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Residual Fate of Chlorphenamidine in Rice Plant and Paddy Soil

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Chlorphenamidine [*N'*-(4-chloro-*o*-tolyl)-*N*,*N*-dimethylformamidine] is a broad spectrum insecticide which is effective for all stages of insects and mites including eggs and adults. Chlorphenamidine hydrochloride has been used for the control of the rice stem borer in Japan.

The major metabolites by plants are *N'*-(4-chloro-*o*-tolyl)-*N*-methylformamidine (desmethyl chlorphenamidine), *N*-formyl-4-chloro-*o*-toluidine and 4-chloro-*o*-toluidine (GUPTA and KNOWLES 1969, KNOWLES 1970, EHRHARDT and KNOWLES 1970).

This report describes residual fate of chlorphenamidine in rice plant and paddy soil. Chlorphenamidine hydrochloride was applied as a granule on rice plant, and residues of chlorphenamidine, desmethyl chlorphenamidine, *N*-formyl-4-chloro-*o*-toluidine and 4-chloro-*o*-toluidine in rice grains, straws and soil were determined.

MATERIALS and METHODS

Chemicals Chlorphenamidine hydrochloride and 4-chloro-*o*-toluidine hydrochloride were supplied from Nihon-Noyaku Industries Co.,Ltd., Tokyo Japan. *N'*-(4-chloro-*o*-tolyl)-*N*-methylformamidine and *N*-formyl-4-chloro-*o*-toluidine were supplied from Laboratory of Insect Toxicology, The Institute of Physical and Chemical Research, Wakoshi, Saitama, Japan. Purities of these compounds were more than 99% (MORIKAWA et al. 1975). 3% Chlorphenamidine hydrochloride granules used for field test were obtained from Nihon-Noyaku Industries Co.,Ltd.

Preparation of rice plant and soil 20-day-old rice seedlings, variety Reihō, were transplanted to paddy field on 20 June and grown free from any insecticide. Paddy fields were divided into four plots of 60 sq.m each by surrounding with vinyl fence. First plot was treated with 240g (7.2g a.i.) granules of chlorphenamidine hydrochloride on 29 September, Second plot with the same dosage on 16 and 29 September, Third plot on 31 August, 16 and 29 September, and Plot 0 was untreated. Rice plants were harvested 42 days after the last treatment. Rice grains were powdered and passed through 100-mesh sieve, and straws were finely chopped by means of cutter after being air-dried. Paddy soils were also sampled at harvest

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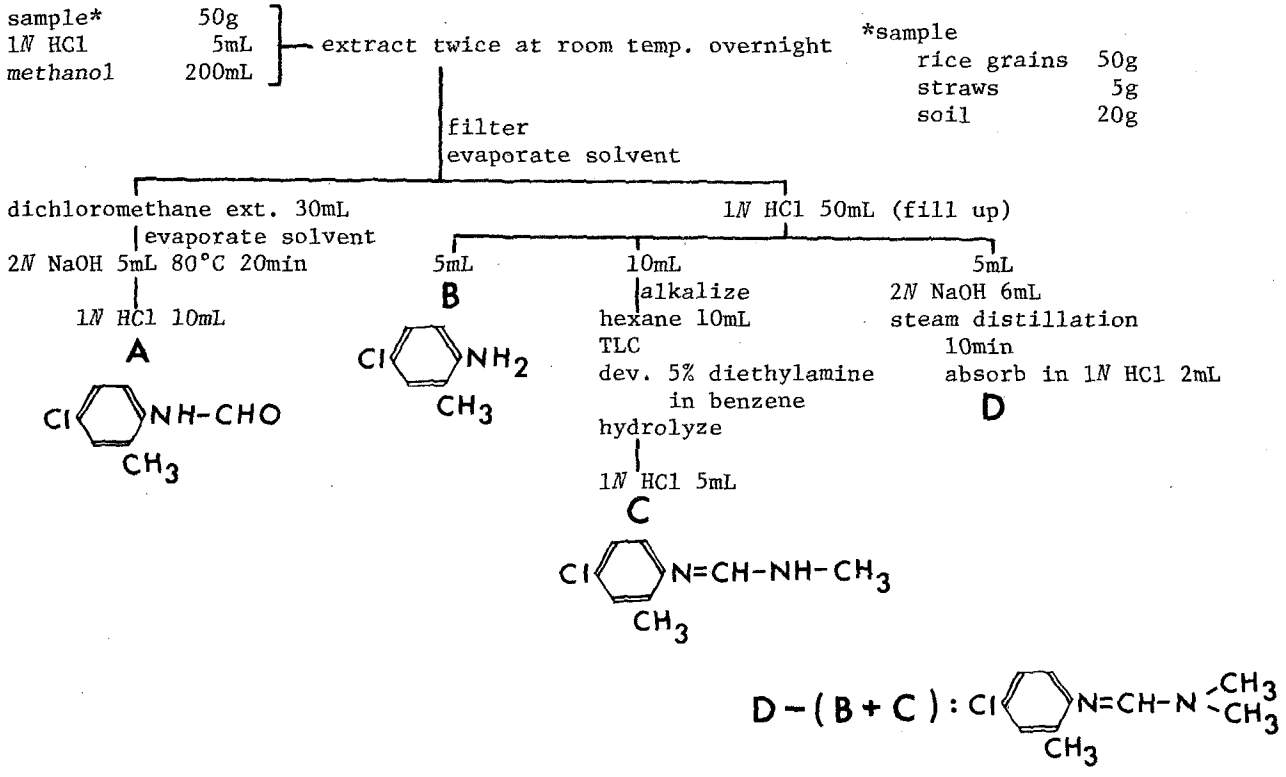

Fig. 1 Scheme of Analytical Procedure for Chlorphenamidine and Its Degradation Products

and separated into two portions : one was from surface to 5cm depth and the other was from 5 to 10cm depth. They were also air dried prior to analysis. Texture of paddy soil was as follows: coarse sand 7.5%, fine sand 22.4%, silt 42.0%, clay 28.1% and organic matter 3.47% (SEINO et al. 1971), pH 6.1.

Analytical procedure Determination of chlorphenamidine, desmethyl chlorphenamidine, *N*-formyl-4-chloro-*o*-toluidine and 4-chloro-*o*-toluidine were conducted according to the procedure reported by KOSSMANN et al.(1971) and GEISSBUHLER et al.(1971). Scheme of cleanup method is shown in Fig. 1.

Diazotization and iodination : After cleanup 1*N* HCl solutions, which contained chlorphenamidine, desmethyl chlorphenamidine, *N*-formyl-4-chloro-*o*-toluidine and 4-chloro-*o*-toluidine, were transfered into 25mL stoppered tube, then diazotized with 1mL of 2% $NaNO_2$ at 0°C for 25 min. Excess nitrite was destroyed by adding 1mL of 20% sulfamic acid, and the diazotized solution was iodinated with 0.5mL of potassium iodide-iodine solution (1g I_2 in 20mL of 10 % KI) at 80°C for 20 min. Excess iodine was destroyed by adding about 0.1g of sodium sulfite powder, and then the solution become colorless. This solution was alkalized by adding 2mL of 6N NaOH, and extracted with 5mL of hexane. The hexane solution was dried with sodium sulfate, and used for gas chromatography.

Gas chromatography : ECD gas chromatograph Simadzu Model 4BM-PE was used for the determination of iodine derivative of 4-chloro-*o*-toluidine. The glass column, 1m x 3mm i.d. packed with 5% OV-17 on Gas Chrom Q 60-80 mesh. The temperature of the oven, inlet and detector : 150, 200 and 250°C, respectively. Carrier gas N_2 was 60mL per min. Standard solution was prepared by dissolving 4-chloro-*o*-toluidine hydrochloride in 1*N* HCl, and treated in the same way as the procedure described previously. The iodine derivative of 4-chloro-*o*-toluidine had a retention time of 3 min.

Residues of chlorphenamidine was calculated by subtracting the amount of 4-chloro-*o*-toluidine (B) and desmethyl chlorphenamidine (C) from that of total 4-chloro-*o*-toluidine (D).

The detection limit for chlorphenamidine and three degradation products in soil and plant were 0.1 ppb.

RESULTS and DISCUSSION

The results of analysis for chlorphenamidine, desmethyl chlorphenamidine, *N*-formyl-4-chloro-*o*-toluidine and 4-chloro-*o*-toluidine in rice grains and straws are shown in Table 1. As expected, the residues in straws were much higher than that in rice grains. The concentration of residues in straws decreased in the order of chlorphenamidine, 4-chloro-*o*-toluidine, *N*-formyl-4-chloro-*o*-toluidine and desmethyl chlorphenamidine, while that in rice grains decreased in the order of 4-chloro-*o*-toluidine, chlorphenamidine, *N*-formyl-4-chloro-*o*-toluidine and desmethyl chlorphenamidine.

TABLE 1

Residues of Chlorphenamidine and Three Degradation Products in Rice Grains and Straws

		chlorphenamidine	desmethyl chlorphenamidine	*N*-formyl-4-chloro-*o*-toluidine	4-chloro-*o*-toluidine
	No.	ppb	ppb	ppb	ppb
rice grains	0	4	0.2	12	3
	1	23	1	10	25
	2	48	0.4	15	53
	3	45	0.2	38	61
straws	0	260	10	67	80
	1	4000	58	260	1600
	2	9500	180	460	7200
	3	9700	180	500	6900

This results suggested that chlorphenamidine did not penetrate so easily into plant tissues. Although small amounts of chlorphenamidine penetrated into plant tissues underwent the degradation gradually, and the concentration of 4-chloro-*o*-toluidine surpassed that of the parent compound in rice grains, but the concentration of desmethyl chlorphenamidine was extremely low.

The analytical results with paddy soil are shown in table 2.

TABLE 2

Residues of Chlorphenamidine and Three Degradation Products in Soil

		chlorphenamidine	desmethyl chlorphenamidine	*N*-formyl 4-chloro-*o*-toluidine	4-chloro-*o*-toluidine
	No.	ppb	ppb	ppb	ppb
soil 0-5cm	0	35	15	8	2
	1	1100	5	380	9
	2	3400	6	270	34
	3	2900	9	190	68
soil 5-10cm	0	33	1	4	t
	1	65	1	4	1
	2	28	4	9	20
	3	150	1	8	20

In the soil, the residues of chlorphenamidine were very high level in upper layer of the soil (0-5cm), but that in the lower layer (5-10cm) was extremely low. Chlorphenamidine and its degradation products were tightly retained in the surface layer of paddy soil, and downward movement was minimal.

Percentage of residues of chlorphenamidine and its degradation products against total residues of these compounds in rice grains, straws and soil are shown in Fig. 2.

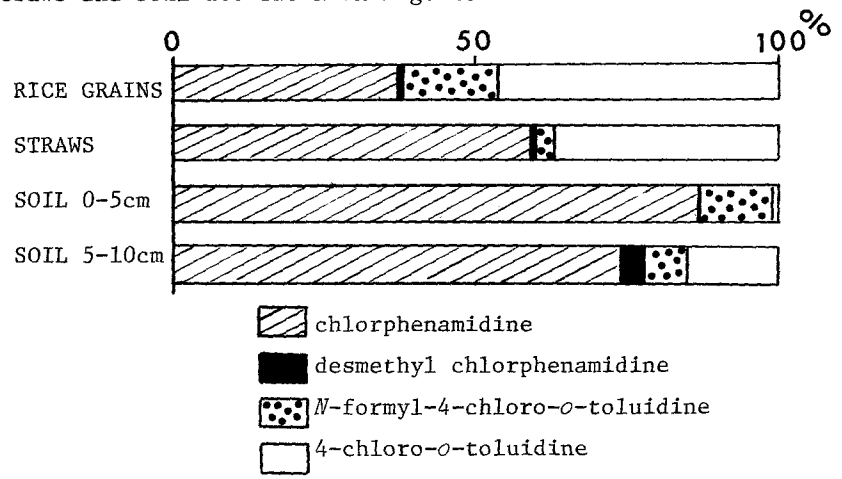

Fig. 2. Residue Pattern of Chlorphenamidine and Its Degradation Products in Rice Plant and Soil.

As shown in Fig. 2 residue pattern in the soil was quite different from that of rice grains or straws. Greater part of residue in soil was occupied by chlorphenamidine itself, and the production of degradation products was comparatively low. High concentration of 4-chloro-*o*-toluidine was found in rice plant, but that was negligible in the soil. Therefore this compound would be produced by biological degradation during the procedurs of translocation in rice plant.

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