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Fluorinated Sulfonamides: A New Class of Delayed Action Insecticides

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[a] This paper presents the results of preliminary research only and will be published later through established channels with appropriate editing. The paper and data should not be referred to in literature citations until they appear in press. Mention of a proprietary product does not constitute a recommendation by the United States Department of Agriculture nor does it imply registration under FIFRA as amended.

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ABSTRACT

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A new class of delayed action toxicant with the generalized formula $R_fSO_2NR_1R_2$ were presented. R_f is a fluoroaliphatic radical and R_1 and R_2 can be any chemically compatible groups. Structure activity-relationships showed that activity was lost if the steric bulk of R_1 or R_2 was great (i.e. R_1=H, R_2=t-Butyl). Unsaturated hydrocarbon substituents gave fast kill if the unsaturation was directly attached to the nitrogen; however, if a methylene group was placed between the nitrogen and double bond, delayed activity was observed. Mono-alcohol substituents showed delayed activity, but diols were inactive. Polyether substituents, either hydrogen or methyl-end capped, all showed similar delayed activity. The C_8F_{17} fluorcarbon radical yielded the best activity, and it was demonstrated that both the fluorocarbon and sulfone groups are essential to the activity of this class of compound. Both water soluble and oil soluble members of the class make them versatile in several different control situations and for several different types of insect pests.

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We would like to introduce a new class of fire ant toxicant that has only been alluded to at past meetings. All of the compounds presented were obtained from 3-M Company, St. Paul, Minnesota. The results are from our primary screening bioassay. The general bioassay procedure is outlined in Table I. In most of the examples the length of the bioassay was extended to 21 days, and unless otherwise specified the samples were dissolved in soy bean oil.

All of the toxicants fit into the general structure R_fSO_2A, where R_f is a fluoroaliphatic radical and A is any structurally compatible residue. Most of the compounds fall into the sulfonamide general formula, $R_fSO_2NR_1R_2$, where R_1 and R_2 are any compatible structures.

The activity of these compounds and their structure-activity relationships can be illustrated by keeping R_f constant and varying R_1 and R_2. Remember that for fire ant control we want delayed action over as wide a range of activity as possible.

Table II illustrates the simplest examples where R_1 and R_2 = H are alkyl groups. We see excellent delayed activity in almost all of the compounds in this series. However, when the steric bulk of the alkyl group is increased to t-butyl (10713) all activity is lost. Interestingly, the diethyl (10707) and the dodecyl (29777) both show delayed action.

When the substituent is unsaturated (Table III), we found that if the unsaturation was directly attached to the nitrogen (10717 and 10715) fast kill at 1.0% was observed. However, if a methylene group was placed between the nitrogen and unsaturation delayed action resulted. Compound 10710 looks especially good!

If R_1 or R_2 are monoalcohol groups (Table IV), delayed action results. Increasing the length of the N-alkyl group (29782, 29754, 29765) did not

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appreciably change the delayed toxicity. However, 2 hydroxyls on 1 group (10732) or one each on R_1 and R_2 (10731) resulted in no activity. In contrast the ester (29771) had delayed activity (Table IV).

We also tested a number of polyethers, some ending in a hydrogen (29753, 29773, 29772) and others capped with a methyl group (10749 and 29769). In both cases the compounds exhibited delayed toxicity (Table V).

Addition of any other functionality, with the exception of 10733 and 29778 (Table VI), gave non-toxic compounds. For example the epoxide (10705), amine (29761), amide (10706) and phosphate (29752) were inactive.

To look at the other end of the molecule we kept $-SO_2NH_2$ constant and varied the fluorocarbon radical. Table VII shows the results of decreasing the fluorocarbon chain length. Below $R_f = C_6F_{13}$ there is no activity except for $R_f = CF_3$, which may be due to fumigant action and not ingestion. Based on these results we feel that $R_f = C_8F_{17}$ or C_6F_{13} provides the best activity. We have demonstrated the importance of both the fluorocarbon and sulfone part of the molecule by the inactivity of compounds 10721 and 10739 (Table VIII).

All previous compounds were oil soluble, but the generality of this class of toxicants is due to the water solubility of certain members of the group. Table IX illustrates the excellent results obtained from several sulfonic acids and salts formulated in honey-water.

This general class of compounds have also been shown to be effective against cockroaches, flies and mosquitoes. Fluoronated sulfonamides and related compounds have a lot of potential and we look forward to following their progress in the pesticide field.

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Table I. Primary Screening Method for Evaluation of Chemicals as Bait Toxicants Against the Imported Fire Ant

1. Three reps of 20 worker ants placed in 30ml cups for 14 days.
2. Test chemicals dissolved in soybean oil or honey-water (1:1).
3. Toxic solution offered to ants on cotton swabs for 24 hrs.
4. Toxic solution removed from cups, ants remain w/o food for 24 hrs.
5. Cotton swabs saturated with soybean oil placed in cups for remainder of test period.
6. Knockdown and mortality counts recorded at intervals of 1, 2, 3, 6, 8, 10, and 14 days.
7. Preliminary tests with all chemicals conducted at 1.0%.
8. Chemicals giving >89% kill are retested at 1.0, 0.1 and 0.01% or until the minimum concentration giving >89% kill is determined.
9. Delayed kill is defined as <15% kill after day 1 and >85% kill after day 14 at any dosage. Promising toxicants have delayed kill over a 10-fold or greater range of concentrations.

Table II. Primary Screening Results for Alkyl Substituted Sulfonamides.

NUMBER	STRUCTURE	CONC. %	PERCENT MORTALITY AT SPECIFIED DAYS 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
		0.1	0	0	0	2	33	77	92	95	98
		1.0	43	85	98	100					
29758	$C_8F_{17}SO_2NHCH_3$	0.01	0	0	2	3	7	7	7	23	40
		0.1	0	0	7	88	97	98	100		
		1.0	17	93	100						
29757	$C_8F_{17}SO_2NHC_2H_5$	0.01	0	0	0	0	2	2	10	22	50
		0.1	0	0	2	80	97	97	98	98	100
		1.0	25	100							
10712	$C_8F_{17}SO_2NHCH(CH_3)_2$	0.01	2	2	2	2	2	3	5	27	65
		0.1	0	0	10	75	93	98	100		
		1.0	83	97	100						
10713	$C_8F_{17}SO_2NHC(CH_3)_3$	1.0	0	0	0	0	0	0	5		
10707	$C_8F_{17}SO_2N(C_2H_5)_2$	0.01	0	0	0	2	5	10	20	50	60
		0.1	0	7	13	78	92	98	100		
		1.0	30	100							
29777	$C_8F_{17}SO_2NHC_{12}H_{25}$	0.01	0	0	0	5	5	5	7	13	17
		0.1	0	0	0	0	2	2	20	50	80
		1.0	0	2	3	78	97	100			

Table III. Primary Screening Results for Unsaturated Sulfonamides.

NUMBER	STRUCTURE	CONC. %	PERCENT MORTALITY AT SPECIFIED DAYS 1	2	3	6	8	10	14	17	21
10717	$C_8F_{17}SO_2N(CH_3)CH{=}CH_2$	0.01	0	0	0	8	8	13	25	37	57
		0.1	0	7	33	77	90	92	100		
		1.0	100								
10710	n-$C_8F_{17}SO_2N(H)CH_2CH{=}CH_2$	0.01	2	2	2	2	2	2	12	37	75
		0.1	3	3	3	48	60	78	93	98	100
		1.0	13	53	80	100					
10709	$C_8F_{17}SO_2N(C_2H_5)CH_2C{=}CH$	0.01	5	5	5	5	5	5	15	15	30
		0.1	2	2	2	2	3	5	43	73	87
		1.0	0	0	0	2	45	60	90	93	100
10715	n-$C_8F_{17}SO_2N(H)C_6H_5$	0.01	2	2	2	2	2	2	3	12	27
	(recrystalized	0.1	0	0	0	18	63	87	90	95	98
	linear isomer)	1.0	88	92	93	97	98	98	98	98	100
29767	$C_8F_{17}SO_2N(C_2H_5)CH_2C_6H_5$	0.01	0	0	0	0	0	3	3	3	3
		0.1	0	0	0	2	2	3	8	18	42
		1.0	0	0	0	2	42	83	100		

Table IV. Primary Screening Results for Mono- and Di Alcohol Substituted Sulfonamides.

NUMBER	STRUCTURE	CONC. %	1	2	3	6	8	10	14	17	21
			PERCENT MORTALITY AT SPECIFIED DAYS								
29782	$C_8F_{17}SO_2N(C_2H_5)C_2H_4OH$	0.01	0	0	2	2	2	2	2	2	3
		0.1	0	0	0	0	2	2	8	40	60
		1.0	0	0	0	45	67	88	98	100	
29754	$C_8F_{17}SO_2N(C_4H_9)C_2H_4OH$	0.01	0	0	0	0	0	0	0	0	2
		0.1	0	2	2	3	3	3	25	48	78
		1.0	0	0	0	0	0	40	92	98	100
29765	$C_8F_{17}SO_2N(C_{12}H_{25})C_2H_4OH$	0.01	0	0	0	0	0	0	0	0	0
		0.1	0	0	0	0	0	0	2	3	15
		1.0	0	0	0	0	2	32	77	88	100
29756	$C_8F_{17}SO_2N(CH_3)C_4H_8OH$	0.01	0	0	2	5	8	8	8	10	13
		0.1	0	0	0	2	5	30	75	85	92
		1.0	0	2	10	83	85	95	100		
10731	$C_8F_{17}SO_2N(C_2H_4OH)_2$	1.0	0	0	0	2	5	10	35		
10732	$C_8F_{17}SO_2N(CH_3)CH_2CH(OH)-CH_2(OH)$	1.0	0	0	0	2	2	2	5		
29771	$C_8F_{17}SO_2N(C_2H_5)C_2H_4OC(O)C_{17}H_{35}$	0.01	0	0	0	0	0	8	10	13	18
		0.1	2	2	2	7	10	17	20	32	58
		1.0	0	0	2	87	98	98	98	98	98

Table V. Primary Screening Results for Polyether Substituted Sulfonamides.

NUMBER	STRUCTURE	CONC. %	1	2	3	6	8	10	14	17	21
			PERCENT MORTALITY AT SPECIFIED DAYS								
29753	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_3H$	0.01	0	0	0	0	3	7	7	13	20
		0.1	0	0	0	0	0	0	3	7	27
		1.0	0	0	2	52	87	98	99	100	
29773	$C_8F_{17}SO_2N(C_2H_5)C_2H_4O(C_3H_6O)_8H$	0.01	0	0	0	0	0	0	0	0	0
		0.1	0	0	0	0	0	0	0	3	17
		1.0	0	0	0	3	5	23	37	45	60
29772	$C_8F_{17}SO_2N(C_4H_9)C_2H_4O(C_3H_6O_8H$	0.01	0	0	2	2	2	2	2	2	2
		0.1	0	0	0	0	0	3	3	15	45
		1.0	0	2	2	2	2	40	87	97	100
10749	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_7CH_3$	0.01	2	3	3	3	3	5	8		
		0.1	5	5	8	15	20	23	40		
		1.0	2	5	5	38	57	80	88		
29769	$C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_{17}CH_3$	0.01	0	0	0	3	7	7	10	13	17
		0.1	0	0	0	2	3	5	10	25	48
		1.0	0	0	32	100					

Table VI. Bioassay Results for Oddball Nitrogen Substituents.

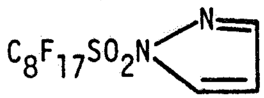
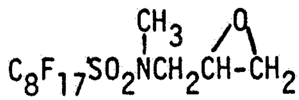
NUMBER	STRUCTURE	CONC. %	PERCENT MORTALITY AT SPECIFIED DAYS 1	2	3	6	8	10	14	17	21
10733	$C_8F_{17}SO_2N(C_2H_5)C_2H_4C_1$	0.01	0	0	0	0	3	3	5	23	47
		0.1	0	0	2	22	83	95	97	100	
		1.0	57	87	98	100					
29778		0.01	2	3	3	8	8	8	13	15	18
		0.1	0	2	3	10	10	52	67	80	88
		1.0	0	2	17	92	100				
10705		1.0	2	2	2	3	8	15	30		
29761	$C_8F_{17}SO_2N(H)C_2H_4NH_2$	1.0	2	2	2	2	2	2	10		
10706	$C_8F_{17}SO_2N(CH_3)\text{-}C_2H_4C(=O)NH_2$	1.0	0	0	0	0	3	5	10		
29752	$C_8F_{17}SO_2N(C_2H_5)C_2H_4OP(=O)(OH)_2$	1.0	2	3	3	3	3	3	10		

Table VII. Effects of Decreasing the Fluorocarbon Chain Length.

NUMBER	STRUCTURE	CONC. %	PERCENT MORTALITY AT SPECIFIED DAYS 1	2	3	6	8	10	14	17	21
10703	$CF_3SO_2NH_2$	0.01	0	0	0	3	3	5	7	8	17
		0.1	3	3	3	5	5	5	17	27	58
		1.0	2	8	18	33	42	50	67	73	82
10744	$C_2F_5SO_2NH_2$	1.0	3	17	22	35	40	45	50		
10745	$C_4F_9SO_2NH_2$	1.0	0	0	0	3	3	3	5		
10702	$C_6F_{13}SO_2NH_2$	0.01	0	0	0	2	2	2	2	5	12
		0.1	3	7	7	7	7	17	63	77	92
		1.0	0	3	30	67	75	87	95	98	100
29759	$C_8F_{17}SO_2NH_2$	0.01	0	0	0	3	7	7	10	20	23
		0.1	0	0	0	2	33	77	92	95	98
		1.0	43	85	98	100					

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Table VIII. Illustration of Fluorocarbon and Sulfone Activity Requiements.

NUMBER	STRUCTURE	CONC. %	PERCENT MORTALITY AT SPECIFIED DAYS 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
		0.1	0	0	0	2	33	77	92	95	98
		1.0	43	85	98	100					
10721	$C_8H_{17}SO_2NH_2$	1.0	5	7	8	12	12	12	12		
110754	$CF_3CH_2SO_2NH_2$	1.0	0	0	0	2	3	5	13		
10739	$C_7F_{15}C(=O)NH_2$	1.0	0	0	0	2	2	2	2		

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Table IX. Primary Screening Results for Several Sulfonic Acids and Salts.

NUMBER	STRUCTURE	CONC. %	1	2	3	6	8	10	14	17	21
			PERCENT MORTALITY AT SPECIFIED DAYS								
50950	$C_8F_{17}SO_3K$	1.0	2	2	23	87	100				
10700	$C_8F_{17}SO_2N(H)Na$	1.0	2	37	73	98	100				
10701	$C_8F_{17}SO_2N(CH_3)Na$	1.0	62	97	100						
10750	$C_8F_{17}SO_3^- \; \overset{+}{N}(C_2H_5)_4$	1.0	10	47	95	100					
10727	$C_8F_{17}SO_3H$	1.0	0	37	62	95	100				
10728	$C_6F_{13}SO_3H$	1.0	15	77	95	100					

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PRELIMINARY ELECTROPHYSIOLOGICAL EVALUATION OF THE EFFECTS OF AVERMECTIN AND A FLUORINATED SULFONAMIDE ON THE RED IMPORTED FIRE ANT

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ABSTRACT

Two potential fire ant toxicants, Avermectin, a macrocyclic lactone glycoside, and a fluorinated sulfonamide, both dissolved in dimethyl sulfoxide (DMSO) were bath-applied to preparations of fire ant indirect flight muscles. Electrophysiological recordings were made of the resting membrane potentials and miniature postsynaptic potentials (MPSP) of these dorsal longitudinal muscles. The records of the MPSP were then analyzed using a microcomputer program with signal averaging capabilities. Preliminary results indicate a lowering of fire ant resting potentials after application of Avermectin at doses up to 12 uM. Miniature postsynaptic potentials exhibited slight decreases in amplitude and frequency with application of Avermectin at the same doses. The fluorinated sulfonamide showed increases in resting potential and amplitudes of the MPSP at doses up to 10 uM. There were some increases in the frequency of the MPSP. The results, though preliminary, indicate some trends which are being examined in greater detail.

Current Research with Toxic Baits

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The number of chemicals evaluated by the USDA as bait toxicants against the red imported fire ant (*Solenopsis invicta* Buren) from 1958 through June, 1983 was 7,435. Eighty-six percent of these were not effective. Eight percent gave rapid kill of workers and were therefore not usable as bait toxicants. The remaining 6% of the total number exhibited delayed toxicity and were therefore further tested as bait toxicants. Of these compounds, 5% showed delayed action over 1 to 9-fold dosage range while less than 1% showed delayed activity over 10 to 99-fold dosage range. Only two compounds mirex and avermectin B_1 (effects on queens only) showed delayed action over a 100-fold dosage range.

Of the total 7,435 chemicals screened, approximately 60 have actually reached the field testing stage. In this group, only three chemicals have been commercially developed for public use, mirex, Amdro® (American Cyanamid Company) and Pro-Drone® (Stauffer Chemical Company). Mirex, as most everyone knows, is no longer available for fire ant control, having had its registrations cancelled by the Environmental Protection Agency in 1978. Two other chemicals that are very promising

[a/] This paper presents the results of preliminary research only and will be published later through established channels with appropriate editing. Therefore, the paper and data should not be referred to in literature citations until it appears in publication. Mention of a proprietary product does not constitute a recommendation by the USDA .

as bait toxicants and ones which the companies have applied for conditional registrations are Affirm® (alias avermectin B_1), (MK-936) (M-895) by Merck and Company, and Logic® (alias RO13-5223) by Maag Agrochemicals Company.

For the present, we have decreased laboratory and field screening tests of chemicals. Large numbers of chemicals are no longer being screened as bait toxicants because we have now made available several chemical tools to the public for use for control of fire ants. We are still testing several insect growth regulators and two of these look very promising in laboratory tests and will probably be tested in small field tests soon.

The results of field tests with the fluoronated sulfonamides from 3M Company are shown in Tables 1 and 2 and although some of the results are erratic, a few of these compounds showed promise. The first field test was conducted at Lake City, Florida in 1982 (Table 1). The Chemical AI3-29759 gave excellent control of fire ants at 6 and 12 weeks post-treatment while AI3-29758 gave 99% control at 6 weeks, but decreased to 73% after 12 weeks. In the second field test (Quitman, Georgia, 1982), AI3-29757 looked very good giving 90 and 96% control after 15 and 24 weeks respectively. The third field test (Table 3) was conducted at Homerville, Georgia in 1983. In addition to the original three fluoronated sulfonamides (AI3-29757, 29758, and 29759), several other promising ones were evaluated. Because of dry conditions during the evaluation periods the results overall did not look very good; however, AI3-10702 and 29759 did perform the best giving 90 and 80% control respectively, after 18 weeks posttreatment. Additional field tests are planned with the most promising of the fluoronated sulfonamides in 1984 and hopefully the best chemical can be selected for large scale field tests in late 1984 and early 1985.

Research on the use of house fly and/or eye gnat pupae as bait-carriers of chemicals for controlling the fire ant is continuing. A major problem of all current toxic baits used for fire ant control is that they rely on the chemical being dissolved in soybean oil, which is the food attractant. Unfortunately, soybean oil is also highly attractive to other nontarget ant species, many of which are very beneficial. We presented a new approach to this dilemma in our report at the IFA Conference in Starkville, Mississippi in 1983. By using a new carrier, fly pupae, which is attractive to fire ants but not to many other ants, we hoped to protect nontarget ants, which will not feed on the pupae. After several promising tests with Amdro and fenoxycarb (Maag R013-5223) in the laboratory and in the field, we decided to continue with this research. An update of recent field results is shown in Table 3. The results clearly indicate that house fly pupae and eye gnat pupae treated with fenoxycarb (Maag R013-5223) offer promise as attractant-carriers containing toxicants for controlling the red imported fire ant. Although the results after 8 and 16 weeks posttreatment with all the various combinations did not give as good control as the standard (fenoxycarb bait using soybean oil on pregel defatted corn grits), lower application rates were used and therefore the grams of active ingredients per acre were much smaller. Additional field tests of this research are underway. Also, publication of this information will be forthcoming soon.

Table 1. Effects of granular soybean oil baits containing fluoronated sulfonamides on populations of the red imported fire ant in Florida and Georgia.[a/]

Chemical AI3-No.	Toxicant concn (%) In SBO	Application rate g AI/A	Mean % reduction in population index after wks indicated 6	12	15	24
		Lake City, FL 1982				
29757	1.0	1.56	83	73		
29758	1.0	1.42	99	84		
29759	1.0	1.36	81	75		
29759	2.5	3.40	95	91		
CHECK			0	0		
		Quitman, GA 1982[b/]				
29757	1.0	1.61			90	96
29758	1.0	1.53			71	62
29759	1.0	1.61			85	82
10702	1.0	1.61			81	73
CHECK					13	9

a/ Avg. of three 1-acre plots. Baits consisted of 70% pregel defatted corn grits impregnated with 30% of the SBO - toxicant solution.

b/ Evaluations in this test were not conducted at 6 and 12 wks. Also, the results of the first 3 chemicals are only for one plot while the results of 10702 were an average of 2 plots. The reason for this is that the other plots were plowed under by the landowner.

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9.24

Table 2. Continued effects of granular soybean oil baits containing fluoronated sulfonamides on populations of the red imported fire ant in Homerville, Georgia 1983.[a/]

Chemical AI3-No.	Toxicant concn (%) in SBO	Application rate g AI/A	Mean % reduction in population index after wks indicated 6	12	18
10702	1.0	1.28	75	67	90
10707	1.0	1.43	30	37	45
10710	1.0	1.36	30	51	42
10712	1.0	1.29	49	52	42
10733	1.0	1.47	60	75	59
29757	1.0	1.50	81	52	74
29758	1.0	1.44	40	46	58
29759	1.0	1.46	80	64	80
CHECK			16	46	30

a/ Avg. of three 1-acre plots. Baits consisted of 70% pregel defatted corn grits impregnated with 30% of the SBO - toxicant solution.

Table 3. Effects of house fly pupae and eye gnat pupae baits containing fenoxycarb (Maag RO 13-5223) on populations of RIFA. Alachua County, FL, June, 1983. (Avg. of three 1-acre plots.)

Bait treatment[a/]	Application rate lbs/A	Mean % reduction in population index after indicated weeks 8	16
HFP (6%)	0.125	84	68
	0.25	85	75
	0.5	84	69
HFP (12%)	0.125	81	73
	0.25	81	85
	0.5	91	81
HFP (18%)	0.125	92	76
	0.25	83	87
	0.5	88	79
EGP (6%)	0.125	87	58
	0.5	82	76
Logic (Std.)	1.0	92	96
Amdro (Std.)	1.0	93	84
CHECK		29	22

a/ Pupae were dipped in acetone - toxicant solution for 24 hours, washed in clean acetone for 5 sec and air dried for 24 hrs. HFP = housefly pupae; EGP = eye gnat pupae. Figures in ( ) equals concentration of acetone solution of fenoxycarb into which pupae were dipped.

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SUPERCOOLING STUDIES ON FOUR SPECIES OF FIRE ANTS

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ABSTRACT.--The phenomenon of cooling water below the incipient freezing point (0°C) is termed supercooling. The freezing point of water can be depressed by mixing it with substances which have a lower freezing point (such as alcohol or ethylene glycol) and are thus known as "anti-freezes", or by eliminating any impurities in the water which might act as ice nucleators. Supercooling is an adaptive physiological response found in many animals which occur in environments subject to freezing temperatures; and insects found in temperate zones often have seasonally depressed supercooling points to protect them from potentially injurious winter temperatures. Although there are many possible injurious effects from cold, a reliable indicator of survivability by insects in cold temperatures is their supercooling point. Winter-kill has been cited in the literature as an important factor limiting the northward spread of fire ants in general, and of imported fire ants in particular. The implication being that despite some protection from cold temperatures received by the ants from moving deep underground where temperatures are not as cold as at the surface and actually seldom fall below freezing, fire ants are thought to have limited or no ability to supercool.

We determined the supercooling points of worker larvae, worker pupae, minor workers, medium workers, major workers, reproductive larvae, and male and female pupae and adults in four species of fire ants: *Solenopsis aurea* Wheeler, *Solenopsis geminata* (Fabricius), *Solenopsis invicta* Buren, and *Solenopsis xyloni* McCook. The worker caste has a slightly lower supercooling point than the reproductive caste in the four species. Within each species adults have a higher supercooling temperature (-7°C to -12°C) than immatures, and larvae have a higher supercooling temperature (-8°C to -16°C) than pupae (-16°C to -24°C).

Airborne Venom Dispersal in *Solenopsis*: Functional Correlates of Insecticidal and Antibiotic Venom Properties

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ABSTRACT

Venom Dispersal in *Solenopsis*: Functional Correlates of Insecticidal and Antibiotic Properties of Venom Alkaloids

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Solenopsis invicta, *S. richteri*, and *S. geminata* exhibit venom extrusion and "gaster-flagging" when they encounter heterospecifics in the foraging arena. Behavioral and gas-liquid chromatographic studies demonstrated that in addition to wiping venom on antagonists, *S. invicta* repels them via airborne droplets released during "gaster-flagging". The size of the observable droplets vary from 150mm to an aerosol-like 2aμm particle. Data suggest that this same aerosol venom dispersal mechanism is used in applying much smaller particles of the antibiotic venom to *S. invicta* brood. Carefully controlled chemical analysis of brood for worker venom alkaloids gave 0.9 - 1.1 ng/immature. Our discoveries of new antagonistic and beneficial uses for fire ant venom alkaloids help further elucidate their adaptive significance to the colony.

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Solenopsis invicta Buren (Myrmicinae) is an indigenous South American ant species that has attained introduced pest status in the southeastern United States. It is perhaps best known for the large mounds it constructs and for the painful sting from which it derives its common name - the fire ant. As with other hymenopteran venoms, research has focused on the effects of fire ant venom in vertebrate models. However, as early as 1958, Blum et al. recognized the insecticidal and antibiotic properties of the alkaloids that constitute over 95% of the fire ant venom (see also Jouvenaz et al., 1972). We were interested in the adaptive significance of these venom characteristics, particularly with respect to "gaster flagging" behavior (Adams and Traniello, 1981) observed in *S. invicta* colonies by ourselves and others (Bhatkar et al., 1972). During "gaster flagging" workers raise and vibrate the gaster while extruding the sting. We hypothesized that during gaster flagging, *S. invicta* workers dispersed venom through the air. However, in *S. invicta* young workers tend brood, while older workers do most of the foraging (Mirenda and Vinson, 1981; cf wilson, 1978), and we had observed gaster flagging by both worker types. It therefore occurred to us that the function of airborne venom

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dispersal might be different in brood tending and foraging contexts. Venom directed to the brood or the surrounding brood chamber would reduce the likelihood of microbial infection, while venom directed at heterospecifics encountered in the foraging arena would function as a repellent.

Our hypotheses concerning venom dispersal and its adaptive significance were based on the following combination of existing studies and personal observation.

A. During careful observations of confrontations between *S. invicta* and foragers of both *Pheidole dentata* (Myrmicinae) and *Camponotus floridensis* (Formicinae) we had noted violent withdrawal, antenna dragging and other grooming behavior on the part of ants that approached gaster flagging *S. invicta* from the rear, but did not actually contact the fire ant's sting. This strongly suggested that venom was being dispersed through the air. Moreover, other Myrmicines including species of *Solenopsis* are known to wipe repellent venom on antagonists as part of either raiding (Höldobbler 1973; Blum et al., 1980), or interference competition strategies (reviewed in Adams and Traniello, 1981).

B. Antimicrobial exocrine products are not without precedent in ants (Maschwitz et al., 1970). Indeed, Wilson (1971) has suggested that the evolution of antibiotic exocrine products was crucial to the development of subterranean existence among ants.

To test our hypotheses, we initiated studies designed to (1) more fully describe gaster-flagging by *S. invicta*, (2) determine whether venom was dispersed through the air by gaster flagging during heterospecific confrontations and (3) determine whether worker-derived venom was present on the surface of the brood.

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Study 1: Analysis of Gaster Flagging Behavior

Methods

Ants tested were members of monogynous queen-right colonies collected four to six months previously and maintained at the USDA Fire Ant Project Laboratories, Gainesville, Florida. Colonies contained more than 10,000 individuals and included immatures at all developmental stages. Colonies were maintained in plastic petri dish cells with Castone® floors at 26-27°C on a diet of honey-water, fly pupae and hard-boiled egg. These brood chambers were placed in Fluon®-coated plastic trays that served as foraging arenas.

Ant behavior in the brood chamber was observed in three different *S. invicta* colonies under ambient and fluorescent light during a total of 260 minutes. Confrontation behavior was observed following introduction of individual *S. invicta* foragers or brood tenders into the foraging tray of heterospecific (*S. geminata*) colonies (N = 11 trials). Data were collected for 10 minutes post introduction. Interspecific interactions in the petri dish arenas were observed under a dissecting microscope fitted with an ocular micrometer. These interactions were also filmed with a Fujica ZC1000 Single-8 camera fitted with a Tamron Tele-Macro lens (1:1).

Results

We recognized three distinct types of gaster flagging in *S. invicta*, hereafter referred to as the "headstand", "aggressive waggle" and "brood flag". The former two were exhibited only by workers during interspecific encounters.

Interspecific encounters. Both brood tenders and foragers exhibited

Control of Imported Fire Ants With New Insect Growth Regulator and Fluorocarbon Baits

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Two experimental insect growth regulators (IGR) from Union Carbide, UC-84572 and UC-86874, produced excellent suppression of worker brood production in laboratory colonies of red imported fire ants (RIFA). Dosages of 10 and 20 mg/colony of either compound produced total suppression of worker brood production by 6 weeks posttreatment in queen-right colonies of 50,000 or more workers. The suppression of brood caused a reduction of 80-85.6 percent in the colony index. No further production of worker brood occurred through 32 weeks posttreatment and all colony indices had been reduced by greater than 98 percent at that time (Table 1). Field tests with UC-86874 are planned for summer 1986.

The IGR S-31183 from Sumitomo Chemical Company produced total suppression of worker brood production at 10 mg/colony in queen-right colonies of 50,000 or more workers within 4 weeks posttreatment. All colonies had been reduced to less than 500 workers by 24 weeks posttreatment when the test was terminated. Field tests with pregel defatted corn grit baits containing 0.5 or 1.0% active ingredient (AI) and applied at rates equivalent to 5.26 to 23.4 g/ha AI produced reductions of 96.0 to 98.2 % in the population index within 13 weeks posttreatment. Logic at 12.18 g/ha AI had reduced the population index by 97.7% at the same interval (Table 3).

A series of fluorinated sulfonamides from 3-M Company were shown by Vander Meer et al. (J. Econ. Entomol. 78: 1190-7, 1985) to possess good delayed-action toxicity to red imported fire ants. Griffin Corporation, Valdosta, Georgia, has selected one of the more promising of this group of chemicals for commercial development as a bait toxicant for control of fire ants. We initiated a study in the fall of 1985 to evaluate the effectiveness of this compound, designated by Griffin as GX-071, in baits against natural infestations of red imported fire ants. Tests were conducted on ungrazed permanent pasture near Lakeland, Florida with pregel defatted corn grit baits containing GX-071 at 0.3 and 0.6%. Applications were made at rates equivalent to 2.58, 3.75, and 5.16 g/ha AI with the 0.3% bait, and to 5.07, 7.20, and 10.14 g/ha AI with the 0.6% bait. Amdro was applied at 9.64 g/ha AI as a standard. After 13 weeks the GX-071 baits had produced reductions in the population index of 80.7 to 93.7%. The highest rate of application of the 0.6% bait was the most effective. Amdro had produced a reduction of 82.1% in the population index (Table 4).

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Classification of Laboratory Colonies of Imported Fire Ants Based On Estimated Number of Worker Ants and Quantity of Worker Brood

Estimated Number Workers	Index	Value	Quantity Worker Brood (ml)	Index	Value
<100	1	1	None	A	1
100-5000	2	2	1-5 ml	B	5
5000-20000	3	3	5-10 ml	C	10
20000-35000	4	4	10-20 ml	D	15
35000-50000	5	5	20-30 ml	E	20
>50000	6	6	>30 ml	F	25

TABLE 1. Effectiveness of Union Carbide Insect Growth Regulators Against Laboratory Colonies of Red Imported Fire Ants. Avg. of 3 replications.

Dosage mg/colony	Pretreatment Colony Index	Percent reduction in colony index after indicated weeks posttreatment: 4	6	12	20	28	32
		AI3-29865(UC 84572)					
10	150	85.3	96.2	96.9	97.8	98.7	98.7
20	150	85.3	96.0	96.4	97.6	98.0	98.2
		AI3-29866(UC 86874)					
10	142	85.6	96.2	96.7	97.4	98.1	98.4
20	142	80.0	96.0	96.5	97.2	98.1	98.3
		Untreated Check					
-	150	0	0	-	32.4	32.7	32.7

Table 2. Effectiveness of the Insect Growth Regulator Sumitomo S-31183 (AI3-29835) Against Laboratory Colonies of Red Imported Fire Ants (Avg. of 3 replications).

Dosage mg/colony	Pretreatment Colony Index	Percent reduction in colony index after indicated weeks posttreatment 4	8	12	16	20	24
10	133	80.0	96.5	97.8	96.5	99.0	100
Check	100	11.7	+3.3	+3.3	5.0	+23.3	+1.3

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RATING OF FIELD COLONIES OF IMPORTED FIRE ANTS

BASED ON WORKER POPULATION AND BROOD STATUS

NUMBER OF WORKER ANTS	WORKER BROOD ABSENT		WORKER BROOD PRESENT	
	FIELD RATING	INDEX	FIELD RATING	INDEX
<100	1	1	6	5
100-1000	2	2	7	10
1000-10000	3	3	8	15
10000-50000	4	4	9	20
>50000	5	5	10	25

Table 3. Effectiveness of the Insect Growth Regulator Sumitomo S-31183 (AI3-29835) Against Natural Infestations of Red Imported Fire Ants. Polk Co., FL. 1984-85.

Formulation	Rate of Application		Pretreatment		Percent Reductions after indicated weeks			
					No. nests		Pop'n Index	
	Bait(kg/ha)	AI(g/ha)	No. active nests	Pop'n Index	6	13	6	13
70% PDCG	1.05	5.26	27	650	11.1	88.9	88.6	98.2
29.5% ORSBO								
0.5% S-31183	2.1	10.5	25	596	32.0	72.0	92.1	97.2
70% PDCG	1.17	11.71	25	554	44.0	68.0	92.3	96.0
29.0 % ORSBO								
1.0% S-31183	2.34	23.39	25	593	12.0	80.0	88.2	96.6
70% PDCG								
29.0 % ORSBO	1.22	12.18	31	731	22.6	80.6	90.7	97.7
1.0% fenoxycarb								
(standard)								
Check	-	-	27	612	27.2	29.6	27.2	24.8

Table 4. Effectiveness of the Griffin Fluorocarbon GX-071 in Baits Against Natural Infestations of Red Imported Fire Ants, Polk Co., FL. 1985-86.

Formulation	Rate of Application: Bait(kg/ha	Rate of Application: AI(g/ha)	Pretreatment: No. active nests	Pretreatment: Pop'n Index	Percent reduction in population index after indicated weeks posttreatment: 6	Percent reduction in population index after indicated weeks posttreatment: 13
70.0% PDCG 29.7% ORSBO 0.3% GX-071	0.86	2.58	26	615	66.0	82.0
	1.25	3.75	25	533	63.2	81.8
	1.72	5.16	25	565	75.9	84.2
70.0% PDCG 29.4% ORSBO 0.6% GX-071	0.845	5.07	26	610	78.0	80.7
	1.20	7.20	27	615	80.8	83.9
	1.69	10.14	26	600	88.5	93.7
AMDRO 0.88% (standard)	1.096	9.64	24	560	82.1	82.1
Check	-	-	41	900	+3.6	13.3

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