Insecticidal Activity of a New Synthetic Compound, S-5602 〔α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-isovalerate〕 on Tobacco Cut Worms (*Spodoptera litura* Fabricius).

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14. 新合成殺虫剤 S-5602〔α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl) isovalerate〕のハスモンヨトウ (*Spodoptera litura* Fabricius) に対する殺虫特性

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新しい合成殺虫剤 S-5602〔α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl) isovalerate〕はハスモンヨトウ (*Spodoptera litura* Fabricius) 幼虫に対し，食薬散布試験で市販殺虫剤であるメソミルやサリチオン以上の高い活性を示した．

メソミルはハスモンヨトウに対し経口投与の場合にも経皮投与の場合にもほぼ同等の活性を示した．一方 S-5602は，経口投与の場合にはメソミルの約4分の1の活性しか示さなかったが，経皮投与では2～4倍に達した．また，この化合物にはサリチオンで認められるようなガス効果や，メソミルで認められるような浸透移行による殺虫作用は認められなかった．

これらの殺虫特性は一般のピレスロイド系殺虫剤と類似しており，S-5602 はシクロプロパンカルボン酸エステルではないが，殺虫特性から考えるとピレスロイド系殺虫剤の一種と言える．

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 synthetic pyrethroidal compounds were discovered such as allethrin[2], tetramethrin[3], resmethrin[4], furamethrin[5], proparthrin[6], phenothrin[7] and permethrin[8]. But these compounds except permethrin and phenothrin were not tried as agricultural insecticides[7,9].

Ohno *et al.* reported that α-substituted phenylacetic acid esters possessed insecticidal activities[10]. And among various derivatives of these compounds, S-5602 〔α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-isovalerate〕 possessed the highest efficacy against many species of insect pests[11].

This paper describes the efficacy and the mode of action of S-5602 on tobacco cut worms (*Spodoptera litura* Fabricius).

Materials and Methods

I) Test insects

The larvae of tobacco cut worms (*Spodoptera litura* Fabricius) were reared on artificial diet[12] in our laboratory (16L 8D 27°C RH 60%).

II) Insecticides

S-5602: Technical grade (98.1%) was synthesized in this institute and 20% EC was formulated from the technical grade.

Methomyl: Technical grade (98.4%) was synthesized in this institute and 45% WP was purchased from Nippon Noyaku Co., Ltd.

Salithion: 25% EC was purchased from Kumiai Kagaku Co., Ltd.

III) Testing methods

(1) Foliar spray method

Each insecticide (EC and WP) was diluted with water and sprayed to potted Chinese cabbage plants. After air-drying the treated leaves were cut out and put in a plastic cup (φ 11cm) and 10 larvae (4th instar) of tobacco cut worms were released. Mortality counts were made after 48 hours. This experiment was performed in triplicate. The LC_{50} value was calculated by Finney's graphic approximate method based on the mortality at 48 hours.

(2) Topical application method

Half a μl of acetone solution of each technical grade insecticide was applied to the ventral thorax of test insects with a microsyringe. Thirty larvae were used at each dosage. Mortality counts were made after 48 hours. The LD_{50} value was calculated by Finney's graphic approximate method based on the mortality at 48 hours.

(3) Film contact method

One ml of acetone solution of each technical grade insecticide was applied to a glass dish (ϕ 9cm). After acetone had evaporated off, 10 larvae (4th instar) were released into the treated dish. Agonized larvae were counted at 30, 60, 90, 120 and 180 minutes after releasing. And also alive and dead larvae were counted after 24 hours. This experiment was performed in triplicate.

(4) Feeding method

Chinese cabbage leaves were cut out at the size 0.7cm in diameter with a cork borer. Half a μl of acetone solution of each technical grade insecticide was applied to the leaf disc with a microsyringe. After acetone had evaporated off, the treated leaf was sandwiched with an untreated leaf by Campbell and Filmer's method[13]. Each disc was put into a plastic cup (ϕ 7cm) and a 5th instar larva was released. Thirty larvae were used at each dosage. Mortality counts were made after 24 hours. The LD_{50} value was calculated in the same manner as in experiment 2.

(5) Vapor effect test method

Each insecticide (EC and WP) was diluted with 100ml water and poured into a one l glass beaker at the rate of 1.7mg a.i./beaker (200g a.i./10 a). A 50 mesh wire net was placed in the beaker 3cm above the bottom to avoid direct contact with the insecticide. After release of ten larvae (4th instar), the top of the beaker was covered with cheese cloth. Mortality counts were made after 24 hours. This experiment was performed in triplicate.

(6) Systemic activity test method

Each insecticide (EC and WP) was diluted with water and applied to the surface of the soil in a pot (ϕ 9cm), where three Chinese cabbage plants were grown to 3-leaf stage. The leaves were cut out 3 and 72 hours after the application, and put in a plastic cup (ϕ 11cm), then 10 larvae (4th instar) were released. Mortality counts were made 48 hours after the release of larvae. This experiment was performed in triplicate.

Results and Discussion

The insecticidal efficacy of S-5602 against tobacco cut worms (*Spodoptera litura* Fabricius) was about two times higher than that of salithion and one and a half times higher than that of methomyl by foliar spray method as shown in Table 1. At a concentration above 10 ppm, S-5602 killed most larvae. At 2.5 or 5.0 ppm, the insecticidal activity was partial, but the damage caused to the leaves was only slight. On the other hand, sublethal concentrations of methomyl and salithion did not prevent leaf damage. Therefore, S-5602 seems to control tobacco cut worms to a greater extent than it might appear on the bases of its LC_{50} value.

Table 1. Efficacy of S-5602 and other insecticides against the 4th instar larvae of tobacco cut worms by foliar spray method.

Insecticide	Concentration and mortality (%) at 48 hrs					LC_{50}
	2.5	5.0	10	20	40	ppm
S-5602	6.7	53.3	96.7	100		4.8
Methomyl		26.7	76.7	83.3	83.3	7.5
Salithion		3.3	43.3	90.0	100	11.0

Meanwhile, effects of dermal and oral applications on efficacy of S-5602 against tobacco cut worms were investigated in comparison with methomyl. As the average body weight of test insects at each application was different, the efficacy was compared by the dose per body weight. As the result, the LD_{50} value ($\mu g/g$) of methomyl in topical application was the same as that in feeding method as shown in Tables 2 and 4. On the other hand, the relative efficacy of S-5602 in topical application was two times of methomyl, but the relative efficacy of this compound in feeding method was one fourth of methomyl. In other words, the oral and the dermal toxicity of methomyl against tobacco cut worms seemed almost equal in these experiments regarding as the respective LD_{50} values ($\mu g/g$). And as for S-5602, the dermal toxicity was eight times higher than the oral toxicity, if each toxicity of S-5602 was calculated based on methomyl. When these insecticides were compared by film contact method, the efficacy of S-5602 was higher than that of methomyl as shown in Table 3, namely, the KT_{50} value and the mortality at 0.05mg/m^2 of S-5602 were almost equal to the respective values of methomyl at 0.2mg/m^2. The result of film contact method showed the similar tendency as in the case of topical application. The efficacy of S-5602 as contact poison was far higher than that as stomach poison in these experiments. It has been reported that the contact poison of pyrethrins are higher than the stomach poison against insects[14].

Furthermore, investigation was carried out to ascertain if S-5602 possesses vapor effect and systemic activity in comparison with salithion and methomyl. Salithion possessed high vapor effect against tobacco cut worms, but as for S-5602, this type of effect was not observed as shown in Table 5. Methomyl possessed systemic insecticidal activity against tobacco cut worms, but this type of activity was not observed with S-5602 as shown in Table 6. Vapor effect and systemic activity have not been recognized with pyrethroidal insecticides like pyrethrins, phenothrin and permethin[15].

The chemical structure of S-5602 is different

Table 2. Efficacy of S-5602 and methomyl against tobacco cut worms by topical application.

Insecticide	Regression equation	LD_{50} μg/larva*	LD_{50} $\mu g/g$	Relative efficacy
S-5602	Y=4.890+2.119 (X−2.274)	0.021	0.70	205
Methomyl	Y=4.885+1.664 (X−1.572)	0.043	1.43	100

* Average body weight: 30mg

Table 3. Efficacy of S-5602 and methomyl against the 4th instar larvae of tobacco cut worms by film contact method.

Insecticide	Dosage mg/m^2	Percentage of agonized larvae 30′	60′	90′	120′	180′	KT_{50}	Mortality (%)
	0.013	0	0	0	0	0		0
S-5602	0.05	0	10.0	10.0	52.3	63.3	110	80.0
	0.2	0	53.3	73.3	80.0	83.3	56	100
	0.013	0	0	0	0	0		7.4
Methomyl	0.05	0	0	0	0	0		0
	0.2	3.4	13.8	44.8	62.1	72.4	110	65.5
Untreated		0	0	0	0	0		0

Table 4. Efficacy of S-5602 and methomyl against tobacco cut worms by feeding method.

Insecticide	Regression equation	LD_{50} μg/larvae*	μg/g	Relative efficacy
S-5602	Y=4.610+2.242(X−1.750)	0.84	6.5	25
Methomyl	Y=4.589+3.548(X−3.198)	0.21	1.6	100

* Average body weight : 130mg

from those of other pyrethroidal insecticides in that S-5602 does not have cyclopropane ring in the acid moiety as shown in Fig. 1. However, the molecular shape of S-5602 seems to be similar to those of pyrethroidal compounds based on molecular model analysis (Ohno *et al.*[10,11]). Furthermore, in this investigation, mode of action of this compound against tobacco cut worms was shown to be similar to that of pyrethroidal compounds. With these results, it is concluded that S-5602 belongs to the group of insecticides called pyrethroids.

Table 5. Vapor effect of S-5602 and other isecticides against tobacco cut worms.

Insecticide	Dosage g (a.i.)/10 a	Mortality (%) at 24 hrs
S-5602	200	0
Methomyl	200	14.8
Salithion	200	100
Untreated		0

Table 6. Systemic activity of S-5602 and other insecticides against tobacco cut worms.

Insecticide	Mortality (%) at 48 hrs time after application to the soil 3 hrs	72 hrs
S-5602	0	0
Methomyl	80.0	100
Salithion	0	3.6
Untreated	0	0

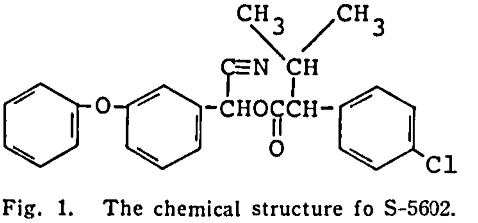

Fig. 1. The chemical structure fo S-5602.

Summary

S-5602 [α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-isovalerate] exhibited high efficacy against tobacco cut worms (*Spodoptera litura* Fabricius) by foliar spray method in comparison with methomyl and salithion. The dermal toxicity of this compound against the pest was about eight times higher than the oral toxicity. This compound exhibited neither vapor effect nor systemic activity against tobacco cut worms. It seems that the mode of action of this compound against tobacco cut worms is similar to that of pyrethroidal compounds.

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References

1) La Forge, F. B.: *J. Amer. Chem. Soc.*, 58, 1777 (1936).
2) Schechter, M. S., Nathan Green and F. B. La Forge: *J. Amer. Chem. Soc.*, 71, 3165(1949).
3) Kato, T., K. Ueda and K. Fujimoto : *Agr. Biol. Chem.*, 28, 914 (1964).
4) Elliot, M., A. W. Farnhan, N. F. Janes, P. H. Needham and B. C. Pearson : *Nature*, 213, 493 (1967).
5) Katsuda, Y., T. Chikamoto, H. Ogami., H. Hirobe and T. Kunishige : *Agr. Biol. Chem.*, 33, 1361 (1969).

6) Nakanishi, M., A. Tsuda, A, Abe, S. Inamasu and T. Mukai: *Botyu-Kagaku*, 35, 91 (1970).
7) Fujimoto, K., N. Itaya, Y. Okuno, T. Kadota and T. Yamaguchi : *Agr. Biol. Chem.*, 37, 2631 (1973).
8) Elliot, M., A. W. Farnham, N. F. Janes, P. H. Needham, D.A. Pulman and J. H. Stevenson : *Nature*, 246, 169 (1973).
9) Davis, J. W., J. A. Harding and D.A. Wolfenbargar: *J. Econ. Entomol.*, 68, 373 (1975).
10) Ohno, N., K. Fujimoto, Y. Okuno, T. Mizutani, M. Hirano, N. Itaya, T. Honda and H. Yoshioka: *Agr. Biol. Chem.*, 38, 881 (1974).
11) Ohno, N., K. Fujimoto, Y. Okuno, T. Mizutani, M. Hirano, N. Itaya, T. Honda and H. Yoshioka: *Pestic. Sci.*, 7, 241 (1976).
12) Yasudomi, N., H. Okamoto and K. Ozaki : *Proc. Assoc. Pl. Prot. Sikoku*, 10, 77 (1975).
13) Campbell, F.L. and R.S. Filmer : *Trans. IV Inter. Cong. Ent.*, 1928, 523 (1929).
14) Metcalf, R. L.: *Org. Insecticide*, 57 (1955).
15) Hirano, M.: Unpublished data.

Studies on Insecticidal Aerosol Formulations[I]. Stability of Tetramethrin and Other Pyre throids in Water-Based Aerosol Formulations. Takashi Yamaguchi, Isao Nishibe and Chuji Hirose (Research Department, Pesticides Division, Sumitomo Chemical Co., Ltd., Takarazuka, Hyogo, 665, Japan) Received Feb. 21, 1977. *Botyu-Kagaku*, 42, 104, 1977.

15. 殺虫エアゾール製剤に関する研究（第一報）水性エアゾール製剤におけるテトラメスリンおよびその他のピレスロイドの安定性 山口堯士，西部勲，広瀬忠嗣（住友化学工業株式会社，生物科学研究所，農薬事業部研究部，兵庫県宝塚市高司4丁目）52. 2. 21受理

水性エアゾール製剤に関し，(1)pH の異なる乳化剤を用いた製剤中のテトラメスリンの安定性と製剤のpH変化の関係，(2)保存された製剤と新しく調合された製剤間のイエバエに対する効力比較，(3)長期間保存された製剤中における各種ピレスロイドの安定性について調べ，次の点を明らかにした．

(1)製剤の pH は経時的に低下する傾向があり，使用された乳化剤によっては，たとえ着手時にアルカリ性であっても，ある時点で酸性に変化するものがあった．この変化は有効成分を含まない製剤中でも起こっており，乳化剤自身の変化によるものであると考えられた．(2)テトラメスリンは，アルカリ性製剤中で不安定であったが，pH が酸性に変化した後の分解は非常に少なかった．また，アルカリ性製剤を製造時に酸性に調節した場合には，テトラメスリンは，幾分安定化された．(3)酸性製剤では，35°C にて1年間保存された試料と新しく調合された試料との間には，効力面での有意差は認められなかったが，アルカリ性製剤では，両者間に差が認められ，製剤を酸性にすることは，効力的にも有効であった．(4)テトラメスリン，d-フェノトリン，レスメスリン，d-アレスリンは，酸性製剤において，室温で少なくとも2年間は極めて安定であった．

Water-based aerosol formulation has been studied since 1950s, mainly for the purpose of lowering cost of the conventional oil based aerosol. Water-based aerosols can be classified into two types, two-phase and three-phase aerosols. Two-phase type consists of two layers, namely, gaseous phase composed of vaporized propellant, and liquid phase composed of active ingredients, solvent, water, emulsifier, and liquefied propellant. Three-phase type consists of vaporized gas phase, water phase and another phase composed of active ingredients, solvent and liquefied gas. In the latter case, the containers have to be shaken before spraying for unification of the layers. Three-phase type has been widely used as a household insecticidal formulation owing to their better stability of active ingredients and generally less corrosion risk of container.

Compatibility of many active ingredients with water-based formulations has been studied. Glessner[1] has described that chlordane, heptachlor, and organo-phosphates such as DDVP and mala-