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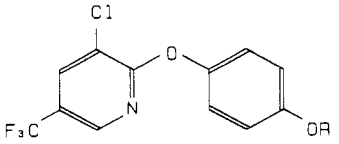
Transformation and Persistence of the Herbicide [^{14}C]Haloxyfop-Methyl in Soil under Laboratory Conditions

Allan E. Smith

The transformation of the herbicidal ester [^{14}C]haloxyfop-methyl (methyl 2-[4-((3-chloro-5-(trifluoromethyl)-2-pyridinyl)oxy)[*ring-U*-^{14}C]phenoxy]propanoate) was studied in three prairie soils at 20 ± 1 °C. In all soils the ester was rapidly hydrolyzed to the corresponding [^{14}C]haloxyfop acid, providing there was moisture in excess of the wilting point. In air-dried soils little hydrolysis of the ester to acid occurred. In moist nonsterile soils, there was a loss of solvent extractable radioactivity with time. These losses followed first-order kinetics, with half-lives of 27, 38, and 92 days respectively in the sandy loam, heavy clay, and clay loam soil types. Traces of a second transformation product and [^{14}C]carbon dioxide were noted. Prolonged treatment of the solvent extracted soils with dilute sodium hydroxide released further small amounts of [^{14}C]haloxyfop acid.

The experimental herbicide haloxyfop-methyl (**1**, R = $CH(CH_3)CO_2CH_3$) is currently being evaluated on the Canadian prairies, at rates up to 0.5 kg/ha, as postemergence treatments for the control of annual and perennial grasses in a variety of broad-leafed crops.



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Although applied to the growing crop, some of the herbicidal spray will inevitably come into contact with the soil making it necessary to study the fate of haloxyfop-methyl in the soil. Research has indicated (Ryder et al., 1983) that the herbidical ester is rapidly converted to haloxyfop acid (**1**, R = $CH(CH_3)CO_2H$) in the soil and that the acid in turn is degraded with a half-life of between 27 and 100 days.

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Table I. Composition and Physical Characteristics of Soils

soil	composition, % clay	silt	sand	organic content	field capacity, %	pH
clay loam	30	40	30	11.7	35	6.0
sandy loam	10	25	65	4.0	20	7.6
heavy clay	70	25	5	4.2	40	7.7

In the studies to be described, the hydrolysis of [^{14}C]-haloxyfop-methyl to [^{14}C]haloxyfop acid was investigated in three Saskatchewan soils at different moisture levels. The persistence and transformation of the [^{14}C]ester in the three soil types was also examined.

MATERIALS AND METHODS

Soils. The composition and physical characteristics of the soils used in these studies are presented in Table I.

Soil samples were collected from the 0–5 cm soil horizon of fallow areas that had received no crops for several years during Aug, 1984, and after screening through a 2-mm

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sieve, the soils were immediately used for the current experiments.

Chemicals. [^{14}C]Haloxyfop-methyl (methyl 2-[4-((3-chloro-5-(trifluoromethyl)-2-pyridinyl)oxy)[*ring-U*-^{14}C]-phenoxy]propanoate), with a specific activity of 10.6 mCi/mmol and a radiochemical purity in excess of 99%, was provided by The Dow Chemical Co., Midland, MI, as were the samples of analytically pure haloxyfop-methyl (1, R = $CH(CH_3)CO_2CH_3$) and haloxyfop acid (2-[4-((3-chloro-5-(trifluoromethyl)-2-pyridinyl)oxy)phenoxy]-propanoic acid, 1, R = $CH(CH_3)CO_2H$).

The [^{14}C]haloxyfop-methyl was dissolved in methanol (5 mL) and a solution prepared containing 3.06 μCi/mL and an ester content of 106 μg/mL. Methanolic solutions of nonradioactive haloxyfop-methyl and haloxyfop acid were also prepared containing 1 mg of the respective ester or acid per milliliter.

Short-Term Hydrolysis Study. Moistened samples (20 g) of the clay loam, heavy clay, and sandy loam at 20%, 65%, and 100% of their respective field capacities were weighed into 125-mL capacity glass-stoppered flasks and treated with [^{14}C]haloxyfop-methyl (20 μL, 2 μg) and nonradioactive ester solution (18 μL, 18μg). This rate was equivalent to 1.0 ppm of haloxyfop-methyl based on moist soil weight. After thorough mixing, the stoppered flasks were incubated at 20 ± 1 °C. Duplicate samples of all treated soils were extracted after 24 and 48 h and analyzed radiochemically for [^{14}C]haloxyfop-methyl and [^{14}C]haloxyfop acid.

To each flask was added sufficient extracting solvent (acetonitrile, water, glacial acetic acid in the proportions 80:20:2.5) so that the combined volume of solvent together with water present in the soil was equivalent to 50 mL. The flask was shaken on a wrist-action shaker for 1 h and the slurry then centrifuged at 3500 rpm for 4 min. An aliquot (25 mL) of the supernatant was added to 5% aqueous sodium bicarbonate solution (100 mL) and shaken with *n*-hexane (2 × 25 mL). Any [^{14}C]haloxfop-methyl extracted into the organic phase was assayed by determining the amounts of radioactivity in portions (5 mL) of the hexane solution.

The alkaline aqueous phase following hexane extraction was acidified by the addition of 12 N hydrochloric acid (10 mL) and shaken with diethyl ether (2 × 25 mL). Combined ether extracts were evaporated to dryness under reduced pressure and the residue taken up in methanol (25 mL). Amounts of [^{14}C]haloxyfop acid present were calculated by determining the radioactivity in an aliquot (5 mL) of the methanolic solution.

To confirm the identities of the [^{14}C]ester and [^{14}C]acid in the hexane and methanol solutions, the solvents were evaporated under reduced pressure to approximately 0.5 mL and the extracts examined by thin-layer chromatographic and radiochemical techniques (see later).

Laboratory Degradation Studies. Moistened samples (50 g) of the three soil types, at 85% of their respective field capacities, were weighed into 250-mL capacity styrofoam cartons fitted with loose fitting lids and incubated at 20 ± 1 °C for 7 days. Distilled water was added, with stirring, every second day to maintain the moisture contents. After equilibration, [^{14}C]haloxyfop-methyl (100 μL, 10 μg ester) and nonradioactive ester (40 μL, 40 μg ester) were added to the soils to yield treatments containing 1 ppm of the herbicidal ester based on moist soil weight. All soils were thorougly stirred to evenly distribute the chemicals. The cartons were loosely capped to permit circulation of air but reduce water evaporation and incubated in the dark at 20 ± 1 °C. Distilled water was added, with stirring, every second day to replace evaporated moisture. This moisture loss was less than 1 g so that the soil moisture of 85% of field capacity was essentially maintained. Duplicate treatments were extracted and analyzed after 1, 4, 8 and 12 weeks to determine the amounts of radioactivity recovered and the number of transformation products present.

The soil from each carton was placed in a 250-mL glass-stoppered flask and extraction solvent added (acetonitrile, ammonium hydroxide solution (30% w/v) in the proportion 90:10) so that the combined volume of solvent together with the water present in the soil was equivalent to 100 mL. The flask and contents were shaken on a wrist-action shaker for 1 h when the soil was allowed to remain in contact with the extraction solvent for a further 20 h before being shaken for another 1-h period. The soil extracts were centrifuged at 3500 rpm for 10 min and solvent extractable radioactivity determined by radioassay of the extract (5 mL).

Further portions of the extract (20 mL, equivalent to 10 g of moist soil) were evaporated to dryness at 35 °C with a rotary evaporator. The residue was taken up in methanol (20 mL), aliquots of which (5 mL) were assayed for radioactivity. The remaining methanolic solution was evaporated under reduced pressure to approximately 0.5 mL and examined by using thin-layer and radiochemical techniques for the presence of ^{14}C-containing compounds.

Alkaline Soil Extraction. After the 12-week incubation period, the solvent extracted soils were collected by vacuum filtration and washed successively with methanol (100 mL) and acetone (100 mL). These washings were discarded since no radioactivity was removed from the soils by these solvents. Each soil was dried for 4 h at 90 °C and samples were subjected to combustion analysis to determine solvent-nonextractable radioactivity. Further samples (20 g) of the dried solvent-extracted soils were shaken on a wrist-action shaker for 24 h with 1 N sodium hydroxide solution (50 mL) and after acidification of the alkaline extract were separated into a soluble fulvic acid fraction and a humic precipitate. Full details of this procedure have been reported (Smith and Muir, 1980).

A portion (1 mL) of the fulvic acid solution was examined for radioactivity, and the remaining solution was decanted into a separatory funnel containing water (50 mL) and shaken with ether (2 × 25 mL). The combined ether extracts were evaporated to dryness and the residue dissolved in methanol (10 mL), a portion of which (1 mL) was assayed for radioactivity. The remaining methanolic extract was evaporated to about 0.5 mL and examined by thin-layer chromatographic and radiochemical analysis.

[^{14}C]Carbon Dioxide Evolution. Duplicate samples (50 g) of the sandy loam were weighed into Bartha and Pramer flasks (Bartha and Pramer, 1965) and incubated in the dark at 20 ± 1 °C for 7 days. After the incubation period, the soils were treated exactly as above with [^{14}C]haloxyfop-methyl solution (100 μL, 10 μg) and nonradioactive ester (40 μL, 40μg). To the side arm of the flasks were added 25 mL of 0.2 N aqueous sodium hydroxide solution to absorb any [^{14}C]carbon dioxide evolved (Fournier et al., 1981); this solution was replaced with fresh every 4 days. After treatment, the flasks were incubated in the dark at 20 ± 1 °C. Samples (1.0 mL) of the sodium hydroxide solution were assayed for radioactivity every second day, and the cumulative amounts released calculated as a percentage of the total radioactivity originally applied to the soil.

Thin-Layer Chromatography. Precoated TLC plates (Silica Gel 60 F-254) were obtained from E. Merck,

Table II. Hydrolysis of [^{14}C]Haloxyfop-methyl to [^{14}C]Haloxyfop Acid in Soils at Different Moisture Levels at 20 ± 1 °C after 24 and 48 h

	% of applied radioactivity extract at[a] 24 h						% of applied radioactivity extracted at[a] 48 h					
	20% of FC		65% of FC		100% of FC		20% of FC		65% of FC		100% of FC	
soil type	ester	acid	ester	acid	ester	acid	ester	acid	ester	acid	ester	acid
clay loam	100	<1	19	79	19	79	97	<1	15	78	12	76
heavy clay	100	<1	7	92	6	84	100	<1	6	79	6	76
sandy loam	99	<1	13	74	12	74	98	<1	10	71	9	72

[a] Initial herbicide concentration of 1 ppm. Average from duplicate experiments. Variation <5%.

Darmstadt, Germany. After development to a height of 10 cm above the origin, the plates were air-dried and examined for radioactive compounds with a thin-layer radiochromatogram scanner. Nonradioactive compounds run for comparative purposes were detected by viewing the developed chromatograms under a short-wave ultraviolet lamp. The *Rf* values of the haloxyfop-methyl and haloxyfop acid in a mixture of benzene and methanol (10:1) were 0.96 and 0.28, and in a mixture of toluene, ethyl acetate, and acetic acid (50:50:1) were 0.97 and 0.44 respectively. By comparing peak areas from the chromatogram scans, and knowing the amounts of radioactivity extracted from each soil, quantification of the various radioactive compounds present was achieved.

Radioactivity Determination. The radioactivity in the various solutions was measured with a liquid scintillation spectrometer. The scintillation solution consisted of an equivolume mixture of toluene and 2-methoxymethanol containing PPO (0.4%) and POPOP (0.1%). Counting efficiencies were determined with an external [^{226}Ra]standard. Radioactivity associated with the soils was measured by combustion analysis as described (Smith and Muir, 1984).

Prior experiments confirmed that untreated control soils contained no substances that interfered with the radioactive analyses.

RESULTS AND DISCUSSION

The results of the hydrolysis studies are summarized in Table II, and there was excellent agreement between the duplicate experiments. Aqueous acidic acetonitrile was selected as extraction solvent, since this extractant has proved most satisfactory for the recovery of other herbicidal esters from the soils used in the present studies (Smith, 1976, 1977, 1981, 1985; Smith and Hayden, 1980).

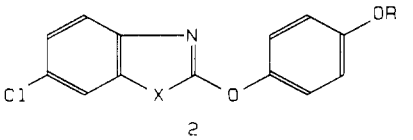
The results of the hydrolytic study (Table II) indicated that after 24 and 48 h in the soils at 20% of their field capacity moisture levels, over 97% of the applied radioactivity was in the form of [^{14}C]haloxyfop-methyl and less than 1% was present at [^{14}C]haloxyfop acid. This indicated a complete lack of hydrolysis of the ester to the acid on any of the three soil types. The data also confirmed that the extraction procedure was not significantly contributing to the hydrolysis of the ester to the carboxylic acid.

In contrast, in the soils at 65% and 100% of their field capacity moistures extensive hydrolysis occurred (Table II). For each soil type, at the two higher moisture levels the amount of hydrolysis that had occurred after 24 and 48 h was very similar. After 24 h, between 6% and 19% of the initial ester remained, while [^{14}C]haloxyfop acid accounted for 74% to 92% of the applied radioactivity. The identities of the [^{14}C]ester and [^{14}C]acid were confirmed by thin-layer chromatographic analysis of the various extracts, as described, when it was observed that the *Rf* values of the [^{14}C]compounds, in both solvent systems, were identical with those of authentic standards run for comparative purposes. After 48 h, between 6% and 15% of the applied radioactivity was attributable to [^{14}C]haloxyfop-methyl, while [^{14}C]haloxyfop acid accounted for between 71% and 79% of the initial radioactivity. Although the total radioactivity recovered from the dry soils after 24 and 48 h was over 97%, the total radioactivity recovered from the moist soils after 24 h ranged from 86% to 99%; after 48 h radioactivity recoverd from the soils ranged from 81% to 93% of that applied. Thus it was inferred that, with time, [^{14}C]haloxyfop acid was not being as efficiently recovered from the soils as was the [^{14}C]ester (Table II).

From these data (Table II) it was determined that in soils with moisture levels greater than 65% of field capacity almost complete hydrolysis of haloxyfop-methyl to haloxyfop acid had occurred after 48 h. Thus, the soil hydrolysis of this herbicide is almost as rapid as for the esters of the phenoxyalkanoic acid herbicides to their respective acid anions (Smith, 1976; Smith and Hayden, 1980) or for the hydrolysis of the experimental herbicides fenoxaprop-ethyl and fenthiaprop-ethyl to their respective acid anions (Smith, 1985) and faster than the hydrolysis of diclofop-methyl to its corresponding acid anion (Smith, 1977). The hydrolytic data for [^{14}C]haloxyfop-methyl to the acid is also in good agreement with a half-life value of approximately 24 h, previously reported (Ryder et al., 1983).

For the laboratory degradation studies, several solvent systems were compared to determine which would recover the maximum amounts of radioactivity from the treated soils. After 7 days of incubation under laboratory conditions, neutral extractants such as 10% aqueous methanol, 10% aqueous acetonitrile, or the aqueous acidic acetonitrile used to recover haloxyfop-methyl from soils recovered less than 70% of the applied radioactivity from any of the soil treatments. This would indicate, that after formation, haloxyfop acid became strongly adsorbed onto soil organic matter.

The ammoniated acetonitrile extraction solvent system used, was selected since it had proved to be an efficient solvent for the extraction of aged residues of atrazine, picloram, and simazine from prairie field soils (Smith, 1981; Smith and Milward, 1983). The ammoniated acetonitrile was also the solvent for choice (Smith, 1985) for the extraction of the carboxylic acids formed in soil by hydrolysis of the oxyphenoxypropanoate herbicides fenoxaprop-ethyl (**2**, X = O, R = $CH(CH_3)CO_2C_2H_5$) and fenthiaprop-ethyl (**2**, X = S, R = $CH(CH_3)CO_2C_2H_5$). It was also noted that



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the 22-h extraction procedure was necessary, since this method recovered up to 25% more radioactivity than did a simple 1-h shaking. In this regard, haloxyfop acid be-

Table III. Radioactivity Recovered from Soils Treated with 1 ppm [^{14}C]Haloxyfop-Methyl following Incubation at 20 ± 1 °C and 85% of Field Capacity

	% of applied ^{14}C[a] in														
	clay loam after (days)					heavy clay after (days)					sandy loam after (days)				
	7	28	56	84	$T^1/_2$[b]	7	28	56	84	$T^1/_2$[b]	7	28	56	84	$T^1/_2$[b]
solvent extractable radioactivity	97	80	67	53	92	90	57	39	20	38	90	48	24	10	27
haloxyfop acid	94	74	57	47		86	52	35	18		89	47	21	7	
compound A	3	6	10	6		4	5	4	2		1	1	3	3	
radioactivity in soil via soil combustion after solvent extraction	[c]	[c]	[c]	34		[c]	[c]	[c]	46		[c]	[c]	[c]	57	
total accountable radioactivity	[c]	[c]	[c]	87		[c]	[c]	[c]	66		[c]	[c]	[c]	67	
radioactivity in fulvic acid fraction	[c]	[c]	[c]	8		[c]	[c]	[c]	18		[c]	[c]	[c]	19	
ether soluble radioactivity in fluvic acid fraction	[c]	[c]	[c]	3		[c]	[c]	[c]	8		[c]	[c]	[c]	7	
haloxyfop acid	[c]	[c]	[c]	2		[c]	[c]	[c]	6		[c]	[c]	[c]	5	
radioactivity in humic and humin fractions[d]	[c]	[c]	[c]	26		[c]	[c]	[c]	28		[c]	[c]	[c]	38	

[a] Average from duplicate experiments. [b] Half-life. [c] Not determined. [d] Obtained by subtracting amounts of fulvic-associated radioactivity from that determined by combustion of the solvent extracted soils.

Table IV. Cumulative Release of [^{14}C]Carbon Dioxide from Moist Sandy Loam Treated with 1 ppm of Phenyl-Labeled [^{14}C]Haloxyfop-Methyl following Incubation at 20 °C

days	% of applied ^{14}C evolved as CO_2[a]
2	0.9
7	5.6
14	11.2
21	15.3
28	20.0

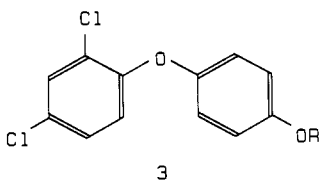
[a] Average from duplicate experiments. Variation <5%.

haved similarly to fenoxaprop acid (**2**, X = O, R = CH(CH_3)CO_2H) and fenthiaprop acid (**2**, X = S, R = CH(CH_3)CO_2H) (Smith, 1985). This extraction procedure effected complete hydrolysis of the haloxyfop-methyl to haloxyfop acid. However, this was not considered important since the results of the hydrolysis experiments, mentioned above, showed that after 48 h the hydrolysis of the haloxyfop-methyl to the acid was almost complete.

The results from the laboratory degradation experiments are compared in Table III, and there was excellent agreement between the results from the duplicate experiments. Evaporation of the ammoniated acetonitrile extracts and subsequent treatment of the residues with methanol resulted in no loss of radioactivity, confirming that no volatile [^{14}C]compounds were being solvent extracted from any of the soils. There was a loss of solvent extractable ^{14}C from all soils with time and this loss appeared to follow first-order kinetics since for all soils regression analysis on the data obtained by plotting the logarithm of percentage radioactivity recovered against incubation time yielded straight lines with regression mean square values of 0.99. The calculated half-lives (Table III) indicated that the breakdown of the herbicide in the soil was fastest in the sandy loam and slowest on the clay loam.

Chromatographic separation of the solvent extractable radioactivity using the two solvent systems described followed by radiochemical analysis indicated the presence of two radioactive products. The major product had identical chromatographic properties with [^{14}C]haloxyfop acid, but a minor product designated compound A was also present in all soils at all sampling times (Table III). Amounts of compound A in the heavy clay and sandy loams were very low, accounting for less than 5% of the applied radioactivity. Slightly more compound A was observed in the clay loam (Table III) where up to 10% of the initial activity was attributable to such a source.

It is interesting to speculate that compound A could be 2-[4-(3-chloro-5-(trifluoromethyl)-2-pyridinyl)oxy]phenol (**1**, R = H) formed in the soil by a side chain cleavage reaction. A similar cleavage is known to occur with the structurally related herbicidal ester diclofop methyl (**3**, R = CH(CH_3)CO_2CH_3) which is transformed in the soil (Smith, 1977, 1979; Martens, 1978) to the phenol (**3**, R = H) and also with fenoxaprop-ethyl and fenthiafop-ethyl which are similarly converted in the soil to their corresponding phenols (**2**, X = O, R = H and **2**, X = S, R = H) (Smith, 1985).



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The *Rf* values of compound A would support such a tentative assignment. In the benzene/methanol solvent system the *Rf* value was 0.61, and in the ethyl acetate/toluene/acetic acid mixture 0.83, thus indicating that the unknown compound is less polar than haloxyfop acid. The oxyphenols derived from diclofop-methyl, fenoxaprop-ethyl, and fenthiaprop-ethyl show similar *Rf* values in these solvents systems (Smith, 1977, 1985).

No other degradation products were extracted from any of the soils at any sampling time. Thus, no phenetole (**1**, R = C_2H_5) appeared to be formed as a result of a decarboxylation mechanism that is known to occur with the oxyphenoxypropanoate herbicides diclofop-methyl, fenoxaprop-ethyl, and fenthiaprop-ethyl (Smith, 1977, 1979; 1985).

From Table III, it can be noted that the half-life values for [^{14}C]haloxyfop acid ranged from about 4 weeks in the sandy loam to about 13 weeks in the clay loam. These values are also in agreement with the 27–100 day half-life data reported for haloxyfop acid in a variety of soil types (Ryder et al., 1983).

Since the loss of radioactivity was most rapid from the treated sandy loam (Table III), this soil was selected to determine whether, in soil, the [^{14}C]benzene ring of the labeled haloxyfop-methyl was being converted into [^{14}C]carbon dioxide. The data (Table IV) indicated that over a 28-day period, 20% of the radioactivity was released as [^{14}C]carbon dioxide. Thus, in the soil, the phenoxy ring system of haloxyfop acid is cleaved with the formation of

carbon dioxide, in a manner similar to that reported for diclofop acid (Martens, 1978).

At the end of the 84 day incubation period, the solvent extracted soils were analyzed by combustion to determine radioactivity remaining in an unextractable form. Between 34 and 57% of the aplied radioactivity remained on the soil (Table III). Thus the amounts of radioactivity that could be accounted for were 87, 66, and 67% of that applied to the clay loam, heavy clay, and sandy loam, respectively (Table III). The remaining radioactivity was presumably lost as [^{14}C]carbon dioxide, which was not assayed for in these experiments.

Alkaline extraction of the solvent extracted soils released between 8 and 19% of the applied radioactivity, and of this, about one-half was ether soluble and shown to consist mainly of [^{14}C]haloxyfop acid (Table III). No attempts were made to further isolate and characterize the radioactivity remaining in the aqueous fulvic acid extracts after ether extraction. Radioactivity associated with the humic and humin fractions ranged from 26 to 38% of that initially applied (Table III).

Treatment of the solvent extracted soils with 1 N sodium hydroxide for 24 h would result in the extraction of fulvic acid and humic acid soil components containing incorporated radioactivity derived from [^{14}C]fragments of the herbicide. The sodium hydroxide could also remove other [^{14}C]compounds that were either not, or only partially, removed from the soils by the ammoniated acetonitrile.

In summary, it has been demonstrated that on the three prairie soils, haloxyfop-methyl undergoes rapid hydrolysis to haloxyfop acid which itself is further transformed.

ACKNOWLEDGMENT

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Registry No. 1 (R = $CH(CH_3)CO_2CH_3$), 69806-40-2; 1 (R = $CH(CH_3)CO_2H$), 69806-34-4; 1 (R = H), 69045-89-2; CO_2, 124-38-9.

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1,4-Disubstituted 2,6,7-Trioxabicyclo[2.2.2]octanes: A New Class of Insecticides

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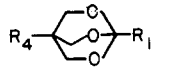
A new class of insecticides, the 1,4-disubstituted 2,6,7-trioxabicyclo[2.2.2]octanes, was prepared either by acid-catalyzed condensation of a 2-substituted 2-(hydroxymethyl)-1,3-propanediol with a trimethyl orthocarboxylate or by Lewis acid catalyzed rearrangement of a 3-substituted 3-[(acyloxy)methyl]oxetane. Compounds of high toxicity to houseflies or American cockroaches have 4-substituents such as *n*-propyl, isopropyl, *n*-, *sec*- or *tert*-butyl, cyclopentyl, cyclohexyl, or phenyl and 1-substituents such as cyclohexyl, cycloheptyl, 4-cyanophenyl, 4-nitrophenyl, 4-halophenyl, or 3,4-dichlorophenyl. The toxicity to houseflies is generally increased by injection and by piperonyl butoxide indicating that the insecticidal activity is limited by the penetration rate and oxidative detoxification. The bicycloorthocarboxylates have a positive temperature coefficient in poisoning houseflies and act at the cockroach neuromuscular junction to inhibit GABAergic synaptic transmission possibly by closing off chloride channels.

INTRODUCTION

New types of insecticides are discovered by many approaches, one of which starts from known toxicants for other organisms and modifies their structure for potency on insects (Casida, 1976). Bicyclophosphorus esters such as *i*-Pr-$C(CH_2O)_3P{=}O$ might be considered as candidate prototypes but they have little or no insecticidal activity (Casida et al., 1976; Milbrath et al., 1979) except to houseflies on injection (Ozoe et al., 1983) and they are highly toxic to mammals (Bellet and Casida, 1973; Casida et al., 1976; Milbrath et al., 1979). The related bicycloorthocarboxylates are similar to the bicyclophosphorus esters in their mode of action (Casida et al., 1976; Milbrath et al., 1979; Squires et al., 1983) and offer considerable opportunity for structural modification in the 1- and 4-positions for optimizing insecticidal potency, penetration, and selective toxicity. This report considers the structural optimization of 1,4-disubstituted 2,6,7-trioxabicyclo-[2.2.2]octanes for insecticidal activity.



R_1, R_4 = alkyl or aryl

MATERIALS AND METHODS

Bioassays. Houseflies (*Musca domestica* L.) were adult females (~20 mg each) of the SCR strain used 3–5 days

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