A Simple Procedure for the Confirmation of Residues of α- and β-Endosulfan, Dieldrin, Endrin, and Heptachlor Epoxide

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Several methods have been reported for the characterization of organochlorine insecticides, with oxygen- or sulfur- containing small rings. Although gas chromatography retention times have been used as confirmation in themselves, chemical derivatization and subsequent gas chromatographic analysis of the products is a much more satisfactory method of confirmation.

The bromo-acetate derivatives of dieldrin have previously been prepared by O'Donnell et al (1955) using a mixture of hydrobromic acid and acetic anhydride. This method has been subsequently applied more generally for the confirmation of other organochlorine insecticides (Hamence, 1965). Derivatives of endrin and dieldrin have been prepared using zinc chloride and hydrochloric acid (Wiencke and Burke, 1969) and derivatives of heptachlor and endrin using chromous chloride (Chau and Cochrane, 1971). Another interesting technique for the preparation of derivatives involved passage of the insecticide through a glass micro column packed with solid reactant followed by GLC analysis. It has been used to characterize insecticides, including heptachlor epoxide (Chau and Lanouette, 1972) and α- and β-endosulfan (Chau and Terry, 1972; Chau, 1972).

This note describes a simple modification of the Hamence procedure (1965) which can be used to identify α- and β-endosulfan, dieldrin, endrin, and heptachlor epoxide. The derivatives are prepared using a mixture of hydrochloric acid and acetic anhydride and analyzed by gas chromatography.

The hydrochloric acid-acetic anhydride mixture is prepared by adding acetic anhydride (20 mls) dropwise and with swirling to an ice cooled solution of hydrochloric acid (10 ml; S.G. 1·19). The flask is sealed and allowed to stand at room temperature for 30 mins. This can subsequently be stored without apparent decomposition for

1 month at 1 C in a brown bottle.

A suitable extract containing the insecticide was evaporated to ∿½ ml in a 12 ml centrifuge tube after which 0.5 ml of the hydrochloric acid-acetic anhydride reagent was added. The tube was rotated so that the contents were thoroughly wetted and then covered while the mixture was heated to 100±1 C in an oven for 45 min. After cooling to room temperature distilled water (1.5 ml) was added, followed by saturated sodium carbonate solution with vortex agitation until evolution of carbon dioxide ceased. Hexane (1 ml) was added and the products extracted from the aqueous layer by brisk agitation for 1 min. on a vortex mixer. The layers were allowed to separate and the organic layer analyzed by gas chromatography.

The reaction products were analyzed on a Hewlett-Packard 5710 gas chromatograph fitted with an ^{63}Ni electron capture detector. The column used was 0.91 m x 0.73 cm Pyrex glass packed with 10% OV-1 on GHP 80-100 mesh. Carrier gas was 95% argon-5% methane, Linde speciality gas mixture, which had been dried by passing through molecular sieve. The flow rate was 50 ml/min. Attenuation was 32 with column and detector temperatures 200 C and 250 C respectively.

In the conventional clean up procedure for organochlorine insecticides the compounds are eluted with mixtures of hexane/ethyl ether on a glass column packed with activated florisil. In the present study ethyl ether/hexane solutions of 5/95, 15/85, and 50/50 concentrations were used. The derivatives were prepared from the appropriate eluate and analyzed by gas chromatography.

The retention times of each insecticide and its derivatives, together with the peak areas, are listed in Table 1. All the compounds within a given fraction can be resolved. There was no detectable blank from the reagent.

Direct spiking of soils (20 g dry weight) with insecticide showed that the limit of detection was in the range 0.5-1.0 p.p.b. The presence of 5-10 p.p.b. of dieldrin and endosulfan isomers in rivers silts has been confirmed by this method.

Previously reported methods for the derivatization and confirmation of endosulfan isomers (Chau and Terry, 1972; Chau, 1972) tend to be lengthy because the appropriate solid columns have to be activated. The method reported here is more rapid and all the insecticides examined can be confirmed using a single reagent.

TABLE 1

Retention times relative to aldrin (R_{aldrin}) and relative peak areas of insecticides and products resulting from treatment with hydrochloric acid and acetic anhydride.

Compound	R_{aldrin}	R_{aldrin} derivative and (peak area)	Eluant composition
Heptachlor epoxide	1.22	2.04(1·00),2.46(0.38)	5/95
α-endosulfan	1.56	2.54 (1.00)	5/95 + 15/85
β-endosulfan	2.09	2.26(0.15),2.51(1.00)	50/50
endosulfan sulfate	2.71	no reaction	50/50
endrin	2.03	2.30(0.28), 3.46(1.00)	5/95 + 15/85
dieldrin	1.81	3.66(0.59),4.21(1.00)	5/95 + 15/85

Absolute retention time of aldrin was 4.8 min.

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