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Note

Derivatization of endrin, aldrin and dieldrin in biological material on thin-layer plates

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

Regional Forensic Science Laboratory, State of Maharashtra, Civil Lines, Nagpur (India)

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Two methods which have been employed for the confirmation of endrin are the use of zinc chloride in hydrochloric acid[1] and the sulphuric acid-catalyzed isomerization[2] of endrin to endrin ketone. Endrin is known to isomerize thermally[3], photochemically[4] and chemically in the presence of boron trifluoride[5]. Identification of dieldrin is based on its chemical transformation into the corresponding acetate, which on alkaline hydrolysis yields dieldrin ketone[1]. The endrin ketone has been characterized by its IR spectrum and the gas–liquid chromatographic (GLC) retention time, whereas the dieldrin derivative has been identified as the chlorohydrin of dieldrin by mass spectrometry and IR spectroscopy[3]. These derivatization processes are carried out in test-tubes followed by extraction of the derivative with *n*-hexane. Recently, efforts have been made to derivatize endrin as endrin ketone on a solid alumina–sulphuric acid matrix in a microcolumn[6]. However, this method is tedious and cannot be used for the routine detection of these insecticides.

This paper describes a simple and quick method for the derivatization of endrin, dieldrin and aldrin on thin-layer plates and the subsequent identification of the derivative as well as the parent compound on the same plate.

EXPERIMENTAL

Reagents

Anhydrous zinc chloride, *n*-hexane and acetone were all AnalaR reagents obtained from BDH (India). Silica gel G was purchased from E. Merck (Darmstadt, G.F.R.). The derivatizing reagent was prepared by dissolving 0.1 g of $ZnCl_2$ in 2 ml of concentrated hydrochloric acid and diluting to 25 ml with absolute ethanol. The Schiff reagent 0.2 g was prepared by dissolving of basic fuchsine in 120 ml of hot water, cooling, adding 20 ml of 10% w/v sodium hydrogen sulphite solution and 2 ml of HCl and finally diluting to 200 ml.

Procedure

The standard glass plates (10 × 20 cm) were coated to a thickness of 0.25 mm with a slurry of silica gel G in water (1:2) and then activated at 110° for 1 h before

* To whom correspondence should be addressed.

use. Ten micrograms of endrin, aldrin or dieldrin in hexane were spotted on to the pre-activated thin-layer plates which were then allowed to dry. The derivatization reagent was sprayed on to the dry spots and the plate was heated to 100° in an oven for 10 min. The plate was allowed to cool and then developed in a previously saturated chamber using hexane–acetone (4:1). After a run of *ca.* 12 cm, the plate was removed and allowed to dry at room temperature. The chromatogram was examined under UV radiation, then sprayed with the Schiff reagent. The R_F values of the different spots were noted (Fig. 1). Biological material containing low levels of lipids required no purification, whereas a clean-up step was necessary for material containing high levels of lipids[7].

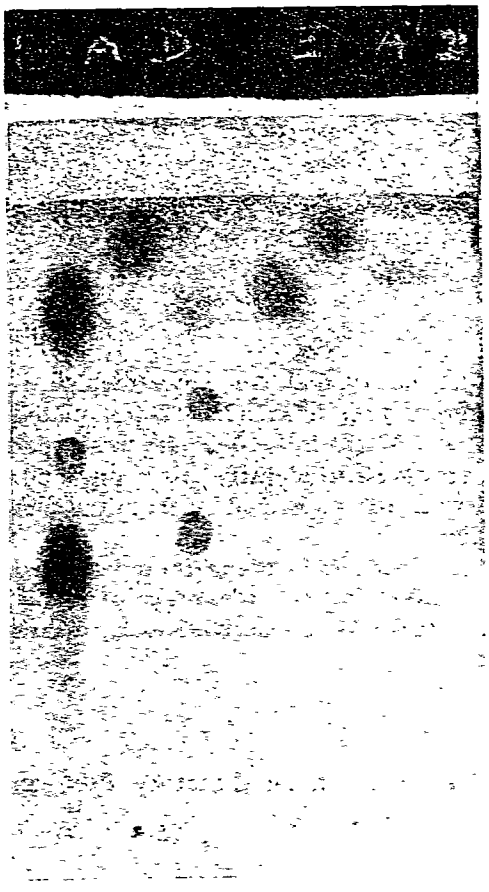

Fig. 1. The separation of endrin (E′), aldrin (A′) and dieldrin (D′) and their respective derivatives (E, A and D).

RESULTS AND DISCUSSION

A green fluorescence was observed for all of the spots when the plate was examined under UV radiation, and the spots gave purple colour with the Schiff reagent.

The R_F values are given in Table I. Endrin gives three (R_F 0.78, 0.36 and 0.56), dieldrin three (R_F 0.73, 0.39 and 0.61), and aldrin only one spot (R_F 0.92). The spot at R_F 0.78 was identified as that of endrin on the basis of a similar R_F value given by pure endrin in the same solvent system. The spot at R_F 0.36 was predominant, whereas that at 0.56 was very weak. It is known that endrin can be isomerized to the half-cage ketone as the major product and the aldehyde as the minor product[2]. Therefore it is obvious that the spot at R_F 0.36 is due to endrin ketone and that at R_F 0.56 is due to endrin aldehyde.

TABLE I

R_F VALUES OF ENDRIN, DIELDRIN, ALDRIN AND THEIR DERIVATIVES IN HEXANE–ACETONE (8:2)

Compound	R_F
Endrin	0.78
Endrin ketone	0.36
Endrin aldehyde	0.56
Dieldrin	0.73
Dieldrin ketone	0.39
Unknown	0.61
Aldrin	0.92

The spot at R_F 0.73 has been identified as that of dieldrin. Since dieldrin is converted largely into dieldrin ketone giving a major peak in GLC[2], it is postulated that the predominant spot at R_F 0.39 could be that of dieldrin ketone; the weak spot at R_F 0.61 could not be identified and work is in progress to identify this compound. Aldrin could not be converted into any of its derivatives, as is evident from the fact that it gave only one spot corresponding to aldrin.

The derivatization of endrin, dieldrin and aldrin *in situ* by the method described here is sensitive to 5 μg of each pesticide. The method has the advantage of simultaneous identification of the parent compounds as well as their derivatives by means of a simple thin-layer chromatography technique.

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