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Note

Direct determination of propoxur in plant tissues by gas chromatography with an alkali flame-ionization detector

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Propoxur, the common name for 2-isopropoxyphenylmethyl carbamate, is a non-systemic insecticide with rapid knock-down and long residual action. It is particularly destructive to insects such as cockroaches, flies and mosquitoes. Foliage sprays have resulted in effective control of aphids, lygus bugs, grasshoppers and other insects that attack various crops.

Residues of propoxur in various substrates can be determined by gas–liquid chromatography (GLC) with an electron-capture detector after hydrolysation to the corresponding phenol, and derivatization with 1-fluoro-2,4-dinitrobenzene[1–3] or trifluoroacetylation[4].

However, as these methods are time consuming, we have devised an alternative technique based on the direct GLC determination of propoxur. Direct GLC of N-methylcarbamates is often complicated by their tendency to decompose on many columns[5]. Lorah and Hemphill[6], however, demonstrated that a column packing of Chromosorb W, surface modified with Carbowax 20M, has excellent properties for the GLC of intact carbamates (carbaryl, methiocarb, promecarb, mexacarbate).

The utility of support-bonded Carbowax 20M column packings for the direct GLC of carbamates was further confirmed by Moseman[7] and by Hall and Harris[8]. The latter authors determined carbamate residues in soil following this principle.

In our method, Ultrabond, a commercially prepared Carbowax 20M-modified column packing, is used. The extraction and clean-up procedure developed is less laborious than the often quoted method of Holden[2]. This fact, in combination with the more rapid, direct GLC determination, makes the method reported especially suitable for determining propoxur residues in vegetable and fruit samples obtained, for instance, in field trials.

EXPERIMENTAL

Gas–liquid chromatography

A Tracor 550 gas chromatograph with a Tracor 702-N-P nitrogen detector was used, with a glass column (1.8 m × 2.7 mm I.D.) packed with Ultrabond 20M (100–120 mesh), stock number 4904, obtained from Alltech (Arlington Heights, IL, U.S.A.).

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The flow-rates of the carrier and detector gases were 20 ml/min for helium, 3.5 ml/min for hydrogen and 100 ml/min for air. The temperatures of the column oven, injector and detector were 175, 225 and 270°C, respectively. A 1-mV f.s.d. recorder, chart speed 1 cm/min, was used.

Reagents and apparatus

Propoxur standard was obtained from Dr. Siegmund and Irmengard Ehrenstorfer (Fritz Hinternayer Strasse 3, D-9800 Augsburg, G.F.R.). Standard solutions in dichloromethane are stable for at least 1 year when stored in a refrigerator at 4°C. Silica gel 60 [0.05–0.2 mm, 70–270 mesh (ASTM)] for column chromatography was obtained from Machery, Nagel & Co. (Düren, G.F.R.). The silica gel was heated overnight in an oven at 130°C. After cooling, 95.0 g of the gel was deactivated with 5.00 g of water. The mixture was homogenized and, before use, allowed to equilibrate overnight in a tightly stoppered bottle. All other chemicals were of analytical-reagent grade and were checked for interfering impurities by means of blank determinations. The fruit and vegetable samples were macerated in an Ultra-Turrax mixer with solvent.

A centrifuge (830 *g*) with a centrifuge beaker was used. For evaporation a rotary evaporator was used (water-bath at 40°C). A chromatographic column (350 × 6 mm) with a reservoir (50 ml) packed with silica gel, was used to separate propoxur from impurities.

Procedure

Extraction. A 50-g ground and homogenized sample was weighed in a centrifuge beaker. Dichloromethane (100 ml) was added and the mixture was blended for 2 min. The lower layer, dichloromethane, was separated and dried over anhydrous sodium sulphate. To 20 ml (≡5 g of sample) were added 10 ml of isooctane and the mixture was concentrated to about 2 ml. Then 5 ml of isooctane were added and the mixture was concentrated to *ca.* 2 ml.

Column chromatographic clean-up. A plug of glass-wool was tamped into the bottom of a chromatographic column, which was filled with approximately 10 ml of *n*-hexane. Subsequently, 1.00 g of silica gel (deactivated with 5% of water) and 0.5 g of anhydrous sodium sulphate were slowly poured in, in succession and allowed to settle. The *n*-hexane was drained until the level had reached the top of the silica gel. The isooctane extract was transferred into the column and allowed to sink in. The flask and column were rinsed three times with about 1 ml of isooctane, then the column was eluted with 55 ml of 10% ethyl acetate in *n*-hexane.

The first 20 ml were discarded and the remaining 35 ml were concentrated to approximately 5 ml and transferred into a graduated test-tube. The liquid was further concentrated to 0.50 ml with the aid of a gentle stream of dry air. Then aliquots of the propoxur standard and of the concentrate were alternately injected into the gas chromatograph: one standard, one concentrate, one standard, one concentrate.

The propoxur concentration in the sample was calculated on the basis of the mean peak heights obtained for the sample and the standard.

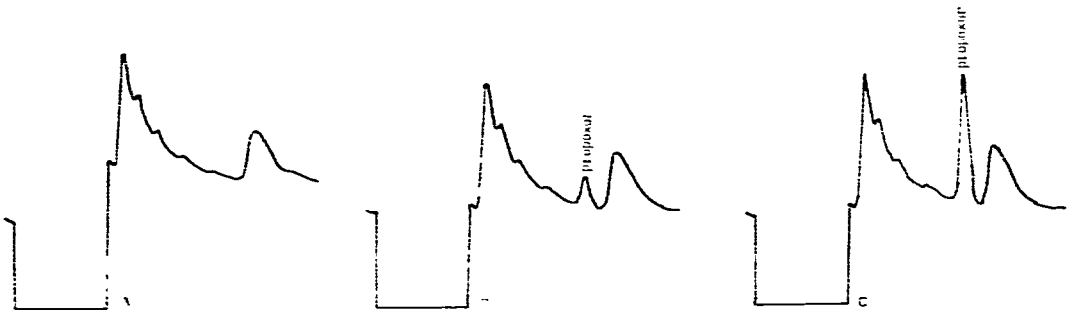

Fig. 1. Chromatogram obtained on a column packed with Ultrabond 20M (100–120 mesh). (A) 12.5 mg of cauliflower; (B) 12.5 mg of cauliflower fortified with 0.02 mg /kgof propoxur; (C) 12.5 mg of cauliflower fortified with 0.1 mg/kg of propoxur.

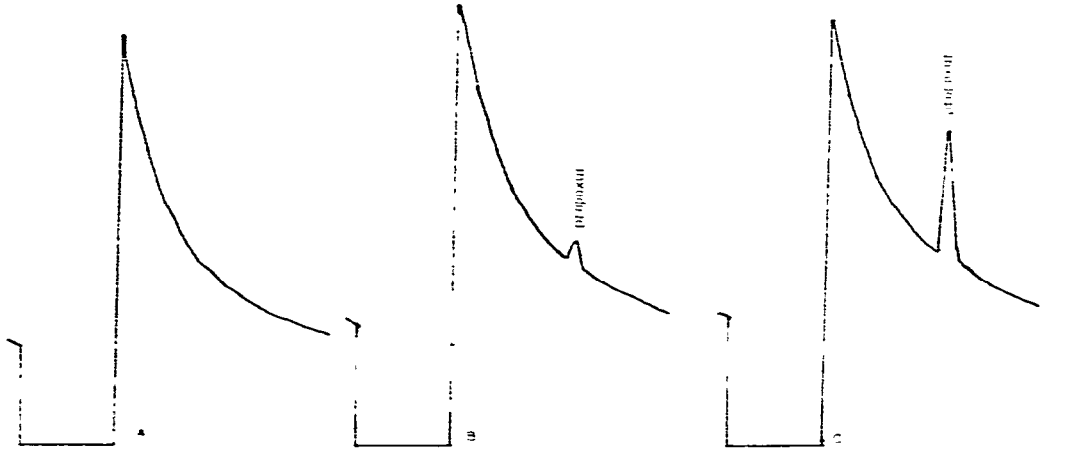

Fig. 2. Chromatogram obtained on a column packed with Ultrabond 20M (100–120 mesh). (A) 12.5 mg of cherries; (B) 12.5 mg cherries of fortified with 0.02 mg/kg of propoxur; (C) 12.5 mg of cherries fortified with 0.1 mg/kg of propoxur.

RESULTS AND DISCUSSION

Recovery experiments were carried out by adding known amounts of propoxur to untreated samples prior to extraction. The results are given in Table I.

It was necessary to condition the GLC columns by injecting a few positive samples until the response of the detector towards propoxur stabilized. It is further advisable to inject alternately standards and samples giving approximately the same peak heights into the gas chromatograph.

In Figs. 1 and 2 typical chromatograms are shown of untreated fortified samples of cauliflower and cherries, analysed with the method described.

In order to check the repeatability of the method, a homogenate of a positive sample of cherries was analysed six times. The following results for propoxur were obtained: 0.105, 0.094, 0.087, 0.099, 0.108 and 0.095 mg/kg. The coefficient of variation was 7.8%.

TABLE I

RESULTS OF RECOVERY EXPERIMENTS

Results given are percentage recoveries.

Sample	*Propoxur added (mg/kg)*					
	0.05	*0.10*	*0.25*	*0.50*	*1.0*	*2.0*
Apples					88	97
Cauliflower		100,110*		90,111*	84	
Cherries		99		90	108	
Currants					86	102
Peas	120			100	106,108*	
Radishes			100			
Savoy cabbage				100		

* In order to check the reproducibility recoveries were determined in duplcate.

In order to find out whether propoxur is detected as such when the GLC system described is applied, the following experiment was carried out. A 500-ng amount of propoxur was injected into the gas chromatograph. The compound eluting at the retention time of the relevant peak was collected in a micro-trap, connected to the outlet of the column. The fraction collected was analysed by thin-layer chromatography according to the technique described by Ernst and Schuring[9]. One spot was found, which had the same R_F value as propoxur. From this experiment, it was concluded that the chromatographic peak used for the determination can be attributed to propoxur.

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