Toxicity-Metabolism Relationship of the Photoisomers of Cyclodiene Insecticides in Freshwater Animals

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The residual cyclodiene insecticides aldrin (A), dieldrin (D), heptachlor (H) and isodrin (I) can be converted by sunlight and ultraviolet light to their corresponding respective photoisomers photoaldrin (PA), photodieldrin (PD), photoheptachlor (PH) and photoisodrin (PI) (1,2,3,4). PA, PD and PH appear to be more toxic than their parent compounds to adults of the housefly, Musca domestica L. and larvae of the mosquito, Aedes aegypti L. (3,5,6). The increased toxicity of PA, PD and PH observed with faster speed of their toxic action is related with their metabolism to more toxic lipophilic ketones (5,7). On the other hand, the toxicity of PI is greatly reduced due to its rapid detoxification by these insects (3,5).

The toxicity-metabolism relationship of the photoisomers of cyclodienes has not been investigated in freshwater animals. Since these extensively used cyclodiene insecticides will persist in the environment, the photoisomers and their lipophilic ketones may cause ecological hazards if introduced in animal food chains (8). A study was therefore carried out to determine if the increased toxicity of these photoisomers to freshwater animals (9) was due to the faster onset of their toxic symptoms and whether this could be related with their metabolism as observed with insects. Results of a preliminary investigation of the toxicity-metabolism relationship of these photoisomers are presented for freshwater crustacea, fish and tadpoles.

Experimental

The animals were either collected in the field or purchased from local suppliers. Bass and bluegills were donated by the Illinois State Hatchery. The animals were acclimated gradually from habitat water to distilled water for at least 5 days before testing. Fish, tadpoles and crayfish were exposed to insecticide suspension in 200 ml water in 1-pint mason jars which were constantly aerated. Each jar contained no more than 4 animals with at least 5 replicates. Microcrustacea were exposed in 25 ml of water in plastic petri dishes using 5 replicates of 10 animals per dish.

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Each experiment was repeated at least two times and the average % mortality values were plotted against log exposure time to determine LT_{50} (lethal time to kill 50% of test animals during continuous exposure to a fixed concentration of the insecticide).

To study the production of the photodieldrin ketone from PD, the animals were injected with 120 nanogram of PD in methylcellusolve. The products were extracted with hexane and analyzed by gas chromatography using authentic compounds (5).

Results and Discussion

Species differences in susceptibility to the photoisomers of cyclodiene insecticides have been reported. For example, based on the LC_{50} values, the sensitivity of animals to photoisomers decreases in the following order: mosquito larvae > isopods > minnows > bluegills (9). Also, PA is the most and PI the least toxic to these animals. The increased toxicity of the photoisomers over their parent compounds is due to faster speed of toxic action as seen in Table 1.

Table 1

Animal	LT_{50}:x10 min. of continuous exposure*					
	A	PA	D	PD	I	PI
1. *Daphnia pulex*	29	20	28	22	18	38
2. *Asellus* spp.	16	8	8	5	4	6
3. *Gammarus* spp.	20	10	18	8	15	35
4. *Cambarus* spp.	114	39	100	20	20	100
5. *Gambia affinis*	-	-	9	3	6	13
6. *Pimephalus promelas*	9	7	10	8	6	13
7. *Lepomis macrochirus*	36	10	>36	7	36	44
8. Tadpoles	-	-	5	3	-	-

* The concentrations (p.p.m.) used were: 1 for animal No. 1, 2, 3, 5 and 8; 1.8 for No. 4; 0.7 for No. 6; 0.24 of A, D, PA, PD and 0.24 of I and PI for No. 7.

Considering the LT_{50} values isopods, tadpoles and fish seem to be more sensitive than crayfish and amphipods to cyclodienes. PA and PD are faster in their action than A and D while PI is the slowest acting compound. These differences are species specific. The toxicity of PA and PD is increased 3-5 fold for crayfish, bluegills and minnows and 1.3-2.2 fold for the other animals. On the other hand, PI is 3-5 times less toxic to crayfish and about 1.2-2.3 times less to the other animals. Thus the photoisomerization of A and D to PA and PD, respectively can be hazardous to the crayfish, bluegills and minnows.

In houseflies and mosquitoes, the increased toxicity as compared with A and D has been shown to be due to their rapid conversion to more toxic photodieldrin ketone (5,7). PDK produced from PA and PD is 2-3 times more toxic than PA and PD to these insects (5,7). A similar relationship between toxicity and metabolism may be possible in these aquatic animals. The rate of *in vivo* formation of PDK from PD correlates well with the toxicity of the latter to these animals (Table 2).

Table 2

Animal	LT_{50} to PD: min.	Amount Recovered ng/animal PD	PDK
Crayfish	20	30.8	82.4
Guppies	40	58.9	40.6
Goldfish	90	87.9	13.2
Tadpoles	20	24.0	78.4

These results obtained by injecting PD also indicate that the degree of sensitivity of these animals may depend mainly on their metabolism. Experiments are in progress to evaluate the toxicity of PDK to these animals to confirm these findings.

Since cyclodiene insecticides, especially aldrin and dieldrin, have been and are still being used extensively, their residues will persist in the environment for several years. As these residues can be converted to photoisomers by sunlight (1-4) and microorganisms (10), which in turn can be metabolized to lipophilic ketones in animals as in the case of PA and PD and possibly PH, their hazard can be greatly

magnified by accumulation and biological concentration of the ketones through food chains. Thorough investigations of the analysis of these photoisomers and their ketone in the environment and in animal food chains must be carried out now to prevent ecological hazards (8,11,12).

Summary

The onset of toxic symptoms of photoaldrin and photodieldrin is 3-5 times faster than aldrin and dieldrin in crayfish, bluegills and minnows and 1.3-2.2 times in other animals. Photoisodrin is 3-5 times slower than isodrin in its toxic action against other animals tested. The increased toxicity of photoaldrin and photodieldrin is apparently related to the rate of *in vivo* formation of more toxic ketones as observed with photodieldrin.

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