

Fluoroaliphatic Sulfones: A New Class of Delayed-action Insecticides for Control of *Solenopsis invicta* (Hymenoptera: Formicidae)¹

ROBERT K. VANDER MEER, CLIFFORD S. LOFGREN,
AND DAVID F. WILLIAMS

Insects Affecting Man and Animals Research Laboratory,
Agricultural Research Service, U.S. Department of Agriculture,
P.O. Box 14565, Gainesville, Florida 32604

J. Econ. Entomol. 78: 1190-1197 (1985)

ABSTRACT Extensive laboratory testing of fluoroaliphatic sulfones (R_fSO_2R) showed that, in particular, sulfonamide ($R_fSO_2NR_1R_2$) analogs have potential as delayed-action toxicants for control of the red imported fire ant, *Solenopsis invicta* Buren. Delayed activity was observed when R_1 and $R_2 = H$ or alkyl with one exception ($R_1 = H$, $R_2 = t$ -butyl). Dependent on the double-bond position, unsaturated hydrocarbon substituents gave either fast kill or delayed activity. Monoalcohol substituents showed delayed activity, but diols were inactive. Polyether substituents, either hydrogen or methyl end-capped, showed similar delayed activity. The C_8F_{17} fluorocarbon radical yielded the best activity. Both the fluorocarbon and sulfone groups were essential to the activity of this class of compounds.

THE RED IMPORTED fire ant (RIFA), *Solenopsis invicta* Buren, is a serious medical and crop pest in the southern United States (Lofgren et al. 1975, Lofgren and Adams 1982). Efforts to control this pest have included soil residual treatments with heptachlor and dieldrin. Later, a bait formulation with mirex as the active ingredient was used. Environmental Protection Agency cancellation of the registration of these compounds (mirex registration was cancelled in late 1977; Johnson 1976) triggered a search for alternative toxicants.

RIFA are difficult to control because fast-acting toxicants formulated on baits affect only a small percentage of foraging workers with little effect on the total colony. In addition, the foraging workers pass ingested toxicants to other members of the colony, thus diluting the effects of the toxicant. Delayed toxicity over a range of concentrations is needed. During the past 10 years, our laboratory has conducted an intensive program to identify delayed-action toxicants. Only ca. 5% of the >7,000 compounds tested had any delayed action and <1% had delayed action over a range of concentrations. We have identified suitable toxicants or insect growth regulators such as Amdro (tetrahydro-5,5-dimethyl-2(1H)-pyrimidinone [3-[4-trifluoromethyl]-1-[2-[4-(trifluoromethyl)phenyl]ethenyl]-2-propenylidene] hydrazone; American Cyanamid AC 217300; Williams et al. 1980, Vander Meer et al. 1982), Affirm (Avermectin B_{1a}, a macrocyclic lactone glycoside isolated from *Streptomyces avermitilis*, Merck Sharp and Dohme; Lofgren and Williams 1982), Logic (Ethyl[2-(p-phenoxyphen-

oxy)ethyl]carbamate, Maag Agrochemicals; Banks et al. 1983), and Bant (N-[2-amino-3-nitro-5-(trifluoromethyl)phenyl]-2,2,3,3-tetrafluoro-propanamide, Eli Lilly; Williams and Lofgren 1981). All but one of these chemicals have been or are expected to be developed commercially. Some of these compounds are active against other pest species (Ostlind et al. 1979); Amdro represents a new structural class of insecticide (Lovell 1979).

We report here the discovery of another new class of insecticides especially effective against RIFA and against other insect pests (Vander Meer et al. 1983a).

Materials and Methods

All compounds used in this study were provided by 3M Company, St. Paul, Minn., as technical-grade compounds. The materials were used without further purification. The general procedure for primary screening for RIFA toxicants has been discussed in detail by Williams et al. (1980). The general procedure with specific modifications was as follows. Each test consisted of three replicates of 20 brood-tending worker ants chosen at random and maintained in plastic medicine cups (30 ml) for 14-21 days. The test material was dissolved in once-refined soybean oil or, in the case of water-soluble compounds, honey/water (1:1). For each test series, a set of soybean oil or honey water controls were run as well as a mirex standard. If the control mortality at the end of the test was >15%, the entire series was repeated. Results for compounds not soluble in either system are not included in this report. The toxicant solution was absorbed onto cotton swabs, and presented to the test ants.

¹ This article reports the results of research only. Mention of a pesticide or a proprietary product does not constitute an endorsement or a recommendation for its use by USDA.

Table 1. Toxicity of alkyl substituted sulfonamides to RIFA workers

AI3-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
29759	$C_8F_{17}SO_2NH_2$	0.01	0	0	0	3	7	7	10	20	23	III
		0.1	0	0	0	2	33	77	92	95	98	
		1.0	43	85	98	100						
29758	$C_8F_{17}SO_2NCH_3$	0.01	0	0	2	3	7	7	7	23	40	III
		0.1	0	0	7	88	97	98	100			
		1.0	17	93	100							
29757	$C_8F_{17}SO_2NC_2H_5$	0.01	0	0	0	0	2	2	10	22	50	III
		0.1	0	0	2	80	97	97	98	98	100	
		1.0	25	100								
10712	$C_8F_{17}SO_2NCH(CH_3)_2$	0.01	2	2	2	2	2	3	5	27	65	III
		0.1	0	0	10	75	93	98	100			
		1.0	83	97	100							
10713	$C_8F_{17}SO_2NC(CH_3)_3$	1.0	0	0	0	0	0	0	5			I
10707	$C_8F_{17}SO_2N(C_2H_5)_2$	0.01	0	0	0	2	5	10	20	50	60	III
		0.1	0	7	13	78	92	98	100			
		1.0	30	100								
29777	$C_8F_{17}SO_2NC_{12}H_{25}$	0.01	0	0	0	5	5	5	7	13	17	III
		0.1	0	0	0	0	2	2	20	50	80	
		1.0	0	2	3	78	97	100				
10867	$(CH_3NHSO_2(CF_2)_4)_2$	1.0	0	0	2	3	3	17	82			I

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

After 24 h, the cotton swabs were removed and the ants remained without food for the next 24 h. Cotton swabs saturated with untreated soybean oil were placed in the cups for the remainder of the test period. Mortality counts were recorded at intervals of 1, 2, 3, 6, 8, 10, and 14 days. However, in some cases, mortality counts were also made at 17 and 21 days. Preliminary tests with all the chemicals were conducted at 1.0% wt/wt (AI). Toxicants that caused >80% mortality at the end of the test period were tested again at 1.0, 0.1, and 0.01%. All test results were expressed as the mean percent mortality at the specified day and toxicant concentration.

The toxicant classification system was adapted from Lofgren et al. (1967) and provides for easy comparisons within a group and with previous results. Class I compounds cause <90% kill at 1.0% at the end of the test period. Class II compounds kill too fast at the higher concentrations (>15% mortality after 24 h and >90% at the end of the test period), and cause <90% total kill at lower concentrations. Class III compounds show delayed action (<15% kill after 24 h but >90% at the end of the test period) over a 1- to 9-fold range of concentrations. Class IV compounds are similar to Class III toxicants except that they show delayed action over a 10- to 99-fold range of dosages. The

rare Class V compounds show delayed activity over a 100-fold or greater concentration range.

Results and Discussion

Over several years a number of organofluorine compounds was screened for RIFA toxicity (Vander Meer et al. 1983b). Several of these compounds, containing a variety of functional groups (i.e., alcohols, ketones, and a carboxylic acid), exhibited Class III delayed toxicity. Thus, we expected our standard bioassay procedures to detect delayed toxicity from fluorinated sulfonamide surfactants (Ahlbrecht and Brown 1957). The availability of a large number of analogs and related compounds made it possible to attempt to correlate structure with activity.

All of the active compounds discussed in this paper are of the general structure R_fSO_2A , where R_f is a fluoroaliphatic radical and A is theoretically any compatible chemical structure. The formula of most of the compounds, however, was that of the fluorinated sulfonamide, $R_fSO_2NR_1R_2$, where R_1 and R_2 are any chemically compatible structures. The activity of these compounds and their structure-activity relationships can be best illustrated by first examining analogs where the fluoroaliphatic radical, R_f , is held constant and R_1 and

Table 2. Toxicity of unsaturated sulfonamides to RIFA workers

AI3-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
10717	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NCH}=\text{CH}_2 \end{array}$	0.01	0	0	0	8	8	13	25	37	57	III
		0.1	0	7	33	77	90	92	100			
		1.0	100									
10710	$\begin{array}{c} \text{H} \\ \\ n\text{-C}_8\text{F}_{17}\text{SO}_2\text{NCH}_2\text{CH}=\text{CH}_2 \end{array}$	0.01	2	2	2	2	2	2	12	37	75	IV
		0.1	3	3	3	48	60	78	93	98	100	
		1.0	13	53	80	100						
10709	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NCH}_2\text{C}\equiv\text{CH} \end{array}$	0.01	5	5	5	5	5	5	15	15	30	III
		0.1	2	2	2	2	3	5	43	73	87	
		1.0	0	0	0	2	45	60	90	93	100	
10714	$\begin{array}{c} \text{H} \\ \\ n\text{-C}_8\text{F}_{17}\text{SO}_2\text{NC}_6\text{H}_5 \\ \text{(recrystallized} \\ \text{linear isomer)} \end{array}$	0.01	0	0	0	2	3	3	7	17	27	III
		0.1	0	2	2	8	53	70	93	95	98	
		1.0	83	87	88	95	97	97	100			
29767	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NCH}_2\text{C}_6\text{H}_5 \end{array}$	0.01	0	0	0	0	0	3	3	3	3	III
		0.1	0	0	0	2	2	3	8	18	42	
		1.0	0	0	0	2	42	83	100			
Mirex		0.01	0	0	0	0	17	38	58	63	92	V
		0.1	0	0	50	73	90	98	100			
		1.0	5	83	97	100						

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test.

R₂ are varied. The R₁ radical with the most abundant analogs was the heptadecafluorooctyl group (R₁ = C₈F₁₇). The synthetic preparation of structures containing this radical (Ahlbrecht and Brown 1957, Olson 1974) is such that the products are composed of several structural isomers, of which the straight chain isomer dominates. However, branched chain isomers are also present.

Table 1 illustrates the effects of altering the size and configuration of alkyl substituents on the nitrogen. In all but the t-butyl compound (10713), Class III delayed activity was observed. The actual cause of the inactivity of the t-butyl analog is unknown, but may be due to increased steric bulk or to the absence of a proton α- to the nitrogen. All of the other analogs (unsubstituted sulfonamide, 29759, and substituted sulfonamides methyl, 29758; ethyl, 29757; isopropyl, 10712) were Class III toxicants and came close to Class IV activity except for high mortality at the 1% concentration. If the perfluorinated eight-carbon chain was sandwiched between 2 N-methyl sulfonamide groups (10867) activity was lost, indicative of the importance of an unencumbered fluoroaliphatic radical.

We found that N-substituents containing a double bond gave either fast action or delayed action at the 1% level (Table 2). Definition of the possible relationships between structure and activity is difficult because the N-methyl and N-ethyl groups

on analogs 10717 and 29767, respectively, precluded exact comparison with N-allyl (10710) and N-phenyl (10714) derivatives. However, the consistent delayed action of N- and N,N-dialkyl analogs (Table 1) strongly suggested that if the unsaturation was directly attached to the sulfonamide nitrogen (N-vinyl, 10717; N-phenyl, 10714), fast kill would have been observed. However, when a methylene group was placed between the nitrogen and unsaturation, it resulted in delayed activity. This suggestion was further supported by results for the N-propargyl analog (10709), which we predicted to have delayed action. Compound 10710 ranked high in this bioassay; in fact, it qualified as a Class IV compound and its activity was comparable with that of a mirex standard (Table 2).

Bioassay results where R₁ or R₂ equal mono-alcohols are given in Table 3. The first three compounds maintained the same two carbon alcohol but the N-alkyl group was varied (29782, 29754, 29765). Increasing the length of the N-alkyl group did not significantly alter the compound activity, since they were all Class III toxicants. Extending the alcohol chain length by two carbons increased the activity (29756, Class IV) compared with the closest analog (29782, Class III). However, addition of an N-monoalcohol group extended (in time) the delayed activity of the toxicants (compare 29782 and 29756 [Table 3] with 29757 and 29758

Table 3. Toxicity of mono- and di-alcohol-substituted sulfonamides to RIFA workers

A13-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class	
			1	2	3	6	8	10	14	17	21		
29782	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NC}_2\text{H}_4\text{OH} \end{array}$	0.01	0	0	2	2	2	2	2	2	2	3	III
		0.1	0	0	0	0	2	2	8	40	60		
		1.0	0	0	0	45	67	88	98	100			
29754	$\begin{array}{c} \text{C}_4\text{H}_9 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NC}_2\text{H}_4\text{OH} \end{array}$	0.01	0	0	0	0	0	0	0	0	0	2	III
		0.1	0	2	2	3	3	3	25	48	78		
		1.0	0	0	0	0	0	40	92	98	100		
29765	$\begin{array}{c} \text{C}_{12}\text{H}_{25} \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NC}_2\text{H}_4\text{OH} \end{array}$	0.01	0	0	0	0	0	0	0	0	0	0	III
		0.1	0	0	0	0	0	0	2	3	15		
		1.0	0	0	0	0	2	32	77	88	100		
29756	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NC}_4\text{H}_8\text{OH} \end{array}$	0.01	0	0	2	5	8	8	8	10	13	IV	
		0.1	0	0	0	2	5	30	75	85	92		
		1.0	0	2	10	83	85	95	100				
10731	$\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_4\text{OH})_2$	1.0	0	0	0	2	5	10	35			I	
10732	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NCH}_2\text{CH}-\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	1.0	0	0	0	2	2	2	5			I	

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

[Table 1], respectively). This effect was accentuated with almost complete loss of activity when two hydroxyl groups were on R₁ or R₂ (10731) and when there was one hydroxyl each on R₁ and R₂

(10731). In general, the introduction of alcohol functionalities to R₁, R₂, or both, appears to be detrimental to effectiveness.

We tested several polyethers (Table 4), some

Table 4. Toxicity of polyether-substituted sulfonamides to RIFA workers

A13-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
29753	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_4\text{O})_3\text{H} \end{array}$	0.01	0	0	0	0	3	7	7	13	20	III
		0.1	0	0	0	0	0	0	3	7	27	
		1.0	0	0	2	52	87	98	99	100		
29773	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NC}_2\text{H}_4\text{O}(\text{C}_3\text{H}_6\text{O})_8\text{H} \end{array}$	0.01	0	0	0	0	0	0	0	0	0	I
		0.1	0	0	0	0	0	0	0	3	17	
		1.0	0	0	0	3	5	23	37	45	60	
29772	$\begin{array}{c} \text{C}_4\text{H}_9 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NC}_2\text{H}_4\text{O}(\text{C}_3\text{H}_6\text{O})_8\text{H} \end{array}$	0.01	0	0	2	2	2	2	2	2	2	III
		0.1	0	0	0	0	0	3	3	15	45	
		1.0	0	2	2	2	2	40	87	97	100	
10749	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_4\text{O})_7\text{CH}_3 \end{array}$	0.01	2	3	3	3	3	5	8			I
		0.1	5	5	8	15	20	23	40			
		1.0	2	5	5	38	57	80	88			
29769	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_4\text{O})_{17}\text{CH}_3 \end{array}$	0.01	0	0	0	3	7	7	10	13	17	III
		0.1	0	0	0	2	3	5	10	25	48	
		1.0	0	0	32	100						

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

Table 5. Toxicity of some active sulfonamides with various nitrogen substituents

A13-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
29778		0.01	2	3	3	8	8	8	13	15	18	III
		0.1	0	2	3	10	10	52	67	80	88	
		1.0	0	2	17	92	100					
10845		0.01	0	0	0	0	0	0	2			III
		0.1	2	2	2	2	3	8	20			
		1.0	0	0	3	33	43	70	93			
10849		0.01	0	0	0	0	0	0	0	0	0	III
		0.1	0	0	0	0	0	10	30	73		
		1.0	7	35	50	50	92	97	100			
10840		1.0	0	0	2	50	87	92	97			III
10869		0.01	0	0	0	2	2	7	10			III
		0.1	0	0	0	28	40	60	85			
		1.0	2	5	18	62	70	93	100			
10733	$C_8F_{17}SO_2NC_2H_4Cl$	0.01	0	0	0	0	3	3	5	23	47	III
		0.1	0	0	2	22	83	95	97	100		
		1.0	57	87	98	100						
10870	$C_8F_{17}SO_2NSCCl_3$	0.01	0	0	2	2	2	2	7			III
		0.1	0	2	5	43	45	70	80			
		1.0	7	25	97	100						

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

ending in a hydrogen (29753, 29773, 29772) and others capped with a methyl group (10749, 29769). The activity and the way the polyether was end-capped did not appear to be related. Similarly, no

trends were observed based on activity and length of the polyether (29753, 10749, 29769) or whether the polyether contained ethoxy (29753) or propoxy (29773) units. In general, activity in polyethers

Table 6. Toxicity of some other nitrogen substituents

A13-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
10705		1.0	2	2	2	3	8	15	30			I
29761		1.0	2	2	2	2	2	2	10			I
10706		1.0	0	0	0	0	3	5	10			I
29752		1.0	2	3	3	3	3	3	10			I
10864		1.0	0	0	0	0	2	2	2			I

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

Table 7. Effects of decreasing the fluorocarbon chain length on toxicity to RIFA workers

AI3-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
10703	CF ₃ SO ₂ NH ₂	0.01	0	0	0	3	3	5	7	8	17	I
		0.1	3	3	3	5	5	5	17	27	58	
		1.0	2	8	18	33	42	50	67	73	82	
10744	C ₂ F ₅ SO ₂ NH ₂	1.0	3	17	22	35	40	45	50			I
10745	C ₄ F ₉ SO ₂ NH ₂	1.0	0	0	0	3	3	3	5			I
10702	C ₆ F ₁₃ SO ₂ NH ₂	0.01	0	0	0	2	2	2	2	5	12	IV
		0.1	3	7	7	7	7	17	63	77	92	
		1.0	0	3	30	67	75	87	95	98	100	
29759	C ₈ F ₁₇ SO ₂ NH ₂	0.01	0	0	0	3	7	7	10	20	23	III
		0.1	0	0	0	2	33	77	92	95	98	
		1.0	43	85	98	100						
29764	$\begin{array}{c} \text{H} \\ \\ \text{C}_{10}\text{F}_{21}\text{SO}_2\text{N}(\text{C}_2\text{H}_7\text{O})_{14}\text{H} \end{array}$	1.0	0	0	0	0	0	0	17			I

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

compared with their monoalcohol precursor (29782) (Table 3) did not appear to improve. Therefore, as in the monoalcohols, we concluded that addition of polyethers to the nitrogen of the sulfonamide moderated activity when compared to the corresponding N-alkyl derivatives (Table 1).

A number of heptadecafluorooctylsulfonamide analogs were active but did not fit into any distinct functional groups (Table 5). We noted that two compounds with the sulfonamide nitrogen incorporated in a heterocyclic ring (29778, 10845) showed Class III activity. Two urea-like analogs (10840, 10869) showed good delayed activity. Reducing the carbonyl to a methylene, as in 10849, did not cause loss of activity. Compounds 10733 and 10870 also exhibited excellent delayed toxicity; they were related only by their chlorines. These

compounds (Table 5) may aid in the search for other types of sulfonamide toxicants with specific activity. For instance, many other derivatives could be prepared that incorporated the sulfonamide nitrogen in a ring system (i.e., pyridine, oxazole, piperidine, thiazole, pyrrole).

Most compounds that we have discussed had very good delayed-action toxic properties. Some examples of inactive compounds that may indicate the limitations of possible structural variation are an epoxide (10705), amine (29761), amide (10706), phosphate (29752), and an aromatic carboxylic acid (10864), all of which were inactive in our bioassay (Table 6).

To examine the effects of alterations at the fluorocarbon end of the molecule, we kept -SO₂NH₂ constant and varied the fluorocarbon radical. Ta-

Table 8. Importance of fluorocarbon and sulfone moiety of molecules on toxicity

AI3-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
29759	C ₈ F ₁₇ SO ₂ NH ₂	0.01	0	0	0	3	7	7	10	20	23	III
		0.1	0	0	0	2	33	77	92	95	98	
		1.0	43	85	98	100						
10721	C ₈ H ₁₇ SO ₂ NH ₂	1.0	5	7	8	12	12	12	12			I
10739	$\begin{array}{c} \text{O} \\ \\ \text{C}_7\text{F}_{15}\text{CNH}_2 \end{array}$	1.0	0	0	0	2	2	2	2			I
10703	CF ₃ SO ₂ NH ₂	0.01	0	0	0	3	3	5	7	8	17	I
		0.1	3	3	3	5	5	5	17	27	58	
		1.0	2	8	18	33	42	50	67	73	82	
10752	FCH ₂ SO ₂ NH ₂	1.0	0	0	2	30	33	43	53			I
10753	HCF ₂ SO ₂ NH ₂	1.0	0	2	2	13	18	20	30			I

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

Table 9. Toxicity of several sulfonic acids and salts to RIFA workers

A13-no.	Structure	Concn (%)	% Mortality at specified days ^a									Activity class
			1	2	3	6	8	10	14	17	21	
50950	C ₈ F ₁₇ SO ₃ K	1.0	2	2	23	87	100					III
10700	$\begin{array}{c} \text{H} \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NNa} \end{array}$	1.0	2	37	73	98	100					III
10701	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_8\text{F}_{17}\text{SO}_2\text{NNa} \end{array}$	1.0	62	97	100							II
10750	$\begin{array}{c} - + \\ \text{C}_8\text{F}_{17}\text{SO}_3\text{N}(\text{C}_2\text{H}_5)_4 \end{array}$	1.0	10	47	95	100						III
10727	C ₈ F ₁₇ SO ₃ H	1.0	0	37	62	95	100					III
10728	C ₆ F ₁₃ SO ₃ H	1.0	15	77	95	100						III

^a Percentages are the mean of three replicates. The soybean oil control had <15% mortality at the end of the test, and the mirex standard had normal delayed activity (see Table 2).

ble 7 illustrates the effects of decreasing the fluorocarbon chain length. Below R_f = C₆F₁₃, there was no activity above Class I. Based on these results, the best activity was obtained when R_f equaled C₆F₁₃ or C₈F₁₇. The only example of R_f > C₈F₁₇ was the polyether 29764 which showed no activity (Table 7). All R_f = C₈F₁₇ polyethers (Table 4) showed significant toxicity.

The importance of the fluorocarbon or sulfone part, or both, of the molecule to activity of this class of toxicants was tested with appropriate substitutions (Table 8). The aliphatic sulfonamide, 10721, was inactive and demonstrated the necessity for the presence of the fluoroaliphatic moiety. However, the fact that R_f must also be combined with the sulfone group was illustrated by the lack of activity for fluoroaliphatic amide 10739. In addition, extrapolation from results for R_f = CF₃ (10703) and one and two proton substitutions (10752, 10753), R_f = CFH₂ and CF₂H, respectively, indicated that any R_f less than perfluorinated will have greatly diminished activity.

Large-scale RIFA control is most effectively done with toxicants formulated in baits. Formulations consist of the toxicant dissolved in soybean oil and then absorbed onto a suitable carrier (i.e., corn grits, pregel defatted corn grits). Solid suspensions are not suitable because the RIFA workers have a sophisticated and efficient mechanism for filtering submicron particles from ingested food (Glancey et al. 1981). Consequently, oil solubility is an essential property for any potential RIFA toxicant. All of the compounds discussed above were soluble to at least 1% in soybean oil. However, a group of compounds that fit the generalized R_fSO₂A structure were water-soluble. These materials were formulated in honey/water (1:1) and tested against the RIFA in the standard bioassay. All of the compounds exhibited excellent delayed activity except 10701 (kill was too fast) (Table 9). The two sulfonic acids (10727 and 10728) and the two sulfonate

salts (50950 and 10750) had similar activity. However, the sodium salt (10700) of unsubstituted sulfonamide 29759 (Table 1) apparently gave better delayed action. The sodium salt (10701) of the N-methyl sulfonamide (29758, Table 1) showed increased toxicity. Although the solubility properties of the compounds listed in Table 9 make them poor candidates for RIFA control, they do suggest the versatility of the compounds and suggest other potential uses.

The results discussed in this paper cannot readily be explained in a mechanistic fashion until a more exact mode of action for this class of compound is determined. Successful whole-colony laboratory tests with many of the active compounds has ruled out fumigant action (unpublished results). Therefore, we suggest that, until further toxicological studies are conducted, the compounds should be considered stomach poisons.

Preliminary bioassay results against other insects have shown that certain compounds in this new class of toxicant have excellent activity against house fly adults, American and German cockroaches, and mosquito larvae (Vander Meer et al. 1983a).

Acknowledgment

We thank 3M Company for providing chemical samples and Ken Plumley for technical assistance.

References Cited

- Ahlbrecht, A. H., and H. A. Brown. 1957. Perfluoroalkylsulfonamidoalkanols and sulfates. *Chem. Abstr. Org. Chem.* 52: 2054-2055.
- Banks, W. A., L. R. Miles, and D. P. Harlan. 1983. The effects of insect growth regulators and their potential as control agents for imported fire ants (Hymenoptera: Formicidae). *Fla. Entomol.* 66: 172-181.
- Glancey, B. M., R. K. Vander Meer, A. Glover, C. S. Lofgren, and S. B. Vinson. 1981. Filtration of

- microparticles from liquids ingested by the imported fire ant, *Solenopsis invicta* Buren. *Insectes Soc.* 28: 395-401.
- Johnson, E. L.** 1976. Administrator's decision to accept plan of Mississippi Authority and order unpending hearing for the pesticide chemical mirex. *Fed. Reg.* 41: 56694-56704.
- Lofgren, C. S., and C. T. Adams.** 1982. Economic aspects of the imported fire ant in the United States. *In* M. D. Breed, C. A. Michner, and H. E. Evans [eds.], *The biology of social insects*. Westview, Boulder, Colo.
- Lofgren, C. S., and D. F. Williams.** 1982. Avermectin B_{1a}, a highly potent inhibitor of reproduction by queens of the red imported fire ant. *J. Econ. Entomol.* 75: 798-803.
- Lofgren, C. S., W. A. Banks, and B. M. Glancey.** 1975. Biology and control of the imported fire ant. *Annu. Rev. Entomol.* 20: 1-30.
- Lofgren, C. S., C. E. Stringer, W. A. Banks, and P. M. Bishop.** 1967. Laboratory tests with candidate bait toxicants against the imported fire ant. *U.S. Dep. Agric. Agric. Res. Serv. [Rep.]* 81-14.
- Lovell, J. B.** 1979. Amidinohydrazones, a new class of insecticides, pp. 575-582. *In* Proceedings, British Crop Protection Conference, Pest Disease No. 2.
- Olson, M. H.** 1974. Use of soluble fluoroaliphatic oligomers in resin composite articles. U.S. patent 3,787,351 (other patents of interest include 2,003,615; 2,346,612; 2,732,378; 2,759,019; 2,915,554; and 3,398,182).
- Ostlind, D. A., S. Cifelli, and R. Lange.** 1979. Insecticidal activity of the anti-parasitic avermectins. *Vet. Rec.* 105: 168.
- Vander Meer, R. K., C. S. Lofgren, and D. F. Williams.** 1983a. A method for control of insects. U.S. patent application SN 455,727.
- Vander Meer, R. K., D. F. Williams, and C. S. Lofgren.** 1982. Degradation of the toxicant AC 217,300 in Amdro® imported fire ant bait under field conditions. *J. Agric. Food Chem.* 30: 1045-1048.
- 1983b.** Efficacy of organofluorine compounds against the red imported fire ant, 1980. *Insectic. Acaric. Tests* 8: 252.
- Williams, D. F., and C. S. Lofgren.** 1981. Eli Lilly EL-468, a new bait toxicant for control of the red imported fire ant. *Fla. Entomol.* 64: 472-477.
- Williams, D. F., C. S. Lofgren, W. A. Banks, C. E. Stringer, and J. K. Plumley.** 1980. Laboratory studies with 9 amidinohydrazones, a promising new class of bait toxicants for control of red imported fire ants. *J. Econ. Entomol.* 73: 798-802.

Received for publication 31 January 1985; accepted 1 August 1985.
