

2017 ISCE/APACE

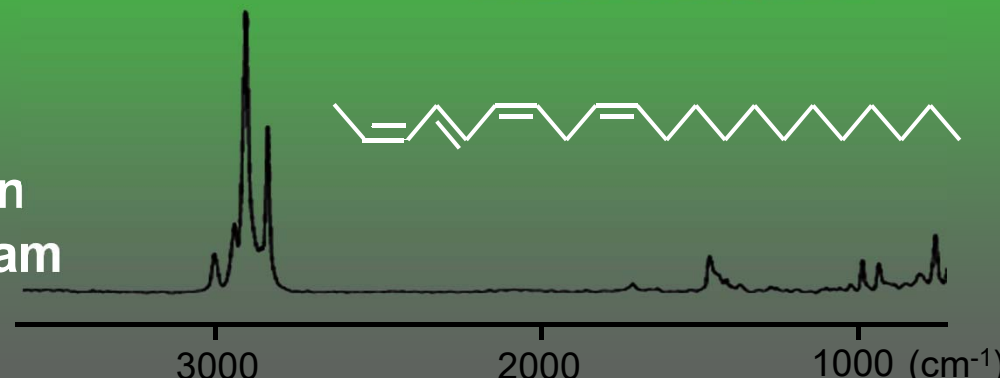
Kyoto, Japan (August 24, 2017)

GC / FT-IR analysis of a novel 2,4,6,9-tetraene
occurring in a female pheromone gland of
Parasemia plantaginis (Lepidoptera: Arctiidae)

Yuta Muraki, Hideshi Naka,
Atsushi Honma, Johanna Mappes,
Kaisa Suisto, and Tetsu Ando*



* Tokyo University of Agriculture
and Technology, Japan
JICA, Can Tho University, Vietnam
E-mail: antetsu@cc.tuat.ac.jp



Representative lepidopteran sex pheromones

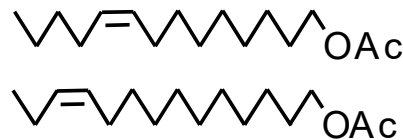
Sex pheromones have been identified from more than 670 species.
Male attractants have been reported for other 1300 species.

Type I

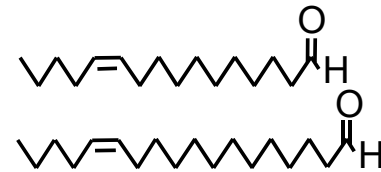
silkworm moth



smaller tea tortrix



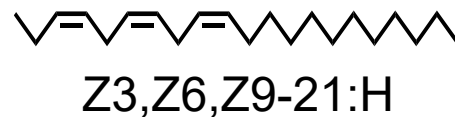
rice stem borer



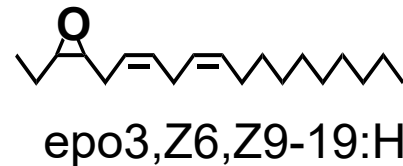
Unsaturated fatty alcohols, acetates and aldehydes with a C₁₀ – C₁₈ chain
Found most commonly (75%)

Type II

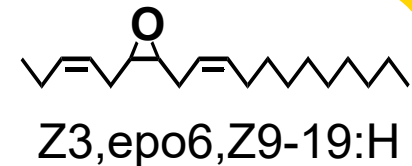
Polyunsaturated hydrocarbons and their epoxides with a C₁₇ – C₂₃ chain
Identified from evolved-insect groups (15%)



plum cankerworm moth



Milionia basalis



giant geometrid moth

Phylogenetic tree of Lepidoptera



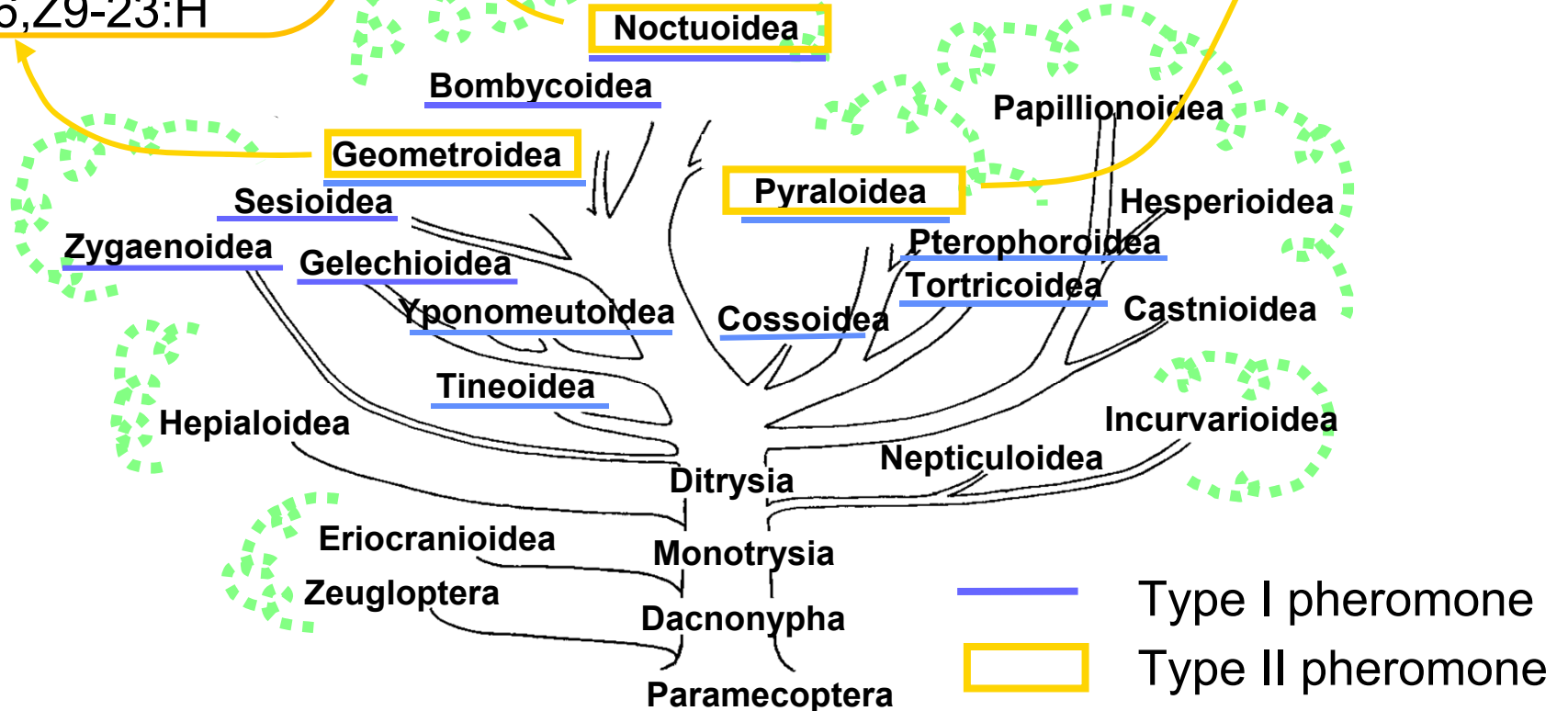
plum cankerworm moth
Z3,Z6,Z9-21:H
Z3,Z6,Z9-23:H



satin moth
Z3,epo6,epo9-21:H

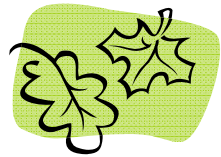


yellow peach moth
E10-16:Ald
Z3,Z6,Z9-23:H



Chemical structures of Type II pheromones

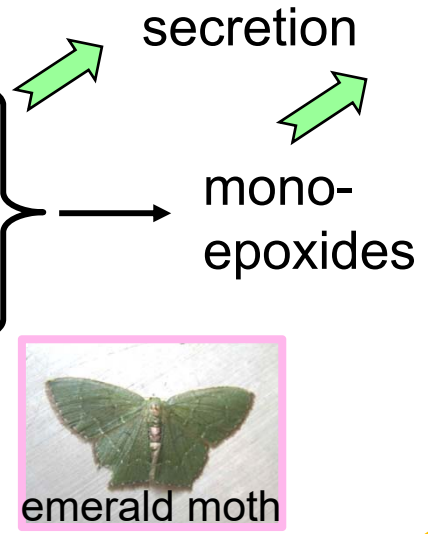
Linoleic acid



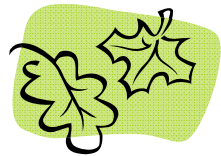
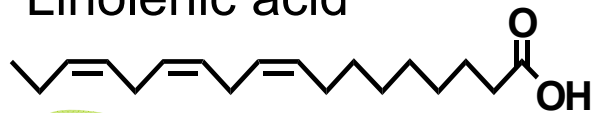
desaturation

Z6,Z9-dienes

- E4,Z6,Z9-trienes
- Z6,Z9,E11-trienes
- Z6,Z9,Z12-trienes



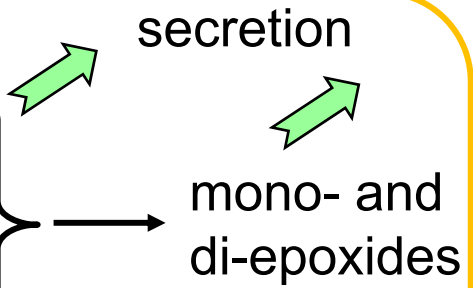
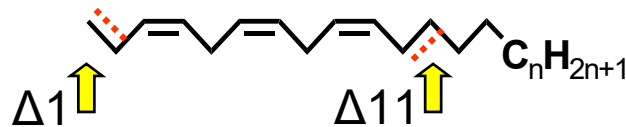
Linolenic acid



desaturation

Z3,Z6,Z9-trienes

- 1,Z3,Z6,Z9-tetraenes
- Z3,Z6,Z9,E11-tetraenes
- Z3,Z6,Z9,Z11-tetraenes



The known chemical diversity is still limited.
Novel compounds must be found.

Noctuoidea species and their sex pheromones

Taxonomy		Type of pheromone	Japanese species number	
Super-family	Family	Sub-family		
Noctuoidea	Notodontidae	I	124 [0]	
	Nolidae	II	107 [0]	
	Noctuidae	<Trifinae>	I	787 [34]
		<Quadritinae>*	II, others	489 [4]
	Lymantriidae*		II, others	59 [16]
	Arctiidae*	Lithosiinae	II, others	79 [4]
		Syntominiinae	II	4 [1]
Arctiinae		II, others	51 [3]	

*Erebidae

[] indicate number of species whose sex pheromone has been identified.

Parasemia plantaginis, wood tiger moth
(Arctiidae; Arctiinae)

Four subspecies are recorded in Japan.

P. p. macromera *P. p. melanissima*

P. p. jezoensis *P. p. melanomera*



GC-EAD analysis of the pheromone extract

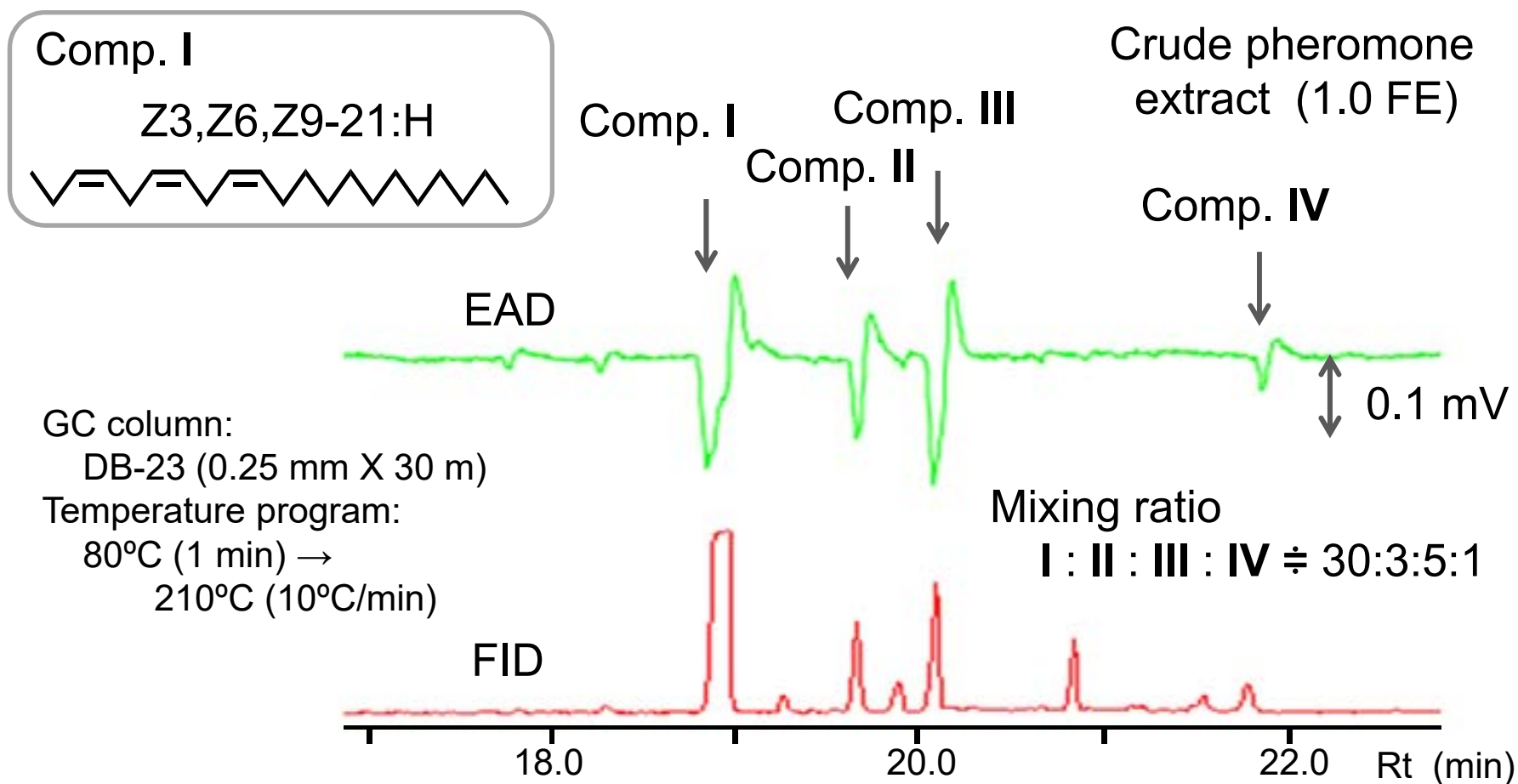
Parasemia plantaginis, wood tiger moth

(Arctiidae; Arctiinae)

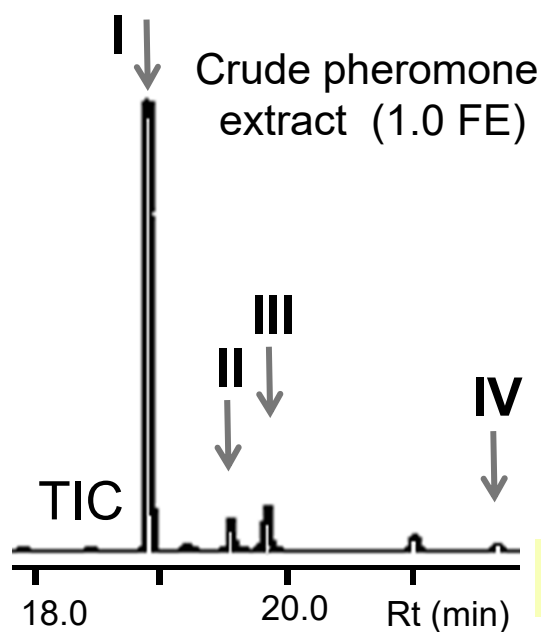
Four subspecies are recorded in Japan.

P. p. macromera *P. p. melanissima*

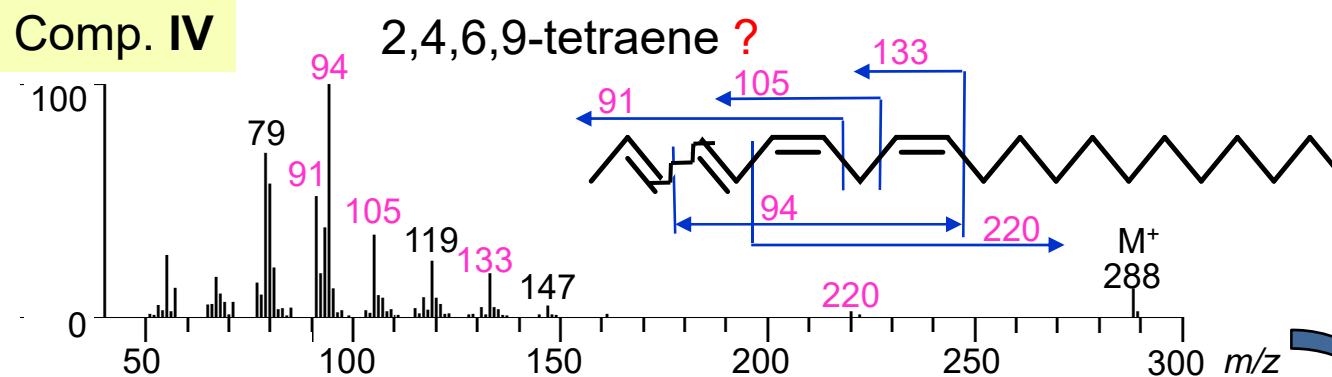
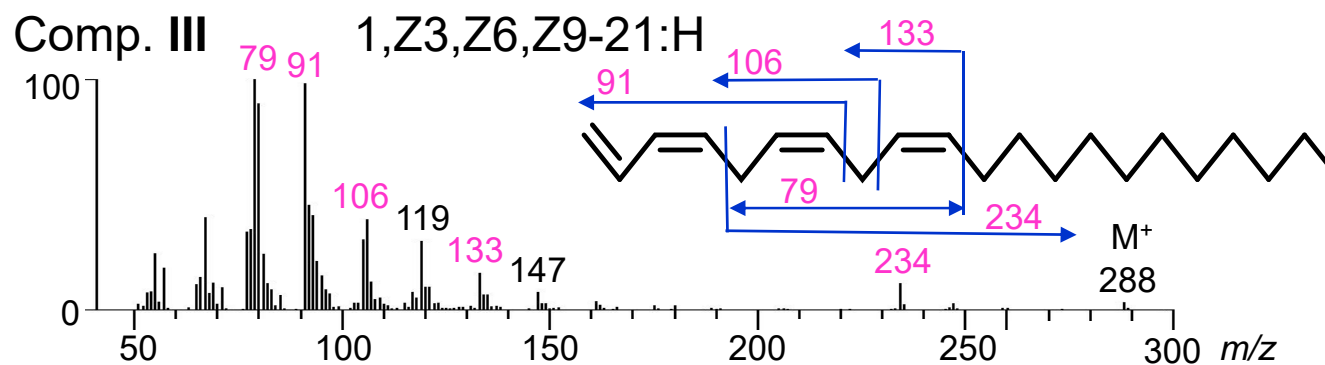
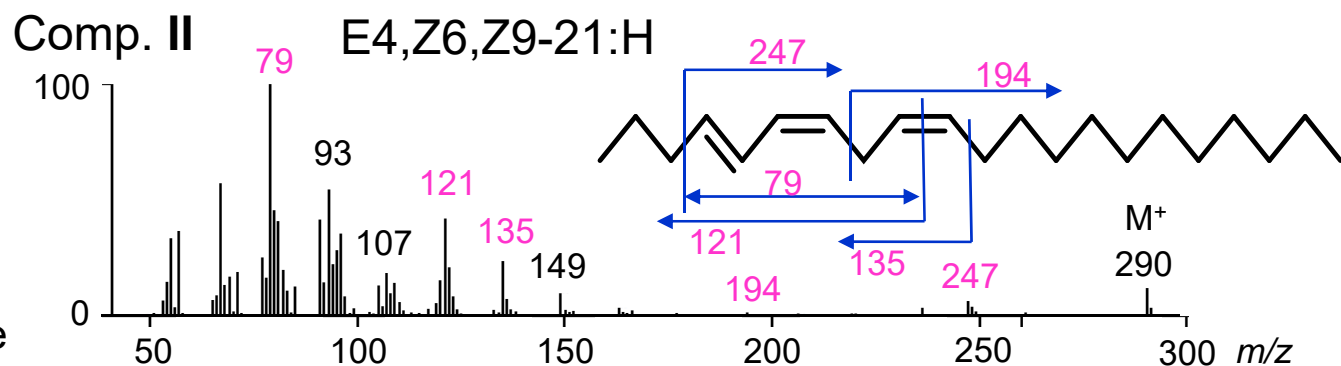
P. p. jezoensis *P. p. melanomera*



GC / MS analysis of the pheromone extract



GC column:
DB-23
(0.25 mm X 30 m)
Temperature program:
80°C (1 min) →
210°C (8°C/min)



GC/FT-IR ← No information on the configurations

Merits of IR analysis



Functional group → OH

Carbon chain length → 16

Double bond

Number → 2

Position → 10, 12

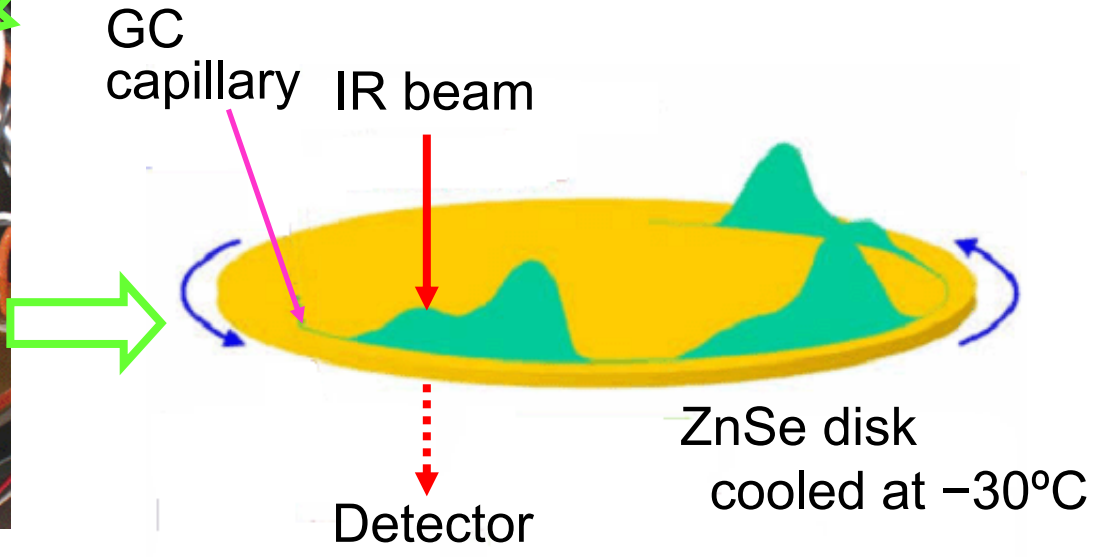
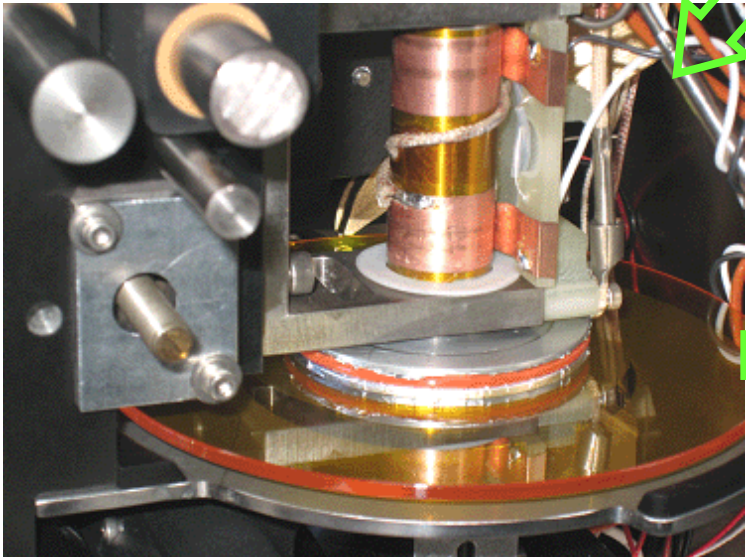
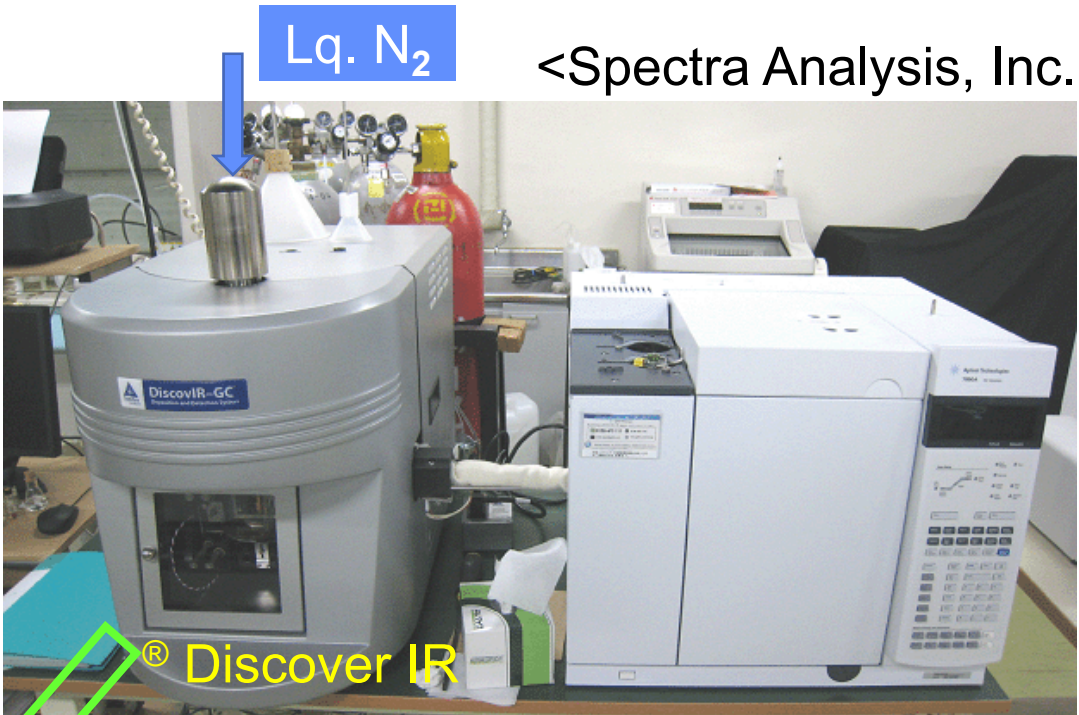
Configuration → E, Z

Determined by the IR spectrum,
if a large amount of the pure pheromone is available.

IR analysis is not utilized, because
the species-specific pheromones are composed of multiple components,
which are produced at μg level, at most.

GC / FT-IR

- Capillary GC
 - High separation
- FT-IR (solid phase)
 - High sensitivity
 - Familiarized spectrum

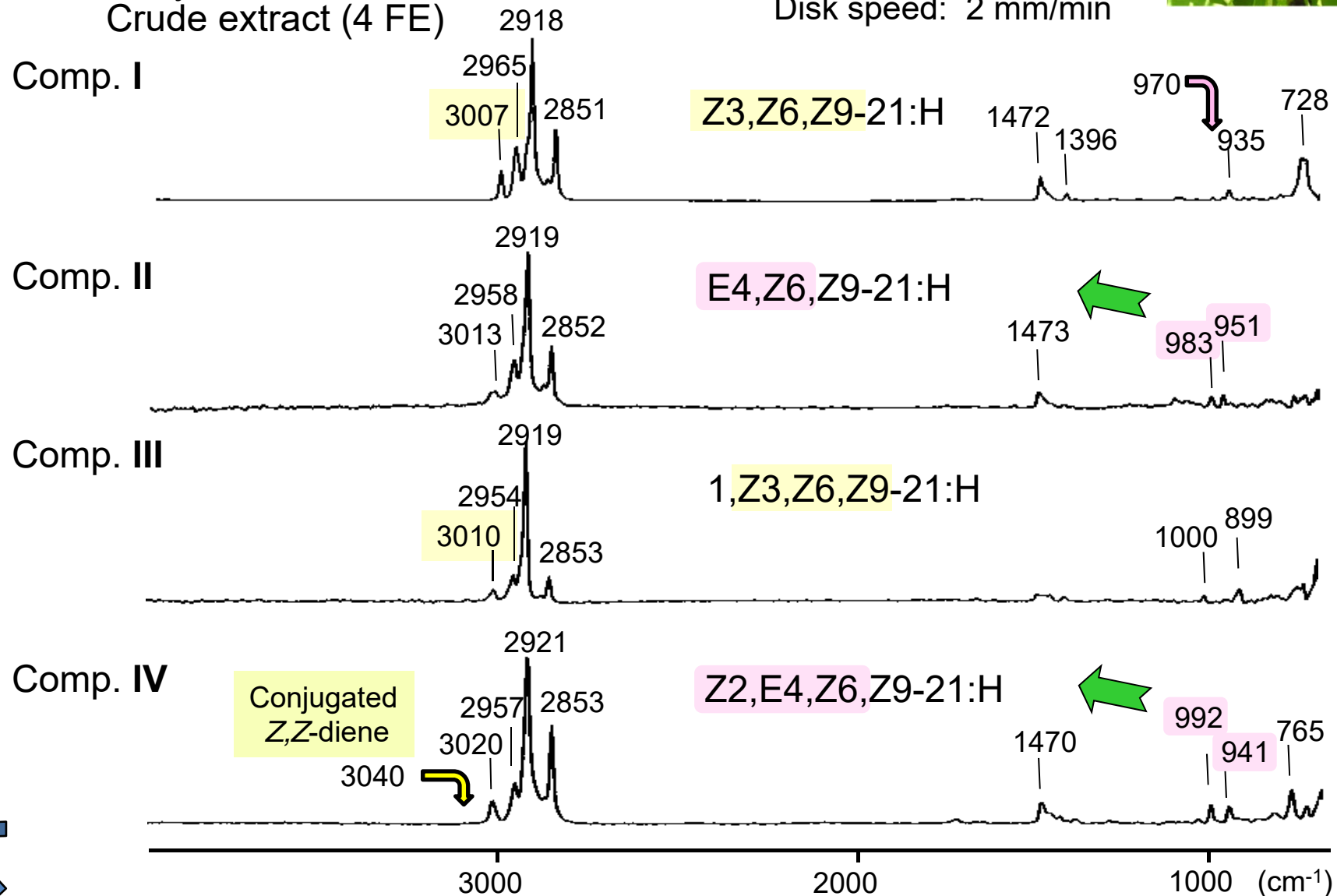


IR spectra of four EAG-active components



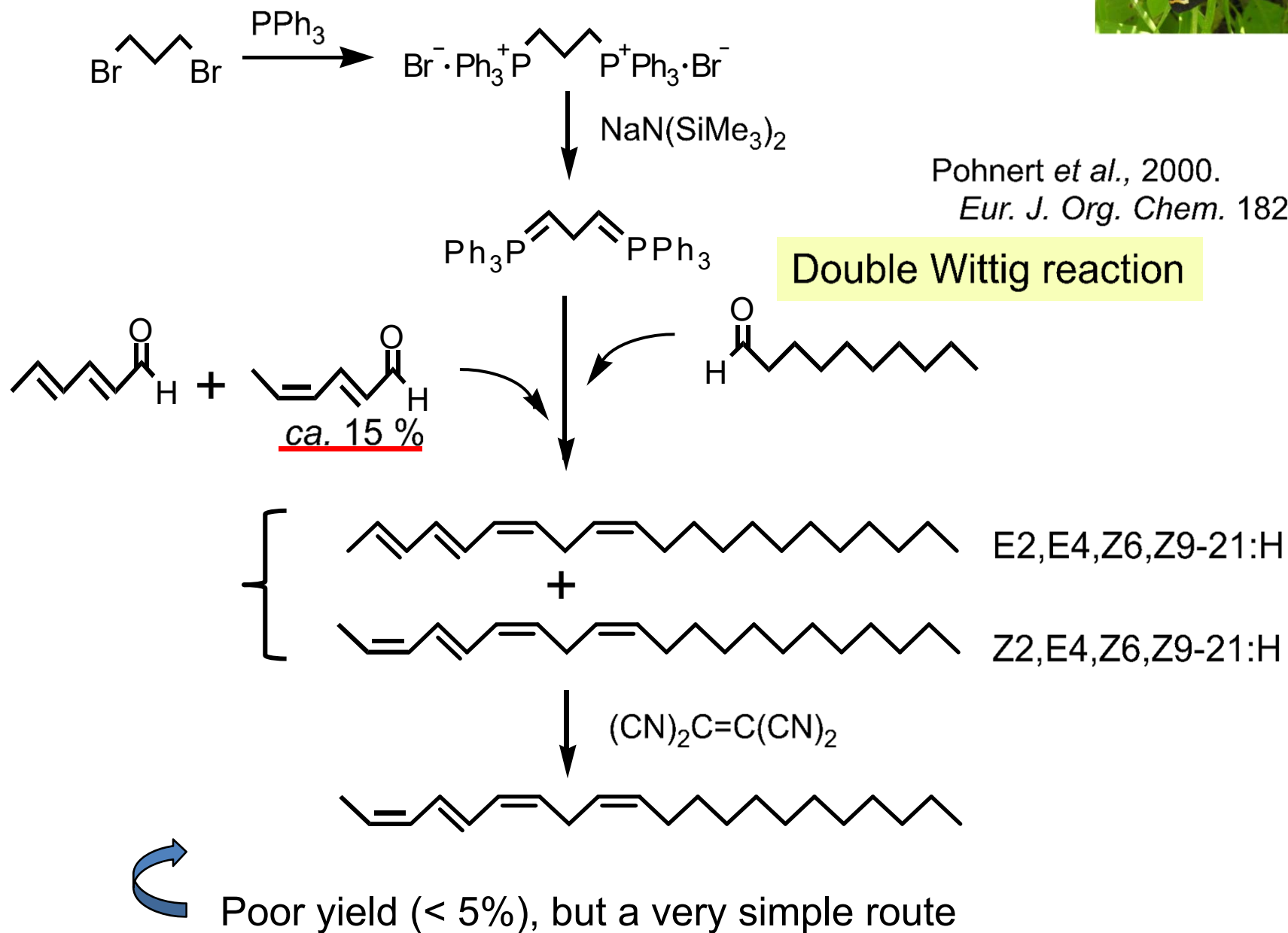
Measured by GC/FT-IR
Crude extract (4 FE)

Disk temperature: -30°C
Disk speed: 2 mm/min



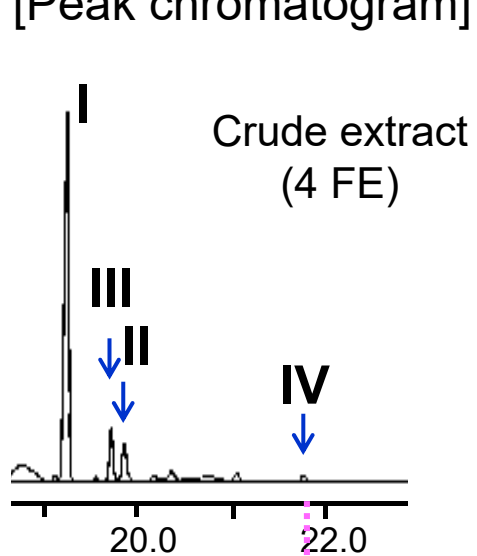
Comp. IV includes *E,Z* conjugated systems, and no *Z,Z* conjugation.

Synthesis of 2,4,6,9-tetraene

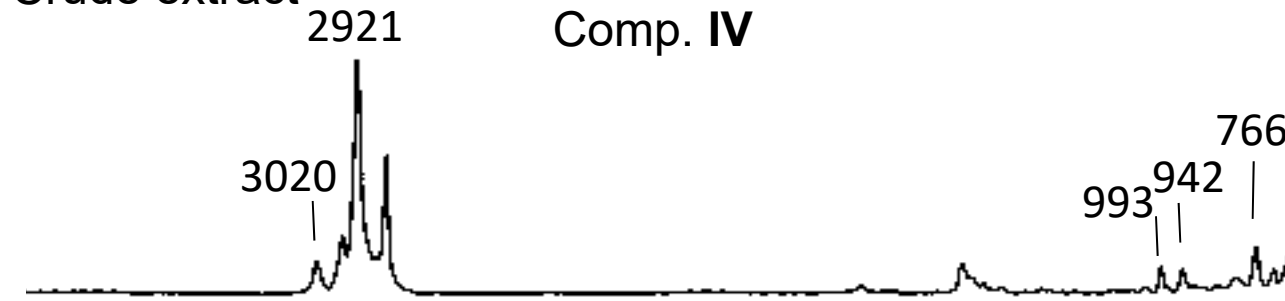


GC/FT-IR analyses of natural and synthetic 2,4,6,9-tetraene

[Peak chromatogram]

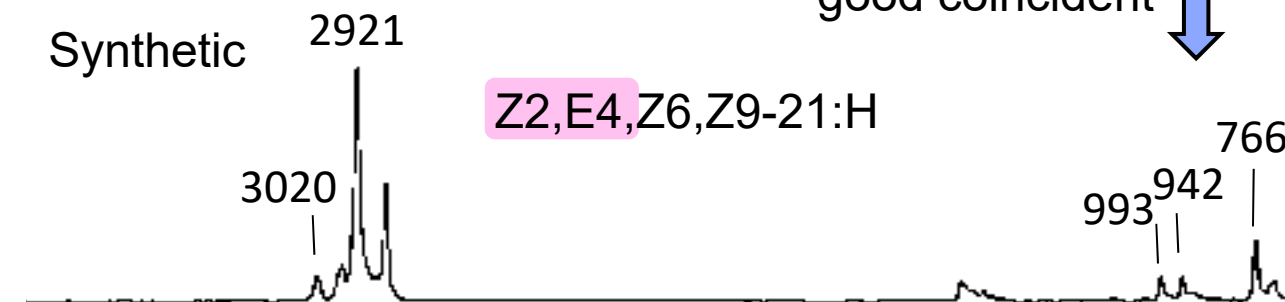


Crude extract



Comp. IV

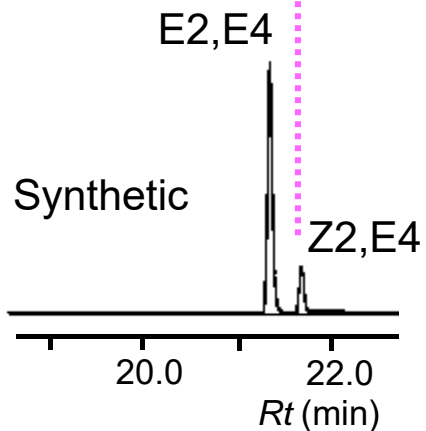
Synthetic



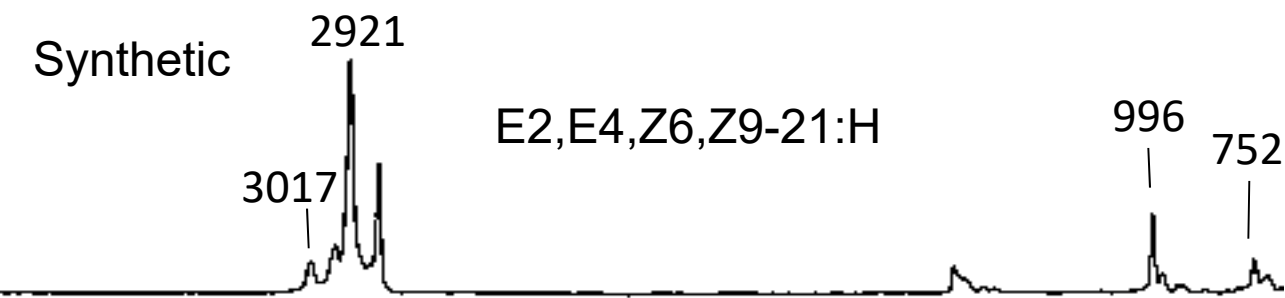
good coincident



Synthetic



Synthetic



Column: HP-5

(0.25 mm X 30 m)

3000

2000

1000 (cm⁻¹)

Summary & discussion



- 1) Four EAG-active components were found in the pheromone grand of *P. p. melanomera* and a Finnish subspecies.
- 2) GC/MS and GC/FT-IR analyses showed the following structures.


Comp. I	Z3,Z6,Z9-21:H	(← linolenic acid)
Comp. II	E4.Z6,Z9-21:H	(← linoleic acid)
Comp. III	1,Z3,Z6,Z9-21:H	(← linolenic acid)
Comp. IV	Z2,E4,Z6,Z9-21:H	(← linoleic acid)

Mixing ratio; I : II : III : IV \doteq 30 : 3 : 5 : 1
- 3) An IR spectrum of the minor Comp. IV measured by a high-sensitive GC/FT-IR instrument indicated its 2Z,4E configuration.
- 4) The structure of Comp. IV was confirmed by synthesis utilizing the double Wittig reaction.
- 5) Male attraction by synthetic lures in the field has not succeeded, indicating necessity of additional pheromone component(s).



Thank you for attention !!

**Present address: Can Tho University (CTU) in Can Tho City, Vietnam
Chief advisor of JICA's project for "Building Capacity for CTU"**



https://lepipheromone.sakura.ne.jp/index_eng.html