クロロメタンスルホンアミドのワタおよびミカン葉中の濃度とニセナミハダニおよびミカンハダニに対する殺ダニ活性との関係

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Original Article

Residual Concentration-Acaricidal Activity Relationship of Chloromethanesulfonamide in Cotton and Orange Leaves against Carmine Mites and Citrus Red Mites*

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A concentration-acaricidal activity relationship of chloromethanesulfonamide (CMSA) against the carmine mite, *Tetranychus cinnabarinus* BOISDUVAL was examined by dipping cotton plant roots into CMSA solution. A relationship between CMSA concentration on/in the leaves and the acaricidal activity against the citrus red mite, *Panonychus citri* MCGREGOR, was also examined by foliar spray to mandarin orange trees. CMSA concentration in cotton leaves reached a peak 3 days after treatment and remained the same level thereafter. The acaricidal activity against the carmine mite increased gradually with time. By foliar spray CMSA concentration on/in the leaves declined rapidly as time elapsed, and so did the acaricidal activity. CMSA concentration in washed citrus leaves was at its highest 24 hr after spraying. The acaricidal activity of CMSA against the citrus red mite was parallel to its concentration in the citrus leaves.

INTRODUCTION

The authors previously reported[1] that chloromethanesulfonamide (CMSA) has a systemic acaricidal action when applied to mandarin orange trees by painting or through soil treatment, and that adult females of citrus red mites, *Panonychus citri* MCGREGOR, are killed when they suck plant juice containing CMSA.

Fukuda & Koremura[2] analyzed the residual amount of the insecticides in cowpea plants, whose seeds had been soaked in 0.1% phorate or disulfoton solution, or dressed with 0.1% phorate dust. Most part of the chemicals in the cowpea plants disappear 7 days after treatment. Phorate concentration reaches 1 ppm 13 days after treatment, and so does disulfoton concentration. Their toxicity against the green peach aphid, *Myzus persicae* SULZER is observed up to 20 days after treatment, but there is no effect after 30 days. Halberstadt[3] reported that the concentration of tetradifon absorbed into the leaves of apple tree reaches a peak one day after spraying and the chemical remains in the leaves for over one month. It is, therefore, important to clarify the nature of the systemic action of CMSA.

This paper reports the results of our study on relationships between concentrations of CMSA translocated in plants and its acaricidal activity.

MATERIALS AND METHODS

1. Materials

1.1 Chemical

Chloromethanesulfonamide (96%) was synthesized in our chemical institute as described previously[1] and its 80% wettable powder was formulated from the technical material.

1.2 Mites

Carmine mites, *Tetranychus cinnabarinus* BOISDUVAL, and citrus red mites, *Panonychus*

* Acaricidal Activity of Chloromethanesulfonamide against Phytophagous Mites (Part 3). For Part 2, see Ref. 6).

citri McGregor, used in this study were the same strains as reported previously.[1)]

1.3 Crops

Cotton: Species Acala SJ-1 provided by the College of Agriculture of the University of Arizona, U.S.A. Mandarin orange tree: 2 years old, cultivated in pots.

1.4 Reagent and apparatus for analysis

Organic solvents: reagents for pesticide residue analysis, Wako Pure Chemical, Ltd. Silica: silicic acid, 100 to 200 mesh, Mallinkrodt. Celite 545: John Malnville Sales Crop. Anhydrous sodium sulfate: guaranteed reagents, Nihon Rikagaku Yakuhin Co., Ltd.

Gas chromatograph and its operating condition: A Shimadzu 5A instrument equipped with a flame photric detector (S filter 394 nm) was used. Column: spiral glass tube (3 mm i.d. and 150 cm long) containing 60 to 80 mesh Gaschrom Q coated with 3% Polyethylene glycol 20M (PEG 20M). Temperature: column oven 185°C, detector 260°C and injection port 240°C. Gas flow rate: nitrogen 60 ml/min as carrier gas, hydrogen 40 ml/min and air 40 ml/min.

2. Methods of Bioassay

2.1 Acaricidal activity by root-dipping

Cotton seeds were sown in a nursery in a greenhouse. After cultivation, the plants were pulled out when they had 12 leaves, and their root portions were washed with water. The roots were then put in 300 ml flasks containing 200 ml of CMSA solution of different concentrations. The plants were supported with absorbent cotton. About 100 ml of water was added to the flasks 5 days after the roots were put into the solution. Twenty-four hours after treatment, adult females of carmine mites were transferred onto the surface of the cotton leaves with a small brush. At intervals of 1, 3, 5, 7 and 9 days thereafter, the number of mites dead or alive was counted and mortality was calculated on the basis of the number of mites immediately after transferring. Average temperature during the experiment was 21.5°C. CMSA concentration in the leaves was examined at different times by an analytical method using gas chromatography as described later.

2.2 Acaricidal activity by spraying

Thirty milliliters of solution diluted to different concentrations was sprayed with a spray gun on a 2-year-old mandarin orange tree planted in a 9-cm diameter pot. At intervals of 3, 24 and 72 hr after spraying, six leaves from each pot were picked. Three of them were washed carefully with water so as to remove any CMSA adhering to the surface and the rest was left unwashed. The leaves were placed on 0.4% agar in a 9-cm diameter petri dish.[4)] Adult females of citrus red mites were then transferred onto the upper surface of the leaves with a small brush. The mites were kept at a constant temperature of 25°C and mortality was recorded 48 hr after treatment. The mortality was corrected by Abott's formula.[5)] CMSA concentration remaining on/in washed and unwashed leaves was determined by gas chromatography as described later.

3. Analytical method of CMSA in/on mandarin orange or cotton leaves

Ten grams of fresh leaves of cotton or mandarin orange samples were homogenized with 200 ml of a solvent mixture of distilled water and acetone (1: 3, v/v) for 3 min. The acetone and water extract was separated by filtration and the residue was rinsed twice with 50 ml of acetone and filtrated. The filtrates were combined and acetone was evaporated under reduced pressure at 45°C (evaporation of organic solvents was performed under reduced pressure, hereinafter) and the residual water was extracted twice with 50 ml of ethyl acetate. After dehydration with anhydrous sodium sulphate, ethyl acetate was evaporated. The residue was dissolved in 5 ml of a solvent mixture of *n*-hexane and acetone (3: 1, v/v) and transferred to the top of silica column bed prepared by packing 15 g of a mixture of silicic acid and celite 545 (2: 1, w/w) into the chromatographic tube (20 mm i.d., 40 cm long) using the same solvent mixture as a solvent. The elution with the same solvent mixture as above was followed. The first 50 ml of the eluate was discarded and the next 100 ml of the eluate was collected. The solvent was evaporated and the residue was dissolved in acetone to attain a fixed volume over 1 to 5 ml (A ml). Then suitable aliquotes of the solution between 1 to 5 μl (B μl) were taken in a microsyringe and injected into the gas chromatograph described

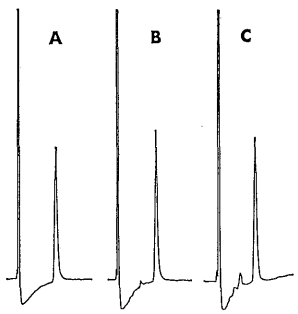

Fig. 1 Gas chromatograms of chloromethanesulfonamide (CMSA) standard on mandarin orange and cotton leaf extracts.

A: CMSA (2.0 ng), B: Mandarin orange leaves, C: Cotton leaves.

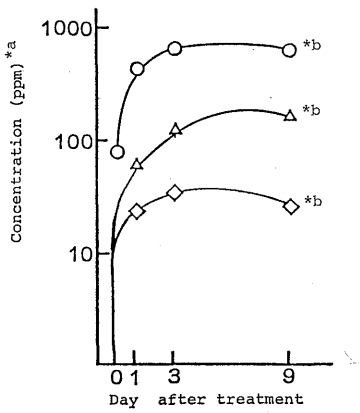

Fig. 2 Concentration of chloromethanesulfonamide (CMSA) in cotton leaves.

*a: Logarithum scale, *b: Concentration of CMSA diluted with water at the test starting, ○: 400 ppm, △: 100 ppm, ◇: 25 ppm.

above. The peak height of CMSA was measured and converted to the amount of injected CMSA (C ng) by using a standard calibration curb. CMSA concentration (R ppm) in the mandarin orange or cotton sample was calculated according to the following formula:

$$R = A \times C / B \times 10$$

The gas chromatograms of CMSA standard on mandarin orange and cotton leaf extracts are shown in Fig. 1.

RESULTS

Figure 2 shows CMSA concentration in cotton leaves after root application, and Fig. 3 the

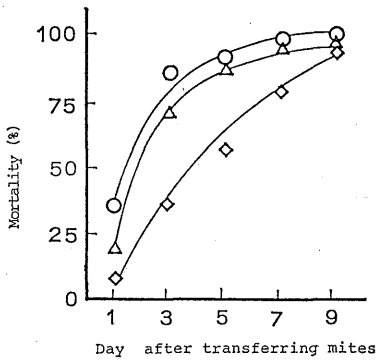

Fig. 3 Relationship between the time elapsed and mortality of carmine mites.

○: 400 ppm*, △: 100 ppm, ◇: 25 ppm. * Concentration of chloromethanesulfonamide diluted with water at the test starting.

acaricidal activity against adult female carmine mites after treatment. The acaricidal activity increased with time.

Table 1 shows the concentration-acaricidal activity relationship of CMSA against adult females of citrus red mites in mandarin orange leaves 3, 24 and 72 hr after treatment, and Table 2 their LC_{50} values. In mandarin orange leaves washed with water, CMSA concentration reached a peak 24 hr after treatment and decreased thereafter. As CMSA concentration in/on unwashed decreased with time, the mortality of citrus red mites lowered.

DISCUSSION

When carmine mites were transferred onto cotton plants whose roots were in CMSA solutions of different concentrations, their mortality ranged from 97% to 100% up to 9 days after transferring. This high mortality suggests that CMSA is accumulated in the mite body and amounts to a lethal dose when the mites are continuously exposed to CMSA integrated in the leaves. By foliar spray, CMSA concentration remaining in the citrus leaves reached a peak about 24 hr after spraying. Our experiment suggested that the changes of CMSA concentration in the citrus leaves were linked to the changes of the acaricidal activity.

The acaricidal activity of CMSA was lowest on washed leaves 3 hr after spraying and highest after 24 hr. CMSA concentration in/on

Table 1 Relationships between chloromethanesulfonamide (CMSA) concentration in/on citrus leaves and mortality of adult female citrus red mites.[a)]

Time after treatment (hr)	CMSA concentration[b)] (ppm)	CMSA concentration[c)] (ppm)	Mortality on washed leaves: Number of mites	Mortality (%)	Corrected mortality (%)	CMSA concentration[c)] (ppm)	Mortality on unwashed leaves: Number of mites	Mortality (%)	Corrected mortality (%)
3	1600					557	110	100	100
	800	17	140	10.7	5.2	296	126	99.2	99.2
	400	1.7	137	5.7	0	120	83	65.1	63.0
	200	0.8	142	4.9	0	96	147	57.1	54.5
	100	0.6	117	4.3	0	38	142	36.6	32.7
	non-treatment	—	173	5.8	—	—	173	5.8	—
24	1600	133	133	94.7	93.8	259	131	99.2	99.1
	800	37.2	118	88.1	87.4	107	124	86.8	86.0
	400	15.7	109	32.9	28.8	42	152	42.1	38.5
	200	7.5	154	16.2	11.0	14.6	151	24.5	19.9
	non-treatment	—	155	6.4	—	—	155	6.4	—
72	1600	25.9	120	41.7	38.1	36.1	127	68.5	66.1
	800	9.4	140	27.9	22.4	14.2	135	23.5	17.9
	400	1.1	170	18.2	11.9	2.7	155	11.6	4.8
	non-treatment	—	156	5.8	—	—	156	5.8	—

a) Mortality was recorded 48 hr after citrus red mites were inoculated to leaves.
b) Applied concentration.
c) Analyzed concentration in/on citrus leaves.

Table 2 Comparison of LC_{50} values of chloromethanesulfonamide against adult female citrus red mites transferred on the leaf surface washed or unwashed.

Time after treatment (hr)	LC_{50} value on the washed leaf surface: Regression curve	LC_{50} (ppm)	Pr	LC_{50} value on the unwashed leaf surface: Regression curve	LC_{50} (ppm)	Pr
3		>17		$Y=5+4.33\ (X-1.97)$	93.3	<0.01
24	$Y=5+2.57\ (X-1.34)$	21.9	<0.01	$Y=5+2.36\ (X-1.63)$	42.6	<0.01
72		34[a)]		$Y=5+1.77\ (X-1.44)$	27.7	<0.01

a) Value calculated by the diagram method.

unwashed citrus leaves declined rapidly with time after foliar spraying, reaching almost the same level of concentration remaining in leaves whose surfaces were washed 72 hr after spraying. CMSA remaining on the leaf surface may disappear by evaporation and photodecomposition. Our experiment showed that CMSA concentration on/in the leaves was roughly parallel to the acaricidal activity. In comparison of LC_{50} values at 24 hr after spraying, the LC_{50} values on washed leaves were lower than those on unwashed leaves. This suggests that citrus red mites ingest CMSA deposited on the leaf surface.

It is reported that CMSA would show a stronger acaricidal action against mites when taken orally than by body contact.[6)] In other words, it is likely that mites ingest CMSA in leaves much more than that on leaves.

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要　　約

クロロメタンスルホンアミドのワタおよびミカン葉中の濃度とニセナミハダニおよびミカンハダニに対する殺ダニ活性との関係*

小川温樹，嶋津朋徳，大石利治

ワタの根部から吸収させたクロロメタンスルホンアミド（以下 CMSA と略す）の葉中濃度とニセナミハダニ雌成虫に対する殺虫力の関係を経時的に追跡すると，葉中濃度は処理3日後から5日後に最高に達し，その後減少傾向を示し，ニセナミハダニに対する殺虫力は9日間連続し追跡すると経時的に強くなった．ミカン苗木に CMSA を散布後葉面を水洗し，葉中への移行濃度を調べると散布24時間後に最も高く，72時間後では減少していた．また葉表を水洗せずそのまま葉体濃度を追跡すると，時間の経過とともに減少した．同時に，ミカンハダニ雌成虫に対する所定時間後の殺虫率は，これらの濃度と平行して変動した．散布24時間後において，葉面を水洗した場合の葉中濃度と水洗しなかった場合の葉体濃度における殺虫力は，前者が後者より低薬量で高い殺虫力を示した．

* クロロメタンスルホンアミドのハダニ類に対する活性（第3報）