

(*Z,E*)-3,5-TETRADECADIEN-1-OL ACETATE  
SEX ATTRACTANT FOR THE CARPENTERWORM  
MOTH, *Prionoxystus robiniae* (Peck)  
(LEPIDOPTERA: COSSIDAE)

R.E. DOOLITTLE,<sup>1</sup> W.L. ROELOFS,<sup>2</sup> J. D. SOLOMON,<sup>3</sup>  
R.T. CARDÉ,<sup>2</sup> and MORTON BEROZA<sup>4</sup>

<sup>1</sup> *Agricultural Research Service, USDA  
Insect Attractants, Behavior and Basic Biology Research Laboratory  
Gainesville, Florida*

<sup>2</sup> *New York State Agricultural Experiment Station  
Geneva, New York*

<sup>3</sup> *Southern Forest Experiment Station, Forest Service, USDA  
Stoneville, Mississippi*

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**Abstract**—Electroantennogram analyses of female gland extract and of male antennal responses to synthetic standards suggested that (*Z,E*)-3,5-tetradecadien-1-ol acetate is a pheromone component for the carpenterworm moth, *Prionoxystus robiniae* (Peck). The four 3,5-geometrical isomers were synthesized and bioassayed in the laboratory and the field in 1972, 1973, and 1974. The *Z,E* isomer was found to be active in the laboratory and a good attractant in the field. The synthesis of the *Z,E* isomer also produced considerable quantities of the *E,E* isomer, which is difficult to remove completely. The *E,E* isomer does not inhibit the response of males to the *Z,E* isomer when it is present in amounts up to 20% of the *Z,E* isomer. The addition of a keeper, a volatility modifier, or an antioxidant prolonged the activity of the attractant for as much as 43 days. (*Z,E*)-3,5-Tetradecadien-1-ol acetate may be a natural pheromone, but it has not been chemically defined from female extract. There is EAG evidence that a second pheromonal component may be present. The attractant nevertheless provides a tool for population survey, behavioral studies, evaluation of economic impact, and possibly control.

**Key Words**—carpenterworm moth, *Prionoxystus robiniae*, (*Z,E*)-3,5-tetradecadien-1-ol acetate, pheromone, electroantennogram.

<sup>4</sup> Dr. Beroza, formerly with the Organic Chemical Synthesis Laboratory, Agricultural Research Service, USDA, Beltsville, Maryland, is retired. His present address is 821 Malta Lane, Silver Springs, Maryland 20901.

## INTRODUCTION

The sex pheromone of the adult female carpenterworm, *Prionoxystus robiniae* (Peck), a destructive insect pest of southern hardwood forests that tunnels extensively in tree trunks, was first reported by Solomon and Morris (1966) and partially characterized by Solomon et al. (1972) as an acetate of a 14- or 16-carbon unsaturated alcohol. The pheromone is potentially valuable for population surveys and control of this pest. However, the insect is difficult to rear (Solomon, 1967; Leppla et al. 1974), which means that the classic isolation and identification methods used successfully to elucidate the chemical structures of the pheromones of many other species were not practical. Therefore, the electroantennogram (EAG) technique (Roelofs and Comeau, 1971a; Roelofs et al. 1971) was tried. In this procedure, retention times of active components in female pheromone gland extracts are determined by assaying the gas (liquid) chromatographic (GLC) effluent from polar and nonpolar columns by EAG analysis. A complete series of monounsaturated standards is then assayed by EAG analysis to determine possible positions and configuration of unsaturation for the compounds of the chain length and functional group suggested by the GLC-EAG analysis.

## METHODS AND MATERIALS<sup>5</sup>

### *Electroantennogram Assays*

EAG analyses were conducted as previously described (Roelofs and Comeau, 1971b; Roelofs et al., 1971). Moths used for these analyses were collected in the field in Mississippi and sent live to New York. Female abdominal tips were extracted with methylene chloride. The GLC columns (2 m × 4 mm ID, glass) employed were OV-1® (3% methyl silicone on 100–120 mesh Gas Chrom® Q) and CHDMS® (3% cyclohexanedimethanol succinate on 100–120 mesh Chromsorb® W-AW-DMCS). Pheromone component retention times were determined before the 1971 flight season, when very few insects were available, by injecting the methylene chloride extract of 10 female abdominal tips (10 FE) onto the OV-1 column (170°C) or the CHDMS column (180°C), and collecting 1-min fractions from each for EAG analysis. The response profiles measured with a series of nonunsaturated acetates were recorded during the 1971 season, when an abundance of males was available.

<sup>5</sup> Mention of a commercial or proprietary product in this paper does not constitute a recommendation or an endorsement by the USDA.

### *Laboratory and Field Bioassays*

Laboratory bioassays were conducted as previously described (Solomon et al., 1972). Field bioassays were conducted by placing the candidate materials in traps in the forest and recording the number of males captured. Through 1972, these were screen traps (Solomon and Morris, 1966). A sticky trap (Solomon and Doolittle, 1976) was used for the 1973 and 1974 tests. All traps were suspended from branches 1.5 m above the ground and positioned about 300 m apart. Candidate chemicals were dissolved in 0.250 ml nanograde hexane, 99 mol% hexane, or spectroscopic grade isooctane, either with or without a keeper or preservative. The solution was placed on pieces of cotton dental roll (2 cm  $\times$  1 cm OD), which were placed in the traps during the afternoon, when the moths were most active. Test samples were assigned randomly to trap site, and rerandomized for each of 2–5 replicates. Catches per trap were recorded daily during the flight season, mid-May to early July, until the baits were no longer attractive. Tests were conducted with different quantities, isomeric mixtures, and preservatives.

### *Chemical Synthesis*

Instrumentation used in the chemical synthesis included a Perkin-Elmer Model 137 infrared spectrophotometer, Varian Aerograph® Models 1522-B and 2100 gas chromatographs, Varian Associates Models HA-100 and T-60 NMR spectrometers, and a high-pressure liquid chromatographic system consisting of a Waters Model 6000 solvent delivery system, a septum injector, and a Lab Data Control refractive index detector.

*Synthesis of (Z,Z) and (E,Z)-3,5-Tetradecadien-1-ol Acetates (VI and VII).* The synthetic routes used are outlined in Fig. 1, scheme A. The first three steps in the synthesis of the *E,Z* and *Z,Z* isomers (scheme A) were essentially the same as those reported by Rodin et al. (1970) and Celmer and Solomons (1953), though there were some modifications. The lithium salt of 1-decyne in tetrahydrofuran (THF) was treated with acrolein to give the secondary alcohol I in 68% yield. Treatment of I with phosphorous tri-bromide in ether-pentane produced a mixture of primary bromides II in 55% yield. Cuprous cyanide in dimethylformamide with a catalytic amount of sodium cyanide converted II to a mixture of ene-yne nitriles III in 70% yield. Methanolic hydrogen chloride converted III to a mixture of the ene-yne methyl esters IV and V in a yield of 86%. The IR spectra and physical constants of I–III and the mixture of IV and V were in agreement with those reported earlier by Rodin et al. (1970). The pure *Z* and *E* isomers IV and V were separated by GLC on 45  $\times$  0.80 cm ID aluminum columns containing 20% HiEFF-8BP® on 60/70 mesh Anachrom® ABS at 185°C with a N<sub>2</sub>

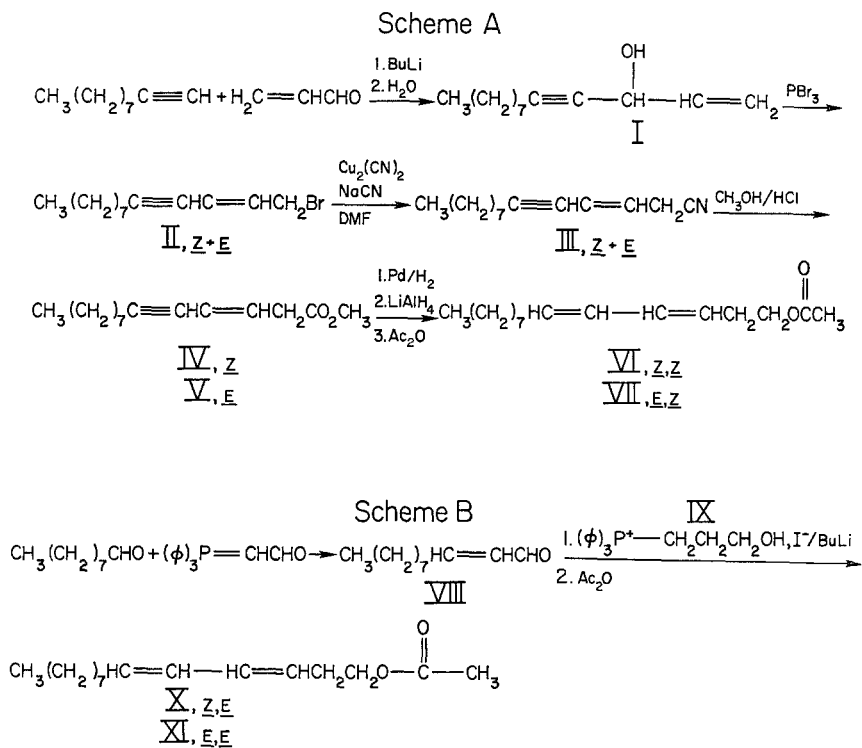


FIG. 1. Synthesis of the four isomers of 3,5-tetradecadien-1-ol acetate.

flow rate of 80 ml/min. The column effluent which was monitored by a thermal conductivity detector (250°C), was collected in 1.2-m lengths of Teflon tubing. From a total of 1.35 g mixed esters, 0.468 g IV (shorter retention time) and 0.675 g V (longer retention time) were obtained; accordingly, the ratio of *Z* to *E* isomers produced in the rearrangement of I to II was about 1:1.4. The IR spectrum of IV had bands at 3040  $\text{cm}^{-1}$  (olefinic C-H), 2220  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ -), 1745  $\text{cm}^{-1}$  (ester  $\text{C}=\text{O}$ ), and 1170  $\text{cm}^{-1}$  (ester  $\text{C}-\text{O}-\text{R}$ ). The IR spectrum of V had bands at 3040  $\text{cm}^{-1}$  (olefinic C-H), 2220  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{C}$ -), 1745  $\text{cm}^{-1}$  (ester  $\text{C}=\text{O}$ ), 1160  $\text{cm}^{-1}$  (ester  $\text{C}-\text{O}-\text{R}$ ), and 960  $\text{cm}^{-1}$  ( $\text{E}-\text{HC}=\text{CH}-$ ). The esters were analyzed on a 1.8 m  $\times$  2 mm ID column of 3% HiEFF-8BP on 100/120 mesh Anachrom ABS at 175°C with a  $\text{N}_2$  flow rate of 30 ml/min. The purity of IV determined by GLC was 96%; that of V was 90%.

The individual methyl esters IV and V were converted to the acetates VI and VII by semihydrogenation over Lindlar catalyst (Lindlar, 1952), followed by reduction with lithium aluminum hydride in ether. The crude

alcohols from the hydride reduction were converted to the acetates with acetic anhydride and pyridine in benzene at reflux. The diene esters VI and VII were purified by preparative GLC with a  $60 \times 0.80$  cm ID column containing 10% HiEFF-8BP on 60/70 mesh Anachrom ABS at  $185^\circ\text{C}$  with a  $\text{N}_2$  flow rate of 80 ml/min. The IR spectrum of the *Z,Z* isomer (VI) had bands at  $3015\text{ cm}^{-1}$  and  $3042\text{ cm}^{-1}$  (olefinic C-H),  $1745\text{ cm}^{-1}$  (ester  $\text{-C=O}$ ),  $1240\text{ cm}^{-1}$  (acetate), and  $1040\text{ cm}^{-1}$  (ester  $\text{-CH}_2\text{-O-C}$ ). The IR spectrum of the *E,Z* isomer VII had bands at  $3010\text{ cm}^{-1}$  and  $3025\text{ cm}^{-1}$  (olefinic C-H),  $1745\text{ cm}^{-1}$  (ester  $\text{-C=O}$ ),  $1240\text{ cm}^{-1}$  (acetate),  $1035\text{ cm}^{-1}$  (ester  $\text{-CH}_2\text{-O-C}$ ), and 985 and  $950\text{ cm}^{-1}$  (characteristic of a *Z,E* or *E,Z* conjugated diene). The UV spectra of the pure diene acetates had the following absorptions: VI ( $\lambda_{\text{max}}$  isooctane at 234 nm  $\epsilon_{\text{max}}$  35,000); VII, ( $\lambda_{\text{max}}$  isooctane at 233 nm,  $\epsilon_{\text{max}}$  25,000). The mass spectra of VI and VII had peaks at 192 ( $\text{M}^+ \text{-CH}_3\text{CO}_2\text{H}$ ), consistent with a molecular weight of 252. These analytical data are compatible with the assigned structures.

*Synthesis of (Z,E) and (E,E)-3,5-Tetradecadien-1-ol Acetate.* Initially the *Z,E* isomer was obtained by lithium aluminum hydride reduction of (*Z,E*)-3,5-tetradecadienoic acid in THF solution, followed by work-up with 1% sulfuric acid and extraction with hexane. The hexane extract was dried, the solvent was removed, and the residual oil was acetylated with acetic anhydride in the usual manner. The mixture of acetates was separated by preparative GLC on the same column described for the purification of the *Z,Z* and *E,Z* isomers. The IR spectrum of the product had bands at  $1745\text{ cm}^{-1}$  (ester  $\text{-C=O}$ ),  $1235\text{ cm}^{-1}$  (acetate),  $1040\text{ cm}^{-1}$  (ester  $\text{-CH}_2\text{-O-C}$ ), and 985 and  $950\text{ cm}^{-1}$  (characteristic of a *Z,E* or *E,Z* conjugated diene).

The *Z,E* and *E,E* isomers were synthesized as described in Fig. 1, scheme B. 2-Undecenal was prepared by heating freshly distilled nonanal with (triphenylphosphoranylidene) acetaldehyde (Trippett and Walker, 1961; m.p.  $178\text{--}180^\circ\text{C}$ ) at reflux in dry benzene under a  $\text{N}_2$  atmosphere for 48 hr. The product was redistilled on a spinning band still to give pure 2-undecenal (b.p.  $54^\circ\text{C}/0.01\text{ mm}$   $n_D^{20}$  1.45625). The IR spectrum had bands at  $2750\text{ cm}^{-1}$  and  $2880\text{ cm}^{-1}$  ( $\text{-C-H}$ ),  $1715\text{ cm}^{-1}$  (conj.  $\text{-C=O}$ ), and  $985\text{ cm}^{-1}$  ( $\text{E-HC=CH-}$ ).

(3-Hydroxypropyl) Triphenylphosphonium iodide (IX). The reaction of 3-iodopropanol with triphenylphosphine in benzene resulted in a 91% yield of white crystalline product m.p.  $208\text{--}209^\circ\text{C}$  (uncorrected) that was used without further purification.

(*Z,E*) and (*E,E*)-3,5-Tetradecadien-1-ol Acetate (X and XI). The reaction was run in a dry,  $\text{N}_2$ -swept 250-ml 4-neck flask fitted with a mechanical stirrer, thermometer,  $\text{N}_2$  inlet, and septum stopper. Sodium hydride (1.32 g, 0.055 mol) in the form of 2.32 g of a 57% dispersion in mineral oil was added to the flask and washed free of mineral oil by repeated decantation with

pentane. Dry dimethyl sulfoxide (50 ml) was added via a syringe, and the flask was heated in a water bath with stirring to 60–65°C until foaming stopped. THF (15 ml) was added, and the reaction mixture was cooled to 0°C in an ice-salt bath. An Erlenmeyer flask (50 ml) containing 24.66 g (0.055 mol) IX was connected to one neck of the flask with a piece of Gooch tubing, and the phosphonium salt was slowly added with stirring while the temperature was kept below 5°C. After the salt had been added, 25 ml (0.055 mol) of a hexane solution of butyllithium was added dropwise with stirring to the reaction mixture while the temperature was kept as close to 0°C as possible. After addition of the butyllithium was complete and the dropping funnel was rinsed with 5 ml THF, the deep-red reaction mixture was held at 0°C for 1 hr; then 2-undecenal (8.41 g, 0.05 mol) was added dropwise. The reaction mixture was stirred and allowed to come to room temperature overnight. Then it was worked up by adding 3.5 ml (0.20 mol) ice water and extracting 4 times with pentane. The pentane extracts were washed with water and brine and then dried over sodium sulfate. The drying agent was removed by filtration, and the solvent was evaporated.

The residual oil was converted to a mixture of acetates (X and XI) in the usual fashion. GLC analysis showed 2 products in a ratio of about 2:1, either on a 1.8 m × 2 mm ID column packed with 3% HiEff-8BP on 100/120 mesh Gas Chrom Q: (175°C and a N<sub>2</sub> flow rate of 15 ml/min) or on a 1.8 m × 2 mm ID column packed with 3% Carbowax® 20 M on 120/140 mesh acid-washed and silanized Chromosorb W (175°C with a N<sub>2</sub> flow rate of 20 ml/min). The crude mixture of acetates was passed through a column of silica gel (J. T. Baker No. 3405) with 5–10% ether in hexane as eluant to remove any triphenylphosphine oxide remaining. When this reaction was run using two equivalents of sodium hydride to generate the phosphorane from IX, very little product was obtained, and no characteristic red color was observed during the reaction. This reaction is under further investigation.

The solvents were removed, and X and XI were separated several ways. Initially, the pure isomers were obtained by preparative GLC using the same columns and conditions reported for VI and VII. The IR spectrum of the isomer with the shorter retention time had bands at 3030 cm<sup>-1</sup> (olefinic -CH), 1745 cm<sup>-1</sup> (ester -C=O), 1235 cm<sup>-1</sup> (acetate), 1040 cm<sup>-1</sup> (ester -C-O-), and 950 and 985 cm<sup>-1</sup> (Z,E conjugated diene), and the IR spectrum of the peak of longer retention time had bands at 3020 cm<sup>-1</sup> (olefinic C-H), 1745 cm<sup>-1</sup> (ester -C=O), 1240 cm<sup>-1</sup> (acetate), 1035 cm<sup>-1</sup> (ester -C-O-), and 990 cm<sup>-1</sup> (E,E conjugated diene). The mass spectra of both X and XI had peaks at 192 (M<sup>+</sup>-60), and the UV spectra showed for X ( $\lambda_{\max}$  isooctane at 232 nm,  $\epsilon_{\max}$  32,000) and XI ( $\lambda_{\max}$  isooctane at 229 nm,  $\epsilon_{\max}$  31,000). These data are consistent with the assigned structures X and XI. The isomers are produced in a ratio of 1:2, X:XI. Although distillation of the mixture of

acetates on a spinning band still failed to completely resolve the isomeric mixture, it was possible to produce one fraction (88–92°C/0.004 mm) that contained a minimum of 95% X and another (91–93°C/0.002 mm) that contained a minimum of 90% XI. Several intermediate fractions (90–91°C/0.002 mm) contained mixtures of X and XI. The still-pot residue, after distillation in a short-path still, was found by GLC analysis to be 98% XI. High pressure liquid chromatography was used to prepare X 99+ % pure. A column of 10- $\mu$ m Lichrosorb® (50 cm  $\times$  0.44 cm ID) was developed with 3% ether in hexane flowing at 3.0 ml/min and 750 psig. Between 20 and 40  $\mu$ l of material was injected in each run; fractions collected were freed of solvent by evaporation, and the residue was distilled (70°C/0.05 mm) in a short-path still to give X as a clear oil.

## RESULTS AND DISCUSSION

EAG analysis of the fractions collected from the OV-1 column showed activity (1.2 mV vs 0 mV from other fractions) at 9–11 min. 1-Tetradecanol and 1-hexadecanol acetate on this column had retention times of 9.2 and 22.0 min, respectively. The portions collected from the CHDMS column (180°C) gave EAG activity at 9–10 min (1.4 mV vs 0.2 in previous fractions) and 14–17 min (2.0 mV); 1-tetradecanol and 1-hexadecanol acetate had retention times of 9.7 and 21.2 min, respectively. The major component had retention times that suggested either a 14-carbon chain acetate with more than one double bond or a 16-carbon aldehyde. Solomon et al. (1972) concluded that the pheromone is not an aldehyde.

Male antennal responses to the series of monounsaturated 12-, 14-, and 16-carbon chain alcohols and acetates showed good responses with 14-carbon chain acetates (Fig. 2), with unsaturation in the 3, 4, 5, and 9 positions. Interpretation of the GLC and the EAG data suggested that (*Z,E*)-3,5-tetradecadien-1-ol acetate could be one of the pheromone components. This result is in agreement with the earlier report that the pheromone is likely either a doubly unsaturated 14-carbon chain acetate or a mono-unsaturated 16-carbon chain acetate (Solomon et al., 1972).

(*Z,E*)-3,5-Tetradecadienoic acid (kindly furnished by W. Burkholder of the University of Wisconsin, Madison) was reduced and acetylated (see "Methods and Materials") to produce a mixture that was resolved by a combination of thin-layer and gas chromatography. The major product, presumably (*Z,E*)-3,5-tetradecadien-1-ol acetate, gave positive results in the laboratory and in field tests during the 1971 flight season. Consequently, all four isomers of 3,5-tetradecadien-1-ol acetate were synthesized.

The retention times of the four isomers of 3,5-tetradecadien-1-ol acetate on CHDMS relative to 1-tetradecanol acetate were: *Z,E*, 1.66; *E,Z*, 1.56;

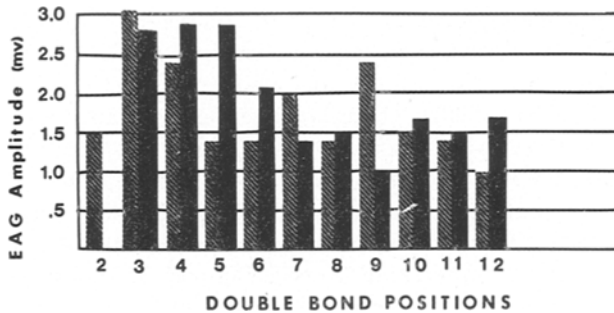


FIG. 2. Electroantennogram responses of male carpenterworm antennae to 10  $\mu$ g 14-carbon acetates on filter paper. Crosshatching represents the *Z* isomer; solid bars, the *E* isomer.

*Z,Z*, 1.76; and *E,E*, 2.00. The major active component of female extracts had a relative retention time of 1.44–1.75, which eliminated the *E,E* isomer. EAG analysis replicated 5 times produced the following order of activity: *Z,E* ( $3.3 \pm 1$  mV); *Z,Z* ( $2.9 \pm 0.7$  mV); *E,E* ( $2.4 \pm 0.9$  mV); *E,Z* ( $2.4 \pm 0.4$  mV); *Z-3* ( $2.7 \pm 0.9$  mV); and *E-5* ( $2.0 \pm 0.9$  mV). Therefore, the *Z-3*, *E-5* isomer had the correct retention time and was the most active by response of the male antennae.

At concentrations of 1  $\mu$ g/ $\mu$ l in the laboratory bioassay, of the four isomers, only (*Z,E*)-3,5-tetradecadien-1-ol acetate produced the characteristic responses (equal to or greater than 60%) of males to female extracts or to live virgin females: vibrating of wings, opening of genital claspers, and rapid crawling and dancing.

During the field bioassays conducted during the 1972 emergence season, 1–12 male carpenterworm moths were attracted to each screen trap (Solomon and Morris, 1966) in 6 experiments baited with 250  $\mu$ g (*Z,E*)-3,5-tetradecadien-1-ol acetate, but no males were attracted to traps containing as much as 1250  $\mu$ g of each of the other three isomers. Since geometrical isomers have been shown to increase or decrease attractiveness of the primary pheromonal component of many insect species, tests were conducted to measure the effect of the other three isomers on the attractiveness of the *Z,E* isomer.

Traps containing from 2.5 to 250  $\mu$ g of either the *Z,Z* or the *E,Z* isomer in admixture with 250  $\mu$ g of the *Z,E* isomer caught no moths, though 250  $\mu$ g of the *Z,E* isomer or caged virgin females caught from 6 to 14 males/day for 1–4 days during this same period. Traps baited with 250  $\mu$ g of the *Z,E* isomer plus 2.5 to 250  $\mu$ g of the *E,E* isomer were as effective as traps baited with the *Z,E* isomer only. Thus, the *Z,Z* and the *E,Z*, isomers might be inhibitory, while the *E,E* isomer was not.

TABLE 1. ATTRACTION OF MALE CARPENTERWORM MOTHS TO MIXTURES OF (Z,E)- AND (E,E)-3,5-TETRADECADIEN-1-OL ACETATE [(Z,E)- AND (E,E)-TDDA]

Isomer mixture ( $\mu\text{g}$ ) <sup>a</sup>		Number of males trapped (mean $\pm$ SD)	
(Z,E)	(E,E) <sup>b</sup>	June 6-30, 1973 <sup>c</sup>	June 19-July 8, 1974 <sup>c</sup>
250	25	13.0 $\pm$ 14.1	5.0 $\pm$ 3.0
250	50	22.0 $\pm$ 5.7	5.0 $\pm$ 3.0
250	125	94.5 $\pm$ 65.8	2.3 $\pm$ 0.6
250	250	39.5 $\pm$ 17.7	2.7 $\pm$ 0.6
250	500	38.0 $\pm$ 47.0	5.7 $\pm$ 4.0
500	50	11.5 $\pm$ 16.3	7.0 $\pm$ 6.2
500	100	181.0 $\pm$ 200.8	22.3 $\pm$ 16.0
500	250	101.0 $\pm$ 90.5	5.0 $\pm$ 5.6
500	500	17.5 $\pm$ 3.5	6.3 $\pm$ 4.5
500	1000	82.0 $\pm$ 67.0	5.0 $\pm$ 4.0
50	0	0.5 $\pm$ 0.7	1.0 $\pm$ 1.0
100	0	15.5 $\pm$ 21.9	0.3 $\pm$ 0.6
250	0	69.5 $\pm$ 92.6	2.3 $\pm$ 0.6
500	0	55.0 $\pm$ 69.3	1.7 $\pm$ 0.6
Virgin females		74.5 $\pm$ 7.8	15.0 $\pm$ 11.0

<sup>a</sup> Trioctanoin included as keeper at a ratio of 10 $\times$  the total isomer mixture.

<sup>b</sup> Pure E,E isomer captured no males.

<sup>c</sup> Two replications in 1973 and 3 replications in 1974.

Additional tests were made during 1973 and 1974 to further assess the effect of the E,E isomer on the attractiveness of the Z,E isomer (Table 1). The striking differences among catches during the two test periods reflect differences in populations of moths. The large deviations within each test period reflect the influence of such variables as weather and trap placement. However, again, the addition of up to 20% of the E,E isomer did not appear to inhibit the attractiveness of the Z,E isomer. The absence of inhibition of the Z,E isomer by the E,E isomer is fortuitous, since the synthesis produces a mixture of the two isomers. Moreover, it is relatively easy to produce the Z,E isomer in up to 90% purity by distillation, but it would be expensive to produce it in a purity greater than 90%.

In 1974, 50-2000- $\mu\text{g}$  quantities of the Z,E isomer plus a 10-fold amount of trioctanoin keeper were bioassayed for attractiveness. Although all amounts were attractive, quantities of 250  $\mu\text{g}$  or more were most attractive (Table 2). Statistical analysis of variance indicated that the higher quantities were comparable with virgin females in both total catches and duration of attractancy. During the first several days, traps baited with 250 and 500  $\mu\text{g}$

TABLE 2. ATTRACTION OF MALE CARPENTERWORM MOTHS TO (Z,E)-3,5-TETRADECADIEN-1-OL ACETATE ON JUNE 4-12, 1974

Quantity of attractant <sup>a</sup> ( $\mu$ g)	Number of males trapped <sup>b</sup> (mean $\pm$ SD)	Number of days attraction (mean $\pm$ SD)
50	4.2 $\pm$ 1.2	1.2 $\pm$ 0.4
100	4.0 $\pm$ 1.6	1.6 $\pm$ 0.5
250	16.8 $\pm$ 3.2	3.2 $\pm$ 0.4
500	23.4 $\pm$ 5.0	5.0 $\pm$ 1.2
1000	20.4 $\pm$ 4.8	4.8 $\pm$ 1.3
2000	27.0 $\pm$ 7.4	7.4 $\pm$ 1.7
Virgin females	29.5 $\pm$ 4.5	4.5 $\pm$ 2.1

<sup>a</sup> Trioctanoin included as keeper at a ratio of 10 $\times$  the total synthetic attractant.

<sup>b</sup> Each test was replicated 5 times.

were generally more attractive than those baited with 1000 and 2000  $\mu$ g; however, the higher quantities remained attractive longer.

In a separate test, a volatility depressant containing an anti-oxidant was compared with trioctanoin, which only reduced the volatility of the attractant (Table 3). The food preservative, Sustane-6<sup>®</sup>, which contains 4% antioxidant (BHA and BHT) in vegetable oil, was added in ratios of 2:1, 5:1, 10:1, and 20:1 to various amounts of Z,E isomer (100, 250, and 500  $\mu$ g). The mixtures of Sustane-6 with Z,E isomer were consistently more attractive than the mixtures with trioctanoin or no additive. For example, 500  $\mu$ g Z,E isomer combined with Sustane-6 in ratios of 2:1, 5:1, 10:1, and 20:1 attracted means of 161, 132, 174, and 349  $\sigma\sigma$ , compared with means of 17, 39, 10, and 12  $\sigma\sigma$  for corresponding samples containing trioctanoin. Moreover, the antioxidant greatly increased the duration of attractancy: 500  $\mu$ g Z,E isomer plus antioxidant at the same ratios was attractive an average of 9, 14, 20, and 37 days, compared with 5, 5, 4, and 5 days for those containing trioctanoin. An analysis of variance indicated that the antioxidant was more effective than the trioctanoin at all three levels of attractant.

The effects on attractiveness of certain monounsaturated isomers suggested by the EAG analysis should be tested.

In summary, Z,E-3,5-tetradecadien-1-ol acetate with as much as 20% E,E isomer was a good attractant for male carpenterworm moths. The addition of Sustane-6 antioxidant helped to increase attractiveness and longevity of the lure.

The Z,E isomer has GLC retention times that correspond with those of

TABLE 3. COMPARISON OF TRIOCTANOIN AND SUSTANE-6 AS KEEPERS IN FIELD ATTRACTANCY OF (Z,E)-3,5-TETRADECADIEN-1-OL ACETATE TO MALE CARPENTERWORM MOTHS BETWEEN JUNE 6 AND JULY 16, 1974

Quantity of Z,E-TDDA ( $\mu$ g)	Quantity of keeper ( $\mu$ g)		Number of males trapped <sup>a</sup> (mean $\pm$ SD)	Number of days' attraction (mean $\pm$ SD)
	Trioctanoin	Sustane-6		
100	200	0	5 $\pm$ 0	1.0 $\pm$ 0.0
100	500	0	7 $\pm$ 4	1.0 $\pm$ 0.0
100	1,000	0	18 $\pm$ 22	2.0 $\pm$ 0.0
100	2,000	0	3 $\pm$ 4	0.5 $\pm$ 0.7
100	0	200	25 $\pm$ 16	1.5 $\pm$ 0.7
100	0	500	22 $\pm$ 9	2.5 $\pm$ 0.7
100	0	1,000	17 $\pm$ 11	4.0 $\pm$ 0.0
100	0	2,000	50 $\pm$ 0	7.0 $\pm$ 1.4
100	0	0	18 $\pm$ 21	1.0 $\pm$ 0.0
250	500	0	11 $\pm$ 10	2.5 $\pm$ 2.1
250	1,250	0	26 $\pm$ 11	2.5 $\pm$ 0.7
250	2,000	0	7 $\pm$ 3	2.5 $\pm$ 0.7
250	5,000	0	14 $\pm$ 8	2.5 $\pm$ 0.0
250	0	500	22 $\pm$ 15	4.5 $\pm$ 0.7
250	0	1,250	57 $\pm$ 48	7.0 $\pm$ 4.2
250	0	2,000	93 $\pm$ 76	11.0 $\pm$ 1.4
250	0	5,000	94 $\pm$ 8	14.0 $\pm$ 1.4
250	0	0	46 $\pm$ 40	1.5 $\pm$ 0.7
500	1,000	0	17 $\pm$ 10	5.0 $\pm$ 2.8
500	2,000	0	39 $\pm$ 48	5.0 $\pm$ 4.2
500	5,000	0	10 $\pm$ 11	3.5 $\pm$ 0.7
500	10,000	0	12 $\pm$ 3	4.5 $\pm$ 2.1
500	0	1,000	161 $\pm$ 76	8.5 $\pm$ 0.7
500	0	2,000	132 $\pm$ 76	14.0 $\pm$ 0.0
500	0	5,000	174 $\pm$ 112	19.5 $\pm$ 3.5
500	0	10,000	394 $\pm$ 115	36.5 $\pm$ 9.2
500	0	0	28 $\pm$ 21	3.0 $\pm$ 1.4
Virgin females			32 $\pm$ 26	4.8 $\pm$ 2.4

<sup>a</sup> Each test replicated twice; tests with virgin female replicated 8 times.

the primary pheromonal component in the extract of the female gland, it elicited the greatest EAG response of all the compounds tested, and it was itself active in laboratory and field behavioral tests. However, rigorous chemical proof is still needed to demonstrate that the material is the primary pheromonal component. A related compound, (E,Z)-3,5-tetradecadienoic acid, has been reported (Silverstein et al., 1967) as a pheromone of the black carpet beetle, *Attagenus megatoma* (F.).

The effectiveness of (Z,E)-3,5-tetradecadien-1-ol acetate as an attractant for male carpenterworms provides a potential tool for population survey, behavioral studies, evaluation of economic impact, and possibly control.

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