Chlorinated Hydrocarbon Insecticide Residues in Ground Beetles (*Harpalus pensylvanicus*) and Iowa Soil[1]

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Predation of ground beetles (Coleoptera: Carabidae) upon western corn rootworms, *Diabrotica virgifera* LeConte, and European corn borer, *Ostrinia nubilalis* (Hübner), has been observed (KIRK 1971, 1973). Because of these observations, the potential of carabid beetles as biological control agents of insect pests of corn is under investigation. Because of the large quantities of insecticides applied to corn cultivars, carabids may be adversely affected by both short-lived organophosphorous and carbamate insecticides as well as by the more persistent chlorinated hydrocarbon insecticides. Quantities of the latter found in the bodies of carabids (*Harpalus pensylvanicus*) taken from Iowa cornfields are reported herein.

MATERIALS AND METHODS

Carabids were obtained during the summer of 1973 by pitfall trapping (THORVILSON 1969). Live beetles were returned to the laboratory and held in tightly closed glass jars at -10°C until analyzed. With the methods of THOMPSON (1972) as a guide, batches of approximately 50 beetles were weighed, then ground with Na_2SO_4 and hexane (Nanograde®, Mallinckrodt Chemical Works, St. Louis, MO) with a mortar and pestle. After vacuum filtration, the beetle fragments and Na_2SO_4 were placed in a glass thimble and extracted with hexane for 2 hr in a Soxhlet apparatus. The mortar and Soxhlet extracts were combined and partitioned with acetonitrile to separate lipids from insecticides, which were then partitioned back into hexane. Extracts were cleaned up on Florisil columns by the method of FAY and NEWLAND (1972).

The gas chromatograph used was a Packard, Model 7821, with dual-column oven equipped with an electron capture detector. Operating temperatures (°C) were: injector 220, column 190, detector 220, outlet 200. Aliquots were injected into glass

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columns (4-mm x 132-cm) packed with 1.5% OV-17/1.95% QF-1 on a solid support of Chromosorb WHP, 100/120 mesh. The carrier gas flow rate was 100 ml/min of prepurified nitrogen (Matheson Gas Products, Joliet, IL). The column used for confirmation of insecticide identity was packed with 5% OV-210 on Chromosorb WHP, 80/100 mesh, with a nitrogen flow rate of 60 ml/min. Column packing materials were obtained from Supelco, Inc. Bellefonte, PA.

Quantities of insecticide residues were determined by the peak height ratio method by using known standards. The limit of detectability of each of the standards was 5 ppb. Recovery of known amounts of standard insecticides from blank samples was 90-100%; therefore, the residue data were not corrected for percentage recoveries.

Thin-layer chromatography was used to confirm identifications made by gas chromatography. The methods outlined in U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE (1969) were used with some modifications as noted. To insure detectable quantities of insecticide, five 5-ml samples of each Florisil column eluate were pooled and reduced to ~0.05 ml. Most of the sample was then spotted on aluminum oxide F-254, neutral type E, coated on aluminum sheets (Brinkmann Instruments, Inc., Des Plaines, IL). The sheet spotted with the 5%-ether Florisil column eluate was developed in one direction only with heptane. The 15%-ether eluate (containing dieldrin) was spotted on another plate, developed in acetonitrile for a distance of 15 cm, dried, turned 180°, and redeveloped in heptane [see section 411.5(3), U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE (1969)].

Visualization of standards (400 ng each) was by $AgNO_3$ spray and UV light, but insecticides in the beetle extracts were detected by eluting them from the Al_2O_3 coating and injecting them into the GLC. Details of this technique are given in THOMPSON (1972) section 12, B-VIII.

Extraction of residues from soil was by shake extraction (NASH et al. 1973) followed by Florisil column clean-up and gas-liquid chromatography. Ten-gram samples of soil were used for each extraction.

RESULTS

The quantities and kinds of chlorinated hydrocarbon insecticides are listed in Table 1. Amounts are expressed as parts per billion; i.e., ng of insecticide/g wet weight.

TABLE 1
Chlorinated hydrocarbon insecticide residues in carabid beetles from Iowa cornfields, 1973.

Sample/ replicate	Residues (ppb)[a] Aldrin	Dieldrin	Hepta-chlor	Heptachlor epoxide	p,p'-DDE	p,p'-DDT
1/1[b]	2.4	29.1	1.7	10.2	98.1	2.4
1/2	4.4	31.8	tr	9.3	94.2	3.2
1/3	4.2	34.4	2.9	7.2	67.7	1.5
1/4	3.0	26.4	2.9	7.3	55.9	1.7
1/5	2.1	38.6	2.0	tr	76.4	3.1
1/6	3.1	34.5	1.6	7.6	60.3	1.4
2/1	3.1	27.6	2.4	8.8	60.7	1.7
3/1	11.1	87.1	4.3	15.5	104.4	tr
3/2	11.9	66.7	2.6	17.4	115.5	3.1
3/3	2.4	28.1	1.7	10.2	119.4	4.2
3/4	22.8	29.3	2.7	13.3	113.3	6.7
3/5	20.4	30.4	6.9	tr	114.0	4.0
3/6	4.3	48.2	1.6	10.0	68.1	3.8
Average	7.3	39.4	2.6	9.0	88.3	2.8

[a]Expressed as ng of insecticide per gram of wet weight of beetles

[b]Number of beetles per replicate ranged from 23 to 50; total number of beetles analyzed: 562

The finding of an average amount of 88 ppb of p,p'-DDE is somewhat surprising since DDT (the parent compound) had not been used on this field for several years. It is possible, of course, that these highly motile beetles actually picked up the reside in another area. The recovery of approximately 40 ppb of dieldrin is understandable because aldrin (the parent compound) has been widely used for corn rootworm control, although not in this particular field, in the last few years. The persistence of these compounds is well documented and is verified in the present study. Smaller amounts of p,p'-DDT and heptachlor were found, probably because these are metabolized to p,p'-DDE and heptachlor epoxide, respectively,

The lipid content of each batch of beetles was determined and plotted against total insecticide residue recovery. The graph did not reveal a linear relationship in which greater amounts of lipid contained greater amounts of insecticide as one might expect. KORSCHGEN (1970) also noted this lack of relationship between lipid and insecticide content, even though this class of insecticides is highly soluble in lipids. The actual amounts of insecticides recovered by KORSCHGEN (1970) from Harpalus pensylvanicus taken from aldrin-treated fields in Missouri were 0.11 ppm aldrin, 0.99 ppm dieldrin, and 0.26 ppm DDT + DDE + DDD. These amounts are greater than those reported in Table 1.

Insecticides from soil taken near the beetle-collecting sites in Iowa are presented in Table 2.

TABLE 2

Chlorinated hydrocarbon insecticide residues in soil[a] from location where carabid beetles were collected for residue analysis, 1973.

Sample[b]	Residues (ppb)					
	Aldrin	Dieldrin	Hepta-chlor	Heptachlor epoxide	p,p'-DDE	p,p'-DDT
A	tr	3.0	-[c]	-[c]	44.7	49.4
B	6.4	84.0	-	-	3.0	14.0
C	tr	2.4	-	-	21.5	24.2
D	10.6	65.8	-	-	27.2	37.3
Average	4.2	38.8	-	-	24.1	31.2
Composite[d]	4.0	45.2	-	-	27.3	34.5

[a]Clarion-Webster soil type

[b]Each sample from separate collecting site

[c]Not detected

[d]Soil samples A-D mixed before extraction

Because individual samples (A-D) varied in residue content, a composite was made preceding extraction. Insecticidal content of this composite agreed closely with the average of the individual samples. Amounts of aldrin and dieldrin were similar to those found in the beetles. In contrast, soil amounts of DDT were higher, and amounts of DDE lower, than in beetles. It is reasonable to assume that carabid beetles are like most other insects in that they can metabolize DDT (toxic) to DDE (nontoxic) (O'BRIEN 1967) and therefore accumulate DDE in their body tissue.

KORSCHGEN (1970) found approximately 15 times more aldrin and 5 times more dieldrin in aldrin-treated soils in Missouri, but the combined amounts of DDT, DDE, and DDD from those fields were almost exactly the same as the quantity of DDT plus DDE reported in this study of Iowa soil. As indicated in Table 2, no heptachlor or heptachlor epoxide was detected in the Iowa soil samples.

DISCUSSION

Although amounts of chlorinated hydrocarbon insecticides ranging from ~2 to 90 ppb have been detected in carabid beetles, the relationship of these quantities to LD_{50} values has not been established. Future bioassays will determine the extent of resistance of these beetles, not only to chlorinated hydrocarbon insecticides, but also to organophosphorus and carbamate insecticides.

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