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Note

High-performance liquid chromatographic determination of kadethrin, permethrin and piperonyl butoxide in spray solutions

ULRICH NEHMER* and NENO DIMOV
Analytical Department, Chemical-Pharmaceutical Research Institute, Ul. "Kl. Ochridski" 1a, Sofia 1156 (Bulgaria)
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Many aerosols and liquid household insecticides contain a combination of piperonyl butoxide (PBO) and other compounds. PBO {5-[2-(2-butoxyethoxy)ethoxymethyl]-6-propyl-1,3-benzodioxole} is the most widely used synergist of pyrethrins and certain pyrethroids[1]. Permethrin [3-phenoxybenzyl-(±)-*cis,trans*-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropan-1-carboxylate] is a residual pyrethroid with outstanding insecticidal activity against a broad spectrum of insect species[1,2]. Kadethrin [5-benzyl-3-furylmethyl-3,3-dimethyl-2-(2,3,4,5-tetrahydro-2-oxothien-3-ylideneme-thyl)cyclopropane-1-carboxylate] is a pyrethroid known to have valuable insecticidal properties[3].

Methods published to date for the determination of permethrin include gas chromatography (GC)[4,5] and high-performance liquid chromatography (HPLC)[6]. Several methods have also been described for the determination of PBO, including GC[7] and HPLC[8]. However, at present no method is available for the assay of solutions containing kadethrin, permethrin and PBO.

This paper describes an HPLC method for the determination of the above three pesticides in spray solutions prepared with ethanol as solvent.

EXPERIMENTAL

Equipment and materials

A Pye Unicam LC-XPD analytical pump coupled with a Pye Unicam LC–UV detector and a Rheodyne 7120 injection valve (sample loop 20 μl) was used, with a Perkin-Elmer 056 recorder. The UV detector was operated at 280 nm. The LC column was a pre-packed LiChrosorb RP-18 column (25 cm × 4 mm I.D.; particle size 10 μm) from Merck (Darmstadt, F.R.G.). The mobile phase was methanol–deionized water (80:20, v/v). A flow-rate of 2 ml/min was optimal for this analysis. All the solvents were of analytical-reagent grade and were filtered before use.

Standards of kadethrin (97.6%), permethrin (93.6%) and technical PBO (80%) were supplied by Wellcome Research Labs. (Berkhamsted, U.K.). Fluoranthene (analytical-reagent grade) was obtained from Fluka (Buchs, Switzerland).

Samples of spray solutions containing 3.07% (w/w) of Neopybutrin 15 R (Wellcome Research Labs.) were obtained from our Institute.

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The UV detector was initially set to monitor 0.32 a.u.f.s. After the kadethrin, PBO and internal standard had been eluted, the setting range was changed to monitor 0.08 a.u.f.s. in order to gain a higher sensitivity for permethrin.

Fluoranthene internal standard

A 75-mg amount of fluoranthene was weighed into a 250-ml volumetric flask and dissolved in absolute ethanol.

Preparation of standard solution

A solution of 20 mg of permethrin and 6 mg of kadethrin in 100 ml of ethyl acetate was prepared. A 40-mg amount of PBO was weighed into a second 100-ml volumetric flask, 20 ml of the permethrin–kadethrin solution and 20 ml of the internal standard solution were added by pipette to this flask and the volume was made up to 100 ml with absolute ethanol. A 20-μl volume of the standard solution was injected into the LC column.

Sample preparation

A 20-ml volume of the spray solution was measured into a 100-ml volumetric flask, 20 ml of the internal standard solution were added and the volume was made up to with absolute ethanol. A 20-μl volume of this solution was injected into the LC column. All samples and the standard solution were run in duplicate.

Calculations

Calculations of the content of kadethrin, permethrin (sum of *cis-* and *trans-*) and PBO were carried out by use of the internal standard technique. The peak-height ratio of the particular component to the internal standard was used as the response ratio.

RESULTS AND DISCUSSION

All spray solutions contained 3.07% (w/w) of Neopybutrin 15 R and 0.1% (w/w) of a perfume composition. Fig. 1 shows the chromatogram of a spray solution sample. The dotted line indicates the sample baseline. The retention times are 3.8 min for kadethrin (peak 2), 4.9 min for PBO (peak 3), 7.5 min for the internal standard (peak 5) and 10.6 min (*trans*) and 13 min (*cis*) for permethrin (peaks 6 and 7, respectively). Peaks 1 and 4 are compounds of the perfume composition, and peak 8 is associated with impurities in the technical PBO.

The results of the analysis of spray solutions are: kadethrin, 0.0146, permethrin 0.049 and PBO 0.490% (w/w), with relative standard deviations of 2.1, 3.0 and 0.6%, respectively.

The linearity of the UV detector was examined in the ranges 0.1–3 μg for kadethrin, 1–40 μg for PBO and 0.3–5 μg for permethrin [the analysis of a 3.07% (w/w) spray solution by this method corresponds to amounts injected of 0.24 μg of kadethrin, 8 μg of PBO and 0.8 μg of permethrin].

The peaks of kadethrin, PBO and permethrin do not interfere with any peaks of the perfume composition used or of the byproducts of technical PBO.

The detection limits (defined as a signal twice the magnetude of the noise) were

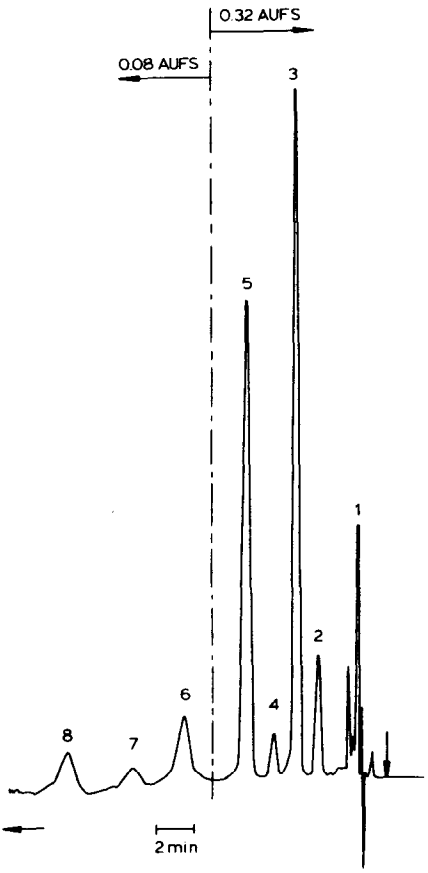

Fig. 1. Chromatogram of spray solution sample. Column, 250 × 4 mm I.D., stainless steel; packing, LiChrosorb RP-18 (10 μm particle size); temperature, ambient; detection, 280 nm; eluent, methanol–water (80:20, v/v); flow-rate, 2 ml/min; pressure, 10 MPa. Peaks: 1,4 = compounds of the perfume composition; 2 = kadethrin; 3 = PBO; 5 = internal standard (fluoranthene); 6 = *trans*-permethrin; 7 = *cis*-permethrin; 8 = byproduct of technical PBO.

2 ng for kadethrin, 10 ng for PBO and 60 ng for permethrin.

In conclusion, an HPLC procedure had been developed for the separating kadethrin, PBO and permethrin from components of a perfume composition and the byproducts of technical PBO and for the determination of these three active ingradients in a spray solution.

REFERENCES

1 A. M. Taha, W. F. Banout, D. C. Stewart and J. S. Martin, *PANS*, 25 (1979) 371.
2 F. Barlow and A. B. Hadaway, *PANS*, 21 (1975) 233.
3 J. Lhoste and F. Rauch, *Pestic. Sci.*, 7 (1976) 247.
4 R. A. Chapman and C. R. Harris, *J. Chromatogr.*, 166 (1978) 513.
5 R. A. Chapman and C. R. Harris, *J. Chromatogr.*, 174 (1979) 369.
6 P. G. Baker and P. Bottomley, *Analyst (London)*, 107 (1982) 206.
7 V. J. Meinen and D. C. Kassera, *J. Ass. Offic. Anal. Chem.*, 65 (1982) 249.
8 R. L. Perez, *J. Ass. Offic. Anal. Chem.*, 66 (1983) 789.