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Note

High-pressure liquid chromatography of a new pyrethroid insecticide, sumicidin

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Sumicidin (Shell WL 43775), (±)-α-cyano-3-phenoxybenzyl (±)-2-(4-chlorophenyl)-3-methylbutyrate, is a new insecticide referred to as a pyrethroid by the manufacturer, although it lacks the dimethylcyclopropanecarboxylic acid function common to other pyrethroids; it is a mixture of two diastereoisomers in a constant ratio.

Gas–liquid chromatographic (GLC) methods with flame ionization or electron-capture detection have been reported for determining sumicidin[1]; however, during GLC, thermal decomposition may occur, thereby impairing quantitative estimation. By contrast, high-pressure liquid chromatography (HPLC) would appear to be more suitable for the analysis of pyrethroid insecticides, as recently pointed out in a paper on permethrin[2]. Here, we describe the HPLC analysis of sumicidin at ambient temperature with two systems, one a reversed-phase system and the other involving adsorption chromatography.

EXPERIMENTAL

Chromatographic system

A Varian LC 8500 high-pressure liquid chromatograph was used, with a variable-wavelength UV detector operated at 235 nm. The columns used (each 15 cm × 4.7 mm I.D.) were of Lichrosorb RP-8 (Merck, Darmstadt, G.F.R.), particle size 10 μm, and of LiChrosorb Si-60 (Merck), particle size 5 μm. In each instance, the flow-rate was maintained at 80 ml/h (column pressure 500 p.s.i.).

Chemicals

The reference sample of sumicidin was a generous gift from the Sumitomo Chemical Co. (Osaka, Japan). All the solvents were of analytical-reagent grade, and the hexane and isopropyl ether were anhydrous.

Analytical method

In the reversed-phase system, isocratic elution was carried out with acetonitrile–aqueous 1% sulphuric acid (70:30); for the silica gel column, isocratic elution was with hexane–isopropyl ether (90:10).

RESULTS AND DISCUSSION

On the RP-8 column (see Fig. 1a), the sumicidin diastereoisomers have similar chromatographic properties and consequently the same retention time. Even when the proportions of acetonitrile and sulphuric acid were altered, there was no separation. Fig. 1b shows the separation of sumicidin isomers on the silica gel column. In each instance, analyses were carried out with internal standards of pentachlorobenzene and diphenylamine, respectively. In the normal-phase study, the order of

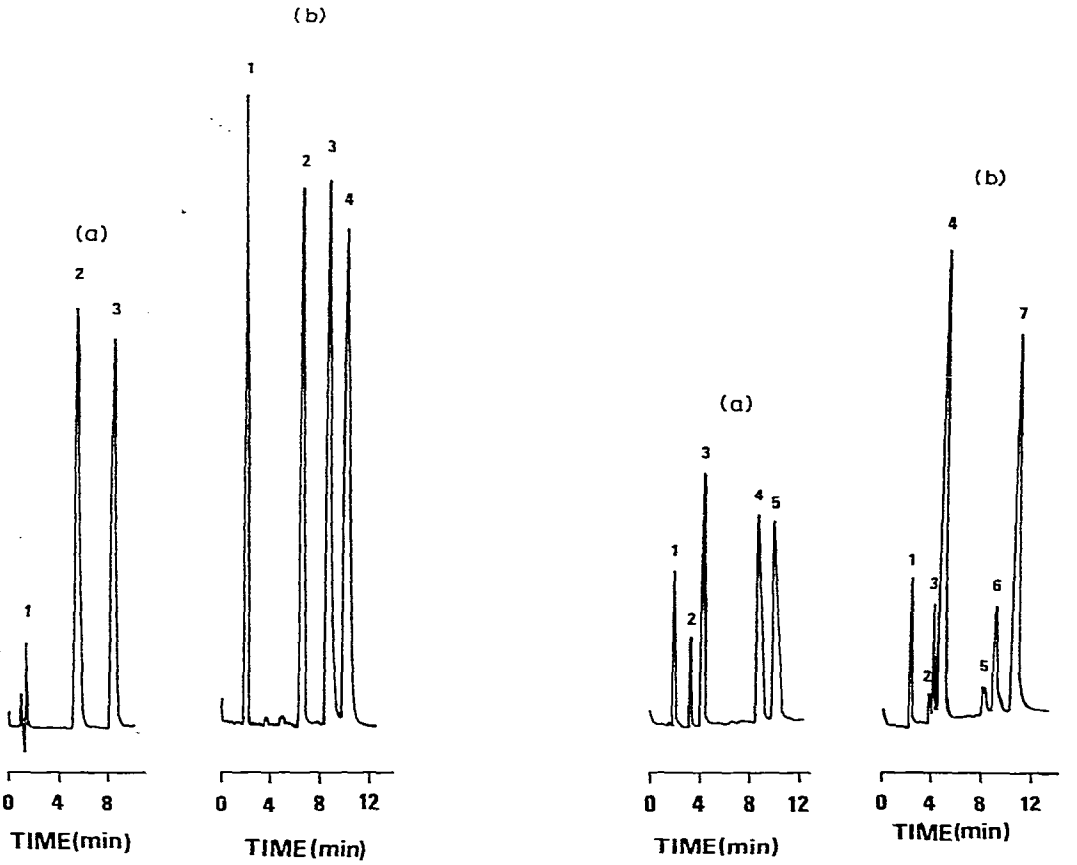

Fig. 1. HPLC of sumicidin in reversed- and normal-phase modes. (a) LiChrosorb RP-8 column; mobile phase acetonitrile–1% sulphuric acid (70:30); flow-rate 80 ml/h; detector sensitivity 0.5 a.u.f.s. Peaks: 1, injection artefact; 2, pentachlorobenzene (internal standard); 3, sumicidin (1 g/l in chloroform). (b) LiChrosorb Si-60 column; mobile phase anhydrous hexane–anhydrous isopropyl ether (90:10); other conditions as in (a). Peaks: 1, injection artefact; 2, diphenylamine (internal standard); 3, 4, sumicidin isomers (1 g/l in chloroform).

Fig. 2. HPLC of pyrethrin and pyrethroid insecticides on a LiChrosorb Si-60 column. (a) Conditions as in Fig. 1b. Peaks: 1, injection artefact; 2, *cis*-permethrin; 3, *trans*-permethrin; 4, 5, sumicidin isomers. Sample solution, permethrin and sumicidin (1 g/l of each in chloroform). (b) Mobile phase anhydrous hexane–anhydrous isopropyl ether (40:60); other conditions as in Fig. 1b. Peaks: 1, injection artefact; 2, jasmolin I; 3, cinerin I; 4, pyrethrin I; 5, jasmolin II; 6, cinerin II; 7, pyrethrin II. Sample solution pyrethrin (0.25 g/l) in cyclohexane.

elution was diphenylamine and the two sumicidin diastereoisomers, the retention times being 370, 510 and 600 sec, respectively. Under our experimental conditions, complete separation required approximately 10 min.

In the normal-phase system, replicate injections led to decreasing retention times of the sumicidin components, with consequently poorer resolution of the two isomers. By pumping pure isopropyl ether through the silica gel column for 2 min and then allowing the system to stabilize, excellent reproducibility of retention times was attained. We suspect that the decrease in retention time is due to deactivation of the column by some residue of sumicidin synthesis (perhaps an alcohol).

In the reversed-phase system, the most critical factor was not reproducibility of retention time, but interference from alkylbenzenes used in sample formulations. However, alkylbenzenes were eluted with the solvent front in the normal-phase system and thus did not interfere.

CONCLUSION

The simple and rapid method described allows the presence of sumicidin to be detected in commercially available insecticidal preparations with use of a silica gel column. The assay is unaffected by the presence of the alkylbenzenes used in such formulations, and, by selection of a suitable internal standard, quantitative analysis is possible. This method would also be useful in the quality control of raw materials and in the detection of residues. In fact, the sensitivity is improved by operating the detector at 235 nm (the absorption maximum of sumicidin). The method also offers an efficient procedure for identification of the residues of most commonly used pyrethroids and pyrethrin insecticides. Fig. 2a shows a typical chromatogram of the separation of sumicidin and permethrin. Natural pyrethrins have already been separated by HPLC on a silica column[3]; however, in our system, with a different ratio of hexane to isopropyl ether (*ca.* 60:40), their separation and identification are still possible (see Fig. 2b).

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