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SEX ATTRACTANT OF THE FALL ARMYWORM MOTH

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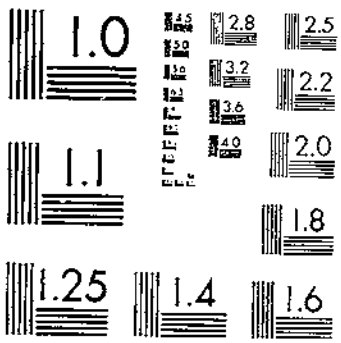

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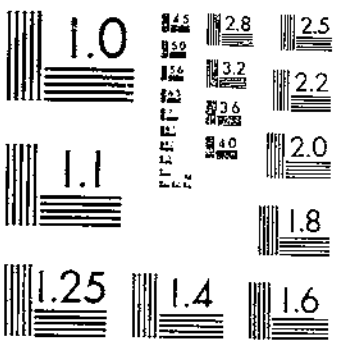

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SEX ATTRACTANT OF THE FALL ARMYWORM MOTH

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ABSTRACT

Z-9-Dodecen-1-ol acetate is either the sex attractant or the major component thereof for the fall armyworm moth, *Spodoptera frugiperda* (J. E. Smith). The structure was verified by synthesis, and its attractiveness was confirmed in the field.

INTRODUCTION

The fall armyworm moth, *Spodoptera frugiperda* (J. E. Smith), is a serious pest of corn and other important crops. In 1965 and 1967 it was shown that the female fall armyworm emitted a substance which sexually stimulated caged male moths (*5*, *6*).[2] In 1967, the sex pheromone was identified as *Z*-9-tetradecen-1-ol acetate (*7*). The synthesized pheromone, although a strong elicitor of sexual excitation and copulatory attempts among caged males in the laboratory, failed to attract males in field trials.[3] Upon reinvestigation we found that the female secretes at least one other substance, identified as *Z*-9-dodecen-1-ol acetate (1) (*Z*-9-dda), which is identical with the sex attractant of the grape berry moth, *Paralobesia viteana* (Clemens) (*4*). We report in this study the synthesis of *Z*-9-dda and the results of several field trials using this sex attractant as bait for traps.

MATERIALS AND METHODS

Laboratory-reared fall armyworms were sexed in the pupal stage and placed in separate cages. Virgin female moths were used as the source of the sex attractant. Methylene chloride extract prepared from 65,000 tips (last two abdominal segments) of female moths was dissolved in 20 volumes of dry acetone and the solution kept at −20° C overnight. The precipitated white solid was filtered through a cold Büchner funnel; after being washed with cold acetone, the solid was dissolved, precipitated, filtered, and washed three more times. The combined acetone filtrates and washes were freed of solvent at 25 millibars of mercury. The residual yellow oil (10 grams) was dissolved in 10 milliliters of *n*-pentane while being cooled in an ice bath and stirred continuously, and was then

1 Present address: Southern Regional Research Center, Agricultural Research Service, New Orleans, La.

2 Italic numbers in parentheses refer to items in "Literature Cited," p. 5.

3 Sparks, A. N., and Snow, J. W. Personal communication.

treated with 100-mesh silicic acid to obtain a free-running powder. This was transferred to the top of a chromatographic column dry-packed with 100 grams silicic acid. The powder was eluted successively with *n*-pentane and with 0.5, 1, 3, 6, and 10 percent ethyl ether in *n*-pentane. The active fractions were combined and evaporated to dryness under reduced pressure. The resultant active oil was purified further by column chromatography on silica gel impregnated with 20 percent silver nitrate and eluted successively with *n*-pentane and with 1, 5, 10, and 25 percent ether in *n*-pentane. The active fractions which were eluted with 5 percent ether in *n*-pentane were combined and concentrated.

A portion of the partially purified material was used to gain information on the nature of the active attractant. Saponification, acetylation, hydrogenation, and bromination suggested the attractant to be an unsaturated acetate. Gas-liquid chromatography (GLC) mobilities of the saponified material coincided with retention times offered by both *Z*-9-dodecenol and *Z*-9-tetradecenol.

The concentrate was subjected to GLC using a Varian Aerograph series 1200 gas chromatograph. The columns used were stainless steel (3.05 meters by 0.32 centimeter, outside diameter) packed with 3 percent Carbowax 20M on 60- to 80-mesh GasChrom Q for the polar phase and with 5 percent SE 30 on the same support for the nonpolar phase. Only two peaks were observed; in both polar and nonpolar columns, the faster eluting component showed the same retention time as *Z*-9-dodecen-1-ol acetate, and the slower eluting component had the same retention time as *Z*-9-tetradecen-1-ol acetate.

The active material having the lower retention time was isolated by preparative GLC. An Aerograph Autoprep A–700 gas chromatograph with a stainless-steel column packed with 10 percent Carbowax 20M on 60- to 80-mesh GasChrom Q (3.04 meters by 0.63 centimeter, outside diameter) was used. Column temperature was 195° C, and helium flow was 60 milliliters per minute.

Reductive cleavage of the ozonide of the collected material, carried out in pentyl acetate and in *n*-pentane, produced fragments identified as propionic aldehyde and 9-acetoxynonanal (*1*).

The structure consistent with these data is that of either *Z*- or *E*-9-dda. Geometrical configuration was assigned by infrared spectra after both isomers were synthesized. Reaction of the tetrahydropyranyl ether of 8-bromooctan-1-ol with a slight excess of lithium salt of 1-butyne in liquid ammonia followed by acid hydrolysis gave 9-dodecyn-1-ol (II); upon catalytic semihydrogenation, (II) gave the desired *Z*-alcohol (*2*, *3*). The *E*-alcohol was obtained by reduction of (II) with sodium in liquid ammonia. Acetylation of the alcohols with acetic anhydride gave the acetates.

RESULTS AND DISCUSSION

Several field tests were conducted to determine the efficacy of the synthetic *Z*-9-dda and *E*-9-dda in attracting and capturing male fall armyworm adults in pie-plate traps coated with Stikem. The *E*-9-dda failed to catch males during these tests. In one 4-day test, *Z*-9-dda rates of 1, 2, 4, 8, and 16 milligrams were used to bait each of two traps for each rate. Table 1 indicates that *Z*-9-dda application rates from 2 to 16 milligrams per trap were about equally effective. The higher rates tended to last longer and catch as many males as four virgin females over a 4-day period. An additional sample of *Z*-9-dda from another source was equally effective in field studies.

Tributylin, tripalmitin, trilaurin, nujol, and olive oil were tested as extenders for the pheromone in the field. Preliminary studies indicated that olive oil produced the most consistent results. Therefore, a 5-day field test was conducted in which 8 milligrams of *Z*-9-dda per trap was mixed with sufficient olive oil so that the pheromone accounted for 0.2, 2.0, and 20.0 percent of the mixture.

TABLE 1.—*Male fall armyworm moths caught per trap per day with four virgin females or Z-9-dda*

Bait	Catch per trap on— 1st day	2d day	3d day	4th day	Total catch
4 virgin females	8.5	7.0	1.5	7.0	50
1 mg Z-9-dda	3.5	1.0	.5	.0	10
2 mg Z-9-dda	14.0	3.5	1.5	.0	38
4 mg Z-9-dda	9.0	6.5	2.5	2.0	40
8 mg Z-9-dda	12.0	8.0	3.0	1.5	49
16 mg Z-9-dda	18.5	7.5	.5	3.0	59

Each treatment was replicated four times. Table 2 indicates that at the termination of the test the mixture containing 20 percent Z-9-dda had captured as many fall armyworm males as the virgin females and over 2½ times as many as the nonextended pheromone.

Another field test was designed to determine the effect of olive oil extender on the attractiveness and persistence of five amounts of Z-9-dda left in the field over a 10-day testing period. The olive oil extender was used to dilute the pheromone to 20 percent of the total bait used per trap. These data, shown in table 3, transformed to $\sqrt{x+1}$, were subjected to analysis of variance, and means were separated by Duncan's multiple-range test. The data indicate that extender added to less than 8 milligrams of Z-9-dda per trap did not significantly increase performance.

TABLE 2.—*Male fall armyworm moths caught per trap per day with virgin females or 8 milligrams of Z-9-dda extended with olive oil*

Bait	Average catch per trap on— 1st day	2d day	3d day	4th day	5th day	Total catch
4 virgin females ..	9.5	14.5	0.0	1.0	2.5	55
8 mg Z-9-dda plus 4,000 mg olive oil (Z-9-dda=0.2% of bait)	2.0	1.5	.5	.5	.0	9
8 mg Z-9-dda plus 400 mg olive oil (Z-9-dda=2.0% of bait)	2.0	11.0	2.0	2.0	1.0	36
8 mg Z-9-dda plus 32 mg olive oil (Z-9-dda=20% of bait)	10.5	13.5	4.0	.5	1.0	59
8 mg Z-9-dda	6.5	4.5	.0	.5	.0	22

However, the addition of the extenders to 8 or 16 milligrams of Z-9-dda per trap significantly increased catch over the 10-day period. Although the virgin-female trap was supplied fresh females each day, at the end of the test the 16-milligram rate plus extender had captured 84.7 percent as many males as the virgin females.

Figure 1 depicts the average effect of the extender added to 8 and 16 milligrams of Z-9-dda per trap compared to Z-9-dda alone. Also graphed are the daily catches of males in virgin-female

TABLE 3.—*Male fall armyworm moths caught in 10-day field test in traps baited with virgin females, undiluted* Z-9-dda, *or* Z-9-dda *extended with 80 percent olive oil*

Bait	Mean catch per day[1] (with and without extender)	Percentage of catch by virgin females	Mean[1] catch per day Without extender	With extender
4 virgin females[2]	17.35c	...	...	...
1 mg Z-9-dda	2.00a	11.5	2.20a	1.90a
2 mg Z-9-dda	2.00a	11.5	1.70a	2.30a
4 mg Z-9-dda	2.90a	16.7	2.40a	2.40a
8 mg Z-9-dda	6.05b	34.9	3.90a	7.80b
16 mg Z-9-dda	9.30b	53.6	4.30a	14.70c

[1] Means followed by the same letter are not significantly different at the 95-percent level of confidence.

[2] Supplied fresh daily.

traps to show the general activity of the adult male fall armyworm moth in the field at that particular time. The extender added to the *Z*-9-dda resulted in significantly higher catches throughout the 10-day period. The rise and fall in numbers of males captured in traps baited with *Z*-9-dda plus extender mimicked those of virgin-female traps, indicating that the native male's response to the *Z*-9-dda plus extender was near normal.

A test was then designed to determine the smallest quantity of pheromone required per day to catch males in quantities comparable to those attracted by

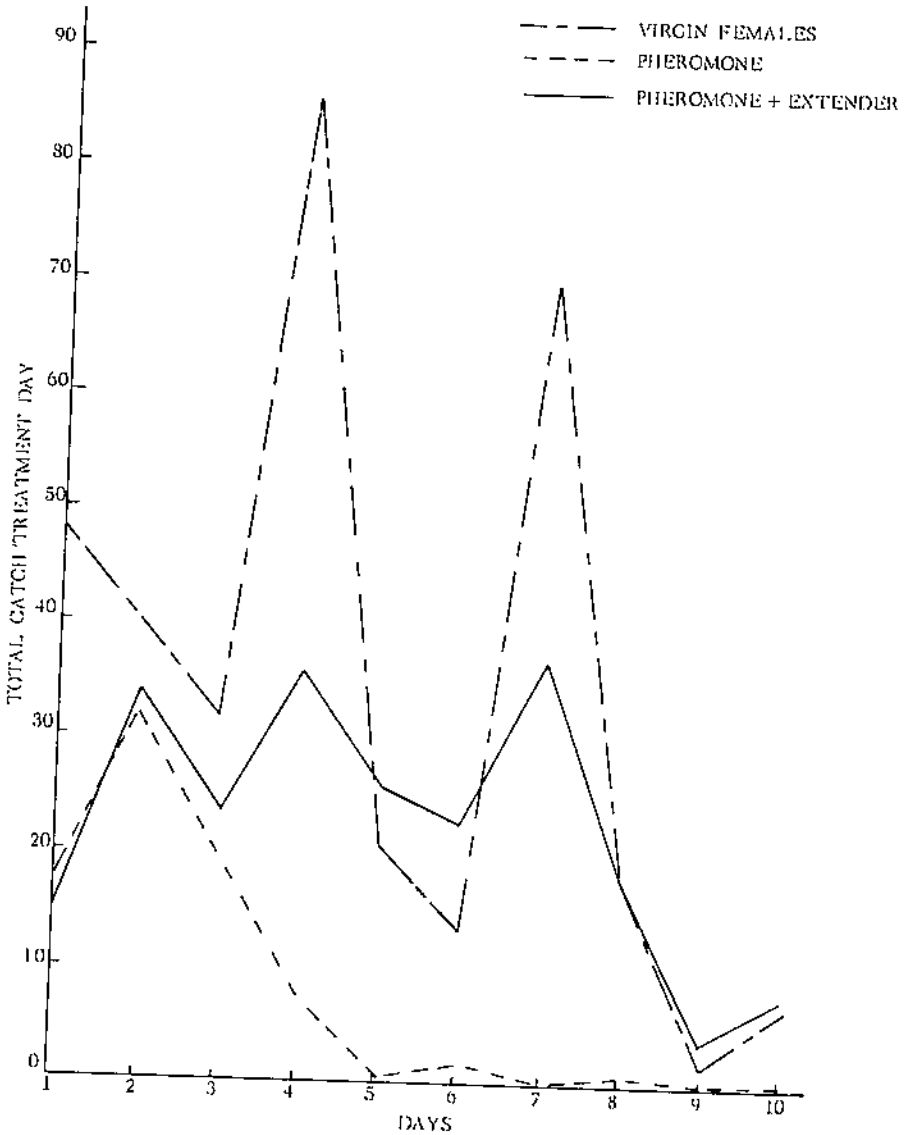

FIGURE 1.—Comparative catches of male fall armyworm adults in Stikem traps baited with four virgin females, *Z*-9-dda, and *Z*-9-dda plus extender.

TABLE 4.—*Male fall armyworm moths caught per trap per day with virgin females or* Z-9-dda; *all traps baited fresh daily for 13 days*

Bait	Mean catch per trap per day[1]	Percentage of catch by virgin females
4 virgin females	16.50a	100.0
1,600 µg Z-9-dda	8.48b	51.4
800 µg Z-9-dda	7.46c	45.2
400 µg Z-9-dda	7.27c	44.1
200 µg Z-9-dda	3.90d	23.6
100 µg Z-9-dda	2.87e	17.4

[1] Means followed by the same letter are not significantly different at the 95-percent level of confidence.

TABLE 5.—*Response of heavy populations of* Spodoptera frugiperda *to virgin-female traps and to* Z-9-dda *on cotton wicks in sticky traps near Belle Glade, Fla.*

Bait	Mean male catch per trap per day[1]
4 virgin females	36.50d
2 mg	100.25a
1 mg	69.50ab
500 µg	62.50bc
250 µg	40.00c
125 µg	26.25cd
62.5 µg	11.50d
31.25 µg	10.50d
2 mg[2]	61.50bd

[1] Means followed by the same letter are not significantly different at the 95-percent level of confidence.

[2] Commercial preparation, 94- to 96-percent pure.

four 1-day-old virgin females, supplied fresh daily. Baiting rates were 100, 200, 400, 800, and 1,600 micrograms of pure *Z*-9-dda per trap per day. All treatments were replicated four times daily and the data were collected for 13 days. Table 4 shows that the 1,600-microgram rate caught approximately 50 percent as many males as four virgin females over this 13-day test.

Although the *Z*-9-dda captured male *Spodoptera frugiperda* during these tests, its catch compared to that of four virgin females was quite different from what was expected. Therefore, another sample of commercial synthetic *Z*-9-dda, which proved to be 94- to 96-percent pure, was further purified and was tested as an attractant in an area of high adult fall armyworm population near Belle Glade, Fla. (table 5). These data indicate the immense differences that can result from testing pheromones in different locations. These differences can be attributed to differences in population levels associated with ecological niches near Tifton, Ga., and Belle Glade, Fla., and purity of the compound tested. In this particular test, 250 micrograms of synthetic *Z*-9-dda caught as many moths as did four virgin females. The 500 micrograms of purified synthetic equaled the catch of 2 milligrams of synthetic that was 94- to 96-percent pure.

CONCLUSIONS

We believe that *Z*-9-dda is the sex pheromone of the fall armyworm or the major component of the pheromone complex. *Z*-9-dda alone is sufficiently attractive to be used efficiently as a survey tool in conjunction with sticky or grid traps and warrants large-cage or small-scale field tests as an atmospheric permeation chemical in mating-inhibition studies.

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