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# Synthesis and Characterization of 3,13- and 2,13-Octadecadienyl Compounds for Identification of the Sex Pheromone Secreted by Clearwing Moths

T. Ando,* H. Naka, M. Yamamoto,
T. Nakazawa, M. Sugie,
K. Matsuoka and Y. Arita

*Graduate School of BASE, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan
E-mail: antetsu@cc.tuat.ac.jp

# Introduction (1)

Insect photos: from web

## Studies of sex pheromones in Sesiidae

Diurnal species with wasp-mimic clear wings and body

1) First identification

Tumlinson *et al.*, *Science,* 185, 614-616 (1974)

*Synanthedon pictipes*

E3,Z13-18:OAc

*S. exitiosa*

Z3,Z13-18:OAc

2) In Japan

Yaginuma *et al*., *Appl. Entomol. Zool.*, 11, 266-268 (1976)

*Synanthedon hector*

E3,Z13-18:OAc
+ Z3,Z13-18:OAc (1:1)

*S. tenuis*

Attractant and
mating disruptant
(ca. 4,000 ha plum orchard)

# Introduction (2)

## Pheromone components of Sesiidae

Identified from 15 species as an essential component for the male attraction. Some species produce multi components.

| | | Number of species | | |
|---|---|---|---|---|
| | | OH | OAc | Ald |
| 3,13-Diene | Z3,Z13 | 4 | 3 | 0 |
| | E3,Z13 | 3 | 3 | 0 |
| | Z3,E13 | 0 | 1 | 0 |
| | E3,E13 | 0 | 0 | 0 |
| 2,13-Diene | Z2,Z13 | 0 | 0 | 0 |
| | E2,Z13 | 0 | 5 | 1 |
| 13-Monoene | Z13 | 0 | 1 | 0 |

Do the females produce E13 compounds ? Z2 compounds ?

aldehydes unsaturated at the 3-position ?

# Introduction (3)

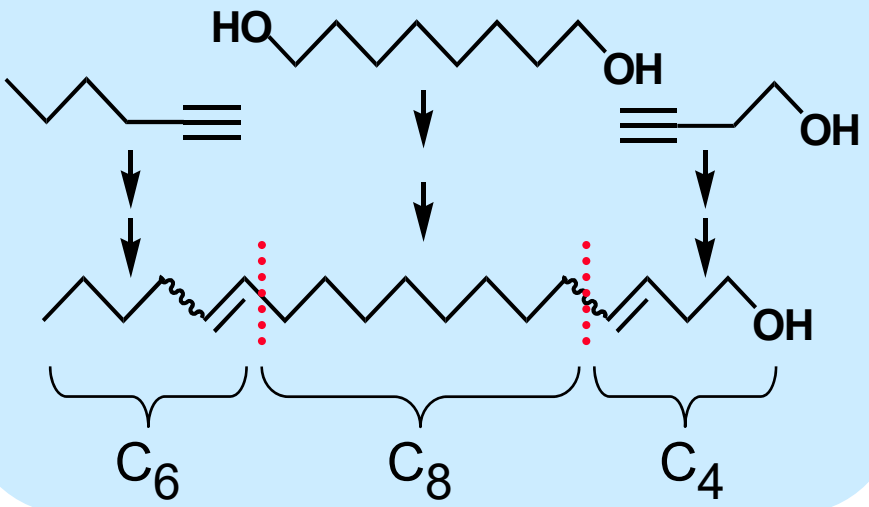
## Japanese sesiid species and pheromone studies in the world

| Sub-family / Tribe | Genus | Japanese species | Sp. reported phero. + attr. * |
|---|---|---|---|
| Tintiinae | *Trichocerata* | 3 sp. | 0 + 0 sp. |
| | *Paranthrenopsis* | 1 sp. | 0 + 0 sp. |
| | *Pennisetia* | 3 sp. | 0 + 3 sp. |
| | *Milisipepsis* | 1 sp. | 0 + 0 sp. |
| Sesiinae | | | |
| Sesiini | *Sesia* | 1 sp. | 1 + 3 sp. |
| | *Scasiba* | 3 sp. | 0 + 0 sp. |
| Melittini | *Melittia* | 4 sp. | 2 + 0 sp. |
| | *Macroscelesia* | 2 sp. | 0 + 0 sp. |
| Paranthrenini | *Nokona* | 5 sp. | 0 + 0 sp. |
| | *Paranthrene* | 1 sp. | 3 + 4 sp. |
| Cissuvorini | *Toleria* | 2 sp. | 0 + 0 sp. |
| Synanthedonini | *Synanthedon* | 12 sp. | 4 + 35 sp. |
| | *Scalarignathia* | 1 sp. | 0 + 0 sp. |
| Osminiini | | | |

* Pheromones from 15 species and attractants from 87 species have been reported.

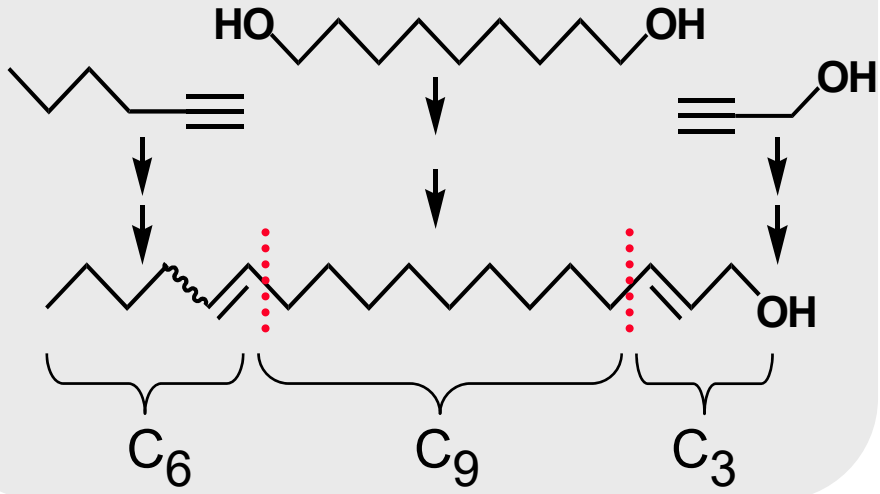
# Synthesis of all geometrical isomers

1) 3,13-Diene system




$\xrightarrow[\text{Pd-BaSO}_4\text{-Qi}]{\text{H}_2}$ (*Z*)-double bond

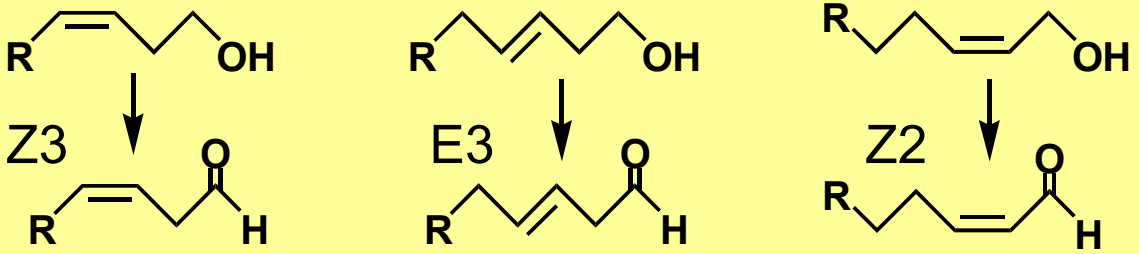
2) 2,13-Diene system



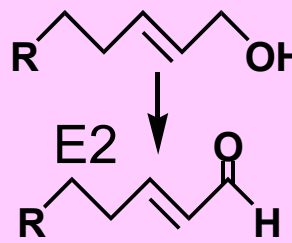

$\xrightarrow[\text{EtNH}_2]{\text{Li}}$ (*E*)-double bond

3) OH ⟶ Ald

Dess-Martin periodinane oxidation



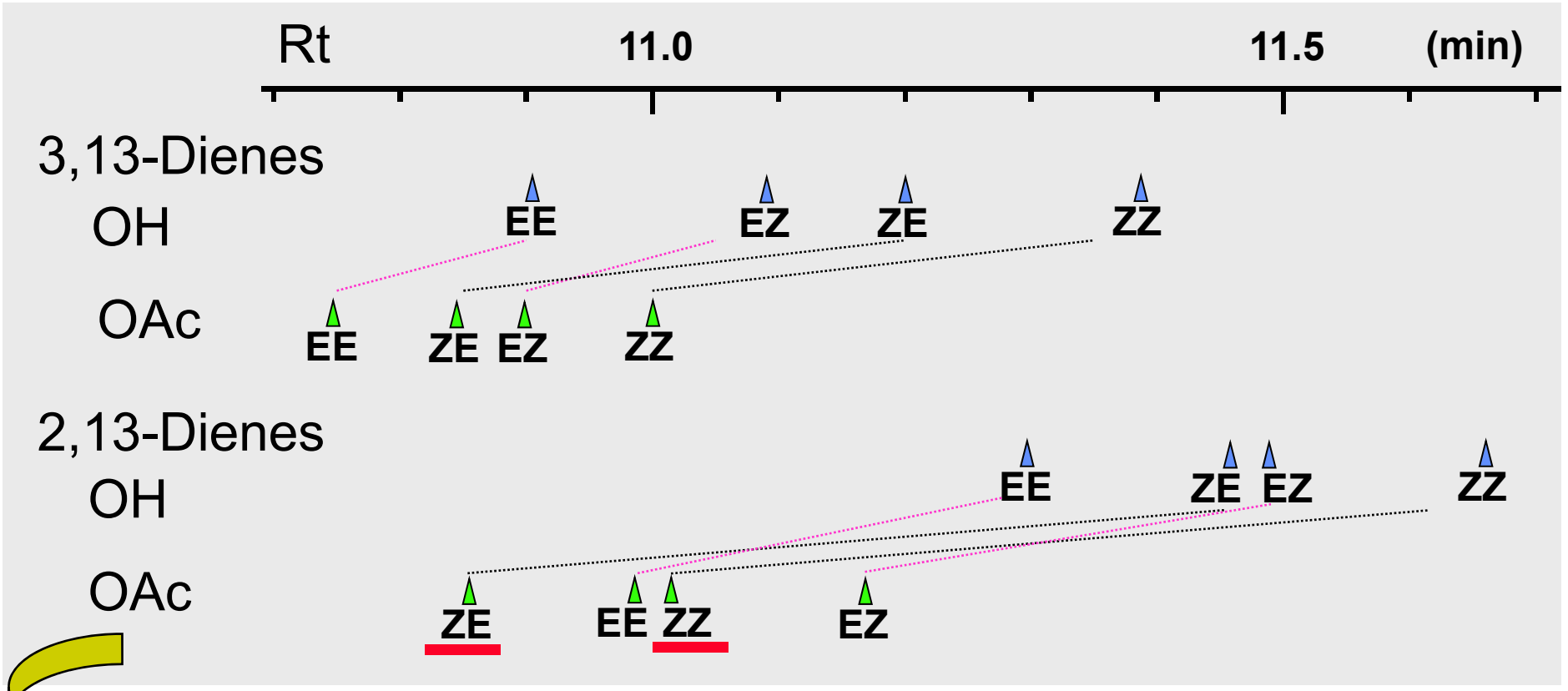

PCC oxidation




stable

# GC analysis of alcohols and acetates

**DB-23 (0.25 mm X 30 m)**
**100 °C (2 min) → 175 °C (20 °C/min) → 220 °C (6 °C/min)**



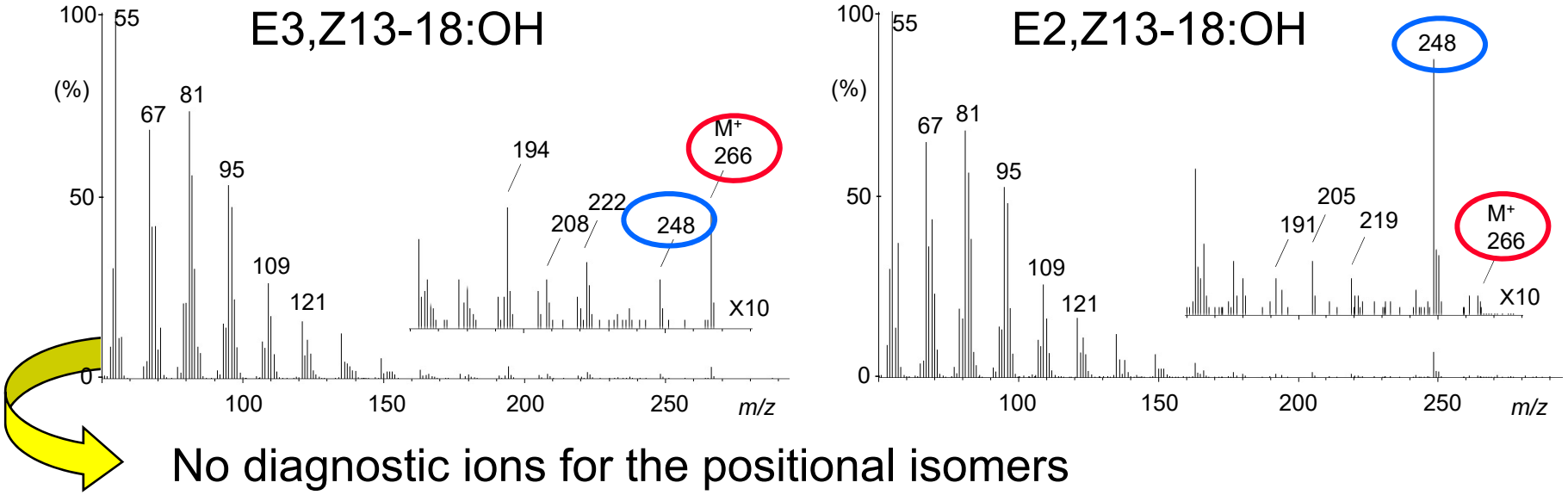

Rt OH: E3 < Z3, E13 < Z13, E2 < Z2

OAc: E3 < Z3, E13 < Z13, Z2 < E2

Elusion order of OAc is different from that of OH.

# Mass spectra of alcohols and acetates

## 1) Alcohols




No diagnostic ions for the positional isomers

But, $M^+$ 3,13-**diene** > 2,13-**diene** $[M-18]^+$ 3,13-**diene** < 2,13-**diene**

## 2) Acetates

3,13-Dienes and 2,13-dienes showed almost the same spectra.

## 3) DMDS derivatives

Mono-DMDS adduct at the 13-position OK

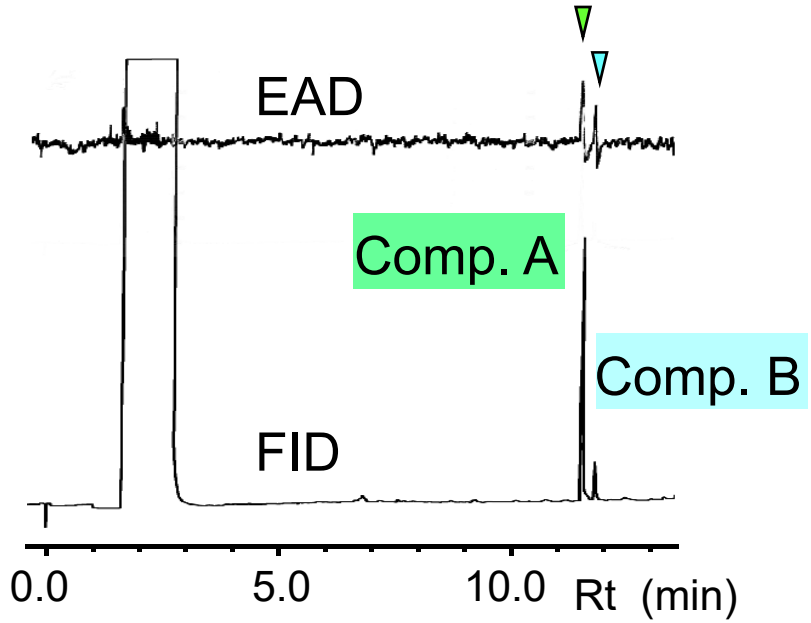
Di-DMDS adduct at the 3,13- or 2,13-positions ?

Vincenti *et al.*, *Ann. Chem.*, 59, 694-699 (1987)

# Sex pheromone of *Nokona pernix*


Distribution: Japan, China
Host plant: *Paederia scandens* (Rubiaceae)

(A) GC-EAD analysis




(B) GC-MS analysis

Comp. A E3,Z13-18:OH
Comp. B Z3,Z13-18:OH

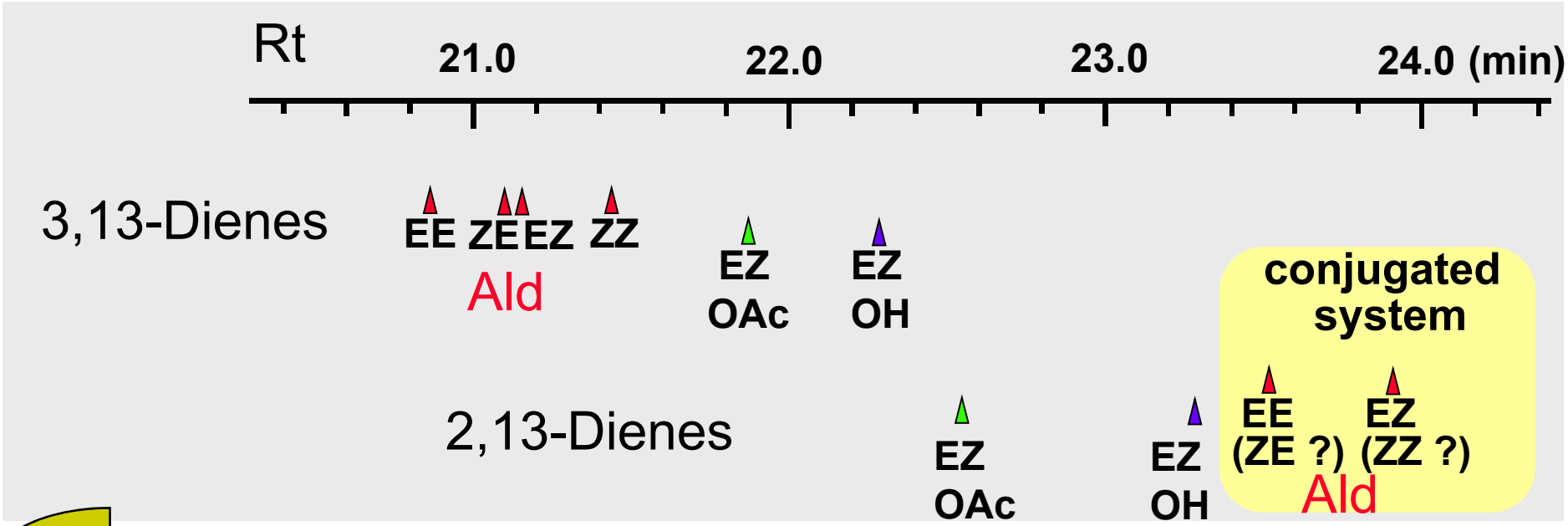
(C) Field attraction by synthetic rules

| Lure (mg/septum) E3,Z13 | Z3,Z13 | males/trap | |
|---|---|---|---|
| 1.00 | 0 | 0 | |
| 0.99 | 0.01 | 0 | |
| 0.95 | 0.05 | 8.7 ± 6.5 | a |
| 0.90 | 0.10 | 20.7 ±13.4 | a |
| 0.70 | 0.30 | 7.7 ± 3.8 | a |
| 0.50 | 0.50 | 1.3 ± 1.5 | b |
| 0 | 0 | 0 | |

June 15 –
July 12, 2004

# GC analysis of aldehydes

**DB-23 (0.25 mm X 30 m), cool-on column injector**
**50 °C (2 min) → 160 °C (10 °C/min) → 230 °C (4 °C/min)**



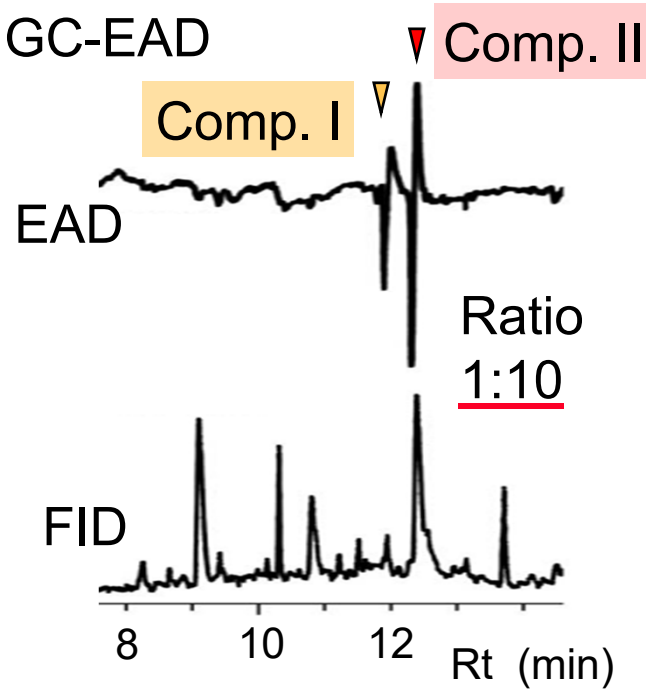

Rt 3,13-Diene: Ald < OAc < OH

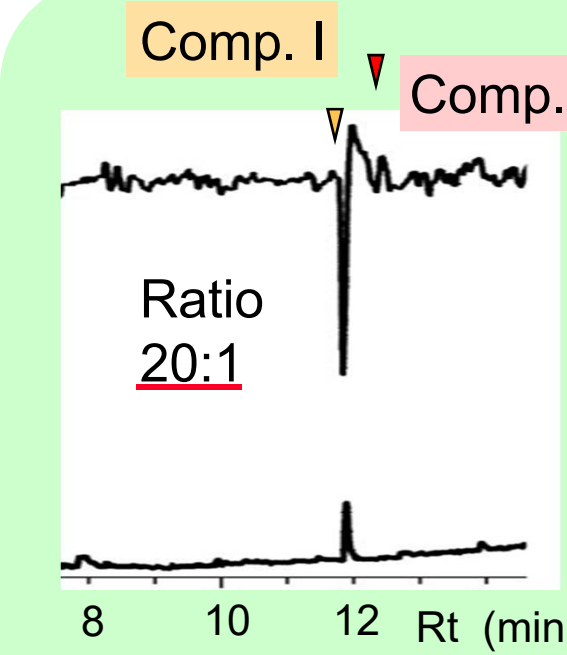
2,13-Diene: OAc < OH < Ald

3,13-Dienals were mainly isomerized to 2,13-dienal with E2.
Z2-Configuration were completely changed to E2-configuration.

# Sex pheromone of *Macroscelesia* spp.

*M. Japona* (Hampson)
Distribution: Japan
Host plant: *Gynostemma pentaphyllum* (in copse)




Comp. I E2,Z13-18:OH

GC-MS ⟶ OH, 2,13-diene, EZ-isomer

Comp. II E2,Z13-18:Ald

GC-MS ⟶ Ald, 2,13-diene? EZ-isomer?

$NaBH_4$ reduction ⟶ E2,Z13-18:OH

⇨ HPLC, LC-MS analyses

*M. longipes yamatoensis* Arita
Distribution: Japan
Host plant: *Actinostemma lobatum* (in riverbed)

# Field evaluation of *Macroscelesia* pheromones

(A) Field attraction in a cospe (June 17 - July 16,2004)

| E2,Z13-18 (mg/septum) OH | Ald | males/trap | |
|---|---|---|---|
| 0 | 1.00 | 1.0 ± 1.0 | b |
| 0.01 | 1.00 | 13.0 ± 7.0 | a |
| 0.05 | 1.00 | 2.3 ± 3.2 | b |
| 0.10 | 1.00 | 0.3 ± 0.6 | b |
| 0.30 | 1.00 | 0 | |
| 0 | 0 | 0 | |

1:100

*M. Japona*

Different habitats and sex pheromones

Reproductive isolation

*M. longipes*

(B) Field attraction in a river side (August 12-23, 2004)

| E2,Z13-18 (mg/septum) OH | Ald | Total males Attracted | | Touched | |
|---|---|---|---|---|---|
| 1.00 | 0 | 6.3 ± 1.7 | b,c | 3.0 ± 1.8 | b,c |
| 1.00 | 0.05 | 13.8 ± 3.3 | a | 9.8 ± 2.2 | a |
| 1.00 | 0.10 | 13.0 ± 6.1 | a,b | 5.3 ± 2.9 | b |
| 1.00 | 0.30 | 13.3 ± 2.5 | a | 5.5 ± 1.3 | b |
| 0 | 0 | 0 | | 0 | |

20:1

# Co-workers


**Dr. Hideshi NAKA**

Department of Biological Safety,
National Institute for Agro-Environmental Sciences (NIAES),
Tsukuba, Ibaraki 305-8604, Japan
Present address:
JT Biohistory Research Hall



**Prof. Yutaka ARITA**

Faculty of Agriculture, Meijo University
Tempaku-ku, Nagoya 468-8502, Japan


Book written
by Prof. Arita