US EPA ARCHIVE DOCUMENT

FILE COPY 8-31-79

Date Out EFB:

To: Product Manager Mautz (16)
TS-767

Through: Dr. Gunter Zweig, Chief
Environmental Fate Branch

From: Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 10182-EA

Chemical: 3-[3-(4'-bromo[1,1'-biphenyl]4-yl)-1,2,3,4-tetrahydro-1-naphthalenyl]4-hydroxy-2H-1-benzopyran-2-one (brodifacoum)

Type Product: Rodenticide

Product Name: Talon

Company Name: ICI Americas, Inc.

Submission Purpose: Outdoor

ZZB Code: Sec. 3

Date in: 5/25/79

Date Completed: 8-31-79

Deferrals To:

___ Ecological Effects Branch

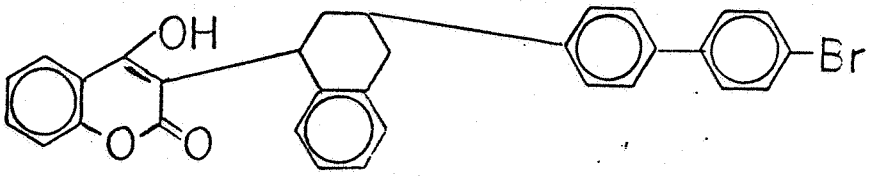
___ Residue Chemistry Branch

___ Toxicology Branch

I. Introduction

This submission by ICI Americas, Inc. is for the registration of TALON™ rodenticide pellets for control of commensal rats and mice in and around homes, industrial and agricultural buildings.

TALON is a new product containing 99.995% inert ingredients and 0.005% (50ppm) active ingredient brodifacoum = 3-[3-(4-bromo[1,1'-biphenyl] 4-yl)-1,2,3,4-tetrahydro-1-naphthalenyl]4-hydroxy-2H-1-benzopyran-2-one; chemical structure:



Other names: Brodifacoum
Code names: PP581 and WBA8119

Applicant has also submitted an application for the registration of Brodifacoum technical and Brodifacoum concentrate for formulating use only.

II. Directions for Use

For Norway and roof rats, place at least 4 oz. of bait at intervals of 15 - 30 feet, and for house mice, place at least 2 oz. of bait at intervals of 8 - 12 feet, along walls or runways in rat burrows and in sheltered areas where rats are known to live or feed. Maintain uninterrupted supply of fresh bait for 10 - 15 days or until signs of rat activity cease.

Use:

Place bait in areas which are inaccessible to children, pets, domestic animals and wildlife or in a tamper-proof bait box.

III. Discussion of Data

BRODIFACOUM - Its Hydrolysis in Aqueous Systems in the Dark - (Report No. RJ0047A) P. Hendley, Y. Lightfoot, and F. J. Hemingway, ICI, R & D Dept., 21 Nov. 1978.
(EPA acc.# 10182-EA)

Procedure

A stock solution of ^{14}C-brodifacoum (uniformly labeled in the phenyl ring of the coumarin moiety) in acetone containing a 0.355 mg/l of trans isomer and 0.642 mg/l of cis isomer was prepared at concentrations of 10 and 1 ppm in four sterile solutions, (pH 4, pH 7, pH 9 and dist. water).

One pair of flasks from each solution was stored in the dark at 20°C, and the other pair was shaken at 45°C in a thermo water bath.

Duplicate aliquots (10 mls) of each solution were taken on 0, 3, 7, 13 and 30 day. All samples stored at -20°C until analyzed.

Analytical Method

The aqueous samples were extracted with CH_2Cl_2. Organic phase was dried with anhydrous $MgSO_4$ and filter-wash residue with CH_2Cl_2. Organosolubles were radioassayed and then concentrated for TLC in 2 solvent systems 1:4 Dioxan & Petroleum Spirit (40:60), and ethylacetate = dichloromethane (5:95). Aqueous phase was combined with the organic phase filtrate and radioassayed by LSC.

Results

- Isomers ratio after hydrolysis was 61.4%cis = 38.6% trans (vs. 65% = 35% before) concentration of radioactivity in solutions remained unchanged between 3 and 30 days in the pH 7, and pH 9 solutions at 1 and 10 ppm sol. in dist. water.

- For the pH 4 solution at both temperatures and concentrations, and in 10 ppm distilled water solution at 45°C, there was a drop in the level of radioactivity.

- Extractable radioactivity from aqueous phase into dichloromethane averaged 96% for all samples except the 10 ppm dist. water solutions (possibly due to precipitation/absorption onto the glass walls).

- Organosolubles radioactivity accounted for as brodifacoum (combined isomers) in solvent system I and II were 95% of the values of the 10 ppm solutions and 78% of the values for the 1 ppm solutions.

An unidentified compound Y was found in the 10 and 1 ppm solutions with relatively higher levels present in the 1 ppm solutions suggesting that some factor in the work-up was converting brodifacoum to compound Y.

Conclusion

1. Concentration of radioactivity in the pH 7 and pH 9 solutions at 1 and 10 ppm and 20° and 25°C remained unchanged between 3 and 30 days, indicating absence of volatiles.

2. Brodifacoum is stable to hydrolysis under the conditions used with no significant formation of 4-hydrocoumarin found.

3. Ratio of brodifacoum isomers was essentially unchanged throughout the study.

Brodifacoum - The Degradation of the Pesticide in Soil Under Laboratory Conditions. D. J. Arnold, J. H. Kapley, and M. S. Weissler (Rep. # RJ0040B) 7 Nov. 1978 EPA acc# 10182-EA26.

Procedure

Three soil types (coarse sandy loam, coarse sand, and clay loam) were treated with 3 preparations of ^{14}C-brodifacoum and incubated at 25°C, aerobically in the dark under lab conditions with the pesticide applied at 0.5 and 5.0 kg/ha to some soils. Coarse sandy loam will also be aerobically incubated under flooded conditions.

Soil Characteristics

Soil Type & Classification	pH	% organic matter content	Coarse sand	Fine sand	Silt	Clay	CEC	Moisture Holding Capacity
'Peartree 7' Coarse Sandy Loam	7.2	6.3	38.0	22.0	17.0	23.0	16.5	84.1
'Gore' Clay Loam*	8.0	11.7	5.3	27.1	14.3	53.3	29.7	154.2
'Lilyfield' Coarse Sand	5.5	1.9	67.5	22.5	2.9	7.1	1.8	30.2

* Contained approximately 15% carbamates

Soil Treatments and Sampling

Pesticide isomer (^{14}C labeled)	Pesticide application rate kg/ha	Incubation conditions	'PEARTREE 7' 0 2 6 12	'GORE' 0 2 6 12	'LILYFIELD' 0 2 6 12
cis			+ + + +		
trans	0.5	aerobic	+ + + +		
cis,trans		25°C	+ + + +	+ + + +	+ + + +
cis,trans	5.0		+ + + +	+ + + +	+ + + +
cis,trans	0.5	flooded 25°C	+ + + +		

Summary of Pesticide isomers preparations
cis = c, trans = t

Preparation #	Rate of Pesticide Appl. (kg/ha)	Pesticide Appl. per soil pot (mg)	brodifacoum isomers
1	0.515	0.0645	only c
2	0.502	0.0627	only t
3	0.546	0.0682	c:t = 60:40
4	5.0	0.6614	c:t = 64:36

Analytical Methodology

1. Quantification of radioactivity in all zero time treated soils was determined by refluxing extraction in solvent dichloromethane:methanol (80:20) for 2-18 hr. periods and mixed extracts and washings were reextracted and analyzed separately. Cold extraction was used for soil samples at 2, 6, and 12 weeks where soils were cold shaken at 25°C. After first 18 hr. extraction, the soils were centrifuged, washed and recentrifuged. Extracts and washings were combined and additional 18 hr. extraction was carried out. Radioactivity remaining in soils was quantified by combination of aliquots and LSC.

Distribution of total radioactivity at 0.5 kg/ha

Brodifacoum and degradation products		'PEACHTREE 7' (c,t/A 0.5/PT 7)				'GORE' (c,t/A 0.5/GORE)				'LILYFIELD' (c,t/A 0.5/LF)			
		Weeks Incubation				Weeks Incubation				Weeks Incubation			
		0	2	6	12	0	2	6	12	0	2	6	12
In extracts of soil	1 cis	51.4	47.8	46.2	45.7	50.4	43.3	40.1	36.5	53.5	58.7	47.3	51.7
	1 trans	38.8	29.8	26.4	20.4	33.5	22.6	20.2	13.3	39.1	29.0	37.3	26.5
	II	1.8	0.3	0.5	1.3	1.0	1.5	0.7	1.2	0.2	1.1	0.7	1.6
	x	4.0	7.9	9.0	11.0	4.8	17.0	15.9	18.9	0.1	4.4	5.8	9.3
	remainder of radioactivity	3.0	7.3	6.2	2.4	8.5	6.3	10.2	7.6	6.5	3.3	5.5	3.3
	radioactivity in 2nd extract	Q	0.5	1.6	Q	Q	1.5	3.7	3.1	Q		Q	1.6
	$^{14}CO_2$	<0.001	1.9	5.0	7.9	<0.001	1.6	3.3	7.3	<0.001	0.4	0.6	1.6
Bound (non-extractable radioactivity		1.0	4.5	5.1	11.3	1.8	6.2	5.9	12.1	0.4	1.1	2.8	4.4

Cis: trans ratio of ^{14}C-brodifacoum in soil at 0.5 and 5.0 kg/ha

Soil Treatment	Pesticide isomer	'PEACHTREE 7'				'CORE'				'LILYFIELD'			
		Weeks Incubation				Weeks Incubation				Weeks Incubation			
		0	2	6	12	0	2	6	12	0	2	6	12
c,t/A 0.5	cis	57.1	61.6	63.6	69.1	60.1	65.7	66.5	73.3	57.8	66.9	55.9	66.1
	trans	42.9	38.4	36.4	30.9	39.9	34.3	33.5	26.7	42.2	33.1	44.1	33.9
c,t/A 5.0	cis	63.4	62.7	63.2	68.1	62.3	64.7	65.4	71.4	62.4	62.3	61.2	57.3
	trans	36.6	37.3	36.8	31.9	37.7	35.3	34.6	28.6	37.6	37.7	38.8	42.7
c,t/F 0.5[b]	cis	58.6	ND	ND	61.9								
	trans	41.4	ND	ND	38.1								

Brodifacoum and its degradates identified and quantified by TLC and comparison to reference compounds

a) 4,hydroxy coumarin II
b) brodifacoum I
c) cis, 3(3-[4'-bromobiphenyl-4-yl]-1,2,3,4-tetrahydronaphth-1-1-yl)-4-hydroxycoumarin-cis-I

d) trans, 3-(3-[4-bromobiphenyl-4-yl]-1,2,3,4-tetrahydronaphth-1-yl)-4-hydroxy coumarin-trans-I

Results

Material balance was 94% with range 68% to 110%. Gore clay loam showed the lower material balance.

Conclusion

1. Brodifacoum as cis and trans isomers degraded with various degrees in all soils incubated under aerobic and flooded conditions.

   In the coarse sandy loam, trans-isomer degraded more rapidly than cis-isomer, yielding 50% and 33% degradation in 8 and 12 weeks, respectively.

   In the clay soil 50% of the cis,trans brodifacoum degraded most rapidly in 12 and estimated 20 weeks; pesticide applied at 0.5 and 5.0 kg/ha.

2. The degradation of brodifacoum at 0.5 kg/ha resulted in the formation of <2% of 4,hydroxy coumarin (II) in all soils and on unidentified product "X" (up to 19% of recovered radioactivity). Amount of product "X" were slightly less in the flooded soil and soils treated at 5.0 kg/ha.

3. In all soils bound residues were generally small ranging from 1 - 12% of recovered radioactivity.

4. Ratio of cis:trans-brodifacoum in the coarse sandy loam and clay loam changed from 60:40 to approximately 70:30 after 12 wks. In flooded soil this raatio was relatively unchanged, possibly due to slower rate of degradation.

3.3 Brodifacoum Dissipation in Soil (Interim report) January 30, 1979 by J. P. Ussury, ICI, Agrichem Div.

Summary of the Study

A dissipation study of brodifacoum is being conducted at Goldsboro, NC; Champaign, IL; and Visalia, CA. To fallow test plots, technical brodifacoum was applied at 2 and 8 lb ai/and plots then filled to 3" depth.

The NC soil is a loamy fine sand with a pH 5.6; the IL soil is a silty clay loam with a pH 6.0; and the CA soil is a fine sandy loam with pH = 8.4.

Samples were taken from 0-3", 3-6", and 6-12" depth on day of this application and intervals up to 109 days afterwards. Sampling will be continued thru 18 mos.

Soil samples were analyzed by extraction with 30% methanol in chloroform. After filtration residue was redissolved in 15% CH_2Cl_2 in cyclohexane, and then in HPLC mobil phase and analyzed by UV detector with a detectability limit of 0.04 ppm for total brodifacoum.

Reported results indicate that brodifacoum was most unstable in the CA soil where only about 10% of original residue remained after 90 days, while no degradation of residues was noted in the NC soil during the sampling period. In the IL soil, residue from the 2 lb/A treatment were unchanged thru 90 days, while the 90-day sample from the 8 lb/A treatment contained 1/2 of the residue of earlier samples.

Conclusions: Brodifacoum dissipation pattern in the soils treated may restrict its uses geographically.

IV. Summary

1. Brodifacoum isomers are stable to hydrolysis at pH 4, 7, and 9, at temperatures 20° and 45°C, and at concentrations of 1 and 10 ppm brodifacoum.

2. Under aerobic and flooded conditions, it degrades in coarse sandy loam, clay loam and coarse sand soils 40% of their moisture holding capacity.

   Degradation products are CO_2(1 and 12%), d-hydroxy coumarin (up to 3%), and bound residues (1-12%). Flooding reduces evolution of CO_2 significantly. Most rapid degradation occurred in the clay loam soil (pH = 8); t 1/2 = 12 weeks at 0.5 kg/ha application rate.

   Of the two isomers, trans-brodifacoum degraded more rapidly.

pH 5, and 6 alkaline?

3. Brodifacoum dissipation rate was highest in alkaline soils where it was applied at a rate of 1.75 lb/soil (pH 5, 6), degradation of residues was noted at neither 2 nor 5 lb/A application rates while, in the silty clay loam, brodifacoum residues dissipation was considerable (reached 50%) at the 8 lb/A rate and remained unchanged at the 2 lb/A application rate.

V. Recommendation

EFB concurs in the proposed use of brodifacoum in the areas proposed in the directions for use: in and around homes, industrial and agricultural buildings, in tamper-proof bait boxes, or areas inaccessible to children, domestic animals and wildlife. The proposed use is not considered by EFB to be an extensive or dispersive outdoor use and the limited amount of environmental fate information submitted appears adequate. However, any proposed use of brodifacoum in dispersive outdoor environmental use patterns such as ground spray in orchards or bait uses in agricultural fields will require full environmental fate information.

We note that the field dissipation study is an interim report of the experiment in progress. The final report regarding this research should be submitted when available. A discussion of the selected field application rates of 2 and 8 lbs. active ingredient per acre in comparison to label directions of 4 oz. bait at 15 - 30 intervals would be helpful.

Note to EEB

EFB defers to EEB in regard to any additional environmental fate information necessary for EEB assessment of this outdoor domestic use. In addition, EEB should consider EEB data needs of environmentally dispersive uses of this chemical are proposed in the future.

Madeline Nawar
EFB, Section #1