A New Insecticidal Pyrethroid Ester¹⁾

Keimei FUJIMOTO, Nobushige ITAYA,
Yoshitoshi OKUNO, Tadaomi KADOTA
and Takashi YAMAGUCHI

Research Department, Pesticides Division, Takarazuka
Laboratory, Sumitomo Chem. Co., Ltd., 2-1,
4-chome, Takatsukasa Takarazuka, Hyogo

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Since the structure of the insecticidal components of natural pyrethrin was elucidated by LaForge *et al.*,²⁾ many synthetic pyrethroids which are esters of chrysanthemic acid, have been discovered and industrially produced as insecticides of low mammalian toxicity for household use. Among these synthetic esters, the one with the most powerful knock-down

activity is tetramethrin,³⁾ and as for the killing effect, resmethrin is the most active.⁴⁾ Furamethrin⁵⁾ and proparthrin⁶⁾ are superior to allethrin in knock-down activity when used as an active ingredient of mosquito coil.

The present paper reports a new synthetic pyrethroid 'phenothrin' or 3-phenoxybenzyl chrysanthemate (I). The new chrysanthemate showed strong killing activity on various

TABLE I. REFRACTIVE INDEX OF THE CHRYSANTHEMATES

Material	N _D ²⁵
Compound (I) (Phenothrin)	
<i>dl-trans, cis</i>	1.5487
<i>d-trans</i>	1.5482
<i>d-cis</i>	1.5504
<i>l-trans</i>	1.5481
<i>l-cis</i>	1.5507
Compound (II)	1.5482
Compound (III)	1.5749

TABLE II. TOXICITY OF THE CHRYSANTHEMATES TO INSECTS AND MICE

Material ^{a)}	Toxicity				
	House fly ^{c)}		Army worm ^{c)}	Green pea aphid ^{e)}	Mice ^{d)}
	Knock-down KT ₅₀ , sec. (0.5%)	Mortality LC ₅₀ (mg/100 ml)	Mortality LC ₅₀ (ppm)	Mortality LC ₅₀ (ppm)	Mortality, oral LC ₅₀ (mg/kg)
Compound (I) (Phenothrin)					
<i>dl-trans, cis</i>	430	22.0	132	250	>5000
<i>d-trans, cis</i>	345	11.0	50	98	>5000
<i>d-trans</i>	390	11.8	58	100	>10,000
<i>d-cis</i>	258	15.5	43	85	480
<i>l-trans</i>	>1000	>1000	>2000	>2000	>5000
<i>l-cis</i>	>1000	>1000	>2000	>2000	—
Compound (II)	>1000	46.5	333	—	>5000
Compound (III)	>1000	110	980	—	>1000
Tetramethrin	43	135	>2000	700	1220
Pyrethrin	50	120	250	193	130
Resmethrin	180	8.2	71	150	300
Furamethrin	127	58.4	500	>2000	3130
<i>d-Furamethrin</i> ^{b)}	62	31.3	260	>2000	1950
Allethrin	125	144	>1000	980	410 ^{e)}
<i>d-Allethrin</i> ^{b)}	56	68.3	483	500	440 ^{e)}

^{a)} The ratio of *d-cis*, *d-trans*, *l-trans* and *l-cis* isomers is 40:10:40:10.

^{b)} The ratio of *d-trans* and *d-cis* isomers is 80:20.

^{c)} Knock-down: Glass chamber method with oil-based space spray. Mortality of house fly: with Campbell's turn table method. Mortality of army worm and aphid: tested on insects released on the leaf sprayed with an emulsion.

^{d)} Tested with 10% Tween-80 suspension except.^{e)}

^{e)} Tested with 1% CMC suspension.

TABLE III. STABILITY UNDER XENON LAMP IRRADIATION^{a)}

Pyrethroid	Irradiation	Residual rate of pyrethroids ^{b)}			
		11 hr	24 hr	72 hr	120 hr
Phenothrin	+	—	87.7	50.6	18.9
	—	—	—	—	98.7
Resmethrin	+	90.4	46.9	15.1	2.5
	—	—	—	—	99.1

^{a)} 6000~6300 lux, 38~41°C.^{b)} Initial value: Phenothrin, 285 mg/38.5 cm²=100
Resmethrin, 287.5 mg/38.5 cm²=100

species of insects, is least toxic to mice and physicochemically most stable relative to the known pyrethroids.

The compound (I) was prepared by esterifying 3-phenoxybenzyl alcohol with chrysanthemoyl chloride and pyridine. 3-Phenoxybenzyl alcohol was readily synthesized from 3-phenoxy-toluene by either halogenation followed by hydrolysis or oxidation with gaseous oxygen. The compound was colorless liquid and refractive indexes of each isomers are shown in Table I.

As seen from Table II, the killing activities of phenothrin were superior to those of other pyrethroids except resmethrin as compared with the related compounds (II),⁷⁾ (III)⁸⁾ and the representative synthetic pyrethroids. Phenothrin was less active in knock-down effect than the others. Only the esters of *d-cis* and *d-trans* chrysanthemic acid were insecticidally active. Phenothrin was found to be more resistant than resmethrin on irradiation with

ultraviolet light (see Table III).

Because of the outstanding killing activity, the remarkable low toxicity to mammals and good stability to ultraviolet light, phenothrin appears to be one of the most promising insecticides for both sanitary and agricultural purposes. Experimental details will be published elsewhere in the near future.

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REFERENCES

- 1) K. Fujimoto, Y. Okuno, N. Itaya, K. Kamoshita, T. Mizutani, S. Kitamura, S. Nakai and N. Kameda, Japan Patent 21473 (published June 17, 1971).
- 2) F. B. LaForge and H. L. Haller, *J. Amer. Chem. Soc.*, **58**, 1777 (1936).
- 3) T. Kato, K. Ueda and K. Fujimoto, *Agr. Biol. Chem.*, **28**, 914 (1965).
- 4) M. Elliott, A. W. Farnham, P. H. Needham and B. C. Pearson, *Nature*, **213**, 493 (1967).
- 5) Y. Katsuda, T. Chikamoto, H. Ogami, H. Hirobe and T. Kunishige, *Agr. Biol. Chem.*, **33**, 1361 (1969).
- 6) M. Nakanishi, T. Mukai, S. Inamasu, A. Tsuda and T. Abe, *Botyu-Kagaku*, **35** (1970).
- 7) K. Fujimoto, Y. Okuno, N. Itaya, S. Kitamura, T. Mizutani and K. Kameda, Japan Patent 26359 (published July 30, 1971).
- 8) K. Fujimoto, Y. Okuno, N. Itaya, K. Kanoshita, T. Mizutani, S. Kitamura, S. Nakai and N. Kameda, Japan Patent 21474 (published June 17, 1971).