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Insecticidal Activity and Properties of TIA-230 (Pyraclofos*)

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TIA-230 (pyraclofos*), *O*-[1(4-chlorophenyl)-4-pyrazolyl]o-ethyl S-propyl phosphorothiolate showed high insecticidal activity against the Lepidopterous, Coleopterous, Hemipterous, and Dipterous insect pests, such as Spodoptera litura, Mamestra brassiase, Pseudaletia separata, Plutella xvlostella, Pieris rapae, Adoxophyes orana, Chilo suppressalis, Aulacophora femoralis, Phyllotreta striolata, Phaedon brassicae, Henosepilachna vigintioctopunctata, Lissorhoptrus orizophilus, Aphis gossypii, Aphis glycines, Myzus persicae, Hyalopterus pruni, Musca domestica and Culex pipiens molestus. The compound also showed a high acaricidal activity against Tetranychus urticae, Tetranychus kanzawai and Rhizoglyphus echinopus and showed a high nematicidal activity against Meloidogyne incognita. Residual activity by foliar spray of TIA-230 was shown to be higher than those of prothiophos, acephate, methomyl, demethylvinphos, chlorpyrifos-methl, dicofol, fenbutatin oxide and cyhexatin. In field tests, the sprays of 0.017% and 0.035% solution of TIA-230 (wettable powder) were highly effective in controlling the damage to cabbage by Spodoptera litura, Mamestra Brassiase, Plutella xylostella, Pieris rapae and Myzus persicae.

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1. Introduction

TLA-230 (pyraclofos), *O*-[1(4-chlorophenyl)-4-pyrazolyl]o-ethyl *S*-propyl phosphorothiolate was a newly developed organophosphorous agent insecticide by Takeda Chemical Industries, Ltd.

The synthetic method was already reported by Okada and Kono¹⁾. It was shown that the manifestation mechanism of insecticidal activity was the inhibition of acetylcholinesterase activity by an activated oxidant in the central nervous system, and it was different from the action mechanism of conventional organophosphorous agents.

Therefore, anticipating the potency of this insecticide to be different from that of conventional organophosphorous agents, we investigated the effects and properties against the *Lepidopterous, Coleopterous, Hemipterous, Dipterous, Orthpteraous*, acarina and nematoda, then discussed its practical use as an agricultural insecticide.

2. Materials and Methods

2.1 Tested insecticides.

TIA-230 was tested in the forms of technical grade substance (purity 90.4%), 50% emulsion concentrate, and 35% wettable powder. As controls, the following insecticides were used: Acephate technical substance [concentration?] (purity 98.9%), 50% wettable powder (Takeda Chemical Industries, Ltd); Prothiophos 50% emulsion concentrate (Nihon Tokusyu Nouvaku, Ltd); Methomyl 45% wettable powder (Takeda Chemical Industries, Ltd); Chlorpyrifos-methyl 25% emulsion concentrate (Nissan Chemical Industry, LTD); Dimethylyinphos 50% wettable powder (Shell Chemical Industry, Ltd); Cartap 50% soluble powder (Takeda Chemical Industries, Ltd); Malathion 50% emulsion concentrate (Takeda Chemical Industries, Ltd); Dimethoate 43% emulsion concentrate (Takeda Chemical Industries, Ltd); DDVP 75% emulsion concentrate (Takeda Chemical Industries, Ltd), Amitraz 20% emulsion concentrate (Nissan Chemical Industry, LTD), Dimethoate-fenvalerate emulsion concentrate (Sumitomo Chemical Co., Ltd); Fenbutatin oxide 25% wettable powder (Takeda Chemical Industries, Ltd); BPPS 30% wettable powder (Shionogi & Co., Ltd); Dicofol 40% emulsion concentrate (Takeda Chemical Chlorobenzilate 21% emulsion concentrate (Sankyo Co., Ltd); Industries, Ltd); Cyhexatin 25% wettable powder (Nissan Chemical Industry, Ltd). When these wettable and soluble powders and emulsion concentrates were tested, they were diluted to appropriate concentrations with water including 0.3% spreader, Dain (Takeda Chemical

Industries, Ltd). The technical substance [concentration?]s were dissolved in acetone solution including 20% Tween20, then diluted to be appropriate concentrations.

2.2 Insects.

The kinds of insect pests and developmental stages used for insecticidal tests in a laboratory and greenhouse are listed on table I. *Lepidopterous* 7 species, *Coleopterous* 7 species, *Hemipterous* 9 species, *Dipterous* 2 species, *Orthpteraous* 1 species, acarina 5 species and nematoda 1 species, totalling 32 species of insect pests used. Of these insects, 9 species, *Pieris rapae crucivora, Aulacophora femoralis, Phyllotrela striolata, Plagiodera versicoradistincta, Phaedon brassicae, Chrysolina auricholcea, Lissorhoptrus oryzophilus, Hyalopterus pruni* and *Panonychus ulmi* were collected from the outdoors. The others were insecticide-susceptible strains that have been maintained in our laboratory.

2.3 Insecticide test.

2.3.1 Spray tests.

The tests of insecticidal activity by foliar spray are described below. The appropriate concentrations of insecticides were sprayed onto pot-cultivated host plants; for *Spodoptera litura* (host-plant: soybean, strain Okuwase, 20 days after seeding) *Mamestra brassiase* (cabbage, Shikidori, 40 days after seeding), *Plutella xylostella* (daikon radish, Golden cross bantam, 35 days after seeding), *Pieris rapae crucivora* (cabbage, same days as above), *Psudaletia sepatrata* (corn, Golden cross bantam, same days as above), *Aulacophora femoralis* (cucumber, Yotsuba, 10 days after seeding), *Phyllotreta striolata* (daikon radish, same strain, same days). After the insecticides were sprayed (10 – 20 ml/ a plant) and the plants were air dried, then part of the leaves and stems of the plants were released into each cup, incubated for 2 days at 25 °C, then the numbers of dead bodies were counted.

Delphacidae and *Cicadellidae*: For *Nephotetlix cincticeps, Laodelphax striatellus, Nilaparvata lugens* (rice, Kinbyoubu, 35 days after transplanting) and *Lissorhoptrus orizophilus* (rice, Kinbyoubu, 20 days after seeding), the hosts were covered with a column cage after one day spraying, then adult insects were released into it. The plants were incubated for one day at 28 °C in a greenhouse, then the dead insect bodies were counted.

For *Chilo suppressalis* (rice, strain same, 35 days after transplanting), aphids: *Aphis gossyppii, Myzus persicae, Aphis glycines* (cucumber, cabbage, soybean, same as above), *Unaspis yanonensis* (bengal quince, 60 days after seeding) and Spider Mite: *Tetranychus*

urticae, Tetranychus kanzawai, Panonychus citri and *Panonychus ulmi* (kidney bean, Honkintoki, bengal quince, apple; Fuji, 2 years old tree), the insect pests were inoculated on the pot-cultivated host plants one day before the appropriate concentrations of insecticides were sprayed. After spraying, the plants were incubated at 28 °C for 2 to 20 days, then the number of dead bodies were counted.

Ten adults of *S. litura* were put into a metal cage (10 cm diameter, height 15 cm). 20 ml of insecticides were sprayed from outside the cage. The cages were incubated at 25 $^{\circ}$ C for 2 days and the dead bodies were counted.

2.3.2 Dipping tests.

The hosts or seeds for *Adoxophyes orana* (stems and leaves of soybean), *Nezara antennata* (seeds of soybean), *Plagiodera versicoradistincta*, (stems and leaves of *Salix koriyanagi*), *Chrysolina auricholcea* (stems and leaves of mugwort), *Henosepilachna vigintioctopunctata* (pieces of sliced potato) and *Rhizoglyphus echinopus* (pieces of lily bulb) were dipped in appropriate concentrations of insecticides for 10 seconds, then dried. They were put in plastic cups or 9 cm diameter dishes, then 10 larvae or adults per cup were put into them. The dead bodies were counted after the cups were incubated for 2 days in a room. The eggs of *S. litura*, and *A. orana* of Spider Mite and pupae of *S. litura* were dipped in insecticide solutions for 20 seconds and dried. They were put in plastic cups of a solutions for 20 seconds and dried.

The larvae of *Culex pipiens molestus* and *Meloidogyne incognita* were put into insecticide solutions for 2 days and the dead bodies counted.

2.3.3 Dermal treatments and oral administrations.

When the epidermis of larvae of *C. suppressalis, S. litura* and *A.orana* or adults of *Musca domestica* were treated by the insecticides, acetone solution of technical grade material was dropped 0.5 microliter each on the abdominal and dorsal regions of larvae and adults with micro syringes. The oral administrations were done to inject 1 microliter of insecticide to a mouthpart by inserting micro syringes after the larvae were anesthetized with carbon dioxide. The 10 treated larvae and adults were removed to dishes with the hosts or 10% of sugar water. After 2 days incubation in a room, the dead bodies were counted.

2.3.4 Dry film method.

1 ml of the acetone solution was put in 9 cm glass dishes. After evaporation of the acetone, 10 of adults of *Blattella germanica* were put in the dishes, incubated for 2 days and the dead bodies counted.

- 2.4. Field test.
- 2.4.1 Test 1.

The nursery plants of cabbage (Rokujyu-nichi Kansyo) were planted 30 cm apart on April 11 1984 at our institute (Itijyouji, Sakyo-ku, Kyoto). The number of larvae of *S. litura*, eggs of *M. brassiase* and colonies of *M. persicae* were counted on the plants on May 23 and May 30 (one day before insecticide spraying). The first day of spraying was May 24 and the second day was June 1. At 1.5 1 / test field (30 plants) of insecticides, TIA-230 wettable powder (dilutions of 1000 and 2000 X) and Acephate wettable powder (dilution strength 1000 X), were sprayed with a shoulder sprayer. Each test field contained 30 plants and the spraying tests were repeated once. Individuals of *M. brassiase* and *M. persicae* migrated from outside of the fields. In case of *S. litura*, the hatched larvae from eggs that inoculated on May 9, 7 and 24 were counted.

2.4.2 Test 2.

The nursery plants of cabbage (Tenpou) were planted on July 12 1984 and the number of eggs and larvae of *P. rapae crucivora*, larvae and pupae of *P. xylostella*, and eggs and larvae of *Plusia nigrisigna* were counted on July 20, August 1 (one day before spray day) and August 15 (last counting day). The first days of spraying were on July 23 and August 2. At 11/ test field (10 plants) of insecticides, TIA-230 wettable powder (dilution 1000 X), Acephate wettable powder (dilution 1000 X) and Dimethoate-fenvalerate (dilution 2000 X) were sprayed with a foliar sprayer. The test was not repeated.

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3. Results

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3.1 Insecticidal activity of TIA-230.

The test results of spraying, dipping and dermal treatment were used to determine LC_{50} and LD_{50} with a computer program based on the Logit method by Ipsen and Feigl⁵⁾ (Table I).

The LC50 of TIA-230 was less than 25 ppm for early stage 3^{rd} instar larvae of *S. litura, M. brassiase, P. sepatrata, P. xylostella, P. rapae crucivora* and *A. orana* in *Lepidoptera*. The value was 26ppm for the 6^{th} instar larvae of *S. litura*, 107 ppm (*sic: Table I shows 93.9*) against *M. brassiase* and 36ppm for *P. sepatrata*, so the activity was high, even against later stages of larvae. The LD₅₀ was less than 10 microgram / g for the 6^{th} instar larvae of S. litura, the 5^{th} instar of *A. orana* and *C. suppressalis*. From these results, the dermal toxicity was also as high as the oral toxicity. LC₅₀ for eggs, pupae and adults of *S. litura*, however, were more than 100 ppm.

Although experiments showed that the LC50 for larvae and adult of *Coleoptera, H. vigintioctopunctata* was less than 20 ppm, the value for *Curculionidae*, such as *L. oryzophilus, A. femoralis, P. striolata, P. brassicae* and for *Chrysomelidae* was 100 – 250 ppm. The activities against these pests were lower than for *Lepidoptera*.

The activities for *Hemiptera* were shown to be less than 20 ppm, and even the activities against aphids were dependent on species. But the LC50 for *N. antennata, U. yanonensis, N. cincticeps, L. striatellus* and *N. lugens* were more than 200 ppm, indicating that activities against these pests were lower than for aphids.

The LD50 for adults of the medical pest insect, *M. domestica*, larvae of *C. pipiens molestus* belonging to *Diptera* and adults of *B. germanica* were 10 microgram/g, less than 0.1ppm and 50 microgram/dish. It showed high activities against all of them.

The LC50 for adults of *T. urticae, T. kanzawai* and *R. echinopus* in *Tetranychus* were less than 4 ppm and they were significantly high activities. However, the LC50 for the eggs of were 100 – 400 ppm, indicating activity for killing eggs was low. The LC50 for adults of *Panonychus citri* and *P. ulmi* was 50 – 80 ppm, and it was lower than that of *Tetranychus*.

The LC50 for larvae of *Meloydogyne incognita*, that parasitizes roots of leaf vegetables, was 0.59 ppm, a very high activity.

3.2 The formulation and insecticidal activity.

The emulsion and wettable powder of TIA-230 were compared to differences of LC50 and residual activities to tested insects between the two formulations. The results are shown in Tables II and III.

The LC50 for the emulsion against larvae of *S. litura, M. brassiase, P. sepatrata* and adults of *T. urticae* were 12.1, 26.9, 8.9 and 1.7ppm. They were almost same as 10.0, 25.5, 7.3 and 1.6ppm with the wettable powder. The value of technical substance was also same as these. The LC50 for the emulsion against larvae of *P. xylostella* and *A. gossyppii* were 11.7 and 18.9ppm. The values were smaller than 26.3 and 38.9ppm with the wettable powder.

The residual activities of both formulations were compared with the larvae of *S. litura*. The lethality with 25, 50 and 100 ppm of emulsion 6 days after spraying were 45, 100 and 100%, respectively. However, the values of wettable powder were 92.5, 95.5 and 100%, indicating that the wettable powder had a bit higher residual activity than the emulsion. But there were no large differences in residual activities among the three different formulations.

3.3.1 Insecticidal activity.

The activities of TIA-230 emulsion and wettable powder against *S. litura, M. brassiase, P. sepatrata, A. orana* and *A. gossyppii* were compared with Prothiophos, Acephate, Methomyl, Dimethylvinphos and Chlorpynifos-methyl by foliar spray, and the LC50 values were determined (Table IV). The residual activities are shown in Table V.

The LC50 of TIA-230 wettable powder for larvae of *S. litura* was 10 ppm with leaf spray, 15.4 ppm with body spray. On the other hand, the values of methomyl were 6.6 and 3.2 ppm, the values of chlorpynifos-methyl were 12.3 and 4.3 ppm. These LC50 were somewhat smaller than the values of TIA-230.

The LC50 of TIA-230 wettable powder were 25.5 ppm for larvae of *M. brassiase*, 7.3 ppm for larvae of *P. sepatrata*, 6.9 ppm for larvae of *A. orana* and 13.6 ppm for larvae of *P. xylostella*. There was no insecticide that showed smaller LC50 than that of TIA-230.

The LC50 of wettable powder of TIA-230 against *A. gossyppii* was 38.9 ppm. It was larger than the values of Chlorpynifos-methyl, Methomyl and Dimethylvinphos.

On the other hand, in comparison of the residual activities, the mortality of 25, 50 and 100 ppm of TIA-230 wettable powder in 6 days after spray were very high, 92.5, 95.0 and 100%, but the mortality of 100 ppm of Methomyl, Dimethylvinphos and Chlorpynifos-methyl that had higher insecticidal activities than TIA-230 were 75, 25.0 and 0%, respectively and significantly lower than TIA-230.

3.3.2 Acaricidal activity.

The LC50 and residual effects (growth suppressing effects) against spider mite were

compared among TIA-230 wettable powder and other control insecticides. The results are shown in Tables VI and VII. The LC50 of TIA-230 wettable powder was 1.6 ppm against the adults of *T. urticae*, 3.8 ppm against *T. kanzawai*, and these were significantly lower than 13.9 and 7.8 ppm for prothiophos, 24.1 and 92.7 ppm for fenbutatin oxide wettable powder. But the LC50 against adults and eggs of *P. citri* and *P. ulmi* were very large than it of Fenbutatin oxide wettable powder.

Although the LC50 of TIA-230 wettable powder against *T. urticae* was 1.6 ppm, the LC50 of prothiophos emulsion that showed the highest acaricidal activity was 13.9ppm, the value of Fenbutatin oxide wettable powder was 21.4 ppm, 11.0 ppm for Amitraz emulsion, 3.2ppm for Cyhexatin wettable powder. This indicated activity of TIA-230 wettable powder was the highest among these control insecticides.

The LC50 of TIA-230 in 7 days after spray was 51.5ppm. This value was almost same as 55.8ppm of Fenbutatin oxide and lower than 16.4ppm of Cyhexatin.

3.4 Control effect of TIA230 wettable powder in test fields.

3.4.1 Results of test 1.

The control effect of TIA-230 wettable powder against migrated *M. brassiase* and *M. persicae* and inoculated larvae of *S. litura* were investigated in a field where cabbage was planted in April 11 1984 (Table VIII).

The investigation/observation one day before spraying (May 23) found that inoculated *S. litura* were first to second instars larvae. Because of lower temperatures in this season, the survival rate was low and the plants parasitized by the 231 larvae, totaled 16 out of 40 plants (with tests duplicated). The larvae of *M. brassiase* were not found. Even the eggs of *M. brassiase* were found on 22 plants in 40. Parasitization by aphids was not found.

The number of larvae of *S. litura* in the control field was 236 in the first investigation/observation (June 1) after spraying. The number was almost same as it was before spraying.

The number of surviving larvae was 14 in the test field where 175 ppm of TIA-230 was sprayed. There were no survivors in the test field sprayed with 350ppm. There were also no survivors in the control field where 500 ppm of Acephate wettable powder. The second investigation/observation in June 12 after secondary spraying found that mortality of larvae in the control field also increased along with development of the insects, and the number of surviving larvae decreased to 73. There were also no survivors in the test fields with 175, 350 ppm of TIA-230 and 500 ppm of Acephate.

The effects against *M. brassiase* are described below. The numbers of larvae in the control field were 432 early instars stages and 225 middle instars stages from an investigation/observation (June 1) one day before spraying. However, the numbers treated with TIA-230 were 4 early stages, 22 middle stage larvae in the test field with 175 ppm, and 21 early stages and 6 middle stages in the test field with 350 ppm. The numbers in the field treated with 500 ppm of Acephate were 2 early stage larvae and 3 middle stages. From the secondary investigation/observation, it was shown that the number of survivors was very small; only 4 middle stages and 1 late stage of instar larvae were found in the test field with 175 ppm of TIA-230, although 69 early stages, 205 middle stages and 97 late instar stages of larvae in the negative control field. There was no survivors in the field with Acephate spray.

The number of colonies of *M. persicae* investigated at the same time was 39 in the negative control field, 6 in the test field with 135ppm and 2 in the test field with 350ppm. This indicates that the number of parasites by *M. persicae* was smaller than that of the negative control, the same as that in the test field with Acephate.

3.4.2 Results of test 2.

The control effect of TIA-230 wettable powder against migrated *P. rapae crucivora, P. nigrisigna* and *P. xyloslella* were investigated in a field where cabbage was planted on July 12, 1984. The insecticides were sprayed on July 23 and August 2 following the same method as with test 1. The results are shown in Table IX. The number of eggs and larvae of *P. rapae crucivora* were 19 and 38 per 10 plants in the control field from the observation before spray. The eggs and larvae of *P. nigrisigna* were 40 and 21 per 10 plants and these were quite large number. The number of larvae of *P. xyloslella* was 14 per 10 plants and the density was low because of the higher temperature.

From the results of investigation/observation (August 1) after the first spraying, the number of eggs and larvae of *P. rapae crucivora* in the control were 5 and 10, and decreased a little. The number of eggs and larvae in the test field with 350 ppm TIA-230 spray decreased to 70% compared to before spraying. This rate was almost same as that of tests with 500 ppm Acephate, 500 ppm Cartap and 50ppm of Dimethoate-fenvalerate. The effects of 350 ppm of TIA-230 and other insecticides were low against larvae of *P. nigrisigna* that showed high occurrence. The number of larvae was larger than the number in the control field. Because of high temperatures, increased density of *P. xyloslella* was less. However, the number of individuals in the control field after spraying

was approximately twice the number before spraying. By contrast, the number of larvae and pupae decreased 70%. This efficacy was almost the same as Acephate and had a higher rate of decrease than with Cartap. But this decreasing rate with 350 ppm TIA-230 was lower than 100% than that of Dimethoate-fenvalerate.

Based on the results of the secondary spraying (August 15), the control effect of TIA-230 was not clear because the number of larvae of *P. rapae crucivora* and *P. nigrisigna* showed no significant differences with the number in the control field. Although the density of *P. xyloslella* became three times higher than it was before spraying, the numbers in the test fields with 350 ppm of TIA-230, 500ppm of Acephate and 50ppm of Dimethoate-fenvalerate treatments were approximately the same as before spraying, and densities did not increase.

4. Discussion.

The newly developed insecticide, TIA-230 emulsion and wettable powder showed high insecticidal activity and residual activity by oral and dermal treatments against larvae of the *Lepidopterous* insects such as *S. litura*, *M. brassiase*, *P. sepatrata* in *Noctuida*, *P. xylostella* in *Yponomeutidae*, *P. rapae crucivora* in *Pieridae*, *A. orana* in *Tortridae* and *C. suppressalis* in *Pyralidae*. These activities of TIA-230 were higher than Prothiophos, Acephate, Methomyl, Demethylvinphos, and Chlorpyrifos-methyl. This insecticide also showed higher activity against larvae and adults of *H vigintioctopunctata* in *Coccinellidae* of *Coleopterous* but lower activity against adults of *Chrysomelidae* and *Curculionidae*. It also showed higher activities same as prothiophos against *A. gossyppii*, *H. pruni*, *M. persicae* and *A. glycines* in *Hemiptera*, but the activity was lower against insect pests belonging to *Pentatomorpha, Diaspididae*, *Cicadellidae* and *Delphacidae*. However, it showed potential application to medical pest insects, because of its high activity.

TIA-230 showed a higher activity against *T. urticae* and *T. kanzawai* of *Tetranychus* in Spider Mite than Prothiophos, Methomyl, Acephate, Malathion, DDVP and Dimethoate. It also showed higher or the same level of activity than specific acaricides including Dicofol, Amitraz, BBPS, Chlorobenzilate, Fenbutatin oxide and Cyhexatin. Moreover, it also showed high activity against M. incognita, and this indicated the applicability of this chemical as an insecticide for nematoda.

As described above, the spectrum of TIA-230 emulsion and wettable powder were wide and showed high activities to insect pests for vegetables, fruits and tea as well as medical insect pests. On the other hand, TIA-230 showed species selectivity, in that the activities were low against insects belong to *P. nigrisigna* of *Lepidopterous, Chrysomelidae* and *Curculionidae* of *Coleopterous,* and *Pentatomidae, Delphacidae* and *Diaspididae* of *Hemiptera.* Generally, the species-selective toxicity of insecticides might be raised by differences of epidermal permeability, activation and detoxification abilities of insecticides inside a body, excretion speed and permeability to site of action from midgut. TIA-230 is expressed the insecticidal activity by the inhibition of acetylcholinesterase in nerve cells after oxidized activation of the TIA-230 in the central nerve system, not in the fatbody or hemolymph, such as with thiophosphoryl-type insecticides including Fenitrothion ^{2,3)}. So if there is a difference of activity of the oxidase in the nerve system by insect species, the insecticidal activity would be strongly affected.

From recent studies, it was indicated that nonspecific esterase (AliE) in the insect played an important role for selective toxicity of organophosphorous agents ^{6,7}. TIA-230 has high specific insecticidal activity against *S. litura* larvae, but it did not inhibit AliE in fatbody and hemolymph of the larvae. However, it was clear that fenitrooxon, the oxidized form of fenitrothion that has low activity against *S. litura* larvae, strongly inhibits AliE. These results indicate AliE would be involved in the species selective toxicity of TIA-230 (oxidized form) has low sensitivity to TIA-230. Therefore, we are investigating the binding affinity of TIA-230 to AliE or oxidase activity in the nerve system of insect pests showing lower activity for TIA-230.

On the other hand, the wide spectrum for insecticide of TIA-230 indicates many applications for use. So we investigated the control effect of TIA-230 wettable powder against insect pests for vegetables, especially cabbage, larvae of *P. rapae crucivora, P. xylostella, M. brassiase, S. litura, P. nigrisigna* and *Aphididae*. Those results indicated that TIA-230 had high control effects on all of tested pests except *P. nigrisigna* by spray 175 ppm and 350 ppm of TIA-230 solution twice in 10 days. This effect was the same as 500 ppm of Acephate wettable powder and 50 ppm of Dimethoate-fenvalerate emulsion concentrate and a little bit better than 500 ppm of Cartap 50% soluble powder.

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