1989

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C. S. Lofgren
USDA

W. A. Banks
USDA

R. K. Vander Meer
USDA

D. F. Williams
USDA

The Florida Entomologist, Vol. 72, No. 1 (Mar., 1989), pp. 140-146
Published by: Florida Entomological Society

RESIDUAL TOXICITY OF SOME FLUOROALIPHATIC SULFONES TO THE RED IMPORTED FIRE ANT, *SOLENOPSIS INVICTA* (HYMENOPTERA: FORMICIDAE)

C. S. LOFGREN, W. A. BANKS, R. K. VANDER MEER, AND D. F. WILLIAMS
Insects Affecting Man and Animals Research Laboratory
United States Department of Agriculture
Agricultural Research Service
Gainesville, FL 32604

ABSTRACT

Thirty-six fluoroaliphatic sulfones were tested to determine their residual toxicity to *Solenopsis invicta* Buren in soil. Six of the compounds gave >90% kill of the ants after they were exposed for 4 days at 10 ppm. When tested at 1.0 ppm, only one compound, AI3-10841, gave appreciable mortality. This compound was tested at 10 ppm in soil held outdoors under ambient summer conditions. Mortality 8 days following initial exposure to samples of this soil was 100% for 12 wks and 91 to 100% from 20 to 36 wks.

RESUMEN

Treinta y seis fluoroaliphatic sulfones fueron examinados para determinar su residúo tóxico a *Solenopsis invicta* Buren en la tierra. Seis de los compuestos químicos dieron >90% de mortalidad de las hormigas después de 4 dias de exposicion a 10 ppm. Cuando tratadas a 1.0 ppm, solo un compuesto, AI3-10841, dió motalidad apreciable. Este compuesto fue examinado a 10 ppm en tierra mantenida al ambiente libre durante el verano. La mortalidad 8 dias después de la exposición initial a muestras de esta tierra fue 100% por 12 semanas y 91 a 100% de 20 a 36 semanas.

The black and red imported fire ants (IFA), *Solenopsis richteri* Forel and *S. invicta* Buren were detected in the United States in the late 1920's and early 1940's. They were soon recognized as potential agricultural pests (Eden & Arant 1949) and in the late 1940's Wilson & Eads (1949) reported that they caused significant damage to a large number of field crops. In recent years they have been shown to be major pests of soybeans, citrus trees, and several vegetable crops (Adams 1986). In contrast, IFA's have been found to be beneficial as predators on such arthropods as ticks, horn flies, and sugar cane borer larvae (Lofgren 1986a). Their impact on public health, because of the potential severe after effects of their stings and venom, is a cause of major concern (de Shazo et al. 1984, James 1976, Lockey 1980). Extensive reviews of the economic impact of IFA are provided by Lofgren (1986a,b) and Adams (1986).

The rapid dissemination of the IFA from a small area around Mobile, Alabama to over 90,000,000 ha today has been associated with their transportation in soil attached to various ornamental plants and trees and in grass sod (Culpepper 1953, Lofgren 1986b). This relationship has been confirmed with recent discoveries of IFA in Tennessee, Oklahoma, and Arizona. Almost all of these infestations occurred in nurseries or around new construction sites where plants or sod had been introduced from IFA-infested areas. This has occurred despite regulations requiring specific treatment of the items under the Imported Fire Ant Quarantine (Title 7, part 301.81-1 to 301.81-10. The quarantine is administered by the Animal Plant and Health Inspection Service of the U.S. Department of Agriculture (APHIS), however, their enforcement of the quarantine was hampered in 1979 when registrations of chlordane for this purpose were withdrawn by the Environmental Protection Agency. Since then chlorpyrifos has been utilized for these purposes; however, it is not as effective, especially for field-grown nursery stock, and the treatment costs are much greater (H. Collins, USDA, APHIS, personal communication).

Our main interest in development of insecticides for IFA control has centered on delayed action toxicants for toxic baits (Lofgren 1986c). We have also evaluated numerous fast-acting chemicals for treatment of individual ant nests (Williams & Lofgren 1983) and we have assisted APHIS in their search for chemicals for quarantine treatment. Recently, Vander Meer et al. (1985) and Williams et al. (1987) reported the discovery of a new class of chemicals, fluoroaliphatic sulfones, that are effective, delayed action bait toxicants for control of IFA. Commercial development of one of these compounds, ethyl heptadecafluorooctyl sulfonamide (AI3-29757), is being pursued by Griffin Corporation, Valdosta, Georgia. With the need for effective quarantine treatments, we decided to evaluate a series of the compounds to determine their potential as soil residuals for quarantine treatments. We report here the results of tests with 36 of the chemicals against *S. invicta*.

Materials and Methods

Procedures used in the evaluations were similar to those described by Banks et al. (1964). Small tapered plastic flower pots (6.3 cm diam at top) were used as test chambers. A layer of Castone®, about 1/4-in thick, was poured over the bottom to cover the drain holes. The worker ants are unable to chew through the Castone after it hardens; however, the Castone readily absorbs water when the pots are placed on moist foam plastic on the bottom of plastic holding trays, measuring 7 by 44 by 56 cm. The sandy-loam soil used for the insecticide treatment was collected near the laboratory and sifted to remove larger particles (>16 mesh). Then it was heat-sterilized in an oven for 8 hours at ca. 150°C. Twenty gram lots of the soil were put into large glass beakers and stirred with acetone solutions of the test insecticides and the chlordane standard (5 ml at 0.004%). A similar lot of soil was treated with acetone (5 ml) as the check. After evaporation of the acetone in a fume hood for several hours, the treatment resulted in an insecticide residue in the soil of 10 ppm. Six grams of soil was placed in each of three test pots which then were placed on moist foam plastic. Water was readily transferred from this surface, through the Castone and into the soil before exposure of the ants. Twenty worker ants from laboratory-reared colonies (Banks et al. 1981) were collected and introduced into each test pot. The ants could not escape because the upper inside lip of each pot was treated with Fluon® and each pot was covered with a glass lid. A sheet of plexiglass, the dimensions of the inside of the holding trays, was placed over the pots to retard evaporation of the water from the foam plastic. The ants readily tunneled in the soil. After 4 days the dead ants were counted and percent mortality calculated. All compounds that gave more than 90% mortality at 10 ppm were retested at 10, 1, and 0.1 ppm. Since some of the fluoroaliphatic sulfones are known to be slow-acting, all ants surviving after 4 days were placed in a 30 ml disposable plastic cup with a Castone bottom (see Williams 1983). The cups were covered and placed on wet foam plastic and the ants provided with food (soybean oil on cotton plugs). Mortality counts were made at the time of transfer (4 days) and 10 days following initial exposure.

The most effective compound at 1.0 ppm in the laboratory tests (AI3-10841) was selected for field studies. For these tests, 100g of soil was treated with AI3-10841 or chlordane (10 ppm) as previously described. It was then poured into a large pan with drainage holes cut in the bottom and placed outdoors near our laboratory in Gainesville, Florida. The area was exposed to direct sunlight throughout the day under ambient temperatures and natural rainfall (April 5-December 13, 1984). Samples of the soil were collected at the time it was placed outdoors, after 1, 2, and 4 wks, and at 4 wk intervals until the treated soil was exhausted (36 wks). Immediately after collection, each sample was divided into 3, 6g samples and their residual toxicity determined as in the prior tests. Ants surviving after 4 days were removed and held in separate containers and mortality was determined 4 days later or 8 days following initial exposure.

All of the data was corrected for check mortality utilizing Abbotts formula (Abbot 1925). Mean per cent mortality and standard error were calculated.

TABLE 1. TOXICITY OF 36 FLUOROALIPHATIC SULFONES AS RESIDUES IN SOIL AT 10 PPM.

AI3-No.	Structure	Per cent mortality[a] after 4 days
10704	$C_4F_9SO_2NHCH_3$	23.3 6.0
10702	$C_6F_{13}SO_2NH_2$	0.0
29759	$C_8F_{13}SO_2NH_2$	85.0 ± 10.0
29758	$C_8F_{17}SO_{2N}HCH_3$	78.3 ± 9.3
29820	$C_4F_9SO_2NHC_2H_5$	3.3 ± 1.7
29757	$C_8F_{17}SO_{2N}HC_2H_5$	98.3 ± 1.7
10712	$C_8F_{17}SO_2NHCH(CH_3)_2$	96.4 ± 3.3
10742	$CF_3SO_2N(CH_3)_2$	1.7 ± 1.7
29821	$CF_3SO_2N(C_2H_5)_2$	1.3 ± 6.0
10707	$C_8F_{17}SO_2N(C_2H_5)_2$	66.6 ± 13.3
10764	$CF_3SO_2NHC_4H_9$	15.0 ± 5.8
29777	$C_8F_{17}SO_2NHC_{12}H_{25}$	11.7 ± 4.4
10711	$C_8F_{17}SO_2NHCH_2CH=CH_2$	46.7 ± 6.0
10717	$C_8F_{17}SO_2NCH_3CH=CH_2$	10.0 ± 2.9
10714	$C_8F_{17}SO_2NHC_6H_5$	95.0 ± 5.0
10709	$C_8F_{17}SO_2NCH_2H_5CH_2C\equiv CH$	0.0
29767	$C_8F_{17}SO_2N(C_2H_5)CH_2-C_6H_5$	53.3 ± 6.0
29756	$C_8F_{17}SO_2NCH_3C_4H_8OH$	3.3 ± 1.7
29755	$C_6F_{13}SO_2NC_2H_5C_2H_4OH$	0.0
29782	$C_8F_{17}SO_2NC_2H_5C_2H_4OH$	0.0
29754	$C_8F_{17}SO_2NC_4H_9C_2H_4OH$	6.7 ± 4.4
29753	$C_8F_{17}SO_2NC_2H_5(C_2H_4O)_3H$	3.3 ± 1.7
10733	$C_8F_{17}SO_2NC_2H_5C_2H_{4C}L$	27.5 ± 1.4
29768	$C_8F_{17}SO_2NC_2H_5(C_2H_4O)^1{}_{2.5}CH_3$	1.7 ± 1.7
29771	$C_8F_{17}SO_2NC_2H_5C_2H_4OCC_{17}H_{35}$	0.0
10859	$C_2F_5SO_2NH-C_6H_4-4-CF_3$	100.0
10762	$CF_3SO_2NH-C_6H_4-3-CF_3$	98.3 ± 1.7
10841	$C_8F_{17}SO_2NH-C_6H_4-4-Cl$	97.4 ± 3.3
10775	$CF_3SO_2NH-C_6H_3-3,5\text{-di}(CF_3)$	51.1 ± 29.5
10774	CF_3SO_2NH - (2-naphthyl)	6.7 ± 6.0
10770	$CF_3SO_2NH-C_6H_2-3,4,5\text{-tri-Cl}$	10.0 ± 5.8
10840	$C_8F_{17}SO_{2N}HC(=O)NH(nC_4H_9)$	1.7 ± 1.7
10869	$C_8F_{17}SO_{2N}HC(=O)NHC_6H_{11}$	33.3 ± 14.8
10845	$C_8F_{17}SO_2N-(CH_2)_6$(heterocycle)	6.4 ± 3.3
10849	$C_8F_{17}SO_2NHCH_2N(CH_2CH_2)_2O$	78.3 ± 21.6
10870	$C_8F_{17}SO_2N(C_3H_7)(SCCl_3)$	83.3 ± 3.5

[a]Mean ± SE (N = 3); mortality in checks (N = 5) averaged 3%

Results and Discussion

Six of the 36 fluoroaliphatic sulfones killed >90% of the worker ants during the 4-day exposure at 10 ppm (Table 1). Seven additional chemicals gave mortalities between 50 and 89%. Tests with the 6 most effective chemicals (Table 2) revealed that none of them caused more than 17% mortality at 1 ppm following the 4-day exposure in treated soil; however, 2 of them caused appreciable mortality after 10 days post-exposure (AI3-10712 = 34.0% ± 18.4; AI3-10841 = 75.7% ± 10.7). The Chlordane standard resulted in 100% mortality at 10 and 1 ppm after 4 days; at 0.1 ppm worker ant mortality was 91.6% ± 5.4 after 4 days and 99.2% ± 0.8 after 10 days.

Outdoor residual tests were conducted with AI3-10841 and chlordane (Table 3). Based on the 8-day mortality counts, AI3-084 gave 100% kill through 16 wks and 92 to 100% from 20 to 36 wks at which time the supply of treated soil was exhausted. In comparison, chlordane residues resulted in 100% mortality in 4 days at all time intervals.

The chlorinated cyclodiene insecticides (chlordane, heptachlor, dieldrin, aldrin) are the most effective residual formicides that have been developed and commercialized. Banks et al. (1964), in tests similar to those presented here showed that their LD-90's after a 24-hr exposure in treated soil followed by a 3-day post-exposure period ranged from 0.008 ppm for heptachlor to 0.0377 ppm for chlordane. Unfortunately concerns with environmental hazards and carcinogenicity have forced the withdrawal of registrations for all of these insecticides.

Currently, chlorpyrifos is the only chemical registered as a residual soil toxicant for treatment of commodities for quarantine certification; however, this compound was not included as a standard in the test with AI3-10841. In other unpublished studies, we have found that it killed 100% of the worker ants after a 4-day exposure at concentrations of 10 and 1 ppm and 80% at 0.1 ppm. Observations 6 days after the exposure at 0.01 ppm revealed only a slight increase in mortality (83%).

Collins et al. (1980) compared the toxicity of chlorpyrifos and chlordane applied in potting soil at the rate of 14.6 g ai/0.76m3. Greater than 89% mortality of small groups of isolated workers was obtained within 4 days when they were exposed in chlorpyrifos-treated soil that had been aged outdoors for 39 months. In comparison, chlordane was effective 41 months. It is impossible to directly compare these data with our tests because the exact insecticide concentrations (ppm) are unknown and the soil and method of ant exposure are different. Despite this, the results clearly demonstrated long term toxic residues of chloropyrifos when it is mixed in soil. However, its residual persistence when applied to the soil surface is much shorter, as is the case with grass sod and field grown nursery plants (H. L. Collins, unpublished data). This fact limits its usefulness for treating these products. Whether or not AI3-10841, or another fluoroaliphatic sulfone, would perform in commercial potting soil and provide adequate control for soil surface treatments must await further tests.

Since the ultimate goal of the quarantine regulations is to eliminate the possibility of the shipment of commodities containing IFA queens or queen right colonies into uninfested areas, it is not necessary to find one chemical that will serve all needs. What is needed is a series of procedures that are effective, easy to apply, economical, and environmentally acceptable. Solutions to the problem require investigations into a multiplicity of approaches and, possibly, AI3-10841 or one of the other fluoroaliphatic sulfones may be a useful chemical tool for restricting the spread of IFA.

Acknowledgement

We thank J. Kenneth Plumley for technical assistance in running the necessary tests.

TABLE 2. EFFECT OF CONCENTRATION ON TOXICITY OF SIX FLUOROALIPHATIC SULFONES AS SOIL RESIDUES TO RED IMPORTED FIRE ANTS.

		Per cent moprtality[a] after 4 & 10 days at ppm indicated[b]					
		10 ppm		1.0 ppm		0.1 ppm	
AI3-No	Structure	4	10	4	10	4	10
29757	$C_8F_{17}SO_2NHC_2H_5$	90 ± 5.80	100	0	0	0	0
10712	$C_8F_{17}SO_2NHCH(CH_3)_2$	100	100	0	34 ± 18.4	0	0
10714	$C_8F_{17}SO_2NHC_6H_5$	100	100	0	0	0	0
10762	$CF_3SO_2NH-C_6H_4-3-CF_3$	100	100	4.7 ± 2.3	4.7 ± 2.3	0	0
10841	$C_8F_{17}SO_2NH-C_6H_4-4-Cl$	95 ± 2.9	100	16.7 ± 3.3	75.7 ± 10.7	0	10 ± 6.1
10859	$C_2F_5SO_2NH-C_6H_4-4-CF_3$	100	100	0	0	0	0
9932	Chlordane (std)	100	100	100	100	91.6 ± 5.4	99.2 ± 0.8

[a]Mean ± SE (N = 3)

[b]Worker ants exposed on treated soil for 4 dys, then transferred to insecticide-free holding containers for final 6 days. Data corrected for check mortality (8% at 4 days; 22% at 10 days) by Abbott's formula.

TABLE 3. COMPARISON OF RESIDUAL SOIL TOXICITY OF 10 PPM OF AI13-10841 AND CHLORDANE WHEN HELD OUTDOORS UNDER AMBIENT CONDITIONS.

Weeks exposure of treated soil	% Mortality[a] after days indicated[b]			
	AI3-10841		Chlordane	
	4	8	4	8
0	88.3 ± 4.4	100	100	—
1	100 —	—	100	—
2	100 —	—	100	—
4	100 —	—	100	—
8	100 —	—	100	—
12	100 —	—	100	—
16	98 ± 1.7	100	100	—
20	90 ± 7.6	98 ± 1.7	100	—
24	78 ± 7.3	93 ± 1.7	100	—
28	97 ± 1.7	100	100	—
32	78 ± 7.3	92 ± 4.4[c]	100	—
36	73 ± 13.0	97 ± 1.7	100	—

[a]Mean SE (N = 3)
[b]Worker ants exposed on treated soil for 4 days, then transferred to insecticide-free holding containers for 4 days. Data corrected for check mortality (0-10%) by Abbott's formula.
[c]Mortality count made at 6 days.

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