Bull. Environm. Contam. Toxicol. 25, 950-955 (1980)

Lethality of Permethrin, Cypermethrin and Fenvalerate to Salmon, Lobster and Shrimp

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The 96-h lethal thresholds for the pyrethroid insecticide, permethrin [3-phenoxybenzyl (±) cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, NRDC 143] range between 1 and 140 µg/L for several fish species and between 0.4 and 7 µg/L for aquatic invertebrates (ZITKO et al. 1977, 1979; JOLLY et al. 1978; MULLA et al. 1978; COATS & O'DONNELL-JEFFERY 1979; LINDÉN et al. 1979). Two pyrethroids with α-cyano substitution of the phenoxybenzyl alcohol moiety, cypermethrin [(±)α-cyano-3-phenoxybenzyl (±) cis, trans-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropanecarboxylate, NRDC 149] and fenvalerate [(±)α-cyano-3-phenoxybenzyl (±)α-2-(4-chlorophenyl)-3-methyl butyrate, S 5602] are more toxic to aquatic organisms than permethrin (COATS & O'DONNELL-JEFFERY 1979; MULLA et al. 1978; LINDÉN et al. 1979).

The purpose of this study is to determine the lethality of permethrin, cypermethrin and fenvalerate to juvenile Atlantic salmon (Salmo salar), lobsters (Homarus americanus), and shrimp (C. septemspinosa) as part of a continuing study of the structure-activity relationships of pyrethroids. The lethality of cypermethrin is compared with the lethality-octanol/water partition coefficient relationship derived for pyrethroid insecticides (ZITKO et al. 1979). Uptake of pyrethroids was determined from analysis of dead animals.

EXPERIMENTAL

Materials: Permethrin (Technical, 92.1%) was supplied by Chipman Chemicals Ltd. Cypermethrin (Technical, 98.5%) and fenvalerate (Technical, 98.0%) were obtained from Shell Canada Ltd.

Lethality tests: Pyrethroids were dissolved in ethanol for addition to test solutions. Tests were static and of 96-h duration with temperatures maintained at 10°C (ZITKO et al. 1979). The toxicant solutions were aerated gently and changed at 48-h. Three salmon (average length, 6.2 cm; average weight, 5.3 g) were exposed in 3 L of test solution. Three lobsters (about 450 g each) were tested in 30 L and three shrimp (about 1.3 g each) were tested in 2 L of solution. Each compound was tested with each species at not less than six concentrations for a minimum of 18 animals per experiment.

0007-4861/80/0025-0950 $01.20

Analysis: Concentration of pyrethroids in water was measured in selected lethality tests at 0.5, 2, 6, 24 and 48 h. Water samples (100 mL) were acidified with 2 mL concentrated HCl and passed through 12 g of XAD-2 resin in a 2.5-cm O.D. glass column. For seawater samples, the column was washed with 500 mL distilled water, which was collected and extracted with 9 mL pesticide grade hexane. The extract was later combined with the hexane extract of column eluent. Pyrethroids were eluted from the columns with 60 mL pesticide grade acetone after the solvent equilibrated in the column for 30 min. Compounds were extracted from the eluent with with 30 mL of hexane. These extracts were concentrated on a rotary evaporator and analyzed by gas chromatography. The efficiency of extraction of each compound was determined for water samples fortified at concentrations representative of those in lethality tests.

Whole fish and shrimp, and the hepatopancreas of lobsters were frozen as soon as possible after death of the animals. Tissues were ground with anhydrous sodium sulfate and pyrethroid residues were Soxhlet-extracted. Permethrin was extracted with hexane and cleaned up by the method of ZITKO et al. (1977). Cypermethrin and fenvalerate were extracted with 100 mL of 50:50 pesticide grade acetone-hexane for 1 h . Water was removed from the extract by passing a 30-mL aliquot through 25 g of sodium sulfate and eluting with 20 mL hexane. An aliquot was dried in a rotatory evaporator to determine lipid content. An aliquot not exceeding 50 mg lipid was applied in 1.5 mL of 80:20 pesticide grade hexane-benzene to a glass column (0.7 cm O.D.) containing 6 g alumina prepared as described by ZITKO et al. (1974). The column was washed with 80:20 hexane-benzene and the first 40 mL of eluent discarded. The next 30 mL of eluent was collected and concentrated on a rotatory evaporator. The procedural recovery of pyrethroids from tissue was determined for fortified salmon tissue.

Instrument conditions: Extracts were analyzed on a gas chromatograph equipped with a ^{63}Ni detector. The 2 m x 2 mm I.D. glass column was packed with 3% OV-101 on 80/100 mesh Chromosorb W-HP. Instrument temperatures for permethrin analysis were 240, 215, and 300°C for injector, column and detector, respectively. The column temperature was 230°C for analyses of cypermethrin and fenvalerate.

Calculations: Time to 50% mortality (LT50 in h) at a test concentration was estimated by probit analysis. LC50's (96 h) were calculated as the geometric mean of the highest concentration without and the lowest concentration with 50% mortality. Also, lethal thresholds were calculated from lethality lines by the method of ZITKO (1979).

The average concentrations of compounds in lethality tests were calculated according to ZITKO et al. (1977).

Octanol/water partition coefficients (P) of substituents in position 3 of dimethylcyclopropanecarboxylic acid and of the alcohol moieties of permethrin and cypermethrin were calculated according to LEO (1975).

RESULTS AND DISCUSSION

Concentration in water: Extraction efficiency of permethrin, cypermethrin and fenvalerate averaged 74, 68 and 69% from fresh water and 83, 81 and 74% from seawater, respectively. The concentrations of compounds in lethality tests decreased exponentially according to the equation: $C = ae^{-bt}$, where C = concentration relative to the maximum, t = time in h, and a,b = empirical coefficients. The coefficients a,b for tests with salmon, lobster and shrimp are listed in Table 1.

TABLE 1. Empirical coefficients a and b for the exponential decrease of the concentrations of pyrethroid compounds in lethality tests.

Compound	Salmon tests		Lobster tests		Shrimp tests	
	a	b	a	b	a	b
Permethrin	0.92	0.022	1.0	0.042	0.97	0.028
Cypermethrin	0.82	0.016	0.74	0.022	0.56	0.008
Fenvalerate	1.0	0.013	0.95	0.030	0.92	0.024

Lethality: The 96-h LC50's and the lethal thresholds for salmon, lobsters and shrimp (Table 2) indicate that the two cyano-substituted compounds are more toxic than permethrin, and that the invertebrates are more sensitive than salmon to each of these pyrethroids.

TABLE 2. The 96-h LC50's and lethal thresholds for three pyrethroids to three species.

Test organism	Compound	96-h LC50[a] (µg/L)	Lethal threshold[b] (µg/L)
Salmon	Permethrin	12	5.00
	Cypermethrin	2.0	2.4
	Fenvalerate	1.2	0.46
Lobster	Permethrin	0.73	0.68
	Cypermethrin	0.04[c]	0.04[c]
	Fenvalerate	0.14	0.08
Shrimp	Permethrin	0.13	0.29
	Cypermethrin	0.01	0.005
	Fenvalerate	0.04	0.05

[a]96-h LC50 calculated by geometric mean.
[b]Lethal threshold calculated according to ZITKO (1979).
[c]Partial mortalities (66%) at 0.025 and 0.005 µg/L indicate values may be as low as 0.003 µg/L.

As expected, in most cases the calculated lethal thresholds were similar to or less than the corresponding LC50's. The exception is permethrin and shrimp, where a large difference between the two concentrations used in calculating the geometric mean (0.06 and 0.3 µg/L) may have resulted in an underestimation of the 96-h LC50.

The 96-h LC50 for permethrin and salmon agrees closely with the previously reported value of 8.8 µg/L (ZITKO et al. 1977, 1979). The LC50's for the pyrethroids and salmon were within the range reported for other fish species (JOLLY et al. 1978; MULLA et al. 1978), but below those reported for rainbow trout (COATS & O'DONNELL-JEFFERY 1979). The 96-h LC50 of permethrin for lobsters is an order of magnitude lower than the previously reported value of 7.0 µg/L (ZITKO et al. 1979). Additional tests at that time provided lower LT50's in 7 of 10 tests and the current results indicate that the previously reported value was overestimated. The values for permethrin and lobsters and shrimp were similar to the LC50 reported for a freshwater crayfish (JOLLY et al. 1978).

ZITKO et al. (1979) concluded that the α-cyano substitution of the phenoxybenzyl alcohol moiety increases the lethality of pyrethroids, and that pyrethroids with (1R)-cis isomers of the acid moiety are more lethal than corresponding cis, trans racemates. Like other α-cyano substituted pyrethroids, cypermethrin is more toxic to salmon than predicted from the relationship between octanol/water partition coefficients and 96-h LC50's (Table 3). Also, the LC50's of cypermethrin for salmon (2.0 µg/L) and lobsters (0.04 µg/L) are higher than those of its (1R)-cis isomer, NRDC 168S (salmon, 0.74 µg/L; lobsters, 0.0003 µg/L; ZITKO et al. 1979).

Since the acid moiety of fenvalerate does not consist of dimethylcyclopropane carboxylic acid but consists of chlorophenyl butyric acid, the octanol/water partition coefficient-lethality relationship for salmon cannot be tested for this compound.

TABLE 3. Partition coefficient (Σ log P*) and observed and predicted 96-h LC50's (µmole/L).

Compound	log P*[a]	LC50 (µmole/L) x 10^3		
		Salmon	Lobster	Shrimp
Permethrin	3.95	15.4[b] (12)[c]	1.9	0.33
Cypermethrin	2.44	2.4[b] (12)[c]	0.09	0.02
Fenvalerate	-	2.9	0.33	0.10

[a]Sum of calculated log octanol/water partition coefficients of the alcohol moiety and 3-substituent on the cyclopropane ring.
[b]Observed LC50's divided by 2 to correct for presence of cis, trans racemates (ZITKO et al. 1977).
[c]Predicted LC50's in brackets calculated from Z = 0.397 Σlog P* 0.448, where Z = log 96-h LC50 (µmole/L) relative to that of pyrethrins (ZITKO et al. 1977).

However, the 96-h LC50 of fenvalerate to salmon (Table 3) is within the range of LC50's for three other pyrethroids with -cyano substitution of the phenoxybenzyl alcohol moiety. They are cypermethrin (Table 3), decamethrin and NRDC 168S with LC50's of 3.9 and 1.8 µmoles/L, respectively (ZITKO et al. 1979). The log P values of these three pyrethroids and fenvalerate, calculated for the entire compound, range from 4.2 to 4.5 (ZITKO, unpublished). This range is too narrow to permit the derivation of a relationship between lethal threshold and log P.

Uptake from water: Our procedural recovery for permethrin, cypermethrin and fenvalerate from fortified salmon tissue were 96, 73 and 55%, respectively. Over approximately 96-h, salmon concentrated the pesticides by factors of 73 for permethrin, 7 for cypermethrin and 200 for fenvalerate (Table 4). The relatively low concentration factors (CF) for salmon and permethrin approximate previous data (ZITKO et al. 1977). The octanol/ water partition coefficients determined by COATS & O'DONNELL-JEFFERY (1979) for permethrin (3,100), cypermethrin (30,000) and fenvalerate (27,000) indicate that cypermethrin is the most lipid-soluble of the three pyrethroids. The low CF's for cypermethrin (Table 4) may indicate rapid metabolism and elimination of the compound by salmon. Pyrethroids were not detected (detection limit = 5 ng/g) in lobster hepatopancreas or in shrimp, probably as a result, in part, of the low test concentrations.

TABLE 4. Concentration and concentration factors (CF = conc. in fish/conc. in water) for pyrethroids in salmon from various toxicity tests.

Compound	Conc. in water (µg/L)	Exposure time (h)	Conc. in fish (µg/g)	CF
Permethrin	85	10	1.2	14
	42	14	1.0	24
	21	17	0.90	43
	6.9	89	0.50	73
Cypermethrin	12	12	0.04	3.5
	7.8	21	0.02	2.6
	3.0	62	0.02	6.7
	1.4	96	0.01	7.1
Fenvalerate	9.3	16	0.37	40
	4.1	54	0.43	100
	2.0	54	0.30	150
	0.8	96	0.16	200

Acknowledgements. J. Galbraith assisted in laboratory work. Manuscript was reviewed by K. Haya and D. J. Wildish.

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