Journal of Chemical Ecology, Vol. 11, No. 6, 1985

SEX ATTRACTANTS FOR GEOMETRID AND NOCTUID MOTHS

Field Trapping and Electroantennographic Responses to Triene Hydrocarbons and Monoepoxydiene Derivatives[1]

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(Received June 6, 1984; accepted September 27, 1984)

Abstract—Male moths belonging to 17 species of Geometridae and nine species of Noctuidae were captured in traps baited with synthetic chemicals as part of a field screening program. The compounds tested were the C_{18}–C_{22} homologs of: (1) (3*Z*,6*Z*,9*Z*)-triene hydrocarbons; (2) mixtures containing equal quantities of (3*Z*,6*Z*)-*cis*-9,10-expoxydienes, (3*Z*,92*Z*)-*cis*-6,7-epoxydienes, and (6*Z*,9*Z*)-*cis*-3,4-epoxydienes; (3) (3*Z*,6*Z*)-9*S*,10R-epoxydienes; (4) (3*Z*,6*Z*)-9*R*,10S-epoxydienes; and (5) (3*Z*,6*Z*,9*Z*,11*E*)-nonadecatetraene. Field captures and electroantennographic assays revealed a high degree of specificity in the responses of many species to the synthetic chemicals. In several species the ability of males to discriminate between the 9*S*,10*R* and 9*R*,10*S* enantiomers of the monoepoxydiene isomers was clearly shown. Synergists and inhibitors were discovered for several of the reported attractants, some of which were not previously known to have semiochemical activity. The geometrid moths captured included *Epirrhoe sperryi* (Herbulot), *Mesoleuca ruficillata* (Guenée), *Triphosa haesitata* (Guenée), *Metanema inatomaria* (Guenée), *Prochoerodes transversata* (Drury), *Cabera erythemaria* (Guenée), *Synaxis jubararia* (Hulst), *Dysstroma brunneata ethela* (Hulst), *Eulithes testata* (Linnaeus), *Sicya macularia* (Harris), *Xanthorhoe iduata* (Guenée), *X. abrasaria aquilonaria* (Herrich-Schäffer), *X. munitata* (Hübner), *Itame loricaria* (Eversmann), *Eupithecia annulata* (Hulst), *E. rovocastaliata* (Packard) and *E. satyrata dodata* (Taylor). The noctuid moths captured included *Bleptina caradrinalis* (Guenée), *Idia americalis* (Guenée), *I. aemula* (Hübner), *Rivula propinqualis* (Guenée), *Lomanaltes eductalis* (Walker), *Spargaloma sexpunctata* (Grote), *Caenurgina distincta* (Neumuller), *Euclidia cuspidea* (Hübner), and *Zale duplicata* (Bethune). Six of

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[1] Issued as NRCC No. 24314.

the nine noctuid species captured belong to three subfamilies for which sex attractants had not been reported previously. Details for the stereospecific synthesis of (3*Z*,6*Z*)-*cis*-9,10-epoxydienes are also reported.

Key Words—Sex attractants, Lepidoptera, Geometridae, Noctuidae, stereospecific synthesis, (3*Z*,6*Z*,9*Z*)-triene hydrocarbons, (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxydienes, (3*Z*,6*Z*,9*R*,10*S*)-9,10-epoxydienes, electroantennogram.

INTRODUCTION

Sex pheromones and sex attractants are known for approximately 150 species of North American Noctuidae (Roelofs, 1979; Steck et al., 1982). Although specific sex attractants have been developed for most of the economically important noctuid pests, these represent only a small fraction of the 2925 species in 18 subfamilies which inhabit America north of Mexico (Hodges et al., 1983). Until very recently, noctuid species for which sex pheromones or attractants were known belonged to only nine of these subfamilies (Table 1).

In North America, the Geometridae consists of 1404 species of moths divided into six subfamilies and is second in size to the Noctuidae (Hodges, 1983). Despite the large number of species, sex pheromones have only recently been reported for the winter moth (Roelofs et al., 1982; Bestmann et al., 1982), the giant looper (Becker et al., 1983), and the fall cankerworm (Wong et al., 1984a,b).

The failure of noctuid species from the nine subfamilies listed on the right in Table 1 and geometrid species to respond to our annual field surveys conducted between 1978 and 1981 with over 300 saturated and olefinic, straight-

TABLE 1. NOCTUIDAE SUBFAMILIES[a] AND CHEMICALLY DEFINED SEX ATTRACTANTS

Subfamilies for which attractants have been reported to 1983	Subfamilies having no known sex attractants to 1983
Plusiinae (74)[b]	Herminiinae (83)
Acontiinae (178)	Rivulinae (16)
Pantheinae (23)	Hypenodinae (21)
Acronictinae (99)	Hypeninae (49)
Amphipyrinae (548)	Catocalinae (391)
Cuculliinae (352)	Euteliinae (16)
Hadeninae (425)	Sarrothripinae (14)
Noctuinae (415)	Nolinae (16)
Heliothinae (179)	Agaristinae (26)

[a] The system used is that of Hodges et al. (1983) and refers only to North American species, north of Mexico.

[b] The number of species within the subfamily is in parentheses.

chain acetates, aldehydes, and alcohols led us to suspect that some of these noctuid and geometrid moths may utilize pheromones whose structures are significantly different from the majority of known lepidopteran pheromones, and stimulated us to perform a study. Our investigation of lepidopteran pheromones and attactants is based on two approaches: (1) identification of the insect-derived pheromone, and (2) field screening of potential attractants. We have successfully utilized the first approach for identification of pheromones for two geometrid species, the fall cankerworm, *Alsophila pometaria* (Harris), and the spring cankerworm, *Paleacrita vernata* (Peck) (Underhill et al., unpublished), and one noctuid species, the forage looper, *Caenurgina erechtea* (Underhill et al., 1983). The second approach, field screening of potential attractants, has also been successful and is the subject of this report. Compounds tested as candidate lures were (3*Z*,6*Z*,9*Z*)-eicosatriene and (3*Z*,6*Z*,9*Z*)-heneicosatriene, pheromone components of *C. erechtea*. Other compounds tested included the C_{18}, C_{19}, and C_{22} homologs of the above triene hydrocarbons, several monoepoxydiene analogs, and (3*Z*,6*Z*,9*Z*,11*E*)-nonadecatetraene, a pheromone component of the fall cankerworm (Wong et al., 1984a). We also report details of a stereospecific synthesis of (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxyheneicosadiene, the saltmarsh caterpillar pheromone, along with C_{18}, C_{19}, C_{20}, and C_{22} homologs, and a homologous series of 9*R*,10*S* enantiomers.

METHODS AND MATERIALS

Synthesis. General procedures along with chromatographic and analytical instrumentation have been previously described (Wong et al., 1984b). Abbreviations used to describe PMR signals are as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad singlet (bs). Unless otherwise noted, product isolation was accomplished by drying the organic phase derived from product extraction over anhydrous magnesium sulfate followed by filtration and concentration under reduced pressure in a rotary evaporator.

Optical rotations were measured with a Perkin-Elmer model 141 polarimeter on chloroform solutions (C in g/100 ml) contained in a 10-cm path length cell. Determinations of enantiomeric purities of the epoxyalcohol intermediates (Va and Vb) were achieved by PMR observations on the complexes formed between the epoxyalcohols and *tris*-(*d*,*d*-dicampholylmethanato)europium (III) (Alfa Products) or the (+)-α-methoxy-α-(trifluoromethyl)phenylacetate derivatives of the epoxyalcohols (Dale et al., 1969).

Unsaturated Hydrocarbons. The (3*Z*,6*Z*,9*Z*)-triene hydrocarbons (C_{18}–C_{22}) [(3*Z*,6*Z*,9*Z*)-X:H where *X* = 18–22] used in the field survey and for electroantennoghraphic (EAG) assays were synthesized from methyl linolenate (NuChek Corp., Elysian, Minnesota) via a copper-catalyzed Grignard coupling as previously described (Underhill et al., 1983). More recently we have prepared these trienes from ethyl linolenate (Sigma, St. Louis, Missouri) by the coupling of (9*Z*,12*Z*,15*Z*)-1-tosyloxy-octadecatriene with an appropriate lithium dialkylcuprate reagent (Conner et al., 1980; Heath et al., 1983). Other unsaturated hydrocarbons used primarily for EAG assays include (6*Z*,9*Z*)-diene hydrocarbons (C_{18}–C_{22}) and (6*Z*,9*Z*,12*Z*)-triene hydrocarbons (C_{18}, C_{20}, C_{21}, and C_{22}), and were also prepared by one or both procedures described above from methyl linolenate and methyl-γ-linolenate (NuChek Corp.), respectively. Two tetraenes, (6*Z*,9*Z*,12*Z*,15*Z*)-20 : H and (6*Z*,9*Z*,12*Z*,15*Z*)-22 : H, were prepared by lithium tetrahydroaluminate reductions of the tosylate derivatives of (5*Z*,8*Z*,11*Z*,14*Z*)-20 : OH (arachidonyl alcohol) and (7*Z*,10*Z*,13*Z*,16*Z*)-22 : OH (both from NuChek Corp.). The purities of all unsaturated hydrocarbons were greater than 98% as determined by GC analysis on capillary columns.

Linolenyl Alcohol, Acetate, and Aldehyde. These compounds were also used primarily for EAG assays. Linolenyl alcohol and linolenyl acetate (both 99%) were purchased from NuChek Corp. and used without further purification. The aldehyde [(9*Z*,12*Z*,15*Z*)-18 : Ald] was prepared by oxidation of linolenyl alcohol with pyridinium chlorochromate (Corey and Suggs, 1975).

Monoepoxydiene Derivatives of (3Z,6Z,9Z)-Triene Hydrocarbons. Mixtures comprised of approximately equal quantities of (3*Z*,6*Z*)-*cis*-9,10-epoxydienes, (3*Z*,9*Z*)-*cis*-6,7-epoxydienes, and (6*Z*,9*Z*)-*cis*-3,4-epoxydienes, all from 18 to 22 carbons in length, were prepared by *m*-chloroperbenzoic acid oxidations of the parent hydrocarbons. Details for the preparation of the monoepoxydienes of (3*Z*,6*Z*,9*Z*)-19 : H, which shall be referred to as the combined monoepoxides of (3*Z*,6*Z*,9*Z*)-19 : H [CME-(3*Z*,6*Z*,9*Z*)-19 : H], will be given as a representative example and are as follows: *m*-chloroperbenzoic acid (345 mg, 2 mmol) was added to 524 mg of (3*Z*,6*Z*,9*Z*)-19 : H dissolved in 10 ml of dichloromethane. The reaction mixture was stirred at 22°C for 1 hr, diluted with 20 ml dichloromethane, and washed successively with 30-ml portions of 5% aqueous sodium bicarbonate and saturated aqueous sodium chloride. Product isolation afforded 530 mg of crude product composed of unreacted (3*Z*,6*Z*,9*Z*)-19 : H (22.4%), CME-(3*Z*,6*Z*,9*Z*)-19 : H (57.6)%, and overoxidized products (20.0%). Isolation of the CME-(3*Z*,6*Z*,9*Z*)-19 : H was accomplished by flash chromatography on a 20-cm × 3.5-cm-ID column of Kieselgel 60 (20-ml fractions). Elution with hexane followed by hexane–ether (95 : 5, v/v) afforded a fraction containing 259 mg of a colorless oil which revealed three partially separated peaks accounting for 99% of the sample on GC analysis. Ions at 279 (M + 1) and 261 [(M + 1) − 18] were found in the chemical ionization mass spectra of all three peaks which were completely resolved by the 60-m × 0.32-mm-ID DB-5 column used in the GC-MS analysis. These ions and other characteristic ions that were present were consistent with the molecular weight and structures of the desired monoepoxydiene isomers [(3*Z*,6*Z*)-*cis*-9,10-epoxy-19 : H, (3*Z*,9*Z*)-*cis*-6,7-epoxy-19 : H, and (6*Z*,9*Z*)-*cis*-3,4-epoxy-19 : H]. Signals in the 90-MHz [^{1}H]NMR spectrum of the product mixture were also consistent with the desired structures: δ 5.7–5.1 (4H, m, vinyl), 3.0–2.7 (3.3H, m, bis-allylic and epoxide), 2.4–1.9 (5.3H, m, allylic), 1.1 (14H, bs, methylene), 0.95–0.75 (6H, 2t, methyl).

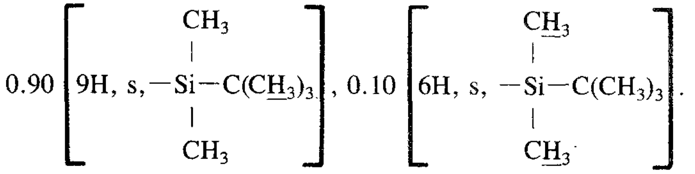
The combined monoepoxides of (3*Z*,6*Z*,9*Z*)-18:H, -20:H, -21:H, and -22:H were prepared by the procedure described above. Satisfactory spectroscopic analyses and purities of 99% were obtained for all four product mixtures.

2,5-Octadiyn-1-ol(I). 1-Tetrahydropyranyloxy-2-propyne (56 g, 400 mmol) was prepared from 2-propyn-1-ol by the procedure of Parham and Anderson (1948) and added to a freshly prepared solution of ethylmagnesium bromide in THF (440 mmol). After 1 hr at 5°C, the Grignard reagent was treated with 2.3 g (8 mmol) of cuprous bromide (98%, Aldrich) followed, after 0.5 hr, by the slow addition of 1-tosyloxy-2-pentyne [95.2 g, 400 mmol; prepared from 2-pentyn-1-ol (Farchan) by the method of Sendega et al. (1968)]. The reaction mixture was then warmed to 21°C, stirred for 5 hr, and quenched with 400 ml of saturated aqueous ammonium chloride. Ether extraction followed by product isolation afforded crude 1-tetrahydropyranyloxy-2,5-octadiyne which was treated with 300 ml of 2.5% *p*-toluenesulfonic acid (*p*-TsOH) in methanol for 2 hr at 21°C to effect hydrolysis of the protecting group. The crude product obtained after standard work-up procedure was distilled through a 10-cm Vigreux column to afford 39.2 g of pure 2,5-octadiyn-1-ol (80.4% yield); bp 72–75°C (0.5 torr). [^{1}H]NMR (90 MHz, $CDCl_3$):δ 4.23 (2H, t, $J = 2.1$ Hz, $-C\underline{H}_2-OH$), 3.17 (2H, quintet, $J = 2.2$ Hz, $-C{\equiv}C-C\underline{H}_2-C{\equiv}C-$), 2.4–2.0 (3H, m, $CH_3-C\underline{H}_2-$ and $-O\underline{H}$), 1.10 (3H, t, $J = 7.3$ Hz, $C\underline{H}_3-$).

1-Tosyloxy-2,5-octadiyne (II). Freshly powdered potassium hydroxide (42 g) was added over 0.5 hr to an ether solution of I (36.6 g, 300 mmol) and *p*-toluenesulfonyl chloride (*p*-TsCl) maintained at −20°C. The reaction mixture, which turned dark brown on addition of potassium hydroxide, was stirred at −20°C for 2 hr, warmed to −10°C and stirred for an additional 2-hr period. Water (30 ml) was added to the reaction and the ether phase separated. The aqueous layer was extracted with ether (2 × 200 ml) and the combined ether extracts worked up in the usual manner to give the dark brown crude tosylate. Partial purification was achieved by elution of the crude product through a column (20 cm × 4.5 cm ID) of Kieselgel 60 with 1.6 liter of hexane–ethyl acetate (85:15, v/v). Solvent removal left 76.2 g (92.0% yield) of 1-tosyloxy-2,5-octadiyne which GC analysis revealed to be 76% pure: [^{1}H]NMR (90 MHz, $CDCl_3$): δ 7.80 (2H, d, $J = 9.0$ Hz, aromatic), 7.30 (2H, d, $J = 9.0$ Hz, aromatic), 4.67 (2H, t, $J = 2.2$ Hz, $-CH_2-O-Ts$), 3.0 (2H, quintet, $J = 2.2$ Hz, $-C{\equiv}C-C\underline{H}_2-C{\equiv}C-$), 2.4 (3H, s, $C\underline{H}_3-C_6H_4-$), 2.1 (2H, tq, $J = 2.2$ Hz and 7.5 Hz, $CH_3-C\underline{H}_2-$), 1.07 (3H, t, $J = 7.5$ Hz, $C\underline{H}_3-CH_2-$).

*1-*tert*-Butyldimethylsilyloxy-2,5,8-undecatriyne (III).* A THF solution of 1-*tert*-butyldimethylsilyloxy-2-propyne (34.0 g, 200 mmol), prepared by standard procedure from 2-propyn-1-ol (Corey and Venkateswarlu, 1972), was cooled to 4°C and treated with 100 ml of a 2 M solution of ethylmagnesium bromide in

THF (Aldrich). The resultant mixture was stirred for 1 hr and treated with 1.14 g (4 mmol) of cuprous bromide. After another hour, a solution of 1-tosyloxy-2,5-octadiyne (72.6 g of 76% purity, ~ 200 mmol) in 50 ml THF was added dropwise. The reaction mixture was warmed to 21°C, stirred for 3 hr, and quenched with 400 ml of saturated aqueous ammonium chloride. Extraction with ether (3 × 250 ml) followed by product isolation afforded the crude triyne. Vacuum distillation through a 10-cm Vigreux column gave 34.8 g of 1-t-butyldimethylsilyloxy-2,5,8-undecatriyne (63.5% yield); bp 126–128°C (0.3 torr). GC analysis revealed a purity of 93.5%. [^{1}H]NMR (90 MHz, $CDCl_3$): δ 4.23 (2H, t, J = 2.2Hz, $-C\underline{H}_2-O$), 3.08 (4H, m, $-C{\equiv}C-C\underline{H}_2-C{\equiv}C-$), 2.10 (2H, tq, J = 2.2 Hz and 7.5 Hz, $CH_3C\underline{H}_2-$), 1.10 (3H, t, J = 7.5Hz, $C\underline{H}_3-$),



$$0.90\left[9H,\ s,-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-C(C\underline{H}_3)_3\right],\ 0.10\left[6H,\ s,\ -\overset{\displaystyle C\underline{H}_3}{\underset{\displaystyle C\underline{H}_3}{\overset{|}{\underset{|}{Si}}}}-C(CH_3)_3\right].$$

(2Z,5Z,8Z)-Undecatrien-1-ol (IV). Borane–dimethylsulfide complex (24 ml of 10 M liquid, Aldrich) was added to a vigorously stirred solution of dry cyclohexene (39.4 g, 480 mmol) dissolved in 175 ml of dry THF and maintained below 10°C. After 1 hr, 10.96 g (40 mmol) of III was added to the white precipitate of dicyclohexylborane. The resultant mixture was warmed to 21°C, stirred for 20 hr, and treated with 55 ml of glacial acetic acid for 4 hr at 60°C. Then the mixture was cooled in an ice bath, made basic with 200 ml of 6 N sodium hydroxide and cautiously treated with 57 ml of 30% hydrogen peroxide. Ether extraction (3 × 100 ml) followed by product isolation afforded the crude (2Z,5Z,8Z)-1-*t*-butyldimethylsilyloxy-2,5,8-undecatriene together with cyclohexanol. This crude product was combined with the crude product from a second experiment performed on 30 mmol of III and treated with 100 ml of 1 M tetrabutylammonium fluoride in THF (Aldrich) for 15 hr at 21°C. The product obtained after aqueous work-up and ether extraction was partially purified by vacuum distillation (bp 80–83°, 0.4 torr) to remove the cyclohexanol. Flash chromatography of the distillate (25-cm × 4.0-cm-ID column; hexane–ethylacetate, 4 : 1) afforded 5.45 g of pure (2Z,5Z,8Z)-undecatrien-1-ol (46.9% yield); [^{1}H]NMR (90 MHz, $CDCl_3$): δ 5.80–5.14 (6H, m, vinyl protons), 4.20 (2H, d, J = 6.0 Hz, $-C\underline{H}_2-OH$), 2.80 (4H, m, bisallylic methylenes), 2.03 (2H, m, $CH_3-C\underline{H}_2$), 1.37 (1H, bs, $-OH$), 0.91 (3H, t, J = 7.5 Hz, CH_3-).

(2S,3R,5Z,8Z)-2,3-Epoxy-5,8-undecadien-1-ol (Va). To 175 ml of dry dichloromethane maintained at −23°C under argon was added titanium tetraisopropoxide (7.43 ml, 25 mmol), (+)-diisopropyl-L-tartrate (5.25 ml, 25 mmol), (2Z,5Z,8Z)-undecatrien-1-ol (3.98 g, 25 mmol) and, after 10 min, 8.9

ml of a 5.65 M solution of *t*-butylhydroperoxide in dichloromethane [prepared by the procedure of Sharpless and Verhoeven (1979)]. The reaction mixture was kept in a freezer at −20°C for 24 hr and then treated with 75 ml of 10% aqueous tartaric acid. The mixture was stirred vigorously until it reached 21°C and then transferred to a separatory funnel. The dichloromethane layer was separated and the aqueous phase extracted twice with 75 ml of dichloromethane. Product isolation yielded epoxyalcohol (Va) together with (+)-diisopropyl-L-tartrate. Removal of the tartrate ester was accomplished by stirring an ice-cold ether solution of the crude product with 60 ml of 1 N sodium hydroxide for exactly 15 min. Extractive work-up afforded crude Va which was purified by flash chromatography (25-cm × 4-cm-ID column, 20-ml fractions). Elution with hexane–ethyl acetate (2 : 1) gave 2.78 g (83.0% yield) of (2*S*,3*R*,5*Z*,8*Z*)-2,3-epoxy-5,8-undecadien-1-ol which was > 98% pure by GC analysis; [^{1}H]NMR (360 MHz, $CDCl_3$): δ 5.52 (1H, dtt, J = 10.7, 7.3, and 1.5 Hz, $-C_6\underline{H}=C_5H-$), 5.40 (2H, m, $-C_8\underline{H}=C_9\underline{H}$), 5.27 (1H, dtt, J = 10.7, 7.3, and 1.5 Hz, $-C_6H=C_5\underline{H}-$), 3.84 (1H, ddd, J = 12.1, 7.1, and 4.3 Hz, $-\underset{\underline{H}_A}{\underset{|}{C}}H_B-OH$), 3.71 (1H, ddd, J = 12.1, 6.5, and 5.3 Hz, $-\underset{\underline{H}_B}{\underset{|}{C}}H_A-OH$), 3.15 (1H, ddd, J = 6.5, 4.3, and 4.3, Hz $-\overset{O}{C_3H-C_2\underline{H}}-$), 3.05 (1H, ddd, J = 6.5, 6.5, and 4.3 Hz, $-\overset{O}{C_3\underline{H}-C_2H}-$), 2.78 (2H, dd, J = 7.1 and 7.1 Hz, $-CH=CH-C\underline{H}_2-CH=CH-$), 2.45 (1H,m, $-\underset{\underline{H}_A}{\underset{|}{C_4}}H_B-$), 2.25 (1H, m, $-\underset{\underline{H}_B}{\underset{|}{C_4}}H_A-$), 2.05 (2H, dq, J = 7.5 and 7.5 Hz, $CH_3C\underline{H}_2$), 1.72 (1H, dd, J = 7.1 and 5.3 Hz, $-O\underline{H}$), 0.96 (3H, t, J = 7.5 Hz, $C\underline{H}_3-$); $[\alpha]_D^{23} = -11.9°$ (C = 9.24, $CHCl_3$).

*(2*R*,3*S*,5*Z*,8*Z*)-2,3-Epoxy-5,8-undecadien-1-ol (Vb).* The procedure used for the preparation of this compound was identical to that described for the 2*S*,3*R* enantiomer (Va) except that (−)-diisopropyl-D-tartrate was employed in the epoxidation step. Flash chromatography afforded 4.75 g of the 2*R*,3*S* enantiomer (87.0% yield); $[\alpha]_D^{23} = 11.3°$ (C = 9.44, $CHCl_3$); the 360 MHz [^{1}H]NMR spectrum of the 2*R*,3*S* enantiomer was identical to that of the 2*S*,3*R* enantiomer.

*(2*S*,3*R*,5*Z*,8*Z*)-1-Tosyloxy-5,8-undecadiene (VIa) and (2*R*,3*S*,5*Z*,8*Z*)-1-Tosyloxy-5,8-undecadiene (VIb).* Tosylations of Va and Vb were carried out under identical conditions. To an ether solution (−10°C) of the epoxyalcohol and *p*-TsCl (1.05 equivalents) was added three equivalents of freshly powdered potassium hydroxide. After 45 min, extractive work-up yielded the crude product which was purified by flash chromatography (20 cm × 4.0 cm ID; hexane–ethyl acetate, 7 : 1) to afford 93.5% yields of each tosylate: (2*S*,3*R*,5*Z*,8*Z*)-1-tosyloxy-5,8-undecadiene (VIa); [^{1}H]NMR (90 MHz, $CDCl_3$): δ 7.83 (2H, d, J =

9.0 Hz, aromatic), 7.37 (2H, d, $J = 9.0$ Hz, aromatic), 5.64–5.06 (4H, m, vinyl protons), 4.13 (2H, m, $-\mathrm{C\underline{H}_2-OTs}$), 3.20–2.87 (2H, m, epoxide protons), 2.70 (2H, m, $-\mathrm{CH{=}CH-C\underline{H}_2-CH{=}CH}-$), 2.40 (3H, s, $\mathrm{C\underline{H}_3-C_6H_4}-$), 2.30–1.86 (4H, m, allylic protons), 0.93 (3H, t, $J = 7.5$ Hz, $\mathrm{C\underline{H}_3-CH_2}-$); $[\alpha]_D^{23} = -22.6°$ (C = 10.2, $CHCl_3$). (2*R*,3*S*,5*Z*,8*Z*)-1-tosyloxy-5,8-undecadiene (VIb); 90-MHz [^{1}H]NMR identical to spectrum of 2*S*,3*R* enantiomer; $[\alpha]_D^{23} = 23.5°$ (C = 10.4, $CHCl_3$).

(3Z,6Z,9S,10R)-9,10-Epoxyheneicosadiene. The procedure for preparation of the title compound [(3*Z*,6*Z*)-9*S*,10*R*-epoxy-21 : H], the saltmarsh caterpillar pheromone, is representative of the preparations of all the homologous epoxydienes and was carried out as follows: To a freshly prepared ether solution of lithium-di-*n*-decylcuprate (2.4 mmol), maintained under nitrogen at −25°C, was added 685 mg (2.04 mmol) of VIb in 5 ml of anhydrous ether. After 20 min, the reaction was quenched with 50 ml of saturated aqueous ammonium chloride and the crude product obtained by ether extraction (3 × 50 ml). Purification was achieved by HPLC on a Magnum ODS-3 column (Whatman). Gradient elution from methanol–water (75 : 25) to 100% methanol over 20 min at 4 ml/min afforded 401 mg (64% yield) of (3*Z*,6*Z*)-9*S*,10R-epoxyheneicosadiene which was greater than 98% pure by GC analysis; [^{1}H]NMR (90 MHz, $CDCl_3$): δ 5.64–5.10 (4H, m, vinyl protons), 3.0–2.7 (4H, m, epoxide and bis-allylic protons), 2.3 (2H, m, $-\mathrm{CH{=}CH-C\underline{H}_2-}\overset{\mathrm{O}}{\mathrm{CH{-}CH}}-$), 2.03 (2H, m, $\mathrm{CH_3C\underline{H}_2}$), 1.47 (2H, m, $-\overset{\mathrm{O}}{\mathrm{CH{-}CH}}\mathrm{-C\underline{H}_2-CH_2}-$), 1.26 (18H, bs, $\mathrm{CH_3(C\underline{H}_2)_9}-$), 0.93 (3H, t, $J = 7.5$ Hz, $\mathrm{C\underline{H}_3CH_2CH{=}CH}-$), 0.86 (3H, deformed t, $J = 7.5$ Hz, $\mathrm{C\underline{H}_3(CH_2)_9}-$); $[\alpha]_D^{23} = 3.4°$ (C = 8.67, $CHCl_3$). The 90-MHz [^{1}H]NMR spectrum reported above is virtually identical to the 100-MHz spectrum (C_6D_6) reported by Hill and Roelofs (1981) for the saltmarsh caterpillar pheromone.

Satisfactory spectral analyses were obtained on the higher (C_{22}) and lower (C_{18}–C_{20}) homologs of (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21 : H prepared under similar conditions with the appropriate cuprate reagent. The specific rotations for the homologs are as follows: (3*Z*,6*Z*)-9*S*,10*R*-epoxy-18 : H, $[\alpha]_D^{23} = 4.8°$ (C = 7.94, $CHCl_3$); (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19 : H, $[\alpha]_D^{23} = 3.5°$ (C = 8.57, $CHCl_3$); (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20 : H, $[\alpha]_D^{23} = 4.3°$ (C = 8.28, $CHCl_3$); (3*Z*,6*Z*)-9*S*,10*R*-epoxy-22 : H, $[\alpha]_D^{23} = 2.5°$ (C = 8.47, $CHCl_3$).

The homologous series of (3*Z*,6*Z*)-9*R*,10*S*-epoxydienes were prepared in identical manner to the 9*S*,10*R* enantiomers except that (2*S*,3*R*,5*Z*,8*Z*)-1-tosyloxy-2,3-epoxy-5,8-undecadiene was employed in the cuprate coupling reaction instead of the (2*R*,3*S*)-tosylate. The specific rotations of the products are as follows: (3*Z*,6*Z*)-9*R*,10*S*-epoxy-18 : H, $[\alpha]_D^{23} = -4.2°$ (C = 5.74, $CHCl_3$); (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H, $[\alpha]_D^{23} = -4.3°$ (C = 8.89, $CHCl_3$);

(3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H, $[\alpha]_D^{23} = -3.7°$ (C = 12.7, $CHCl_3$); (3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H, $[\alpha]_D^{23} = -3.4°$ (C = 15.9, $CHCl_3$); (3*Z*,6*Z*)-9*R*,10*S*-epoxy-22:H, $[\alpha]_D^{23} = -1.7°$ (C = 8.26, $CHCl_3$).

Field Trapping. Experiments were performed with Pherocon 1CP® traps (Zoecon Corp., Palo Alto, California) baited with 500 μg of synthetic chemicals impregnated in rubber septa (A. H. Thomas, No. 8753-D22).

Twenty-one synthetic compounds or mixtures of compounds consisting of (3*Z*,6*Z*,9*Z*,11*E*)-19:H, the C_{18}–C_{22} homologs of (3*Z*,6*Z*,9*Z*)-trienes, combined monoepoxides of (3*Z*,6*Z*,9*Z*)-trienes, (3*Z*,6*Z*)-9*S*,10*R*-epoxydienes, and (3*Z*,6*Z*)-9*R*,10*S*-epoxydienes were used in our experiments. In the field survey these compounds were set out individually and as binary mixtures which comprise the 118 different treatments shown in Table 2. Field survey treatments were duplicated and set out in complete randomized block designs at two locations 5 km apart. Traps were hung in a line on tree branches approximately 1.5 m above ground and at least 20 m apart and tended twice a week between May and September 1983. Captured specimens were identified at Biosystematics Research Institute, Ottawa, Canada. Similar procedures were followed for specific experiments except that treatments were 3X replicated.

Trap capture data were transformed $[(x + 0.5)^{1/2}]$, subjected to analysis of variance, and the means compared by Duncan's new multiple-range test.

Electroantennography (EAG). EAG measurements were performed as previously described (Chisholm et al., 1975). The compounds tested include all those used in the field survey, as described above, and the following groups; saturated and monounsaturated, C_{10}, C_{12}, C_{14}, C_{16} acetates, alcohols, and aldehydes with *Z* and *E* unsaturation ranging from 5 to 11; saturated hydrocarbons C_{11}–C_{24}; (6*Z*,9*Z*)-diene hydrocarbons, C_{18}–C_{22}; (6*Z*,9*Z*,12*Z*)-triene hydrocarbons, C_{18}–C_{22}, and linolenyl acetate, alcohol, and aldehyde.

RESULTS

Stereospecific synthesis of (3*Z*,6*Z*,9*S*,10*R*)-9,10-epoxyheneicosadiene was achieved in six steps from I with an overall yield of 12.5%. Although our synthetic route is similar to one reported by Mori and Ebata (1981), we obtained a much higher yield; 23.5% from III compared to less than 6% from a similar triyne intermediate in Mori and Ebata's synthesis. Improvements in yield were mainly due to our use of dicyclohexylborane for triyne reduction instead of P-2 nickel catalyst which is unsuitable for triynes (Huang et al., 1983). We also obtained significantly better yields for the asymmetric epoxidation and lithium dialkylcuprate coupling reactions. On the basis of the specific rotations of the key epoxyalcohol intermediates (Va and Vb), the enantiomeric purities of our products are higher than those prepared by Mori and Ebata. High-field $[^1H]$NMR

TABLE 2. COMPOUNDS AND BLENDS USED AS TRAP LURES IN 1983 FIELD SURVEY[a]

Compound/blend
(3*Z*,6*Z*,9*Z*)-18:H
+(3*Z*,6*Z*,9*Z*)-19:H
+CME-(3*Z*,6*Z*,9*Z*)-18:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-18:H
(3*Z*,6*Z*,9*Z*)-19:H
+(3*Z*,6*Z*,9*Z*)-20:H
+CME-(3*Z*,6*Z*,9*Z*)-19:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H
(3*Z*,6*Z*,9*Z*)-20:H
+(3*Z*,6*Z*,9*Z*)-21:H
+CME-(3*Z*,6*Z*,9*Z*)-20:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H
(3*Z*,6*Z*,9*Z*)-21:H
+(3*Z*,6*Z*,9*Z*)-22:H
+CME-(3*Z*,6*Z*,9*Z*)-21:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H
(3*Z*,6*Z*,9*Z*)-22:H
+CME-(3*Z*,6*Z*,9*Z*)-22:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-22:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-22:H
CME-(3*Z*,6*Z*,9*Z*)-18:H
+CME-(3*Z*,6*Z*,9*Z*)-19:H
CME-(3*Z*,6*Z*,9*Z*)-19:H
+CME-(3*Z*,6*Z*,9*Z*)-20:H
CME-(3*Z*,6*Z*,9*Z*)-20:H
+CME-(3*Z*,6*Z*,9*Z*)-21:H
CME-(3*Z*,6*Z*,9*Z*)-21:H
+CME-(3*Z*,6*Z*,9*Z*)-22:H
CME-(3*Z*,6*Z*,9*Z*)-22:H
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-22:H
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-22:H
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-18:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H
+(3*Z*,6*Z*)-9*S*,10*R*-epoxy-22:H
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-22:H
(3*Z*,6*Z*,9*Z*,11*E*)-19:H
+(3*Z*,6*Z*,9*Z*)-19:H
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H
+(3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H

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[a] Compounds tested as single components are underlined. Binary blends consisted of the underlined compound and each of the compounds listed below at ratios of 1:4, 1:1 and 4:1. All lures contained a total of 500 μg.

analysis of the (+)-α-methoxy-α-(trifluoromethyl)phenyl acetate derivatives of Va and Vb revealed enantiomeric excesses of 93% and 92%, respectively.

During 1982, a preliminary field screening of unsaturated hydrocarbons, combined monoepoxides of (3*Z*,6*Z*,9*Z*)-trienes, and linolenyl derivatives was performed. Field captures and strong EAG responses by male geometrids and noctuids, primarily to (3*Z*,6*Z*,9*Z*)-trienes and the combined monoepoxydiene derivatives, suggested the importance of these compounds as sex attractants (Underhill et al., unpublished). Consequently, we focused our 1983 field survey on these compounds together with two homologous series of enantiomerically enriched (3*Z*,6*Z*)-*cis*-9,10-epoxydienes (C_{18}–C_{22}). A component of the fall cankerworm moth pheromone, (3*Z*,6*Z*,9*Z*,11*E*)-19 : H, was added to the survey following its identification and synthesis (Wong et al., 1984a,b). The other unsaturated hydrocarbons and linolenyl derivatives described in Methods and Materials were only used for EAG assay.

Between May and September 1983, males belonging to 17 species of Geometridae were captured in our traps. All of these species belonged to the subfamilies Larentiinae or Ennominae which make up 87% of the Geometridae of North America north of Mexico (Hodges et al., 1983). Males of nine noctuid species from the subfamilies Catocalinae, Herminiinae, Hypeninae, and Rivulinae were also captured. Multiple captures of conspecific males to specific lures were recorded for several species from both families. Prior to discussions of individual species, it is important to note, with the methodology employed here, that comparisons of lure attractancy to virgin females were not possible. Since we had no information on the population size of the various species, the potency of our attractants could only be judged on a relative basis. Low numbers of insects caught may be an indication of poor attractancy or a low population of the species in our region.

Only one species, the geometrid *Epirrhoe sperryi*, responded to a (3*Z*,6*Z*,9*Z*)-triene as a single-component lure. In 1982, Pherocon 1CP traps baited with 500, 200, and 50 μg of (3*Z*,6*Z*,9*Z*)-19 : H caught 35, 22 and 4 *E. sperryi* males, respectively, in a 3X replicated experiment (June 21–July 12, 1982). These results were confirmed and expanded by data obtained during the 1983 field survey (Table 3). The only single-component lure which effectively produced multiple captures of *E. sperryi* was (3*Z*,6*Z*,9*Z*)-19 : H. Captures of *E. sperryi* males by (3*Z*,6*Z*,9*Z*)-19 : H were unaffected by (3*Z*,6*Z*,9*Z*)-18 : H at the 4 : 1 ratio, but greatly reduced or completely blocked by various doses of (3*Z*,6*Z*,9*Z*)-20 : H. The apparent synergistic effect of (3*Z*,6*Z*,9*Z*,11*E*)-19 : H was not confirmed by a second experiment. The reduction in total males captured between the 4 : 1 and 1 : 1 ratios of (3*Z*,6*Z*,9*Z*)-19 : H plus (3*Z*,6*Z*,9*Z*)-18 : H, CME-(3*Z*,6*Z*,9*Z*)-19 : H, or (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H cannot be clearly attributed to either dose of (3*Z*,6*Z*,9*Z*)-19 : H or effect of the second component since a comparison of dose of (3*Z*,6*Z*,9*Z*)-19 : H versus captures of *E. sperryi*

TABLE 3. CAPTURE OF *Epirrhoe sperryi* MALES IN SURVEY TRAPS

Lure composition (μg)	Total males captured[a]
(3*Z*,6*Z*,9*Z*)-19:H (500)	46
(400) + (3*Z*,6*Z*,9*Z*)-18:H (100)	42
(250) + (3*Z*,6*Z*,9*Z*)-18:H (250)	3
(400) + (3*Z*,6*Z*,9*Z*)-20:H (100)	4
(400) + (3*Z*,6*Z*,9*Z*,11*E*)-19:H (100)	73
(250) + (3*Z*,6*Z*,9*Z*,11*E*)-19:H (250)	23
(400) + CME-(3*Z*,6*Z*,9*Z*)-19:H (100)	47
(250) + CME-(3*Z*,6*Z*,9*Z*)-19:H (250)	9
(100) + CME-(3*Z*,6*Z*,9*Z*)-19:H (400)	7
(400) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H (100)	52
(250) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H (250)	16
(100) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H (400)	13
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H (500)	1
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (100)	7
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (250)	13
(100) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (400)	2

[a] Total males captured in 2X replicated survey traps between May 30 and June 27, 1983.

was not carried out. This comment applies in general to the other species captured and must be kept in mind during interpretation of results. Note here that in Table 3 and other tables, absence of an experimental treatment used in the survey indicates no captures of the species described in the Table heading. While additions of CME-(3*Z*,6*Z*,9*Z*)-19:H or (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H to (3*Z*,6*Z*,9*Z*)-19:H failed to produce any obvious effects, (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H appeared to reduce captures of *E. sperryi*. However, this effect was not observed during a 3X replicated experiment designed to test the effect of various doses of epoxydienes (data not shown).

Thus the effect of epoxides, if any, on the attractancy of (3*Z*,6*Z*,9*Z*)-19:H to *E. sperryi* remains unclear. An EAG assay was performed on *E. sperryi* in 1982 with all of the compounds described in Methods and Materials except for (3*Z*,6*Z*,9*Z*,11*E*)-19:H and the enantiomers of (3*Z*,6*Z*)-*cis*-9,10-epoxydienes. Responses were strongest for (3*Z*,6*Z*,9*Z*)-19:H and CME-(3*Z*,6*Z*,9*Z*)-19:H and adjacent higher and lower homolog (Figure 1). Although not shown in Figure 1, EAG responses by *E. sperryi* were near background for all of the other groups of compounds used in electroantennography, including the saturated and monounsaturated acetates, alcohols and aldehydes, saturated hydrocarbons, (6*Z*,9*Z*)-diene hydrocarbons, (6*Z*,9*Z*,12*Z*)-triene hydrocarbons, and linolenyl derivatives. This statement also applies to the other geometrid and noctuid moths captured in the survey (Figures 2–5). EAG responses were elicited principally by the (3*Z*,6*Z*,9*Z*)-triene hydrocarbons, their combined monoepoxydiene analogs, and the (9*S*,10*R*)- and (9*R*,10*S*)-monoepoxydienes. In general, those

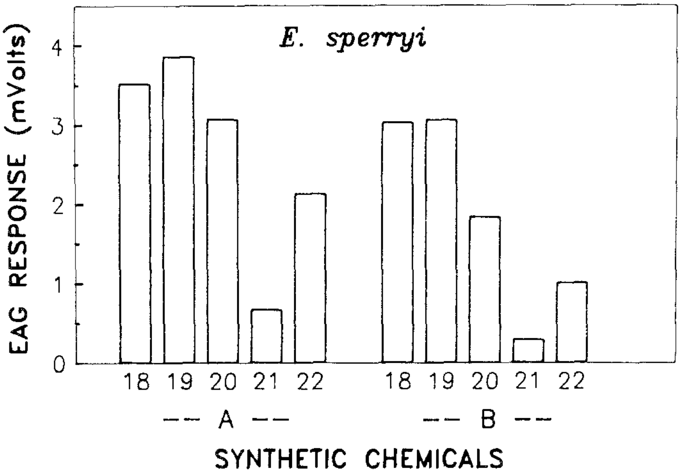

FIG. 1. EAG responses of *E. sperryi* to synthetic chemicals. Letters (A and B) refer to (3Z,6Z,9Z)-*X*: H and CME-(3Z,6Z,9Z)-*X*: H, respectively. Numbers (18–22) refer to the length of the carbon chain (*X*).

compounds which attracted moths in the field also elicited the strongest EAG signals. Recently, (3*Z*,6*Z*,9*Z*)-19:H has been identified as a pheromone component for the giant looper, *Boarmia (ascotis) selenaria* (Becker et al., 1983), the spring cankerworm, *Paleacrita vernata* (Underhill et al., unpublished), and the fall cankerworm moth, *Alsophila pometaria* (Wong et al., 1984a).

Two geometrid species, *Mesoleuca ruficillata* and *Triphosa haesitata affirmata* (Guenée), both of the Hydriomenini tribe, were captured by lures consisting predominantly of (3*Z*,6*Z*,9*Z*)-trienes. Single captures of *M. ruficillata* occurred with five binary lures in which the principal components were (3*Z*,6*Z*,9*Z*)-19:H, (3*Z*,6*Z*,9*Z*)-20:H, or (3*Z*,6*Z*,9*Z*)-21:H. The minor components of these lures did not share any obvious common features. The best lure for *M. ruficillata*, (3*Z*,6*Z*,9*Z*)-21:H (400 μg) + (3*Z*,6*Z*,9*Z*)-22:H (100 μg), captured five males, and also captured one of the two specimens of *T. haesitata affirmata* taken during 1983. The other specimen was caught in a survey trap baited with (3*Z*,6*Z*,9*Z*)-21:H (450 μg) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (50 μg). Although these captures alone are not conclusive, data from 1982 suggest (3*Z*,6*Z*,9*Z*)-trienes may be components of an attractant. Survey traps baited with (3*Z*,6*Z*,9*Z*)-20:H (200 μg) + linolenyl aldehyde (10 μg), (3*Z*,6*Z*,9*Z*)-20:H (200 μg) + linolenyl acetate (10 μg), and (3*Z*,6*Z*,9*Z*)-21:H (200 μg) + linolenyl acetate (10 μg) captured two, seven, and five males of *T. haesitata affirmata*, respectively, between May 18 and June 9, 1982. These results suggest that a combination of a (3*Z*,6*Z*,9*Z*)-triene (C_{20} and/or C_{21}) and linolenyl acetate may be required for attraction of *T. haesitata affirmata*.

TABLE 4. CAPTURE OF *Metanema inatomaria* AND *Prochoerodes transversata* MALES IN SURVEY TRAPS

	Total males captured	
Lure composition (μg)	*M. inatomaria*[a]	*P. transversata*[b]
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-18:H (400) + (3*Z*,6*Z*,9*Z*)-18:H (100)	0	1
(250) + (3*Z*,6*Z*,9*Z*)-18:H (250)	0	1
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H (500)	7ef	1
(400) + (3*Z*,6*Z*,9*Z*)-18:H (100)	31de	0
(250) + (3*Z*,6*Z*,9*Z*)-18:H (250)	6f	0
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (400) + (3*Z*,6*Z*,9*Z*)-19:H (100)	0	56
(250) + (3*Z*,6*Z*,9*Z*)-19:H (250)	0	47
(100) + (3*Z*,6*Z*,9*Z*)-19:H (400)	0	7
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H (500)	80bc	0
(400) + (3*Z*,6*Z*,9*Z*)-19:H (100)	2f	1
(250) + (3*Z*,6*Z*,9*Z*)-19:H (250)	0	4
(400) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H (100)	85bc	0
(250) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H (250)	38cd	0
(100) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H (400)	11def	0
(400) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (100)	116ab	0
(250) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (250)	44c	0
(100) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (400)	6ef	0
(400) + (3*Z*,6*Z*,9*Z*,11*E*)-19:H (100)	169a	0
(250) + (3*Z*,6*Z*,9*Z*,11*E*)-19:H (250)	101ab	0
(100) + (3*Z*,6*Z*,9*Z*,11*E*)-19:H (400)	48c	0

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[a] Total males captured in 2X replicated Pherocon 1CP traps between June 7 and July 25, 1983. Values followed by the same letter are not significantly different ($P = 0.05$).

[b] Total males captured in 2X replicated Pherocon 1CP traps between June 17 and September 7, 1983.

Several species of geometrids were specifically attracted to survey traps baited with an epoxide as the major component. Captures of *Metanema inatomaria* and *Prochoerodes transversata* clearly illustrate this attraction (Table 4). *M. inatomaria* males were caught by (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H and the less potent (3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H as single-component lures. The specificity of this response is shown by the absence of captures to the opposite (9*S*,10*R*)-epoxydiene isomers. (3*Z*,6*Z*,9*Z*)-Trienes appeared to have opposite effects on the two epoxydiene attractants. Although not statistically significant, (3*Z*,6*Z*,9*Z*)-18:H appeared to be synergistic with (3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H, while (3*Z*,6*Z*,9*Z*)-19:H blocked the attraction of *M. inatomaria* to (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H. Combination of the two attractive epoxydienes did not cause a synergistic response. Two compounds appeared to increase the attractancy of (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H. Captures of *M. inatomaria* males were increased slightly by (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H, while addition of (3*Z*,6*Z*,9*Z*,11*E*)-19:H produced a significant twofold increase. The synergistic effect of (3*Z*,6*Z*,9*Z*,11*E*)-19:H was confirmed by a 3X replicated experiment conducted between June 21 and July 7, 1983. Traps baited with (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H and (3*Z*,6*Z*,9*Z*,11*E*)-19:H, (400:100 μg) and (475:25 μg), captured 83 and 60 males of *M. inatomaria*, respectively, compared to 16 males caught by 500 μg of the epoxydiene alone.

Another experiment revealed that the attractancy of (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H was blocked by its enantiomer or the combined monoepoxides of (3*Z*,6*Z*,9*Z*)-19:H (Table 5). No males of *M. inatomaria* were captured by a 1:1 (racemic) mixture of (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H and its (9*S*,10*R*)-enantiomer. Inhibition by *CME-(3Z,6Z,9Z)*-19:H is complete at the 25-μg dose, which indicates that one or both of the other isomers, (3*Z*,9*Z*)-*cis*-6,7-epoxy-

Table 5. Effect of Dose of (3*Z*,6*Z*)-9*R*,10*S*-Epoxy-19:H, (3*Z*,6*Z*)-9*S*,10*R*-Epoxy-19:H, and CME-(3*Z*,6*Z*,9*Z*)-19:H on Captures of *Metanema inatomaria*

Lure composition (μg)	Total males captured[a]
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-19:H (500)	35a
(250)	25ab
(50)	7bc
(475) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (25)	66a
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (100)	40ab
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (250)	0c
(475) + CME-(3*Z*,6*Z*,9*Z*)-19:H (25)	0c

[a] Total males captured in 3X replicated Pherocon 1CP traps between June 17 and July 7, 1983. Values followed by the same letter are not significantly different ($P = 0.05$).

19 : H or (6Z,9Z)-*cis*-3,4-epoxy-19 : H, is responsible, since the quantity of (3Z,6Z)-9S,10R-epoxy-19 : H present (4.2 μg) is insufficient for complete inhibition. The antennal responses of *M. inatomaria* to synthetic compounds (Figure 2) were consistent with field capture data and were strong for compounds which are attractants, synergists, and inhibitors. It is interesting to note that

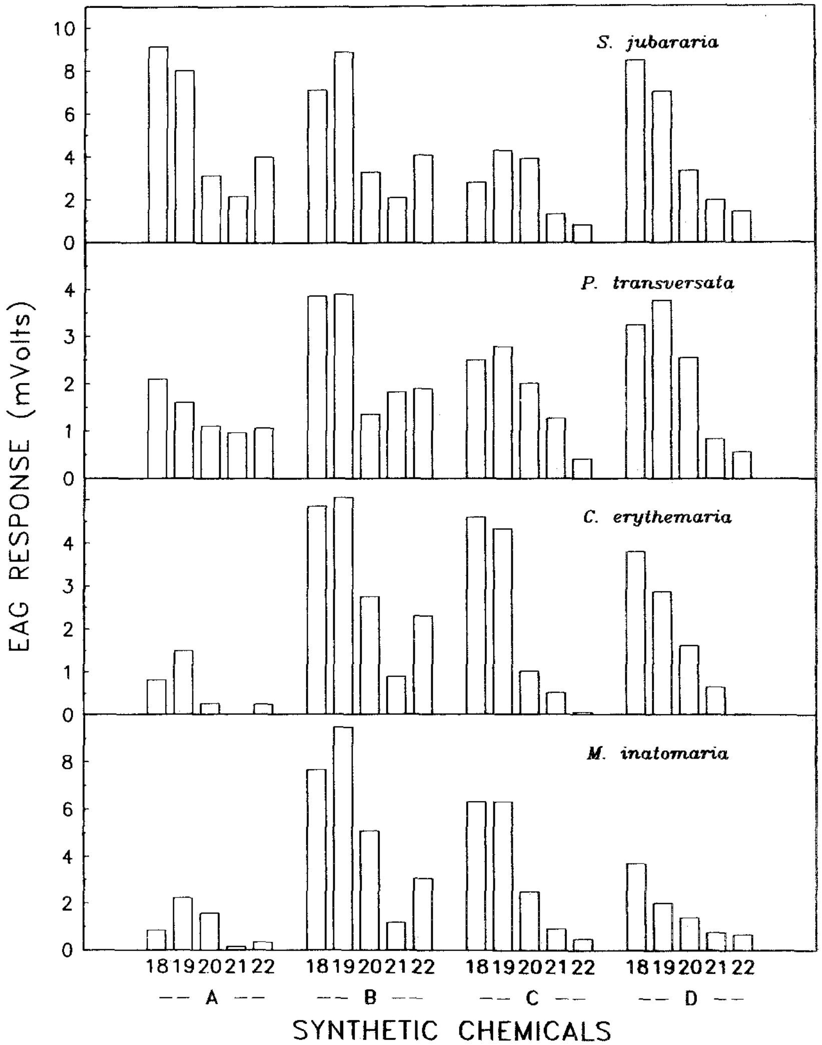

FIG. 2. EAG responses of *M. inatomaria, C. erythemaria, P. transversata*, and *S. jubararia* to synthetic chemicals. Letters (A–D) refer to (3Z,6Z,9Z)-X: H, CME-(3Z,6Z,9Z)-X: H, (3Z,6Z)-9R,10S-epoxy-X: H, and (3Z,6Z)-9S,10R-epoxy-X: H, respectively. Numbers (18–22) refer to the length of the carbon chain (X).

principal attractants, (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H and -18 : H, elicited stronger antennal responses than the unattractive 9*S*,10*R* enantiomers. Hill et al. (1982) have reported that *Hyphantrea cunea* produces larger antennal responses to (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21 : H than its 9*R*,10*S* enantiomer.

Another geometrid moth, *Cabera erythemaria*, gave an EAG profile (Figure 2) very similar to that of *M. inatomaria*. This moth was not attracted by any of the lures used in the field survey and was captured in experiments designed to determine the effect of lure composition on captures of *M. inatomaria*. Lures composed of (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H and (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19 : H, 475 : 25 μg and 400 : 100 μg, captured *M. inatomaria* males and no *C. erythemaria* males (Table 5) while a 1 : 1 mixture of these compounds captured 21 males of *C. erythemaria* and no *M. inatomaria*. This phenomenon of attraction of one species and inhibition of a second species by a specific ratio of enantiomers is similar to the situation reported for the responses of *Lymantria dispar* and *L. monacha* to (+)- and (−)-disparlure mixtures (Hansen et al., 1983). Further experiments disclosed that (3*Z*,6*Z*,9*Z*)-19 : H was required for improved captures of *C. erythemaria*. The addition of 10 μg and 50 μg of (3*Z*,6*Z*,9*Z*)-19 : H to a racemic mixture of the 9*S*,10*R* and 9*R*,10*S* enantiomers (500 μg) led to captures of 71 and 34 males, respectively. These captures were significantly greater ($P = 0.05$) than the capture of three males by a treatment consisting of 500 μg of the racemate alone (3X replicated, July 11–18, 1983).

The large maple spanworm, (*Prochoerodes transversata*), is commonly found in oak and maple and is distributed throughout the temperate regions of North America. In our region, two flights occur during June–July and August–September. While single captures of *P. transversata* were recorded for several survey lures, most males were caught by binary mixtures of (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19 : H and (3*Z*,6*Z*,9*Z*)-19 : H (Table 4). The absence of captures for either compound alone indicated an absolute requirement for a combination of both compounds. This was confirmed by a 3X replicated experiment (August 18–September 4, 1983) which resulted in captures of 41 and 54 males in traps baited with (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19 : H and (3*Z*,6*Z*,9*Z*)-19 : H at doses of 250 : 250 μg and 400 : 100 μg compared to no captures for 500 : 10 μg and 500 : 1 μg mixtures.

Single captures of *P. transversata* by mixtures of (3*Z*,6*Z*)-9*S*,10*R*-epoxy-18 : H + (3*Z*,6*Z*,9*Z*)-18 : H may be indicative of weak activity by these compounds (Table 4). Weak attraction by lower homologs of principal attractants was also observed for *M. inatomaria* and could suggest a certain degree of flexibility in the specificity of receptor sites for the principal attractants that allows lower homologs to fit into these sites. Captures of *P. transversata* by lures containing (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H may be due to weak activity by the 9*R*,10*S* enantiomer or to the 9*S*,10*R* isomer present in the sample. However, the small quantity of the 9*S*,10*R* isomer present (3.5%) makes the latter explanation unlikely. The EAG profile for *P. transversata* (Figure 2) contained strong responses to compounds identified as attractants or inhibitors by the field experiments. Note that the response is higher for the more attractive (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19 : H compared to the 9*R*,10*S* isomer.

Synaxis jubararia, which belongs to the same tribe (Ourapterygini) as *P. transversata*, gave strong antennal responses to the compounds which also stimulated *P. transversata* (Figure 2). In survey traps, four, one, two, and two males of *S. jubararia* were captured in traps baited with (3*Z*,6*Z*,9*Z*)-19 : H (400 μg) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H (100 μg), (3*Z*,6*Z*,9*Z*)-19 : H (250 μg) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H (250 μg), (3*Z*,6*Z*,9*Z*)-19 : H (400 μg) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19 : H (100 μg), and (3*Z*,6*Z*,9*Z*)-19 : H (400 μg) + CME-(3*Z*,6*Z*,9*Z*)-19 : H (100 μg), respectively. These captures suggest that (3*Z*,6*Z*,9*Z*)-19 : H, as a major component, together with one enantiomer or a specific combination of both enantiomers of (3*Z*,6*Z*)-*cis*-9,10-epoxy-19 : H may be required for attraction of *S. jubararia*.

Another geometrid moth captured by lures consisting solely or principally of an epoxide was *Dysstroma brunneata ethela*. Lures consisting only of (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20 : H or (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21 : H captured *D. brunneata ethela* males (Table 6). Captures of *D. brunneata ethela* by the C_{20} epoxide were completely blocked by addition by of (3*Z*,6*Z*,9*Z*)-20 : H but were not obviously affected by the other compounds tested in the survey, The EAG profile of *D. brunneata ethela* (Figure 3) is very consistent with the field trapping data and shows stronger responses for the attractive (9*S*,10*R*)-epoxydiene isomers than the inactive 9*R*,10*S* isomers.

Twelve specimens of a second *Dysstroma sp.*, tentatively identified as *citrata* (the dark marbled carpet moth), were captured in 10 traps baited with binary lures. All of the lures contained (3*Z*,6*Z*,9*Z*)-20 : H or (3*Z*,6*Z*,9*Z*)-21 : H plus one of the following: CME-(3*Z*,6*Z*,9*Z*)-20 : H, CME-(3*Z*,6*Z*,9*Z*)-21 : H, (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20 : H, (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20 : H, (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21 : H, or (3*Z*,6*Z*)-9*R*,10*S*-epoxy-21 : H. Although a principal attractant was not discerned from the field-capture data, some combination of a triene hydrocarbon (C_{20} and/or C_{21}) and an epoxydiene (C_{20} and/or C_{21}) appears to be required.

Several noctuid moths were also specifically attracted by lures consisting primarily of an epoxide. Lures which contained (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20 : H, alone or in a number of combinations, consistently attracted *Spargaloma sexpunctata* (subfamily Hypeninae). Table 7 summarizes the captures of this species in the survey (test 1) and one other field test. The greatest number of males captured was in traps baited with (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20 : H alone. The attraction, which appeared to be stereospecific, was not enhanced by additions of other components and may have been inhibited by some. Although mixtures of the C_{20} and C_{21} combined monoexpoxydiene hydrocarbons captured a few

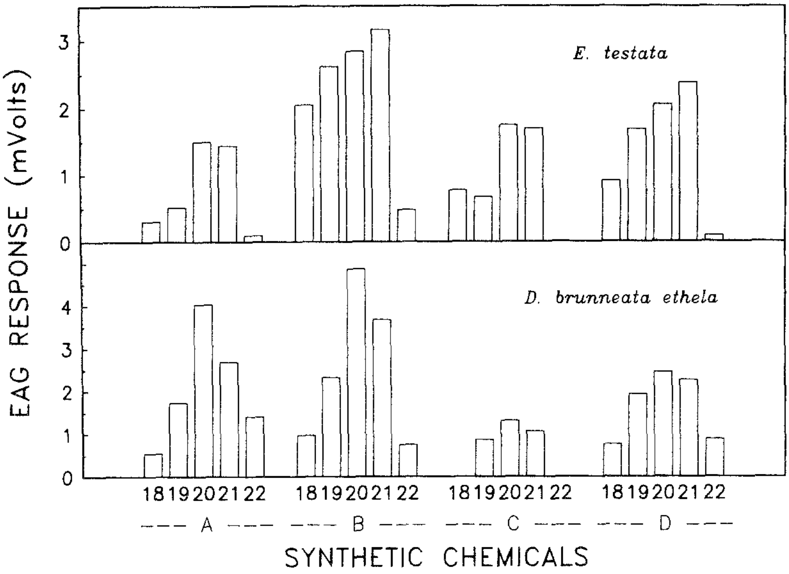

FIG. 3. EAG responses of *D. brunneata ethela* and *E. testata*. Letters (A–D) refer to (3*Z*,6*Z*,9*Z*)-*X*:H, CME-(3*Z*,6*Z*,9*Z*)-*X*:H, (3*Z*,6*Z*)-9*R*,10*S*-epoxy-*X*:H, and (3*Z*,6*Z*)-9*S*,10*R*-epoxy-*X*:H, respectively. Numbers (18–22) refer to the length of the carbon chain (*X*).

TABLE 6. CAPTURE OF *Dysstroma brunneata ethela* IN SURVEY TRAPS

Lure composition (μg)	Total males captured[a]
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H (500)	41a
(250) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (250)	21abc
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (100)	14abc
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (250)	6bc
(100) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (400)	2c
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H (100)	30ab
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H (250)	30ab
(100) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H (400)	21abc
(400) + (3*Z*,6*Z*,9*Z*)-20:H (100)	0c
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H (500)	4bc
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-22:H (100)	14abc
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-22:H (250)	9abc
(100) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-22:H (400)	4bc

[a] Total males captured in 2× replicated Pherocon 1CP traps from July 11 to August 4, 1983. Values followed by the same letter are not significantly different ($P = 0.05$).

TABLE 7. CAPTURE OF *Spargaloma sexpunctata* IN 1983 FIELD TESTS

Lure composition (μg)	Males caught[a]	
	Test 1	Test 2[b]
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H (500)	47	21a
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (100)	20	
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (250)	7	
(400) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H (100)	17	
(250) + (3*Z*,6*Z*)-9*S*,10*R*-epoxy-21:H (250)	4	
(250) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (250)	19	
(450) + CME-(3*Z*,6*Z*,9*Z*)-20:H (50)		0b
(400) + CME-(3*Z*,6*Z*,9*Z*)-20:H (100)	0	3b
(250) + (3*Z*,6*Z*,9*Z*)-20:H (250)	4	
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (500)	3	
(400) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H (100)	5	
CME-(3*Z*,6*Z*,9*Z*)-20:H (250) + CME-(3*Z*,6*Z*,9*Z*)21:H (250)	10	

[a] Total number of target males captured. Test 1: field survey data from 2X replicated Pherocon 1CP traps. Moths were caught between June 14, and July 21, 1983. Test 2: 3X replicated Pherocon 1CP, July 10–18, 1983.

[b] Values followed by common letters do not differ at the 5% level.

specimens, CME-(3*Z*,6*Z*,9*Z*)-20:H alone failed to capture any and, in a 3X replicated test (test 2), its addition to (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H significantly decreased the number of males captured, suggesting one or more of the other isomers present in the mixture to be inhibitory. The capture or lack of capture of moths by several lure combinations are at present unaccountable and further field testing is required. This was particularly noticeable with binary mixtures of (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H plus (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H which, at 1:4 and 4:1, failed to capture any *S. sexpunctata* but at 1:1 (the racemate) was attractive. In response to the test series of synthetic compounds, major antennal stimulation was elicited by CME-(3*Z*,6*Z*,9*Z*)-20:H, (3*Z*,6*Z*)-9*S*,10*R*-epoxy-20:H, and (3*Z*,6*Z*,9*Z*)-20:H; by comparison the response to the 9*R*,10*S* isomer was low (Figure 4).

Two other species within the Hypeninae subfamily were also captured and both appeared to respond to a specific epoxide. A total of 18 specimens of *Lomanaltes eductalis* were captured and all, except one, were attracted to (3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H-based lures. No males were caught in CME-baited traps, which suggests that one or more of the isomeric monoepoxydienes in the mixtures was inhibitory. A small number (six) of a *Bomolocha* sp., [probably *palparia* (Walker)] were also captured. These were all taken by traps baited with the next lower homolog (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H.

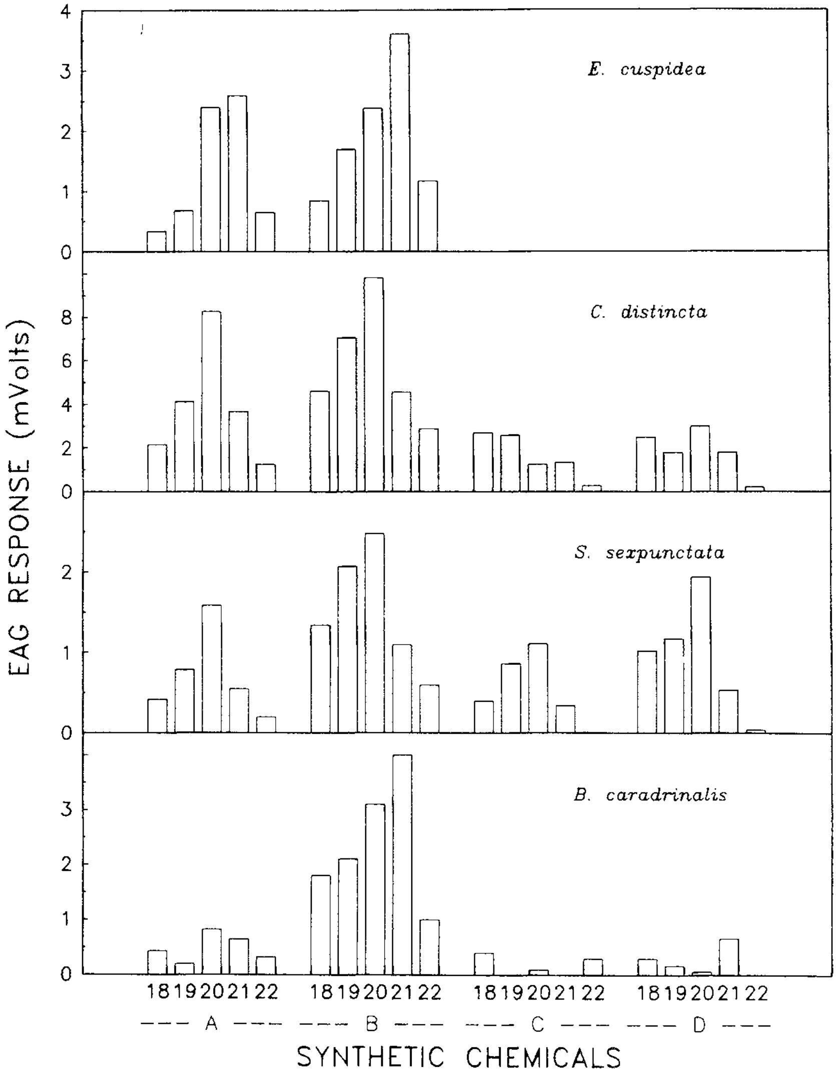

FIG. 4. EAG responses of *E. cuspidea*, *C. distincta*, *S. sexpunctata*, and *B. caradrinalis*. Letters (A–D) refer to (3*Z*,6*Z*,9*Z*)-*X*: H, CME-(3*Z*,6*Z*,9*Z*)-*X*: H, (3*Z*,6*Z*)-9*R*,10*S*-epoxy-*X*: H, and (3*Z*,6*Z*)-9*S*,10*R*-epoxy-*X*: H, respectively. Numbers (18–22) refer to the length of the carbon chain (*X*).

Several survey traps captured the noctuid *Caenurgina distincta*, subfamily Catocalinae (Table 8). Traps containing (3*Z*,6*Z*,9*Z*)-20: H alone took a few specimens. Blends of this hydrocarbon with its next lower or higher homologs produced no synergistic effects and the captures, which were all less than seven, were deleted from Table 8. However, binary lures containing (3*Z*,6*Z*,9*Z*)-20: H

TABLE 8. CAPTURE OF *Caenurgina distincta* MALES IN 1983 SURVEY TRAPS

Lure composition (μg)	Males caught[a]
(3Z,6Z,9Z)-20:H (500)	7
(3Z,6Z,9Z)-20:H (400) + CME-(3Z,6Z,9Z)-20:H (100)	33
(250) + CME-(3Z,6Z,9Z)-20:H (250)	35
(100) + CME-(3Z,6Z,9Z)-20:H (400)	14
CME-(3Z,6Z,9Z)-20:H (500)	3
(3Z,6Z,9Z)-20:H (400) + (3Z,6Z)-9R,10S-epoxy-20:H (100)	19
(250) + (3Z,6Z)-9R,10S-epoxy-20:H (250)	56
(100) + (3Z,6Z)-9R,10S-epoxy-20:H (400)	71
(3Z,6Z,9Z)-20:H (400) + (3Z,6Z)-9S,10R-epoxy-20:H (100)	91
(250) + (3Z,6Z)-9S,10R-epoxy-20:H (250)	113
(100) + (3Z,6Z)-9S,10R-epoxy-20:H (400)	73
(3Z,6Z)-9S,10R-epoxy-20:H (500)	2

[a] Total number of target males captured in 2× replicated Pherocon 1CP traps. Captures occurred between May 25, and July 18, 1983.

plus any one of CME-(3Z,6Z,9Z)-20:H, (3Z,6Z)-9R,10S-epoxy-20:H, and (3Z,6Z)-9S,10R-epoxy-20:H resulted in large increases in captures. Traps which contained these three additives as single components captured only a few males or none. The EAG response profile obtained with *C. distincta* males showed only two major peaks of activity in response to (3Z,6Z,9Z)-20:H and CME-(3Z,6Z,9Z)-20:H (Figure 4). Considering the field capture data, it is somewhat surprising that major antennal responses were not elicited by (3Z,6Z)-9S,10R-epoxy-20:H and (3Z,6Z)-9R,10S-epoxy-20:H as well.

Two other species from the large Catocalinae subfamily were also captured in the field survey traps, *Euclidia cuspidea* and *Zale duplicata*. The EAG response profile of *E. cuspidea* (Figure 4) shows similarly strong responses were elicited by both the C_{20} and C_{21} (3Z,6Z,9Z)-triene hydrocarbons and their combined monoepoxydiene analogs. The (9R,10S)- and (9S,10R)-monoepoxydiene enantiomers were not available at the time these analyses were done. In our survey, *E. cuspidea* were only captured in traps baited with mixtures of the C_{21} triene hydrocarbon and its epoxides. Of 45 specimens taken, 25 were attracted to mixtures of (3Z,6Z,9Z)-21:H + CME-(3Z,6Z,9Z)-21:H and the remainder to mixtures of the hydrocarbon and its (9R,10S)- and (9S,10R)-monoepoxydiene enantiomers. These results indicate that a combination of (3Z,6Z,9Z)-21:H and an epoxide are required for attraction of *E. cuspidea*. A total of 13 specimens of *Zale duplicata* were captured in the survey, and all but one were taken by traps in which (3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H was the only or major component present.

Several noctuid species from the subfamilies Herminiinae and Rivulinae were captured in traps baited principally with combined monoepoxydiene mixtures. Three species from the Herminiinae were captured in the survey traps, namely *Bleptina caradrinalis, Idia americalis*, and *I. aemula. B. caradrinalis*, a noctuid widely distributed from central Canada to the Gulf of Mexico and westward to the Rocky Mountains, was regularly taken in traps baited with CME-(3*Z*,6*Z*,9*Z*)-21:H (Table 9). The largest number of specimens was captured in traps baited with CME-(3*Z*,6*Z*,9*Z*)-21:H alone. Only a few males were caught in traps baited with CME-(3*Z*,6*Z*,9*Z*)-20:H alone and none by the C_{22} homolog. The data indicate that none of the binary mixtures were synergistic in the three ratios tested. It is not known which of the *cis*-3,4-,*cis*-6,7- or *cis*-9,10-epoxides present in the CME mixture stimulated *B. caradrinalis* male attraction; however, no specimens were taken in traps containing either the C_{21} 9*R*,10*S* or 9*S*,10*R* isomers as single components and neither elicited appreciably strong EAG responses (Figure 4).

EAG responses to the synthetic compounds listed in Methods and Materials were measured using *B. caradrinalis* males captured in the survey traps (Figure 4). Major responses were only elicited by the field-active compounds, CME-(3*Z*,6*Z*,9*Z*)-20:H and CME-(3*Z*,6*Z*,9*Z*)-21:H, the others giving lower or near background responses. Antennal responses to (*Z*)- and (*E*)-monounsat-

TABLE 9. CAPTURE OF *Bleptina caradrinalis* IN 1983 SURVEY TRAPS

Lure composition (μg)	Males caught[a]
CME-(3*Z*,6*Z*,9*Z*)-21:H (500)[b]	46
CME-(3*Z*,6*Z*,9*Z*)-21:H (400) + (3*Z*,6*Z*,9*Z*)-21:H (100)	12
(250) + (3*Z*,6*Z*,9*Z*)-21:H (250)	4
(100) + (3*Z*,6*Z*,9*Z*)-21:H (400)	1
CME-(3*Z*,6*Z*,9*Z*)-21:H (400) + CME-(3*Z*,6*Z*,9*Z*)-20:H (100)	14
(250) + CME-(3*Z*,6*Z*,9*Z*)-20:H (250)	18
(100) + CME-(3*Z*,6*Z*,9*Z*)-20:H (400)	2
CME-(3*Z*,6*Z*,9*Z*)-21:H (400) + CME-(3*Z*,6*Z*,9*Z*)-22:H (100)	20
(250) + CME-(3*Z*,6*Z*,9*Z*)-22:H (250)	9
CME-(3*Z*,6*Z*,9*Z*)-20:H (500)	4
CME-(3*Z*,6*Z*,9*Z*)-20:H (250) + (3*Z*,6*Z*,9*Z*)-20:H (250)	5

[a] Total number of target males captured in 2X replicated Pherocon 1CP traps. Captures occurred between June 27, and July 25, 1983.

[b] CME represents an equal mixture of the monoepoxydiene hydrocarbons derived from the triene hydrocarbon, here from (3*Z*,6*Z*,9*Z*)-21:H.

urated C_{20} hydrocarbons were also measured to determine if those with unsaturation corresponding in position and geometry to the field-active compounds would display elevated responses. Near background responses resulted from all. Thus, while some lepidopteran species give elevated EAG responses to monoolefinic analogs of their dienyl acetate, alcohol, or aldehyde pheromones and thus yield information regarding the positions of unsaturation, it would appear this phenomenon does not hold for these polyunsaturated hydrocarbons.

Although fewer specimens of two species of *Idia* were trapped, epoxide isomers were also involved in their capture. A total of 20 specimens of *I. americalis* were taken. Of these, 17 were caught in traps baited with epoxide-based lures and 11 in traps containing CME-(3*Z*,6*Z*,9*Z*)-20 : H. The other species, *I. aemula*, was captured only in traps baited with monoepoxydiene hydrocarbons and eight of the 13 specimens were taken in traps containing CME-(3*Z*,6*Z*,9*Z*)-21 : H. EAG analyses were not conducted on either of these species.

Traps baited with lures containing CME-(3*Z*,6*Z*,9*Z*)-19 : H as the major component captured 10 out of a total of 11 specimens of *Rivula propinqualis* (subfamily Rivulinae), an insect whose range extends from Nova Scotia to Texas and across the continent as far as the Rocky Mountains. None were captured in traps containing either of the singly baited C_{19} (9*R*,10*S*)- or (9*S*,10*R*)-monoepoxydienes, which suggests mixtures of these two enantiomers or another postional epoxide isomer in the CME mixture to be the attractant.

Specific attraction to lures containing primarily CME mixtures was also displayed by several geometrid species. The chevron moth, *Eulithes testata*, which belongs to the same tribe (Hydriomenini) as the *Dysstroma* sp. gave strong EAG signals in response to all of the CME homologs except for the C_{22} homolog (Figure 3). As observed for the *Dysstroma* sp. tentatively identified as *citrata*, all captures of *E. testata* were in traps baited with combinations of (3*Z*,6*Z*,9*Z*)-20 : H or (3*Z*,6*Z*,9*Z*)-21 : H plus a C_{20} or C_{21} CME or (9*S*,10*R*)-epoxydiene isomer. Although the results do not indicate a specific attractant, responses to the combined monoepoxides may indicate involvement by epoxydiene isomers other than the 9,10-epoxydienes.

Several other species of geometrids were also caught by lures consisting primarily of combined monoepoxydiene mixtures. The EAG profiles for these moths (Figure 5) were similar to each other and showed strong responses to CME-(3*Z*,6*Z*,9*Z*)-trienes and in some cases (3*Z*,6*Z*,9*Z*)-trienes. EAG responses to the (9*S*,10*R*)- and (9*R*,10*S*)-epoxydienes were background or near background for all of these species. In some cases, field captures of these moths also correlated well with their EAG profiles. For example, a *Semiothisa* sp., tentatively identified as *signaria dispuncta* (Walker), gave its strongest antennal response to CME-(3*Z*,6*Z*,9*Z*)-18 : H and was captured only by lures containing CME-(3*Z*,6*Z*,9*Z*)-18 : H. Captures of eight, seven, seven, and one males were recorded for survey traps baited with CME-(3*Z*,6*Z*,9*Z*)-18 : H (500 μg), CME-(3*Z*,6*Z*,9*Z*)-18 : H (400 μg) + (3*Z*,6*Z*,9*Z*)-18 : H (100

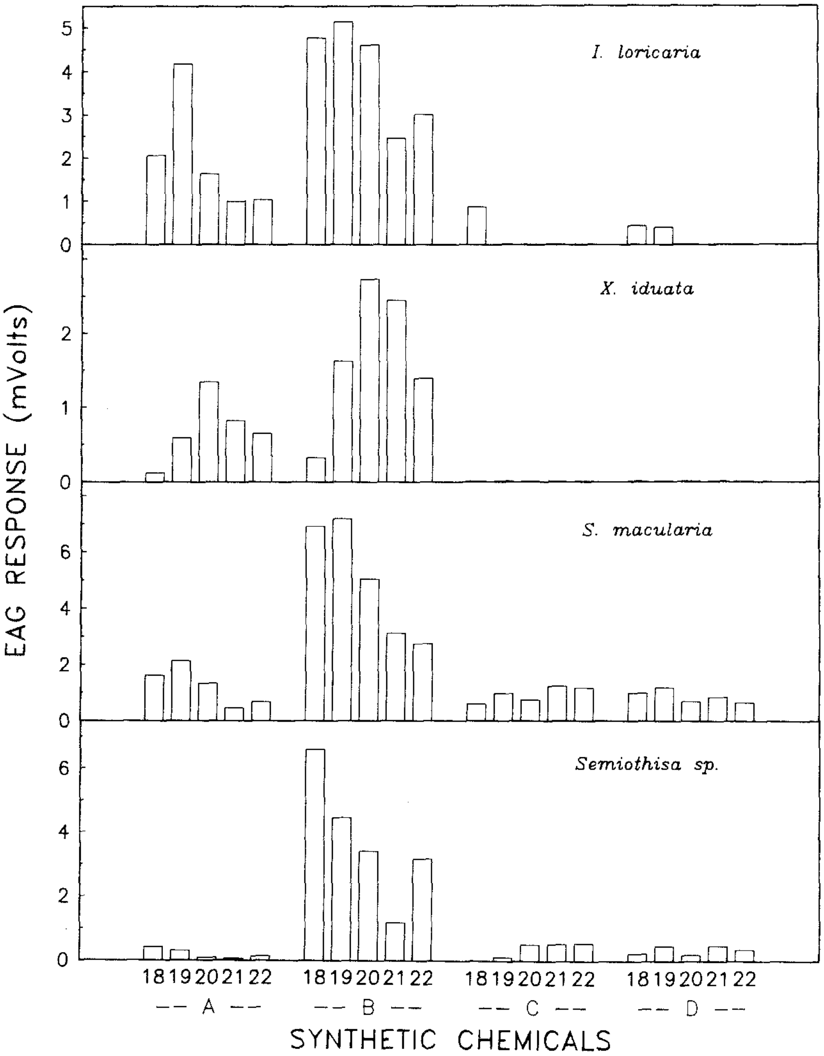

FIG. 5. EAG responses of *I. loricaria, X. iduata, S. macularia*, and a *Semiothisa* sp. Letters (A–D) refer to (3*Z*,6*Z*,9*Z*)-*X*: H, CME-(3*Z*,6*Z*,9*Z*)-*X*: H, (3*Z*,6*Z*)-9*R*,10*S*-epoxy-*X*: H, and (3*Z*,6*Z*)-9*S*,10*R*-epoxy-*X*: H, respectively. Numbers (18–22) refer to the length of the carbon chain (*X*).

μg), CME-(3*Z*,6*Z*,9*Z*)18 : H (250 μg) + (3*Z*,6*Z*,9*Z*)-18 : H (250 μg), and CME-(3*Z*,6*Z*,9*Z*)-18 : H (250 μg) + CME-(3*Z*,6*Z*,9*Z*)-19 : H (250 μg), respectively. These captures, together with the absence of captures to (3*Z*,6*Z*)-9*S*,10*R*-epoxy-18 : H or the 9*R*,10*S* isomer, suggest the involvement of (3*Z*,6*Z*)-

cis-3,4-epoxy-18 : H and/or (3*Z*,6*Z*)-*cis*-6,7-epoxy-18 : H in attraction of this species.

Two single captures of *Sicya macularia* were recorded during the 1983 field survey in traps baited with (3*Z*,6*Z*,9*Z*)-20 : H (400 μg) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20 : H (100 μg) and (3*Z*,6*Z*)-9*R*,10*S*-epoxy-19 : H (400 μg) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20 : H (100 μg). Although these captures are not meaningful on their own, the EAG profile of *S. macularia* (Figure 5) is very similar to that of the *Semiothisa* sp. and suggests the potential involvement of other monoepoxydiene isomers.

Multiple captures were obtained for three species of *Xanthorhoe* during 1983 and are shown in Table 10. All three species responded to lures consisting primarily of combined monoepoxydienes with exceptions of single captures of *X. abrasaria aquilonaria* and *X. munitata*. Again there was good correlation between field captures and EAG responses as exemplified by *X. iduata* (Figure 5). The EAG profile of *X. munitata* (not shown) is virtually identical to that of *X. iduata* with strongest responses recorded for the C_{20} and C_{21} homologs of CME-(3*Z*,6*Z*,9*Z*)-trienes. An EAG profile was not recorded for *X. abrasaria aquilonaria*.

The EAG profile of *Itame loricaria* (Eversmann) (Figure 5) is similar to the others in the figure except that responses are somewhat higher for (3Z,6Z,9Z)-trienes. Single captures of *I. loricaria* were obtained for 10 different lures consisting of (3Z,6Z,9Z)-trienes, combined monoepoxydienes, and specific epoxydiene enantiomers. A specific attractant was not discerned from these results. Unlike *Xanthorhoe* sp. and *Semiothisa* sp., whose field captures were predicted by their EAG profiles, the failure of field captures of *I. loricaria* to correspond to its EAG profile may indicate both attraction and inhibition by different epoxydiene isomers within the combined monoepoxydiene mixtures.

Multiple captures of *Eupithecia annulata* were recorded for several lures during 1983. While an EAG profile was not recorded, field captures (Table 11) indicated that *E. annulata* may belong to the group of moths that respond to epoxydienes other than the 9,10 isomers. However, the lack of response to the (9*R*,10*S*)- and (9*S*,10*R*)-epoxydienes does not rule out the possibility that a specific combination of the two enantiomers is responsible for attraction. CME-(3Z,6Z,9Z)-20 : H appears to be the strongest attractant and was not potentiated by other compounds tested in the survey.

Three single captures each of *E. rovocastaliata* (Packard) and *E. satyrata dodata* (Taylor) were recorded in the survey. All of the lures consisted of a (3Z,6Z,9Z)-triene (C_{19} or C_{21}) plus a specific epoxide enantiomer or CME mixture of the same chain length.

DISCUSSION

Our choice of potential attractants for field screening was based on the structures of pheromones for two noctuid species and several arctiid species.

TABLE 10. CAPTURE OF *Xanthorhoe abrasaria aquilonaria*, *X. iduata*, AND *X. munitata* IN SURVEY TRAPS

Lure composition (μg)	Total males captured		
	X. a. aquilonaria[a]	*X. iduata*[b]	*X. munitata*[c]
CME-(3*Z*,6*Z*,9*Z*)-21:H (100) + (3*Z*,6*Z*,9*Z*)-21:H (400)	5	7	0
(250) + (3*Z*,6*Z*,9*Z*)-21:H (250)	1	8	0
(400) + (3*Z*,6*Z*,9*Z*)-21:H (100)	0	1	2
(3*Z*,6*Z*,9*Z*)-19:H (250) + (3*Z*,6*Z*,9*Z*)-20:H (250)	1	0	0
CME-(3*Z*,6*Z*,9*Z*)-21:H (500)	0	0	3
(400) + CME-(3*Z*,6*Z*,9*Z*)-20:H (100)	0	0	1
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H (500)	0	0	2

[a] Total males captured in 2X replicated Pherocon 1CP traps from July 18 to August 4, 1983.
[b] Total males captured in 2X replicated Pherocon 1CP traps from July 4 to July 28, 1983.
[c] Total males captured in 2X replicated Pherocon 1CP traps from May 25 to June 3, 1983.

TABLE 11. CAPTURE OF *Eupithecia annulata* IN SURVEY TRAPS

Lure composition (μg)	Total males captured[a]
CME-(3*Z*,6*Z*,9*Z*)-18:H (400) + CME-(3*Z*,6*Z*,9*Z*)-19:H (100)	2
(100) + CME-(3*Z*,6*Z*,9*Z*)-19:H (400)	3
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-18:H (500)	1
CME-(3*Z*,6*Z*,9*Z*)-19:H (500)	2
(400) + (3*Z*,6*Z*,9*Z*)-19:H (100)	2
(400) + CME-(3*Z*,6*Z*,9*Z*)-20:H (100)	8
(250) + CME-(3*Z*,6*Z*,9*Z*)-20:H (250)	9
(100) + CME-(3*Z*,6*Z*,9*Z*)-20:H (400)	17
CME-(3*Z*,6*Z*,9*Z*)-20:H (500)	16
(400) + CME-(3*Z*,6*Z*,9*Z*)-21:H (100)	5
(250) + CME-(3*Z*,6*Z*,9*Z*)-21:H (250)	4
(100) + CME-(3*Z*,6*Z*,9*Z*)-21:H (400)	1
CME-(3*Z*,6*Z*,9*Z*)-21:H (400) + CME-(3*Z*,6*Z*,9*Z*)-22:H (100)	2
(3*Z*,6*Z*)-9*R*,10*S*-epoxy-21:H (400) + (3*Z*,6*Z*)-9*R*,10*S*-epoxy-20:H (100)	1
(3*Z*,6*Z*)-9*S*,10*R*-epoxy-19:H (250) + (3*Z*,6*Z*,9*Z*)-19:H (250)	1

[a] Total males captured in 2× replicated Pherocon 1CP traps from May 16 to June 30, 1983.

The discovery of (3Z,6Z,9Z)-21:H as a pheromone component for *Utetheisa ornatrix* (Conner et al., 1980), and the discovery of this compound together with (3Z,6Z,9Z)-20:H as pheromone components for *Anticarsia gemmatalis* (Hübner) (Heath et al., 1983) and *Caenurgina erechtea* (Underhill et al., 1983), revealed the methylene interrupted triene moiety which had not appeared in previously reported lepidopteran pheromones. The discovery of (3Z,6Z)-*cis*-9,10-epoxy-21:H as a pheromone component for the saltmarsh caterpillar moth, *Estigmene acrea* (Drury) (Hill and Roelofs, 1981), and the fall webworm moth, *Hyphantrea cunea* (Drury) (Hill et al., 1982) indicated the potential importance of monoepoxidized derivatives of the (3Z,6Z,9Z)-trienes as lepidopteran attractants.

Field screening of (3Z,6Z,9Z)-triene hydrocarbons and monoepoxydiene derivatives has resulted in the discovery of specific attractants for males of several species of geometrids from the two major subfamilies of Ennominae and Larentiinae. The specificity of response by captured species was very high, and for some species, *M. inatomaria*, *C. erythemaria*, *P. transversata*, and *D. brunneata ethela*, the ability to discriminate between opposite enantiomers or a particular ratio of enantiomers was clearly demonstrated by field captures and EAG responses. Although many examples of chiral insect pheromones are known (Brand et al., 1979), only two examples have been clearly identified for lepidopteran species. These are *cis*-7,8-epoxy-2-methyloctadecane (disparlure) from the gypsy moth (Bierl et al., 1970), and (*R*)-1-methybutyl decanoate from the bagworm moth, *Thyridopteryx ephemeraeformis* (Haworth) (Leonhardt et al., 1983). Some evidence for the involvement of chirality in the pheromone system of *E. acrea* and *H. cunea* has been reported (Hill and Roelofs, 1981; Hill et al., 1982). Tamaki et al. (1983) have also reported a chiral pheromone component, 10-methyldodecyl acetate, for the smaller tea tortrix moth. The results of our field screening, performed with compounds which have been identified as pheromone or homologs of pheromone, suggest a wider involvement of chirality in lepidopteran pheromone systems.

The data presented here and elsewhere (Heath et al., 1983; Underhill et al., 1983) also expands the structural group of chemicals associated with male noctuid sex attraction to include (3Z,6Z,9Z)-triene hydrocarbons and a number of their monoepoxydiene hydrocarbon analogs. Although only a few species were captured, our survey has increased the number of noctuid subfamilies linked to defined chemical attractants from nine to 13. Further field tests to improve lure efficiency and further define optimal chemical attractants for these noctuid and geometrid species are planned. On the basis of the data presented here, we believe that unsaturated hydrocarbons and monoepoxydiene derivatives may function as pheromones for some geometrid and noctuid species.

Acknowledgments—We are very grateful for the excellent technical assistance provided in this work and over the past several years by B.K. Bailey and S.J. Peesker, both of whom were involved in a fatal traffic accident while conducting these field experiments. We thank the staff of the Biosystematics Research Institute (Ottawa) for their generous assistance in identification of species.

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