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Vancouver, Canada (July 25, 2011)

Characterization of Epoxytrienes Derived from  
(3Z,6Z,9Z)-1,3,6,9-Tetraenes, Sex Pheromone  
Components of Arctiid Moths and Related Compounds

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# Representative lepidopteran sex pheromones

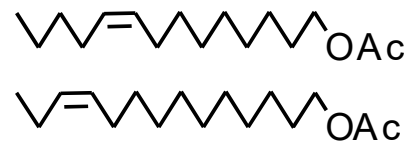
Sex pheromones have been identified from about 620 species.  
Male attractants have been reported for other 1200 species.

## Type I

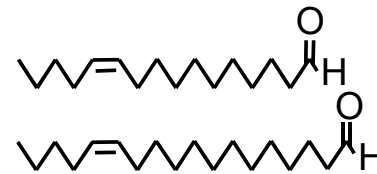
Silkworm moth



Smaller tea tortix



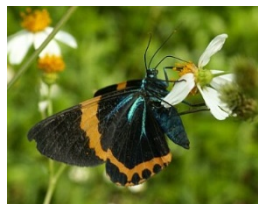
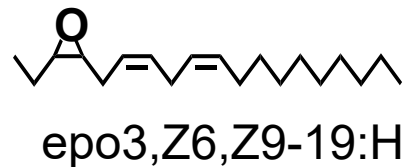
Rice stem borer



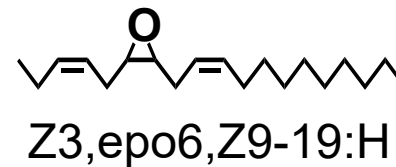
Unsaturated fatty alcohols, acetates and aldehydes with a C<sub>10</sub> – C<sub>18</sub> chain  
Found most commonly (75%)

## Type II

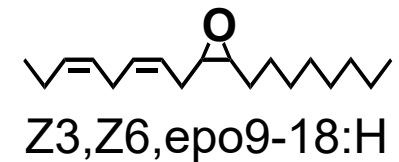
Polyunsaturated hydrocarbons and their epoxides with a C<sub>17</sub> – C<sub>23</sub> chain  
Identified from evolved-insect groups (15%)



*Milionia e basalis*



Giant geometrid moth



Mulberry looper

# Phylogenetic tree of Lepidoptera



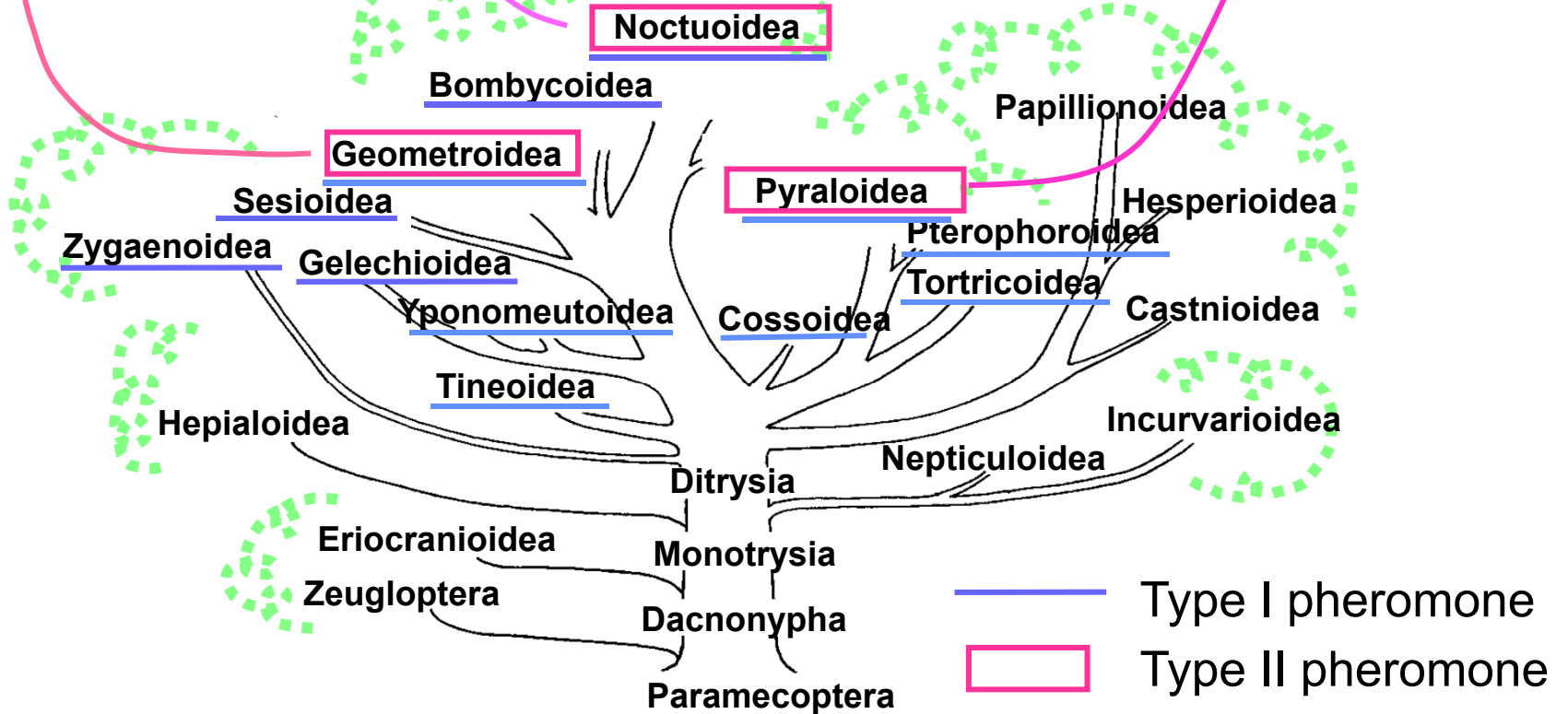
Plum cankerworm moth  
 Z3,Z6,Z9-21:H  
 Z3,Z6,Z9-23:H



Lichen moth  
 Z3,Z6,Z9-21:H  
 Z3,Z6,Z9-23:H



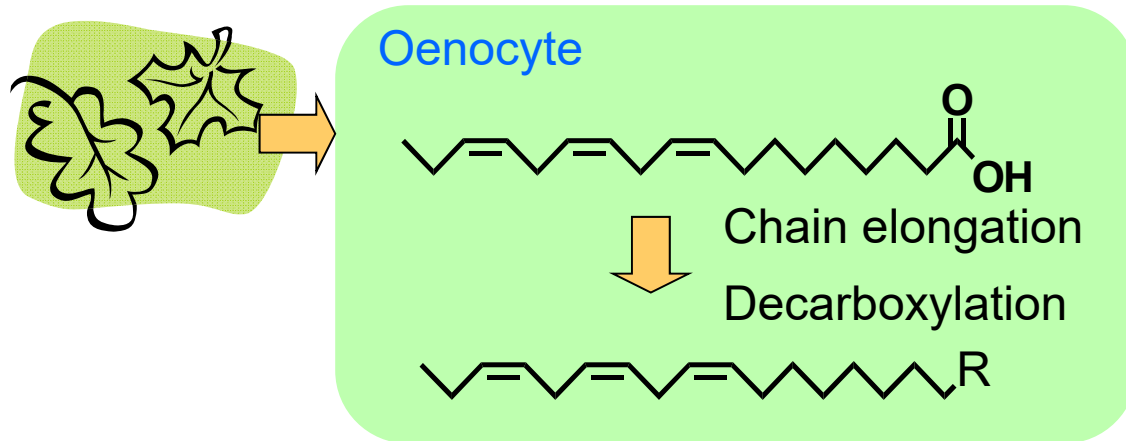
Yellow peach moth  
 E10-16:Ald  
 Z3,Z6,Z9-23:H



## Speciation of the groups, which produce Type II pheromones

Taxonomy								
Super-family	Family	Sub-family	Type of pheromone	Japanese species				
Geometroidea	Uraniidae							
		Geometridae	Ennominae	II, others	339			
	Geometrinae		II	86				
	Sterrhinae		I	109				
	Larentiinae		II	346				
	Alsophilinae		II	14				
Noctuoidea	Notodontidae		I	124				
		Lymantriidae		II, others	59			
			Nolidae		II	107		
				Noctuidae		I, II, others	1276	
					Pantheidae			13
						Arctiidae	Lithosiinae	II, others
	Syntominiinae	II	4					
	Arctiinae	II, others	51					

# Biosynthesis of Type II sex pheromones



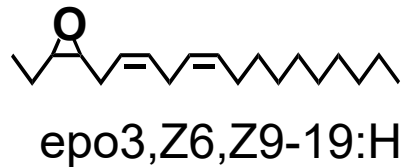
Transport by lipophorin

Pheromone gland

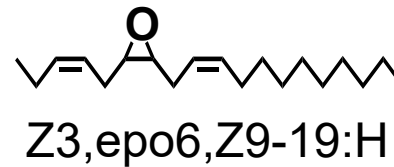
Epoxidation

## Type II

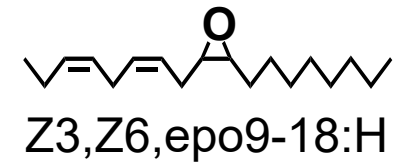
Polyunsaturated hydrocarbons and their epoxides with a C<sub>17</sub> – C<sub>23</sub> chain Identified from evolved-insect groups (15%)



*Milionia e basalis*

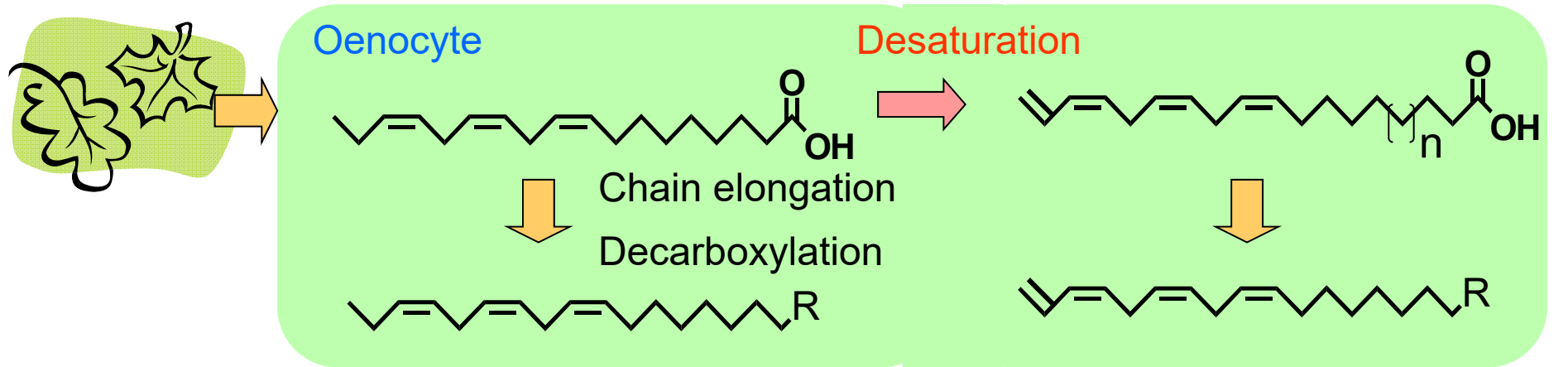


Giant geometrid moth

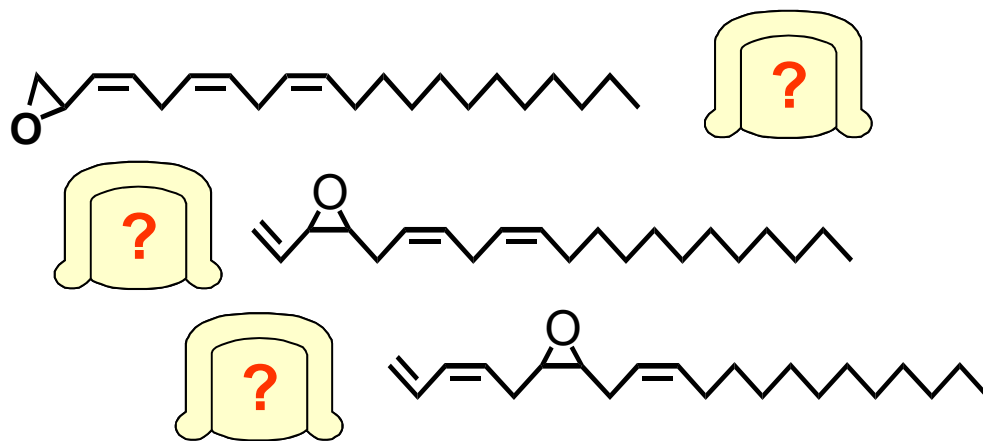


Mulberry looper

# Biosynthesis of Type II sex pheromones



## Epoxytrienes

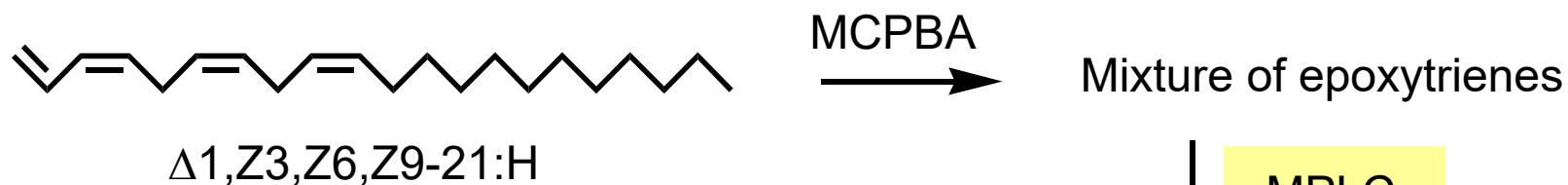
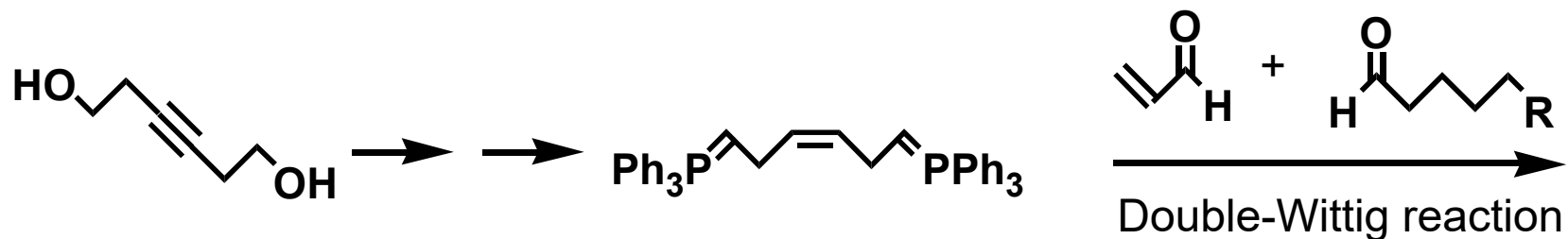


Fall webworm



Mulberry tiger moth

# Synthesis of epoxytrienes



Lobar column (LiChroprep Si 60)

eluent: 0.5% THF in Hx

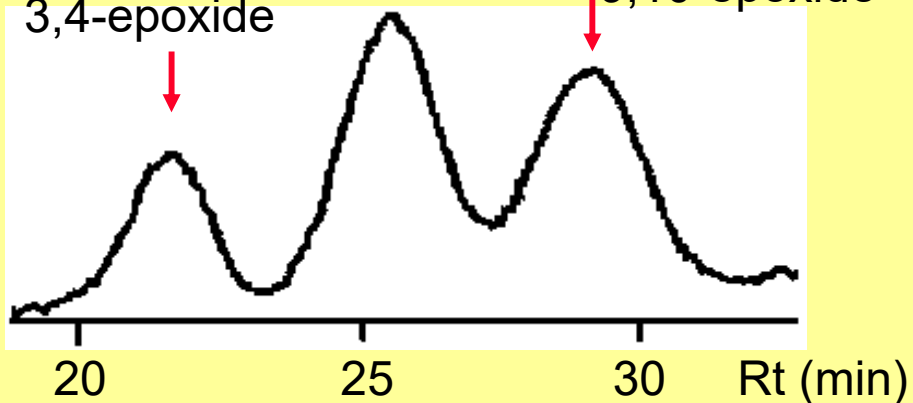
flow rate: 3.0 ml/min

detector: RI

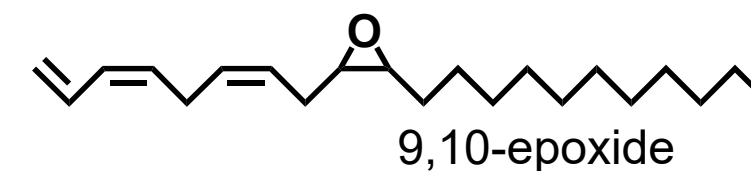
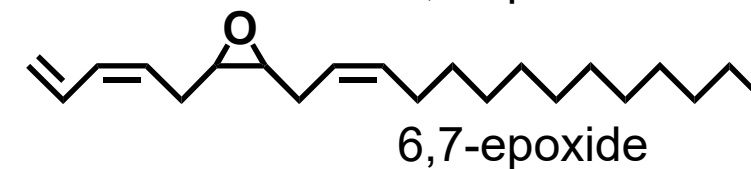
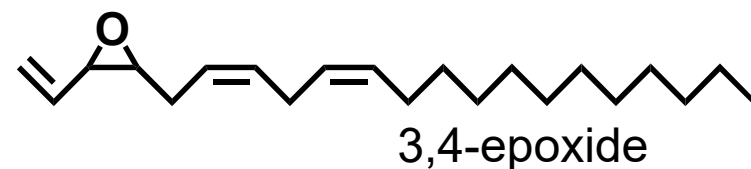
3,4-epoxide

6,7-epoxide

9,10-epoxide

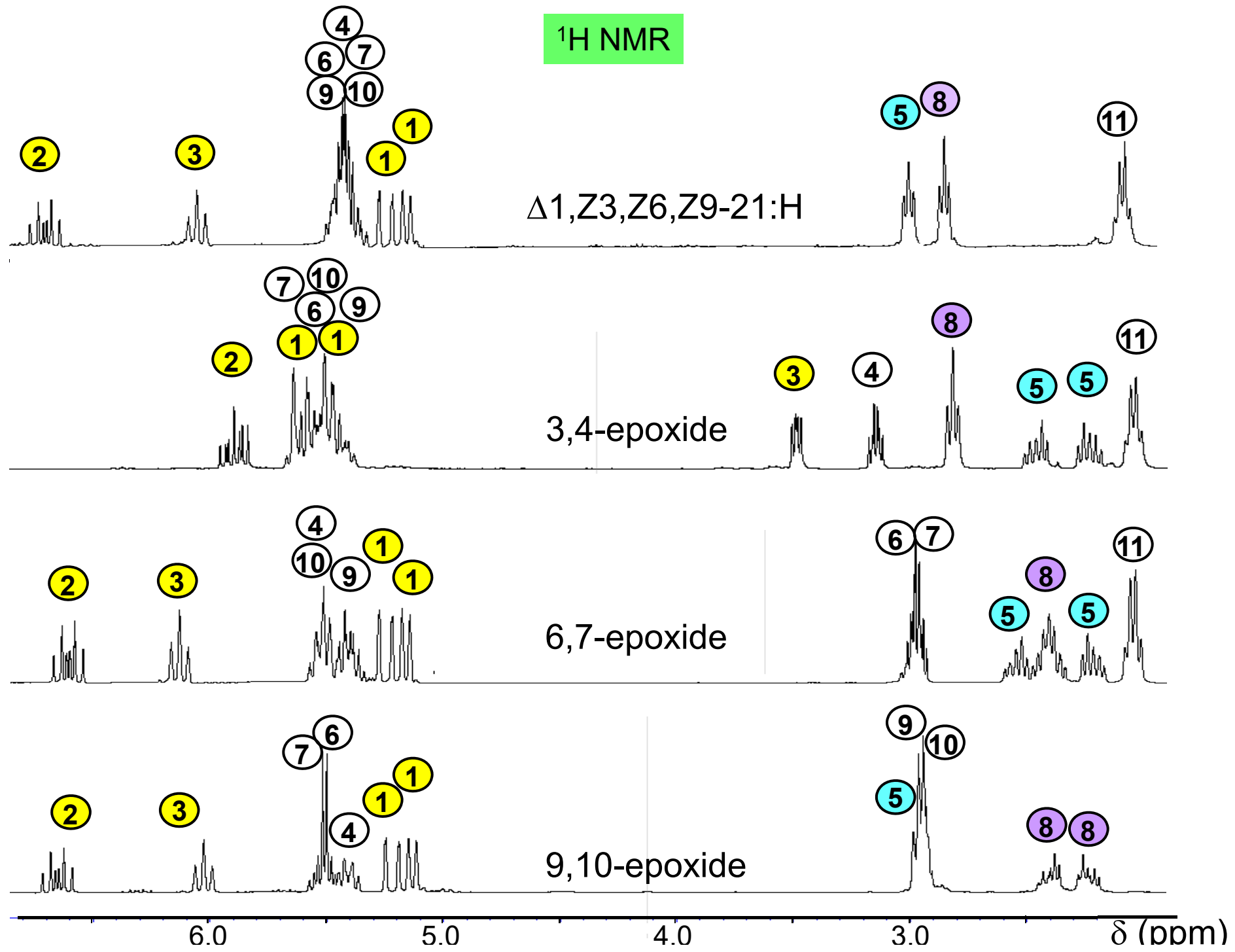


MPLC



1,2-Epoxy was not produced.

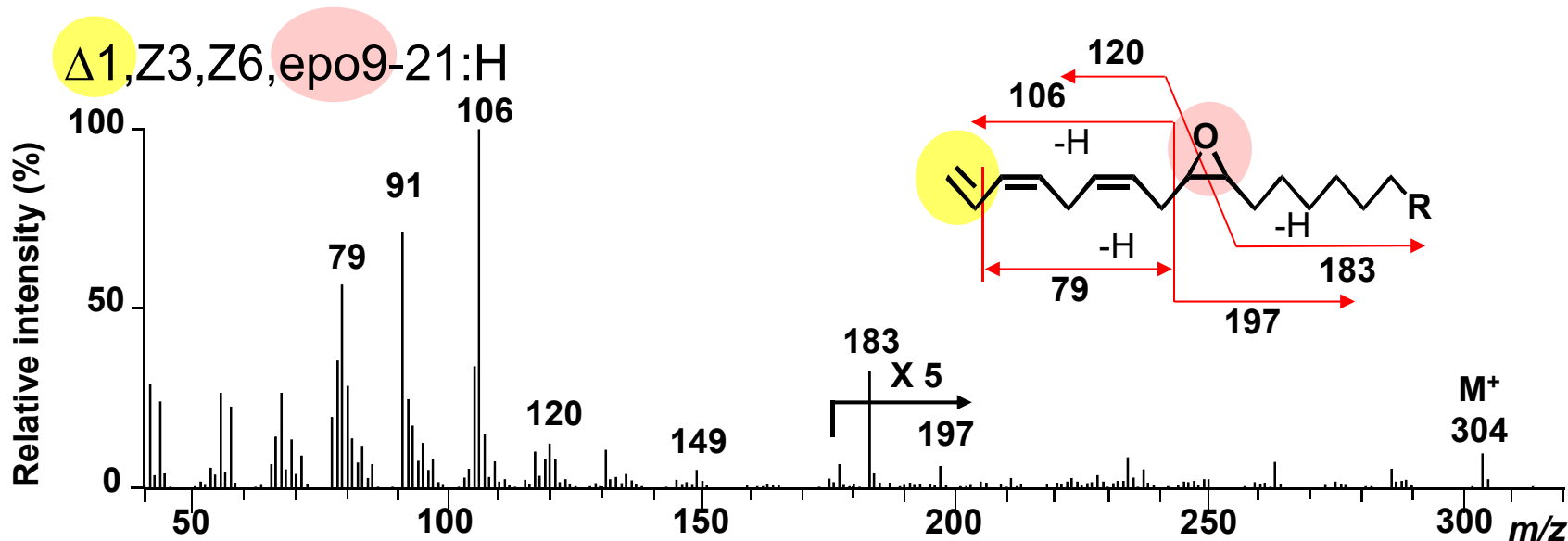
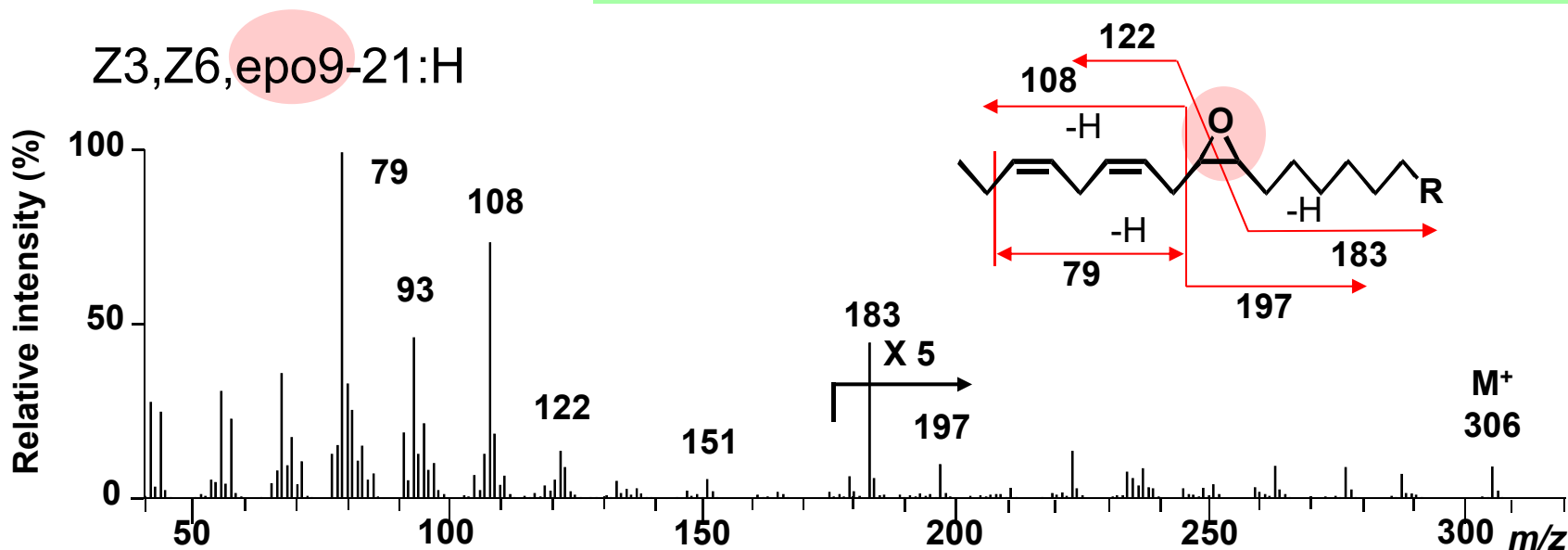
<sup>1</sup>H NMR





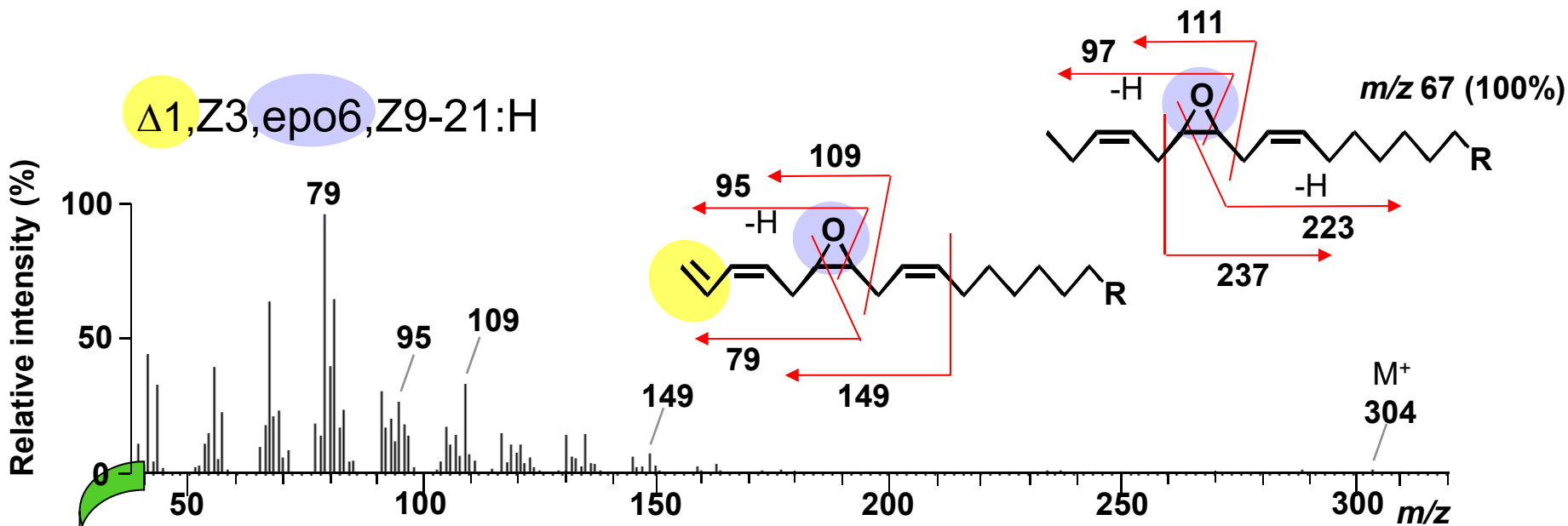
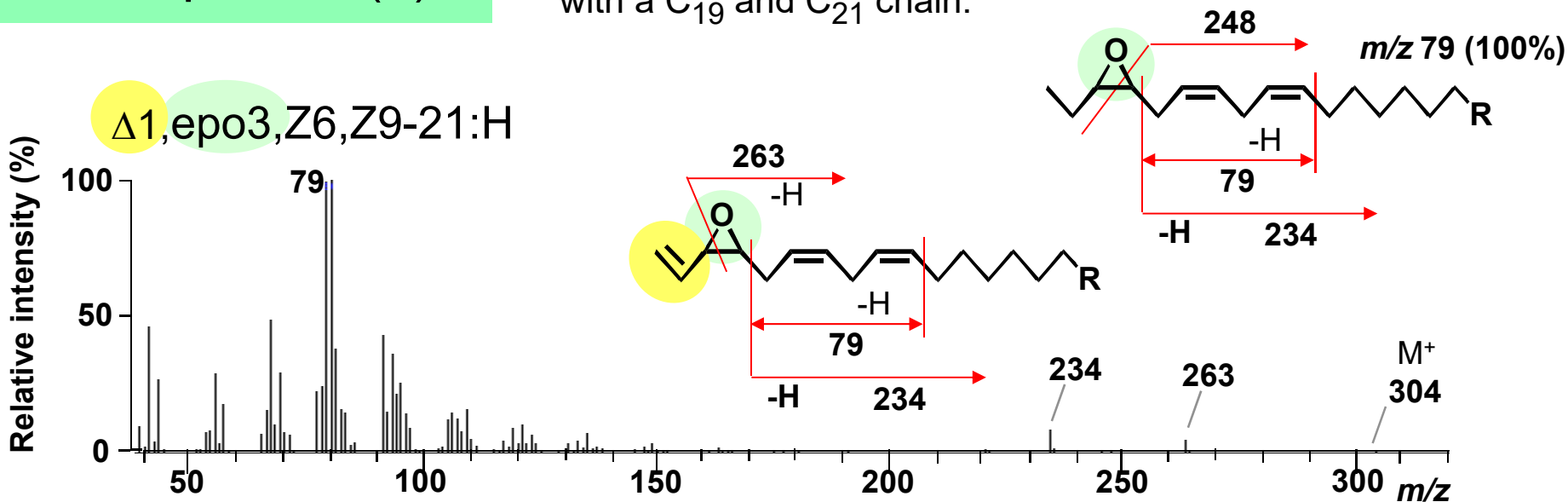
# Mass spectra (1)

The 9,10-epoxytriene characteristically showed some ions corresponding to diagnostic ions of the 9,10-epoxydiene.  
The terminal double bond did not effect strongly on the fragmentation.



## Mass spectra (2)

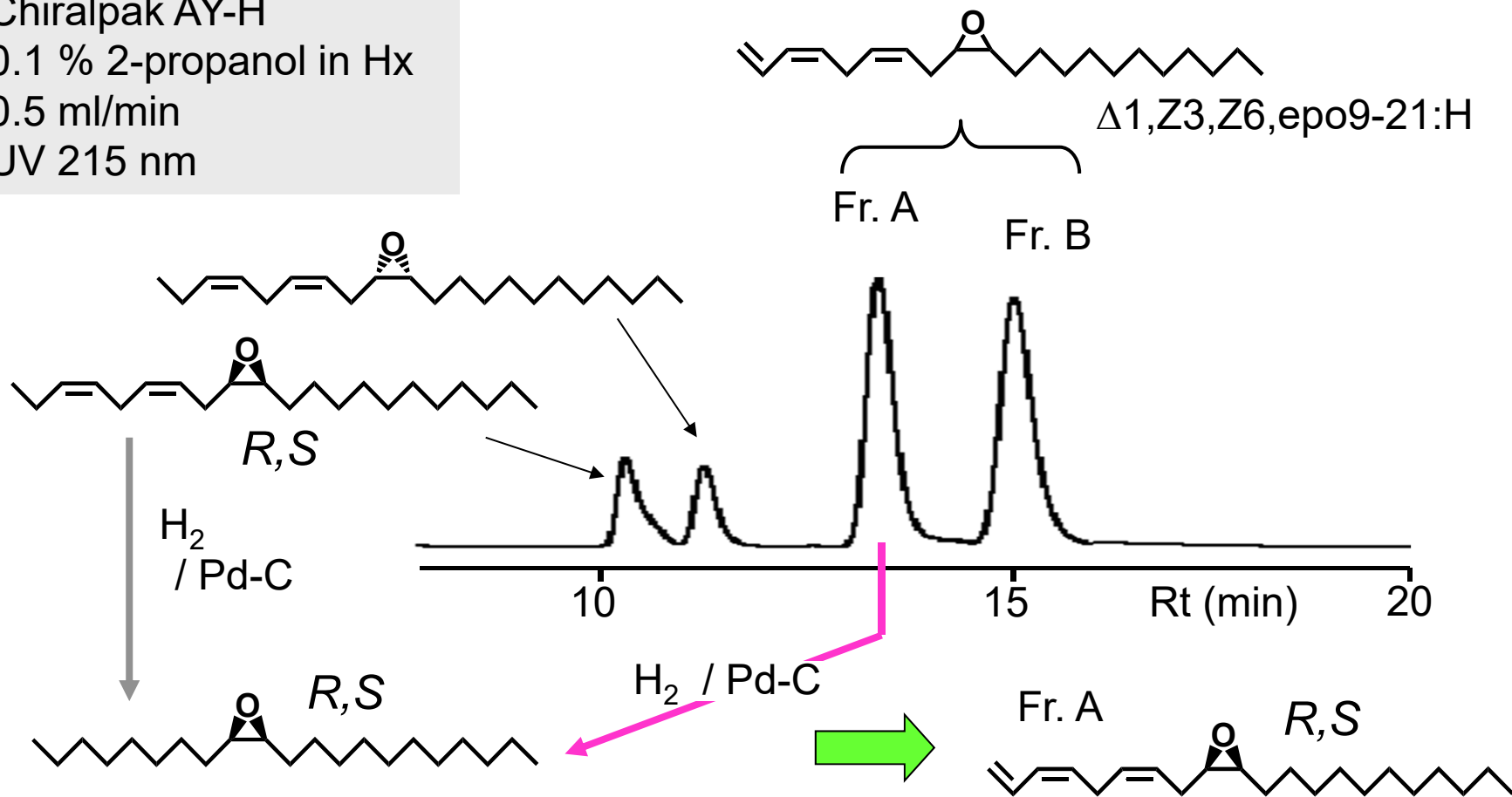
Similar fragmentations were also observed for compounds with a C<sub>19</sub> and C<sub>21</sub> chain.



These diagnostic fragment ions are useful to find new pheromone components.

# Resolution of epoxytrienes by chiral HPLC

Chiralpak AY-H  
 0.1 % 2-propanol in Hx  
 0.5 ml/min  
 UV 215 nm



epo3,Z6,Z9-21:H  
 $\Delta^{1,\text{epo}3,Z6,Z9}\text{-}21\text{:H}$

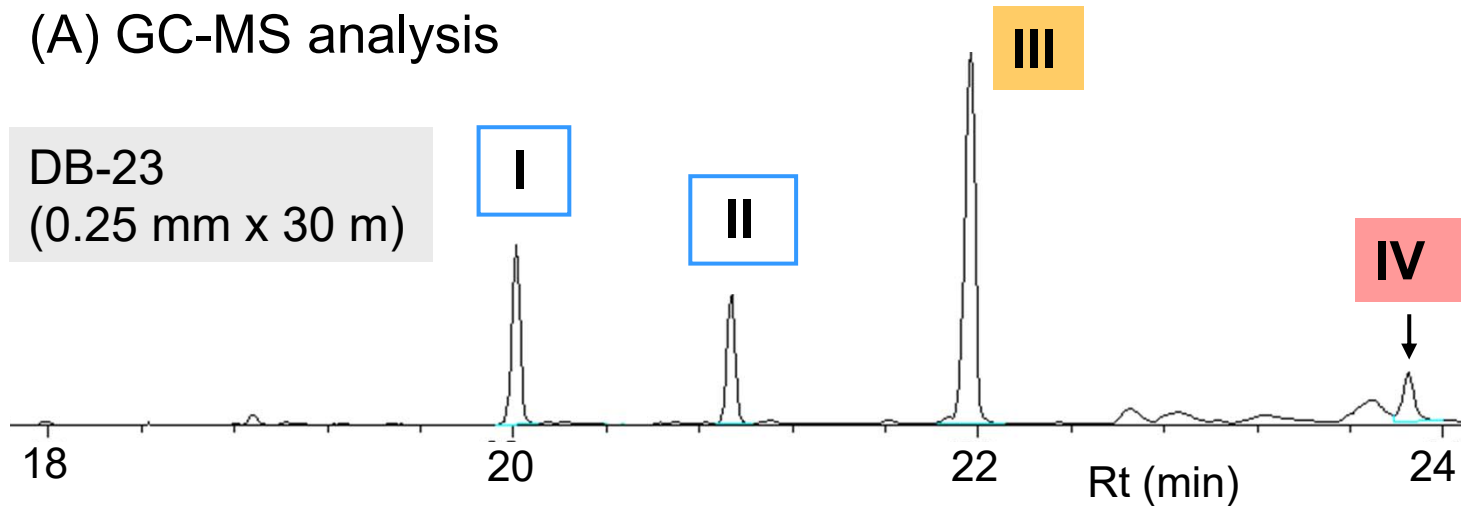
Z3,epo6,Z9-21:H  
 $\Delta^{1,Z3,\text{epo}6,Z9}\text{-}21\text{:H}$

S,R-isomer  
 $\rightarrow$  R,S-isomer

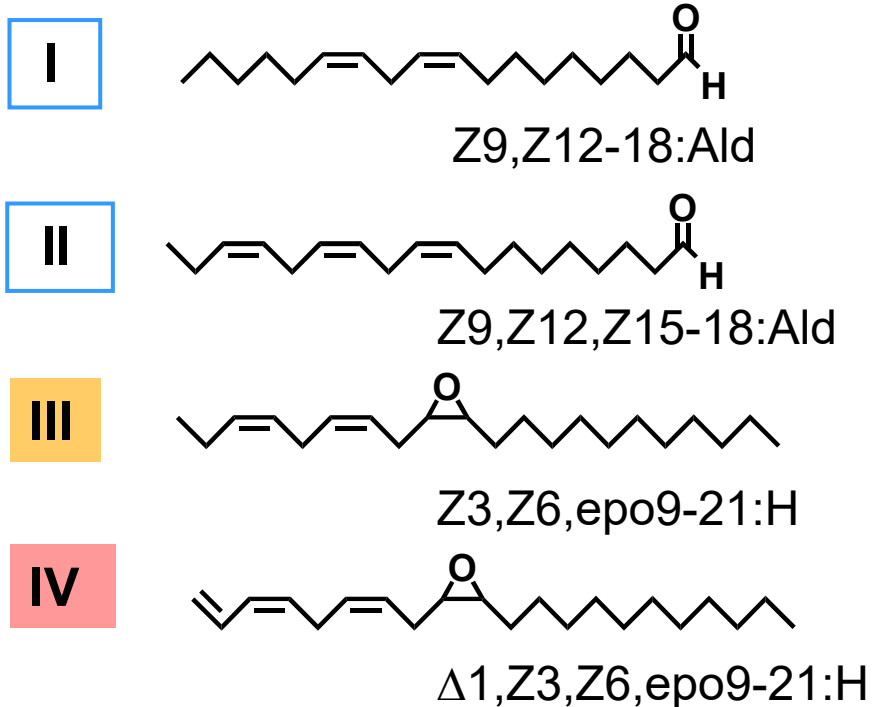
# Stereochemistry of the *H. cunea* pheromone (1)

## (A) GC-MS analysis

DB-23  
(0.25 mm x 30 m)

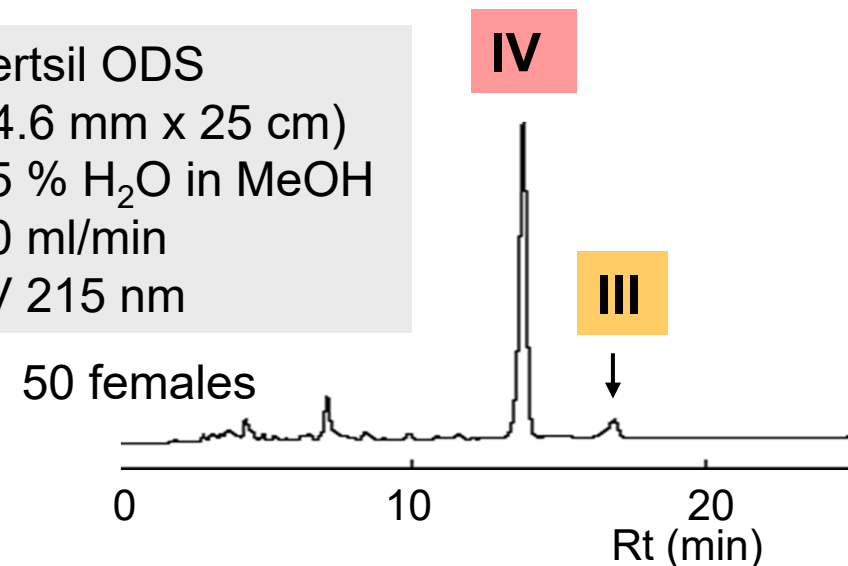


Fall webworm  
*Hyphantria cunea*  
(Arctiidae)



## (B) Preparative HPLC

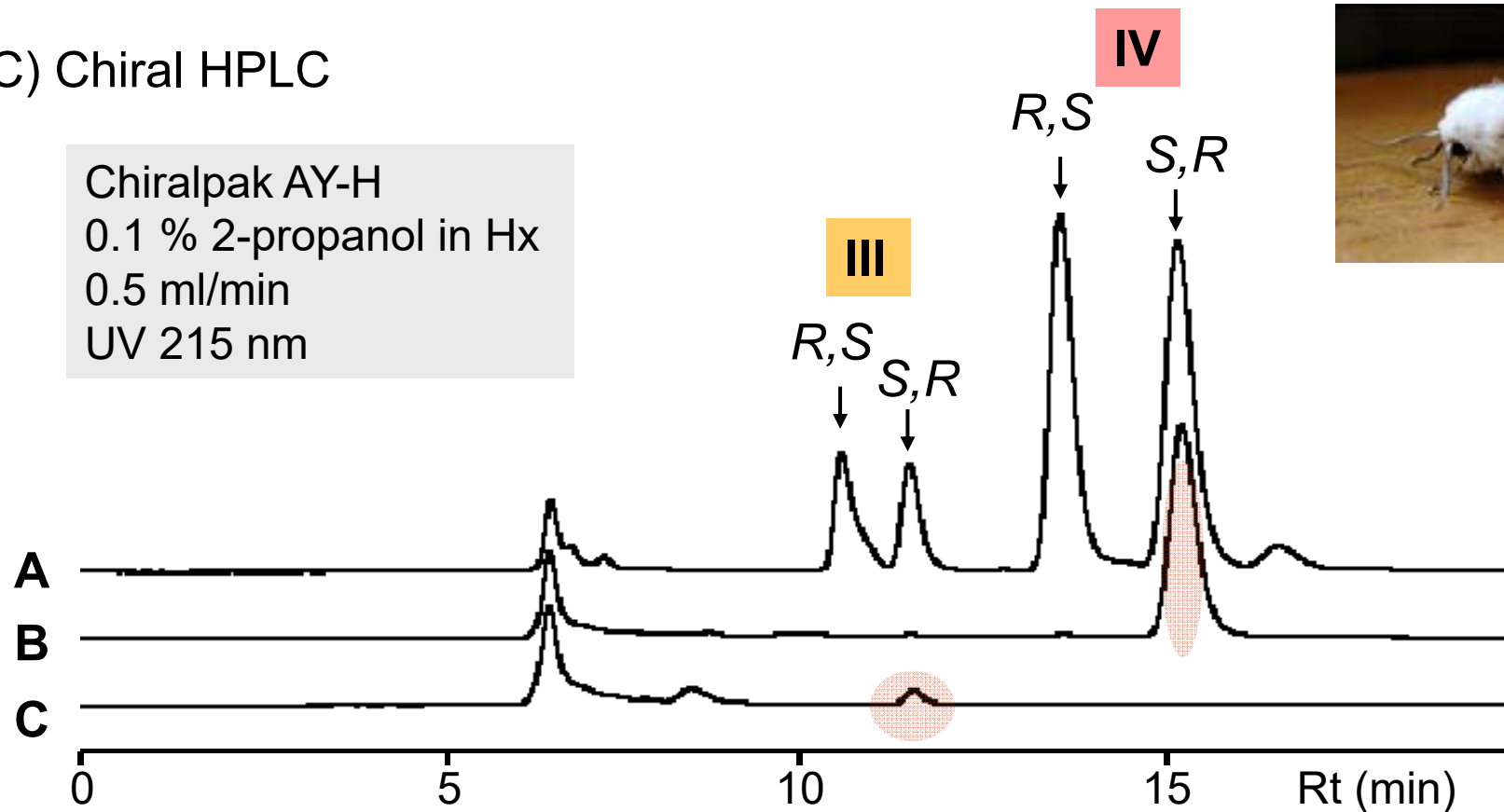
Inertsil ODS  
(4.6 mm x 25 cm)  
3.5 % H<sub>2</sub>O in MeOH  
1.0 ml/min  
UV 215 nm



# Stereochemistry of the *H. cunea* pheromone (2)

## (C) Chiral HPLC

Chiralpak AY-H  
0.1 % 2-propanol in Hx  
0.5 ml/min  
UV 215 nm



**A:** Synthetic racemic mixtures (10  $\mu\text{g}$  of **III** and 1  $\mu\text{g}$  of **IV**)

**B:** Natural pheromone (Fr. **IV**,  $\Delta^1,Z^3,Z^6,epo^9-21:H$ )

**C:** Natural pheromone (Fr. **III**,  $Z^3,Z^6,epo^9-21:H$ )

**(9S,10R)-Isomers**

Male attraction in the fields

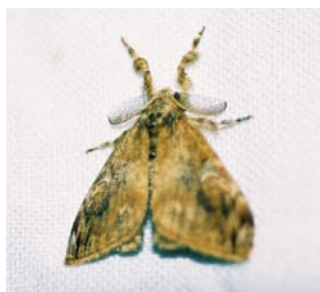
## Further studies

### Epoxytrienes derived from $\Delta^1,Z^3,Z^6,Z^9$ -tetraenes

1. Synthesis and characterization of 1,2-epoxytrienes
2. Field screening tests of the synthetic pheromone candidates to find new male attractants of the species in Arctiidae, Geometridae, and *etc.*

### Epoxy compounds derived from $Z^6,Z^9,E^{11}$ -trienes and $Z^3,Z^6,Z^9,E^{11}$ -tetraenes

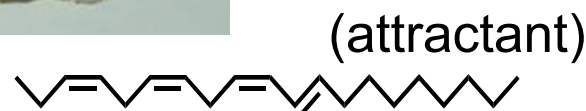
1. Synthesis of a mixture of epoxides and separation by MPLC
2. GC-MS analysis to find diagnostic fragment ions
3. Optical resolution by chiral HPLC



Tussock moth  
*Orgyia postica*  
(Lymantriidae)



Winter moth  
*Inurois fletcheri*  
(Geometridae)



(attractant)

Wakamura *et al.*, *Tetrahedron Lett.*, **42**, 687

Yamamoto *et al.*, 2008 *J. Chem. Ecol.*, **34**, 1057

# Acknowledgments

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