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Persistence of IBP and Isoprothiolane in Rice Plant

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水稻體중 IBP와 Isoprothiolane의 殘留消長

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Abstract

Effect of the application time on the persistence of IBP and isoprothiolane in rice plant was studied in the field and effects of the water depth and soil texture on their persistence were also tested as a pot experiment. When granules were applied to the rice paddy water, two fungicides were readily absorbed through the root system and rapidly translocated to the upper parts of the plant. The concentrations of two fungicides in rice plant reached to the maximum within 24 hr regardless of the application time. When applied at the maximum tillering stage, the persistence pattern of two fungicides in plant showed similar trends; that is, residue levels of two compounds declined rapidly upto 7 days after application but more slowly thereafter. When applied at the heading stage, the persistence pattern of IBP in plant was similar to the maximum tillering stage while isoprothilane was quite different; 3 ppm reached on 3rd days after application was maintained almost constant for further 25 days.

There was no effect of the water depth on the persistence of two compounds in plant and IBP concentration in plant was also not affected by soil texture. However, isoprothiolane in plant was higher in sandy loam than in loam and clay loam. Isoprothiolane residues in plant were much higher than those of IBP.

Introduction

Rice production in Korea has long suffered from blast disease caused by *Pyricularia oryzae.* Many kinds of fungicides are used to control this disease. Among them IBP and isoprothiolane are included in the most important fungicides using for this purpose.

IBP and isoprothiolane have similarities in the systemic nature and in the mode of action; when granules were applied to the rice paddy water, they were readily absorbed through the root system and rapidly translocated to the upper parts of the plant[1,2] and strains with higher resistance to IBP also have a cross resistance to isoprothiolane[3]. As shown in table

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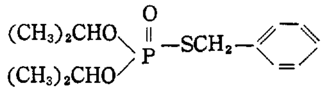
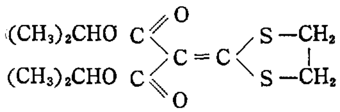
Table 1. Chemical structure and water solubility of IBP and isoprothiolane

Fungicide	Structure	Water solubility (ppm)	References
IBP		500 (at 18°C) 1,000 (at 18°C)	Yoshinaga[1] Eto[4]
Iso prothiolane		48 (at 20°C) 48 (at 20°C)	Tsumura[2] Thomson[5]

1, water solubility of isoprothiolane is very low as compared to that of IBP. Isoprothiolane does not contain a phosphorus atom but two fungicides have similarities in their structures. They have sulfur atom (s) in common but the sulfur atom in IBP is in thioester linkage and those in isoprothiolane are in thioether linkages. The sulfur atom(s) in two compounds might be important for their fungicide activity[6].

Because of some advantages that granules reduce drift, granules are easy to apply with accurate control of rate and placement, and they are also safer to applicators[7], Korean farmers have used more granular products than any other formulations. Weber and Weed[8] reported that pesticide performance was different from such soil properties as organic matter and texture. Adsorption decreased the rate of release of pesticide from soil and thereby decrease their biological activity and movement. There are some papers related to the uptake of IBP by the rice plant[9] and the persistence of isoprothiolane in rice plant[10]. Although the application time is very important for the effective control of rice blast, neverthless, it seems to be a little report related to the effects of the application time on the persistence of IBP and isoprothiolane.

This paper deals with the effect of the application time of IBP and isoprothiolane on their persistence in rice plant. Effects of water depth and soil texture on their persistence were also tested in the pot. These results will give some information for the effective control of rice blast.

Materials and Methods

Effect of application time

Fungicide application: IBP (O,O-diisopropyl S-benzyl phosphorothiolate) 17% and isoprothiolane(diisopropyl 1,3-dithiolane-2-ylidene malonate) 12% granules were applied evenly onto paddy water at the maximum tillering stage (July 14, 1979) and heading stage (Aug. 16, 1979) of rice plant (var. Milyang #23) at the rate of 6.8 and 4.8 kg AI/ha for IBP and isoprothiolane, respectively.

Soil used in this experiment was sandy loam with pH 6.2, organic matter content 1.76%, and CEC 11.6 8 me/100 g soil.

Plant samples for residue analysis were taken 1, 3, 7, 15, and 30 days after the application. All plant materials were chopped and stored in polyethylene bags at −20°C in freezer until extraction and analysis of fungicide residues.

Effect of texture and water depth

A pot experiment was carried out to study the effects of soil texture and water depth on the persistence of two fungicides in rice plant. A pot of 1/2000 a contraining 15 kg of each soil with 3 kinds of soil textures (sandy loam, loam, and clay loam) was submerged for 24 hr and maintained to 0, 2.5, and 5.0 cm surface water depth during the experimental period without drainage. The amount reduced by evaporation was watered occasionally. The soil used in the experiment had pH 6.2, 4.7, and 5.4 and organic matter content 0.33, 1.47, and 1.95% for sandy loam, loam, and clay loam, respectively. 3 seedlings of rice plant (var. Milyang #23) were transplanted to each pot on June 5, 1980. Two granular fungicides were applied on June 30, July 5, 10, and 15 to the surface water in each pot at the rate of 0.34 and 0.24 g AI/pot for IBP and isoprothiolane, respectively. All plant samples were taken on Aug. 5, 1980 and prepared for residue analysis.

Residue analysis

Isoprothiolane residues in plant were analyzed as described by Hattori and Kanauchi[11]. The plant sample prepared was homogenized with 150 ml of acetone-benzene mixture (1 : 1, V/V). The filtrate was evaporated to about 5 ml at 40°C under vacuum on a rotary flash evaporator. The concentrate was partitioned with 40 ml of acetonitrile, 80 ml of hexane, and 20 ml of saturated NaCl solution. After evaporating the hexane phases, the concentrate was cleaned up on a Florisil column (15 mm×34 cm) packed with a 20 g of Florisil (Floridin Co.) deactivated with 2% H_2O(W/W). Isoprothiolane residues were eluted with 80 ml of ethylacetate-hexane mixture (1 : 4, V/V).

The method of Mcleod et al.[1] was adopted for the analysis of IBP residues in plant. A 30 g sample of chopped rice plant was homogenized with 100 ml of acetonitrile and 30 ml of H_2O in Waring blender and filtered under vacuum. After evaporation, the filtrate was partitioned with 100 ml of hexane and 20 ml of saturated NaCl solution. Repeat with 50 ml of hexane and combine two organic layers. The hexane phase was cleaned up on a Florisil column (9 mm× 25 cm). Residues were percolated with 100 ml of hexane-petroleum ether mixture (85 : 15, V/V).

Gas chromatography

Isoprothiolane was determined on a Tracor Model 550 gas chromatograph equipped with a Ni^{63} electron capture detector. A 2 m long and 4 mm ID borosilicate glass column packed with 6% DC-200 on 80/100 mesh Chromosorb W was preconditioned at 220°C for 72 hr prior to use. Gas flow rates in ml/min. were carrier (N_2) 70 and purge (N_2) 30. The column oven temperature was maintained at 260°C, and the injection port at 220°C.

IBP was also analyzed on a Tracor Model 550 gas chromatograph equipped with a flame photometric detector sensitive to phosphorus. A 1m long and 4 mm ID borosilicate glass column packed with 3% OV-1 on 80/100 mesh Chromosorb W was used. Gas flow rates in ml/min. were carrier(N_2) 70, hydrogen 100, oxygen 25, and air 40. Injector port temperature was 220°C, detector 190°C, and column oven 190°C.

From the plant fortified with IBP and isoprothiolane, percent recovery was above 90 for two fungicides..

Results and Discussion

Effect of application time

When applied to the rice paddy water at the maximum tillering stage, IBP and isoprothiolane in plant reached to maximum 1 day after treatment(DAT), reaching 6.2 and 7.6 ppm for isoprothiolane and IBP, respectively, and then declined rapidly upto 7 DAT, reaching 1.5-1.8 ppm but more slowly thereafter(Fig. 1). These results imply that both fungicides were

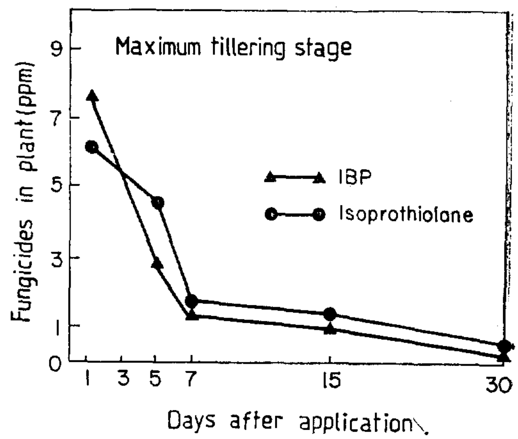


Fig. 1. Changes in concentrations of IBP and isoprothiolane in rice plant on maximum tillering stage (July 14, 1979)

readily absorbed via root system and rapidly translocated into the plant tissues. Concentrations of isoprothiolane were somewhat higher than those of IBP during the whole experimental period except for 1 DAT. On the other hand, when applied at the heading stage, the persistence pattern of IBP was almost same as the maximum tillering stage while that of isoprothiolane was quite different; the maximum concentration of 3.8 ppm reached 1 DAT and then declined showly upto 5 DAT, reaching about 3 ppm, thereafter maintained almost constant level until 30 DAT (Fig. 2). This phenomenon means that the persistence of IBP in plant was not related to the growth stage of the plant but in case of isoprothiolane, the concertrations in plant were higher in later growth stage (heading stage) than in earlier stage (maximum tillering stage).

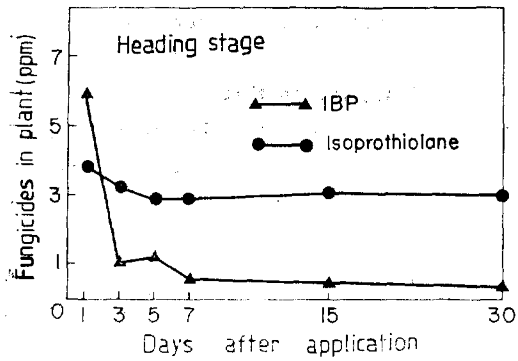


Fig. 2. Changes in concentrations of IBP and isoprothiolane in rice plant on heading stage (August 16, 1979)

The terms required to reach the maximum concentration in plant (1 day) in this experiment were much shorter than previous data; 5∼7 days[13], 14 days[2], and 28 days[14] for isoprothiolane and 10 days[15] and 15 days[1] for IBP.

Yamamoto et al.[9] also reported that IBP in leaf blade reached to a maximum within 24 hr in the application at the tillering stage but 10 days were needed for the maximum in the application at the heading stage. One of the reasons for such different terms might be due to the different soil texture. Soil adopted in this experiment was sandy loam with 1.76% of organic matter while soils used in previous studies were volcanic ash soils with high content of organic matter and different clay mineral constituent, consequently pesticides might be tightly adsorpted and released slowly.

The persistences of two fungicides applied at the milking stage are shown in Fig. 3. This experiment was undertaken to confirm the effect of the application at the later growth stage on the persistence of IBP and isoprothiolane. The persistence patterns of two fungicides were almost the same as the results obtained at the heading stage. To determine more accurately the term required to reach the maximum concentrations in plant, samples were taken 6, 12, and 24 hr after the application. The terms required to reach a maximum concentration' were the same; 24 hr, reaching 5.1 and 6.3 ppm for isoprothiolane and IBP, respectively. However, isoprothiolane was absorbed more rapidly by the root system than IBP within 24 hr.

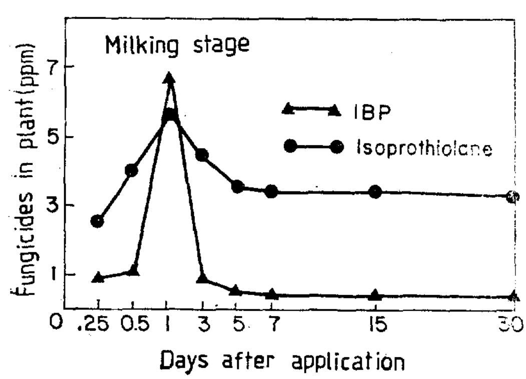


Fig. 3. Persistence of IBP and isoprothiolane in rice plant on milking stage(September 11, 1980)

For the effective control of the rice blast, it may be very important to know the relationship between the time of outbreak of blast disease and the most appropriate application time related to the soil properties. Tsumura[2] reported that the presence of isoprothiolane at 2 ppm in leaf blades was sufficient to protect rice plants from the blast, and Yoshinaga et al.[1] reported the concentration of 3∼5 ppm of IBP in leaves was able to give the good controlling effect. From these points of view, if two fungicides be applied to the rice field of this experiment within 1 day before the initial outbereak of blast, the effective control of blast may be possible. Even if the whole plant sample except for roots was used for the residue analysis, based on 2 ppm pf concentration necessary for giving good controlling effect from rice blast, fungicidal activity of isoprothiolane will be 7 and 30 days for the application at the maximum tillering stage and the heading stage, respectively.

The previous studies related to the effect of application time on the persistence of IBP are different from the reseacher. Yamamoto et al.[9] reported that uptake of IBP by the rice plant was different with the growth stages of the plant, and the rate of uptake was rapid in early growth stage. They described the reason might be attributed to the fact that growth rate and uptake of nutrients in plant declined in the latter application due to the maturing stage of rice plant, consequently uptake of IBP was decreased. However, Nene and Thapliyal[15] reported that if applied at the tillering stage, decomposition of IBP in leaves starts in a very short time. While in case of pre-ear sprouting stage, concentration of IBP in leaves reaches maximum after 10 days and starts to decrease 20 days after application.

On the other hand, persistence of isoprothiolane applied at the heading stage was similar to the report by Kanauchi[10]. He reported that the older the plant, the lesser the decrease, and the reason might be due to the dilution of the chemical by the increased weight of rice plant rather than the decrease by the degradation of the compound.

Effect of water depth and soil texture

The effect of water depth and soil texture on the persistence of two systemic fungicides in rice plant was conducted as a pot experiment. The results are shown in Fig. 4. Although the chemicals applied at early stage of rice plant (tillering), the concentrations of isoprothiolane in plant were considerably high regardless of the treatments. This trend was similar to the result obtained at the heading stage in the field trial. This reason might be attributed to the abnormal climate conditions during this experiment (1980); since air temperature was 2∼3°C lower than the average year, thereby the degradation rate of isoprothiolane might be reduced.

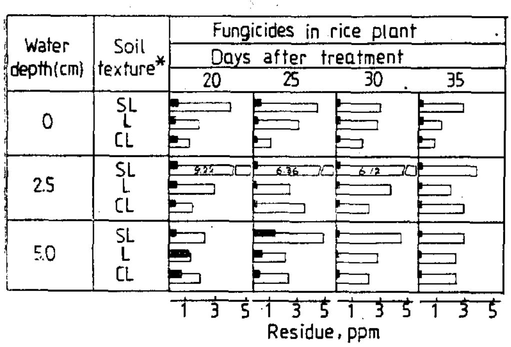


Fig. 4. Effect of water depth and soil texture on the persistence of IBP (■) and isoprothiolane (□)

SL: Sandy loam, L: Loam, and CL: Clay loam

The concentrations of isoprothiolane were the highest levels in the plant grown in the sandy loam soil regardless of the water depth and a little higher in loam soil than in clay loam soil. This phenomenon might be attributed to the adsorption of isoprothiolane by orgnic matter. Since drainage was excepted in this experiment, adsorption might be a principal factor affecting the absorption of isoprothiolane by the rice plant and translocation to the upper parts of the plant. The content of organic matter and clay in soils used in the experiment followed the order of clay loam 〉 loam 〉 sandy loam.

There was little effect of the water depth on the persistences of two fungicides in rice plant but concentration of isoprothiolane in plant was a little higher in the 2.5 cm water depth of the sandy loam soil. In case of IBP, its concentrations in plant were very low since then 20 days after the application regardless of the treatments.

要　約

水稻體中 IBP와 isoprothiolane의 殘留消長에 미치는 撒布時期의 影響이 調査되었으며, 아울러 水深과 土性의 影響도 관찰되었다. IBP(17%, G)와 isoprothiolane(12%, G)을 各各 6.8과 4.8 kg AI/ha의 比率로 湛水土壤에 1回 撒布한 후 時期別로 水稻體中 殘留量을 gas chromatograph로 分析하였다. 撒布時期와는 無關하게 두 殺菌劑는 뿌리조직을 통해 植物體로 신속히 吸收, 轉移되었으며, 稻體中 두 殺菌劑의 濃度는 撒布時期와는 無關하게 24時間 이내에 最高에 이르렀다. 최대분열기 撒布時 두 殺菌劑의 分解樣相은 비슷한 傾向으로 時間의 經過와 더불어 신속히 分解되었다. 한편 출수기 撒布時에 IBP의 分解樣相은 최대분열기 撒布時와 비슷한 傾向이나 isoprothiolane의 그것은 아주 相異하였다. 즉 藥劑撒布後 3日에 나타난 最高濃度가 그후 25日까지 큰 변화없이 維持되었다.

한편 두 殺菌劑의 殘留消長에 미치는 水深의 影響은 별로 없었으며, isoprothiolane의 경우 壤土와 殖壤土에서 보다 砂壤土에서 栽培한 水稻體에서 더 높은 殘留量을 보이는 傾向이었다.

Acknowledgement

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