SEX ATTRACTANTS OF GEOMETRID AND NOCTUID MOTHS: CHEMICAL CHARACTERIZATION AND FIELD TEST OF MONOEPOXIDES OF 6,9-DIENES AND RELATED COMPOUNDS

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Abstract—(*Z*,*Z*)-6,9-Dienes with straight C_{18} - C_{23} chains were synthesized from linoleic acid, and a C_{17} chain was synthesized by hydrogenation of the corresponding 6,9-diyne prepared from propargyl alcohol. Oxidation of the homoconjugated dienes with *m*-chloroperoxybenzoic acid yielded a 1:1 mixture of two monoepoxides that could be separated by repeated medium-pressure liquid chromatography with a Lobar column. The chemical structure of each positional isomer was confirmed by analyses of the ozonolysis products, and the isomers showed characteristic ¹³C signals in their NMR spectra and fragment ions in their El mass spectra. In addition to the (*Z*,*Z*,*Z*)-3,6,9-trieness with straight C_{18} - C_{23} chains and their monoepoxides, field tests using single source lures incorporating one of the above seven dienes and 14 monoepoxymonoenes were carried out in a forest in Tokyo from 1992 to 1994. Consequently, attraction of six geometrid species and five noctuid species was observed for the first time.

Key Words-Sex pheromone, lepidopterous attractant, field test, monoepoxymonoene, monoepoxydiene, mass spectrum, Geometridae, Noctuidae.

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INTRODUCTION

(Z,Z,Z)-3,6,9-Triunsaturated hydrocarbons and their monoepoxides have been identified as sex pheromone components of female moths, mainly in the families Geometridae and Arctiidae (Arn et al., 1992). Furthermore, field screening tests in Canada, Europe, and Japan using synthetic compounds revealed that the trienes and monoepoxydienes attracted not only geometrid species but many noctuid species belonging to the subfamilies Catocalinae, Ophiderinae, Hyperminae, and Herminiinae (Arn et al., 1992; Ando et al., 1993). Recently Ohmasa et al. (1991) reported the major pheromone component of Oraesia excavata Butler (Noctuidae: Ophiderinae) to be (Z)-6-cis-9,10-epoxyheneicosene. Furthermore, the nonadecene analog was tentatively identified from the female gland of Anacamptodes humaria Guenée (Geometridae: Ennominae) by Millar et al. (1991). These results indicate that the monoepoxides of (Z,Z)-6,9-diunsaturated hydrocarbons constitute one group of the lepidopterous sex pheromones. This paper deals with the syntheses and chemical characterizations of monoepoxymonoenes and with their field attractancy as evaluated in a forest in Tokyo, in addition to the parent dienes, (Z,Z,Z)-3,6,9-trienes, and their monoepoxides.

METHODS AND MATERIALS

Synthesis of 6,9-Dienes. Homoconjugated dienes with straight C_{18} - C_{23} chains (Z6,Z9-18:H, Z6,Z9-19:H, and so on)⁴ were synthesized starting from linoleic acid by the same method described for 3,6,9-trienes starting from linolenic acid (Ando et al., 1993). Z6,Z9-17:H was synthesized as shown in Scheme 1. After protecting the hydroxyl group, propargyl alcohol (1) was alkylated with 1-bromoheptane to yield THP ether of 2-decyn-1-ol (2). The THP

⁴Compounds are abbreviated as described in our previous paper (Ando et al., 1993) as follows: Z6,Z9-18:H is (6Z,9Z)-6,9-octadecadiene, epo6,Z9-17:H is (Z)-9-cis-6,7-epoxyheptadecene.



SCHEME 1. Synthetic route of (6Z,9Z)-6,9-heptadecadiene (Z6,Z9-17:H). a: 3,4-dihydro-2*H*-pyran/*p*-TsOH, b: *n*-BuLi/dry THF, and *n*-C₇H₁₅Br/HMPA, c: *p*-TsOH/EtOH, d: MsCl/Et₃N/CH₂Cl₂, e: LiBr/THF, f: *n*-C₅H₁₁C \equiv CMgBr/CuCl/dry THF, g: H₂/Pd-BaSO₄-quinoline/*n*-hexane.

protectional group was removed by acid, and the alcohol (3) was converted to 1-bromo-2-decyne (4) (37% yield from 1) via the mesylate. The bromide (4) was coupled with hept-1-ynylmagnesium bromide, which was prepared with 1-heptyne and ethylmagnesium bromide, in the presence of copper chloride yield-ing 6,9-heptadecadiyne (5) (80% yield from 4). Partial hydrogenation of the diyne (5) to Z6,Z9-17: H was achieved using Pd-BaSO₄ catalyst poisoned with quinoline (86% yield).

Synthesis and Separation of Monoepoxides of 6,9-Dienes. A mixture of epo6, Z9-17: H and Z6, epo9-17: H in a ratio of ca. 1:1 was obtained by oxidation of Z6, Z9-17: H with m-chloroperoxybenzoic acid (MCPBA). The two positional isomers were separated by a medium pressure liquid chromatographic system (MPLC), the components of which were a solvent pump (Yanaco L4000W liquid chromatograph), a Lobar column (Merck LiChroprep Si 60, 10 mm ID \times 240 mm, 40-63 μ m), and an RI detector (Shimadzu RID-2A). Although the mixture (50 mg) applied to the MPLC using 1.0% tetrahydrofuran (THF) in *n*-hexane as a solvent (flow rate: 2.0 ml/min) showed only one peak $(R_t = 77.5 \text{ min})$, even in a recyclic mode (two times), the first half (fraction 1, 70.0-77.5 min) and the latter half (fraction 2, 77.5-83.0 min) of the eluent were recovered separately. By repeating this MPLC separation two more times, we obtained two fractionated compounds [8 mg of each with purity >95% by GC (i.e., TIC trace from GC-MS)], and their chemical structures were determined by ozonolysis experiments. Ozone was passed into the *n*-hexane (1 ml) solution of each compound (ca. 0.1 mg), cooled in a Dry Ice-acetone bath for 1 min, and an aliquot $(1 \mu l)$ of the solution was injected into a capillary column of the GC-MS to analyze the aldehydes, which were produced from the ozonides by heat. Mixtures of two monoepoxides of other diunsaturated hydrocarbons $(C_{18}-C_{23})$ were prepared and separated into two fractions in the same manner. Their structures were determined also by the GC-MS analyses of ozonolysis products.

Synthesis of 3,6,9-Trienes and Their Monoepoxides. Trienes and their monoepoxides with $C_{19}-C_{21}$ chains had been synthesized (Ando et al., 1993). Compounds with C_{22} and C_{23} chains were prepared by the same method, except for utilizing the bromo derivative of linolenic alcohol in a Grignard-type coupling reaction instead of a tosyl derivative (Fukumoto and Yamamoto, 1992). To yield Z3,Z6,Z9-18:H, the tosyl derivative was mixed with LiAlH₄ in dry THF and stirred for one night. The triene was also converted to the 1:1:1 mixture of monoepoxydienes by MCPBA oxidation. These positional isomers were separated more easily by the MPLC with the Lobar column than by the preparative TLC. With a solvent of 1.0% THF in *n*-hexane (flow rate: 2 ml/min), they were well separated from each other after one recycle ($R_1 = 62.3$ min for epo3,Z6,Z9-18:H; 48.5 min for Z3,epo6,Z9-18:H; and 55.9 min for Z3,Z6,epo9-18:H). Monoepoxydienes with C_{22} and C_{23} chains were also separated by the MPLC purification.

Spectroscopy. The NMR spectrum of each compound in CDCl₃ was analyzed with a JEOL EX 270 Fourier transform spectrometer (270.2 MHz for ¹H and 67.9 MHz for ¹³C) using TMS as an internal standard. Electron impact (EI) GC-MS was performed with a JEOL JMS-SX102A mass spectrometer containing a DB-1 capillary column (0.25 mm ID \times 30 m, J&W Scientific). The ionization voltage of every measurement was 70 eV. The ion source temperature was 240°C, and the column temperature program was 40°C for 1 min, 50°C/min to 150°C, and finally 8°C/min to 300°C.

Field Evaluation. In the same manner reported previously (Ando et al., 1993), screening tests with seven 6,9-dienes (C_{17} - C_{23}), six 3,6,9-trienes (C_{18} - C_{23}), and their monoepoxides were carried out from August 1992 to July 1994 in a mixed forest area in the suburbs of Tokyo (Rolling Land Laboratory, Tokyo University of Agriculture and Technology, Hachioji-shi, Tokyo). Each chemical at 1 mg with purity >95% by GC was applied to a rubber septum, which was placed in a sticky-type trap (30 × 27-cm bottom plate with a roof, Takeda Chemical Ind., Ltd., Osaka, Japan). Two traps were used for each chemical.

RESULTS AND DISCUSSION

Characterization of Synthetic Compounds

Identification of Monoepoxides of 6,9-Dienes. Ozonolysis of the compound, which was collected as fraction 1 from the monoepoxides of Z6,Z9-17: H by a Lobar MPLC column, produced 3,4-epoxyundecanal with M^+ at m/z 184 (4%) and characteristic fragment ions at m/z 85 (95%), 127 (63%), 155 (12%), and 166 (19%), while *n*-hexanal, the counterpart of 3,4-epoxyundecanal, was not detected. This small aldehyde eluted from the GC column before starting the measurement of mass spectra. In contrast, ozonolysis of fraction 2 generated two aldehydes, 3,4-epoxynonanal with M^+ at m/z 156 (8%) and fragment ions at m/z 85 (84%), 99 (61%), 127 (22%), and 138 (18%); and *n*-octanal with M^+ at m/z 128 (1%) and fragment ions at m/z 99 (40%) and 110 (29%). These results showed that the compound in fraction 1 is Z6,epo9-17: H and that in fraction 2 is epo6,Z9-17: H. The chemical structures of monoepoxides with $C_{18}-C_{23}$ chains were also determined by the same ozonolysis experiments, and it was revealed that 9,10-epoxides were recovered in fraction 1 and 6,7-epoxides in fraction 2.

It is difficult to distinguish between 6,7-epoxides and 9,10-epoxides by ¹H NMR measurements, since these compounds include a common functional group, an epoxy ring homoconjugated with C=C bond. In ¹³C NMR, however, chemical shifts of some signals of 6,7-epoxides are different from those of the corresponding carbons of 9,10-epoxides, and the ¹³C NMR spectrum of the crude

products of MCPBA oxidation represented some paired signals. Table 1 shows the 13 C NMR assignments (C-1 to C-12) for monoepoxymonoenes of the two types, which were accomplished by two-dimensional experiments and by referring to the 13 C NMR data of monoepoxydienes. In this table, carbons from position 4 to position 12 of the 6,7- and 9,10-epoxides are arranged conversely in order to compare the shift values of each carbon in the common structure represented with C-a to C-h (see the footnote of Table 1). Although the epoxy ring and olefinic carbons (C-c, C-d, C-f, and C-g) of the two positional isomers were at the same chemical shift values, each signal of the C-1, C-a, and C-b of the 6,7-epoxides appeared at a higher field than the corresponding signal of the 9,10-epoxides, and each signal of C-2, C-3, and C-h at a lower field. Particular differences of the shift values of C-3 and C-a are about 0.3 ppm; therefore the synthetic monoepoxide of 6,9-dienes can be identified based on the values of these 13 C signals.

MS Analyses of Monoepoxides of 6,9-Dienes. In EI-MS measurements, each monoepoxide of 6,9-dienes showed M⁺ and [M-18]⁺ ions with the relative intensities of ca. 5 and 10%, respectively. Reflecting the chemical structures, several abundant fragment ions are expected to be produced after the EI ionization as shown in Figure 1. While ions at m/z 71, 153 M-71, and M-153 are listed for both 6,7- and 9,10-epoxides in common, ions at m/z 99, 113, 127, M-127, M-114, and M-100 are nominated as characteristic fragments for the 6,7-epoxides and ions at m/z 97, 110, 124, M-125, M-111, and M-97 for the 9,10-epoxides. Their relative intensities, which were measured in this experiment, are listed in Table 2. Among them, ions at m/z 99, M-114, and M-100 are actually observed to be stronger in 6,7-epoxides, and ions at m/z 124, M-125, and M-111 in 9,10-epoxides than the other epoxides. 6,7-Epoxides showed smaller R_i , than the corresponding 9,10-epoxides on a DB-1 capillary column (see Table 2). These two types of monoepoxymonoenes are distinguished from each other by using a capillary GC-MS system according to their chromatographic behavior and the above characteristic fragment ions.

Fragmentation at the epoxy ring produces ions at m/z 99 from 6,7-epoxides and at m/z 124 from 9,10-epoxides, including a moiety composed of C-1 to C-6 and C-1 to C-9, respectively, and ions at m/z M-100 from 6,7-epoxides and at m/z M-125 from 9,10-epoxides including a terminal carbon. Cleavage of the bond between the allylic carbon and the epoxy ring carbon produces ions at m/z M-114 from 6,7-epoxides and at m/z M-111 from 9,10-epoxides. When one pays attention to the three pairs of ions and divides the intensity of the latter ion by that of the former ion, namely [124]/[99], [M-125]/[M-100], and [M-111]/ [M-114], the intensity ratios of 6,7-epoxides are less than or equal to 1.0, and those of 9,10-epoxides are larger than 1.0 as shown in Table 3. The main pheromonal component of *O. excavata* is Z6,epo9-21: H, the chemical structure

					Ð	nemical shift	(mdd)				
	C-1	C-2	C-3	C-4(a)	C-5(b)	C-6(c)	C-7(d)	C-8(e)	C-9(f)	C-10(g)	C-11(h)
6.7-Epoxide											
epo6.Z9-17:H ^h	14.01	22.60	31.77	26.30	27.76	57.24	56.58	26.24	123.81	132.72	27.46
epo6.Z9-18:H	14.01	22.60	31.75	26.30	27.75	57.24	56.58	26.22	123.80	132.72	27.46
epo6,29-19:H	14.01	22.59	31.76	26.29	27.75	57.25	56.57	26.22	123.82	132.71	27.45
epo6,Z9-20:H	14.01	22.60	31.77	26.30	27.76	57.25	56.58	26.24	123.81	132.74	27.46
epo6,Z9-21:H	14.01	22.61	31.77	26.30	27.75	57.25	56.59	26.24	123.81	132.74	27.47
epo6.29-22 : H	14.01	22.61	31.77	26.31	27.78	57.25	56.59	26.24	123.81	132.74	27.47
epo6,Z9-23 : H	14.02	22.62	31.77	26.31	27.77	57.27	56.59	26.24	123.82	132.74	27.48
	C-1	C-2	C-3	C-12(a)	C-11(b)	C-10(c)	C-9(d)	C-8(e)	C-7(f)	C-6(g)	C-5(h)
9,10-Epoxide											
Z6,epo9-17:H	14.07	22.57	31.52	26.62	27.79	57.24	56.58	26.24	123.83	132.72	27.43
Z6,epo9-18:H	14.07	22.57	31.51	26.62	27.79	57.25	56.58	26.24	123.83	132.72	27.43
Z6,epo9-19:H	14.06	22.57	31.51	26.62	27.81	57.24	56.58	26.25	123.84	132.72	27.43
Z6,epo9-20:H	14.07	22.57	31.51	26.62	27.79	57.25	56.58	26.24	123.83	132.72	27.43
Z6,epo9-21:H	14.06	22.57	31.51	26.62	27.81	57.24	56.58	26.23	123.84	132.72	27.43
Z6.epo9-22 : H	14.07	22.57	31.52	26.62	27.81	57.24	56.58	26.24	123.83	132.72	27.43
Z6,epo9-23 : H	14.06	22.57	31.51	26.62	27.80	57.24	56.58	26.24	123.83	132.73	27.43
"Dienes including th	e common	structure re	unrecented v	vith: C.aC		ہ- <u>ر</u> - ہے- ر- ہ	- م-ن- =				
0) ; ;)) 0))	-			

Table 1. ¹³C NMR Assignments for Monoepoxides of 6,9-Dienes⁴

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^bC-12 to C-14 ~ 29.5 ppm, C-15 31.86 ppm, C-16 22.68 ppm, C-17 14.12 ppm.



FIG. 1. Fragmentation proposed for 6,7-epoxides (A), and 9,10-epoxides (B) of 6,9dienes with $C_{17}-C_{23}$ chains after initial EI ionization at the epoxy oxygen and C=Cbond. Diagnostic ions shown in squares were used in the calculation for Table 3. Molecular ions: C_{17} compounds ($R = n-C_6H_{13}$), m/z 252; C_{18} compounds ($R = n-C_7H_{15}$), m/z 266; C_{19} compounds ($R = n-C_8H_{17}$), m/z 280; C_{20} compounds ($R = n-C_9H_{19}$), m/z294; C_{21} compounds ($R = n-C_{10}H_{21}$), m/z 308; C_{22} compounds ($R = n-C_{11}H_{23}$), m/z322; C_{23} compounds ($R = n-C_{12}H_{25}$), m/z 336.

of which has been identified by ozonolysis and other experiments (Ohmasa et al., 1991). The values of the ratios calculated from the published mass spectrum of the natural pheromone are larger than 1.0 (see Table 3), indicating that it is a 9,10-epoxide. Because these three ratios reflect the position of the epoxy ring, the structure of monoepoxymonoenes of 6,9-dienes can be reliably estimated by examining the intensity ratios.

Characterization of Monoepoxides of 3,6,9-Trienes. The chromatographic behavior of the monoepoxydienes with C18, C22, and C23 chains on a normalphase MPLC correspond to those of the C19-C21 monoepoxydienes on a normalphase TLC plate (Ando et al., 1993). NMR data of the compounds possessing the epoxy ring at the same position are almost the same except for the methylene signals of the long chains. The intensity of the methylene proton signals at ca. 1.3 ppm and the number of methylene carbon signals at ca. 29.5 ppm depends on the chain length. On EI-MS, fragmentation properties of the compounds previously synthesized (Ando et al., 1993) were also observed in the spectra measured for the new compounds as follows: ions at m/z M-29, M-72, and 79 for 3,4-epoxides; at m/z M-29, M-69, and 111 for 6,7-epoxides, and at m/zM-29, M-69, M-109, 108, and 79 for 9,10-epoxides. These results confirmed that these are diagnostic ions for identifying epoxydienes with C₁₈-C₂₃ chains from a natural pheromone extract. By further examination of these spectra, it was revealed that other diagnostic ions, which were produced by fragmentation at the epoxy ring, were additionally characterized as follows: ions at m/z M-58 for 3,4-epoxides, at m/z 97 and M-83 for 6,7-epoxides, and at m/z 122 and M-123 for 9,10-epoxides.

	Q	Base	t M							Rel	ative i	ntensity o	of fragme	nt ions, n	(%) 2/4			:	
	(min)	(<i>z/m</i>)	(12/m)	71	79	66	110	113	124	127	153	M-153	M-127	M-125	M-114	M-111	M-100	79-M	M-71
6.7-Epoxide																			
epo6,Z9-17:H	7.53	81	252	21	48	52	48	23	20	01	17	21	œ	10	27	27	10	7	12
epo6,Z9-18:H	8.46	67	266	28	56	36	33	53	30	10	61	23	6	5	24	16	13	-	11
epo6.29-19:H	9.43	81	280	49	63	85	33	58	20	×	12	8	12	4	17	Н	7	-	13
epo6,Z9-20:H	10.42	67	294	35	46	4	29	35	15	5	12	_	9		6	9	4	-	8
epo6.Z9-21:H	11.48	96	308	35	58	56	46	47	59	×	14	-	4	7	16	13	4		,
epo6,Z9-22:H	12.46	81	322	40	57	49	33	34	21	2	13	Ι	4		8	5	4		6
epo6,Z9-23:H	13.49	67	336	5	48	96	38	45	53	01	17	2	7	2	=	9	7		15
9,10-Epoxide																			
Z6.epo9-17:H	7.54	69	252	17	37	×	56	35	26	10	12	×	Ξ	15	9	12	m	4	13
Z6,epo9-18:H	8.48	81	266	28	45	16	80	23	37	9	22	Ξ	10	21	7	21	2	10	15
Z6.epo9-19:H	9.47	81	280	38	49	6	67	24	26	m	81	ŝ	18	38	e	29	CI	9	12
Z6.epo9-20:H	10.47	81	294	28	43	=	4	19	21	¢1	13	-	4	16	61	16	-	7	10
Z6.epo9-21:H	11.52	81	308	33	50	17	11	32	31	ŝ	20	5	×	24	2	27	7	S	13
Z6,epo9-22:H	12.50	81	322	29	46	7	51	20	24	ŝ	01	0	7	14	-	13		3	6
Z6.epo9-23:H	13.54	8	336	48	4	10	55	17	24	ŝ	18	-	0	38	£,	21	-	9	×
"Each compound wa min, 150°C to 300	ts chroma °C at 8°t	ttograph C/min,	hed on a and 300	DB-1	capi min)	llary . and	colum the N	n (0.2 1S spe	5 mm ctrum	i.d. × was n	c 30 m neasure) under p ed by El	rogramed ionizatior	temperat operated	ure (40°C 1 at 70 eV	C 1 min.	40°C to 1	50°C at	50°C/

TABLE 2. GC-MS DATA OF MONOEPOXIDES OF 6,9-DIENES"

		Intensity ratio									
	AND 2 40.0	Sy	nthetic n	ionoepox	ymonoei	ne"		Natural pheromone ⁶			
Ratio, [ion]/[ion]	C ₁₇	C18	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₁			
6,7-Epoxide											
[124]/[99]	0.9	0.8	0.2	0.3	0.5	0.4	0.2				
[M-125]/[M-100]	1.0	0.4	0.6	0.3	0.5	0.3	0.3				
[M-111]/[M-114]	1.0	0.7	0.6	0.7	0.8	0.6	0.5				
9,10-Epoxide											
[124]/[99]	3	2	3	2	2	3	2	2			
[M-125]/[M-100]	5	11	19	16	12	14	38	65			
[M-111]/[M-114]	2	3	10	8	5	13	7	10			

TABLE 3. INTENSITY RATIOS OF SOME CHARACTERISTIC FRAGMENT IONS OBSERVED IN
Mass Spectra of Synthetic Monoepoxides of 6,9-Dienes and a Main Component
OF NATURAL PHEROMONE OF Oraesia excavata

"Spectra were measured with a JEOL JMS-SX102A mass spectrometer operated at 70 eV.

^bSpectrum was measured with a JEOL JMS-D300 mass spectrometer operated at 70 eV (Ohmasa et al., 1991).

Sex Attractants Discovered by Screening Tests

Field Evaluation from 1992 to 1994. By the field screening tests of 6,9dienes, 3,6,9-trienes, and monoepoxydienes with C_{19} - C_{21} chains, sex attractants for 14 geometrid and four noctuid species had already been found in Japan (Ando et al., 1993). This time field evaluation mainly with their C₁₈, C₂₂, and C_{23} chain analogs and monoepoxymonoenes with chains from C_{17} to C_{23} showed attraction of male moths of another six geometrid and five noctuid species. Table 4 lists the scientific names of the new attracted insects, the abbreviated names of the attractants, the time of flight, and the total number of moths captured by dual traps. All of the six geometrid species belong to the subfamily Ennominae. Recently sex pheromones were investigated in geometrid moths closely related to three of these species. Two C17 components, epo3,Z6,Z9-17:H and Z3,Z6,Z9-17:H, have been identified as sex pheromone components from the pheromone gland of Abraxas grossulariata L., the 10:1 mixture of which attracted the male moths (Tóth et al., 1992), while the corresponding C₁₈ epoxide epo3,Z6,Z9-18:H attracted A. niphonibia in our field test. Other sex pheromones, Z3,epo6,Z9-18: H and Z3,Z6,Z9-18: H, have been identified from the gland extract of Ectropis obliqua Prout (Yao et al., 1991) in China. The monoene derivative epo6, Z9-18: H more effectively attracted E. excellens than the

Family, subfamily, and species	Attractant	Time	flight	Attracted moths (N)
Geometridae				
Ennominae				
Abraxas niphonibia Wehrli	epo3,Z6,Z9-18:H	June		17
Colotois pennaria ussuriensis Bang-Haas ^a	Z3,epo6,Z9-20:H	NovE	Dec	99
Ectropis excellens (Butler)	epo6,Z9-18:H	Apr.	ж.	291
-	Z3,epo6,Z9-18:H			38
	Z6,epo9-18:H			16
Erannis golda Djakonov	Z3,epo6,Z9-18:H	Dec.		6
Menophra senilis (Butler)	epo6, Z9-19: H	AprN	lay	27
Rhynchobapta cervinaria bilineata (Leech)	Z6,Z9-17:H	Aug.		6
Synegia esther Butler	Z6, Z9-21: H	Sep.		10
Noctuidae				
Ophiderinae				
Hypenomorpha calamina (Butler)	Z6,epo9-20:H	June		74
Neachrostia bipuncta Sugi	Z3,Z6,Z9-18:H	SepO	ct.	21
Pangrapta trimantesalis (Walker)	Z3,Z6,epo9-23:H	AugS	ep.	13
Rivula leucanioides (Walker)	Z3,epo6,Z9-18:H	OctN	ov.	11
Herminiinae				
Adrapsa notigera (Butler)	Z3,epo6,Z9-23:H	AugS	ep.	97
-	Z3.epo6,Z9-22 : H	-		14

TABLE 4. SEX ATTRACTANTS DETECTED IN FIELD SCREENING TESTS IN A FOREST IN TOKYO FROM 1992 TO 1994

^aThis species was attracted by epo3,Z6,Z9-20:H and Z3,epo6,Z9-19:H in our previous field tests (Ando et al., 1993).

monoepoxydiene in Japan. The mixture of two C_{19} pheromone components, Z3,epo6,Z9-19:H and Z3,Z6,Z9-19:H (10:3), attracted *Erannis defoliaria* Clerck (Hansson et al., 1990). In this test the C_{18} compound Z3,epo6,Z9-18:H caught males of *E. golda*. Sex pheromones and attractants have not been reported so far for any species in the same genera as the other three species, *Menophra senilis* Butler, *Rhynchobapta cervinaria bilineata* Leech, and *Synegia esther* Butler. In addition to these six species, *Colotois pennaria ussuriensis* Bang-Haas is also listed in this table, since Z3,epo6,Z9-20:H attracted this species more strongly in the winters of 1992 and 1993 than epo3,Z6,Z9-20:H and Z3,epo6,Z9-19:H, which had been announced to be its attractant in the field evaluation in 1991 (Ando et al., 1993).

Noctuid species attracted in this test are Hypenomorpha calamina Butler, Neachrostia bipuncta Sugi, Pangrapta trimantesalis Walker, Rivula leucanioides Walker, and Adrapsa notigera Butler. The first four species belong to the subfamily Ophiderinae, and the last to Herminiinae. Although sex attractants of the species in the genus *Rivula (R. propinqualis, R. sericealis, and R. sasaphila)* are now known (Millar et al., 1990; Ando et al., 1993), no reports have been published concerning the pheromones and attractants of the moths in the other genera—Hypenomorpha, Neachrostia, Pangrapta and Adrapsa.

Structural Peculiarities of Discovered Sex Attractants. By field trials from 1991 to 1994, we finished the evaluation of 3,6,9-trienes with C_{18} - C_{23} chains, 6,9-dienes with C_{17} - C_{23} chains, and all of their monoepoxides. These systematic tests in Japan revealed the sex attractants for a total of 29 species. Although lepidopterous sex pheromones are usually composed of multiple components, not a few species were successfully attracted by single-source lures. The peculiarities of their chemical structures are summarized in Table 5. The number of the species attracted by the trienes and the monoepoxides (monoepoxydienes) is larger than that by the dienes and the monoepoxides (monoepoxymonoenes), and the epoxides attracted more species than the parent hydrocarbons. In particular, a considerable number of noctuid species were trapped by the lures baited with monoepoxydienes. By field evaluation of monoepoxymonoenes of C_{17} - C_{21} in Saskatoon (Canada), Millar et al. (1991) observed attraction of four geometrid species. Our test of the monoepoxymonoenes in Japan showed attrac-

		Geomet	Noctuidae				
Attractant	Ennominae	Oenochrominae	Geometrinae	Larentiinae	Ophiderinae	Herminiinae	Tota
Functional	· · · · · · · · · · · · · · · · · · ·						
group							
Triene	0	1	2	3	1	0	7
Monoepoxy-							
diene	6	2	0	1	5	2	16
Diene	2	0	1	0	0	0	3
Monoepoxy-							
monoene	2	0	0	0	i	0	3
Carbon length							
of chain							
C ₁₇	1	0	0	0	0	0	1
C ₁₈	3	0	0	0	2	0	5
CI9	3	1	0	2	2	0	8
C ₂₀	1	0	3	0	1	1	6
C ₂₁	2	2	0	2	1	0	7
C ₂₂	0	0	0	0	0	0	0
C23	0	0	0	0	1	1	2

 Table 5. Number of Lepidopterous Species, Sex Attractants Found to be Unsaturatei

 Hydrocarbons, and Their Monoepoxides by Field Screening Tests in Japan

tion of two other geometrid species and, interestingly, one noctuid species. While the number of the species attracted by monoepoxymonoenes is much smaller than those attracted by monoepoxydienes, these results indicate that the monoepoxymonoenes are also important pheromonal components of the geometrid and noctuid species.

Carbon lengths of the sex attractants discovered in Japan are mainly C_{18} - C_{21} . Since monoepoxydienes of C_{17} have not been tested, it cannot be concluded that the C_{17} compounds are novel for Japanese Lepidoptera. A biosynthetic pathway has been proposed for the hydrocarbons with a homoconjugated polyene system and their monoepoxides (Rule and Roelofs, 1989). Starting from the fatty acids with the polyene system, linoleic and linolenic acids, which commonly occur in insects, these compounds might be biosynthesized by a combination of chain elongation and reductive decarboxylation. When the chain elongation proceeds only with acetyl CoA, compounds with carbons of odd numbers are selectively produced. However, not a few hydrocarbons and epoxides with an even carbon chain are recognized as pheromone components (Arn et al., 1992). More than one third of the attractants found in our experiments have an even-number carbon chain. It is necessary to understand well the biosynthetic pathways of the geometrid and noctuid pheromones.

Our field tests utilized a racemic mixture of *cis*-epoxides. It is desirable to examine the attractancy of optically pure samples. Another valuable method to obtain further information about the geometrid and noctuid pheromones is the evaluation of multicomponent lures.

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