Note

Gas Chromatographic Determination of Esfenvalerate (Sumi-alpha®) in Technical Preparations

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FIG. 1. Gas Chromatogram of Esfenvalerate in Technical Preparations.

1, solvent (acetone); 2, di-2-ethylhexyl sebacate (IS); 3, X-isomer of esfenvalerate; 4, Y-isomer of esfenvalerate. GC conditions: column, glass (3 mm i.d. $\times$ 2 m) packed with 2% Dexsil 300 GC on Sumikasorb HP, 80~100 mesh; column temp., 250°C; injection port and detector temp., 270°C; carrier gas, nitrogen at 50 ml/min; sensitivity, 1.6×10^{-9} amperes at full scale.

FIG. 2. Gas Chromatogram of A α from a Commercial Column.

1, solvent (acetone); 2, diketone compound (decomposed product); 3, A β (isomerized compound); 4, A α . GC conditions: column, glass (3 mm i.d. $\times$ 2 m) packed with 2% Dexsil 300 GC on Chromosorb W HP, 80~100 mesh. The other conditions were the same as those in Fig. 1.

(S)- α -cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutylate (esfenvalerate, Sumi-alpha®) is a synthetic pyrethroid insecticide, which is an optically active compound of fenvalerate ((RS)- α -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutylate, Somicidin®).¹⁾ The authors have developed an analytical method for the determination of esfenvalerate in technical preparations. Gas chromatography (GC) was applied with a 2% Dexsil 300 GC column that was selected from various GC columns for its ability to separate the relevant impurities and diastereoisomers. Horiba *et al.*²⁾ have reported a method for the determination of fenvalerate in technical preparations that used a 2% Apiezon L column, but the separation of diastereoisomers was not sufficient.

By using the 2% Dexsil 300 GC column (3 mm i.d. $\times$ 2 m), nearly baseline separation was achieved. As an internal standard (IS) for the determination, di-2-ethylhexyl sebacate was found to be suitable (Fig. 1). The early eluted diastereoisomeric peak (named as X) was composed of (R)- α -cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutylate (named as A β) and (S)- α -cyano-3-phenoxybenzyl (R)-2-(4-chlorophenyl)-3-methylbutylate (named as B α), and the last peak (named as Y), of (S)- α -cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutylate (named as A α , which was the active ingredient and main component of the technical preparations) and (R)- α -cyano-3-phenoxybenzyl (R)-2-(4-chlorophenyl)-3-methylbutylate (named as B β). The refined A α was used as an analytical standard for determining the total isomeric (X+Y) content of the technical preparations.

However, the authors found that esfenvalerate, fenvalerate and other α -cyano-3-phenoxybenzyl esters were often decomposed in the column, especially by contact with the support medium (diatomaceous earth). It was assumed that the alkali in the support medium and silanol on its surface caused this decomposition. Figure 2 shows the gas chromatogram of a decomposition example of the

TABLE I. ANALYTICAL RESULTS FOR ESFENVALERATE IN TECHNICAL PREPARATIONS

Analysis	Total isomeric content (%)
1	95.5
2	95.5
3	95.7
4	95.3
5	96.1
	Av. 95.6
	C.V. 0.3

FIG. 3. Gas Chromatogram of A α from a Well-inactivated Column.

1, solvent (acetone); 2, A α . GC conditions: column, glass (3 mm i.d. $\times$ 2 m) packed with 2% Dexsil 300 GC on Sumikasorb HP, 80 ~ 100 mesh. The other conditions were the same as those in Fig. 1.

A α standard. The decomposed products were identified to be 3-(4-chlorophenyl)-4-methyl-1-(3-phenoxyphenyl)-1,2-pentanedione (named as a diketone compound) and A β by GC mass spectrometry and the GC retention times of authentic samples. The diketone compound was formed by the elimination of HCN from A α according to the following scheme:

A β was formed by the epimerization of A α .

The authors tried to prepare a column which did not decompose these α -cyano-3-phenoxybenzyl esters, and developed a well-acid-washed and well-inactivated support medium (named as Sumikasorb HP), which was coated with 2% of Dexsil 300 GC. By using this 2% Dexsil 300 GC on the Sumikasorb HP column, the A α standard could

FIG. 4. Gas Chromatogram of α -Cyano-3-phenoxybenzyl Esters in Technical Preparations from a Well-inactivated Column.

1, solvent (acetone); 2, fenpropathrin; 3, cyphenothrin; 4, cypermethrin; 5, fenvalerate; 6, deltamethrin. GC conditions: column, glass (3 mm i.d. $\times$ 2 m) packed with 3% Silicone OV-101 on Sumikasorb HP, 100 ~ 120 mesh; column temp., 240°C; injection and detector temp., 270°C; carrier gas, nitrogen at 40 ml/min.

FIG. 5. Structures of α -Cyano-3-phenoxybenzyl Esters.

be stably chromatographed without decomposition in the column (Fig. 3), and the total isomeric content of esfenvalerate in technical preparations was accurately determined by the IS method (Fig. 1), the coefficient of variation (C.V.) being 0.3%, as shown in Table I.

Figure 4 shows a gas chromatogram of such other α -cyano-3-phenoxybenzyl esters as fenpropathrin, cyphenothrin, cypermethrin, fenvalerate and deltamethrin (Fig. 5) in technical preparations by 3% Silicone OV-101 on Sumikasorb HP (3 mm i.d. $\times$ 1 m). These pesticides could be stably chromatographed without decomposition, and especially deltamethrin, which was quite unstable for GC by a commercial column, could be stably and quantitatively eluted.

MATERIALS

Analytical standard for esfenvalerate. Recrystallized pure A α (mp, 60.6~61.5°C) was used.

IS solution. Ten ml aliquots of acetone solutions containing about 40 mg of di-2-ethylhexyl sebacate (of analytical reagent grade from Wako Pure Chemical Industries Ltd., Osaka, Japan) were used.

Column packings for GC. Non-silanized diatomaceous earth, Uniport B (80 to 100 mesh, obtained from Gasukuro Kogyo Inc., Tokyo, Japan) was washed by a 1 N phosphoric acid/methanol solution and rinsed by methanol to be neutral, instead of by using an alkali. This diatomaceous earth was dried and silanized with 5% (v/v) dimethyldichlorosilane (DMCS) in a dried dichloromethane solution under refluxing for 30 min. The authors used dichloromethane as a reaction solvent to better mix the reaction mixture and release the hydrochloric acid formed by reacting DMCS with silanol, rather than toluene, which is generally used to silanize diatomaceous earth with DMCS. Dichloromethane has higher specific gravity and lower boiling point in comparison with toluene, and was therefore advantageous for use as the reaction solvent. After successively rinsing by dried dichloromethane and dried methanol, and then drying *in vacuo*, the acid-washed and well-inactivated support (Sumikasorb HP) was obtained and finally coated with 2% of Dexsil 300 GC by the evaporation method.

Gas chromatography. A Shimadzu GC 7A gas chromatograph equipped with a flame-ionization detector

(Shimadzu Corporation, Kyoto, Japan) was used.

Automatic integration. Shimadzu model C-R3A Chromatopac data processing system was used.

METHOD

Preparation of the calibration curve. Samples of 40, 50 and 60 mg each of pure A α were weighed accurately into a 20 ml conical flask, 10 ml of the IS solution was added to each flask, and the contents mixed well to make the standard solutions. One μ l portions of these standard solutions were chromatographed under the GC conditions described in the legend to Fig. 1. A calibration curve of the peak area ratios (A α to IS) versus the weights of A α in these standard solutions was constructed, this giving a straight line with satisfactory reproducibility, the average C.V. being less than 0.4%.

Determination. About 55 mg of a sample was weighed into a 20 ml conical flask, 10 ml of IS solution was added, and the contents mixed well to make a sample solution. A 1 μ l portion of this solution was chromatographed under the GC conditions described in the legend to Fig. 1, and the total isomeric content of the sample was determined by using the calibration curve according to the following equation:

$$\text{Total isomeric content (\%)} = R/W \times 100$$

where R is the weight (mg) obtained from the peak area ratio ((X + Y) to IS) by the calibration curve, and W is the weight (mg) of the sample.

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