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IDENTIFICATION OF THE CALIFORNIA RED SCALE[1] SEX PHEROMONE[2]

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Abstract—Pheromone components of female California red scale, *Aonidiella aurantii* (Maskell) were isolated from airborne collections and found to be 3-methyl-6-isopropenyl-9-decen-1-yl acetate and (*Z*)-3-methyl-6-isopropenyl-3,9-decadien-1-yl acetate. Both enantiomers of the latter compound as well as the corresponding enantiomers of the *E* isomer were prepared from (*S*)- or (*R*)-carvone. Bioassays with each of the four isomers showed that only the *R,Z* isomer attracted male red scale.

Key Words—California red scale, *Aonidiella aurantii*, pheromone, attractant, enantiomer, isomers (*E,Z*)-3-methyl-6-isopropenyl-9-decen-1-yl acetate, (*Z*)-3-methyl-6-isopropenyl-3,9-decadien-1-yl acetate.

INTRODUCTION

The California red scale, *Aonidiella aurantii* (Maskell), is a serious pest of citrus in many parts of the world, particularly in California, Australia, and the Mediterranean countries. Tashiro and Chambers (1967) found that the female scales produce a sex pheromone that can be used to attract male red scales. Rice and Moreno (1969) demonstrated that a trap consisting of sexually mature virgin females on a lemon in a pint carton with an attached

[1] *Aonidiella aurantii* (Maskell) (Homoptera: Diaspididae).
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sticky card was highly effective in catching males in citrus groves, and Shaw et al. (1971) showed that such traps were an excellent substitute for the laborious visual inspection for detecting infestations.

Interest was generated in chemically defining the sex pheromone components because it would represent the first for a Homopteran species, and also because the synthetic pheromone could replace the cumbersome and expensive virgin female traps in the field. Furthermore, the risk of a trap bearing virgin females becoming damaged, allowing mating and subsequent infestation by these females, would be eliminated by a synthetic pheromone. Laboratory rearing procedures were developed (Tashiro, 1966), as well as a good turntable olfactometer for bioassays (Tashiro et al., 1969). Studies (Tashiro and Chambers, 1967) showed that an active extract was obtained with cold-trap condensate from air passed over female red scale-infested lemons and with whole-body extractions. Preliminary identification tests indicated that the pheromone could be an unsaturated acetate (Warthen et al., 1970).

METHODS AND MATERIALS

Pheromone Collection and Bioassay

Our initial studies were conducted with cold-trap condensate that was processed by extracting its steam distillate with ether–hexane (3:1). The resulting extract contained large quantities of contaminating terpenes and other volatiles from the lemons and made the pheromone purification steps more difficult. The host material was changed to potatoes (Rice and Moreno, 1969), and the cold trap was replaced with a Porapak-Q® solid absorption trap (Byrne et al., 1975). This improved system was used to collect an estimated 400 million female day-equivalents of pheromone for the identifiction of two sex pheromone components.

Airborne collections were made by passing air over scale-infested host material contained in a 45-liter glass jar and through a 2.5×30-cm column of Porapak-Q (Waters Associates, Inc.) (Figure 1). Initially male scales were selectively killed while female scales were in the second molt by dipping scale-infested lemons into a 0.5% suspension of dichlorvos (Shaw et al., 1973); the females were used for pheromone collection when sexually mature (approx. 27 days old) for a period of 2 weeks. The same isolation technique was used with various other host materials, such as rose cuttings, butternut squash, banana squash, summer squash, the wild gourd *Cucurbita foetidissima*, oranges, and grapefruit, but lemons were preferred because of their year-around availability, size, and long shelf-life. However, the large quantities of lemon volatiles obtained in airborne collections created problems in

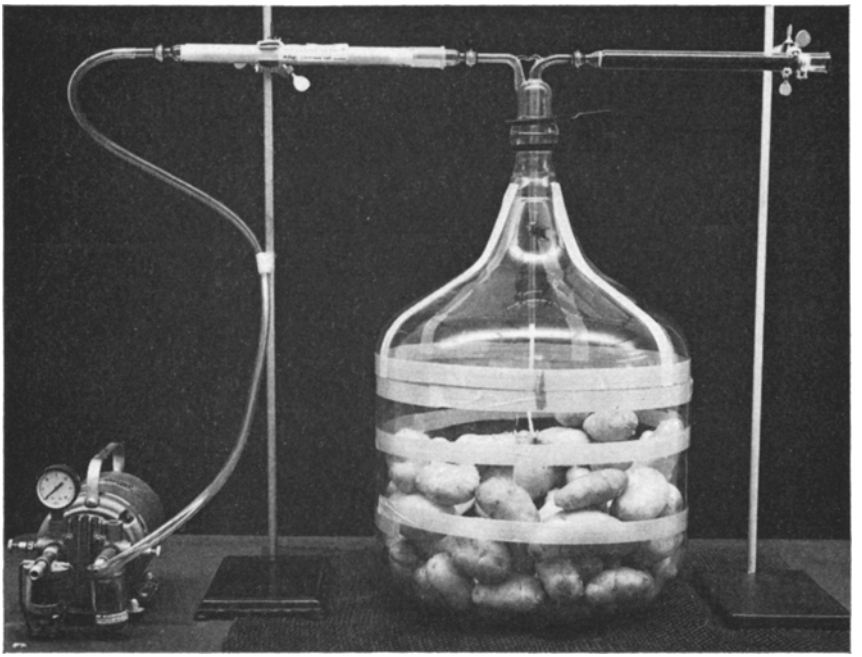


FIG. 1. Airborne collection with Porapak-Q of pheromone emitted by virgin female red scales on potatoes.

the isolation procedure. An alternative host with less volatiles was sought. Rice and Moreno (1969) found that white rose, russett, and sweet potatoes were suitable hosts, although the use of dichlorvos to isolate female scales was not applicable with potatoes because it killed all the scales. Juvenoids were found (Moreno et al., 1976) to selectively prevent male maturation, and so a formulation of 1 ppm of triprene was sprayed on first-molt scales to prevent male metamorphosis. Female scales matured at approx 35 days old, and their pheromone was collected for a period of 2 weeks. Thus, the predominant host in the last year of pheromone collection was potatoes. In a typical run, air was drawn over about 150 infested potatoes per jar for 7 days before changing the Porapak column. The used Porapak was extracted with 200 ml of pentane, the solvent evaporated, and the extracted residue used in further purification steps.

Bioassays were conducted in the greenhouse with a turntable olfactometer modified from Tashiro et al. (1969). The 1.8-m-diam table traveled at the rate of approx. 0.17 rpm. It accommodated 24 Munger cells (Munger and Gilmore, 1963), which contained either a section of lemon with virgin female

scales or test sample on a 2.4-cm-diam filter paper disk placed in a 3.5-cm steel planchet. Treatments were set out in the early afternoon, and male scales emerging the same afternoon from male and female-infested lemons were captured on 7.5×12.7-cm sticky cards (Bird Tanglefoot®) positioned above the Munger cells. Counts were made the next morning.

Pheromone Purification

The oily residue from the airborne collection first was chromatographed on a 1.5×50-cm column of florisil (60–80 PR mesh, Floridin Co.) eluted with 900 ml of a 0–50% gradient of diethyl ether in Skelly B. A 0.25-ml aliquot from every second fraction (15 ml each) was bioassayed.

Active fractions from the florisil column were combined and injected onto a 1×100-cm-high pressure column packed with 10% $AgNO_3$ on Bio-Sil A (20–44 μm, Bio-Rad Laboratories). The column was eluted with 500 ml of 10% diethyl ether in benzene and then with 500 ml of 20% ether in benzene. A 0.25-ml aliquot of every third fraction (15 ml each) was bioassayed, and the fractions containing each active component were combined.

Each component was purified further on a 2×500-mm LiChrosorb® (10 μm) high-pressure column by eluting (1 ml/min) with 20 ml of 1% ethyl acetate in heptane. Fractions (0.5 or 1.0 ml) were bioassayed or assayed by GLC.

GLC columns were 3% OV-1 or 3% OV-101 (methyl silicone) on 100-120 mesh Gas-Chrom Q, and 10% XF-1150 (50% cyanoethyl methyl silicone) or 3% Carbowax 20 M on 100-120 mesh Chromosorb W-AW-DMCS.

Identification

Microchemical reactions were carried out in 3.7-ml (1-dram) vials. The reduction of acetates to alcohols was accomplished by adding $LiAlH_4$ to an aliquot of active component in diethyl ether. A few drops of ethanol were added after 1 hr followed by a few drops of water. The ether was decanted, dried over $MgSO_4$, and assayed by GLC and greenhouse activity. The product was acetylated by adding a few drops of acetyl chloride and evaporating the excess acetyl chloride after 0.5 hr.

Microozonolyses (Beroza and Bierl, 1967) in CS_2 were analyzed by GLC with the Carbowax column. Hydrogenations were carried out at atmospheric pressure with either 5% palladium on calcium carbonate in methanol or with platinum oxide in methanol or hexane. Synthetic 3-oxobutan-1-yl acetate was prepared by acetylating 3-methyl-3-buten-1-ol and ozonizing the resulting acetate.

The pheromone hydrocarbon skeleton was prepared by saponifying the

hydrogenated product with 2% sodium hydroxide in aqueous methanol for 1 hr at 100°C. The product was extracted with ether and the ether removed under N_2 after drying over $MgSO_4$. The resulting alcohol was converted into the corresponding bromide by treating it with an excess amount of triphenylphosphine dibromide prepared according to Sonnet and Oliver (1976). After stirring for 4 hr at room temperature the mixture was filtered and treated with $LiAlH_4$ to produce the hydrocarbon skeleton.

Ultraviolet spectra were obtained with a Cary 15 spectrophotometer using 4×10-mm cells and pentane as the solvent. The mass spectrometer was a Hitachi RMU-6E interfaced with an OV-1 or Carbowax 20 M column. All mass spectra were obtained at 20 eV.

Nuclear magnetic resonance spectra were obtained with either a Varian XL 100 (Fourier transform) spectrometer (College of Environmental Science and Forestry, Syracuse, New York), a Varian HR 300 (Fourier transform) spectrometer (TNO, Delft, The Netherlands), or a Varian HA-100D spectrometer (Geneva, New York).

RESULTS AND DISCUSSION

Crude material from the airborne collections was fractionated on the florisil column (Table 1) and the active fractions (11–22) were combined. The active material was fractionated on the $AgNO_3$ column (Table 1), and activity was found in fractions 11–14 (AI) and fractions 29–38 (AII). The two active components were purified further on the LiChrosorb column (Table 1), and activity in each case was found in the same 0.5-ml fraction (fraction 10). The carbon numbers relative to saturated acetates for AI and AII were 12.25 and 12.06, respectively, on OV-1, and 13.08 and 13.00, respectively, on XF-1150.

The components were shown to be acetates by $LiAlH_4$ reduction to the corresponding alcohols and subsequent acetylation. The alcohol product was inactive, but acetylation restored the activity at the original retention time on OV-1. Hydrogenation of AI and AII produced the same compound, which had carbon numbers relative to saturated acetates of 12.39 on OV-1 and 11.90 on XF-1150. Mass spectra of both hydrogenated products were identical (Figure 2, AH_2) and indicated that the compound was a branched 14-carbon acetate. There was an immediate loss of acetate to give peaks at *m/e* 196 (M-60) and 61, and the next highest mass fragment (*m/e* 153) indicated a facile loss of three carbons. A mass spectrum of the hydrocarbon skeleton (Figure 2, A-Sk) of AH_2 also indicated a branched 14-carbon compound with a molecular ion peak at *m/e* 198 and an immediate three-carbon loss to *m/e* 155.

Mass spectra of AI and AII (Figure 3) showed that AII possesses three

TABLE 1. MALE RED SCALE CATCHES IN GREENHOUSE BIOASSAY OF PURIFICATION COLUMN FRACTIONS

Florisil[a]		$AgNO_3$[b]		LiChrosorb[c]	
Fraction	Males caught	Fraction	Males caught	Fraction	Males caught
2–	0	2–	9	1–	1
4–	3	5–	0	2–	2
6–	1	8–	2	3–	0
8–	1	11–	338	4–	4
10–	1	14–	17	5–	1
12–	92	17–	1	6–	0
14–	225	20–	5	7–	0
16–	212	23–	2	8–	0
18–	252	26–	2	9–	0
20–	135	29–	15	10–	128
22–	26	32–	422	11–	1
24–	3	35–	210	12–	1
26–	8	38–	10	13–	0
28–	2	41–	1	14–	0
30–	2	44–	1	15–	0
32–	3	47–	1	16–	0
				17–	0
48–	2	62–	0		

[a] Crude pheromone extract from airborne collection.
[b] Active fractions (11–22) from florisil.
[c] Active fractions (11–14) from $AgNO_3$.

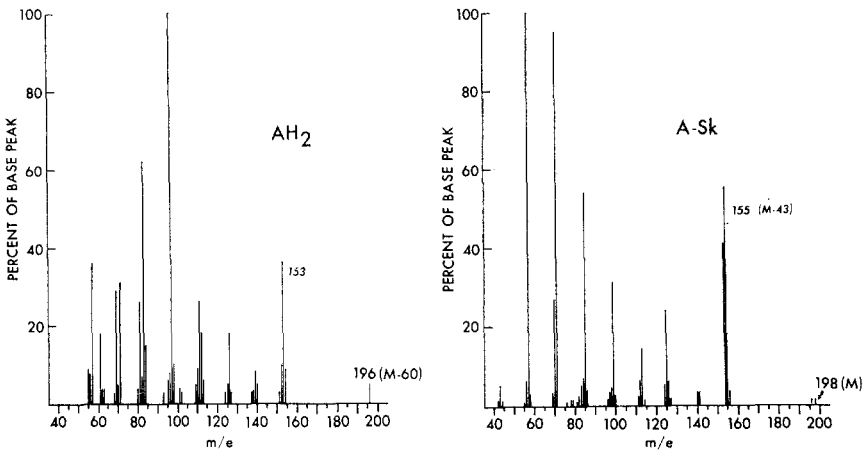


FIG. 2. Mass spectra (20 eV) of hydrogenated AII (AH_2) and of its hydrocarbon skeleton (A-Sk).

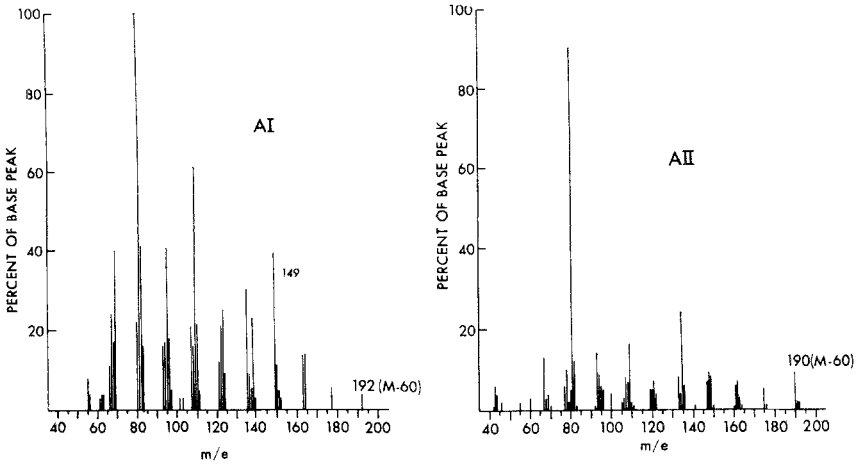


FIG. 3. Mass spectra (20 eV) of AI and AII.

units of unsaturation and AI only two, since the M-60 peaks were found at *m/e* 190 and 192, respectively, compared to 196 for the saturated AH_2.

Ozonolysis of AI did not yield any GLC visible product, but ozonolysis of AII produced one major product that was identified as 3-oxobutan-1-yl acetate by comparison of its retention time on Carbowax 20 M (6.5 min when programed from 80° at a rate of 10°/min) and its mass spectrum with

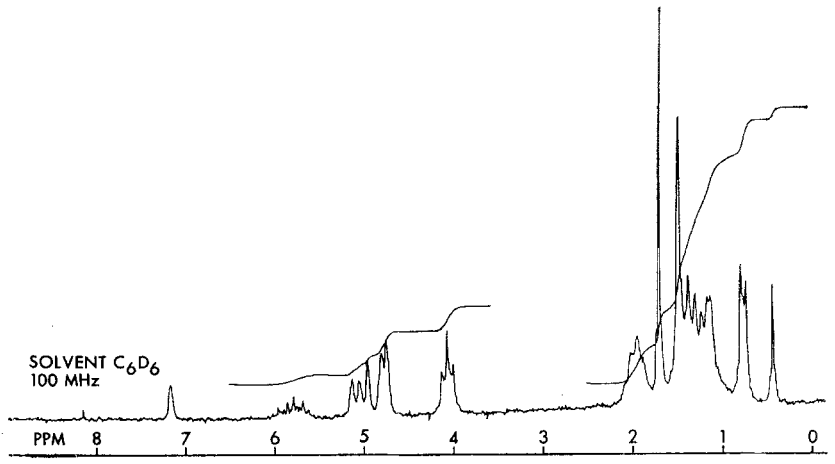
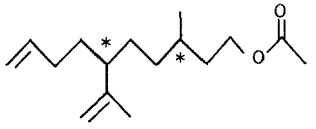


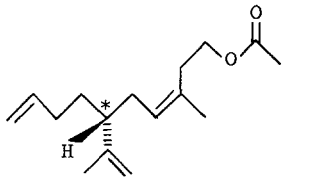
FIG. 4. NMR spectrum of AI (C_6D_6; 100 MHz).

those of a synthetic standard. This information defined a 3-methyl group on both pheromone components, and a double bond in the 3 position for AII. An ultraviolet spectrum did not exhibit any absorption attributable to a conjugated system.

Pheromone was accumulated until approximately 30 μg of each component was available for an NMR spectrum. The spectrum of AI (C_6D_6; 100 MHz) (Figure 4) was consistent with structure I with δ values as follows: 5.75 (1H, *m*), 5.07 (1H, *d*), and 5.02 (1H, *d*) ($\underline{H}_2C{=}C\underline{H}{-}CH_2{-}$); 4.82 (1H, *s*) and 4.76 (1H, *s*) ($R_2C{=}C\underline{H}_2$); 4.09 (2H, *t*, $J = 7$ Hz) and 1.7 (3H, *s*) ($-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-C\underline{H}_3$); 1.95 (3H, *m*, allylic); 1.49 (3H, *s*) ($C\underline{H}_3-\overset{\overset{R}{|}}{C}{=}C-$); 1.1–1.6 (9H, *m*); and 0.77 ppm (3H, *d*, $J = 6$ Hz) ($R_2CH-C\underline{H}_3$).



I



II

The spectrum of AII (CS_2; 300 MHz) (Figure 5) was consistent with structure II with δ values as follows: 5.71 [1H, *m*, "*J*" = 7, 10, 16 Hz (*t,d,d*, respectively)], 4.92 (1H, *d*, "*J*" = 16 Hz), and 4.87 (1H, *d*, "*J*" = 10 Hz) ($H_2C{=}C\underline{H}{-}CH_2{-}$); 5.12 (1H, *t*, "*J*" = 6 Hz) ($R_2C{=}C\underline{H}{-}CH_2{-}$); 4.7 (1H, *s*) and 4.64 (1H, *s*) ($R_2C{=}C\underline{H}_2$); 3.95 (2H, *t*, $J = 7.5$ Hz) and 1.92 (3H, *s*) ($-CH_2-C\underline{H}_2-O-\overset{\overset{O}{\|}}{C}-C\underline{H}_3$); 2.27 (2H, *t*, $J = 7$ Hz) ($-\overset{\overset{R}{|}}{C}{=}C-C\underline{H}_2-CH_2-$); 1.9–2.1 (5H, *m*, allylic); 1.69 (3H, *s*) and 1.60 (3H, *s*) (two $C\underline{H}_3-\overset{\overset{R}{|}}{C}{=}C-$); and 1.39 ppm (2H, *m*).

An alternative structure possessing a vinyl group on the 6 position and a 9-methyl group also is generally consistent with the data, except for the

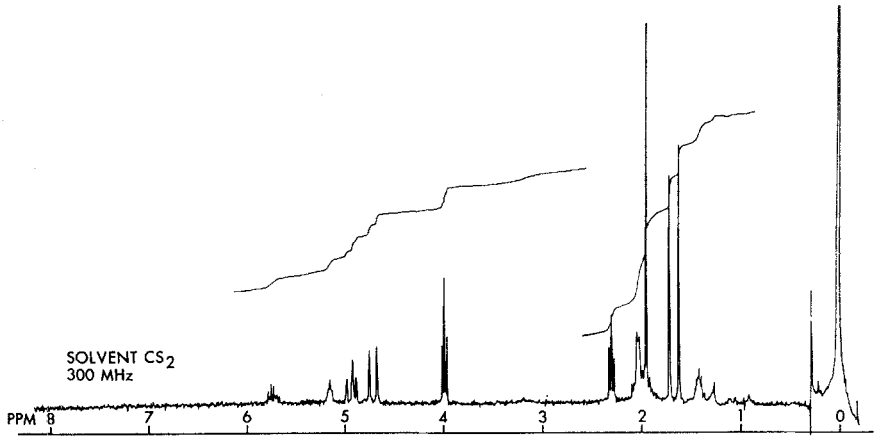


FIG. 5. NMR spectrum of AII (CS_2; 300 MHz).

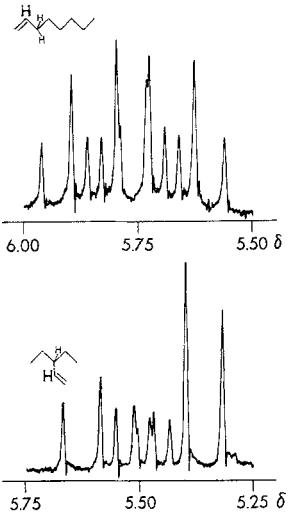


FIG. 6. The NMR splitting pattern of a vinyl proton (bold faced) with two adjacent allylic protons (top, 1-octene) and of a vinyl proton with one adjacent allylic proton (bottom, 3-ethyl-1-pentene).

characteristic splitting pattern of the 9-position vinyl proton of I and II. This proton has two adjacent allylic protons (Figure 6, top), whereas the corresponding vinyl proton of the alternative structure would be adjacent to only one allylic proton (Figure 6, bottom). The NMR spectra of standards in Figure 6 show the splitting patterns produced by the two different systems. The splitting patterns of AI and AII are consistent with that of the vinyl proton adjacent to two allylic protons.

The pheromone component AII was determined to possess a *Z* configuration by comparison of its NMR spectrum and its GLC retention times on OV-101 to those of the synthetic Z and *E* isomers of II. The 3-methyl group of the *E* isomer resonated at δ 1.60 (in CS_2), whereas the 3-methyl group of the *Z* isomer resonated at δ 1.69. The natural component had the same retention time on XF-1150 (2.9 min at 165°C) as the synthetic *Z* isomer, and there was no evidence for the *E* isomer at its retention time (3.8 min).

The NMR spectrum of the natural component AII (300 MHz) was similar to that of synthetic II, and the mass spectra of AII, AH_2, and A-Sk were identical to the corresponding synthetic compounds.

Synthesis of II

Since neither the stereochemistry of the trisubstituted double bond nor the absolute configuration of the pheromone II was known, a synthesis of all four of the possible isomers was designed. Thus the *R,Z* and *R,E* isomers of

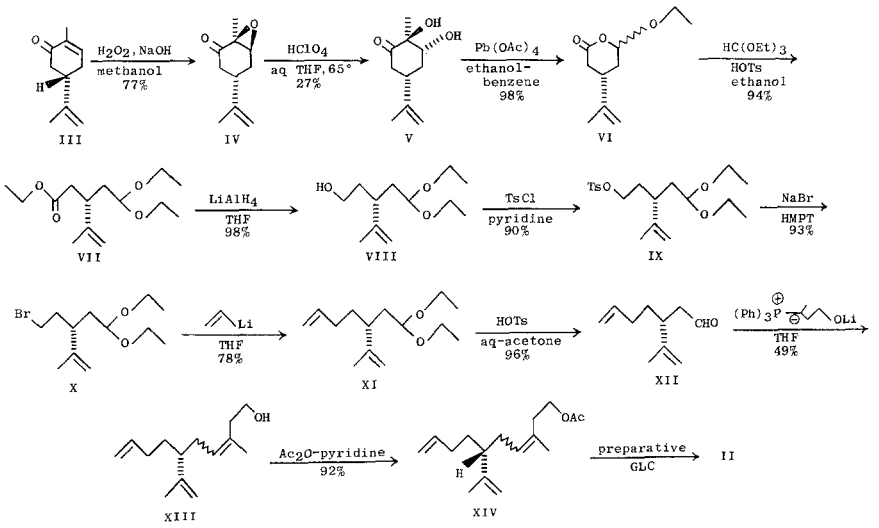


FIG. 7. Synthesis of the *R,Z* and *R,E* isomers of compound II.

compound II were prepared from (*S*)-(+)-carvone as shown in Figure 7, and the *S,Z* and *S,E* isomers were obtained from (*R*)-(−)-carvone in an analogous manner. In each case the *Z* and *E* isomers were readily separable by preparative GLC (OV-1 at 170°C, retention times of 16 and 14 min, respectively).

(*S*)-(+)-Carvone (III) was converted to the epoxide IV with alkaline hydrogen peroxide in methanol (Klein and Ohloff, 1963). Treatment of IV with dilute perchloric acid in tetrahydrofuran (THF) gave a mixture from which the keto diol V crystallized [mp 104–107°C; IR (CCl_4) 3590 and 3490 (OH), 1715 cm^{-1} (C=O); NMR ($CDCl_3$ and D_2O, δ) 4.67 and 4.87 (br *s*, 2H), 3.77 (*d* of *d*, 1H, "*J*" = 5, 11 Hz), 1.78 (*s*, 3H), and 1.37 ppm (*s*, 3H)]. Oxidation of V with 2 equivalents of lead tetraacetate in ethanol–benzene gave directly a mixture of the diastereomeric lactones VI [IR (CCl_4) 3080 ($C=CH_2$), 1760 cm^{-1} (C=0); NMR ($CDCl_3$, δ) 5.35 (*m* 1H), 4.83 (br *s*, 2H), 1.77 (br *s*, 3H), and 1.23 ppm (*t*, 3H, $J = 7$ Hz)], which were converted to the acetal ester VII with triethyl orthoformate in ethanol [VII; IR (CCl_4) 3075 ($H_2C=C$), 1740 cm^{-1} (C=O); NMR ($CDCl_3$, δ) 4.80 (br *s*, 2H), 4.45 (*t*, 1H, $J = 6$ Hz), and 1.70 ppm (br *s*, 3H). Lithium aluminum hydride reduction of VII gave the alcohol acetal VIII [IR (CCl_4) 3630 and 3490 cm^{-1} (OH); NMR ($CDCl_3$, δ) 4.82 (br *s*, 2H), 4.47 (*t*, 1H, $J = 6$ Hz), 1.68 (*s*, 3H), and 1.20 ppm (*t*, 6H, J = 7 Hz)], which on reaction with *p*-toluenesulfonyl chloride in pyridine gave the acetal tosylate IX [NMR ($CDCl_3$, δ) 4.40 (*t*, 1H, $J = 5.5$ Hz), 3.98 (*t*, 2H, $J = 6.5$ Hz), 2.47 (*s*, 3H), and 1.18 ppm (*t*, 6H, $J = 7$ Hz)]. The tosylate was then converted to the bromo acetal X with NaBr in hexamethylphosphoric triamide (HMPT), and reaction of X with vinyllithium in THF gave the diene acetal XI [NMR ($CDCl_3$, δ) 4.43 (*t*, 1H, $J = 6$ Hz), 1.62 (*d*, 3H, $J = 1$ Hz), and 1.18 ppm (*t*, 6H, $J = 7$ Hz)]. Hydrolysis of the acetal produced the key intermediate XII [IR (CCl_4) 3080 ($H_2C=C$), 1730 cm^{-1} (C=O); NMR ($CDCl_3$, δ) 9.75 (*t*, 1H, $J = 2$ Hz) and 1.67 ppm (br *s*, 3H)]. This diene aldehyde XII was then reacted with the ylide generated from the corresponding 3-hydroxy-1-methylpropyltriphenylphosphonium salt to give the triene alcohols XIII [IR (CCl_4) 3625 and 3540 (OH), 3075 cm^{-1} ($H_2C=C$); NMR ($CDCl_3$, δ) 3.67 (*t*, $J = 7$ Hz), 3.61 (*t*, $J = 6.5$ Hz), and 1.62 and 1.70 ppm (both br *s*, 6H)]. GLC analysis of XIII indicated that the *Z* and *E* isomers were formed in the Wittig reaction in a ratio of 52:48, respectively. Acetylation of XIII with acetic anhydride in pyridine gave the corresponding triene acetates XIV [IR (CCl_4) 3080 ($C=CH_2$), 1745 cm^{-1} (C=O); NMR ($CDCl_3$, δ) 4.10 and 4.13 (two *t*, 2H, $J = 7$ Hz), 2.03 (*s*, 3H), and 1.62 and 1.70 ppm (both br *s*, 6H)].

Pure samples of the *R,Z* and *R,E* isomers of XIV were obtained by preparative GLC separation of the mixture. The enantiomeric purity of the

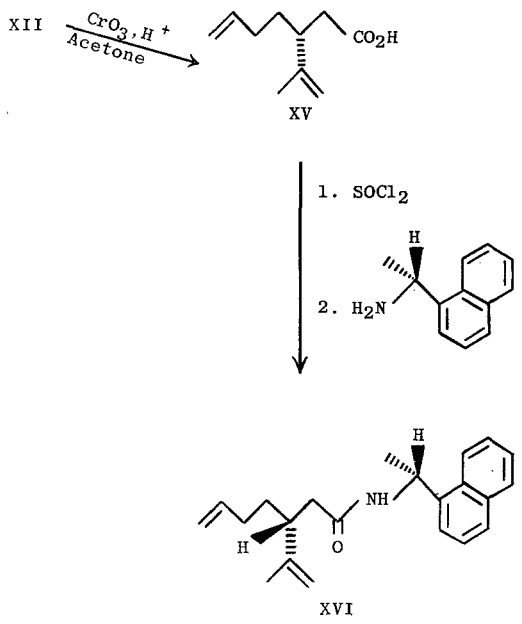


FIG. 8. Preparation of a derivative for determination of enantiomeric purity.

synthetic *R* and *S* isomers of II was determined by using a technique developed earlier in our laboratories (Zoecon) (Figure 8) (Bergot et al., 1978). Thus the *R* diene aldehyde XII was oxidized with excess Jones reagent to give the corresponding acid, XV. This acid was then converted to the acid chloride ($SOCl_2$, ether, catalytic dimethylformamide), which on treatment with (*R*)-(+)-1-(1-naphthyl)ethylamine gave the amide XVI. Similarly, the corresponding diastereomer was prepared from the *S* isomer of XV and (*R*)-(+)-1-(1-naphthyl)ethylamine. These diastereomeric amides were completely resolved by high-performance liquid chromatography (HPLC) (22×0.46 cm Zorbax-SIL, DuPont, eluted with water-saturated 10% ethyl acetate in pentane at 1.8 ml/min). From such a HPLC analysis, the percentage enantiomeric purity of XVI [and hence of (*R*)-XIV and also of the synthetic (*R,Z*)-isomer II)] was shown to be 98.4% (i.e., enantiomeric composition of 99.2% *R* and 0.8% *S*). In a like manner the *S* isomers of II were shown to be of 99.0% enantiomeric purity (i.e., enantiomeric composition of 99.5% *S* and 0.5% *R*).

Bioassays of II

Greenhouse flight tests (Table 2) with the four stereoisomers of II, *R,Z*,

TABLE 2. MALE RED SCALE CATCHES IN GREENHOUSE FLIGHT TESTS

Treatment	$\bar{x}$ males/treatment[a]
Test 1 (25 ng each isomer)	
R,Z	266 a
R,E	7.5 b
S,Z	8.5 b
S,E	9.0 b
Blank	7.5 b
Virgin female[b]	395 a
Test 2 (25 ng each isomer)	
R,Z	141 a
R,Z+*R,E*	123 a
R,Z+*S,Z*	135 a
R,Z+*S,E*	140 a
All 4 isomers	155 a
Virgin female[b]	150 a
Blank	4 b
Test 3 (125 ng each isomer)	
R,Z	219 a
R,Z+*R,E*	246 a
R,Z+*S,Z*	246 a
R,Z+*S,E*	227 a
All 4 isomers	240 a
Virgin female[b]	184 a
Blank	6.5 b

[a] Treatments were replicated twice and run two different days. Means followed by the same letter are not significantly different at the 5% level as determined by Duncan's new multiple-range test.

[b] The two female treatments averaged 33 females/trap.

S,Z, *R,E*, and *S,E*, showed that only the *R,Z* isomer was active by itself (Table 2, test 1). The *R,Z* isomer was competitive with virgin female red scales at load rates of 25 and 125 ng on filter paper. This activity was not diminished when equal amounts of *S,Z* (racemic mixture) or the other isomers were added to *R,Z* (Table 2, tests 2 and 3).

A preliminary field test in California using sticky 1-pint ice cream carton traps showed that 200 μg of II (*R,Z*) on a rubber septum was as attractive as standard traps containing 200 virgin females. In 2 days three replicates of II captured 150 red scale males, the standard female traps captured 9 males, and blank traps caught 1 male. In another test over 28 days with II (*R,Z*+*R,E*; 1:1), the mean number of male red scales caught in five replicates were

14.5, 21.4, and 14.6 for 300 μg, 1000 μg, and 200 virgin females, respectively, compared to 1.2 for the blank traps. Further field testing will be conducted with the various isomers of II and with I when they become available.

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