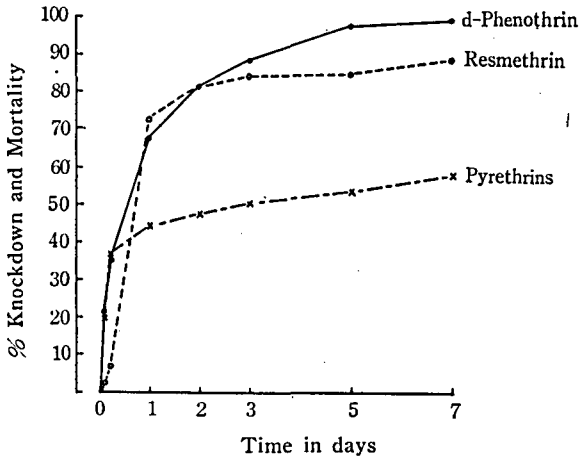


Fig. 3. Residual contact activity of *d*-Phenothrin against roaches by the semi-field test method

thrin, and allethrin, will provide an excellent active ingredient for several kinds of formulations such as aerosol, oil, emulsion and mosquito coil.

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