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Note

Rapid method for the detection of oxygen analogues of fenthion, disulphoton and phorate on thin-layer plates

S. V. MIRASHI*, M. P. KURHEKAR, F. C. D'SOUZA and S. K. MEGHAL

Forensic Science Laboratories, State of Maharashtra, Bombay-400 008 (India)

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Organophosphorus insecticides containing a thionophosphate (P=S) and a thioether group in their molecules, such as fenthion, disulphoton and phorate, are commonly used for agricultural purposes. They are also used for poisoning by administration through food or alcoholic beverages and sometimes they occur as contaminants on grain. Thin-layer chromatography is the method of choice for the identification of these insecticides in biological materials. However, sometimes it is necessary to derivatize these insecticides for their confirmation. Blinn¹ studied 12 oxidants for oxidizing phorate and found that *m*-chloroperbenzoic acid gave the best results, whereas Anderson *et al.*² obtained erratic results with this reagent because of its interference in gas-liquid chromatography (GLC). Bowman and Beroza³ oxidized fenthion, disulphoton, phorate and their metabolites from biological materials with *m*-chloroperbenzoic acid and determined them by GLC using a flame photometric detector. Other workers^{4,5} have also used *m*-chloroperbenzoic acid for the oxidation of different organophosphorus insecticides in test-tubes, the oxidation product being determined by GLC. As this method is tedious and requires pre-cleaning and subsequent use of GLC, we report here a simple method for the oxidation of fenthion, disulphoton and phorate on thin-layer plates.

EXPERIMENTAL

Fenthion, disulphoton and phorate (5 μ g) in diethyl ether were spotted on pre-activated silica gel F plates, then 1 or 2 drops of a 1% solution of *m*-chloroperbenzoic acid in chloroform were applied to the spots. The plate was allowed to stand for 15 min at room temperature, then developed in a previously saturated chamber using *n*-hexane-acetone (3:1). After a run of 12 cm the plate was removed and allowed to dry at room temperature.

Various spray reagents were used for the identification of these insecticides, which were extracted from biological material with diethyl ether and oxidized directly on thin-layer plates as described above.

RESULTS AND DISCUSSION

The thioethers of fenthion, disulphoton and phorate on oxidation with *m*-chloro-

TABLE I

R_F VALUES OF FENTHION, DISULPHOTON, PHORATE AND THEIR OXYGEN ANALOGUES IN *n*-HEXANE-ACETONE (3:1)

Compound	R_F
Fenthion	0.67
Fenthion oxygen analogue	0.25
Disulphoton	0.76
Disulphoton oxygen analogue	0.33
Phorate	0.81
Phorate oxygen analogue	0.43

roperbenzoic acid have been reported to be converted into the sulfoxides or sulphones and the P=S group to a P=O group¹⁻³. The data in Table I show that each insecticide gave two spots, viz., fenthion at R_F 0.67 and 0.25, disulphoton at R_F 0.76 and 0.33 and phorate at R_F 0.81 and 0.43. The spots at R_F 0.67, 0.76 and 0.81 were identified as those of fenthion, disulphoton and phorate, respectively, on the basis of similar R_F values given by the pure insecticides in the same solvent system. The spots at R_F 0.25, 0.33 and 0.43 were oxygen analogues of fenthion, disulphoton and phorate, respectively. The same reaction for each insecticide was carried out in test-tubes³ and the reaction products agreed chromatographically with the oxygen analogues obtained by performing the same reaction on thin-layer plates.

Bowman and Beroza³ used chloroform to extract these insecticides from biological material and added *m*-chloroperbenzoic acid to the extracts. After oxidation at room temperature the material was passed through an alumina column and the eluate was used for GLC studies, whereas in the proposed method the ether extract of biological material is oxidized directly on thin-layer plates, which are then developed.

The solvent system *n*-hexane-acetone (4:1), which otherwise gives good separations of organophosphorus insecticides⁶, failed to separate these insecticides and their oxygen analogues. Different proportions of *n*-hexane and acetone were therefore tried in order to achieve a good resolution of the parent compound and the oxygen analogues simultaneously. *n*-Hexane-acetone (3:1) was found to give better separation of the insecticides and their oxygen analogues, as can be seen in Table I.

Several spray reagents were tried. Mercury(II) nitrate with diphenyl carbazone and mercury(I) nitrate gave white spots on a violet background and black spots on

TABLE II

COLOURS OF SPOTS AFTER SPRAYING WITH DIFFERENT REAGENTS

Spray reagent	Colour of spots
Hg(NO ₃) ₂ + diphenylcarbazon	White spots on violet background
HgNO ₃ and heating	Black spots on white background
Iodine	Brown spots on yellow background
Acidic KMnO ₄	Yellow spots on faint brownish background

a white background, respectively, for the insecticides and their oxygen analogues. Acidic potassium permanganate and iodine vapour gave yellow spots turning to white and brown spots, respectively (Table II).

The oxidation of fenthion, disulphoton and phorate with *m*-chloroperbenzoic acid *in situ* is sensitive to 5 μg and has the advantage of simultaneous identification of the insecticides and their oxygen analogues.

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