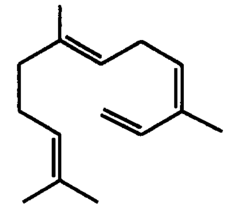
Bioorg. Med. Chem. **1996**, *4*, 283

(*Z*,*E*)-α-Farnesene—An Electroantennogram-Active Component of *Maladera matrida* Volatiles

Gal Yarden,[a] Arnon Shani[a]* and Walter Soares Leal[b]
[a]*Department of Chemistry, Ben-Gurion University of the Negev, Beér-Sheva 84105, Israel,*
[b]*Laboratory of Chemical Prospecting, Department of Insect Technology, National Institute of Sericultural and Entomological Science, Tsukuba, Ibaraki 305, Japan*

(*Z*,*E*)-α-Farnesene, a component of the volatiles of *Maladera matrida* female beetle, was found to be active on male antenna.



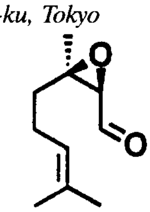
(*Z*,*E*)-α-farnesene
(*Z*3, *E*6)-3,7,11-trimethyldodeca-1,3,6,10-tetraene

Bioorg. Med. Chem. **1996**, *4*, 289

Chemical Ecology of Astigmatid Mites—XLV. (2*R*,3*R*)-Epoxyneral: Sex Pheromone of the Acarid Mite *Caloglyphus* sp. (Acarina: Acaridae)

Naoki Mori,[a]* Yasumasa Kuwahara[a] and Kazuyoshi Kurosa[b]
[a]*Pesticide Research Institute, Koyoto University, Sakyo, Kyoto 606-01, Japan,* [b]*Nishi-Ikebukuro 5-21-15, Toshima-ku, Tokyo 171, Japan*

(2*R*,3*R*)-Epoxyneral was identified as the female sex pheromone from an acarid mite, *Caloglyphus* sp. (Astigmata: Acaridae). The enantiomer of the pheromone, (2*S*,3*S*)-epoxyneral, was inactive and its admixture did not inhibit the activity of the natural pheromone.

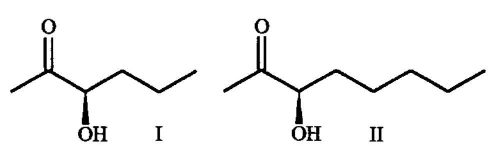


Bioorg. Med. Chem. **1996**, *4*, 297

Assignment of Absolute Stereochemistry to an Insect Pheromone by Chiral Amplification

Xiongwei Shi, Walter S. Leal and Jerrold Meinwald*
Department of Chemistry, Cornell University, Ithaca, NY 14853, U.S.A.

Chiral amplification, a new strategy for determining the absolute configuration of difficultly available natural secondary alcohols or analogous amines, is described. The *R* configuration was assigned to both components (I, II) of the male sex pheromone emitted by the longhorn beetle, *Anaglyptus subfasciatus*.

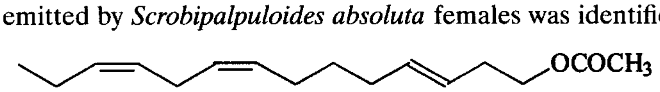


Bioorg. Med. Chem. **1996**, *4*, 305

(3*E*,8*Z*,11*Z*)-3,8,11-Tetradecatrienyl Acetate, Major Sex Pheromone Component of the Tomato Pest *Scrobipalpuloides absoluta* (Lepidoptera: Gelechiidae)

Athula B. Attygalle,[a]* Gulab N. Jham,[a] Aleš Svatoš,[a] Rosa T. S. Frighetto,[a] Fernando A. Ferrara,[b] Evaldo F. Vilela,[b] Manoel A. Uchôa-Fernandes[b] and Jerrold Meinwald[a]
[a]*Baker Laboratory, Department of Chemistry, Cornell University, Ithaca. N.Y. 14853, U.S.A.* [b]*Department of Animal Biology, Universidade Federal de Viçosa, Viçosa, MG 36571, Brazil*

The major sex pheromone emitted by *Scrobipalpuloides absoluta* females was identified and synthesized.

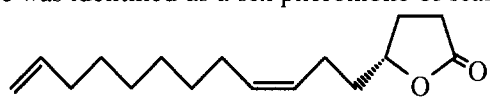


Bioorg. Med. Chem. **1996**, *4*, 315

(*R*,*Z*)-7,15-Hexadecadien-4-olide, Sex Pheromone of the Yellowish Elongate Chafer, *Heptophylla picea*

Walter Soares Leal,[a]* Shigefumi Kuwahara[b], Mikio Ono[c] and Sakae Kubota[d]
[a]Laboratory of Chemical Prospecting, National Institute of Sericultural and Entomological Science, 1-2 Ohwashi, Tsukuba-city 305, Japan, [b]Laboratory of Agricultural Chemicals, Faculty of Agriculture, Ibaraki University, Ami-machi, Inashiki-gun, Ibaraki 300-03, Japan, [c]Fuji Flavor Co. Ltd, 3-5-8 Midorigaoka, Humura-city, Tokyo 190-11, Japan, [d]Shizuoka Tea Experiment Station, Kitugawa, Shizuoka 439, Japan

(*R*,*Z*)-7,15-Hexadecadien-4-olide was identified as a sex pheromone of scarab beetle, *H. picea*.

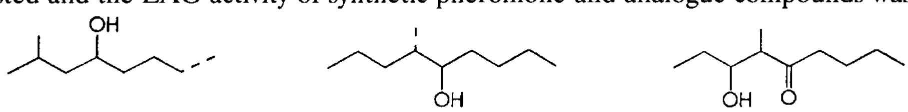


Bioorg. Med. Chem. **1996**, *4*, 323

Chemical Identification, Electrophysiological and Behavioral Activities of the Pheromone of *Metamasius hemipterus* (Coleoptera: Curculionidae)

P. Ramirez-Lucas,* C. Malosse, P.-H. Ducrot, M. Lettere and P. Zagatti
INRA, Unité de Phytopharmacie et Médiateurs Chimiques, Route de Saint-Cyr, 78026 Versailles CEDEX, France

The male-produced aggregation pheromone of *M. hemipterus* was identified. The natural pheromone was behaviorally tested and the EAG activity of synthetic pheromone and analogue compounds was recorded.

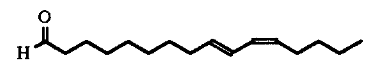


Bioorg. Med. Chem. **1996**, *4*, 331

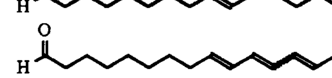
Sex Attractant Pheromone of the Pecan Nut Casebearer (Lepidoptera: Pyralidae)

Jocelyn G. Millar,*[a] Allen E. Knudson,[b] J. Steven McElfresh,[a] Regine Gries,[c] Gerhard Gries[c] and James H. Davis[d]
[a]Department of Entomology, University of California, Riverside, CA 92521, U.S.A. [b]Texas Agricultural Extension Service, The Texas A&M University System, 17360 Coit Road, Dallas, TX 75252, U.S.A. [c]Department of Biological Sciences, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6, [d]New Mexico Department of Agriculture, Corner Gregg and Espinosa Streets, Las Cruces, NM 88003, U.S.A.

9*E*,11*Z*-Hexadecadienal **15** has been identified in subpicogram amounts as a sex pheromone of the pecan nut casebearer. The more highly conjugated triene analogues **18a** and **18b** were not attractive.



15



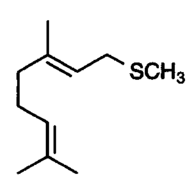
18a: *E*9,*Z*11,*Z*13
18b: *E*9,*Z*11,*E*13

Bioorg. Med. Chem. **1996**, *4*, 341

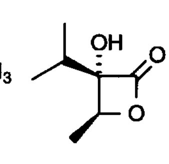
The Pheromone System of the Male Danaine Butterfly, *Idea leuconoe*

S. Schulz*[a] and R. Nishida[b]
[a]Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany
[b]Pesticide Research Institute, Kyoto University, Kyoto, 606-01, Japan

The complex pheromone bouquet of the butterflies consists of several volatile components, of which the active geranyl methyl thioether (**2**) and viridifloric β-lactone (**3**) are especially noteworthy. The volatiles are embedded into a lipidic matrix with more than 150 components.



2



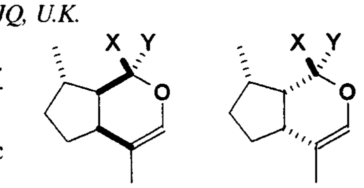
3

Bioorg. Med. Chem. **1996**, *4*, 351

The Aphid Sex Pheromone Cyclopentanoids: Synthesis in the Elucidation of Structure and Biosynthetic Pathways

Glenn W. Dawson, John A. Pickett* and Diane W. M. Smiley
Biological and Ecological Chemistry Dept., IACR-Rothamsted, Harpenden, Herts., AL5 2JQ, U.K.

Aphid sex attractant pheromones comprise the cyclopentanoids **1**, **15**, **16** and **17**. Synthesis based on work by Schreiber and coworkers (1986) provides for large scale field requirements.
Biosynthetic and molecular biological studies employ synthetic acyclic precursors, some ^{3}H-radiolabelled.

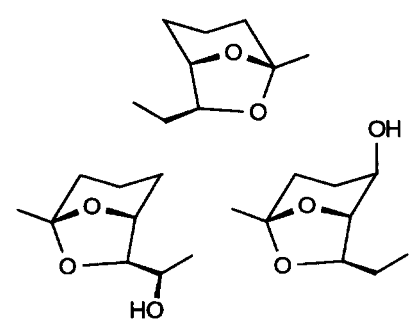


1 X = Y = O **16** X = OH, Y = H
15 X = H, Y = OH **17** X = H, Y = OH

Bioorg. Med. Chem. **1996**, *4*, 363

Identification and Synthesis of New Bicyclic Acetals from the Mountain Pine Beetle, *Dendroctonus ponderosae* Hopkins (Col.:Scol.)

W. Francke,[a]* F. Schröder,[a] P. Philipp,[a] H. Meyer,[a] V. Sinnwell[a] and G. Gries[b]
[a]*Institut für Organische Chemie der Universität, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany;* [b]*Centre for Pest Management, Department of Biological Sciences, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

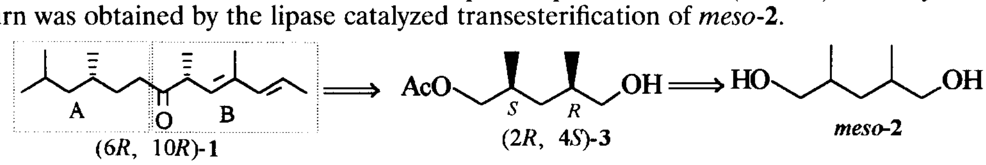


Bioorg. Med. Chem. **1996**, *4*, 375

Enzymatic Synthesis of (2*E*, 4*E*)-(6*R*, 10*R*)-4, 6, 10, 12-Tetramethyl-2, 4-Tridecadien-7-one, the Sex Pheromone of *Matsucoccus matsumurae* Japanese Pine Bast Scale

Guo-Qiang Lin* and Wei-Chu Xu
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

The sex pheromone of *Matsucoccus matsumurae* Japanese pine bast scale (6*R*,10*R*)-**1** was synthesized from **3**, which in turn was obtained by the lipase catalyzed transesterification of *meso*-**2**.

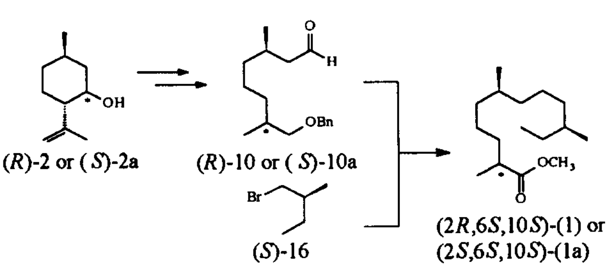


Bioorg. Med. Chem. **1996**, *4*, 381

Pheromone Syntheses: A Tropical Approach. Enantioselective Synthesis of the (2*R*,6*S*,10*S*) and (2*S*,6*S*,10*S*) Isomers of Methyl 2,6,10-Trimethyldodecanoate

J. Tércio B. Ferreira* and Paulo H. G. Zarbin
Laboratório de Síntese de Produtos Naturais, Departamento de Química, Universidade Federal de São Carlos, 13565-905 São Carlos-SP, Brazil

We describe the synthesis of two isomers of methyl 2,6,10-trimethyldodecanoate, out of eight possibles, which was identified as a component of the male-produced pheromone of the stink bugs, *Euschistus obscurus* and *Euschistus heros*.

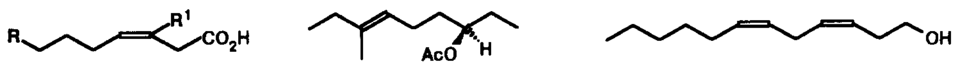


Bioorg. Med. Chem. **1996**, *4*, 389

A Versatile and Convenient Protocol for the Stereocontrolled Synthesis of Olefinic Insect Pheromones

Andrei A. Vasil´ev, Alexei L. Vlasyuk, Galina D. Gamalevich and Edward P. Serebryakov*
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation

A combination of the Horner–Emmons synthesis of alkyl 2,4-dienoates with their 1,4-*cis* hydrogenation over complex L·Cr(CO)$_3$ catalysts (L = 3CO or arene) provides a practical approach to the pheromones of the furniture carpet beetle, dry bean beetle, rusty grain beetle, square-necked grain beetle and of a potent pheromone mimic for subterranean termites.

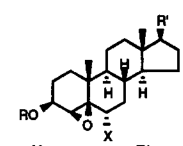


Bioorg. Med. Chem. **1996**, *4*, 401

Synthesis of Some Analogues of Blattellastanoside A, the Steroidal Aggregation Pheromone of the German Cockroach

Kenji Mori,*[a] Tôru Nakayama[a] and Masayuki Sakuma[b]
[a]*Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162, Japan*
[b]*Pesticide Research Institute, Faculty of Agriculture, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-01, Japan*

Four analogues (**1a–d**) of blattellastanoside A (**1e**) were synthesized and bioassayed. The fluoro analogue **1c** was more active than **1e** itself, and **1a** was only slightly less active than **1e**. The analogues **1b** and **1d** as well as the aglycones of **1e** and blattellastanoside B were inactive.



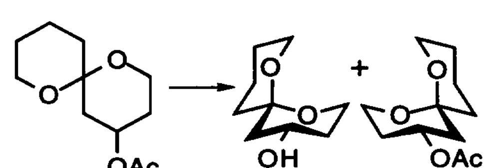
	R	X	R'
1a	D-Glu.	Cl	MeCH(CH$_2$)$_3$CHMe$_2$
b	D-Glu.	Cl	H
c	D-Glu.	F	MeCH(CH$_2$)$_2$CH(Et)CHMe$_2$
d	D-Gal.	Cl	MeCH(CH$_2$)$_2$CH(Et)CHMe$_2$
e	D-Glu.	Cl	MeCH(CH$_2$)$_2$CH(Et)CHMe$_2$

Bioorg. Med. Chem. **1996**, *4*, 409

Enzymatic Preparation of (4*R*,6*R*)-4-Hydroxy-1,7-dioxaspiro[5.5]undecane and its Antipode, the Minor Component of the Olive Fruit Fly Pheromone

Yūsuke Yokoyama, Hirosato Takikawa and Kenji Mori*
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162, Japan

Asymmetric hydrolysis of (±)-**A** with pig liver esterase yielded (4*S*,6*S*)-**B** and (4*R*,6*R*)-**A**.



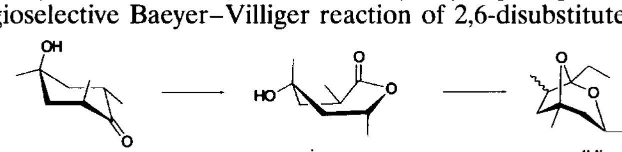
(±)-**A** (4*S*,6*S*)-**B** (4*R*,6*R*)-**A**

Bioorg. Med. Chem. **1996**, *4*, 413

On the Regioselectivity of the Baeyer–Villiger Reaction of 2,6-Dialkyl Cyclohexanones: Application to the Synthesis of Sordidin, a Male Pheromone Emitted by *Cosmopolites sordidus*

Josiane Beauhaire and Paul-Henri Ducrot*
Unité de Phytopharmacie et Médiateurs Chimiques, I.N.R.A., Route de Saint-Cyr F-78026, Versailles Cedex, France

The diastereoselective synthesis of (1*S**,3*R**,5*R**,7*S**)-2,8-dioxa-1-ethyl-3,5,7-trimethylbicyclo[3.2.1]octane (**1d**) has been achieved using as the key step the regioselective Baeyer–Villiger reaction of 2,6-disubstituted cyclohexanone.

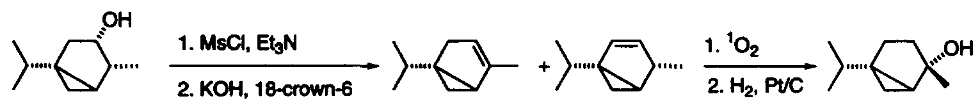


major sordidin

Bioorg. Med. Chem. 1996, 4, 419

A Convenient Synthesis of *trans*-Sabinene Hydrate from (−)-3-Thujol via a Highly Selective Ene Reaction of Singlet Oxygen

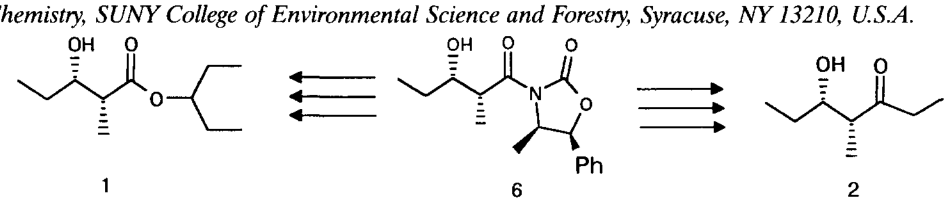
Peter Baeckström,[a]* Bohumir Koutek,[b]* David Šaman[b] and Jan Vrkoč[b]
[a]*Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[b]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague, Czech Republic*



Bioorg. Med. Chem. 1996, 4, 423

Asymmetric Aldol Condensation as a Route to Polypropionate-Derived Pheromones

James P. DiBattista and Francis X. Webster*
Department of Chemistry, SUNY College of Environmental Science and Forestry, Syracuse, NY 13210, U.S.A.



R,S-sitophilate

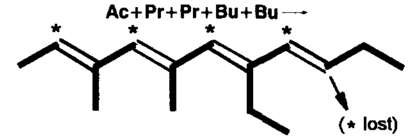
S,R-sitophilure

Bioorg. Med. Chem. 1996, 4, 429

Polyketide Origin of Pheromones of *Carpophilus davidsoni* and *C. mutilatus* (Coleoptera: Nitidulidae)

Robert J. Bartelt* and David Weisleder
Bioactive Constituents Unit, USDA-ARS, National Center for Agricultural Utilization Research, 1815 N. University St., Peoria, IL 61604, U.S.A.

All carbons of the figured tetraene pheromone component and 14 related trienes and tetraenes are derived from the simple acyl units, acetate (Ac), propionate (Pr), and butyrate (Bu). The final structure is determined by the types, order, and number of acyl units. The last unit to be added loses its carboxyl carbon.



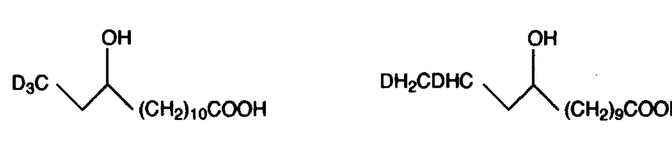
* = carboxyl carbon of acyl unit

Bioorg. Med. Chem. 1996, 4, 439

Synthesis of [14,14,14-$^2H_3$] 12-Hydroxytetradecanoic Acid and [13,14-$^2H_2$] 11-Hydroxytetradecanoic Acid Useful as Tracers to Study a (11*E*)-Desaturation Reaction in *Spodoptera littoralis*

Isabel Navarro, Gemma Fabriás* and Francisco Camps*
Department of Biological Organic Chemistry, CID-CSIC, Jordi Girona 18-25, 080345-Barcelona, Spain

Synthesis of labeled hydroxytetradecanoic acids **1** and **2** is described, as well as their use to investigate the possibility that (11*E*) -tetradecenoic acid is formed by dehydration of either 11- or 12-hydroxytetradecanoic acid in *Spodoptera littoralic* pheromone glands.

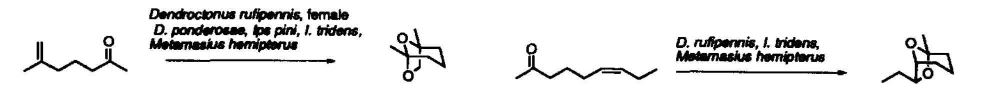


Bioorg. Med. Chem. **1996**, *4*, 445

Transformation of Presumptive Precursors to Frontalin and *exo*-Brevicomin by Bark Beetles and the West Indian Sugarcane Weevil (Coleoptera)

Alice L. Perez,[a] Regine Gries,[b] Gerhard Gries[b] and Allan C. Oehlschlager[a]
[a]Department of Chemistry and [b]Centre for Pest Management, Department of Biological Sciences, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Production of enantiomerically enriched frontalin and *exo*-brevicomin by all the beetles exposed to respective precursors represent nonspecific and nonselective biotransformations, and demonstrate widespread occurrence of nonspecific polysubstrate monooxidases in the Coleoptera.

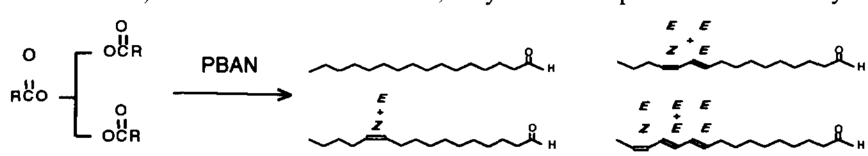


Bioorg. Med. Chem. **1996**, *4*, 451

The Integral Role of Triacyl Glycerols in the Biosynthesis of the Aldehydic Sex Pheromones of *Manduca sexta* (L.)

J. H. Tumlinson, P. E. A. Teal and N. Fang
Insect Attractants, Behavior, and Basic Biology Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Gainesville, FL 32604, U.S.A.

R = Any of the 15-carbon, saturated or unsaturated, alkyl chains depicted in the aldehydes.

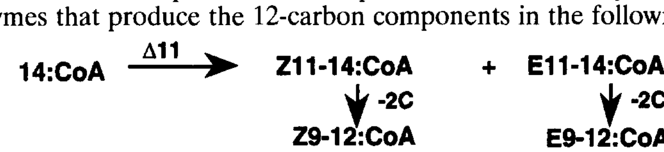


Bioorg. Med. Chem. **1996**, *4*, 461

Biosynthetic Enzymes Regulating Ratios of Sex Pheromone Components in Female Redbanded Leafroller Moths

W. L. Roelofs[a]* and R. A. Jurenka[b]
Department of Entomology,[a] Cornell University, Geneva, NY 14456, U.S.A. and [b]Iowa State University, Ames, IA 50020, U.S.A.

Specific *Z*/*E* ratios of the 14-carbon pheromone components are affected by the activity and specificity of the chain-shortening enzymes that produce the 12-carbon components in the following scheme:

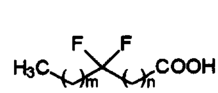


Bioorg. Med. Chem. **1996**, *4*, 467

Difluoropalmitic Acids as Potential Inhibitors of the Biosynthesis of the Sex Pheromone of the Egyptian Armyworm *Spodoptera littoralis*—IV

M. P. Bosch,[a] R. Pérez,[b] G. Lahuerta,[b] D. Hernanz,[b] F. Camps[b] and A. Guerrero[b]*
[a]Departments of Technology of Tensioactives and [b]Biological Organic Chemistry, C.I.D., C.S.I.C., Jordi Girona 18-26. 08034 Barcelona, Spain

Synthesis and biological activity of difluoropalmitic acids **1–3** are presented.



1 : m=13; n=0
2 : m=12; n=1
3 : m=11; n=2

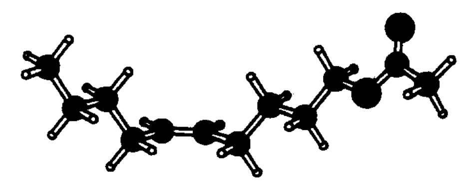
Bioorg. Med. Chem. 1996, 4, 473

Ab Initio Calculations on (Z)-5-Decenyl Acetate, a Component of the Pheromone Complex of *Agrotis segetum* (Lepidoptera: Noctuidae) and Electrophysiological Studies with Chain Elongated Analogues

Hans Jürgen Bestmann, Klaus-Dieter Roth, Claudia Rehefeld, Barbara Leinemann, Friedrich Kern and Otto Vostrowsky
Organic Chemistry Institute, University Erlangen-Nürnberg, Henkestr. 42, 91054 Erlangen, Germany

$$CH_3-(CH_2)_n-\overset{H}{C}=\overset{H}{C}-(CH_2)_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$$

n = 3: *Z*-5–10:Ac; *n* = 4: *Z*-5–11:Ac; *n* = 5: *Z*-5–12:Ac; *n* = 7: *Z*-5–14:Ac; *n* = 9: *Z*-5–16:Ac.



Bioorg. Med. Chem. 1996, 4, 479

New Mimics of the Acetate Function in Pheromone-Based Attraction

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Several analogues of (*Z*)-8-dodecenyl acetate (**1a**), the major pheromone component of the Oriental fruit moth, *Cydia molesta*, with chloroformate and lactone functional groups in place of the acetate moiety, were synthesized and investigated for their biological activity by electroantennography, electrosensillography, short-range sexual stimulation and activation in the flight-tunnel.

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Antennal Response and Field Attraction of the Predator *Elatophilus hebraicus* (Hemiptera: Anthocoridae) to Sex Pheromones and Analogues of Three *Matsucoccus* Spp. (Homoptera: Matsucoccidae)

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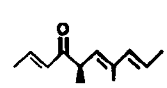
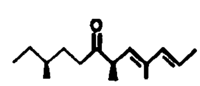
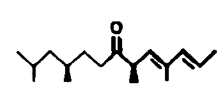
The predator, *Elatophilus hebraicus*, associated only with the Israeli pine bast scale *Matsucoccus josephi*, utilizes the sex pheromone of its prey, as a kairomone. The predator responses also to the sex pheromones of two allopatric species, *M. feytaudi* and *M. matsumurae*, despite the fact that all three species are geographically well isolated.



Matsucoccus josephi



Matsucoccus feytaudi



Matsucoccus matsumurae

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Optimization of Blends of Synthetic Pheromone Components for Trapping Male Limabean Pod Borers (*Etiella zinckenella* Tr.) (Lepidoptera: Phycitidae): Preliminary Evidence on Geographical Differences

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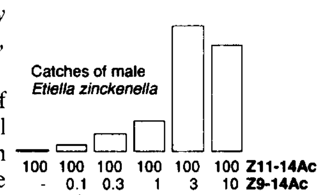
From the five pheromone components of *Etiella zinckenella* the 100:3 mixture of (*Z*)-11-tetradecenyl acetate and (*Z*)-9-tetradecenyl acetate was necessary for maximal attraction of males into traps in Hungary. However, none of the traps baited with combinations of the above compounds captured any moths in Taiwan, suggesting possible pheromonal differences in European and Eastern Asian populations of *E. zinckenella*.



Bioorg. Med. Chem. **1996**, *4*, 499

Conformationally Constrained Analogues of (Z)-5-Decenyl Acetate, a Pheromone Component of *Agrotis segetum*

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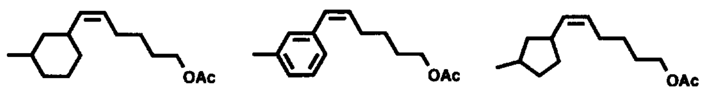
Conformationally constrained analogues of the natural pheromone component have been synthesized and tested by using single-cell electrophysiology.



Bioorg. Med. Chem. **1996**, *4*, 505

Proteins that Smell: Pheromone Recognition and Signal Transduction

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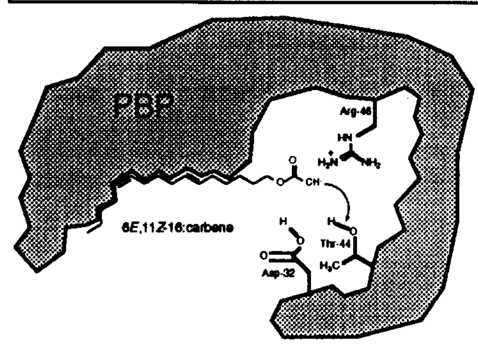
Recombinant pheromone binding proteins (PBPs) show ligand specificity and photoaffinity labeling with a diazoacetate analog maps critical active-site residues. A hypothesis is presented in which the PBP–pheromone complex presents the ligand to the putative transmembrane domain pheromone receptor as a first step in olfactory signal transduction.



Bioorg. Med. Chem. **1996**, *4*, 515

Labial Gland Chemistry of Three Species of Bumblebees (Hymenoptera: Apidae) from North America

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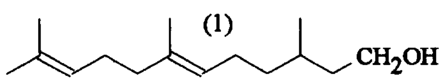
The male labial gland secretion in three North American bumblebees is composed of acyclic isoprenols and straight chain alcohols. The secretions are species-specific and the main components are: (*Z*)-11-octadecen-1-ol in *Bombus sonorus*, *trans*-2,3-dihydrofarnesol (1) in *Bombus huntii* and geranylcitronellol (2) in *Psithyrus insularis*.

(1)



(2)