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SYNTHESIS OF THE TWO COMPONENTS OF THE SEX PHEROMONE SYSTEM OF THE POTATO TUBERWORM MOTH, *Phthorimaea operculella* (ZELLER) (LEPIDOPTERA: GELECHIIDAE) AND FIELD EXPERIENCE WITH THEM

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Abstract—Male potato tuberworm moths are attracted by a mixture of *trans*-4,*cis*-7-tridecadien-1-ol acetate and *trans*-4,*cis*-7,*cis*-10-tridecatrien-1-ol acetate. The synthesis of both compounds is described. Overall yields were 14.4 and 9.5% after distillation. The products were purified by liquid chromatography. Mixtures of these compounds in several ratios and quantities were tested in potato fields in Australia, Peru, and Cyprus. The largest catches were obtained from water pan traps baited with rubber sleeve stoppers containing both components in ratios varying between 1:9 and 9:1. The stoppers were attractive over a period of several months even under hot weather conditions.

Key Words—*Phthorimaea operculella* (Zeller), potato tuberworm moth, sex pheromone, attractant, *trans*-4,*cis*-7-tridecadien-1-ol acetate, *trans*-4,*cis*-7, *cis*-10-tridecatrien-1-ol acetate.

INTRODUCTION

The potato tuberworm moth, *Phthorimaea operculella* (Zeller), is a serious pest in several areas of the world. Adeesan et al. (1969) showed that the female moths release volatile substances to lure the males. Knowledge about the chemistry of these substances could provide another weapon for controlling this insect. Recently two attractive compounds were isolated from female

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abdominal tip extracts. Roelofs et al. (1975) isolated, identified, and synthesized *trans*-4,*cis*-7-tridecadien-1-ol acetate (PTM 1). They also isolated another active component from the extracts but this was not identified. Independently Persoons et al. (1976a,b) found PTM 1 and also demonstrated that the second component of the pheromone system is *trans*-4,*cis*-7,*cis*-10-tridecatrien-1-ol acetate (PTM 2). They discovered that a mixture of PTM 1 and PTM 2 in the ratio 1:4 was much more attractive than each single compound. Other investigators have also tried to elucidate the pheromone system of the potato tuberworm moth (Voerman et al., 1977). Strangely enough Yamaoka et al. (1976) did not find PTM 1 in their extract from adult females and concluded that the pheromone should be one of the geometric isomers of the 4,7,10-tridecatrienyl acetates. A description of the synthesis of PTM 1 was given before (Roelofs et al., 1975; Henrick, 1977). This paper describes the synthesis of both PTM 1 and PTM 2, and the results from more extensive field experiments in Australia, Peru, and Cyprus.

METHODS AND MATERIALS

Synthesis of PTM 1 and PTM 2

The progress of all reactions was followed and all products were checked by gas–liquid chromatography using a column packed with 1.5% SP-2250/1.95% SP 2401 on Supelcon AW-DMCS 100/120 (glass, 2.1 m × 2.4 mm ID) and a column packed with 15.6% OV-275 on Chromosorb W AW-DMCS 100/120 (glass, 5.4 m × 2.4 mm ID). The end-products, PTM 1 and PTM 2, were ultimately purified by liquid chromatography on a silver-loaded resin (glass column, 200 cm × 0.8 cm, packed with Lewatit SP 1080, 170–200 mesh, Ag^+ form, eluent methanol, temperature 20–40°C) (Houx et al., 1974). Purity was checked with HPLC at 21°C (PTM 1) and 37°C (PTM 2) (Houx and Voerman, 1976). They were stored at —20°C under nitrogen after addition of 0.1% 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant (Goto et al., 1974). The reaction sequences for the synthesis of PTM 1 and PTM 2 are shown in Figure 1.

2-(3-Bromopropyloxy)tetrahydropyran (I). To 83 g (0.59 mol) 3-bromopropanol-1 and 4 drops of concentrated HCl, 65 g (0.77 mol) of dihydropyran was slowly added. The mixture was stirred magnetically and cooled in ice water. After stirring for 2 hr at room temperature, 2 g of K_2CO_3 was added and stirring was continued for 1 hr. After filtration, the filtrate was distilled; main fraction 82.9 g (63%), b. 76°C/1.4 mm, n_D^{25} 1.4778.

2-(6-Hydroxy-4-hexynyloxy)tetrahydropyran (II). After stirring 0.2 g $Fe(NO_3)_3 . 9H_2O$ for $\frac{1}{4}$ hr in 600 ml NH_3, 5.6 g lithium (0.76 mol) was added in small pieces. When the blue color had vanished, 21.2 g (0.38 mol)

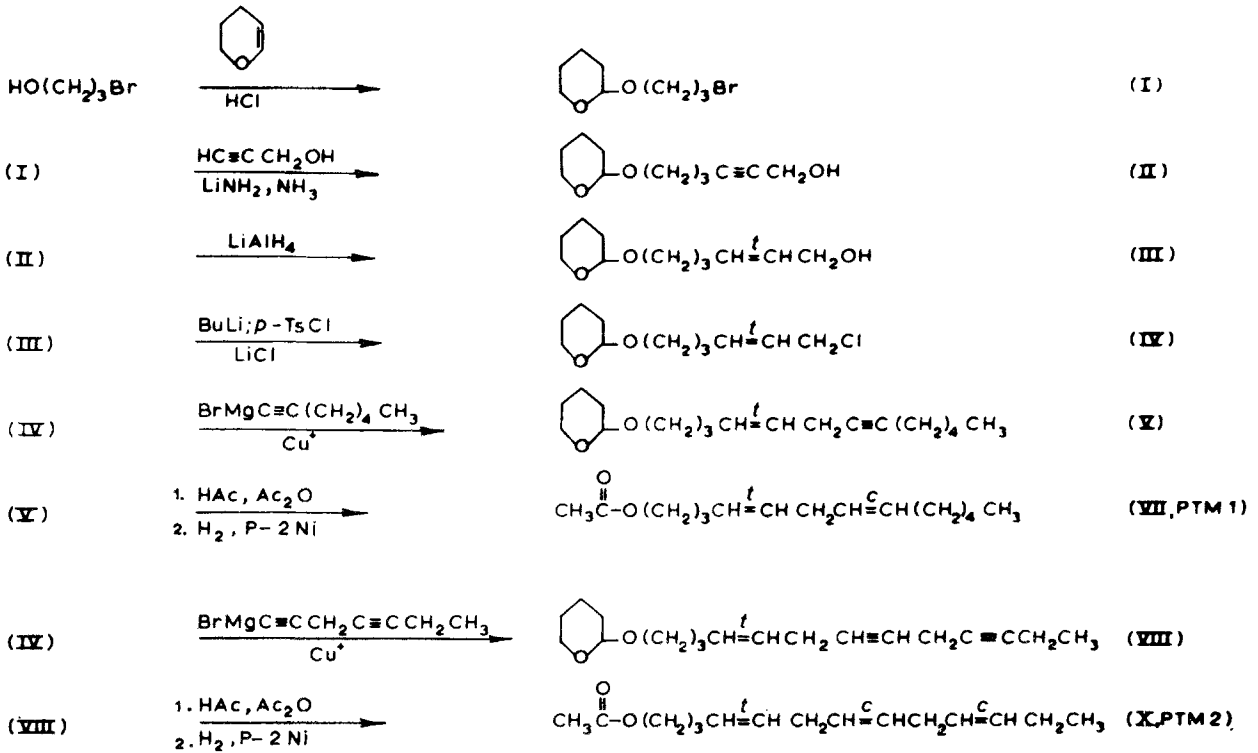

FIG. 1. Reaction scheme for synthesizing PTM 1 and PTM 2.

propargyl alcohol was added. After 2 hr of stirring, 53 g (0.24 mol) (I) diluted with 250 ml tetrahydrofuran was added. After stirring overnight, the mixture was worked up (Ames et al., 1963) and distilled. Main fraction 36.7 g (78.1%), b. 104°C/0.03 mm, n_D^{25} 1.4825.

2-(6-Hydroxy-trans-4-hexenyloxy)tetrahydropyran (III). To a cooled (—80°) mechanically stirred suspension of 4.3 g (113 mmol) $LiAlH_4$ in 90 ml dry ether, 25.0 g (126 mmol) of (II) was added fairly rapidly. After 1 hr of stirring, the cooling bath was removed and the mixture was allowed to warm up. It was gently refluxed for $3\frac{1}{2}$ hr, cooled again, and 12 ml ethyl acetate, 250 ml saturated NH_4Cl, and 200 ml 20% NaCl were added. Stirring was continued for several hours (Raphael, 1955). The organic layer was extracted with ether (some CH_3OH might be helpful to break the emulsion). The extract was washed with 20% NaCl, dried, and distilled; main fraction 18.7 g (74.5%), b. 99–101°C/0.05 mm, n_D^{25} 1.4720.

2-(6-Chloro-trans-4-hexenyloxy)tetrahydropyran (IV). The alcohol (III), 48 g (240 mmol) in 120 ml dry ether and 60 ml dry HMPT, cooled in an ice–salt bath, was provided with an equivalent of butyllithium in hexane as described by Stork et al. (1969). The mixture became brown-red at the equivalence point. After stirring some time at room temperature, the mixture was cooled again to 3°C and 48.6 g (255 mmol) *p*-TsCl dissolved in 120 ml ether and 60 ml HMPT was added followed by 30.9 g (720 mmol) LiCl. After stirring overnight, the mixture was worked up and the product distilled, main fraction 34.3 g (65.4%), b. 82°C/0.10 mm, n_D^{25} 1.4780.

2-(trans-4-en,7-Tridecynyloxy)tetrahydropyran (V). Ethylmagnesium bromide [from 4.9 g (0.20 mol) Mg and 16.3 g (0.15 mol) EtBr] in 70 ml THF was added to 15.4 g (0.16 mol) 1-heptyne in 15 ml THF. The reaction mixture was warmed on a waterbath at 60°C for $\frac{3}{4}$ hr. Afterwards it was decanted from the magnesium and 1 g dry CuCl was added. The suspension was stirred for $\frac{1}{4}$ hr before 21.8 g (0.10 mol) of (IV) and 5 ml THF were added. After stirring overnight at 35°C, the mixture was refuxed at 60°C for $\frac{1}{2}$ day. This resulted in a light green reaction mixture, which was poured out in 120 ml H_2O containing 20 g NH_4Cl and 4 g KCN. The product was extracted with ether, and the extract was washed with 20% NaCl until neutral. After drying on $MgSO_4/K_2CO_3$ and removing the solvent in a rotary evaporator, 26.1 g oil remained (see also Brandsma, 1971).

trans-4,7-Tridecyn-1-ol acetate (VI). 13.0 g of (V) in 50 ml HAc was stirred and heated at 80°C. Then 25 ml Ac_2O was added, and heating and stirring were continued overnight. The mixture was poured out in icewater and worked up in the usual way. Distillation gave 9.0 g (76.2% from IV) b. 82–83°C/0.05 mm, n_D^{25}1.4620.

trans-4,cis-7-Tridecadien-1-ol acetate (VII, PTM 1). To 1.25 g $Ni(OAC)_2 \cdot 4H_2O$ in 50 ml EtOH under H_2, was added 5.0 ml of a $NaBH_4$ solution

(prepared by filtering the solution resulting from 1 g $NaBH_4$, 24 ml EtOH, 1.25 ml 2 N NaOH) (Brown and Ahuja, 1973a,b). After the hydrogen evolution had ceased, 0.7 ml 1,2-diaminoethane and 9.0 g (38 mmol) of (VI) were added. After 959.4 ml H_2 had been taken up, under vigorously stirring, the reaction stopped. The reaction mixture was filtered, diluted with a 20% NaCl solution, and extracted with ether. The extract was washed with 20% NaCl, dried, and distilled giving 7.1 g (78.9%) PTM 1, b. 73°/0.02 mm, n_D^{25} 1.4528. This oil was purified further by liquid chromatography (Houx et al., 1974) giving pure PTM 1, n_D^{25} 1.4542, with satisfactory elemental, GC and LC analyses, and consistent MS, NMR, and IR spectra (Persoons et al., 1976b).

1,4-Heptadiyne. A Grignard reagent, made from 12 g (0.5 mol) magnesium and 39 g (0.36 mol) ethyl bromide in 175 ml THF, was decanted from the excess of magnesium and provided with 30 g (0.56 mol) 1-butyne in 100 ml dry THF (Brandsma, 1971, p. 52). After stirring the mixture $\frac{3}{4}$ hr at 60° and $\frac{1}{4}$ hr at room temperature, 2.0 g dry CuCl and 38 g (0.32 mol) 3-bromopropyne were added. The mixture was stirred overnight. Then a water solution of 52 g NH_4Cl and 6 g KCN was added to the green suspension. The ether extract of the latter was washed with 5% KCN and 20% NaCl until neutral and was then dried and distilled. Main fraction 15.3 g (55%), b. 34–41°/22 mm, n_D^{25} 1.4488 (Kraevskii et al., 1964, found b. 62–63°/80 mm, n_D^{20} 1.4440).

trans-4-en,7,10-Tridecadiyn-1-ol acetate (IX). A Grignard reagent, prepared from 5.0 g Mg (0.21 mol) and 18.3 g (0.17 mol) ethyl bromide in 100 ml THF, was decanted from the excess of magnesium and slowly added to 20.4 g (0.22 mol) 1,4-heptadiyne in 60 ml dry THF. The mixture was warmed at 65°C for $\frac{1}{2}$ hr. Then it was stirred for some time with 2 g dry CuCl after which 32 g (0.146 mol) (IV) was added. The reaction was slightly exothermic, and the mixture became light green. After 36 hr of stirring at room temperature and 1 hr at 55°C, the mixture was poured out into 250 ml water containing 50 g NH_4Cl and 6 g KCN. After extraction with ether and working up as described above, 39.0 g of a red–brown oil was obtained (VIII). From this oil, 16.5 g was converted into the acetate (IX) with 60 ml HAc and 32 ml Ac_2O. The product was distilled; main fraction 7.6 g (53%), b. 108–114°/0.05–0.07 mm, n_D^{25} 1.4830.

trans-,4,cis-7,cis-10-Tridecatrien-1-ol acetate (X, PTM 2). To 2.5 g $Ni(OAc)_2.4H_2O$ in 100 ml EtOH under H_2 was added 10 ml of a $NaBH_4$ solution (see preparation of VII), and after the H_2 evolution ceased, 1.4 ml 1,2-diaminoethane was added. In this mixture 7.6 g (IX) (32.8 mmol) took up 1680 ml H_2. The mixture was worked up as described above. Distillation gave 5.8 g (75.1%) colorless oil, b. 75°/0.02 mm, n_D^{25}1.4650. Part of this oil was purified by liquid chromatography giving pure PTM 2, n_D^{25}1.4660, with

satisfactory elemental, GC, and LC analyses and consistent MS, NMR, and IR spectra (Persoons et al., 1976b).

Field Experiments with PTM 1 and PTM 2

Field trials were undertaken in Australia to determine the influence on male trap captures of baits containing various mixtures of both female pheromone components. The effects of differing dosage levels in baits and the possible role of the components in bringing males to pheromone sources were also examined. Other field tests were carried out in Cyprus on component ratios and male catches. There was also an extended trial in Peru to test the longevity of a single blend.

In Australia, trials were located in and around an experimental potato field. The traps consisted of plastic boxes ($20 \times 10 \times 5$ cm) containing 200 ml of water and 2% wetting agent. The pheromone components, dissolved in methylene chloride, were applied to red rubber sleeve stoppers (Fisher Scientific Company, Pittsburgh, Pennsylvania, catalog No. 14-126A). These were suspended from the lids 2.5 cm above the water (Bacon et al., 1976). Traps were placed 9 m apart on the ground within the rows of potato plants. To obviate significant positional effects, traps were rotated regularly. Trapping methods in Cyprus and Peru were essentially the same as those in the Australian tests.

RESULTS

Ratio of Pheromone Components and Male Captures

PTM 1 and PTM 2 were applied singly or in combination to rubber sleeve stoppers in varying quantities as indicated in Table 1. In the first trial within the potato crop, traps were sampled regularly.

The totals for the entire period (Table 1) indicate that there was no significant difference in male captures at traps baited with blends of PTM 1 and PTM 2 ranging from 9:1 to 1:9, although all were significantly greater than either component alone. PTM 2 was generally significantly more attractive on its own than PTM 1. Statistical analysis of the results obtained during the first and last 15 days of exposure of the baits showed that this pattern of captures was consistent over the period of the tests, although the actual dosage level of each component would have decreased with time. Catches were greatest during the first few days of exposure of the pheromones in previously unsampled areas both in Australia and Cyprus. Adult numbers were high within the potato field and there were very significant differences between inner and outer trap locations within the potato field (mean catch

TABLE 1. MEAN NUMBER OF MALE POTATO TUBERWORM MOTHS CAPTURED WITH VARIOUS BLENDS OF PTM 1 AND PTM2[a]

Treatment		Mean catch per trap[b]	
PTM 1 (μg)	PTM 2 (μg)	Potato field	Pasture field
200	0	131 a	3 a
180	20	854 bc	13 b
160	40	1160 b	17 bc
140	60	782 bc	29 bc
120	80	983 bc	16 bc
100	100	932 bc	16 bc
80	120	1041 b	15 bc
60	140	591 cd	20 bc
40	160	658 bc	21 bc
20	180	748 bc	15 bc
0	200	252 d	5 a
0	0	20 e	0 d

[a] Australia, February 2–March 18, in potato field and March 18–April 5 1977, in pasture field, 5 traps per treatment.
[b] Means followed by the same letter are not significantly different at $P < 0.05$, Duncan's multiple range test $\sqrt{x}$ transformation.

per treatment: outer traps, 1590; inner traps, 674; significant difference at $P<0.05$). For this reason traps had to be redistributed randomly at regular intervals. Blank traps without rubber septa caught relatively few males (Table 1). Less than 3% of captures consisted of females; of these most were mated. Similar numbers of females were taken at all treatments.

It was thought that the similarity in numbers of moths captured at almost all combinations of both components may have been due to the large numbers of males available for capture in the relatively small potato field. However, a second series of tests with the same treatments undertaken in a pasture field several hundred meters away from the potato field produced similar results (Table 1), although overall captures were much lower.

Moth captures in Cyprus (Table 2) also followed this pattern and, as noted in Australia, there was no significant difference in captures at the beginning and end of the 64-day trapping period. The Cyprus tests also demonstrated that most treatments were as effective as virgin female traps (Table 2) each baited with two females.

Quantity of Pheromone and Male Captures

Varying quantities of both PTM 1 and PTM 2 were tested singly and in

TABLE 2. NUMBERS OF MALES CAPTURED WITH VARIOUS BLENDS OF PTM 1 AND PTM 2 (CYPRUS, APRIL 15–JUNE 18, 1977)

Treatment		
PTM 1 (μg)	PTM 2 (μg)	Mean total catch per field[a]
200	0	1290 a
180	20	3334 b
160	40	3895 bc
140	60	3602 bc
120	80	3852 bc
100	100	3694 bc
80	120	3747 bc
60	140	3845 bc
40	160	3856 bc
20	180	3844 bc
0	200	3487 b
0	0	151 d
100	300	6154 e
2 virgin females		4075 c

[a] Figures followed by same letter are not significantly different at $P < 0.05$. Only 1 replicate in each of 5 fields, therefore analysis done on percentage captures per treatment with arcsin transformation; Duncan's multiple range test.

two combinations (4:1, 1:4) in the field in Australia. The results (Table 3) indicate that over the 38-day sampling period maximum male captures were taken at sources containing a total of 1000 μg of both components in both combinations. At the highest dosages of 10,000 μg, catches decreased significantly and, although the pheromone quantities must have diminished with time, remained low throughout the trial. The reduction in captures with PTM 2 was particularly marked (Table 3). Captures at traps baited with only 10 μg of blends of both components were also lower than those containing 1000 μg (Table 3). The difference between captures at 10 and 100 μg was also consistent but not always statistically significant.

Both pheromone components remain active over a prolonged period in the field. Comparisons of relative capture rates at traps baited with 10 and 100 μg of both pheromone blends (4:1, 1:4 PTM 1 and PTM 2) in nine successive samplings over 38 days showed that even low dosages remained active throughout this period. Bait longevity was demonstrated most strikingly in the tests conducted in Peru. Two traps baited with a mixture of 100 μg of PTM 1 and 300 μg of PTM 2 caught nearly 87,000 moths in 4 months of high temperatures, and weekly captures exceeding 1000 males per trap

TABLE 3. QUANTITY OF PTM 1 AND PTM 2 PER TRAP AND MALE CAPTURES (AUSTRALIA, APRIL 13–MAY 20, 1977). MEAN OF 5 TRAPS

Treatment		
PTM 1 (μg)	PTM 2 (μg)	Mean catch per trap[a]
10	0	32 abc
8	2	63 cdef
4	6	125 efghi
0	10	118 efgh
100	0	32 abc
80	20	148 ghij
40	60	193 hijk
0	100	128 fghij
1000	0	42 bcd
800	200	219 jk
400	600	249 k
0	1000	81 defg
10000	0	11 ab
8000	2000	102 afgh
4000	6000	61 cdef
0	10000	7 a

[a] Mean figure represents total of 9 successive samplings per trap; figures followed by the same letter are not significantly different at $P < 0.05$, $\sqrt{x}$ transformation, Duncan's multiple range test.

were still being recorded at the end of this period. The baits were not refreshed in this period. A similar 1:3 bait used in the Cyprus trials also caught significantly more males than the other treatments, (Table 2) suggesting that this combination may be particularly effective; this blend was not tested in Australia.

Role of PTM 1 and PTM 2 in Trapping Males

A field test was undertaken to determine whether the individual components of the pheromone blend differed in their influence on male movements towards a source of the compounds. Concentric rings of cellulose acetate 15 cm apart were placed within a shallow metal tray containing water and 2% detergent; the overall diameter of the trap container was 150 cm.

TABLE 4. NUMBERS OF MALES TRAPPED AT VARYING DISTANCES FROM A PHEROMONE SOURCE (AUSTRALIA, MARCH 17–APRIL 15, 1977)[a]

Distance from pheromone source (cm)	Catches (%) with		
	PTM 1 + PTM 2 (100μg + 100μg)	PTM 1 (200 μg)	PTM 2 (200 μg)
0–15	395 (35)	13 (30)	31 (35)
15–30	264 (23)	12 (28)	14 (16)
30–45	180 (16)	8 (19)	13 (15)
45–60	165 (15)	5 (12)	17 (19)
60–75	133 (12)	5 (12)	13 (15)
Total	1137 (100)	43 (100)	88 (100)

[a] No significant difference between percentages across table; arcsin transformation; Duncan's multiple range test. $N = 3$, replication achieved by analyzing 3 successive samples from individual traps.

Rubber sleeve stoppers baited with PTM 1 and PTM 2 singly or in combination (1:4, 200 μg) were placed in the central area. Numbers of captured males in the various sectors were counted at regular intervals. It was considered that a compound acting solely as long-range attractant (Kennedy, 1977) would have produced a greater proportion of captures in the outer sectors; conversely a short-range substance would have resulted in a greater proportion of captures in the central sector—albeit with lower overall numbers than those taken by the long-range compound in the outer sectors.

The results (Table 4) show that although the total numbers captured differed as expected (Table 1) between the various pheromone treatments, there was no significant difference between the proportion of captures in the various sectors. In all three treatments, captures increased with proximity to the pheromone sources, and there was no evidence to suggest that the two components acted differently over short or long-range distances.

DISCUSSION

The Australian field results confirm and extend the earlier findings of Persoons et al. (1976a,b) and show that there is no obvious optimal ratio of PTM 1 to PTM 2 and that blends are more attractive than the single components. The Cyprus results are similar but, contrary to earlier field tests in that country (Persoons et al., 1976b), traps baited solely with PTM 2 caught as many males as those containing mixtures (Table 2). Both compounds were long-lived under field conditions, and the tests suggested that baits

with 400–1000 μg of both components produced larger catches than lower or higher quantities of the mixtures (Tables 2 and 3). Preliminary field tests failed to reveal any evidence that PTM 1 and PTM 2 had distinct individual roles. Males flew to sources containing either single compound, but when both compounds were present the numbers of moths attracted increased significantly.

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