The Analytical Characteristics of Two Dieldrin Photoconversion Products

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Several products may be formed when the insecticide dieldrin is subjected to sunlight under field conditions or to ultraviolet light in the laboratory (1-6). After agricultural use of dieldrin (or aldrin), photoconversion products of dieldrin (PCPD) are formed and their residues may remain on food or feed products (1,2,4).

Because of this possibility of residue occurrence, we have investigated the application of the official AOAC multiresidue analytical method (7) to the determination of two dieldrin photoconversion products in foods. Several investigators (2,3) have reported that PCPD (Figure 1, proposed structure A) is formed after irradiation of dieldrin with UV light in the laboratory and after exposure of plants sprayed with dieldrin to sunlight. Henderson and Crosby (6) found that PCPD (Figure 1, proposed structure B) was formed when solutions of dieldrin were irradiated with UV light but was not formed when plants sprayed with dieldrin were exposed to sunlight.

Figure 1. Photoconversion products of dieldrin. A. Formed by irradiation of dieldrin with UV light and by exposure of dieldrin-sprayed plants to sunlight. B. Formed by irradiation of solution of dieldrin with UV light.

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Experimental

The AOAC official method for certain chlorinated and organophosphorus pesticides (7) was investigated for recoveries of PCPD-A and PCPD-B. Segments of the method were studied separately; recoveries were then determined with the complete method. Both compounds were carried through the method for fruits and vegetables, but only PCPD-A was studied with the method for dairy products and oils.

Gas Chromatography: Electron Capture

Retention times relative to aldrin and the quantities necessary for one-half full scale recorder deflection (½ FSD) were determined for PCPD-A and PCPD-B on two gas chromatographic columns with different liquid phases and with electron capture detection. Both columns were 6' x 4.5 mm i.d., operated at 200°C and with 120 ml nitrogen/min. The columns were packed with 10% DC-200 on 80/100 Gas Chrom Q and a 1:1 mixture of 15% QF-1 and 10% DC-200 on 80/100 Gas Chrom Q (8). The detector was operated at a sensitivity that gave ½ FSD for 1 ng heptachlor epoxide. Two different columns of each type were used for the determinations.

Thin Layer Chromatography

Migration distance relative to p,p'-TDE was determined for PCPD-A and PCPD-B with two thin layer systems: the plates were 8" x 8" with a 250 μ thickness of aluminum oxide adsorbent, and either n-heptane or 2% acetone in n-heptane (v/v) was used as a developing solvent. One plate for each solvent system was spotted alternately with 100 ng each of PCPD-A, PCPD-B, and p,p'-TDE. Chromatography was stopped when the solvent front had traveled 100 mm, and the spots were made visible with a silver nitrate spray.

Florisil Column Chromatography

The recovery of PCPD-A during Florisil column chromatography was determined on columns prepared from four different production lots of Florisil; these lots had lauric acid adsorption values (9) of 99, 92, 88, and 76 mg/g. The recovery of PCPD-B was determined in quadruplicate on one lot of Florisil having a lauric acid adsorption value of 76 mg/g.

The weight of Florisil used in each column was adjusted on the basis of the Florisil adsorption of lauric acid (9). Two milliliters of hexane containing 40 μg of the respective PCPD was added to each column and consecutive 200 ml portions of 6%, 15%, and 20% ethyl ether (containing 2% ethanol) in petroleum ether were used for elution. Each eluate was analyzed separately by electron capture gas chromatography.

Partitioning: Petroleum Ether to Acetonitrile

Duplicate 3 g portions of butteroil were fortified with 0.3 ppm PCPD-A, dissolved in 15 ml petroleum ether, and extracted with four 30 ml portions of acetonitrile saturated with petroleum ether. Acetonitrile was removed from the combined extracts by dilution with water in the presence of petroleum ether. The petroleum ether solution was cleaned up by Florisil column chromatography and analyzed by electron capture gas chromatography.

Fruits and Vegetables

Recoveries were determined using the appropriate section of the AOAC official method with one modification: 20% ethyl ether in petro-

leum ether was substituted for 15% ethyl ether in petroleum ether as the second eluant of the Florisil column. PCPD-A was added to 100 g samples of spinach at levels of 0.01 and 0.10 ppm and to 100 g samples of broccoli at 0.30 ppm. PCPD-B was added to 100 g samples of apples at 0.10 ppm.

Milk

Recoveries of PCPD-A from milk were determined using the appropriate section of the AOAC method with the same modification in the Florisil column elution as for fruits and vegetables. PCPD-A was added to milk at a level of 0.50 ppm on a fat basis. The second eluate from the Florisil column was saponified, as outlined in the method, to provide a solution sufficiently free of fat to permit gas chromatographic determination. Recovery of PCPD-A was also attempted through the magnesia column cleanup as described in the method.

Results

Results of the various recovery experiments shown in Tables I-V indicate that dieldrin photoconversion products A and B would be determined by the AOAC official method for fruits and vegetables. Use of the 15% ethyl ether in petroleum ether eluant specified in the official method would result in only slightly reduced recoveries, as indicated in Table III.

TABLE I

Gas Chromatography Electron Capture Detection

	RRT_{Aldrin}		Amount Needed for ½ FSD, ng	
Liquid Phase	PCPD-A	PCPD-B	PCPD-A	PCPD-B
10% DC-200	4.3	1.40	6	2
15% QF-1/10% DC-200	7.5	1.86	10	2.3

TABLE II

Thin Layer Chromatography

Migration Relative to p,p'-TDE

Mobile Solvent	PCPD-A	PCPD-B
n-Heptane	0.0	0.42
2% Acetone/n-heptane	0.2	0.85

TABLE III

Florisil Column Chromatography

	Recovery, %	
Eluant[a]	PCPD-A[b]	PCPD-B[c]
6% Ethyl ether/petroleum ether	0	0
15% Ethyl ether/petroleum ether	94	95
20% Ethyl ether/petroleum ether	< 5	0

[a] Successive 200 ml portions.

[b] Average of results from 4 lots of Florisil.

[c] Average of 4 results from single lot of Florisil.

TABLE IV
Recovery of PCPD from Fruits and Vegetables

Added, ppm	Sample	Recovery, %
	PCPD-A	
0.01	Spinach	100, 104
0.10	Spinach	100
0.30	Broccoli	93, 100
	PCPD-B	
0.10	Apples	96, 99, 93

TABLE V
Recovery of PCPD-A from Milk and Butter

Added, ppm	Sample	Recovery, %
0.3	Butter	96, 110
0.5	Milk	86, 81[a,b]

[a] Includes additional cleanup by saponification.

[b] PCPD-A not recovered through magnesia column cleanup.

PCPD-A can be determined in milk and oils, although additional cleanup of the Florisil may be necessary. Recoveries of 81 and 86% were obtained after saponification (Table V); PCPD-A was not recovered through the MgO-Celite column. The method for fatty foods was not applied to PCPD-B.

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