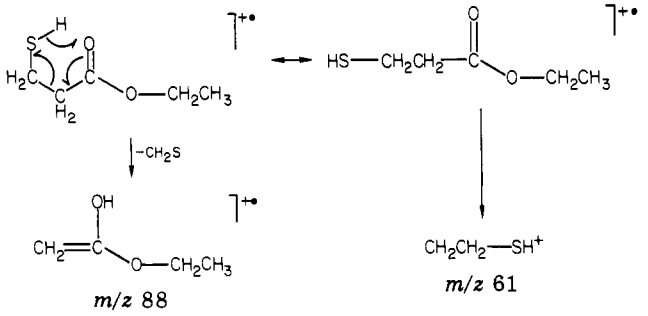
Scheme I



of certain chemicals can have a dramatic effect on their flavor characteristics. Ethyl 3-mercaptopropionate, which has a flavor threshold in water of 0.2 ppm, is a very good example of this phenomenon. At low concentration levels it has a very pleasant, fruity, grapy character, while at higher concentrations its aroma takes a skunky or foxy, animal-like aroma.

Registry No. Ethyl 3-mercaptopropionate, 5466-06-8.

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Poly(ethylene glycol) Pretreatment Reduces Pyrethroid Adsorption to Glass Surfaces

Pretreatment of glass vials with a solution of high molecular weight poly(ethylene glycol) (M_r 20 000; 4% w/v) reduced the adsorption of pyrethroid insecticides to vessel surfaces. This treatment also reduced the adsorption of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, dieldrin, and insect juvenile hormone III, but it increased the adsorption of trifluralin. Surface treatment may prove effective in maintaining aqueous solutions of known concentrations of pyrethroids and some other lipophilic pesticides for use in in vitro assay procedures.

Studies of the action and fate of lipophilic pesticides in aqueous systems are often complicated by the sorption of the test compound to the walls of the vessels used for such experiments. Previous studies have documented the adsorption of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) (Champion and Olsen, 1971), the pyrethroid insecticide permethrin (Sharom and Solomon, 1981), and the dinitroaniline herbicide trifluralin (Sharom and Solomon, 1981; Strachan and Hess, 1982) from aqueous media to glass and plastic surfaces. During the course of our studies of pyrethroid metabolism and action in isolated biochemical preparations, we found it necessary to identify methods to minimize surface adsorption. We now report a surface treatment method that reduces the adsorption of pyrethroids and some other lipophilic pesticides to glass vessels.

MATERIALS AND METHODS

Surface Treatment Procedures. Three poly(ethylene glycols) were tested: Carbowax 20M (M_r 20 000; Fisher Scientific, Rochester, NY); Carbowax 20M–TPA (M_r 20 000; terminated with terephthalic acid; Applied Science, State College, PA); Carbowax 4000 (M_r 4000; Applied Science). Glass scintillation vials (7 mL) were immersed in dilute (0.1–10%) aqueous solutions of each of the above, drained, oven-dried (110 °C) overnight, and used for adsorption assays. Vials were also silanized after base washing with dimethyldichlorosilane (5% in toluene) or were treated with commercial siliconizing agents (Sigmacote, Sigma Chemical Co., St. Louis, MO; Surfasil, Pierce Chemical Co., Rockford, IL) according to manufacturers' instructions.

Radiolabeled Compounds. The following compounds were available from previous syntheses in this laboratory: NRDC 157-^{14}C [3-phenoxybenzyl (1*R*,*cis*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate; Soderlund, 1979]; NRDC 157-*t* (Soderlund et al., 1983a); NRDC 163-^{14}C (the 1*R*,trans isomer of NRDC 157; Soderlund et al., 1983b). The following compounds were obtained as gifts: *trans*- and *cis*-permethrin-^{14}C (FMC Corp., Middleport, NY); fenvalerate-^{14}C (Shell Development Co., Modesto, CA); deltamethrin-^{14}C [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,*cis*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate; Roussel-Uclaf-Procida, Romainville, France]; fluvalinate-^{14}C [(*R*,*S*)-α-cyano-3-phenoxybenzyl (*R*,*S*)-2-[2-chloro-4-(trifluoromethyl)-anilino]-3-methylbutyrate; Zoecon Corp., Palo Alto, CA); trifluralin-^{14}C (J. O. Nelson, Department of Entomology, University of Maryland, College Park, MD). The following compounds were purchased: DDT-^{14}C and juvenile hormone III-*t* (New England Nuclear, Boston, MA); Dieldrin-^{14}C (Amersham Corp., Arlington Heights, IL). All compounds were purified by thin-layer chromatography (silica gel 60 F_{254} chromatoplates, 0.25 mm gel thickness;

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Table I. Effect of Carbowax and Silicone Surface Treatments on the Adsorption of NRDC 157 to Glass Surfaces from Aqueous Solutions[a]

surface treatment	adsorption, %[b]
untreated vial	46.5 ± 2.1
Carbowax 20M, 1%	12.3 ± 4.6
Carbowax 20M-TPA, 1%	23.5 ± 3.5
Carbowax 4000, 1%	48.0 ± 2.8
dichlorodimethylsilane	62.5 ± 0.7
Sigmacote	76.5 ± 9.2
Surfasil, 2%	89.4 ± 0.2

[a] All assays were performed by using 3×10^{-7} M NRDC 157. [b] Results are means ± SD of either two or three determinations.

Table II. Effect of Carbowax 20M Pretreatment on the Adsorption of NRDC 157 to Glass Surfaces from Aqueous Solutions and Suspensions[a]

NRDC 157 concentration, M	Carbowax 20M pretreatment, %	adsorption, % untreated vial	adsorption, % treated vial
5×10^{-8}	1	46.7 ± 6.4	36.3 ± 14.3
	2		8.4 ± 3.9
	3		6.2 ± 1.6
	4		2.5 ± 0.8[b]
3×10^{-9}	4	41.3 ± 3.5	2.0 ± 0.1
1×10^{-8}	4	45.2 ± 1.5	1.3 ± 0.1
1×10^{-7}	4	45.7 ± 3.5	1.4 ± 0.1
1×10^{-6}	4	38.4 ± 1.4	1.1 ± 0.1
1×10^{-5}	4	31.3 ± 0.8	1.6 ± 0.3

[a] Results are means ± SE or four determinations. [b] With the 4% Carbowax treatment, unadsorbed NRDC 157 was recovered as follows: incubation mixture, 90.2 ± 5.0%; buffer wash, 5.0 ± 1.7%; NaOH wash, 2.3 ± 0.7%.

EM Laboratories, Elmsford, NY) in benzene–ethyl acetate (3:1) prior to use.

Adsorption Assays. Glass scintillation vials were treated as described above. Labeled compounds were introduced in 5–10 μL of ethanol to give final nominal concentrations of 3×10^{-9}–1×10^{-5} M in 0.3–1.0 mL of 0.05 M Tris-HCl buffer, pH 7.5. After incubation at 22 °C for 45 min the incubation mixture was removed and the vial was rinsed with buffer (1.0 mL) and 0.1 N NaOH (1.0 mL). The distribution of radioactivity in the incubation medium, the two rinses, and the rinsed vial was determined by liquid scintillation counting.

RESULTS AND DISCUSSION

Adsorption of NRDC 157. We used NRDC 157 as a model for the development of surface treatment procedures because of our continuing interest in this compound in studies of pyrethroid pharmacokinetics and action (Soderlund, 1979; Soderlund et al., 1983a,b). Since this compound is among the least water soluble pyrethroids (Burt and Goodchild, 1977), it also provides a severe test for methods developed to maintain aqueous solutions. We explored two types of surface treatments suggested from previous work: treatment with aqueous solutions of high molecular weight poly(ethylene glycol) (e.g., Carbowax 20M), which has been reported to reduce the adsorption of insect juvenile hormone III (Hammock et al., 1975), and siliconization, which reduced the adsorption of trifluralin (Strachan and Hess, 1982).

In the absence of surface treatment, introduction of NRDC 157 to give nominal concentrations of 3×10^{-9} to 1×10^{-5} M resulted in recovery of 31–47% of the added radiocarbon adsorbed to the surface of the glass vial (Tables I and II). Of the surface treatments examined, Carbowax 20M was most effective in reducing the adsorption of NRDC 157 (Table I). Carbowax 20M terminated with terephthalic acid was less effective, whereas the lower molecular weight poly(ethylene glycol) was ineffective and the three siliconization treatments enhanced the adsorption of NRDC 157. Carbowax 20M increased in effectiveness as its concentration in the pretreatment medium was increased from 1% to 4% (Table II). Using 4% Carbowax 20M, most (>85%) of the added radioactivity was recovered in the initial incubation medium regardless of the nominal NRDC 157 concentration used. At higher concentrations of Carbowax 20M, adsorption was much more variable and the added radioactivity was recovered in the vial rinses as well as in the initial incubation medium. The use of 4% Carbowax 20M effectively reduced the adsorption of NRDC 157 even at concentrations ($>1 \times 10^{-6}$ M) that are far in excess of the probable water solubility of this pyrethroid (Table II).

Table III. Effect of Carbowax 20M Pretreatment of Pyrethroids and Other Lipophilic Compounds to Glass Surfaces from Aqueous Solutions[a]

compound[b]	adsorption, % untreated vial	adsorption, % treated vial
pyrethroids		
cis-permethrin	43.1 ± 3.2	18.3 ± 0.6
trans-permethrin	40.6 ± 4.9	9.9 ± 3.2
NRDC 163	45.9 ± 4.6	15.4 ± 2.4
deltamethrin	21.9 ± 5.3	5.9 ± 1.6
fenvalerate	24.3 ± 8.1	5.7 ± 2.3
fluvalinate	5.8 ± 0.6	3.5 ± 0.8
other compounds		
DDT (5×10^{-7} M)	34.1 ± 2.2	9.9 ± 1.2
dieldrin	15.7 ± 2.5	3.2 ± 0.3
juvenile hormone III (2.7×10^{-7} M)	0.73 ± 0.03	0.08 ± 0.02
trifluralin	3.9 ± 0.4	14.6 ± 0.8

[a] 4% Carbowax 20M was used for all treated vials. Results are means ± SE of four determinations. [b] All compounds were assayed as 1×10^{-7} M solutions except where noted.

The adsorption of NRDC 157 was reduced by Carbowax 20M only under specific conditions of treatment and handling. Rinsing in water after immersion in Carbowax solution and storage of treated vials after drying negated the effectiveness of this treatment, and the effectiveness of Carbowax treatment was not restored when stored vials were reheated.

Adsorption of Other Pyrethroids. The optimal conditions for reducing NRDC 157 adsorption also proved effective in reducing the adsorption of several other pyrethroids (Table III). Among the compounds examined, those lacking an α-cyano substituent were most extensively adsorbed. The effect of the cyano substituent is clearly seen in comparing deltamethrin and NRDC 157, which differ only with regard to the presence or absence of this group. In comparison with the other pyrethroids tested, fluvalinate was only weakly adsorbed.

In all cases, pretreatment of vials with 4% Carbowax 20M reduced the extent of adsorption, but the efficacy of this treatment varied considerably between compounds. The best results were achieved with NRDC 157, the compound used to define optimal conditions. It is possible that specific optimization with other pyrethroids might further reduce the extent of adsorption observed with those compounds. Clearly, surface treatment conditions developed for one pyrethroid cannot be assumed to be equally effective for all compounds.

Adsorption of Other Compounds. We also examined the effect of Carbowax 20M pretreatment on the adsorption of other compounds to glass surfaces (Table III).

Juvenile hormone III and trifluralin have been reported to be removed from aqueous solution by adsorption (Hammock et al., 1975; Sharom and Solomon, 1981; Strachan and Hess, 1982), whereas dieldrin, like DDT and the pyrethroids, is expected to be adsorbed to glass surfaces because of its hydrophobic nature.

The degree of adsorption in the absence of Carbowax 20M treatment varied widely with these compounds. Both DDT and dieldrin were adsorbed to an extent similar to that observed for most of the pyrethroids. Trifluralin adsorption in our studies was less than that observed in previous work (Sharom and Solomon, 1981; Strachan and Hess, 1982). This difference may be attributable to the fact that we measured residual adsorption to glass surfaces after rinsing rather than simply the reduction in trifluralin concentration in the aqueous phase. Previous studies have not reported levels of juvenile hormone III adsorption, but in view of the use of Carbowax 20M pretreatment to prevent adsorption during binding assays (Hammock et al., 1975) it was surprising to find less than 1% of the added juvenile hormone III adsorbed under our assay conditions. Pretreatment of vials with 4% Carbowax 20M effectively reduced the adsorption of DDT, dieldrin, and juvenile hormone III. However, this treatment increased the amount of trifluralin retained in the vial.

These data demonstrate the general utility of Carbowax 20M pretreatment in reducing the adsorptive loss of synthetic pyrethroids and other lipophilic compounds from aqueous solution. Our treatment procedure, optimized using NRDC 157 as the adsorbed pyrethroid, was most effective for this compound. It is possible that specific optimization will improve the efficacy of pretreatment for preventing the adsorption of other compounds as well. The increased adsorption of trifluralin to treated vials is a further reminder that our specific conditions cannot be applied routinely to all adsorbed compounds.

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Registry No. NRDC 157, 55700-98-6; *cis*-permethrin, 61949-76-6; *trans*-permetrhrin, 61949-77-7; NRDC 163, 55667-38-4; deltamethrin, 52918-63-5; fenvalerate, 51630-58-1; fluvalinate, 69409-94-5; DDT, 50-29-3; dieldrin, 60-57-1; insect juvenile hormone III, 22963-93-5; trifluralin, 1582-09-8; poly(ethylene glycol), 25322-68-3; Carbowax 20M, 56592-21-3; Carbowax 20M–TPA, 41479-14-5; Carbowax 4000, 25322-68-3.

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