

**The 3rd International Symposium on
Insect Pheromones
Sweden, 2003 May**

Session II

**Lepidopteran Epoxyalkenyl Pheromones :
Synthesis and Identification**

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Graduate School of BASE

I. Introduction

Lepidopterous sex pheromones: 500 species

Sex attractants: 1200 species

Type I

Unsaturated fatty alcohols, acetates, and aldehydes derivatives (C_{10} - C_{18})



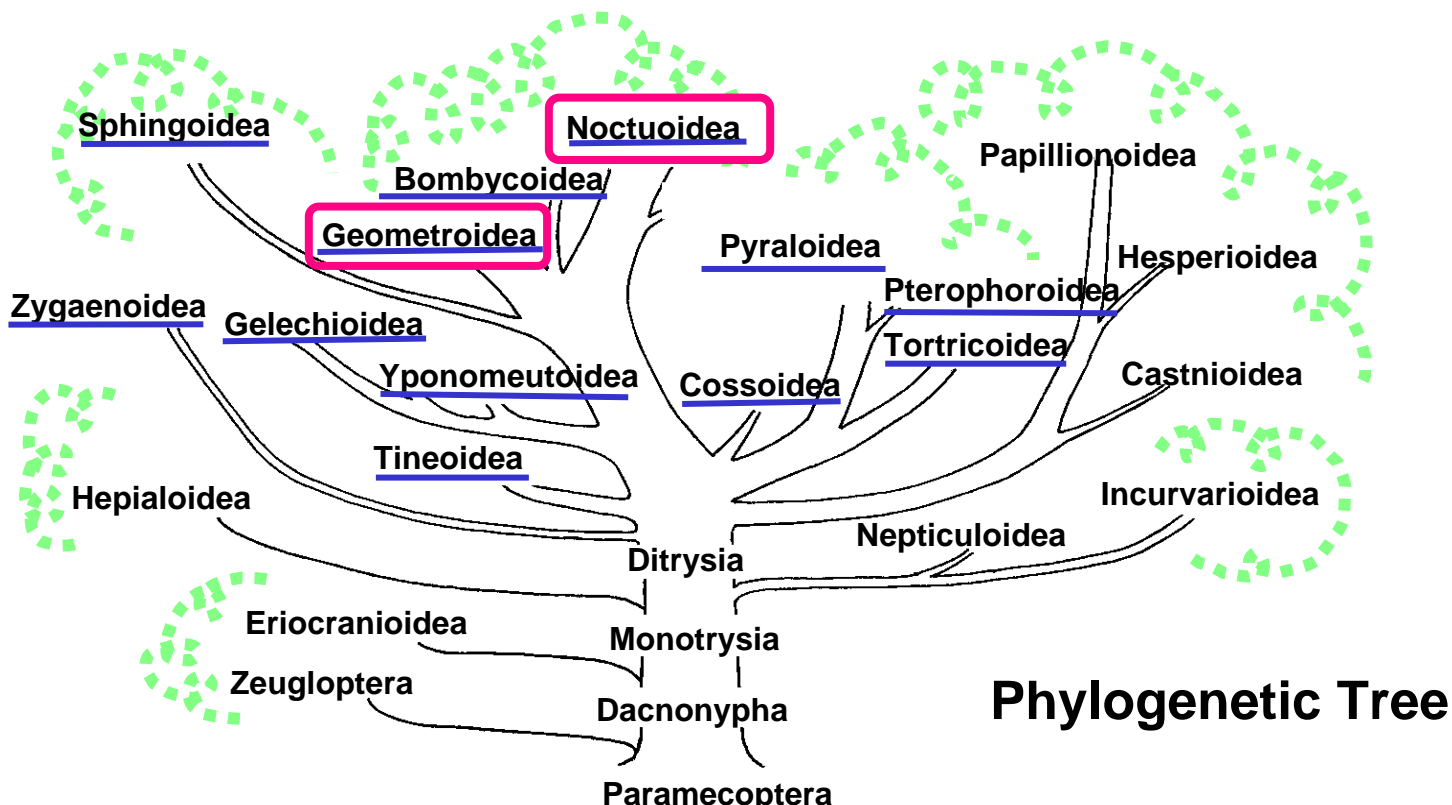
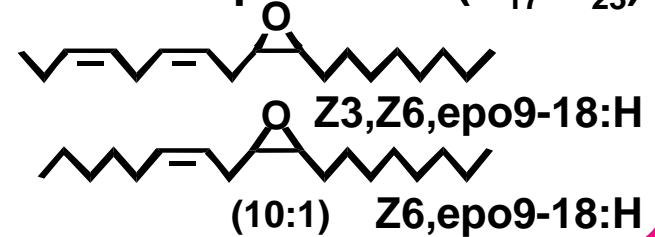
silkworm moth



Type II

(3Z,6Z,9Z)-trienes, (6Z,9Z)-dienes, and their monoepoxides (C_{17} - C_{23})

mulberry looper



I. Introduction

(A) Identification of natural pheromones

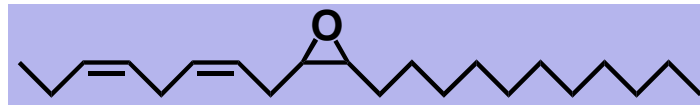
Hill *et al.*, (1981) *J. Chem. Ecol.*, 7: 655

saltmarsh caterpillar moth (*Estigmene acrea*; Arctiidae)

Z3,Z6,epo9-21:H

+ Z9,Z12,Z15-18:Ald

+ Z9,Z12-18:Ald (27:6:1)

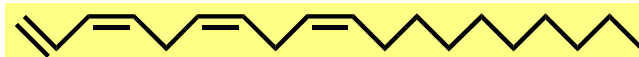


Roelofs *et al.*, (1982) *Science*, 217: 657

Bestmann *et al.*, (1982) *Tetrahedron Lett.*, 23: 4007

winter moth (*Operophtera brumata*; Geometridae)

1,Z3,Z6,Z9-19:H



(B) Systematic synthesis and field evaluations

Millar *et al.*, (1990) *J. Chem. Ecol.*, 16: 2307, 16: 2317

Millar *et al.*, (1991) *J. Chem. Ecol.*, 17: 911

Ando *et al.*, (1993) *J. Chem. Ecol.*, 19: 787

I. Introduction

Studies on Epoxyalkenyl Pheromones

by Chemical Ecology Laboratory in TUAT

(1) Systematic synthesis and field evaluations

Racemates of epoxydienes and epoxymonoenes

Optical resolution by chiral HPLC

(2) Identification of natural pheromones

Typical components from geometrid and noctuid moths

Novel components from lymantriid moths

(3) Biosynthesis

Biosynthetic pathway, substrate specificity, endocrine control

(4) Application for pest control

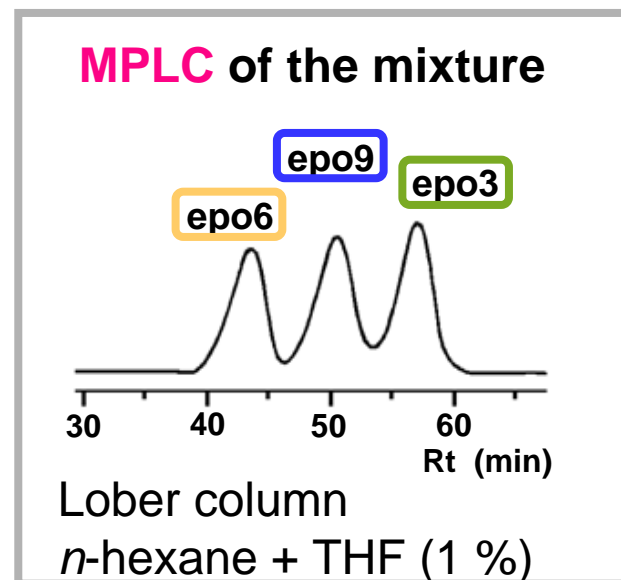
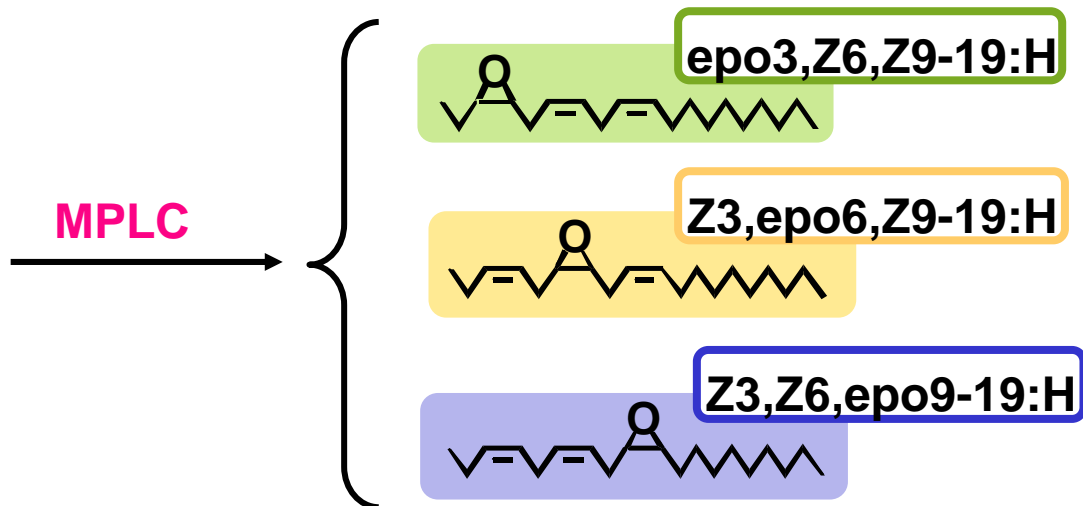
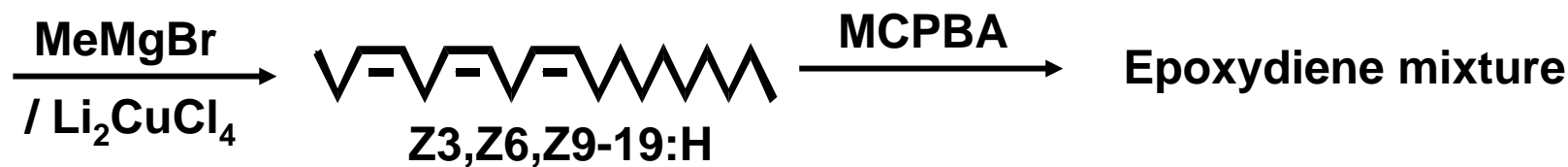
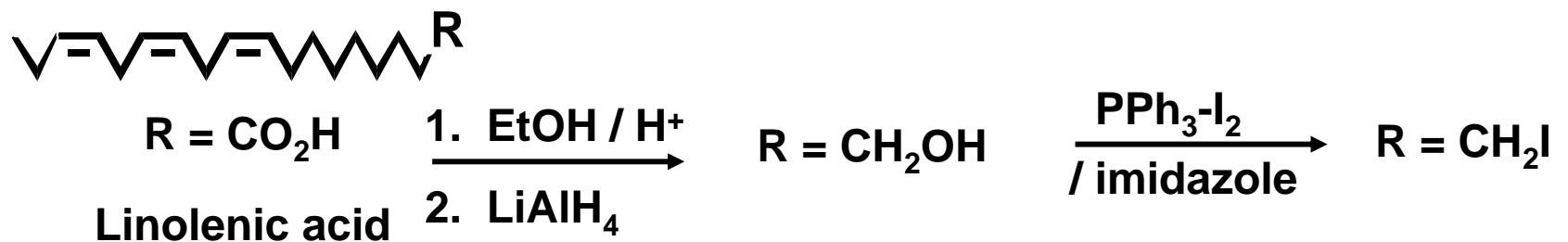
Monitoring tool, disruption



Session III

II. Synthesis and Field Evaluation

(A) Synthesis of racemic epoxyalkadienes



II. Synthesis and Field Evaluation

(B) Sex pheromones and attractants

Known sex pheromone

+ Attractant found
in Japan

Chain length	Diene Z6,Z9	Epoxymonoene	
		epo6,Z9	Z6,epo9
17	no +G(1)	no	no
18	no	no +G(1)	G(1)
19	G(2)	G(2) +G(1)	no
20	G(1),A(1) +G(1)	no	no +N(1)
21	G(1),N(2),A(3) +G(1)	no	N(1),A(1)
22	no	no	no
23	no	no	no

G: Geometridae

N: Noctuidae

L: Lymantriidae

A: Arctuiidae

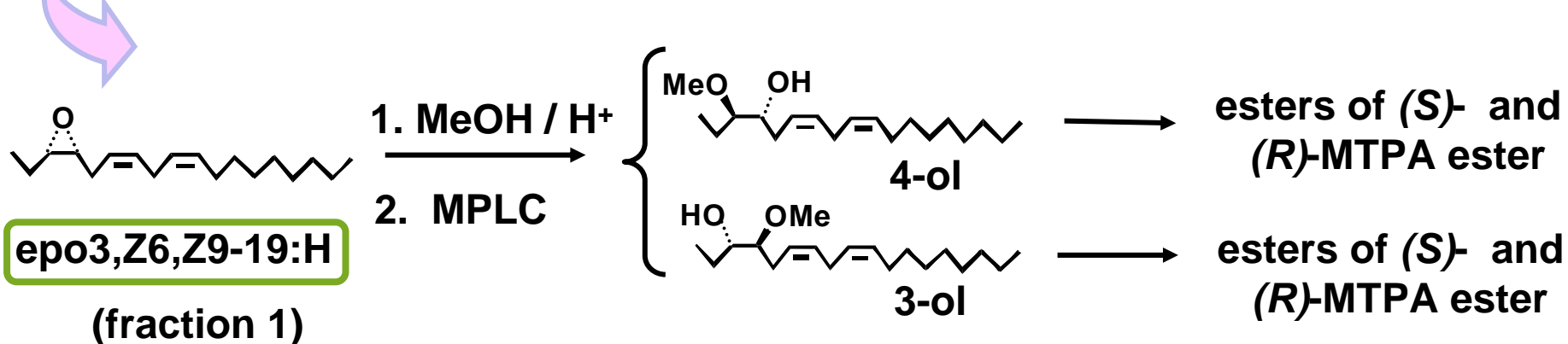
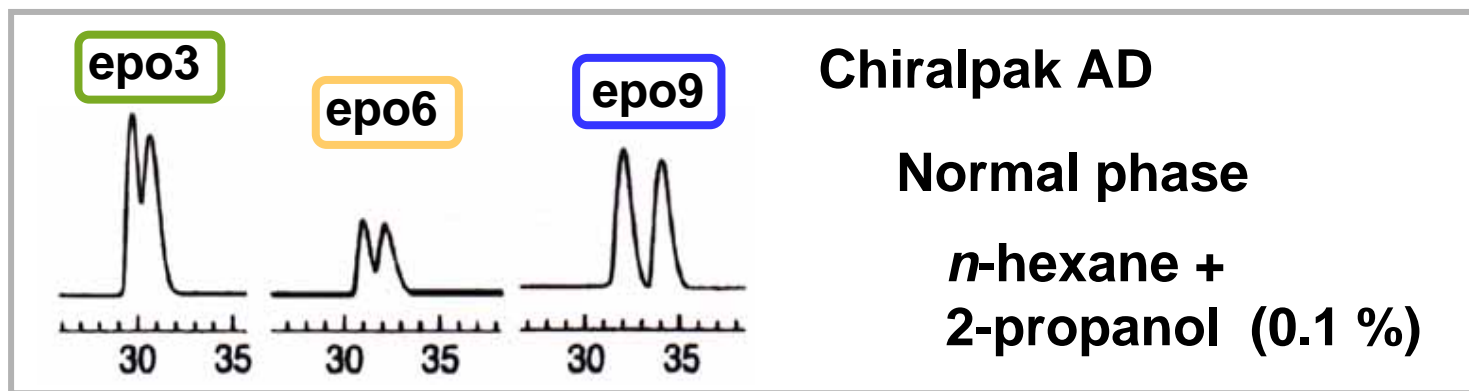
P: Pyralidae

Chain length	Triene Z3Z6,Z9	Epoxydiene		
		epo3,Z6,Z9	Z3,epo6,Z9	Z3,Z6,epo9
17	G(6)	G(6)	no	no
18	G(2) +N(1)	no +G(1)	G(1) +G(1),N(1)	G(6)
19	G(10) +G(2)	G(3) +G(2)	G(4) +G(1),N(2)	L(1)
20	G(1),N(6) +G(2)	no +G(1)	no +G(1),N(1)	N(1),A(2)
21	G(1),N(10),L(1),A(10) +G(2)	no +G(2)	N(1),L(1) +N(1)	N(3),A(12) +G(1)
22	no	no	no	no
23	P(1),A(2)	no	no +N(1)	no +N(1)

II. Synthesis and Field Evaluation

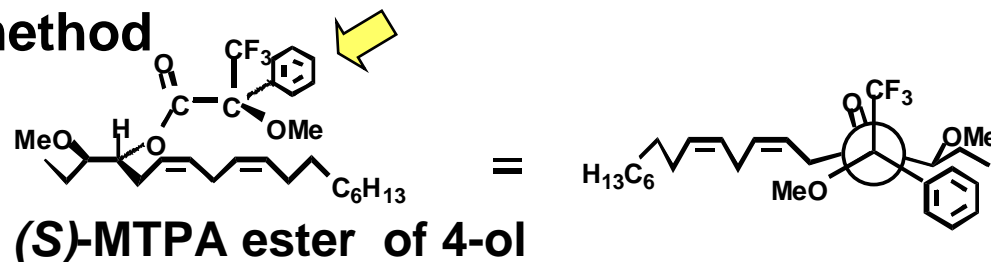
(C) Resolution and stereochemistry of enantiomers

Chiral HPLC



3*S*,4*R*-isomer

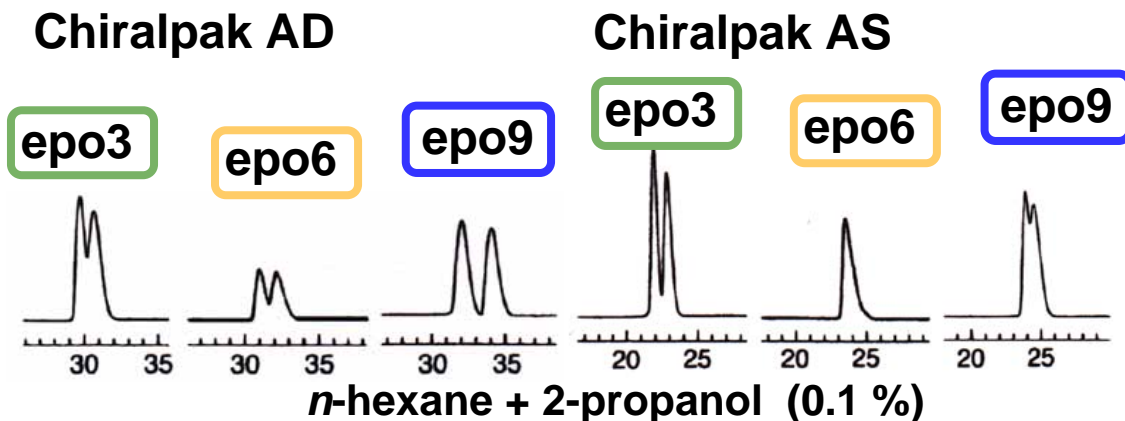
Mosher's method



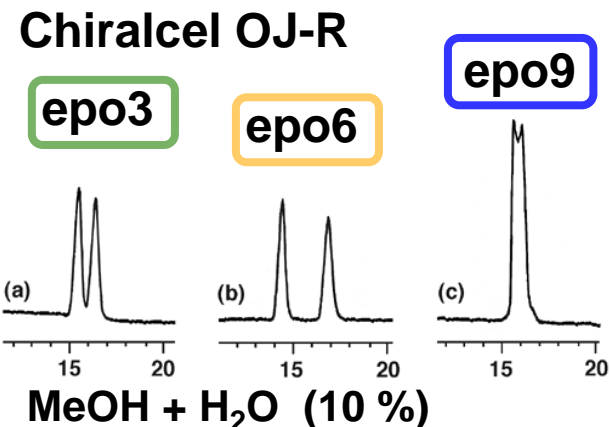
II. Synthesis and Field Evaluation

(D) Summary of resolution

[A] Normal-phase



[B] Reversed-phase



	Normal-phase Chiralpak AD	Chiralpak AS	Reversed-phase Chiralcel OJ-R	Isomer with shorter Rt
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Epoxydiene

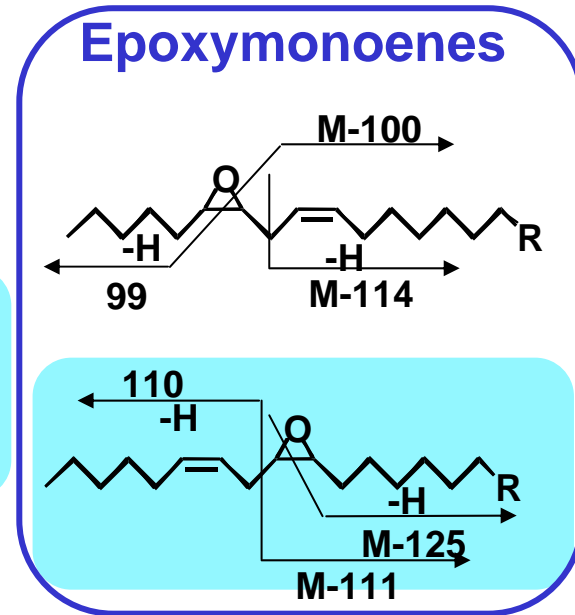
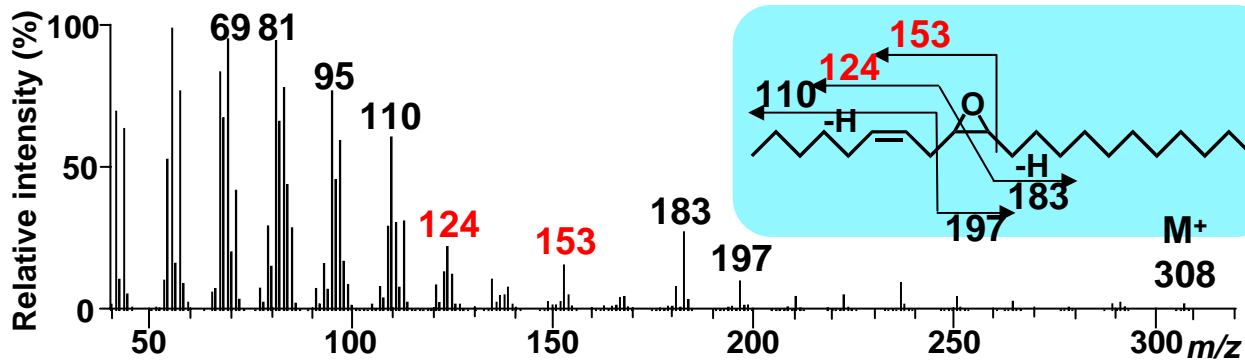
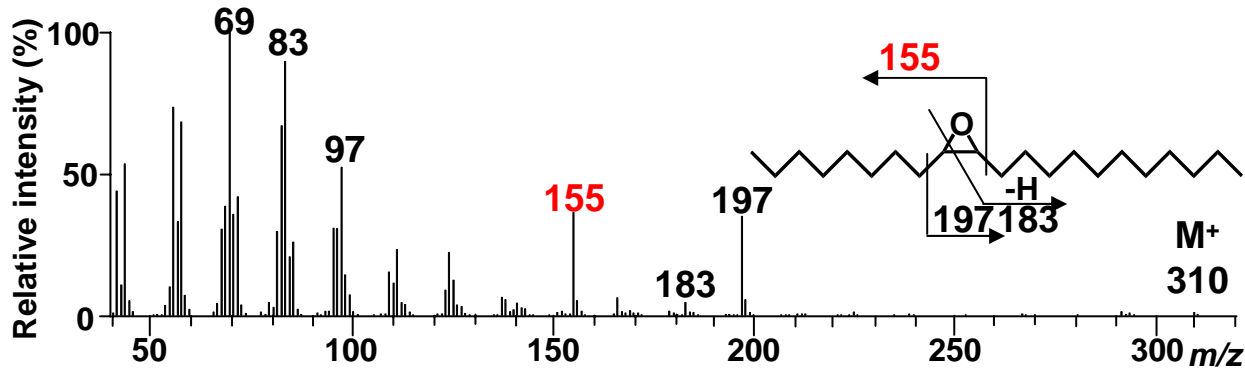
3,4-epoxide				(+)-3 <i>S</i> ,4 <i>R</i>
6,7-epoxide		×		(+)-6 <i>S</i> ,7 <i>R</i>
9,10-epoxide			(17) × (21)	(+)-9 <i>R</i> ,10 <i>S</i>

Epoxymonoene

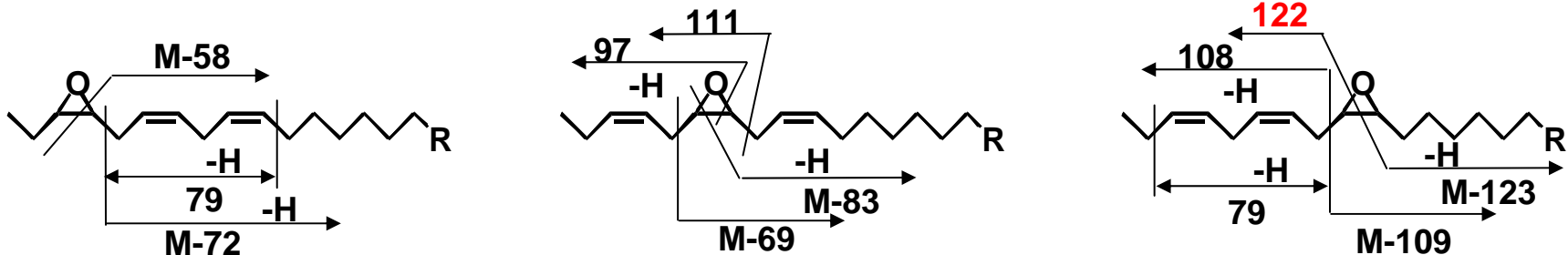
6,7-epoxide		×		(-)-6 <i>S</i> ,7 <i>R</i>
9,10-epoxide		×	(17) (23)	(-)-9 <i>R</i> ,10 <i>S</i>

III. Identification of Typical Components

(A) Diagnostic ions of GC-MS analysis



Epoxydienes

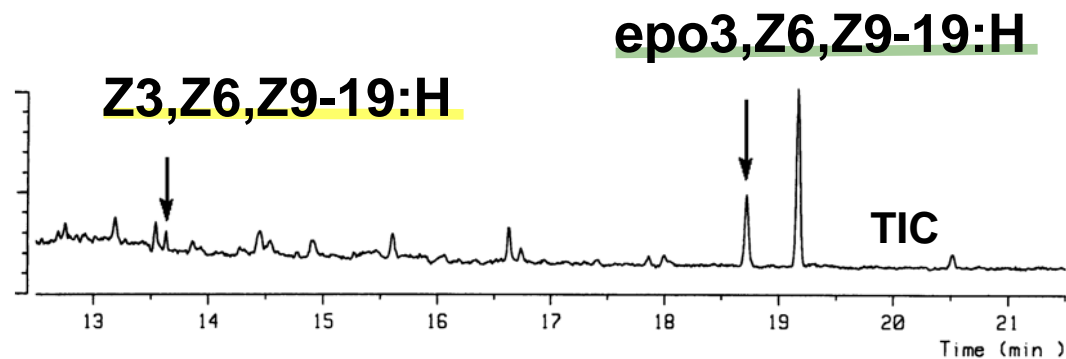


III. Identification of Typical Components

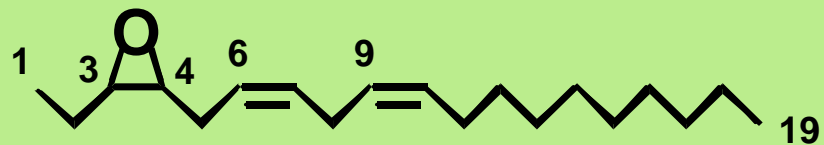
(B) Natural pheromone of *A. s. cretacea* [1]

Ascotis selenaria cretacea (Geometridae: Ennominae)

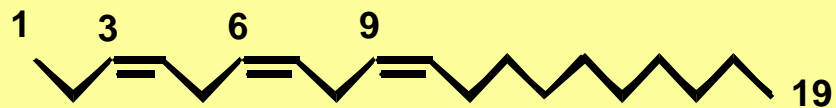
Japanese Giant Looper



(Z,Z)-cis-3,4-epoxy-6,9-nonadecadiene

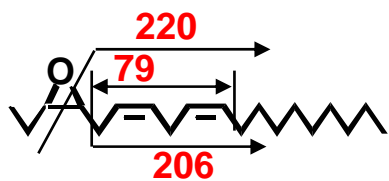


(Z,Z,Z)-3,6,9-nonadecatriene

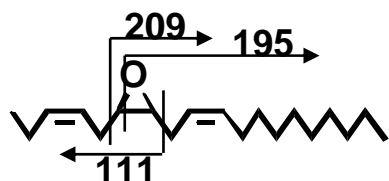


III. Identification of Typical Components

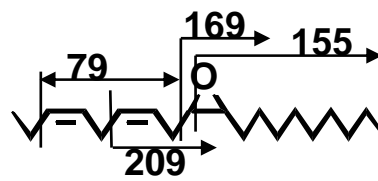
(B) Natural pheromone of *A. S. cretacea* [2]



epo3,Z6,Z9-19:H



Z3,epo6,Z9-19:H

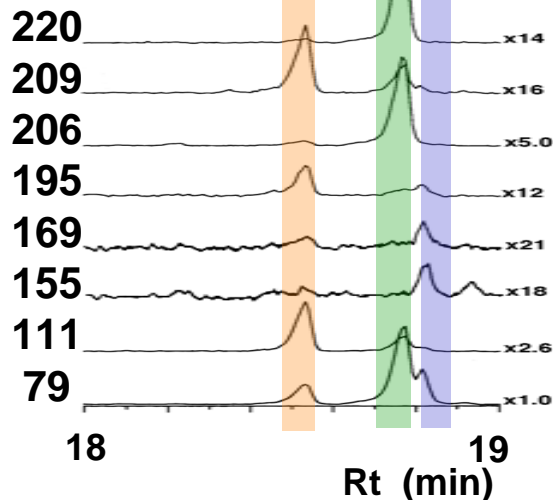


Z3,Z6,epo9-19:H

GC-MS

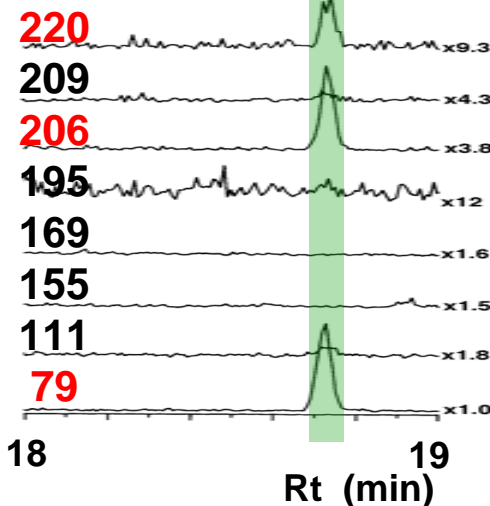
Synthetic mixture + Extract
TIC

Mass chro.
m/z



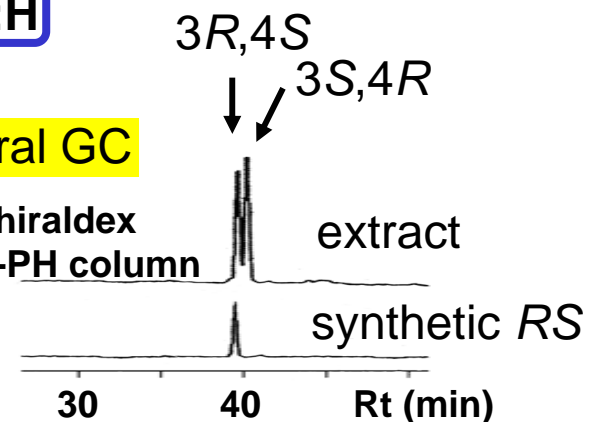
Female
extract (1)

m/z



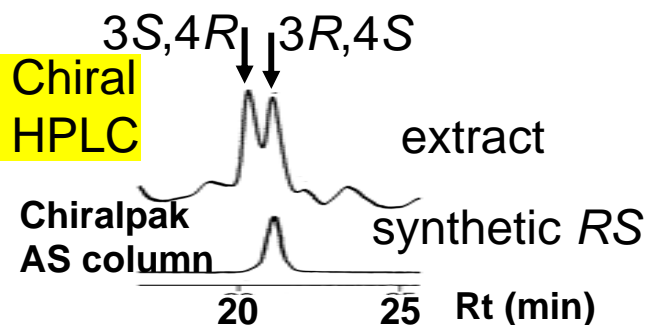
Chiral GC

Chiraldex
A-PH column



Chiral HPLC

Chiralpak
AS column



**Racemate of
epo3,Z6,Z9-19:H**

III. Identification of Typical Components

(C) Natural pheromone of *B. robustum* [1]

Biston robustum (Geometridae: Ennominae)

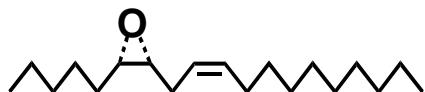
Giant geometrid moth



Comp. I Z6,Z9-19:H



Comp. II Z3,Z6,Z9-19:H



Comp. III epo6,Z9-19:H

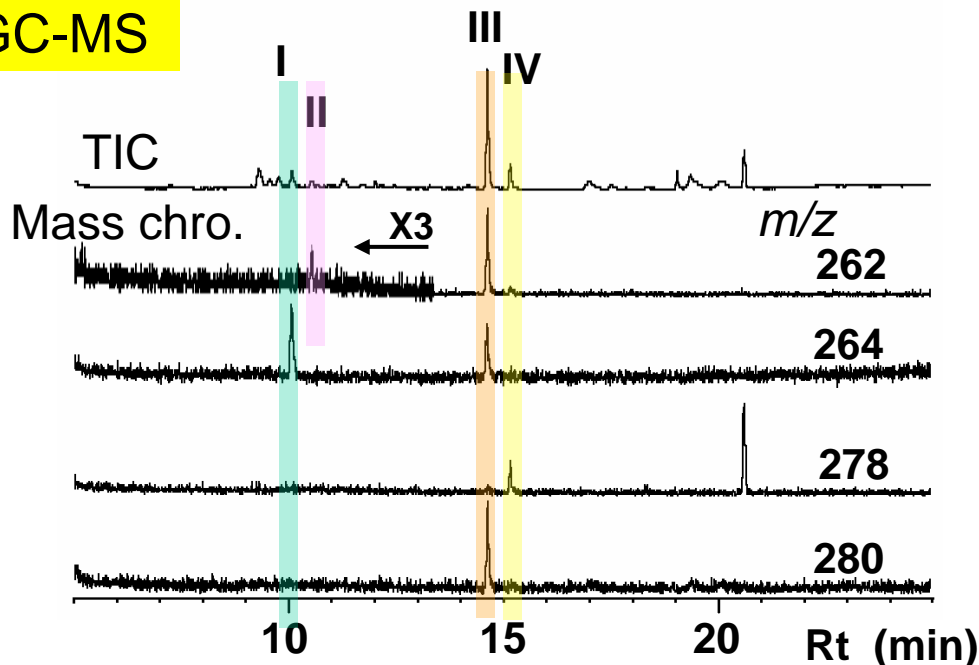


Comp. IV Z3,epo6,Z9-19:H

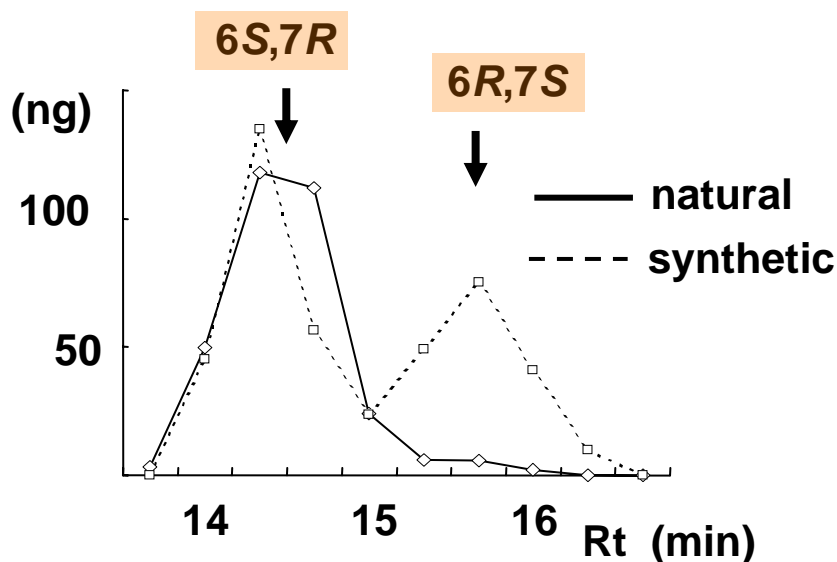
Chiral HPLC

Quantitative GC

GC-MS



Chiralpak AD column

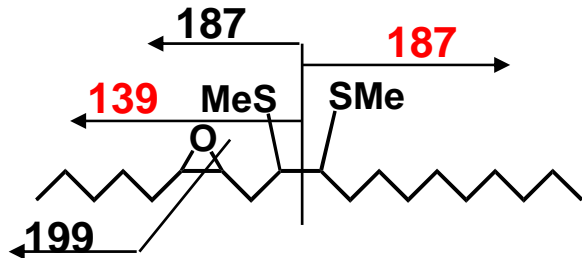


III. Identification of Typical Components

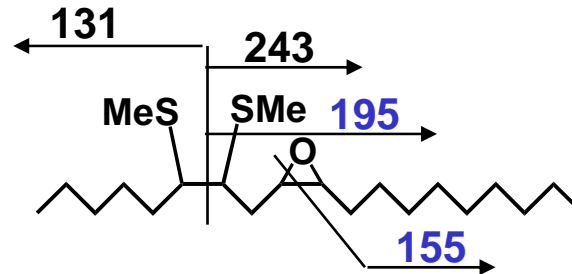
(C) Natural pheromone of *B. robustum* [2]

GC-MS analysis of DMDS Adducts

From epo6,Z9-19:H

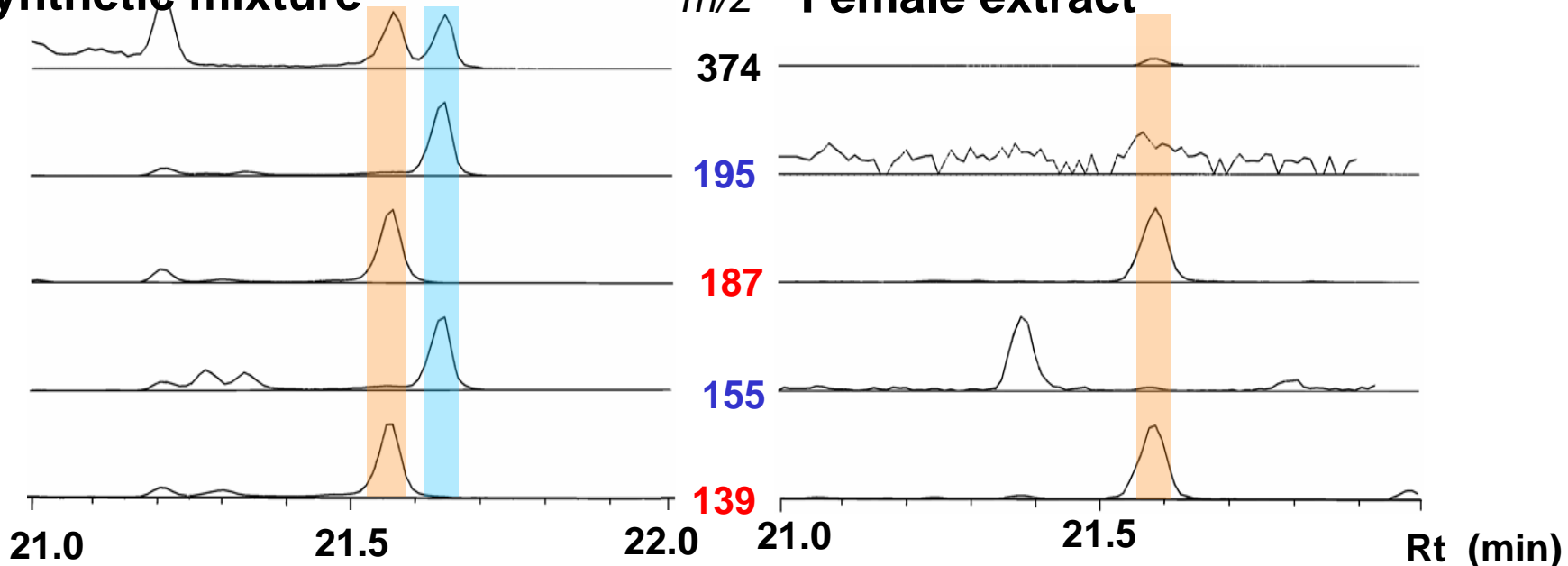


From Z6,epo9-19:H



Synthetic mixture

m/z Female extract

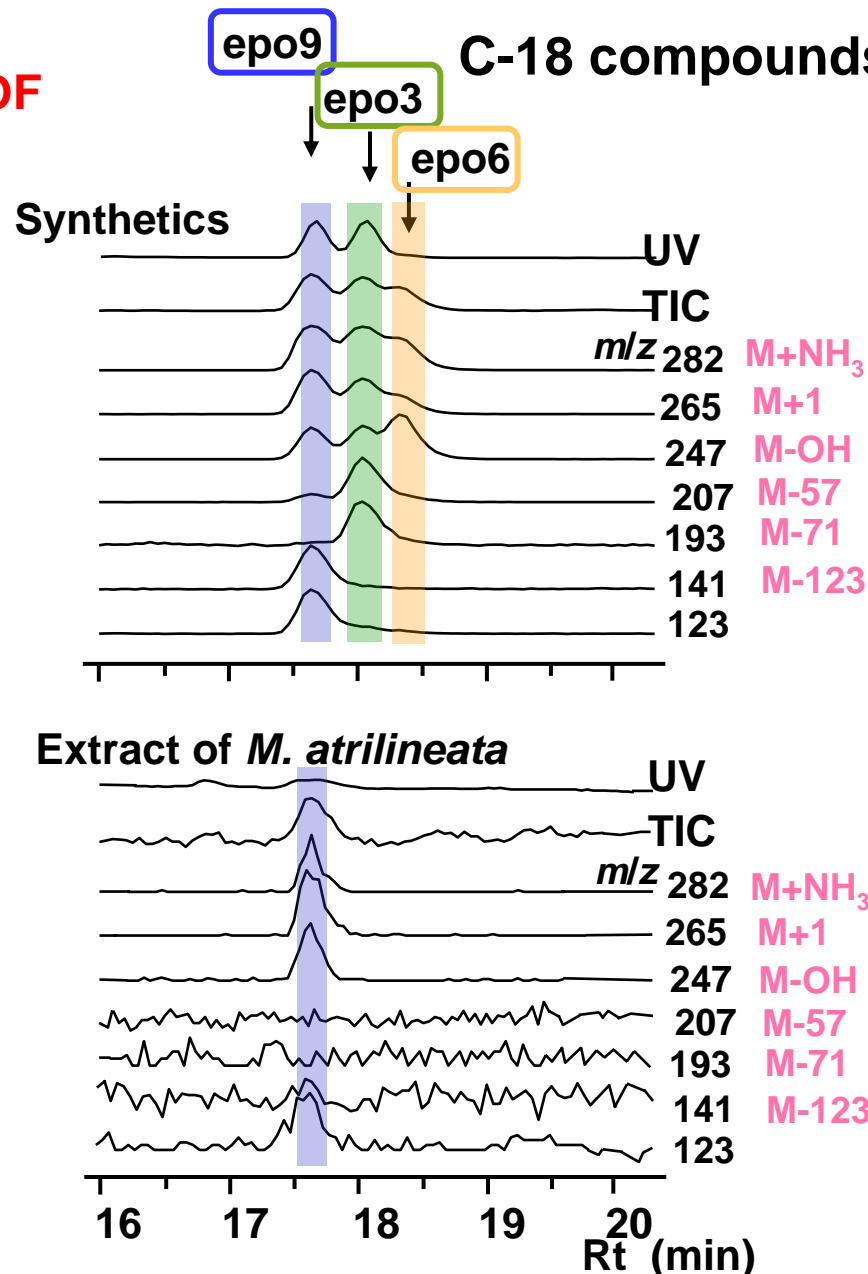
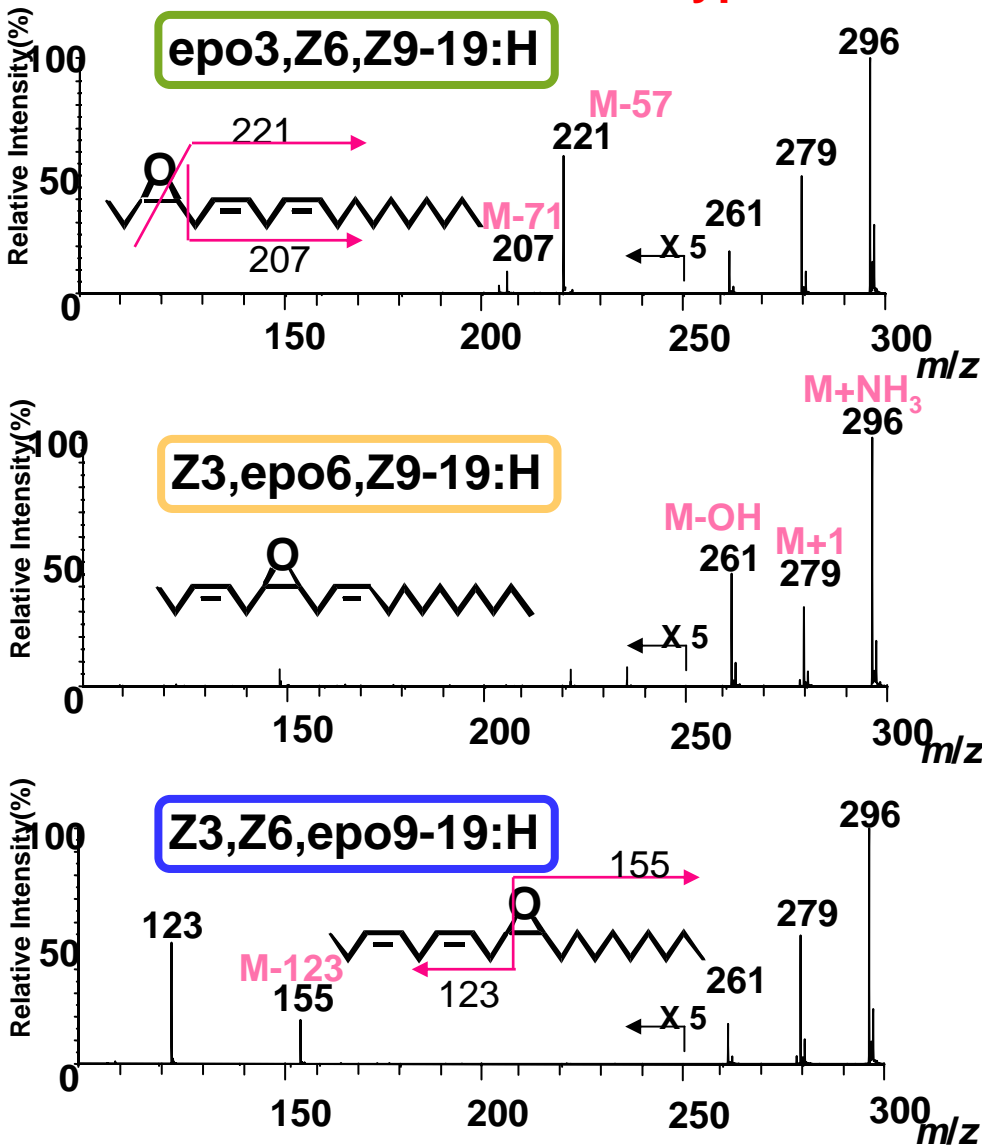


III. Identification of Typical Components

(D) LC-MS analysis

Ionization: ESI
Type of MS: TOF

C-18 compounds



III. Identification of Typical Components

(E) Stereochemistry and attractive activity in a field

Family	Natural pheromone		Field attraction		
	Species	Main component	Configuration	Optimum isomer	Racemate
Geometridae					
	<i>Biston robustum</i> giant geomerid moth	epo6,Z9-19:H	6S,7R	6S,7R + 6R,7S (9:1)	×
	<i>Ascotis selenaira</i> Japanese giant looper	epo3,Z6,Z9-19:H	racemate	3R,4S	○
	<i>Menophra atrilineata</i> mulberry looper	Z3,Z6,epo9-18:H	9S,10R	9S,10R	○
Noctuidae					
	<i>Oraesia excavata</i> fruit-piercing moth	Z6,epo9-18:H	9S,10R	racemate	

IV. Identification of Novel Components

(A) Posticlure from *O. postica* [1]

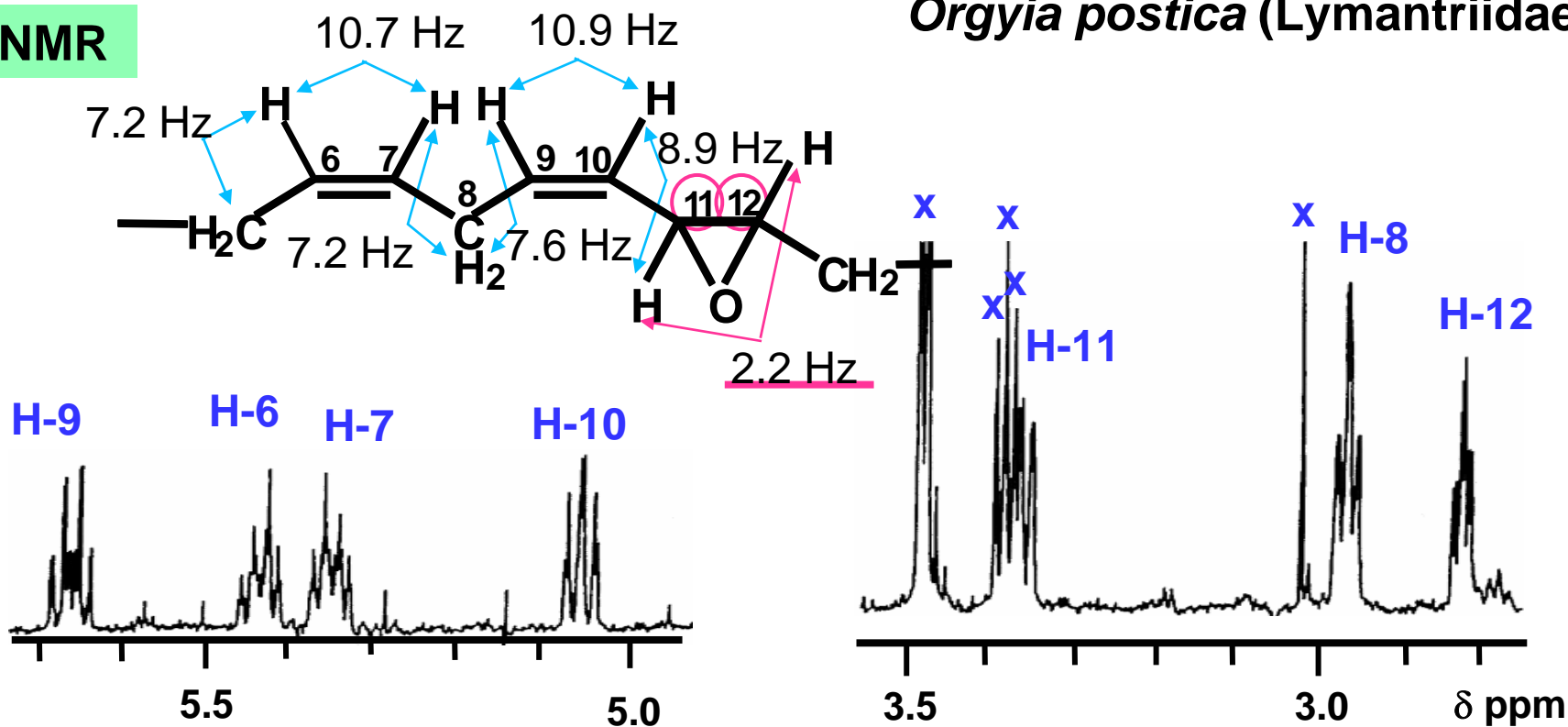


(8.5 μ g from 500)



Orgyia postica (Lymantriidae)

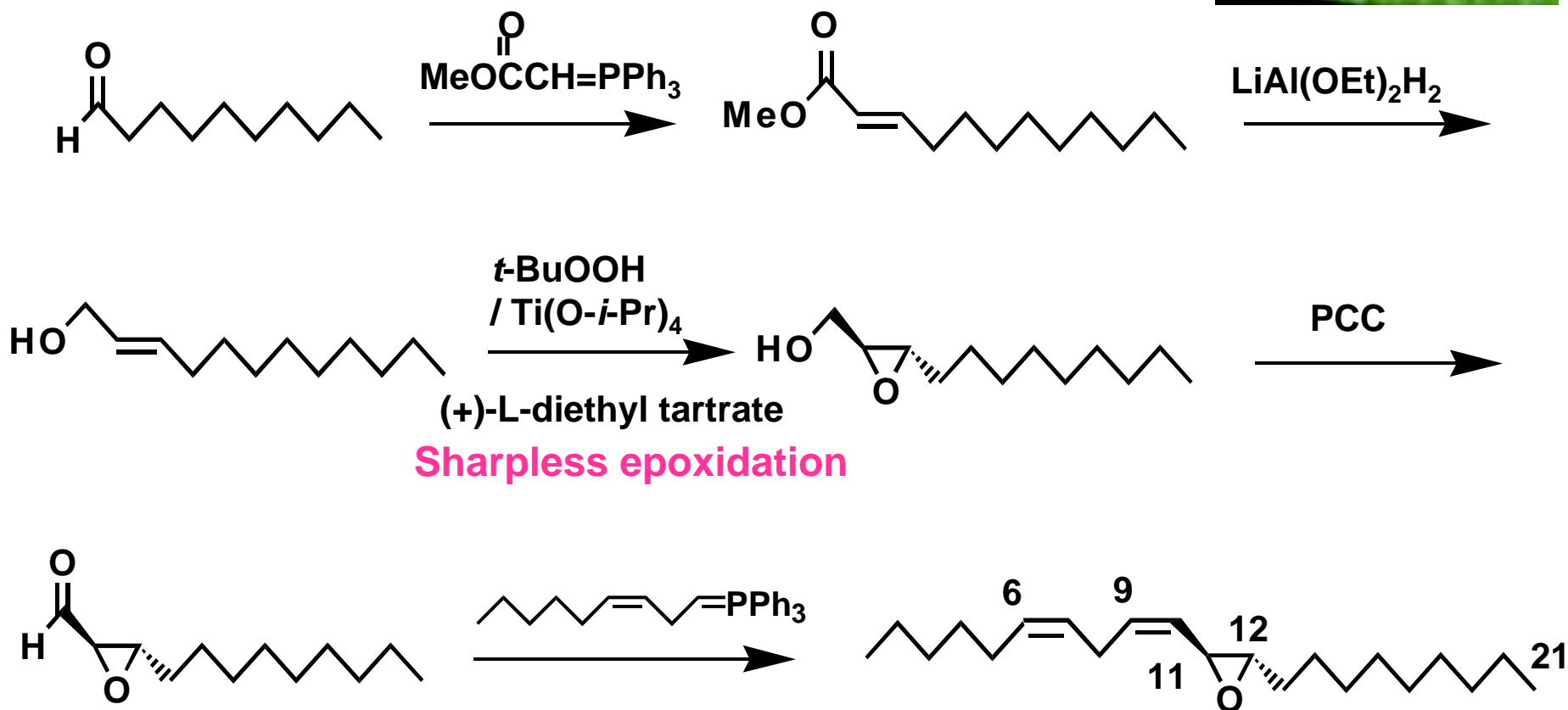
^1H NMR



IV. Identification of Novel Components

(A) Posticlure from *O. postica* [2]

Chiral synthesis of 11*S*,12*S*-posticlure

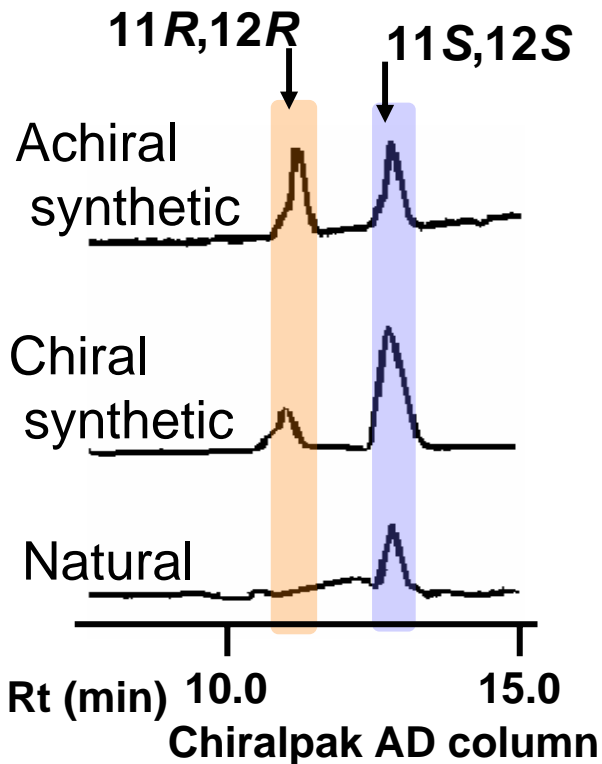


IV. Identification of Novel Components



(A) Posticlude from *O. postica* [3]

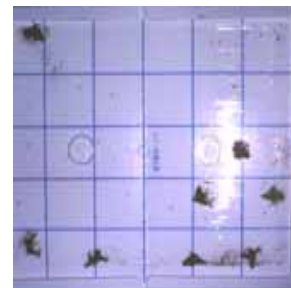
Chiral HPLC



Field tests

Okinawa Island

Posticlude μg		Total captured males Test period (June, 2000)	
11R,12R	11S,12S	16-19	20-26
500	0	0	0
100	0	0	0
0	500	18	30
0	100	8	10
250	250	16	12
50	50	7	3
0	0	0	0
Virgin females		-	122



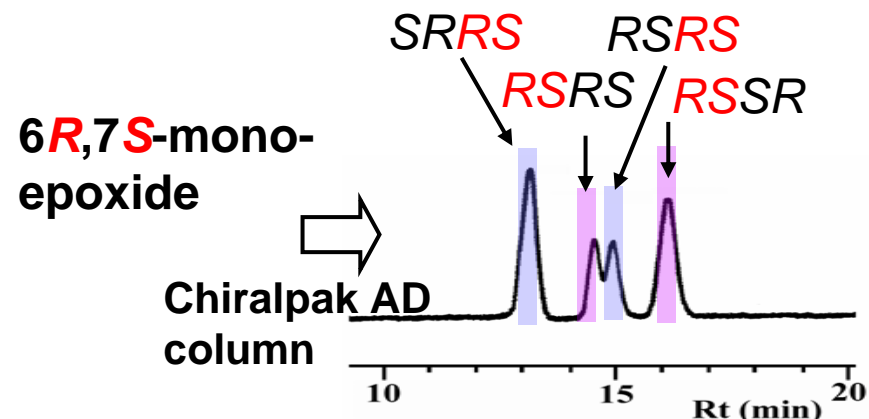
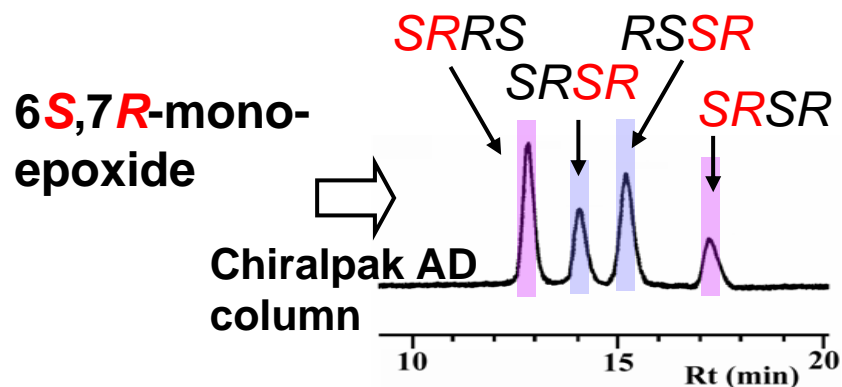
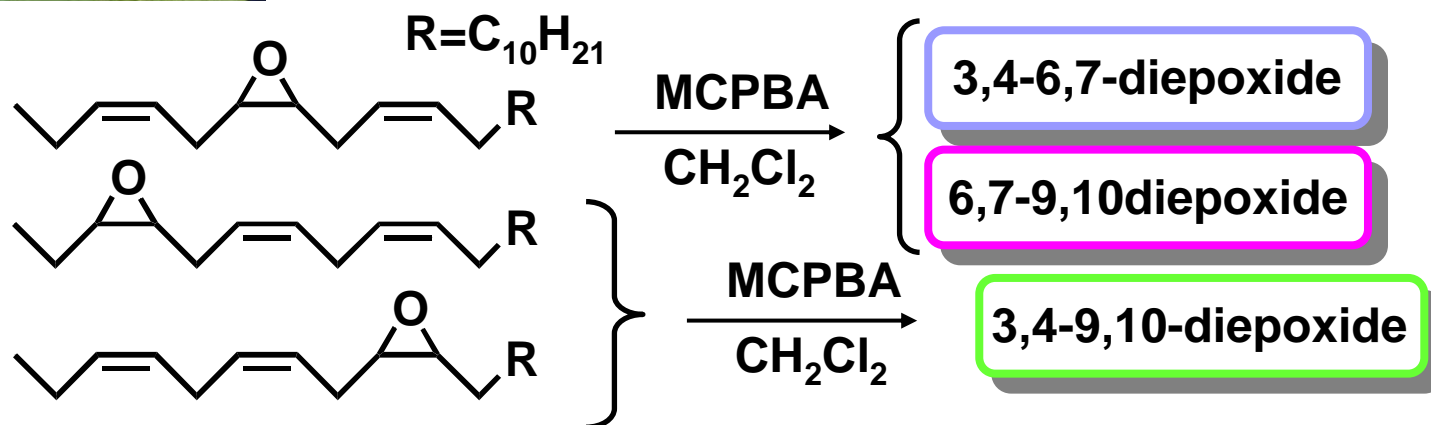
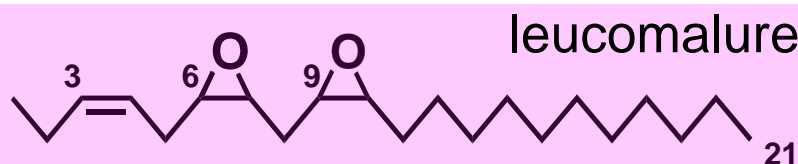
IV. Identification of Novel Components

(B) Synthesis of diepoxyalkenes



Leucoma salicis
(Lymantriidae)
Satin moth

Gries *et al.* (1997) *Naturwiss.* **84**: 219



IV. Identification of Novel Components

(C) Diepoxyalkenes from *P. nuda* [1]

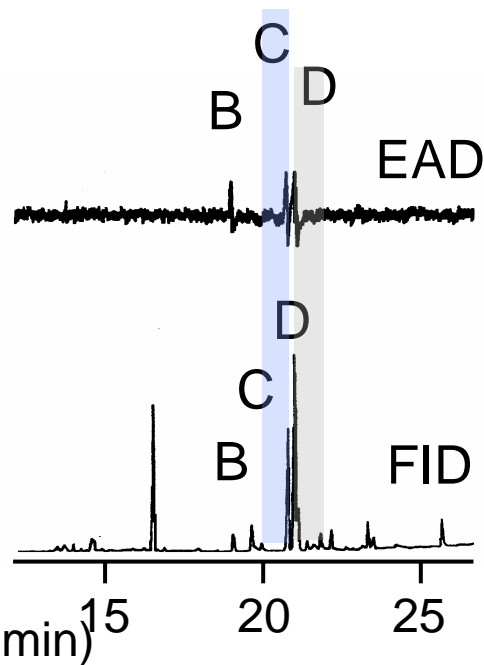
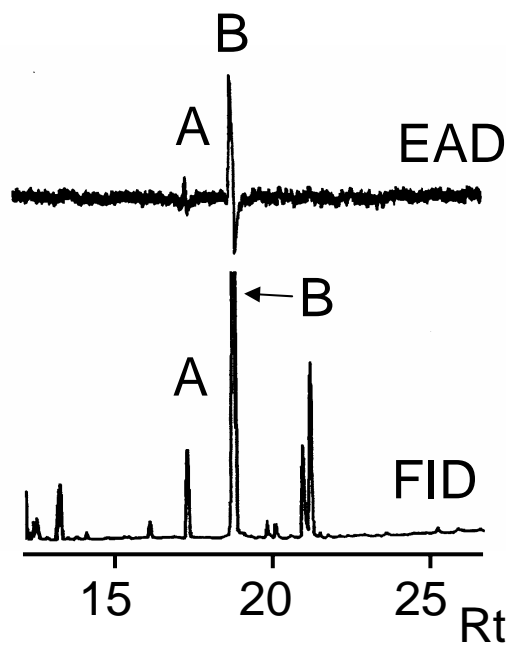


Perina nuda (Lymantriidae)
Clear-winged tussock moth

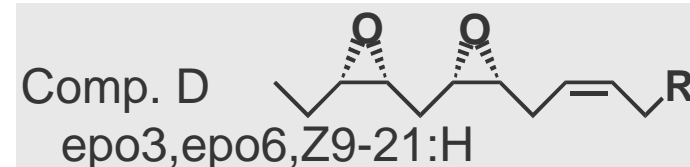
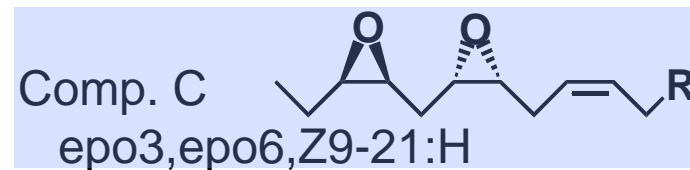
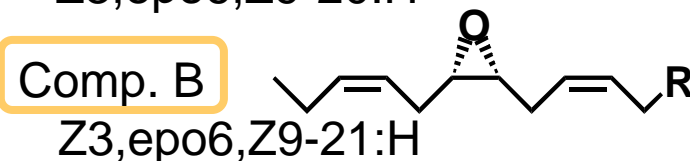
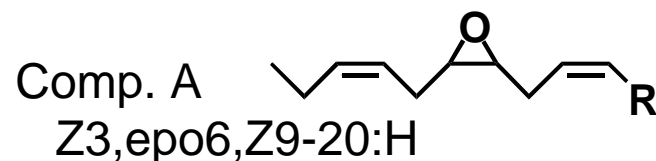
GC-EAD

5%-ether fraction

20%-ether fraction



$R = n-C_{10}H_{22}$

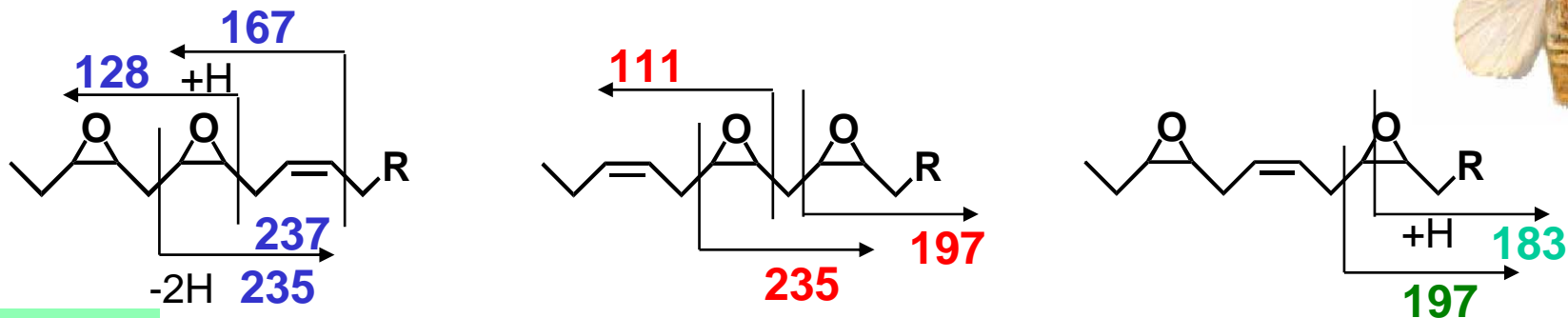


A : B : C : D =
0.4 : 250 : 5 : 8 (ng / FE)

IV. Identification of Novel Components

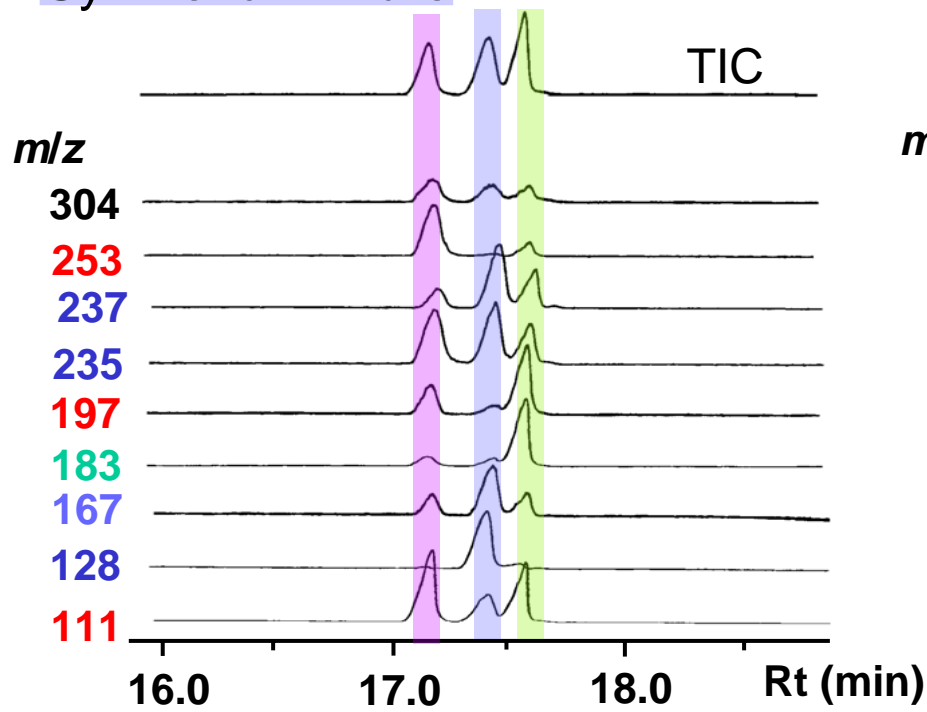


(C) Diepoxyalkenes from *P. nuda* [2]

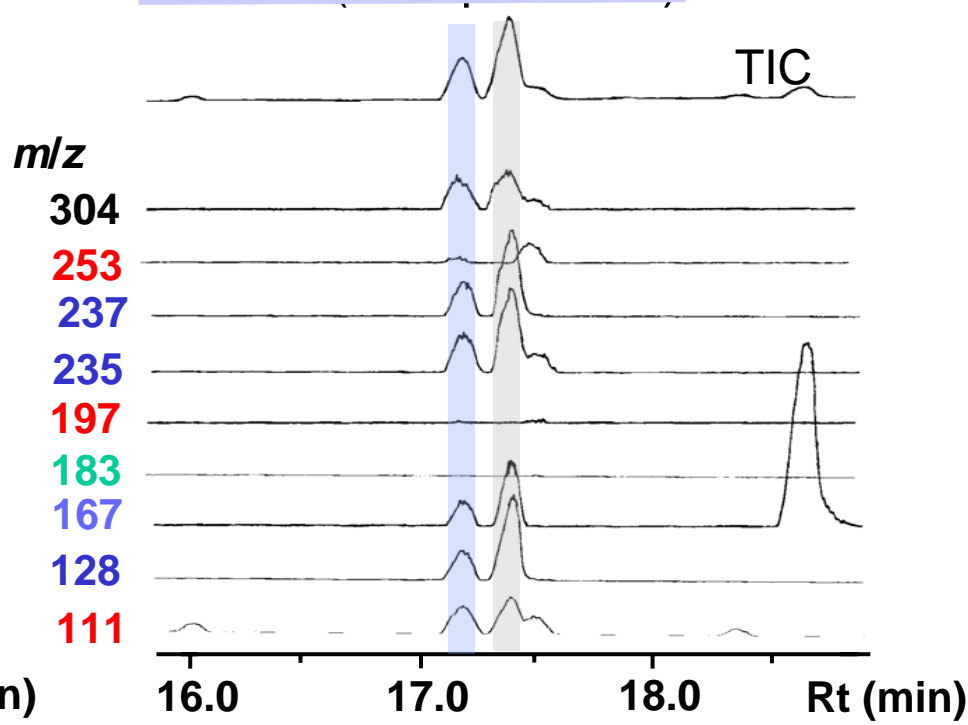


GC-MS

Synthetic mixture



Natural (Comp. C & D)



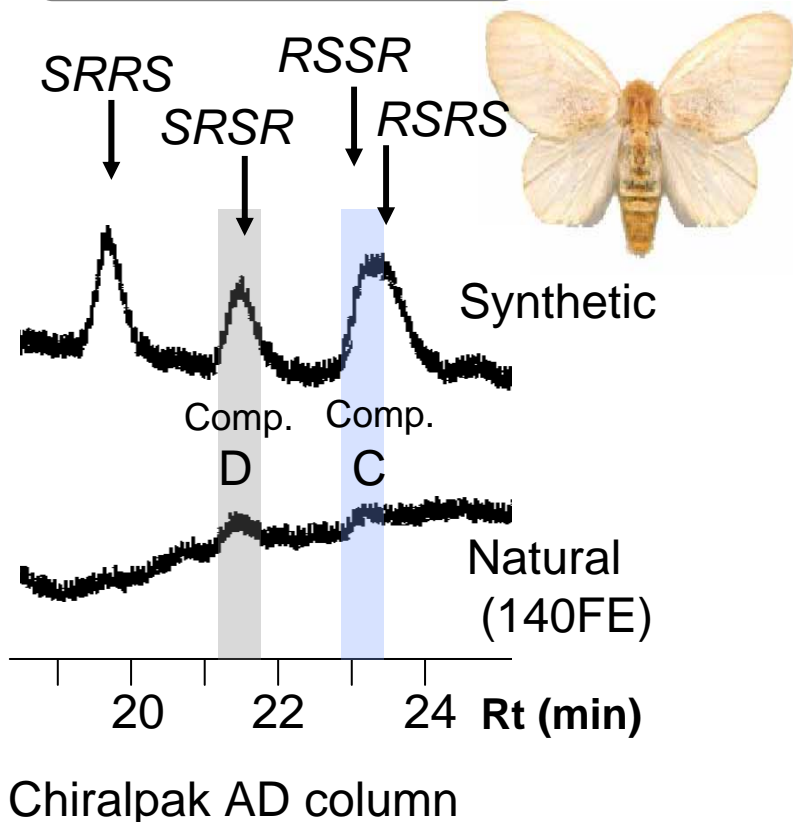
IV. Identification of Novel Components

(C) Diepoxyalkenes from *P. nuda* [3]



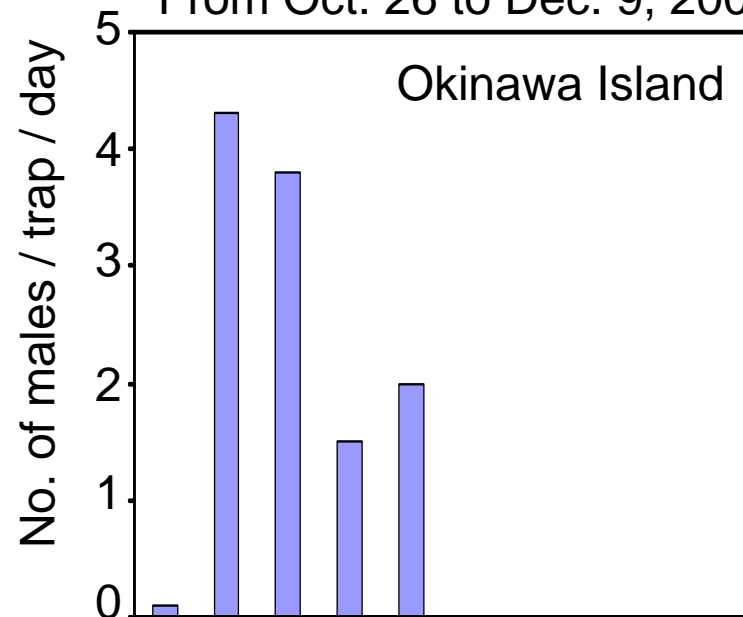
Chiral HPLC

3,4-6,7-diepoxyde



Field test

From Oct. 26 to Dec. 9, 2000



epo3, epo6, Z9 μg

RSSR	0	20	20	0	0	0	20	20	0	0
SRRS	0	0	0	20	20	0	0	0	20	20
SRSR	0	30	0	30	0	0	30	0	30	0
RSRS	0	0	30	0	30	0	0	30	0	30

Z3, epo6, Z9
500 μg

6S, 7R

6R, 7S

Acknowledgments

Co-workers

Dr. S. WAKAMURA

N. ARAKAKI

K. OHTANI

Y. OHMASA

M. KISO

J. TAKEUCHI

G.-Q. PU

S. HASHIMOTO

K. I. KARASAWA

Identification from tussock moths

Identification from tussock moths

Identification from Japanese giant looper

Identification from Fruit-piercing noctuid moth

Identification from giant geometrid moth

Identification from mulberry tiger moth

Identification from mulberry looper

Insect taxonomy

LC-MS

Chemical Ecology Laboratory of TUAT

Dr. X.-R. QIN

Dr. M. YAMAMOTO

Dr. H. YAMAZAWA

Dr. WITJAKSONO

Dr. S. INOMATA

H. OHSAWA

H. KISHI

T. MIYAMOTO

Y. TAKEUCHI

N. NAKAJIMA

W. WEI

T. MURAKAWA



