Effect of Controlled Release Granule on Behavior of SSF-126 in Paddy Water, Paddy Soil and Rice Plant

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(Received June 4, 1996; Accepted January 13, 1997)

When the controlled release granule of SSF-126, (E)-2-methoxyimino-N-methyl-2-(2-phenoxyphenyl)acetamide, was applied to a paddy field, the increases of SSF-126 concentration in the paddy water, paddy soil and rice plants were slower in the earlier stage and the decreases in the later stage were also slower, as compared with those of the non-controlled release granule which was made by extrusion and generally used in Japan. The concentration of SSF-126 became relatively higher on about the 10th day in paddy water, on the 40th day in water at 5 cm deep in paddy soil, on the 72nd day in water at 10 cm deep in paddy soil and on the 20-35th day in rice plants after application than those of non-controlled release one. These results suggested that the SSF-126 concentration in rice plants could be controlled by formulation, and gave a hint that the higher residual activity against rice blast could be obtained by using the controlled release granules of SSF-126.

INTRODUCTION

Methoxyiminoacetamide derivatives are novel antifungal compounds which are being developed as agricultural fungicides.1, 2) Especially, SSF-126, (E)-2-methoxyimino-N-methyl-2-(2-phenoxyphenyl)acetamide, is one of the promising compounds with a broad spectrum and a new mode of action without cross resistance to any current fungicides.3, 4) We studied on the controlled release granule of SSF-126 in order to develop this compound as a rice blast controlling agent.

The controlled release granule (AE-5) showed 60% release of SSF-126 in altogether until the 7th day after application in a beaker compared with the non-controlled release granule (GN-1).5) AE-5 showed not only higher concentration of SSF-126 than GN-1 in paddy water from the 5th day after application but also higher preventive effect against rice blast from the 10th day after application in pot test.6) Therefore, the controlled release of SSF-126 was regarded as an easily available technology to keep more preventive effects for a long period.

From these findings, the effect of the controlled release granule on behavior of SSF-126 in paddy water, paddy soil and rice plants under field conditions is examined.

MATERIALS AND METHODS

1. Chemicals

The chemical structure of SSF-126 is shown in Fig. 1. It was synthesized at Aburahi Laboratories, Shionogi & Co., Ltd. (Shiga, Japan). The compound is colorless, crystalline powder with 99.93% purity and mean particle size of 43.1 μm. It dissolves at 128 mg/l in water at 20°C and easily dissolves in various organic solvents. The melting point is 86.5-87.0°C.

The activated carbon (type; powder) and ethylcellulose (grade; 100 cp.) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Bentonite (brand; Kunigel® VA) was obtained from Kunimine Industries Co., Ltd. (Tokyo, Japan). Kaolin clay (brand; HA Kaolin) was supplied by Sanyo Clay Industries (Okayama, Japan). Sodium lignosulfonate (brand; SanX® P-252) and sodium dodecylbenzenesul-
fonate (brand; Neopelex No. 6F) were purchased from Nippon Paper Industries (Tokyo, Japan) and Kao (Osaka, Japan), respectively. The other chemicals were purchased from Wako Pure Chemical Industries, Ltd.

2. Preparation of SSF-126 Granules

The compositions of the granules are shown in Table 1. After SSF-126 was mixed with powder components, the mixed powder was kneaded with water and extruded through a 0.8 mm screen, then dried as described before. After sieving at 16/32 mesh, the granules, AE-5 and GN-1, containing 6.0% of SSF-126 were obtained. The number of particles, bulk density and moisture content of both granules were 900-1100 particles/g, 1.06-1.08 and ca. 1.2%, respectively. GN-1 disintegrated at 20°C within 3 min after immersion into water, and AE-5 disintegrated after more than 30 min of immersion. Furthermore, AE-5 showed 60% release of SSF-126 in water until the 7th day after application in a beaker, compared with GN-1.

3. Application of SSF-126 Granules

SSF-126 granules were applied into the irrigation water of paddy field at a dose rate of 15.0 g/plot (5 m² = 2 x 2.5 m), equivalent to 3 kg/10 a, on June 25, 1993 in Aburahi Laboratories, Shionogi & Co., Ltd. Rice seedlings (cultivar; Koshihikari) were transplanted on May 10, 1993. The soil property of experimental field was clay soil (Sandy clay loam; Shiga, Japan), and the paddy water was kept between 1 and 5 cm deep. Atmospheric temperature, sunshine hours and rainfall from May to September in 1993 are shown in Table 2.

4. Behavior of SSF-126 Released from Granules in Paddy Water, Paddy Soil and Rice Plant

4.1 Extraction of SSF-126 from paddy water

After application, 100 ml of paddy water was collected periodically. SSF-126 was extracted from the paddy water with n-hexane. The solvent was evaporated and the residue was dissolved in acetonitrile. Then, 1.5 μl of the solution was applied to HPLC.

4.2 Extraction of SSF-126 from paddy soil water and paddy soil

Pipes of 4 cm inner diameter (made of polyvinylchloride and fitted with double nets of 100 mesh at the bottom) were inserted into the soil surface 5 and 10 cm deep. Then, the water in the pipe was collected periodically. SSF-126 in the soil water collected was extracted with n-hexane. The solvent was evaporated and the residue was dissolved in acetonitrile. Then, 1.5 μl of the solution was applied to HPLC. In addition, on the 100th day after application, the soil down to 10 cm deep under the surface was collected here and there by a soil sampling cylinder of 4 cm inner diameter. From those samples, the top layer of 1 cm deep was removed to avoid contamination from the residual granules. The remaining soil was divided into 2 parts of 1-5 and 5-10 cm deep, and SSF-126 in each soil was extracted with MeOH. Then, SSF-126 in MeOH was transferred to n-hexane and was applied to GLC under the conditions described below.

4.3 Extraction of SSF-126 from rice plant

After application, 10 shoots of the rice plants were collected periodically. The collected shoots were homogenized with MeOH and SSF-126 in MeOH was transferred to n-hexane. Then, the hexane phase was cleaned up by the Sep Pak® C18 column (Waters Ltd., MA, U.S.A.) to be applied to GLC.

5. Determination of SSF-126

The concentrations of SSF-126 in the samples above were determined by HPLC or GLC. In brief, the HPLC

Table 1 Composition of granules (w/w %).

<table>
<thead>
<tr>
<th>Component</th>
<th>AE-5</th>
<th>GN-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSF-126</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Bentonite</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Lignosulfonate a)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>DBS b)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Ethylcellulose</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Kaolin clay</td>
<td>51</td>
<td>61</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

a) Sodium salt.
b) Sodium dodecylbenzenesulfonate.
system was composed of equipments (a pump, LC-10A; a detector, SPD-10A; Shimadzu Co., Kyoto, Japan) and an ODS column (YMC-Pack ODS-A, 150×6.0 mm; YMC Co., Ltd., Kyoto, Japan). A mobile phase consisted of 50% acetonitrile in water (v/v) and SSF-126 was detected at 230 nm. The flow rate was 1.5 ml/min.

The GLC analysis was carried out with a Hewlett-Packard HP-5890 (a detector, NPD; Hewlett-Packard Co., Tokyo, Japan) and a capillary column (DB-5, 15 m×0.53 mm; J & W Sci., CA, U.S.A.). The injection and detector temperatures were 250 and 300°C, respectively. The column temperature was programmed; kept at 60°C for 1 min after injection, then the temperature was heightened for 8 min at the rate of 30°C/min and maintained at 300°C for 1 min. The flow rates of He (carrier gas), H₂ and air were 5, 3 and 100 ml/min, respectively.

RESULTS AND DISCUSSION

1. Behavior of SSF-126 Released from Granules in Paddy Water

The concentrations of SSF-126 in paddy water and rainfall after application are shown in Fig. 2. The concentration for respective granules showed the maximum value within 4 days after application and then decreased. A little fluctuation in the concentration obtained was found due to the climatic factors such as rainfall and so on. However, the values for AE-5 became relatively higher than those for GN-1 from 10 days after application. This tendency was very similar to AE-5 and GN-1 in pot test.⁶

2. Behavior of SSF-126 Released from Granules in Paddy Soil Water and Paddy Soil

The concentrations of SSF-126 in paddy soil water at 5 and 10 cm deep are shown in Fig. 3. The values for GN-1 at 5 cm deep increased rapidly towards the 7th day after application, and then almost the constant values were kept until the 65th day, and decreased later. The values for AE-5 at 5 cm deep increased rapidly towards the 14th day. After that, they increased slowly towards the 40th day and then, almost the constant values were also kept until the 65th day, and decreased later. The values for GN-1 at 5 cm deep were relatively higher than those for AE-5 until 40th day, but thereafter the values for AE-5 and GN-1 reversed.

In a case of 10 cm deep, the values for GN-1 increased rapidly towards the 10th day after application, and then increased slowly towards the 65th day, and decreased...
later. The values for AE-5 increased gradually until the 40th to 65th day, and then, decreased. The reversion in concentration between AE-5 and GN-1 appeared on about the 72nd day.

The reversion in concentration in paddy water happened earlier than in soil water. But, in the deeper soils, the transfer of SSF-126 occurred more slowly. As shown in Fig. 4, the time for reversion after application of SSF-126 was highly correlated to depth in paddy soil.

SSF-126 contents at 1–5 and 5–10 cm deep in soil at 100th day after application are shown in Table 3. The contents of SSF-126 in soils of both depth were higher for AE-5 and these results seem to correspond to the tendency shown in the soil water.

3. Behavior of SSF-126 Released from Granules in Rice Plant

The concentrations of SSF-126 in rice plants and atmospheric temperature are shown in Fig. 5. The concentration, though fluctuated to a certain extent, rapidly increased up towards the 30th day after application and then gradually decreased, for both granules. In addition, the values for AE-5 became higher than those for GN-1 20–35 days later.

The above fluctuation in concentration in rice plants was also influenced by the climatical conditions, especially, by the temperature and irradiation time by sunlight.

The time for reversion of the SSF-126 concentration in rice plants was the same as that in soil water at less than 5 cm deep (Fig. 4). This phenomenon can be explained by the fact that a large number of rice roots gathered close to the soil surface and those near the surface can be active to uptake nutrients and chemicals dissolved in water.

Thus, the differences in change of the concentration in paddy water, paddy soil and rice plants after applications of AE-5 and GN-1 seem to be clearly attributed to the different release rate of SSF-126 from the granules. Therefore, it was suggested that SSF-126 concentration in rice plants could be controlled in some levels by controlling the release rate of SSF-126 from granules. Furthermore, the results give a hint that the higher residual activity against rice blast can be obtained by the controlled release granules.

ACKNOWLEDGMENTS

We wish to express our thanks to Dr. Michio Masuko, Shionogi Aburahi Laboratories, for his many helpful suggestions during the study.

REFERENCES

要約
田面水、土壌および稲体中における SSF-126 の挙動に対する放出制御粒子の効果

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SSF-126, (E)-2-methoxyimino-N-methyl-2-(2-phenoxyphenyl)acetamide の放出制御粒子を水田に施用した場合、田面水、土壌および稲体中の SSF-126 の濃度推移は通常の粒剤（非放出粒子）に比べその立ち上がりが緩やかであるが、濃度の減衰速度も小さく、また、田面水、土壌、土壌および稲体のいずれにおいても時間的経過に伴って濃度の逆転、すなわち放出制御粒子区での濃度が通常の粒剤区より高くなった。逆転は、粒剤処理後田面水では约 10 日目、土壌深 5 cm 水で約 40 日目、土壌深 10 cm 水で約 72 日目、稲体で 20 ～ 35 日目であり、稲体での変化は土壌深 5 cm 以内の挙動を反映していると考えられた。以上の結果から、放出制御粒剤により稲体中の SSF-126 濃度が効果的に制御できることが示され、これにより、イネいもち病に対する SSF-126 の残効性を高めることが十分に期待された。

* SSF-126 の放出制御製剤に関する研究（第 3 報）