

Toxicity of Permethrin, Decamethrin, and Related Pyrethroids to Salmon and Lobster

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The lethalities of permethrin [3-phenoxybenzyl (1R)-*cis*, *trans*-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate, NRDC 143], its 1R-*cis*-isomer (NRDC 167), decamethrin [(S)- α -cyano-3-phenoxy benzyl (1R)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate, NRDC 161], and its dichloro analogue (NRDC 168S) to juvenile Atlantic salmon (*Salmo salar*) and adult lobster (*Homarus americanus*) were determined.

As expected from the insecticidal activity patterns (ELLIOTT 1977), 1R-*cis* permethrin is more lethal than permethrin to both salmon and lobsters. The lethalities of the cyano-substituted pyrethroids are higher than one would expect from the lethality-octanol/water partition coefficient relationship, derived previously (ZITKO et al. 1977).

EXPERIMENTAL

Materials

NRDC 143 was obtained from Chipman Chemicals Limited, NRDC 161, 167, and 168S from Procida/Roussel Uclaf. DECIS^R EC-25, a formulation containing NRDC 161 at 25 g/l, was supplied by the Chemical Control Research Institute, Ottawa.

Lethality tests

Pyrethroids, dissolved in ethanol, were added to water in the test containers.

Static tests in 4-l Erlenmeyer flasks with 3 fish/test were conducted as described previously (ZITKO et al. 1976). Juvenile Atlantic salmon, average length 9.6 cm, average weight 9.4 g, were used and the water temperature was 10 C. Test solutions were renewed at 48 h and tests were terminated at 96 h.

The lobster tests were conducted in fibreglass

tanks with 30 l of sea water, 5 lobsters/test with permethrin and 3 lobsters/test with the other compounds. Each lobster weighed about 450 g. The solutions were renewed at 48-h intervals, temperature was 10 C, and salinity was 30‰. Dissolved oxygen was maintained at about 8 ppm by gentle aeration.

Time to 50% mortality (LT50 in h) was estimated by probit analysis (LITCHFIELD 1949). Each compound was tested at 5-6 concentrations. Lethal thresholds (96 h) were calculated as the geometric mean of the highest concentration without and the lowest concentration with mortality. The former was not less than 50% of the latter. The lobster tests were continued beyond 96 h, and longer term thresholds were also calculated where appropriate.

Analysis

The concentrations of the compounds were monitored throughout the lethality tests after 0.5, 2, 4, 8, 24 and 48 h. The treatment of the freshwater samples has been described previously (ZITKO et al. 1977). For sea water, a 1 l sample was siphoned from the test tanks with vacuum assist and passed through a precleaned Amberlite XAD-2 resin column at 50 ml/min. After sampling, the column was washed with 100 ml of distilled water. Pyrethroids were eluted with 25 ml of pesticide-grade acetone. The eluent was partitioned with pesticide-grade hexane (3 x 10 ml). The extracts were combined, concentrated on a rotary evaporator, and analyzed by gas chromatography. Recovery of each compound by XAD-2 resin was determined, using spiked seawater samples covering the range of concentrations to be sampled.

Instrumental conditions

A Varian Model 600D gas chromatograph with a tritium EC detector was used as described by ZITKO et al. (1977), for analysis of the compounds from fresh water and 3 of the compounds from seawater tests. Permethrin (NRDC 143) from seawater tests was analyzed with a Packard Model 803 gas chromatograph with an Analog Technology Corp., wide-range tritium EC detector. A 6 ft x 1/4 inch glass column, containing 4% SE-30 on 100/200 mesh Chromosorb W, was operated at 215 C and a nitrogen flow rate of 80 ml/min.

Partition coefficients

Octanol/water partition coefficients (P) of substituents in position 3 of dimethyl cyclopropane-carboxylic acid and of the alcohol moieties were calculated according to LEO (1975).

RESULTS AND DISCUSSION

Concentration in water

The concentrations of the compounds decreased exponentially during the tests (Table 1) according to the equation $C = a \exp(-bt)$, C = relative concentration, t = time in h, and a, b = empirical coefficients.

TABLE 1

Empirical coefficients a and b for the compounds in fresh and sea water.

<u>Compounds</u>	<u>Fresh Water</u>		<u>Sea Water</u>	
	a	b	a	b
Permethrin (NRDC 143)	0.709 ^a	0.029 ^a	0.894	0.049
(1R)- <i>cis</i> -permethrin (NRDC 167)	0.494	0.038	0.922	0.016
Decamethrin (NRDC 161)	0.515	0.006	0.746	0.033
DECIS ^R 25 EC	0.745	0.016	-	-
NRDC 168S	1.450	0.029	0.867	0.011

^aFrom ZITKO et al. (1977)

Average concentrations during the tests were calculated according to ZITKO et al. (1977).

Lethality

The lethal thresholds and coefficients A and B for the lethality lines [$\log LT50 = A \log C + B$, $LT50$ in h, C in $\mu\text{g}/\ell$] for salmon and lobsters are listed in Table 2.

The lethality of DECIS^R is higher than that of the pure active ingredient (decamethrin), possibly due to the presence of surfactants and other additives.

TABLE 2

96-h Lethal thresholds L ($\mu\text{g}/\ell$) and coefficients A,B of lethality lines ($\log \text{LT}_{50}$) = A \log C+B, LT_{50} in h, c in $\mu\text{g}/\ell$).

Compound	Atlantic Salmon			Lobster		
	L	A	B	L	A	B
Permethrin ^a (NRDC 143)	8.80	-0.31	1.95	7.00 ^b	-0.91	2.69
(1R)- <i>cis</i> -permethrin (NRDC 167)	1.34	-0.84	1.94	0.40 ^c	-1.04	1.54
Decamethrin (NRDC 161)	1.97	-1.17	2.32	0.0014	-0.39	0.65
DECIS ^R 25 EC	0.59	-1.01	1.77	Not tested		
NRDC 168S	0.74	-1.07	1.74	0.0003	-0.64	-0.34

^aFrom ZITKO et al. (1977)

^bL = 0.76 at 650 h

^cL = 0.20 at 160 h

The relationship between octanol/water partition coefficient and lethal threshold to juvenile Atlantic salmon (ZITKO et al. 1977) is not applicable to the cyano-substituted pyrethroids, decamethrin and NRDC 168S, which are considerably more toxic than predicted (Table 3). The presence of an α -cyano group in the alcohol moiety decreases the degradability of the molecule in mammals by both hydrolases and oxidases (SODERLUND and CASIDA 1977), and the data in Table 3 indicate the possibility of a similar effect in salmon and, particularly, in lobster. For comparison, the lethalities of NRDC 167 and decamethrin, relative to permethrin, are 4 and 26 in houseflies, and 2.5 and 6 in Mexican beetles (MARTER and COLAS 1976).

Pyrethroids containing 3-dimethylvinyl chrysanthemic acid moiety appear to be less lethal to juvenile Atlantic salmon than predicted. This has been noticed previously (ZITKO et al. 1977) in the case of dimethrin and additional data (MIYAMOTO 1976) for fenothrin, furamethrin, and tetramethrin seem to confirm this observation.

TABLE 3

Partition coefficients ($\Sigma \log P^*$), lethal thresholds (L, $\mu\text{mole}/\%$) and relative lethality.

Compound	$\Sigma \log P^*{}^1$	L			
		Salmon		Lobster	
		Actual $\times 10^3$	Predicted ² Relative	Actual $\times 10^3$	Relative
Permethrin (NRDC 143)	3.95	22.6	1	17.9	1
(1R)- <i>cis</i> -permethrin (NRDC 167)	3.95	3.44	11.5	1.03	17
Decamethrin (NRDC 161)	2.72	3.90	78.3	2.77×10^{-3}	6500
NRDC 168S	2.44	1.78	12.3	0.73×10^{-3}	24000

¹Sum of calculated octanol/water partition coefficients of the alcohol moiety and 3-substituent on the cyclopropane ring (ZITKO et al. 1977).

²Calculated from $Z = 0.397 \Sigma \log P^* - 0.448$, where $Z = \log L$ ($\mu\text{mole}/\%$), relative to that of pyrethrins (ZITKO et al. 1977).

CONCLUSIONS

(IR)-*cis*-permethrin, decamethrin, and NRDC 168S are extremely lethal to salmon and lobster. The increase in lethality relative to that of permethrin follows qualitatively the patterns established in toxicity studies with insects: (IR)-*cis* isomers are more lethal than (IR)-*trans*, and the presence of an α -cyano group in the phenoxybenzyl moiety increases the lethality. The latter effect is very pronounced for lobsters.

The octanol/water partition coefficient alone is not sufficient for predicting the lethality of pyrethroids to salmon or lobster.

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REFERENCES

- ELLIOTT, M.: Synthetic pyrethroids, IN: Synthetic Pyrethroids, M. Elliott, Editor, ACS Symposium Series 42, Washington, D.C., 1977, p. 1-28.
- LEO, A.J.: Calculation of partition coefficients useful in the evaluation of the relative hazards of various chemicals in the environment. Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms, G.D. Veith and D.E. Konasewich, Editors, IJC, Great Lakes Research Advisory Board, Windsor, Ontario, 1975, p. 151-176.
- LITCHFIELD, S.R., Jr.: J. Pharmacol. Exp. Theor. 97, 399 (1949).
- MARTER and COLAS: Specific activity of some synthetic pyrethroid isomers. Cotton Conference, Las Vegas 1976.
- MIYAMOTO, J.: Environ. Health Persp. 14, 15 (1976).
- SODERLUND, D.M., and J.E. CASIDA: Stereospecificity of pyrethroid metabolism in mammals, IN: Synthetic Pyrethroids, M. Elliott, Editor, ACS Symposium Series 42, Washington, D.C., 1977, p. 162-172.
- ZITKO, V.: Bull. Environ. Contam. Toxicol. 16, 508 (1976).
- ZITKO, V., W.G. CARSON, and C.D. METCALFE: Bull. Environ. Contam. Toxicol. 18, 35 (1977).