The insecticidal activity and the vapor pressure of the pyrethroids containing acyclic alcohol moieties

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Abstract: Twenty kinds of 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane-carboxylic acid esters of acyclic alcohols were synthesized, and their insecticidal activities against houseflies were investigated by three bioassay methods; a topical application, a filter paper contact and a volatile effect test method. Among the α -ethynyl alcohol esters, (*E*)-1-ethynyl-2-methyl-2-pentenyl ester possessed the highest activity by a volatile effect test method. The insecticidal activities of α -cyano alcohol esters were lower than those of corresponding α -ethynyl esters. The insecticidal activities of the other types of esters were low. From these results, α -ethynyl-2-methyl-2-pentenol was selected as an alcoholic moiety, and the insecticidal activities of 4 kinds of esters containing different acidic moieties were investigated. Among these esters, chrysanthemate showed the highest efficacy by the volatile effect test method. This compound was selected as a unique pyrethroid possessing high volatile effect, and is now promised to be developed.

Since the chemical structures of natural pyrethrins were elucidated by LaForge and Haller (1936), a number of studies on analogues of chrysanthemic acid esters have been conducted. Most of these pyrethroidal compounds possess the aromatics in the alcoholic moieties. As for the esters of acyclic alcohol, *trans*-2,5-hexadien-1-yl chrysanthemate (Sota *et al.*, 1973), 1-ethynyl-2-methyl-2-hexen-5-yn-1-yl 3-(2,2-dichlorovinyl) 2,2-dimethylcyclopropane-1-carboxylate (Hirano *et al.*, 1978) and (*E*)-1-ethynyl-2-methylpent-2-enyl (1*RS*)-*cis*, *trans*-chrysanthemate

(Matsuo *et al.*, 1980) were only reported. Though these pyrethroids showed high knock-down and lethal activities by a contact method such as a topical application or a direct spray, it has not been reported the volatile effect to target insects at room temperature.

We gave a specific attention to the high volatile effect of the pyrethroids with acyclic alcohol moieties against houseflies. This paper describes the lethal and knockdown activities and the vapor pressure of the new pyrethroids containing acyclic alcohol moieties.

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MATERIALS AND METHODS

1. Test insects

Houseflies, *Musca domestica* (CSMA strain) were reared in our laboratory at $27 \pm 1^\circ\text{C}$ and $60 \pm 5\%$ in relative humidity.

by Jensen and Schall (1966).

RESULTS AND DISCUSSION

Among the esters containing α -ethynyl alcohol moieties submitted to the experiments, compound 8 showed the highest lethal

activity by a topical application method as shown in Table 1, and the activity was comparable to that of permethrin (Hirano *et al.*, 1978). Although the lethal activity of compound 6 whose R was 1-methyl-1-butenyl by a topical application was about one sixth of the compound 8, the insecticidal

Table 2 Insecticidal activity of α -cyano alcohol esters of 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid against houseflies

Compound No.	Chemical structure R ₁	Vapor effect (50 mg/m ²)		Filter paper contact LC ₅₀ (ppm)
		KT ₅₀ (min)	% Mortality	
9	CH ₃ CH ₂ CH ₂ CH=CH—	> 120	0	81
10	$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{CH}_3\text{CH}_2\text{CH}=\text{C}— \end{array}$	> 120	100	16
11	$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{CH}_3\text{CH}_2\text{CH}=\text{C}— \end{array}$	> 120	0	55
12	CH ₃ CH ₂ CH=CHCH=CH—	> 120	0	200

Table 3 Insecticidal activity of the other 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid esters with acyclic type alcoholic moieties against houseflies

Compound No.	Chemical structure R ₂	Vapor effect (50 mg/m ²)		Filter paper contact LC ₅₀ (ppm)
		KT ₅₀ (min)	% Mortality	
13	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \text{CH}_2=\text{CH} \end{array} \text{CH}—$	> 120	0	200
14	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \\ \text{CH}_2=\text{CH} \end{array} \text{CH}—$	> 120	5	> 500
15	$\begin{array}{c} (\text{CH}_3)_2\text{C}=\text{CH} \\ \text{CH}_3 \end{array} \text{CH}—$	> 120	0	> 500
16	$\begin{array}{c} \text{CH}_2=\text{CHCH}_2 \\ \text{CH}_2=\text{CHCH}_2 \end{array} \text{CH}—$	> 120	3	> 500
17	$\begin{array}{c} \text{CH}_2=\text{CH}(\text{CH}_3)\text{CH} \\ \text{CH}_2=\text{CH}(\text{CH}_3)\text{CH} \end{array} \text{CH}—$	> 120	0	> 500
18	$\begin{array}{c} \text{CH}_3\text{C}\equiv\text{C} \\ \text{CH}_3\text{C}\equiv\text{C} \end{array} \text{CH}—$	> 120	98	6.8

Table 4 Insecticidal activity of (*E*)-1-substituted-2-methyl-2-pentenyl 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylates

Compound No.	Chemical structure R ₃	Topical application LD ₅₀ (μg/female)	Vapor effect (50 mg/m ²)		Filter paper contact LC ₅₀ (ppm)
			KT ₅₀ (min)	% Mortality	
6	HC≡C—	0.17	24	100	1.5
19	CH ₃ —C≡C—	0.21	83	100	6.8
20	CH ₃ —CH ₂ —C≡C—	1.4	>120	3	58
10	N≡C—	0.34	120	100	16

Fig. 3 Relationship between the chemical structures of candidate pyrethroids with acyclic alcohols and the efficacy against houseflies

Figures under the chemical structures mean KT₅₀ value (min) and % mortality by a volatile effect test method. R shows 2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropyl group.

activity by a filter paper contact method was about half. Moreover, the knockdown activity of the compound 6 by a volatile effect test was higher than that of the compound 8. The compound 5 whose R was ethynyl possessed low lethal activity by a topical application method, but this compound showed higher activity by a volatile effect test method than the compound 8. The said results seem as follows. The insecticidal activity by a topical application method is due to contact toxicity only, but the activity by a filter paper contact test method is due to not only contact toxicity but also volatile effect. Namely, compounds 5 and 6 seemed to possess higher vapor pressure than the compound 8. The activities of the other compounds were not so high as those of the compounds 5, 6 and 8.

Among the α -cyano alcohol esters, the compound 10 whose R₁ was identical to that of the compound 6 showed the insecticidal activity by a volatile effect test, and this compound showed the highest activity among the α -cyano esters by a filter paper

contact method as shown in Table 2. The efficacy of this compound was inferior to that of the compound 6. Although among the other pyrethroidal esters containing acyclic alcohol moieties compound 18 showed a lethal activity by a volatile effect test as shown in Table 3, the activities of the other compounds were low.

As the influence of R₃ on the activity was examined, the efficacy of ethynyl moiety was highest among four compounds tested by all of the bioassay methods adopted in this paper as shown in Table 4. The order of activity was as follows: ethynyl > 1-propynyl > cyano > 1-butynyl.

The relationship between the chemical structures and the activity by a volatile effect test was summarized in Fig. 3. From this result, α -ethynyl-2-methyl-2-pentenol was selected as the most efficient alcoholic moiety. The insecticidal activities and the vapor pressure of the 4 kinds of pyrethroidal esters having this alcoholic moiety were shown in Table 5. Although the lethal activity of 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopro-

Table 5 Insecticidal activity against houseflies and the vapor pressure of (*E*)-4-methyl-4-hepten-1-yn-3-yl esters

Compound No.	Chemical structure R ₄	Topical application LD ₅₀ (μ g/female)	Vapor effect (50 mg/m ²)		Vapor pressure at 25°C (mm Hg)
			KT ₅₀ (min)	% Mortality	
21	(1 <i>R</i>)- <i>cis, trans</i> 2 : 8	0.25	14	100	1.1×10^{-3}
6	(1 <i>RS</i>)- <i>cis,trans</i> 4 : 6	0.17	24	100	3.1×10^{-4}
22		0.80	43	52	4.6×10^{-3}
23		0.55	>120	0	1.5×10^{-4}
Allethrin	(1 <i>R</i>)- <i>cis, trans</i> 2 : 8	0.25	>120	3	7.6×10^{-5}
Phenothrin	(1 <i>R</i>)- <i>cis, trans</i> 2 : 8	0.022	>120	0	1.9×10^{-6}

panecarboxylic acid ester (compound 6) by a topical application method was highest, chrysanthemic acid ester (compound 21) showed the highest activity by a volatile effect test method. The order of the activity by this method was as follows; chrysanthemic acid (compound 21) > 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid (compound 6) > 2,2,3,3-tetramethylcyclopropanecarboxylic acid (compound 22) > 2-(4-chlorophenyl) isovaleric acid (compound 23). The vapor pressure of these chemicals depended on the molecular weight. The chrysanthemic acid ester (compound 21) showed the highest efficacy by a volatile effect test method because of not only proper contact toxicity but also its higher vapor pressure than those of the other compounds having the same alcohol moiety. The efficacy of this compound by this experiment was superior to those of (+)-*cis*, *trans*-allethrin and (+)-*cis*, *trans*-phenothrin.

From these results, compound 21 was selected as a promising pyrethroid possessing high volatile effect. This compound is now promised to be developed.

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摘 要

鎖状アルコールを有するピレスロイドの殺虫活性と蒸気圧

鎖状アルコールを有するピレスロイド系化合物のイエバエに対する殺虫活性を、局所施用法、濾紙接触法および蒸散法により検討した。

その結果、1-エチニル-2-メチル-2-ペンテニルアルコールのエステルが蒸散法で最高の活性を示した。そこで本アルコールを選択し、4種のカルボン酸とのエステルの殺虫活性と蒸気圧について検討した。局所施用法では3-(2,2-ジクロロビニル)-2,2-ジメチルシクロプロパンカルボン酸エステルの最も高い致死活性を示したが、蒸散試験では菊酸エステルの最も優れていた。本化合物は高い蒸散効果を有する独特な新しい型のピレスロイドとして開発が期待されている。