N-メチルカーバメート抵抗性ツマグロヨコバイに対するN-メチル,N-プロピルカーバメート混剤の共力殺虫効果

誌名	日本農薬学会誌
ISSN	03851559
著者	高橋, 洋治 興村, 伸夫 山本, 出
巻/号	2巻4号
掲載ページ	p. 467-470
発行年月	1977年11月

J. Pesticide Sci. 2, 467–470 (1977)

Synergistic Insecticidal Action of *N*-Methyl- and *N*-Propylcarbamates to the Green Rice Leafhopper, *Nephotettix cincticeps*, Resistant to Aryl *N*-Methylcarbamates

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(Received July 15, 1977)

The green rice leafhoppers, *Nephotettix cincticeps* Uhler, not only cause direct damage by sucking rice plant juice at heading and ripening stages, but also transmit the agents of rice dwarf and rice yellow dwarf diseases. They had not been the major pest, but destruction of the natural predators at the time of chemical control of the rice stem borer has made them a most serious pest insect in Japanese paddy field. The seriousness is further accelerated by the development of resistance of the insect to all *N*–methylcarbamates which are now widely used. Conventional organophosphorus insecticides are also useless because the insect has been already selected by these insecticides and thus, resistant to them. Recently, we have found that aryl *N*–propylcarbamates, regardless of the ring substituents, were far better inhibitors than the corresponding *N*–methylcarbamates for the acetylcholinesterase (AChE) obtained from the resistant leafhopper.[1] However, the insecticidal activity of *N*–propylcarbamates was still far less than the activity we need to control the resistant insect in the field. This paper reports the finding of synergistic insecticidal action of *N*–methyl– and *N*–propylcarbamates, which reached to the level of practical control.

It was shown that the inhibition of the AChE by *N*–propylcarbamates was negatively correlated to the *N*–methylcarbamate-resistance level.[1] The relationship between the resistance level to *N*–methylcarbamates and the insecticidal activity shown by the *N*–propyl analogs of MIPC (2–isopropylphenyl *N*–methylcarbamate), BPMC (2–*sec*–butylphen yl *N*–methylcarbamate, MTMC (3–methylphenyl *N*–methylcarbamate), MPMC (3,4–dimethylphenyl *N*–methylcarbamate), XMC (3,5-dimethylphenyl *N*–methylcarbamate) and carbaryl is shown in Fig. 1. For convenience, *N*–propyl analog of MTMC is referred to as *N*–propyl-MTMC. The resistance level is indicated by LD_{50} value given by individual *N*–methylcarbamates. With the development of resistance level (S→RN–N→RN–4[1]), the individual *N*–propylcarbamate gave better or inferior insecticidal activity, but in general the insecticidal activity of *N*–propylcarbamates seems not so much affected by the development of the resistance. However, this level of LD_{50} is practically of no use.

Combination of *N*-methyl– and *N*–propylcarbamates gave a remarkable synergism in insecticidal activity. Figure 2 shows the result when MTMC is combined with the corresponding *N*-higher alkylcarbamates in 1 : 1 ratio. The 1 : 1 mixture of *N*–methyl– and *N*–propylcarbamates gave the highest synergism and insecticidal activity. Such synergism or potentiation was also found between other *N*–propylcarbamates and *N*–methylcarbamates. Table 1 shows the synergism between *N*–propyl-MTMC and eight different *N*–methylcarbamates. For RN–4 resistant strain, *N*–

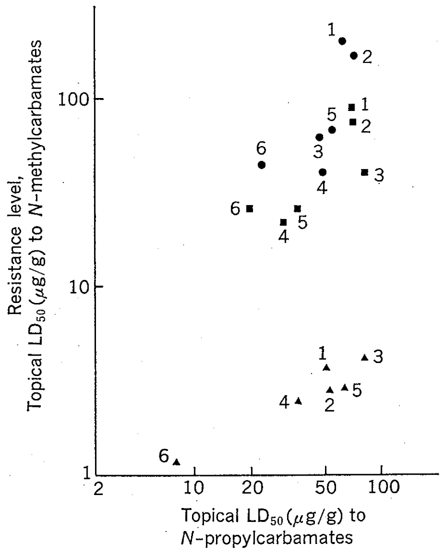

Fig. 1 Relationship between resistance level to *N*–methylcarbamates and insecticidal activity of *N*–propylcarbamates.
1, MIPC; 2, BPMC; 3, MTMC; 4, MPMC; 5, XMC; 6, carbaryl
▲ Susceptible (S), ■ Resistant (RN-N), ● More resistant (RN-4).

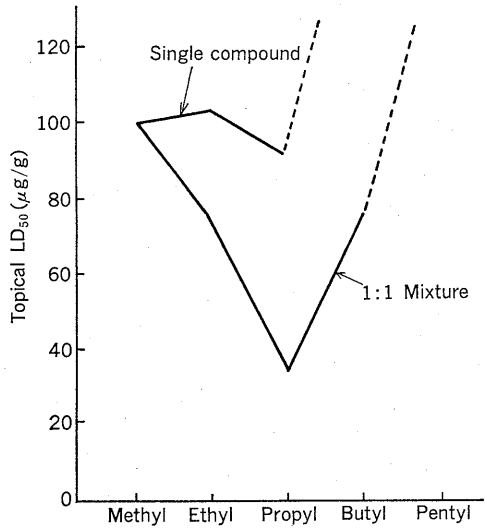

Fig. 2 Synergism in insecticidal activity between *N*–methyl–MTMC and *N*–higher alkyl–MTMC.
Dotted line was used because of unavailability of exact LD_{50} value.

Table 1 Insecticidal synergism between *N*–propyl–MTMC and *N*–methylcarbamates to resistant *N. cincticeps* (RN-4).

	Topical LD_{50} (μg/g)		
	Single compound	1 : 1 Mixture with *N*–propyl–MTMC	Co-toxicity coefficient
N–propyl–MTMC	50		
MTMC	61	19	2.9
MIPC	155	25	3.0
BPMC	148	18	4.2
Propoxur	200	28	2.8
CPMC	54	23	2.2
MPMC	41	19	2.4
XMC	66	22	2.6
carbaryl	44	19	2.4

methylcarbamates became far less effective and useless, LD_{50} being around 50 μg/g or over. *N*–Propyl-MTMC was also poor in insecticidal activity. However, the 1:1 mixtures gave LD_{50} around 20 μg/g by synergism which is indicated in the table by co-toxicity coefficient.[2] This level of insecticidal activity obtained by topical application is well correlated with the results obtained by a bell jar test and field dusting.[3]

Mechanism of the synergism was investigated. Jao and Casida[4] found a synergistic effect of *N*–propyl–carbaryl to synthetic pyrethroids. In this case, *N*–propyl-carbaryl has no insecticidal activity, but inhibits the hydrolytic detoxication of the pyrethroids, thus increasing the insecticidal activity. A small degree of synergism was reported by combining piperonyl butoxide with *N*–methylcarbamates, but there was no difference of the degree between susceptible and resistant strains of the green rice leafhopper.[5] Contribution of detoxication to the mechanism of resistance has not been established, but the degree of resistance can be explained by the great difference of I_{50} values between AChEs from resistant and susceptible strains. Increased activity of aliesterase and its increased sensitivity to *N*-methylcarbamates in the resistant strain is not involved for the higher I_{50} values for AChE from resistant strain.[1]

Table 2 Synergism between *N*-methyl and *N*-propylcarbamates for the inhibition of AChE from resistant *N. cincticeps* (RN-4).

Compound	I_{50} (M)	Co-toxicity coefficient
MTMC	3.3×10^{-4}	
BPMC	1.4×10^{-4}	
N-propyl-MTMC	3.1×10^{-5}	
N-propyl-BPMC	2.9×10^{-5}	
MTMC+*N*-propyl-MTMC*	2.3×10^{-5}	2.5
MTMC+*N*-propyl-BPMC*	2.9×10^{-5}	1.8
BPMC+*N*-propyl-MTMC*	1.6×10^{-5}	3.2
BPMC+*N*-propyl-BPMC*	1.9×10^{-5}	2.5

* Ratio (1 : 1, M/M)

The supernatant of 30,000 *g*, 10 min of the insect homogenate was used and AChE activity was measured by Ellman method.[6]

Synergism does occur at the level of I_{50} as shown in Table 2. For example, I_{50}(M) value was 3.3×10^{-4} for MTMC, while 1 : 1 mixture with its *N*-propyl compound was 2.3×10^{-5}, the co-toxicity coefficient[2] being 2.5. Synergism was observed not only between carbamates with the same aryl group, but also between the carbamates with the different aryl group.

A remarkable synergism was also found from the study of AChE inhibition on acrylamide disk electrophoresis,[6] as shown in Fig. 3. Inhibition by MTMC at 2×10^{-3} M level caused the change in quantity and pattern of the zymograph as compared with those of uninhibited AChE from the resistant strain, whereas *N*-propyl-MTMC at 2×10^{-4} M level did not show much inhibition. Combination of 10^{-3} M of MTMC and 10^{-4} M of *N*-propyl-MTMC gave a remarkable synergistic inhibition of the AChE.

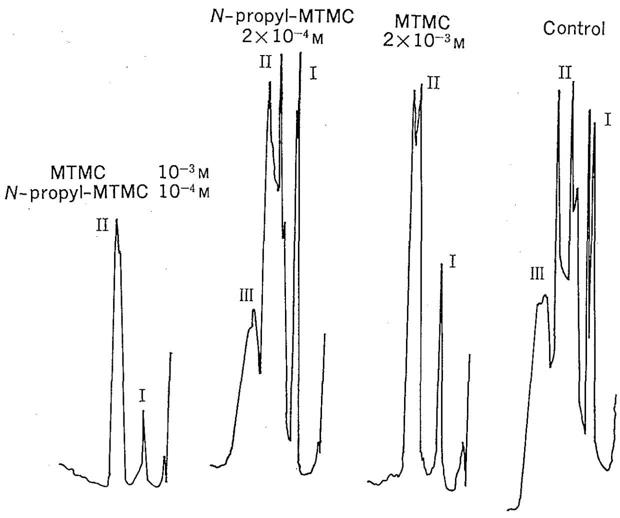

Fig. 3 Electrozymograms of AChE of resistant *N. cincticeps* (RN-4) inhibited by *N*-methyl- and *N*-propylcarbamates, and by the mixture.

Two grams of *N. cincticeps* bodies were homogenized in 20 ml of phosphate buffer (0.02 M, pH 7.4) containing 5% Triton X-100, and thereafter, the homogenate was ultrasonicated (20 kHz, 10 min). The supernatant of 100,000 *g*×60 min of the homogenate was used as the enzyme source. The location of the enzyme was detected by staining the gel by the procedure of Karnovsky and Roots.[7]

ACKNOWLEDGEMENT

The authors wish to thank Dr. H. Yamashina, Dr. K. Wakabayashi and Mr. N. Nakamura, Mitsubishi Chemical Ind. Ltd., for their valuable suggestions during the course of this study.

要　約

Aryl *N*-propylcarbamates が *N*-methylcarbamates 抵抗性ツマグロヨコバイのアセチルコリンエステラーゼ (AChE) を感受性のそれより強く阻害することから殺虫力を検討したが実際の防除に役立つほどの効果はなかった．しかし *N*-methylcarbamate と *N*-propylcarbamate との 1：1 混合物は抵抗性ツマグロヨコバイに対し著しい殺虫効果を示し，実用防除に役立つ程度に達した．この共力効果はベンゼン環上の置換基の種類に関係なく認められ，AChE 阻害の I_{50} 値のレベル，またディスク電気泳動で観察される AChE レベルにおいても認められた．

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