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Note

Separation of permethrin and some of its degradation products by high-performance liquid chromatography

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Pyrethrins are known to be valuable insecticides. Unlike the chlorinated hydrocarbons, phosphates and carbamates, pyrethrins have the important advantages of being biodegradable, having low vapor pressure, and having low mammalian toxicity. Among the synthetic pyrethroids one of the most promising is permethrin [3-phenoxybenzyl (±) *cis*-, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate][1,2]. Permethrin, apart from having the desirable properties of a pyrethrin, is superior in that it is photostable and possesses high insecticidal activity. Already a wide range of applications have been found for the compound[2–13].

It is anticipated that the use of permethrin will increase. Therefore, the insecticide's metabolic products and its residence time in mammals are of great ecological importance. Extensive investigations of the metabolic fate of permethrin in rats have been described[14,15].

Several colorimetric[11] and gas chromatographic[9,10,16,17] procedures for the determination and quantitation of the insectide have been described.

Surprisingly, very little high-performance liquid chromatographic (HPLC) work in the analysis of permethrin and its degradation products has been reported. HPLC has the potential of being the analytical procedure of choice for the analysis of permethrin, since it would require less stringent sample preparation and clean-up. In our laboratory we have investigated briefly the retention characteristic of the compound on silver-loaded aluminosilicate stationary phase[19]. Residue determinations at F.M.C.[18] have also used liquid chromatography. The present paper describes the analysis of permethrin and some of its degradation products using HPLC on a reversed-phased system.

EXPERIMENTAL

The liquid chromatograph consisted of a Milton Roy Pump, Model 396 Laboratory Data Control, Riviera Beach, Fla., U.S.A.) and Tracor 100 (Tracor, Austin, Texas, U.S.A.), UV detector operated at 254 nm having a cell volume of 8 μl. Samples were introduced through a Rheodyne injection valve model 70-10 purchased from Altex (Berkeley, Calif., U.S.A.). The reversed-phase packing was prepared by reacting trimethoxyoctadeylsilane with Partisil 10 (Whatman, Clifton, N.J., U.S.A.). Permethrin, *m*-phenoxybenzyl alcohol and *m*-phenoxybenzoic acid were provided by F.M.C.

(Middleport, N.Y., U.S.A.). All organic solvents were reagent grades obtained from Fisher Scientific (Pittsburgh, Pa., U.S.A.) and were used without purification. Water used for the mobile phase was distilled and passed through an ion-exchange column (Barnstead Sybron, Boston, Mass., U.S.A.).

RESULTS AND DISCUSSION

Previous work on the separation of *cis*- and *trans*-permethrin have indicated that in adsorption chromatography the resolution is extremely sensitive to the amount of the polar modifier in the mobile phase. Therefore a reversed phase seemed more appropriate to the separation of the insecticide. In the present case since one of the compounds is an acid, an acidic mobile phase was used in order to suppress ionic species. Fig. 1 shows a chromatogram of *cis*- and *trans*-permethrin and the two major degradation products, *m*-phenoxybenzyl alcohol and *m*-phenoxybenzoic acid. Obviously a continuous gradient could have been used instead of a step gradient. We prefer the latter approach due to the large differences in polarities between the decomposition products and the parent compounds. The use of a reversed-phase system is especially useful in the analysis of the metabolites; since in mammals, permethrin is quickly hydrolized and enzymatically converted to more polar compounds which are excreted from the body within a short time.

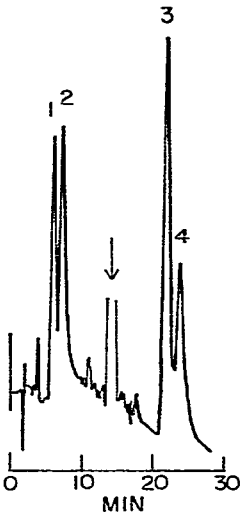

Fig. 1. Separation of permethrin and its major metabolites. Column: reversed-phase, 250 × 4.2 mm I.D.; mobile phase: 5 ml acetic acid, 25 ml chloroform, 470 ml of H_2O (42%) in methanol, pH 2.4. The mobile phase was changed to 5 ml acetic acid, 25 ml chloroform, 470 ml of H_2O (21%), pH 2.5; flow-rate, 1.1 ml/min; detector attenuation 0.32. 1 = *m*-phenoxybenzyl alcohol, 2 = *m*-phenoxybenzoic acid, 3 = *trans* permethrin, 4 = *cis* permethrin.

The procedure discussed here offers still a greater advantage in the case of less stable pyrethrins which would usually undergo thermal isomerization or decomposition[20] during the gas–liquid chromatographic analysis.

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