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ATTRACTION OF REDBANDED LEAFROLLER MOTHS, *Argyrotaenia velutinana*,[1] TO BLENDS OF (Z)- AND (E)-11-TRIDECENYL ACETATES

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Abstract—The pheromone of *Argyrotaenia velutinana* (Walker) is a 92:8:150 mixture of (Z)-11-, (E)-11-tetradecenyl and dodecyl acetates. An 85:15 blend of (Z)-11- and (E)-11-tridecenyl acetates produces a trap catch equivalent to that with the pheromone blend. The sensory input elicited by (Z)-11-tridecenyl acetate appears to substitute for the sensory input of both (Z)-11-tetradecenyl and dodecyl acetates, whereas the input from (E)-11-tridecenyl acetate appears to substitute for that of (E)-11-tetradecenyl acetate. Surprisingly, addition of dodecyl acetate to the tridecenyl acetates mixture decreases trap catches.

Key Words—Redbanded leafroller, *Argyrotaenia velutinana* (Walker), (Z)-11-tridecenyl acetate, (E)-11-tridecenyl acetate, (Z)-11-tetradecenyl acetate, (E)-11-tetradecenyl acetate, dodecyl acetate, attractant, pheromone.

INTRODUCTION

Three sex pheromone components found in the female redbanded leafroller moth, *Argyrotaenia velutinana* (Walker), are (Z)-11-tetradecenyl (Z11–14:Ac), (E)-11-tetradecenyl (E11–14:Ac) and dodecyl (12:Ac) acetates (Roelofs and Arn, 1968; Roelofs and Comeau, 1968; Klun et al., 1973; Roelofs et al., 1975). A 92:8:150 blend of these compounds is a potent attractant

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for males of this species. Roelofs and Comeau (1971a) found that (Z)-11-tridecenyl acetate (Z11–13:Ac) also attracts *A. velutinana* males, although Klun and Robinson (1972) reported that it did not. Comeau (1971) had preliminary evidence that the addition of 12:Ac to Z11–13:Ac results in a lower trap catch, but the effects of the presence of the geometrical isomer, (E)-11-tridecenyl acetate (E11–13:Ac), were not defined at that time. This paper reports an investigation on the attractiveness of Z11–13:Ac alone and in various combinations with E11–13:Ac, E11–14:Ac and 12:Ac.

METHODS AND MATERIALS

The Z11–14:Ac and E11–14:Ac were obtained from Farchan Chemical and the 12:Ac from Eastman Chemical. The Z11–13:Ac and E11–13:Ac were synthesized in our laboratory by the usual alkyne reductions of 11-tridecynyl acetate (Roelofs and Arn, 1968). The Z11–13:Ac was purified by $AgNO_3$ high-pressure liquid chromatography with benzene. Compound purity and treatment compositions were determined by GLC on 3% PDEAS (phenyldiethanolamine succinate on 100–120 mesh Chromosorb W-AW-DMCS) on a 1.8 × 4 mm glass column. All compounds were >99% pure.

Field tests were conducted in abandoned apple orchards in Sodus and Dresden, New York. Test chemicals were placed in natural polyethylene closures (OS-6, Scientific Products) and these dispensers were positioned in the bottom center of Pherocon® 1C traps (Zoecon Corp.). Traps were hung in trees at a height of 1.5 m and separated by 10 m in a randomized complete block design. When checked, traps were cleared of moths and rerandomized within blocks. Data were transformed to $\sqrt{(x+0.5)}$ and submitted to analyses of variance. Differences among means were determined by Duncan's new multiple range test.

RESULTS AND DISCUSSION

Previous field tests with *A. velutinana* pheromone have shown that a low percentage (ca. 8%) of E11–14:Ac is obligatory for trap catch (Klun et al., 1973), with the optimum trapping ratio of these two isomers approximating the naturally occurring blend (Roelofs et al., 1975). Behavioral studies showed that these two components together elicit long-distance upwind anemotaxis (Baker et al., 1976). A field test was conducted, therefore, with Z11–13:Ac in combination with various amounts of its geometrical isomer, E11–13:Ac, to determine if there is an optimum combination of these isomers

TABLE 1. CAPTURES OF MALE *Argyrotaenia velutinana* BY VARIOUS MIXTURES OF 11-TRIDECENYL AND 11-TETRADECENYL ACETATES (TEST CONDUCTED IN DRESDEN, NEW YORK, JULY 12–15, 1974)

Treatment			
Z11–13:Ac	E11–13:Ac	E11–14:Ac	x̄/trap[a]
100 :	0 :	0	0.1 (g)
97 :	3 :	0	4.5 (de)
94 :	6 :	0	7.8 (cd)
91 :	9 :	0	9.1 (c)
88 :	12 :	0	18.2 (a)
85 :	15 :	0	12.7 (ab)
80 :	20 :	0	9.8 (bc)
97 :	0 :	3	7.2 (cd)
94 :	0 :	6	1.5 (fg)
91 :	0 :	9	1.0 (fg)
88 :	0 :	12	0.2 (g)
85 :	0 :	15	0.6 (g)
80 :	0 :	20	0.0 (g)
Pheromone			
10 mg 11–14:Ac's (92:8 of Z:E)+15 mg 12:Ac			14.7 (ab)
10 mg 11–14:Ac's (92:8 of Z:E)			2.7 (ef)
Unbaited trap			0.0 (g)

[a] Treatments contained 3.5 mg sample, unless otherwise noted, and were replicated three times and rerandomized twice. Means followed by the same letter are not significantly different at the 5% level.

for attraction of *A. velutinana* males. The results (Table 1) show that Z11–13:Ac alone did not lure males, but mixtures containing 3–20% E11–13:Ac did. Surprisingly, the 88:12 and 85:15 mixes of Z11–13:Ac to E11–13:Ac were as potent as the three-component pheromone system. These observations were consistent in a number of field tests over two years. In a typical test (also see Table 2), 10 replicate traps containing 10 mg Z/E11–14:Ac (93:7) captured 18 males; treatments combining the three pheromone components [10 mg Z/E11–14:Ac (93:7) and 15 mg 12:Ac] lured 278 males, whereas traps containing Z/E11–13:Ac (91:9) caught 598 males.

The discrepancy between previous reports on the attractiveness of Z11–13:Ac may be due in part to the use of samples of differing purities.[3]

[3] Another difference was in the dispenser load. Klun and Robinson (1972) used 14 μg Z11–13:Ac in 0.7 ml olive oil.

TABLE 2. CAPTURES OF MALE *Argyrotaenia velutinana* BY MIXTURES OF 11-TRIDECENYL, 11-TETRADECENYL, DODECYL, AND UNDECYL ACETATES (TEST CONDUCTED IN SODUS, NEW YORK, FROM JULY 19 TO AUGUST 2, 1973)

Treatment (5 mg)			
Z11–13:Ac		E11–13:Ac	$\bar{x}$/trap[a]
99.4	:	0.6	5.0 (d)
95.1	:	4.9	28.5 (b)
93.1	:	6.9	28.5 (b)
90.7	:	9.3	36.5 (a)
84.5	:	15.5	38.0 (a)
83.9	:	16.1	28.0 (b)
90.7	:	9.3+12:Ac (15 mg)	12.0 (cd)
90.7	:	9.3+11:Ac (15 mg)	6.0 (cde)
90.7	:	9.3+11:Ac (5 mg)	12.5 (c)
Pheromone			
10 mg 11–14:Ac's (91:9 Z:E)+ 15 mg 12:Ac			26.0 (b)
10 mg 11–14:Ac's (91:9 Z:E)			12.5 (c)

[a] Treatments were replicated five times and sampled five times. Means followed by the same letter are not significantly different at the 5% level.

The Z11–13:Ac sample used by Klun and Robinson (1972) contained 5% E isomer (J.A. Klun, personal communication), whereas the sample used by Roelofs and Comeau (1971a) contained ca. 10% of the E isomer.

Behavioral observations of wild males established that 12:Ac acts in conjunction with the 92:8 ratio of Z11– and E11–14:Ac, mediating an increase in the incidence of landing close to the chemical source (Baker et al., 1976). Laboratory behavioral studies (Baker et al., 1976) showed that the 12:Ac enhanced the wing-fanning response of males to Z11–14:Ac, but not to E11–14:Ac, indicating that 12:Ac might be acting in conjunction with the Z receptor sites. EAG (Baker and Roelofs, 1976) and single-cell electrophysiology (O'Connell, 1975) also suggest that 12:Ac interacts synergistically with the Z11–14:Ac antennal acceptors, as hypothesized by Roelofs and Comeau (1971b) in their model of acceptor-site specificity. It is tempting to suggest from the above data that Z11–13:Ac provides the synergized sensory input of Z11–14:Ac+12:Ac, whereas E11–13:Ac replaces E11–14:Ac. The unique chemical structure of Z11–13:Ac makes it structurally similar to Z11–14:Ac and also very similar in overall length to 12:Ac.

Compared to the natural blend of E11– to Z11–14:Ac (ca. 8:92), a high ratio of E11–13:Ac to Z11–13:Ac (ca. 15:85) was required, possibly because of a lower intrinsic activity of the unnatural (E11–13:Ac) compound. When E11–14:Ac, instead of E11–13:Ac, was combined with Z11–13:Ac (Table 1), it was effective at low ratios but not at higher amounts of 6 and 9%. A possible explanation for these data is that the Z11–13:Ac compound replaced both the Z11–14:Ac and the 12:Ac of the natural 92:8:150 blend of Z11–14:Ac, E11–14:Ac and 12:Ac and gave a calculated attractant ratio of 3:97 for E11–14:Ac to Z11–13:Ac. Further research with lower ratios is necessary, however, to determine the optimum attractant blend for these two compounds.

Another test (Table 3) was conducted to substantiate further the roles of E11– and Z11–13:Ac. It was shown that Z11–13:Ac did not effect trap catch when added to the two pheromone components, Z11–14:Ac and 12:Ac, at the 5% level, but addition of E11–13:Ac to these components at the same level did produce an attractive blend. The 8% mix of E11–13:Ac with the components did not attract as many males as the natural blend using 8% E11–14:Ac, but this may be due to a lower intrinsic activity of the 13-carbon compound. These data indicate that E11–13:Ac can partially substitute for E11–14:Ac, but Z11–13:Ac cannot. However, when a high quantity (15 mg) of Z11–13:Ac was substituted for 12:Ac in the blend, trap catches were equivalent to the natural blend. A lower quantity (3 mg)

TABLE 3. CAPTURES OF MALE *Argyrotaenia velutinana* BY VARIOUS MIXTURES OF 11-TRIDECENYL, 11-TETRADECENYL, AND DODECYL ACETATES (TEST CONDUCTED IN DRESDEN, NEW YORK, JULY 9–13, 1974)

	Treatment (mg)					
	Z11–14:Ac	E11–14:Ac	Z11–13:Ac	E11–13:Ac	12:Ac	$\bar{x}$/trap[a]
	10.0	—	—	—	15	0.7 (c)
	9.2	—	0.8	—	15	1.0 (c)
	9.2	—	—	0.8	15	3.5 (b)
Pheromone	9.2	0.8	—	—	15	13.5 (a)
	9.2	0.8	15	—	—	11.4 (a)
	9.2	0.8	3	—	—	5.6 (b)
Unbaited trap						0.0 (c)

[a] Treatments replicated and rerandomized three times. Means followed by the same letter are not significantly different at the 5% level.

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of Z11–13:Ac was not as attractive; similar results were obtained with lowered quantities of 12:Ac (Roelofs et al., 1975).

Although Z11–13:Ac by itself appeared to substitute for the pheromone components Z11–14:Ac and 12:Ac, surprisingly its effectiveness in doing so was reduced when the natural component 12:Ac was added to the lure (Comeau, 1971). This phenomenon has been observed over several years. A typical test (Table 2) shows that (1) maximum trap catch is obtained with Z/E11–13:Ac ratios of 85:15 and 91:9; (2) these 13-carbon acetate combinations are more attractive than the natural pheromone components; and (3) the addition of 12:Ac or undecyl acetate (11:Ac) to the 11–13:Ac's greatly reduces trap catch. Both 12:Ac and 11:Ac were effective in increasing trap catches when combined with the 11–14:Ac pheromone components (Roelofs and Comeau, 1971), but have the opposite effect when combined with the 11–13:Ac's. Possibly the hypothesized role of Z11–13:Ac in substituting for the sensory input of Z11–14:Ac+12:Ac could be diminished with the addition of 12:Ac. In the latter case, the role of Z11–13:Ac could be reduced to substituting only for Z11–14:Ac, in which case it may not be competitive with the natural component, a case similar to the substitution of E11–13:Ac for E11–14:Ac.

In a number of other Lepidoptera, pheromone analogs have been demonstrated to evoke the same behavioral reactions as the pheromones, but only when the analog stimulus was present in a dosage increased over that of the pheromone. For example, Shorey et al. (1976) found in *Pectinophora gossypiella* (Saunders) that at the same dispenser charges, the analog (Z)-7-hexadecenyl acetate was ca. 100-fold less attractive to males than the pheromone, (Z,Z)-7,11- and (Z,E)-7,11-hexadecadienyl acetates in a 1:1 ratio. Voerman et al. (1975) found Z11–13:Ac could be substituted for Z11–14:Ac in thetwo -component Z11–14:Ac and (Z)-9-tetradecenyl acetate pheromones of *Adoxophyes orana* (Fischer von Röslerstamm) and *Clepsis spectrana* (Treitschke), but with reductions in the levels of attractancy.

In contrast, our tests of *A. velutinana* field attraction showed that Z11– and E11–13:Ac in ca. an 85:15 ratio was at least as efficacious as the natural three-component mixture. The criterion of trap catch, however, is only an approximate measure of the complex orientation and precopulatory behaviors mediated by the pheromone. It is possible that at the natural rate of female pheromone emission an equivalent amount of 11–13:Ac's would be less attractive than the pheromone. Additionally, the threshold of response for activation, upwind orientation, and wing fanning (Baker et al., 1976) may be elevated with 11–13:Ac's compared to the pheromone.

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