BIOLOGICAL CHARACTERISTICS OF NEW ACARICIDE MK-239

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ABSTRACT

MK-239 is a new acaricide discovered in 1987 by Mitsubishi Kasei Corporation. MK-239 is of unique chemistry and has a novel mode of action, providing excellent control of various mite species(*Tetranychus* spp., *Panonychus* spp., *Origonychus* spp. and *Eotetranychus* spp.). The compound shows rapid and high activity against all developmental stages of mites, and also has long residual activity. No cross-resistance has been observed to other commercial acaricides, such as dicofol, fenbutatin oxide and hexythiazox. The compound is not systemically active but does show translaminar activity. MK-239 has excellent selectivity on target crops and low toxicity to honeybees. It is now under global development with extensive field trials.

INTRODUCTION

During an intensive research on pyrazole derivatives, a new class acaricidal compound was synthesized and patented by Mitsubishi Kasei Corporation(Okada *et al*, 1988). MK-239 has been elected as the most active compound among the derivatives. This paper describes chemical properties and acaricidal performance.

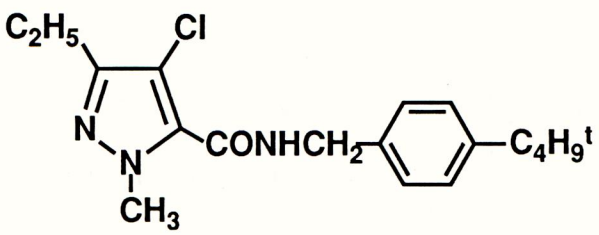
CHEMICAL AND PHYSICAL PROPERTIES

Chemical Name : N-(4-*t*-butylbenzyl)-4-chloro-3-ethyl-1-methyl-pyrazole-5-carboxamide

Empirical Formula : $C_{18}H_{24}ClN_3O$

Molecular Weight : 333.8

Structural Formula :



Appearance :	Off-white crystals
Melting Point :	61-62°C
Vapor Pressure :	1.1×10^{-6} mmHg at 40°C
Partition Coefficient : (n-octanol/water)	4.61±0.10 at 25°C
Water solubility :	2.8mg/l at 25°C

Solubility : Soluble in most organic solvents, such as acetone, methanol, chloroform, acetonitrile, n-hexane, and benzene.

Stability : Stable in water at pH3-11 up to 4 weeks at 37°C

TOXICOLOGY

Mammalian Toxicity

Acute oral	LD50	rat	male	595mg/kg
			female	997mg/kg
		mouse	male	224mg/kg
			female	210mg/kg
Acute dermal	LD50	rat		>2000mg/kg
Skin irritation		rabbit		non-irritating

Fish Toxicity

LC50	carp	0.073mg/l

Avian Toxicity

Acute oral LD50	mallard duck	>2000mg/kg
8-day dietary LC50	mallard duck	>5000mg/l
8-day dietary LC50	bobwhite quail	>5000mg/l

Mutagenecity

No mutagenic effects were observed in the following tests: Ames, Mammalian Micronucleus, *Drosophila* Wing-spot, *in vitro* Cultureed Human Lymphotes, *in vivo* Bone Marrow Erythrocytes, Unsheduled DNA Synthesis, and CHO/HGPRT .

LABORATORY EVALUATION

Acaricidal activity

MK-239 has excellent activity on eggs and adults of *Tetranychus* spp. and *Panonychus citri* (Table 1).

Table 1. Activity of MK-239 and of other acaricides against *Tetranychus* spp. and *Panonychus citri*.

Compound	LC50 (mg/l)							
	T.urticae		*T.cinnabarinus*		*T.kanzawi*		*P.citri*	
	Egg[1]	Adult[2]	Egg[1]	Adult[2]	Egg[1]	Adult[2]	Egg[1]	Adult[2]
MK-239	0.96	3.7	1.8	5.6	6.8	8.4	3.9	0.50
Cyhexatin	521.0	4.5	–	–	> 800.0	6.9	159.0	19.0
Fenbutatin oxide	>1000.0	21.0	> 800.0	28.0	> 800.0	28.0	> 800.0	18.0
Dicofol	48.0	14.0	–	–	257.0	24.0	591.0	297.0
Hexythiazox	0.39	>1000.0	–	–	1.5	–	5.2	>1000.0

[1] Observed at 7 days after treatment
[2] Observed at 2 days after treatment

MK-239 has demonstrated excellent activity against all developmental stages of *Tetranychus urticae* (eggs, larvae, nymphs, chrysalis and adults), with little difference in activity between the stages (Table 2).

Table 2. Activity of MK-239 on each developmental stage of *Tetranychus urticae*

Developmental stage	LC50 (mg/l)
Egg[1]	0.72
Egg[2]	1.9
Larva	1.8
Protochrysalis(nymphochrysalis)	0.93
Protonymph(first nymph)	0.83
Deutochrysalis	1.5
Deutonymph(second nymph)	1.5
Teleiochrysalis(telochrysalis)	1.2
Adults(male)	2.6
Adults(female)	3.7

[1] Immediately after oviposition(before the contractive phase of germ band)
[2] At three days after oviposition(just before hatching)

Residual activity

MK-239 has long residual activity on all stages of *Panonychus* spp. and on larvae of *Tetranychus* spp.. Fig.1 shows the residual activity of MK-239 at 100 mg/l in comparison with cyhexatin at 100 mg/l on adults of *Tetranychus urticae*.

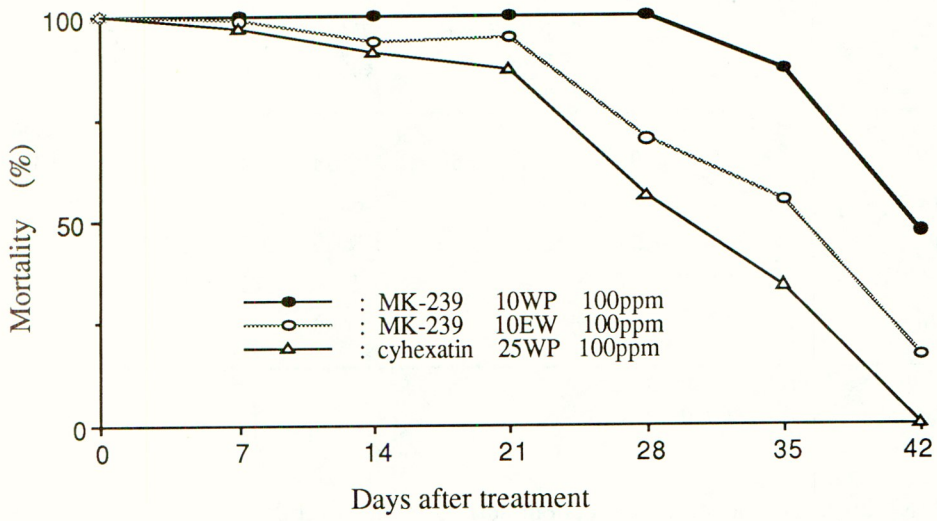


Fig. 1 Residual activity of MK-239 and of cyhexatin on adults of *Tetranychus urticae* under glasshouse conditions.

Temperature/Activity Relationship

The activity of MK-239 and of two other acaricides at three different temperatures were studied on adults of *Tetranychus urticae*. Fig. 2 shows that activity of MK-239 is not temperature-dependent.

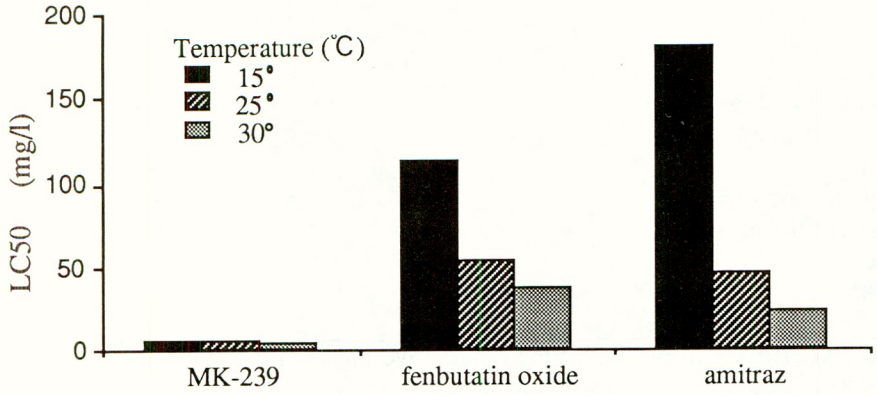


Fig. 2 Temperature/activity relationship of MK-239 and of other acaricides on adults of *Tetranychus urticae*.

Systemic/translaminar activity

In common with fenbutatin oxide and propargite, MK-239 does not show any systemic activity, but MK-239 does show translaminar movement. When applied to the upper leaf surface of kidney bean (*Phaseolus vulgaris*), MK-239 inhibited development of mite eggs on the under surface of treated leaves (Fig.3). Fenbutatin oxide and propargite showed no translaminar activity in these experiment.

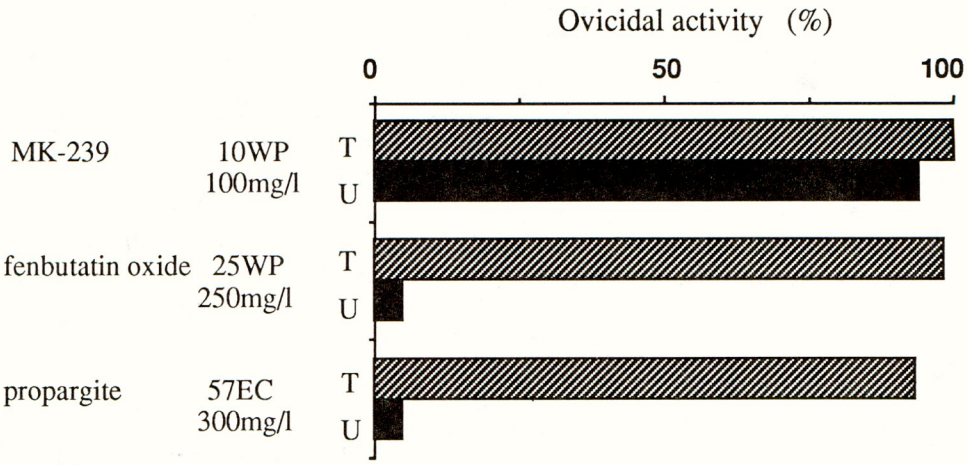


Fig. 3 Translaminar activity of MK-239 on kidney bean leaves.
T Treated surface (Upper surface of leaf)
U Untreated surface (Under surface of leaf)

Cross resistance

MK-239 showed no cross resistance in adult *T.urticae* from strains resistant to dicofol, fenbutatin oxide or organophosphates (Fig. 4) or with hexythiazox on eggs of *Panonychus citri* (Table 3).

Table 3 Acaricidal activity of MK-239 on eggs of resistant *Panonychus citri*.

Compound	LC50 (mg/l) Susceptible	Hexythiazox-Resistant
MK-239	1.5	1.3
Hexythiazox	0.4	13000.

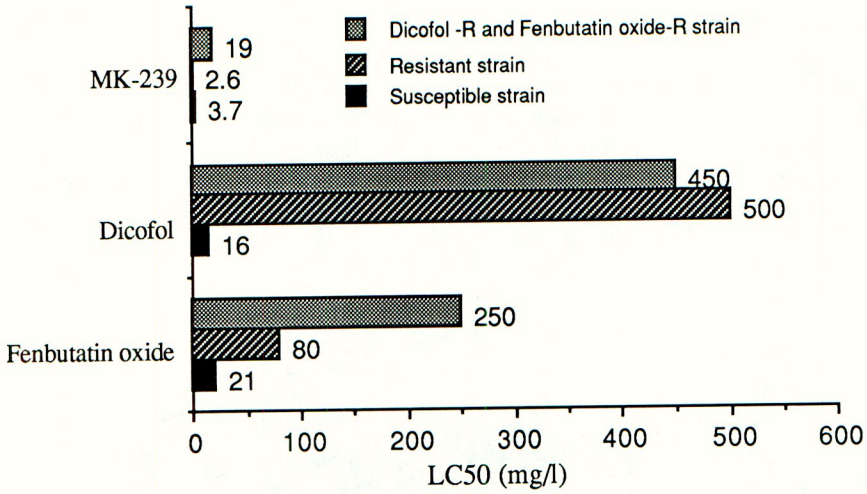


Fig. 4 Acaricidal activities of MK-239, dicofol and fenbutatin oxide on adults from susceptible and resistant strains of *Tetranychus urticae*.

Formulation

The following formulations are available: 10% or 20% wettable powder (WP), 20% emulsifiable concentrate (EC), 60% water dispersible granule (WG) and 10% emulsion, oil in water (EW). Table 4 shows initial activities in different formulations of MK-239 on *Tetranychus urticae* and *Panonychus citri*.

Table 4 Initial activity in different formulations of MK-239 against *Tetranychus urticae* and *Panonychus citri*.

Formulation	LC50 (mg/l)			
	Tetranychus urticae		*Panonychus citri*	
	Adult[1]	Egg[2]	Adult[1]	Egg[2]
20%WP	4.6	1.6	1.4	5.3
20%EC	3.7	1.3	1.0	3.8
10%EW	4.9	1.0	0.8	1.4
60%WG	3.6	1.4	2.2	3.0
10%WP	3.8	0.8	1.2	2.0
Tech.	3.7	1.0	0.5	3.9

[1] Adulticidal activity was observed at 2 DAT.
[2] Ovicidal activity(failure to hatch)was observed at 10 DAT.

Phytotoxicity

Phytotoxic effects of MK-239 have been tested on many crops. No phytotoxicity has been observed on most of the crops at recommended dosage(25-200mg A.I./l). The number of crops and varieties tested so far are shown below.

Fruit	9 families	40 varieties
Tea	1	1
Cereals	3	10
Vegetables	41	160
Ornamentals	4	13

Effect on beneficial species

MK-239 is not toxic to bees and does not appear to influence the behaviour of bees. MK-239 has not caused any adverse effect on *Stethorus punctillum, Chrysopa sp.* or *Typhlodromus occidentalis*, has a slight effect on *Orius sp.* and *Amblyseius longispinosus* .

FIELD EVALUATION

Field evaluations of MK-239 have been conducted in many areas on various crops such as citrus, top fruit, grape, vegetables, tea and ornamentals(Merriam *et al.*,1990). Data from the trials with MK-239 in Japan during 1987-1989 are given as examples of its field activity. MK-239 at 50mgAI/l provided very good control of *P.citri* in citrus for up to 40 days after treatment(Fig. 5). MK-239 at 25mgAI/l also provided control of *T. urticae* in cucumber(Fig. 6).

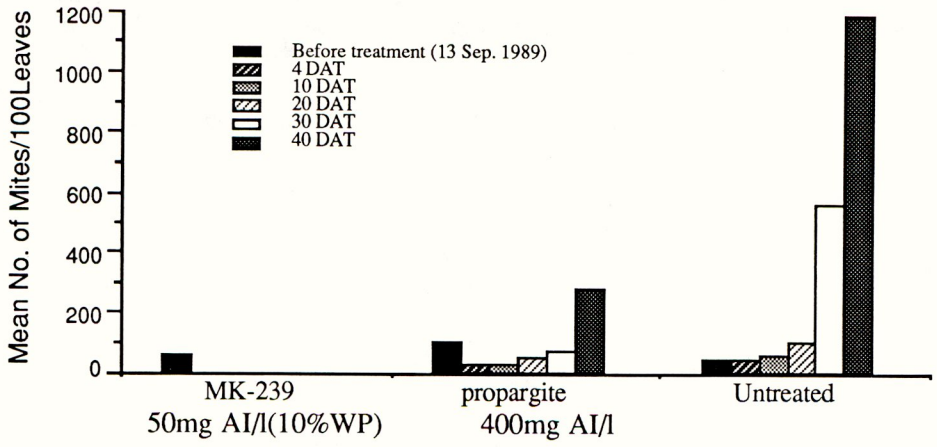


Fig. 5 Effect of MK-239 on *P.citri* on citrus in Japan (Shizuoka prefecture).

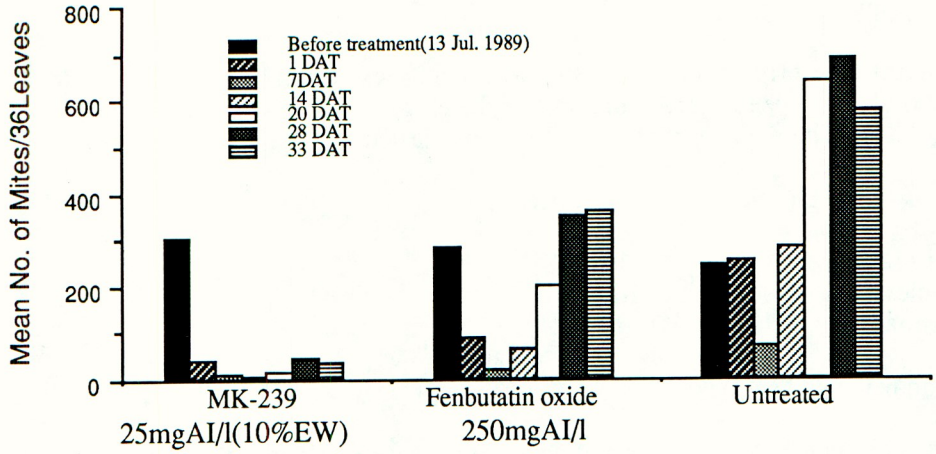


Fig. 6 Effect of MK-239 on *T.urticae* on cucumber in Japan (Iwate prefecture).

CONCLUSION

In laboratory evaluations and field trials, MK-239 has been shown to be an acaricide having a broad spectrum of activity, and giving excellent control at low dosages on many important crops without phytotoxicity under various climatic conditions.

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FIELD EVALUATION OF AC 801,757 (MK-239) ACARICIDE

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ABSTRACT

AC 801,757 (MK-239) is an experimental acaricide discovered by Mitsubishi Kasei Corporation which is being co-developed by American Cyanamid Company. The compound has a broad spectrum of activity on mites, with good knockdown and long residual properties. In field trials conducted in Japan, W. Europe, and the United States during 1989-90, AC 801,757 at rates of 5 to 20 g AI/100 litres provided excellent control of major mite pests of fruit and vine crops, such as *Panonychus ulmi*. Activity on both eggs and motile life stages of mites was demonstrated. AC 801,757 controlled *Tetranychus* spp. on cotton and vegetables and was also active on insect pests such as *Psylla pyricola* on pear, *Aphis gossypii* and *Myzus persicae* on vegetables, *Phorodon humili* on hops, and *Bemisia tabaci* on cotton.

INTRODUCTION

AC 801,757 (MK-239) (*N*-(4-*tert*-butylbenzyl)-4-chloro-3-ethyl-1-methylpyrazole-5-carboxamide) is a new, highly-active acaricide discovered by Mitsubishi Kasei Corporation (Fukuchi *et al.*, 1990). It has unique chemistry and mode of action, and is active on all stages of mites with no cross-resistance to various commercial acaricides in laboratory studies (Kyomura *et al.*, 1990). AC 801,757 is now under development by Mitsubishi Kasei Corporation and American Cyanamid Company. This paper describes the performance of AC 801,757 for control of mites and insects of economically important crops under field conditions from 1989 to 1990.

METHODS

AC 801,757 10% wettable powder (WP), 20% WP and emulsifiable concentrate (EC) formulations were applied with water for the trials. Applications were made in sufficient volume to ensure thorough coverage of the foliage. All treatments were replicated a minimum of four times. Percent control was calculated using the methods of Henderson and Tilton (1955).

RESULTS

Top Fruit

AC 801,757 at dosages of 5 to 20 g AI/100 litres provided excellent control of major mite pests, including *Panonychus ulmi* and *Tetranychus urticae* on apple, pear, peach, and cherry in numerous field trials conducted in Europe, Japan, and the U.S. In France, AC 801,757 20% WP at dosages of 10 g AI/100 litres and greater provided excellent initial and residual control of high populations of *P. ulmi*. The level of control was more consistent and superior to that provided by cyhexatin at 30 g AI/100 litres (Figure 1).

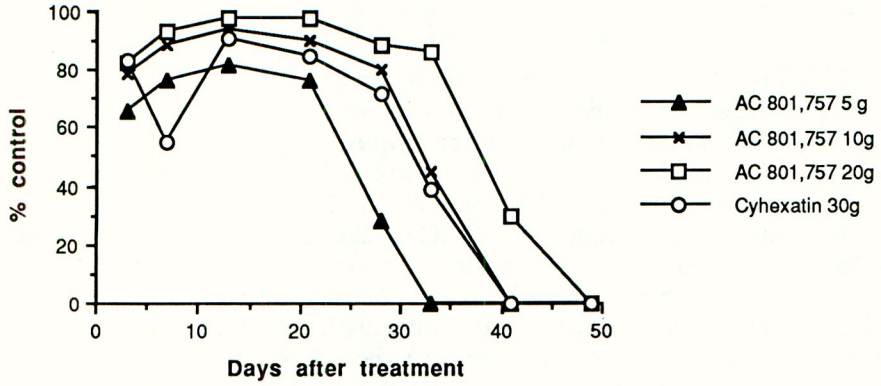

Figure 1. Control of *Panonychus ulmi* by AC 801,757 20% WP in apples in France.

In the U.S., AC 801,757 20% EC at rates as low as 5 g AI/100 litres provided excellent control of *P. ulmi* for at least 34 DAT. The level of control was superior to that provided by fenbutatin oxide at 90 g AI/100 litres (Figure 2).

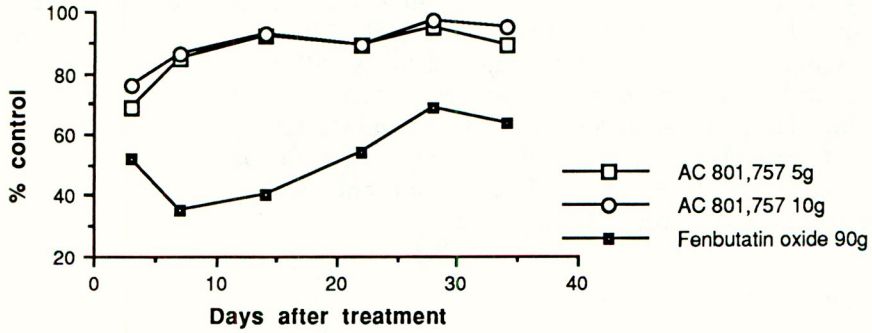

Figure 2. Control of *Panonychus ulmi* by AC 801,757 20% EC in apples in the U.S.

AC 801,757 20% WP was also effective for controlling over-wintering eggs and newly hatched larvae of *P. ulmi* in France (Figure 3). At 10 g AI/100 litres,

AC 801,757 gave performance comparable to clofentezine at 20 g AI/100 litres, and provided control of *P. ulmi* for at least six weeks after treatment.

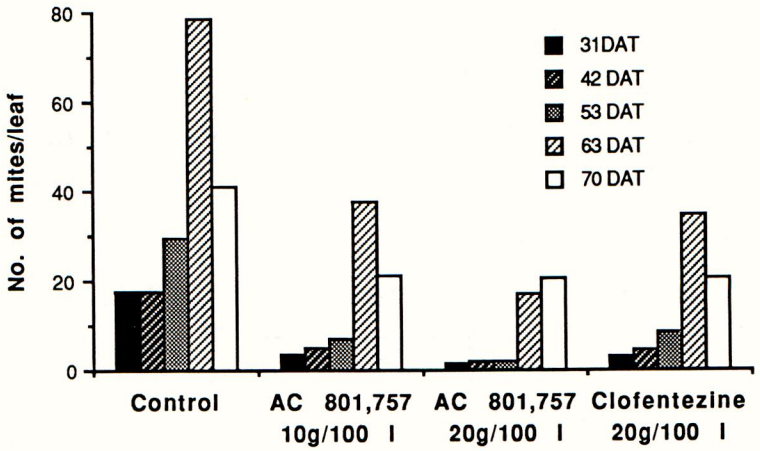

Figure 3. Control of *Panonychus ulmi* on apple, with AC 801,757 20% WP applied at the onset of hatching of over-wintering eggs (France).

At rates from 5 to 20 g AI/100 litres, AC 801,757 also provided excellent control of *P. ulmi* on a variety of fruit crops in trials conducted in Belgium, Italy, Japan, Spain, Switzerland, and W. Germany. Performance was equal or superior to commercial standards. The speed and degree of residual control were directly correlated with dosage. AC 801,757 was also active on *Aculus schlechtendali* on apples in Belgium and W. Germany, and on *Epitrimerus pyri* on pear in the U.S., although effective rates were generally higher than those required for control of *P. ulmi*.

In a trial conducted in the U.S., AC 801,757 20% WP at rates of 20 and 40 g AI/100 litres provided good control of *Psylla pyricola*; similar to that provided by the standard, dicofol plus amitraz (Table 1).

Table 1. Control of *Psylla pyricola* on pear after two applications (June 23 and July 8, 1989) of AC 801,757 or standard in New York, USA

Treatment	Formulation	Rate (g AI/100 l)	% Control at Days after Treatment* 5/1A	11/1A	6/2A	16/2A	30/2A
AC 801,757	20WP	10	87	77	87	65	10
AC 801,757	20WP	20	62	84	96	96	7
AC 801,757	20WP	40	81	90	96	96	34
Dicofol + Amitraz	35WP 1.4 EC	55 45	89	90	82	96	34
Untreated**	–	–	4.7	6.2	2.3	2.9	2.9

* 1A=First Application, 2A=Second Application

** Average number of *P. pyricola* nymphs/leaf

No phytotoxicity or russetting was observed in selectivity trials conducted on apple and pear using AC 801,757 WP and EC formulations at rates as high as 80 g AI/100 litres (4 to 16 times the effective rate).

Citrus

In Japan, AC 801,757 10% WP at rates of 2.5 and 5 g AI/100 litres provided control of *Panonychus citri* superior to that provided by the standards fenbutatin oxide, bifenthrin, and fenpropathrin (Table 2).

Table 2. Control of *Panonychus citri* on citrus in Japan

Treatment	Rate (g AI/100 l)	% Control at Days After Treatment						
		7	14	21	28	35	42	49
AC 801,757 10% WP	5.0	100.0	100.0	100.0	100.0	97.0	94.9	95.3
	2.5	100.0	100.0	100.0	83.1	81.8	90.5	89.6
Fenbutatin oxide	12.5	100.0	87.5	79.9	86.0	63.8	67.0	38.4
Bifenthrin	2	96.5	97.4	88.9	92.8	62.0	73.4	46.4
Fenpropathrin	5	98.2	88.8	91.6	97.0	72.2	76.0	87.6
Untreated*	–	(12.8)	(33.3)	(39.4)	(76.7)	(239)	(460)	(702)

* Number of adults/100 leaves

AC 801,757 20% WP at 5 to 10 g AI/100 litres provided from four to six weeks of residual control of P. *citri* in Spain. In Italy, AC 801,757 at 20 g AI/100 litres and fenbutatin oxide at 60 g AI/100 litres controlled a high population of *T. urticae* on lemon for four weeks after treatment, but AC 801,757 at 10 g AI/100 litres was inferior to these treatments (Figure 4).

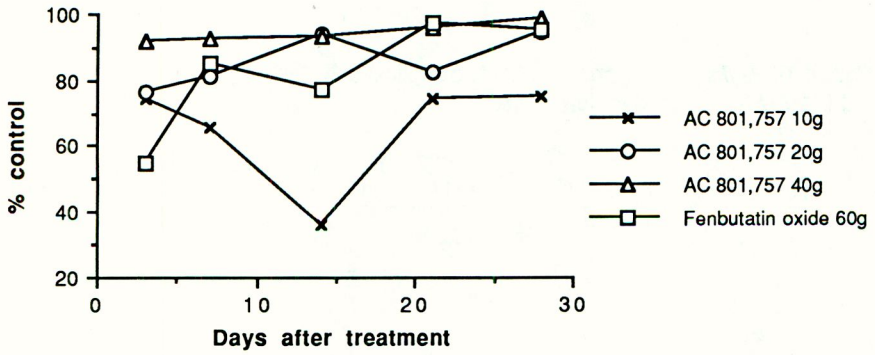

Figure 4. Control of *Tetranychus urticæ* by AC 801,757 20% WP on lemon in Italy.

In the U.S., AC 801,757 at rates of 20 to 40 g AI/100 litres controlled the two most important mites on western citrus, *P. citri* and *T. urticae*, and also demonstrated potential for control of *Eutetranychus banksii* in Texas and *Phyllocoptruta oleivora* in Florida.

Vines

On vines in France, AC 801,757 20% WP at 10 and 20 g AI/100 litres provided good knockdown and residual control of *Eotetranychus carpini* for up to five weeks post-treatment (Figure 5). Efficacy was superior to that provided by dicofol at 50 g AI/100 litres.

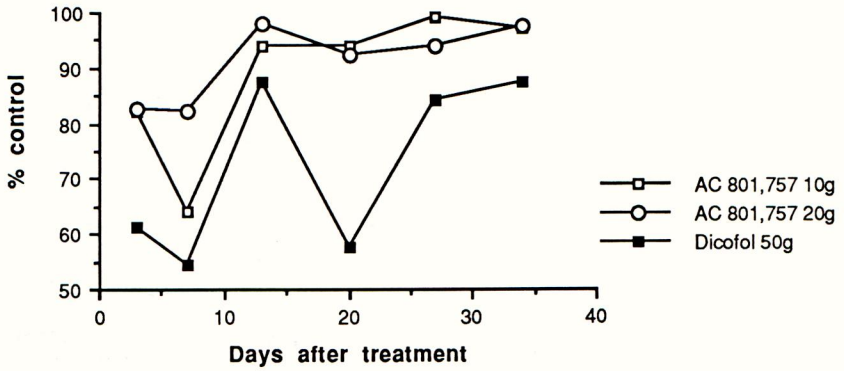

Figure 5. Control of *E. carpini* with AC 801,757 20% WP on vines in France.

At 5 to 10 g AI/100 litres AC 801,757 gave excellent control of *P. ulmi* for at least seven weeks in France, and was superior to dicofol at 50 g AI/100 litres. AC 801,757 was active on *Calepitrimerus vitus* in one trial, with 20 g AI/100 litres providing 78% control at 30 DAT. In the U.S., AC 801,757 at 20 to 40 g AI/100 litres was superior to fenbutatin oxide at 62 g AI/100 litres for control of *T. pacificus* for up to four weeks post-treatment. The same rates provided control of *T. willaumetti* equal to or better than propargite at 75 g AI/100 litres.

Cotton

In Spain, AC 801,757 at 250 g AI/ha provided good control of *T. urticae* for up to four weeks post-treatment, which was superior to that provided by bifenthrin at 80 g AI/ha. AC 801,757 was also active on *Frankliniella* sp. and *Bemisia tabaci* in these trials. In the U.S., AC 801,757 at rates as low as 250 g AI/ha also gave excellent initial and residual control of *T. urticae* on cotton.

Hops

In W. Germany, AC 801,757 20% WP at 10 to 20 g AI/100 litres provided excellent control (>99%) of high *T. urticae* populations on Huller and Northern Brewer variety hops. AC 801,757 at 20 to 40 g AI/100 litres also performed well

(>95% control up to three weeks post-treatment) for control of *Phorodon humili*, but was slightly inferior to cyhalothrin at 6.5 g AI/100 litres. No phytotoxic effects were observed from AC 801,757 treatments.

Vegetables

In trials conducted in Europe and Japan, AC 801,757 at rates from 2.5 to 20 g AI/100 litres controlled *T. urticae*, *T. cinnabarinus*, and *T. kanzawai* on a variety of vegetable crops. In Japan, AC 801,757 at rates as low as 5 g AI/100 litres (spray volume = 2000 l/ha) provided excellent control of *T. urticae* on eggplant for three weeks post-treatment, superior to fenbutatin oxide at 25 g AI/100 litres (Table 3).

Table 3. Control of *Tetranychus urticae* on eggplant in Japan

Treatment	Rate (g AI/100 l)	% Control at Days After Treatment				
		2	7	15	21	29
AC 801,757 20% WP	10	99.7	99.6	99.7	98.3	84.9
	5	98.9	97.9	98.7	90.3	4.7
Fenbutatin oxide	25	78.8	93.6	90.0	72.7	0
Untreated*	–	(606)	(643)	(1,200)	(1,307)	(320)

* Number of adult mites/60 leaves

Under greenhouse conditions in Italy, AC 801,757 20% WP at rates as low as 10 g AI/100 litres (spray volume = 2000 l/ha) provided over 95% control of *T. urticae* on melons for up to four weeks post-treatment, which was superior to that provided by fenpropathrin at 20 g AI/100 litres or fenbutatin oxide at 44 g AI/100 litres (Table 4). In this trial, AC 801,757 was also active on *Aphis gossypii* and *Myzus persicae*, with 10, 20, and 40 g AI/100 litres providing over 90% residual control for 2, 3, and 4 weeks post-treatment.

Table 4. Control of *Tetranychus urticae* on melons grown under greenhouse conditions in Italy

Treatment	(g AI/100 l)	% Control at Days After Treatment				
		3	7	13	21	27
AC 801,757 20% WP	10	98.3	99.4	99.1	97.7	96.2
	20	99.1	98.6	98.7	99.0	96.2
Fenpropathrin	20	93.4	93.2	95.6	86.5	56.7
Fenbutatin oxide	44	98.0	83.5	92.9	80.0	2.7
Untreated*	–	(29.6)	(29.8)	(63.5)	(41.0)	(42.5)

* Mean number of motile mites/leaf

CONCLUSIONS

Results of field trials conducted in W. Europe, Japan, and the United States have shown that AC 801,757 (MK-239) provides excellent initial and residual control of major mite pests on a variety of crops. AC 801,757 was also active on insect pests such as *P. pyricola*, *B. tabaci*, and several species of aphids. No phytotoxic effects were observed on treated crops.

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FENPYROXIMATE (NNI-850), A NEW ACARICIDE

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ABSTRACT

Fenpyroximate (NNI-850) is a novel acaricide discovered by Nihon Nohyaku Co. Ltd. and is now under worldwide development. The chemical belongs to the phenoxypyrazole group, a new chemical category of acaricides, and shows selective activity on important phytophagous mites such as Tetranychidae, Eriophyidae and Tarsonemidae. It has 10 to 100 times higher activity than dicofol and cyhexatin and reveals not only quick knockdown activity on mobile stages but also inhibits moulting of immature stages at lower doses. Fenpyroximate shows no cross resistance with other conventional acaricides and excellent persistent residual activity in the field at doses of 25-50 mg AI/l. It can be used in any season of the year and be used for preventing synthetic pyrethroids from causing resurgence of mites if it is mixed with them. The safe property of the chemical to many kinds of crops also promises its availability for the control of important agricultural mites.

INTRODUCTION

The control of spider mites has become more difficult in recent years with the appearance of populations resistant to conventional acaricides and because of pest resurgence caused by intensive use of synthetic pyrethroids. In order to solve these problems, we focused our research on the development of a new acaricide and discovered fenpyroximate in 1985 among phenoxypyrazole compounds which had been derived from our continuing studies on the new pyrazole chemistry. The chemical was coded as NNI-850 and is now under worldwide development.

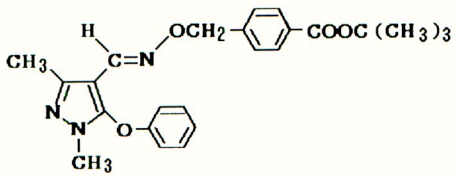
This paper reports technical and biological properties of the chemical, with special reference to the activity on two major species of agricultural mites, Tetranychus urticae and Panonychus citri.

CHEMICAL AND PHYSICAL PROPERTIES

Code Number:	NNI-850
Chemical Name:	tert-butyl (E)-α-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-p-toluate

2—8

Structural Formula:



Molecular Formula: $C_{24}H_{27}N_3O_4$
Molecular Weight: 421.50
Appearance: White crystalline powder
Melting Point: 101.1～ 102.4℃
Vapour Pressure: 5.6×10^{-8} mmHg (25℃)
Solubility (g/l solvent): water 0.015×10^{-3} (20℃)
methanol 15 (25℃)
n-hexane 4 (25℃)
xylene 175 (25℃)
Formulation: 5% Suspension Concentrate

MAMMALIAN TOXICITY

Acute oral LD50:	Rat (male)	480 mg/kg	
	Rat (female)	245 mg/kg	
Acute dermal LD50:	Rat (male)	> 2,000 mg/kg	
	Rat (female)	> 2,000 mg/kg	
Eye irritation:	slight		
Skin irritation:	none		
Mutagenicity:	Ames	negative	
	DNA repair	negative	
	Chromosomal aberration (in vitro)		negative
	Micronucleus (mouse)		negative

AQUATIC TOXICITY

48h LC50: Cyprinus carpio (carp) 6.1 μg /l
3h LC50: Daphnia pulex (water flea) 85 μg /l

BIOLOGICAL PROPERTIES

Acaricidal Spectrum

Fenpyroximate shows high activity on important phytophagous mites such as Tetranychidae, Eriophyidae and Tarsonemidae, whereas its activity is relatively weak on predacious mites such as Phytoseiidae and is almost none on animal-parasitic or soil-living mites such as Ixodidae, Acaridae and Oribatei at the doses (25-50 mg AI/l) recommended for the control of phytophagous mites (Table 1). This indicates that the chemical is a rather selective acaricide. Among Insecta, only Empoasca onukii (tea green leafhopper) can be controlled and Apis mellifera is not affected at all by fenpyroximate at these doses.

TABLE 1. Acaricidal spectrum of fenpyroximate.

Activity at recommended doses (25-50 mg AI/l)		
High	Moderate	Low/None
Tetranychidae (Tetranychus urticae) (T. cinnabarinus) (Panonychus citri) (P. ulmi) etc Eriophyidae Tarsonemidae	Phytoseiidae (Phytoseiulus persimilis)	Phytoseiidae (Amblyseius longispinosus) Ixodidae Acaridae Oribatei

Laboratory Evaluation

The activity of fenpyroximate on several developmental stages of two major species of spider mites was evaluated by the spray-method. The LC50 values for the chemical and reference compounds are shown in Table 2. Fenpyroximate is most effective on larvae followed by nymphs, adults and eggs in both species and its activity on mobile stages is 10 to 100 times higher than those of dicofol and cyhexatin. Even compared with hexythiazox, fenpyroximate has slightly higher activity on immature stages, but its ovicidal activity is lower than that of hexythiazox.

The mode of action of fenpyroximate was further studied with female adults and larvae of T. urticae. The KT50 value (median knockdown time) for

TABLE 2. Activity of fenpyroximate on several developmental stages of T. urticae and P. citri.*

Species and Stage	LC50 value (mg AI/l) fenpyroximate 5 SC	dicofol 40 EC	cyhexatin 25 WP	hexythiazox 10 WP
T. urticae				
egg(24h old)	36	290	210	0.82
larva	0.11	12	1.8	0.49
protonymph	0.17	11	2.1	0.60
adult(♀)	0.32	14	3.1	> 500
P. citri				
egg(24h old)	51	380	160	5.9
larva	1.0	50	12	1.0
adult(♀)	5.5	59	30	> 500

* Each chemical was sprayed on leaf-discs infested by mites. Leaves of kidney bean and grape fruit were used for T. urticae and P. citri, respectively.

TABLE 3. KT50 values for several acaricides on female adults of T. urticae.

Chemical	KT50 value (min) 50	100	500*
fenpyroximate 5 SC	51	48	13
dicofol 40 EC	200	140	51
cyhexatin 25 WP	190	170	110
propargite 57 EC	550	390	150

* Each chemical was sprayed on to mites at the concentration (mg AI/l) indicated.

fenpyroximate on adult mites was 1/3 to 1/10 compared to those of reference compounds (Table 3), indicating the faster knockdown activity of this chemical. It was also observed that affected mites stopped feeding and egg-laying, resulting in minimal plant damage.

Larval mites were knocked down and died quickly at the higher doses shown in Table 4, but at lower doses they survived to the protochrysalis or deutochrysalis stage and then failed to moult. In order to compare the acaricidal properties of fenpyroximate and other acaricides, LC50 values on newly hatched larvae were calculated, based on cumulative mortality at the end of each successive developmental stage (Table 5). Among conventional chemicals tested, binapacryl, dicofol, pirimiphos-methyl, amitraz and cyhexatin mainly revealed quick knockdown activity on mobile larvae. Tetradifon, clofentezine and hexythiazox did not show any knockdown activity against larvae but killed mites at the protochrysalis stage. The mode of action of fenpyroximate seems to be different from those of conventional acaricides tested.

TABLE 4. Dose response mortality of larval T. urticae treated with fenpyroximate.*

Dose (mg AI/l)	Cumulative Mortality (%) ~ larva	~ protochrysalis	~ deutochrysalis
4	100	100	100
2	81.6	100	100
1	49.3	100	100
0.5	17.2	100	100
0.25	4.2	100	100
0.125	0.0	64.9	83.8
0.0625	1.4	49.3	63.8
0.0313	0.0	18.0	42.6
0.0156	0.0	0.0	16.7

* Newly hatched larvae were treated.

TABLE 5. LC50 values for several acaricides on larvae of T. urticae, based on the cumulative mortality at each successive developmental stage.

Chemical	LC50 value (mg AI/l) Larva(A)	Protochrysalis	Deutochrysalis(B)	A/B
fenpyroximate	0.98	0.071	0.041	24
binapacryl	57	50	50	1
pirimiphos-methyl	12	12	12	1
dicofol	11	9.0	9.0	1
amitraz	11	5.6	5.6	2
cyhexatin	17	5.7	5.7	3
tetradifon	> 400	2.8	0.81	>500
clofentezine	> 100	0.69	0.69	>100
hexythiazox	> 500	0.41	0.41	>1000

Cross Resistance

Cross resistance between fenpyroximate and other conventional acaricides was studied with a susceptible laboratory strain and field strains of the three major species of spider mites collected at various locations in Japan from 1985 to 1989. No populations were observed to be resistant to fenpyroximate (Fig. 1), probably because of the unique mode of action of the chemical as mentioned above.

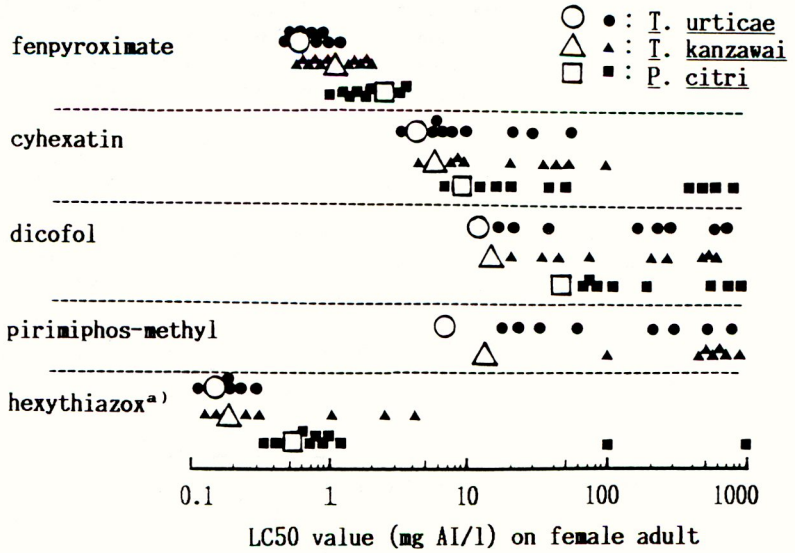


FIG. 1 Acaricide-susceptibility of susceptible (hollow symbols) and field (solid symbols) strains of mites in Japan.

[a)] Ovicidal and larvicidal activity.

Residual Activity

The residual effect of fenpyroximate was studied after citrus trees were sprayed with the chemical in the field. Leaves were cut, placed on agar-gel and infested by female adults of P. citri at one week intervals. The persistence of fenpyroximate efficacy was much better than that of cyhexatin, even at a dose of 1/10 of the reference compound (Table 6).

TABLE 6. Residual effect of fenpyroximate on P. citri on citrus.

Chemical	Dose (mg AI/l)	Corrected Mortality (%)* DAT 0	7	14	20	28
fenpyroximate 5 SC	50	100	100	100	100	73
	25	100	100	77	71	3
cyhexatin 25 WP	250	100	92	15	36	6

* Mortality count was made 2 days after each release.

Field Evaluation

The performance of fenpyroximate against important phytophagous mites such as Tetranychidae and Eryophyidae was evaluated in a series of field trials. As exemplified in Tables 7-11, fenpyroximate provided excellent control efficacy on all species of mites tested, including the population resistant to conventional acaricides (Table 8) at doses ranging from 25-50 mg AI/l. It can be used in any season of the year to control mites and may be used to prevent synthetic pyrethroids causing a resurgence of mites, if it is combined with them as shown in Table 9.

Phytotoxicity

Fenpyroximate (5% SC) shows no phytotoxicity to top fruits, citrus, tea and vegetables at the doses recommended for the control of mites.

TABLE 7. Control of Panonychus ulmi on apple (Aomori Pref., 1988).*

Chemical	Dose (mg AI/l)	No. of mobile mites/leaf DAT 0	4	12	21	32	46
fenpyroximate 5 SC	25	1.5	0.6	0.1	0.03	0.0	0.03
fenbutatin oxide 25 WP	250	1.8	0.1	0.03	0.03	0.0	0.03
hexythiazox 10 WP	50	1.2	0.6	0.0	0.0	0.07	0.0
untreated	-	0.9	0.3	0.1	1.6	1.7	4.1

* The chemical was applied on July 21 at a spray volume of 40 l/tree(1).

TABLE 8. Control of P. citri resistant to conventional acaricides on citrus (Shizuoka Pref., 1987).*

Chemical	Dose (mg AI/l)	No. of female adults/100 leaves DAT 0	2	10	20	30
fenpyroximate 5 SC	25	32	2	0	0	3
fenbutatin oxide 25 WP	125	177	114	53	168	938
amitraz 20 EC	200	126	20	30	40	530
dicofol 40 EC	260	238	40	11	34	332
untreated	-	229	393	669	761	308

* The chemical was sprayed to run-off on June 6[2].

TABLE 9. Combination effect of fenpyroximate and synthetic pyrethroids for the control of P. citri on citrus (Osaka Pref., 1988).*

Chemical	Dose (mg AI/l)	No. of female adults/200 leaves DAT 0	7	14	21	28	35
permethrin	100	88	145	639	810	1457	566
cyhalothrin	25	100	38	96	548	2004	2695
fluvalinate	100	96	12	25	118	713	971
fenpyroximate	50	778	13	9	11	16	21
+ permethrin	50 +100	256	0	14	13	6	1
+ cyhalothrin	50 + 25	175	0	0	0	19	27
+ fluvalinate	50 +100	294	0	1	23	41	18
untreated	-	65	200	374	644	156	135

* The chemical was sprayed to run-off on July 11.

TABLE 10. Control of Aculops pelekassi on citrus (Ehime Pref., 1989). *

Chemical	Dose (mg AI/l)	No. of fruits sampled	No. damaged fruits ranked ** 0	1	2	3	% of fruits damaged
fenpyroximate 5 SC	25	144	144	0	0	0	0.0
dicofol 40 EC	267	150	145	2	2	1	3.3
untreated	-	150	68	6	2	74	54.7

* The chemical was sprayed to run-off on July 5 and fruits were picked on Aug. 11[3].

** 0: no damaged, 1: slightly damaged, 2: up to 1/3 of fruit-surface damaged, 3: more than 1/3 of fruit-surface damaged.

TABLE 11. Control of T. urticae on grape (Osaka Pref., 1987). *

Chemical	Dose (mg AI/l)	No. of female adults / 40 leaves DAT 0	7	14	21	28
fenpyroximate 5 SC	50	72	0	0	0	0
hexythiazox 10 WP	50	44	18	6	0	0
untreated	-	33	198	266	76	93

*The chemical was sprayed on Sep. 21 at a spray volume of 2 l/tree.

CONCLUSIONS

Fenpyroximate is a promising novel acaricide. It provides excellent control efficacy on important phytophagous mites by means of outstanding knockdown activity and residual activity without any phytotoxicity to many kinds of crops at doses of 25-50 mg AI/l. It prevents synthetic pyrethroids from causing resurgence of mites and allows them to control other insect pests. Because of its novel chemistry and mode of action, fenpyroximate also controls mites that are resistant to other conventional acaricides. These properties may facilitate its frequent use. Therefore, alternating application of fenpyroximate with different types of products is recommended since spider mites rapidly develop resistance.

ACKNOWLEDGEMENTS

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GY-81, A NEW CONCEPT IN SOIL FUMIGATION

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ABSTRACT

Water soluble sodium and potassium salts of H_2CS_4, tetrathio(peroxocarbonic acid), have been formulated into highly effective control agents for plant parasitic nematodes, phylloxera and some soil fungi. These compounds exhibit the general property of decomposing in the soil/plant environment to release carbon disulphide, a well known broad spectrum biocide. The formulations exhibit very low phytotoxicity and are environmentally benign. The results of nine years of laboratory and field studies from the United States and Europe are summarized. All studies required by the Environmental Protection Agency in the U.S. have been completed and registrations are pending in several European countries. A commercial formulation of tetrathio(peroxocarbonate) will soon be released under the trade name "ENZONE".

INTRODUCTION

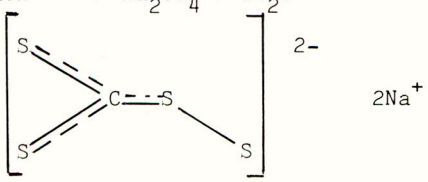
In the late 1970s when it became evident that many standard pesticides were becoming environmentally unacceptable, Unocal Science & Technology Division initiated research to design a new generation of environmentally acceptable chemical pesticides.

One of the first areas of research was the control of plant parasitic nematodes, particularly on perennial crops. After some nine years of research and development we have produced a formulation based on the tetrathio(peroxocarbonated) anion that controls plant parasitic nematodes effectively in irrigated agriculture and is environmentally acceptable. This paper reports details of the chemistry, toxicity, mode of action, effectiveness and environmental behaviour of these compounds.

CHEMISTRY

Disodium tetrathio(peroxocarbonate) is prepared from the reaction of carbon disulphide (CS_2) hydrogen sulphide (H_2S), sulphur (S), and sodium hydroxide. This compound has the structure (Zins, et al., 1975):

1) $CS_2 + H_2S + S + 2\ NaOH \longrightarrow Na_2CS_4 + 2H_2O$



The pure compound is a deep red crystal that is extremely hygroscopic and highly sensitive to air oxidation. It is very soluble in water

(>50% m/m at 20°C). However, in water it rapidly establishes the following equilibrium:

2) $Na_2CS_4 \rightleftharpoons Na_2S_2 + CS_2$

3) $Na_2S_2 + 2H_2O \rightleftharpoons 2\ NaOH + H_2S + S$

Concentrated aqueous solutions of disodium tetrathio(peroxocarbonate) can be stabilized indefinitely by the addition of appropriate quantities of sodium disulphide (Na_2S_2) and sodium hydroxide (Young & Green, 1988). The stabilized aqueous solutions containing 31.8% m/m disodium tetrathio(peroxocarbonate) is the product currently used for soil fumigation. This product has the research designation GY-81.

When GY-81 is added to soil, the disulphide ion (S_2^{-2}), in equilibrium with CS_4^{-2} (equation 2), is irreversibly adsorbed by the soil matrix to liberate CS_2. The rate of CS_2 release is primarily a function of free water in the soil (Table 1). Tetrathio(peroxocarbonate) is not itself adsorbed by soil (Rf value >0.9). Hence, under irrigated agriculture, GY-81 can be placed in the soil at any location and concentration by appropriate manipulation of irrigation methods and rates. In a relatively short time (Table 1), GY-81 produces CS_2 which is the biologically active moiety.

TABLE 1. Half-life of GY-81 in soil

Percent Water Holding Capacity	Half-Life (min)
0	16
50	40
100	510

TOXICITY

With the exception of eye and skin irritation, GY-81 is a relatively benign material posing little hazards to humans or animals (Table 2).

ENVIRONMENTAL BEHAVIOUR

Dispersal in soil

When GY-81 is dispersed in the soil it is rapidly converted to CS_2, H_2S, S and NaOH (Table 1), because of the strong adsorption of H_2S by soil and the precipitation of elemental sulphur. The soil reactions shift the equilibrium shown in equations 1-3 completely to the left. H_2S and sulphur are oxidized in soil by thiobacillus to H_2SO_4 in 1-3 days depending on soil conditions. CS_2 is oxidized similarly to CO_2 and H_2SO_4, but more slowly, in 3-25 days. However, CS_2 is highly volatile and diffuses out of the soil in 3-5 days. Hence, approximately 50-100% of the CS_2 volatilizes from the soil; the remainder is oxidized. In a high porosity sand essentially all the CS_2 volatilizes from the soil. In a low porosity clay soil about half of the CS_2 will volatize; the rest is oxidized. After a period of no more

TABLE 2. Toxicity data for GY-81

Acute Toxicity	
Oral LD_{50} (24 hr, rats)	631 mg/kg
Dermal Toxicity (rabbits)	>2 g/kg
Inhalation (acute, 4 hr, rats)	4.04 g/m^3
Primary Eye Irritation (rabbits)	Moderate
Primary Dermal Irritation (rabbits)	Severe
Dermal Sensitization (guinea pigs)	Negative
Mutagenicity	
Ames Salmonella/Microsome Plate Test	Negative
CHO/HGPRT Cell Mutation	Negative
Unscheduled DNA Synthesis (rat hepatocytes)	Negative
In Vitro Chromosomal Aberration	Equivocal
Developmental	
Teratology (two species, rats and rabbits)	Negative
Subacute-Subchronic	
Inhalation (21-day, rats)	0.11 g/m^3, no observable adverse effect; no systemic effects at any dose

than 30 days the soil residue resulting from GY-81 application consists of sodium salts of carbonate and sulphate.

Dispersal in Water

At low concentrations in ground water GY-81 is hydrolyzed (Equation 4) with a half-life of approximately 30 minutes.

4) $Na_2CS_4 \xrightarrow{\text{excess } H_2O} Na_2S + S + CS_2$

The inorganic compounds are of no toxicological concern. However, CS_2 has a solubility in water of about 2000 ppm, but also has a Henry's Law constant of 4.7×10^5 mm Hg at 25°C. Hence the CS_2 spontaneously leaves the water and enters the adjacent soil-air matrix where it dissipates and is partially converted to carbonate and sulphate by biological processes.

Through several lysimeter and field studies, we have found that the dissipation of CS_2 from deep stagnant aquifers occurs with a half-life of about 18 days. Even if GY-81 were directly injected into an aquifer, no long-term contamination should occur.

CROP RESIDUE

GY-81 is completely decomposed in the soil in a few minutes. The

inorganic metabolites are utilized as ordinary plant nutrients and are of no toxicological concern. Carbon disulphide can persist in the soil for several hours and be taken into crop plants and translocated. For example, heavily dosed tomatoes have shown concentrations as high as 500 ppb in aerial parts of the plant. However, radio carbon label studies have shown that CS_2 rapidly dissipates from the plant, to reach a level of <1.0 ppb in approximately 14 days. After this time there is no detectable residue of CS_2 in GY-81 treated plants. These data have been confirmed in field residue studies on a variety of crops.

MODE OF ACTION

In vitro and in vivo studies have shown that the control of a variety of soil pathogens can be approximated as a function of the concentration of toxicant (C) x time (T):

$$\text{Percent mortality} = f\ (C-C_o)T$$

where C_o equals the "no effect concentration". However since C is much greater than C_o, ignoring the latter term has little effect on the result. Similar methodology has been used for other soil fumigants (McHenry & Thomason, 1974). For example, exposure of a susceptible organism to 10 ppm of CS_2 for 10 h gives approximately the same effect as exposure to 100 ppm of CS_2 for 1 h. Table 3 presents the LC_{50} values in terms of the CT product of some of the organisms we have studied. To obtain an analogous "instantaneous kill" enormous rates of CS_2 must be used; i.e. of the order of magnitude of 2 tons per acre (Ordish, 1972). This is why the use of CS_2 as a soil fumigant has been largely abandoned. The use of GY-81 as a delivery vehicle for CS_2 has allowed the manipulation of the time parameter. This capability allows soil pathogen control with absolute rates of 10 to 20 pounds of CS_2 per acre.

TABLE 3. LC_{50} of CS_2, expressed as CxT (ppm-hours), to selected soil organisms and the no-effect level, Co

Pest/Pathogen	CT, ppm-hrs	Co, ppm
Root knot nematode (Meloidogyne incognita)	300	<10
Citrus nematode (Tylenchulus semipenetrans)	300	<10
Phylloxera (Daktulosphaira vitifoliae)	100	< 5
Pythium ultimum	10,000	100
Phytophthora spp.		
(parasitica)	2,000	100
(citrophthora)	1,000	20
(cinnamoni)	1,500	100

Nematodes, phylloxera and some fungi can be controlled using rates well below the phytotoxic level (Table 4). Nematodes and phylloxera are considerably more sensitive to CS_2 than the fungal species. The latter, however, are still within the range of practical soil treatment levels.

For example, in citrus orchards, both nematodes and Phytophthora spp. can be controlled simultaneously with a single non-phytotoxic rate of GY-81 (Matheron & Matejka, 1988).

TABLE 4. Maximum dose of GY-81 required for pathogen control, compared with minimum phytotoxic dose, both expressed as CxT, ppm-hours.

	Required Dose	Phytotoxic Dose
Citrus Orchards	19,200	>50,000
Grapes	17,400	>50,000
Almond, Peach, Prune Orchard	11,600	>50,000

Field Application

The application rates of GY-81 are not based on conventional pounds of active ingredient per acre, but rather the concentration of active ingredient to be maintained in irrigation water and the length of time it is to be maintained. The actual mass of GY-81 applied to achieve control varies with the type of irrigation system. Tables 5-7 are examples of recommendations for the use of GY-81 on a variety of crops and pathogens. Treatment should not normally begin until the soil temperature has reached 58°F at 6 inches. When the ambient air temperature is expected to exceed 90°F for 5 h on the day of application, the lowest concentrations (ppm A1) listed in the tables should be used or crop injury may occur. Treated crops should be at least 1 year old or crop injury may occur.

We have carried out over 800 field efficacy trials in which we have treated approximately 40,000 acres distributed among grapes, citrus, tomatoes, and potatoes, and minor amounts of other crops. Most of these trials included internal standards consisting of carbofuran, aldicarb, fenamiphos or oxamyl, or some combination of these pesticides. In all cases the pathogen control from the recommended application method of GY-81 was equal to or greater than the internal standards at their recommended rates. The rates of GY-81 are generally higher than these standard materials. However, the cost of pathogen control with GY-81 is comparable.

CONCLUSIONS

GY-81 offers a new approach to soil fumigation that is consistent with current environmental constraints. Its utility is currently practically limited to irrigated agriculture. Our current research is focused on other derivatives of tetrathio(carbonate) that can extend this utility to non-irrigated agriculture.

ACKNOWLEDGEMENTS

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TABLE 5. Control of citrus nematode and management of Phytophthora root rot in citrus orchards by the application of GY-81 in irrigation water.

Irrigation method	PPM A.I.	Hrs. injection	Gal. GY-81/ acre/ treatment	No. treatments/ /yr.	Max gal/ acre/yr
Drip	950-1950	3-8	5-20	2-6	50
Low Volume Emitters	950-2400	3-8	10-30	2-6	100
Flood & Furrow	250-500	1-6	20-60	1-3	100
Shank	-	-	25-50	1-3	100

TABLE 6. Control of plant parasitic nematodes by the application of GY-81 in irrigation water.

Irrigation method	PPM A.I.	Hrs. injection	Gal. GY-81/ acre/ treatment	No. treatments/ /yr.	Max gal/ acre/yr
Drip & Low Volume Emitters	950-1450	3-8	5-30	2-6	75
Flood & Furrow	250-500	1-6	20-60	1-3	100
Shank	-	-	25-50	1-3	100

TABLE 7. Control of grape phylloxera by the application of GY-81 in irrigation water.

Irrigation method	PPM A.I.	Hrs. injection	Gal GY-81/ acre/ treatment	No. treatments/ /yr.	Max gal/ acre/yr
Drip & Low Volume Emitters	700-1450	6-12	5-30	2-6	75
Flood & Furrow	250-500	1-6	20-60	1-3	100
Shank	-	-	25-50	1-3	100

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