

Synthetic studies on female sex pheromones of lepidopteran insects

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The pheromones are classified into (1) type I compounds, (2) type II compounds, (3) methyl-branched compounds, and (4) non-branched other compounds.

The chemical formulae are symbolized by

- 1) the number before the hyphen giving the position of double bond(s) [Z = (Z)-configuration, E = (E)-configuration, Δ = terminal] and/or other structures in the chain as follows, ≡ = triple bond, epo = *cis*-epoxy ring, tepo = *trans*-epoxy ring, and Me = branched methyl group,
- 2) the number before the colon giving the carbon atoms in the straight chain skeleton,
- 3) the words after the colon giving the functional groups as follows, H = hydrocarbon, OH = primary alcohol, OAc = acetate of alcohol, Ald = aldehyde, and one = ketone.

Pheromone	Family and species of moth	Publication of synthesis
<u>(1) Type I compounds</u>		
1-1) 1,3-Dienes		
E3,Z5-12:OAc	Tortricidae (<i>Phtheochroa cranaodes</i>)	Unelius, 1996; Park, 1998; Chong, 1999; Hodgson, 2007
Z3,E5-14:OAc	Cossidae (<i>Holcocerus vicarius</i>)	Rossi, 1982; Doolittle, 1986
E4,Z6-16:OAc	Stathmopodidae (<i>Stathmopoda masinissa</i>)	Nishida, 2003; Awalekar, 2020
Z5,E7-12:OH and/or Z5,E7-12:Ald	Lasiocampidae (<i>Malacosoma disstria</i> , <i>Dendrolimus spectabilis</i> , etc.)	Chisholm, 1981; Ando, 1982; Bestmann, 1982; Trost, 1984; Gardette, 1984; Ando, 1985; Fiandanese, 1989; Khrimian, 2002
E7,Z9-12:OAc	Tortricidae (<i>Lobesia botrana</i>)	Labovitz, 1975; Dressaire, 1980; Rossi, 1981; Ujvary, 1985; Gardette, 1984; Alexakis, 1988; Fiandanese, 1989; Yamamoto, 1989(c); Diego, 2006; Cahiez, 2017

- E8,E10-12:OH
Tortricidae (*Cydia pomonella*)
- E8,Z10-14:Ald
Gracillariidae (*Cameraria ohridella*)
- E9,Δ11-12:OAc
Noctuidae (*Diparopsis castanea*)
- Z9,Δ11-12:OAc
Noctuidae (*Diparopsis castanea*)
- Z9,E11-14:OAc
Noctuidae (*Spodoptera littoralis*)
- E9,E11-14:OAc
Tortricidae (*Epiphyas postvittana*)
- Z9,E11-16:Ald
Crambidae (*Diatraea saccharalis*)
- E9,Z11-16:Ald
Pyralidae (*Acrobasis nuxvorella*)
- E10,Z12-16:OH
Bombycidae (*Bombyx mori*)
- E10,E12-16:Ald
Noctuidae (*Earias insulana*)
- Z11,Z13-16:Ald
Pyralidae (*Amyelois transitella*)
Notodontidae (*Notodonta dromedaries* etc.)
- Z11,E13-16:OAc
Pyralidae (*Herpetogramma licarsisalis*)
- 1-2) 1,4-Dienes
- E4,Z7-13:OAc
Gelechiidae (*Phthorimaea operculella*)
- Z9,E12-14:OAc
- Descoins, 1972; Mori, 1974(a); Samain, 1978; Knox, 1981; Bloch, 1983; Yamada, 1983; Ando, 1985; Chourreu, 2021
- Figueiredo, 2007; Grodner, 2009; Chourreu, 2020
- Nesbitt, 1972; Mori 1974(a); Babler, 1977; [Wollenberg, 1979]; Rossi, 1981; Knox, 1981; Bloch, 1982; Yamada, 1983; Engman, 1985; Nagano, 2002; Cahiez, 2008
- Gardette, 1984; Ishibashi, 1987
- Rossi, 1981; Gardette, 1984; Fiandanese, 1989
- Knox, 1981; Bloch, 1983
- Svirskaya, 1984(b); Tao, 2013
- Passaro, 2003; Figueiredo, 2007
- Negishi, 1973; Bestmann, 1977; Zweifel, 1978; Gardette, 1984; Alexakis, 1988; Fiandanese, 1989; Uenishi, 2000; Khrimian, 2002
- Knox, 1981; Klug, 1982
- Bishop, 1983; Gardette, 1984; Mori, 2009(c), Liu, 2019
- Alexakis, 1988; Gibb, 2007
- Voerman, 1978; Alexakis, 1978; Nishiyama, 1984; Yadav, 1986; Nonoshita, 1990; Hutzinger, 1995; Odinokov, 1997; Vakhidov, 2007; Pan, 2022
- Jacobson, 1970; Bac, 1982; Kasymzhanova, 1992

Noctuidae (*Spodoptera eridania* etc.)
Pyralidae (*Cadra cautella*, etc.)

- 1-3) 1,5-Dienes
E3,Z7-14:OAc Ragoussis, 2008; Awalekar, 2021
Gelechiidae (*Symmetrischema tangolias*)
Z7,Z11-16:OAc and/or Z7,E11-16:OAc Sonnet, 1974; Mori, 1974(b); Su, 1974; Anderson, 1975; Ishihara, 1984;
Gelechiidae (*Pectinophora gossypiella*, Svirskaya, 1984(a); Ducoux, 1992; D'yakonov, 2017
Sitotroga cerealella)
- 1-4) Other dienes
E2,Z13-18:Ald and/or E2,Z13-18:OAc Hukumoto, 1998; Hoskovec, 1990; Grodner, 2006; Naka, 2006; Islam, 2007
Sesiidae (*Vitacea polistiformis*, etc)
E3,Z8-14:OAc Cabezas, 2019
Gelechiidae (*Scrobipalpuloides absoluta*)
Z3,Z13-18:OAc and/or E3,Z13-18:OAc Voerman, 1979; Doolittle, 1980; Gardette, 1983(b); Svirskaya, 1984(a);
Sesiidae (*Synanthedon exitiosa* Yamamoto, 1989(a); Hoskovec, 1990; Naka, 2006;
Synanthedon pictipes, etc.) Armstrong-Chong, 2004
E6,Z11-16:OAc and E6,Z11-16:Ald Kochansky, 1977
Saturniidae (*Antheraea polyphemus*)
- 1-5) Trienes
E3,Z8,Z11-14:OAc Cabezas, 2019
Gelechiidae (*Scrobipalpuloides absoluta*)
E4,E6,Z10-16:OH and E4,Z6,Z10-16:OH Huang, 2017
Gracillariidae (*Conopomorpha cramerella*)
E4,E6,Z11-16:Ald Tomida, 1993
Saturniidae (*Samia cynthia*)
E4,Z7,Z10-13:OAc Voerman, 1978; Pan, 2022
Gelechiidae (*Phthorimaea operculella*)
Z7,Z11,E13-16:Ald Leal, 2006; Moreira, 2006; Vang, 2008
Gracillariidae (*Phyllocnistis citrella*)

Z9,E11,Δ13-14:Ald
 Pyralidae (*Ectomyelois ceratoniae*)
 Elachistidae (*Stenoma cecropia*)
 Baker, 1989; Millar, 1990; Tellier, 1990; Tellier, 1991(a)

E10,E12,Z14-16:OAc or E10,E12,Z14-16:Ald
 Crambidae (*Glyphodes pyloalis*)
 Sphingidae (*Manduca sexta*)
 Ando, 1988; Doolittle, 1990; Tellier, 1991(b); Chen, 2000

1-6) Tetraenes
 Z7,Z13,Z16,Z19-22:OisoBu
 Erebidae (*Euproctis chrysorrhoea*)
 Khrimian, 2008

1-7) 1,3-Enynes
 Z9,≡11,Δ13-14:Ald
 Elachistidae (*Stenoma catenifer*)
 Hoddle, 2009; Zou, 2010

≡11,Z13-16:OAc
 Notodontidae (*Thaumetopoea pityocampa*)
 Gardette, 1983(a); Camps, 1983; Shani, 1983

(2) Type II compounds

Z3,Z6,Z9-19:H and/or Z3,Z6,Z9-21:H
 Geometridae (*Ascotis selenaria*, etc.)
 Conner, 1980; Becker, 1983; Baker, 1984; Underhill, 1983;
 Bestmann, 1985; Mangold, 1987; Langlois, 1990; Ando, 1993
 Yadav, 1998(a); Wang, 2007; Davies, 2007

Δ1,Z3,Z6,Z9-19:H
 Geometridae (*Operophtera brumata*)
 Huang, 1983; Jain, 1983(b); Baker, 1984; Viala, 1991; Pohnert, 2000
 Yamamoto, 2008

Δ1,Z3,Z6,Z9-21:H
 Erebidae (*Utetheisa ornatrix*)
 Jain, 1983(a); Yamamoto, 2008

Z3,Z6,Z9,E11-19:H
 Geometridae (*Alsophila pomataria*)
 Yamamoto, 2008

Z3,Z6,Z9,Z12-20:H
 Geometridae (*Thalassodes immissaria*)
 Yamakawa, 2011(a); Langseter, 2012

epo3,Z6,Z9-18:H (3S,4R) and (3R,4S)
 Geometridae (*Ascotis selenaria*)
 [Ando 1993]; Soulie, 1995; Qin, 1997

Z3,epo6,Z9-18:H (6S,7R)
 Yu, 2017; Xu, 2017

Geometridae (<i>Ectropis obliqua</i>)	
Z3,epo6,Z9-19:H (6S,7R) Geometridae (<i>Erannis defoliaria</i>)	Mori, 1991(c); [Ando 1993]; Qin, 1997
Z6,epo9-19:H (9S,10R) Geometridae (<i>Ennomos subsignaria</i>)	MaGee, 2011; Zhou, 2024(a)
Z6,epo9-21:H (9S,10R) Erebidae (<i>Phragmatobia fuliginosa</i> , etc.) (9R,10S) Erebidae (<i>Teia anartoides</i> , etc.) Z3,Z6,epo9-19:H (9S,10R) Erebidae (<i>Lymantria mathura</i> , etc.)	Brevet, 1992; [Bell, 1993]; [Ando 1995]; Zhang, 2000 Muto, 2003(b); Zhou, 2024(a) [Ando 1993]; Qin, 1997; Khrimian, 2004
Z3,Z6,epo9-21:H (9S,10R) Erebidae (<i>Estigmene acrea</i> , <i>Hyphantria cunea</i> , etc)	Mori, 1981; Mori, 1986; Pougny, 1987; [Bell, 1993]; [Ando 1993]; Qin, 1997; Nakanishi, 2005
Δ1,Z3,Z6,epo9-21:H (9S,10R) Erebidae (<i>Hyphantria cunea</i> , etc.)	Mori, 1989; Yadav, 1998(b); Nakanishi, 2005; Che, 2005; Yamakawa, 2012
Z3,epo6,epo9-21:H (6R,7S,9R,10S, leucomalure) Erebidae (<i>Leucoma salicis</i>)	Yamamoto, 1999; [Yamazawa, 2001]; [Lizarraga, 2001]; Muto, 2003(a) Wimalaratne, 2004
epo3,epo6,Z9-21:H (3S,4R,6S,7R) Erebidae (<i>Perina nuda</i>)	Yamamoto, 1999; [Yamazawa, 2001]
tepo4,Z6,Z9-19:H Geometridae (<i>Bupalus piniarius</i>)	[Yamamoto, 2013]; Kang, 2007
Z6,Z9,tepo11-21:H (11S,12S, posticlure) Erebidae (<i>Orgyia postica</i>)	Wakamura, 2001; Muto, 2001; Fernandes, 2002; Kang, 2007; Fernandes, 2007

(3) Methyl-branched compounds

3-1) Hydrocarbons

Me2-17:H Erebidae (<i>Holomelina aurantiaca</i> etc.)	Dasaradhi, 1987
Me2,Me5-17:H (S) + Me5,Me11-17:H (5R,11S) Geometridae (<i>Lambdina fiscellaria</i>)	[Gries, 1991]; Li, 1993; Mori, 1996; Wang, 2023
Me5,Me9-15:H (5S,9R) Lyonetiidae (<i>Perileucoptera coffeella</i>)	Kuwahara, 2000; Moreira, 2003; [Zarbin, 2004]; Mori, 2008

- Me5,Me9-17:H (5*S*,9*S*)
Lyonetiidae (*Leucoptera malifoliella*)
Mori, 1991(a); Taguri, 2012; Li, 2013; Yu, 2023
- Me7-17:H (S) + Me7,Me11-17:H (meso)
Geometridae (*Lambdina athasaria*, *L. pellucidaria*)
Shirai, 1999; Diaz, 2000; Enders, 2002; [Chow, 2004]; Nagano, 2007
- Me9-19:H (S)
Erebidae (*Alabama argillacea*)
Lamers, 2003; Cao, 2013
- Δ1,Me10,Me14-18:H (10*S*,14*S*)
Lyonetiidae (*Lyonetia prunifoliella*)
Tamagawa, 1999; [Nakamura, 2000(a)]; Summeren, 2005; Taguri, 2014; Yu, 2023
- Δ1,Me14-18:H (S)
Lyonetiidae (*Lyonetia clerkella*)
[Sugie, 1984]; [Manabe, 1985]; Kato, 1985; Mori, 1985; Sonnet, 1987; [Yamamoto, 1989(b)]; Sankaranarayanan, 1995; Zhang, 2013; Ishmuratov, 2013; Wei, 2020; He, 2021; He, 2022
- 3-2) Epoxides
Me2,epo7-18:H (7*R*,8*S*, (+)-disparlure)
Erebidae (*Lymantria dispar*)
Iwaki, 1974; Mori, 1981; Mori, 1986; Fukusaki, 1991; Keinan, 1992; Brevet, 1992; Hu, 1999; Koumbis, 2005; Inkster, 2005; Garg, 2017; Gwon, 2024
- 3-3) Esters of primary alcohol and acid
Me3,Me13-15:Ate with Me2-5:3-OH (3*R*,13*R*,1'*S*)
Psychidae (*Clania variegata*)
Mori, 2009(b); Mori, 2010; Taguri, 2013; Sun, 2017(b); Wang, 2024
- Me10-12:OAc (R)
Tortricidae (*Adoxophyes honmai*)
Suguro, 1979; Hjalmarsson, 1985; Sankaranarayanan, 1995; Geresh, 1998; Chow, 2001
- Me10,Me14-15:OisoBu (R)
Erebidae (*Arna pseudoconspersa*)
Ichikawa, 1995; Sun, 2017(a); Sun, 2024
- 3-4) Secondary alcohols
Me5-17:7-OH (5*R*,7*R*)
Erebidae (*Miltchrista calamine*)
Yamakawa, 2011(b); Muraki, 2014; Yuan, 2022
- Me6,Me10,Me14-15:2-OH (2*R*,6*R*,10*R*)
Pyralidae (*Corcyra cephalonica*, *Aphomia sociella*)
Mori, 1991(b); Nakamura, 2000(b), Shafikov, 2011
- 3-5) Ketones
Me6-18:2-one (S) + Me14-18:2-one (S)
[Yamamoto, 2007]; [Do, 2009]; Mori, 2009(a); [Taguri, 2010];

+ Me6,Me14-18:2-one
Erebidae (*Lyclene dharma*)

Shikichi, 2012; Zhou, 2024(b)

(4) Non-branched other compounds

4-1) Esters of secondary alcohols

17:7-OPr (S) + 17:8-OPr (S)
Erebidae (*Barsine expressa*)

Fujii, 2013

Z12-17:2-OAc (S)
Tineidae (*Kermania pistaciella*)

Gries, 2006; Britton, 2009

4-2) Ketones

Z6-21:11-one
Erebidae (*Orgyia pseudotsugata*)

Smith, 1975; Akermark, 1978; Nishiyama, 1984 Larson, 1985;
Dasaradhi, 1987; Jones, 2006

Z6,E8-21:11-one
Erebidae (*Orgyia pseudotsugata*, *O. vetusta*)

Muto, 2003(b); Jury, 2003; Comeskey, 2004

Z6,Z9-21:11-one
Erebidae (*Orgyia leucostigma*, *Teia anartoides*)

Mayo, 2022

Z7-19:11-one (Z12-19:9-one)
+ Z7-20:11-one (Z13-20:10-one)
Carposinidae (*Carposina sasakii*)

Naoshima, 1981; Yadagiri, 1983; Yamashita, 1988

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