Note

Gas Chromatographic Determination of a New Fungicide, Procymidone (Sumilex®) in Technical Preparation and Formulation

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N-(3,5-Dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide (procymidone, Sumilex®) is a novel fungicide which possesses high antifungal activity especially against *Sclerotinia* rot and gray mould fungi.¹⁾ The mechanism of antifungal action of procymidone has been investigated by Hisada *et al.*²⁾ Figure 1 gives the chemical structure. In this paper an analytical method for technical preparations and formulations has been described.

Gas chromatography (GC) was successfully applied with a 5% silicone XE-60 column; the impurities such as 3,5-dichloroaniline, 1,2-dimethylcyclopropane-1,2-dicarboxylic acid, *N*-(3-chlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide (Monochloro), *N*-(2,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide (2,5-Dichloro isomer) and *N*-(2,4-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide (2,4-Dichloro isomer) which were suspected to be contained in technical procymidone were completely separated from procymidone peak. Figure 2 gives a gas chromatogram and the impurities were identified by the comparison of the retention times of their authentic standards and by GC-MS spectroscopy. Another impurity, 2-[*N*-(3,5-dichlorophenyl) carbamoyl]-1,2-dimethyl-1-cyclopropanecarboxylic acid (Halfamide) which was not eluted by GC was determined spectrometrically measuring the absorbance at 250 nm after alkaline-extraction (5% Na₂CO₃) from technical samples.

The content of procymidone in technical preparations was more than 98% as shown in Table I, and the content

FIG. 1. Chemical Structure of Procymidone.

FIG. 2. Gas Chromatogram of a Technical Procymidone.

(1) 3,5-dichloroaniline; (2) monochloro; (3) 2,4- and 2,5-dichloro isomers; (4) procymidone; (5) dicyclohexyl phthalate (IS).

GC conditions: apparatus, Shimadzu GC-5A equipped with a flame ionization detector; column, a glass column packed with 5% silicone XE-60/Chromosorb W (AW, DMSC, 60 to 80 mesh); column temp., 200°C; injection and detector temp., 250°C; carrier gas, nitrogen at 50 ml/min; hydrogen, 50 ml/min; air, 1000 ml/min; sensitivity $\times$ range, $10^2 \times 64$ (6.4×10^{-9} amperes in full scale); injection volume, 1 μ l (10 mg/ml, chloroform).

TABLE I. ANALYSES OF SOME TECHNICAL PROCYMIDONE SAMPLES

Lot	Analytical values (%)		
	Content	Monochloro	Halfamide
A	98.8		
	98.6	0.1	0.2
	98.7		
B	98.8		
	99.1	0.2	0.1
	98.8		
C	98.4		
	98.3	0.3	0.1
	98.1		

TABLE II. ANALYSES OF PROCYMIDONE
IN A WETTABLE POWDER

Calculated (%)	Found (%)	Recovery (%)
53.1	53.2	100.2
	52.9	99.6
	53.4	100.6
	53.1	100.0
	53.0	99.8
	53.3	100.4
	53.2	100.2
	av. 53.2	av. 100.2
		CV 0.34

of 3,5-dichloroaniline was negligible. Table II gives analytical results of a 50% wettable powder. Procyimdone was quantitatively recovered from substitute materials by extraction with chloroform with a precision of 0.34%.

EXPERIMENTAL

Reagents and apparatus. Procyimdone analytical standard was prepared by recrystallization from methanol, mp. 164~166°C. Internal standard solution was prepared by dissolving 0.8 g of dicyclohexyl phthalate (Tokyo Kasei Co.) in 100 ml of chloroform.

A Iwaki KM shaker model V-D (Iwaki Co.) was used for the extraction of procyimdone from a wettable powder. A Shimadzu model ITG-4A digital integrator was used for peak area measurements of gas chromatogram.

Analytical method. Each of 80, 100 and 120 mg of procyimdone analytical standards was weighed accurately into a 20 ml conical flask, and 10 ml aliquot of internal standard solution was added to each flask to dissolve, and mixed well to prepare calibration standard solutions. Each of one μ l aliquot of calibration standard solutions was chromatographed under the GC conditions described in

Fig. 2. Peak areas of procyimdone and dicyclohexyl phthalate were measured with a digital integrator and peak area ratios of procyimdone to dicyclohexyl phthalate were plotted against their weight ratios to prepare a calibration curve.

About 100 mg of technical procyimdone was weighed accurately into a 20 ml conical flask, 10 ml aliquot of internal standard solution was added accurately to dissolve, and mixed well to prepare a sample solution. One μ l of the sample solution was chromatographed under the same GC conditions as described above and peak area ratio of procyimdone to dicyclohexyl phthalate was converted into weight ratio (R) and the purity was determined as follows;

$$\text{Procyimdone purity (\%)} = R \times (W_i/W_s) \times 100$$

where, W_i and W_s were weights (mg) of dicyclohexyl phthalate and sample in the sample solution, respectively.

In a case of wettable powder, a sample containing about 100 mg of procyimdone was weighed accurately and 10 ml of internal standard solution was added, and shaken for 10 min by using a mechanical shaker. The supernatant solution was chromatographed samely as above.

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