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Chapter 5

Synthesis and Application of Pheromones for Integrated Pest Management in Vietnam

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Additional information is available at the end of the chapter

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Abstract

The negative impacts of conventional pesticides on health, environment, and organisms have involved strong development of integrated pest management (IPM) strategies. The use of insect pheromones becomes an effectively alternative selection in agricultural and forest pest control. Pheromone researches in Vietnam started in the last few decades and in addition to technical factors, recent achievements in the Vietnamese agriculture have an important direct link to the pheromone developments. In this chapter, we review the pheromone researches related to synthesis and field trials of several especial insect pheromones, in which Vietnamese scientists have mainly participated or collaborated with foreign research groups. First, we will discuss an overview of popular insect pheromones in Vietnam, a lot of species of which are also found around the world, as an important reference for scientists who would have especial consideration in this field. Further, synthetic routes of pheromones are summarized with various structures including chiral, racemic, mono- and poly-olefinic pheromones where some schemes have become standard methodologies for synthesis of similar structural compounds. Finally, field evaluations of the pheromones of numerous species are discussed in detail.

Keywords: insect attractant, pheromone trap, synthesis, pest control, integrated pest management, field application

1. Introduction

Nowadays, numbers of pests are becoming increasingly resistant due to the conventional pesticides which cause damage to useful parasites and imbalance in the ecosystem, creating environmental pollution and adverse effect on the economy [1]. This leads to the concept of IPM

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being rapidly developed to solve the problems of pesticide use. IPM allows safer insect control and poses the least risks while maximizing benefits and reducing costs. Although many methods have been employed, the use of pheromones obviously is one of the most effective approaches in pest control which can be achieved by mass trapping and killing the harmful pests selectively [2]. Moreover, the use of pheromone traps minimizes risks to human health and reduces destruction of the living environment.

Because of the tropical climate, Vietnam is generally favourable for many typical pests with rapid breeding which cause damage to the crops and forest trees throughout the year [3]. Since Nguyen group's first report in early 1980s [4], the demand of pheromone for IPM in Vietnam is steadily growing and that generally leads to a strong development of synthesis and field trial of pheromones. Success of the Vietnamese agriculture in the recent years has had important contribution from use of this technique. At the same time, the numerous reports on pheromones in Vietnam from other groups, such as groups of Can Tho University, have been increasing rapidly during the last decades.

Herein, our aim is to review synthesis and field trials of insect pheromones from research groups in Vietnam. The chapter consists of three main parts including introduction of pheromones of popular insects in Vietnam, an overview of synthetic methodology presented in structurally typical order, and finally field trials of several important insect pheromones.

2. Popular insect pheromones in Vietnam

Due to the big difference of weather conditions between the regions of Vietnam, for instance the South of Vietnam having no winter season but the North having four clearly identifiable seasons, numerous insect species have been found in Vietnam [3]. Known pheromones of popular species in the country are summarized in **Table 1** where only major component of pheromones identified at ratios of more than 65% in their mixture is listed with a respective reference. Species specificity is commonly achieved by the use of blends of several pheromone components. The data reveal that Lepidoptera is the best studied insect order related to pheromone, with data available for about 27 species. The pheromones of this order usually consist of alcohols, acetates, or aldehydes of long chain containing double bonds while the other orders mostly possess pheromone molecules bearing chiral carbons.

Order, family and species	**Common name**	**Major component of pheromone***	**Ref.**
Lepidoptera			
Crambidae			
Cnaphalocrocis medinalis G.	Rice leaf folder	*Z*13-18:Ac or *Z*13-18:Ald	[5, 6]
Chilo suppressalis W.	Rice stem borer	*Z*11-16:Ald	[7]
Hellula undalis F.	Cabbage webworm	*E*11*E*13-16:Ald	[8]
Crocidolomia binotalis Z.	Cabbage head caterpillar	*Z*11-16:Ac	[9]

Order, family and species	Common name	Major component of pheromone*	Ref.
Conogethes punctiferalis G.	Yellow peach moth	*E*10-16:Ald	[10]
Scirpophaga nivella F.	Sugarcane top borer	*E*11-16:Ald	[11]
Proceras venosatus W.	Striped sugarcane borer	*Z*13-18:OH	[12]
Noctuidae			
Sesamia inferens W.	Pink stem borer	*Z*11-16:Ac	[13]
Helicoverpa armigera H.	Cotton bollworm	*Z*11-16:Ald	[14]
Spodoptera *exigua* H.	Beet armyworm	*Z*9*E*12-14:Ac	[15]
Spodoptera litura F.	Oriental leafworm	*Z*9*E*11-14:Ac	[16]
Chrysodeixis eriosoma D.	Green garden looper	*Z*7-12:Ac	[17, 18]
Ctenoplusia albostriata B. & G.	Eastern streaked plusia	*Z*7-12:Ac	[18]
Argyrogramma signata F.	Green semilooper	*Z*5-10:Ac	[18]
Ctenoplusia agnata S.	-	*Z*7-12:Ac	[18]
Zonoplusia ochreata W.	-	*Z*7-12:Ac and Z5-12:Ac	[18]
Spodoptera pectinicornis H.	Water lettuce moth	*Z*7-12:Ac	[18]
Gracillariidae			
Phyllocnistis citrella S.	Citrus leaf miner	*Z*7*Z*11*E*13-16:Ald	[19]
Conopomorpha cramerella S.	Cocoa pod borer	*E*4*E*9*Z*10-16:Ac and *E*4*Z*6*Z*10-16:Ac	[20]
Sphingidae			
Agrius convolvuli L.	Convolvulus hawk moth	*E*11*E*13-16:Ald	[21]
Tortricidae			
Homona coffearia N.	Tea tortrix	12:OH	[22]
Archips atrolucens D.	Citrus leaf roller	*Z*11-14:Ac and *E*11-14:Ac	[18, 23]
Adoxophyes privatana W.	Apple leaf-curling moth	*Z*11-14:Ac	[23]
Meridemis furtiva D.	-	Z11-14:Ac	[18]
Pyralidae			
Etiella zinckenella T.	Pea pob borer	*Z*11-14:Ac	[24]
Yponomeutidae			
Prays endocarpa M.	Citrus pock caterpillar	*Z*7-14:OH and *Z*7-14:Ald	[25]
Limacodidae			
Parasa lepida C.	Nettle caterpillar	*Z*7,9-10:OH	[26]
Coleoptera			
Brentidae			
Cylas formicarius elegantulus S.	Sweet potato weevil	*Z*3-dodecen-1-yl *E*2-butenoate	[27]

Order, family and species	Common name	Major component of pheromone*	Ref.
Chrysomelidae			
Phyllotreta striolata F.	Striped flea beetle	6*R*,7*S*-Himachala-9,11-diene	[28]
Dryophthoridae			
Cosmopolites sordidus G.	Banana root borer	1*S*3*R*5*R*7*S*-sordidin	[29]
Scarabaeidae			
Oryctes rhinoceros L.	Coconut rhinoceros beetle	Ethyl 4-methyloctanoate	[30]
Curculionidae			
Rhynchophorus ferrugineus O.	Red palm weevil	4*S*,5*S*-Ferrugineol	[31]
Cerambycidae			
Xylotrechus quadripes C.	Coffee white stemborer	2*S*-Hydroxydecan-3-one	[32]
Hemiptera			
Aphididae			
Aphis glycines M.	Soybean aphid	1*R*4a*S*7*S*7a*R*-Nepetalactol	[33]
Pentatomidae			
Nezara viridula L.	Southern green stink bug	*Trans*-1,2-Epoxy-*Z*-α-bisabolene	[34]
Aphididae			
Myzus persicae Sulzer	Green peach aphid	*E*-β-Farnesene	[35]
Brevicoryne brassicae D.	Cabbage aphid	4a*S*7*S*7a*R*-Nepetalactone	[36]
Pseudococcidae			
Planococcus citri R.	Citrus mealybug	Planococcyl acetate	[37]
Pseudococcus comstocki K.	Comstock mealybug	2,6-Dimethyl-1,5-heptadien-3-yl acetate	[38]
Heteroptera			
Dysdercus cingulatus F.	Red cotton bug	*S*-Linalool	[39]
Thysanoptera			
Thripidae			
Thrips palmi K.	Melon thrips	*R*-Lavandulyl 3-methyl-3-butenoate	[40]
Diptera			
Cecidomyiidae			
Orseolia oryzae W.	Asian rice gall midge	2*S*,6*S*-Diaxetoxyheptane	[41]

***Z*,*E*: *Z*,*E*-double bonds; *R*,*S*: *R*,*S*-enantiomer carbon; number before hyphen: position of a double bond or enantiomer carbon or epoxy; number after hyphen: carbon number of a straight chain; Ac: acetate, OH: alcohol, and Ald: aldehyde.

Table 1. Overview of popular insect pheromones in Vietnam.

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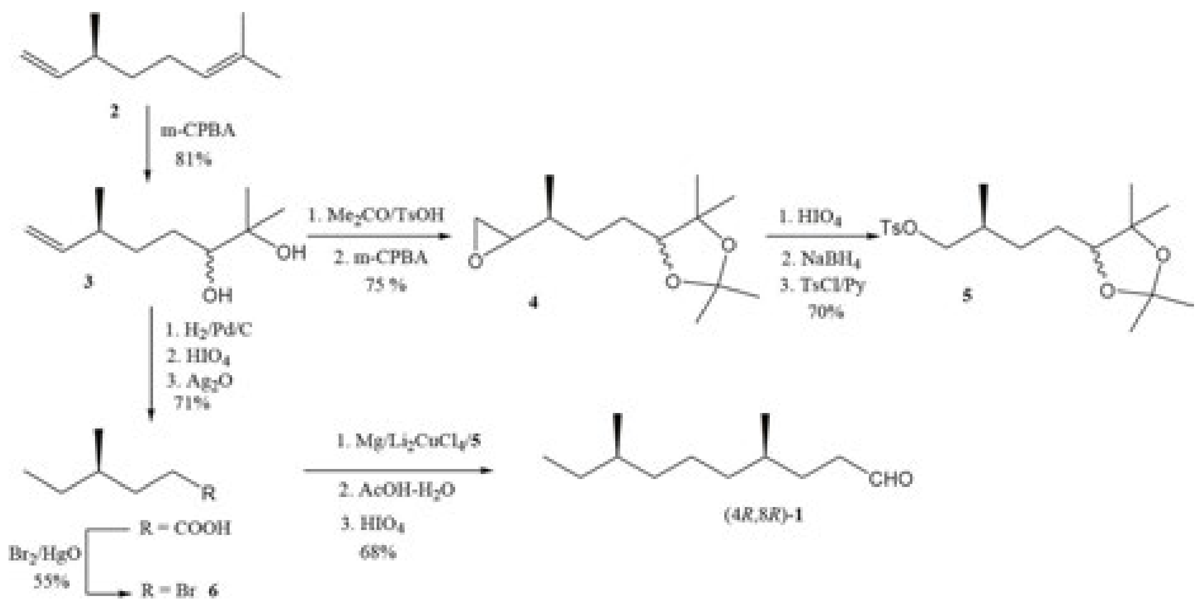
3. Synthesis of pheromones

As discussed above, most of the insect pheromones found in Vietnam possess chiral and olefinic structures. Chiral pheromone is defined as a compound containing at least one asymmetric carbon atom, while olefinic attractant bears one or more double bonds C=C in the carbon chain. Generally, insects are attracted more efficiently by a typical optical or/and configurative isomer than by a mixture of its isomers. Hence, an unambiguous understanding of production of these pheromones is particularly necessary for their application. Herein are summarized important synthetic approaches of pheromones which have been used for field trials in Vietnam over three decades. Synthetic approaches are divided into three main categories as described below.

3.1. Chiral pheromones

3.1.1. 4R,8R-dimethyldecanal (4R,8R-1, 4R,8R-Tribolure, 1)

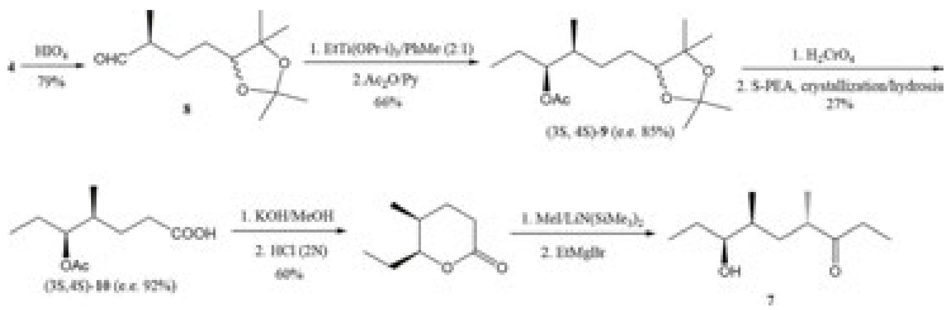
Suzuki *et al.* [42] described the identification and synthesis of tribolure (**1**) as the aggregation pheromone of the *Tribolium* flour beetles, in which the (4*R*,8*R*)-**1** isomer is a major component of the natural pheromone [43, 44]. A simple way for synthesis of (4*R*,8*R*)-**1** has been reported by Nguyen and co-workers [45–47]. The selective peroxidation of (*S*)-3,7-dimethylocta-1,6-diene (**2**) gave an important intermediate diol **3** which was as an initial material for synthesis of both components, the tosylate **5** and the Grignard reagent **6**. The Wurtz condensation of the two components in presence of lithium cuprate, followed by simple conversions, affords the pheromone (4*R*,8*R*)-**1** (**Scheme 1**).



Scheme 1. Synthetic route of 4R,8R-dimethyldecanal.

3.1.2. (4S, 6S, 7S)-7-hydroxy-4,6-dimethylnonan-3-one (Serricornin, 7)

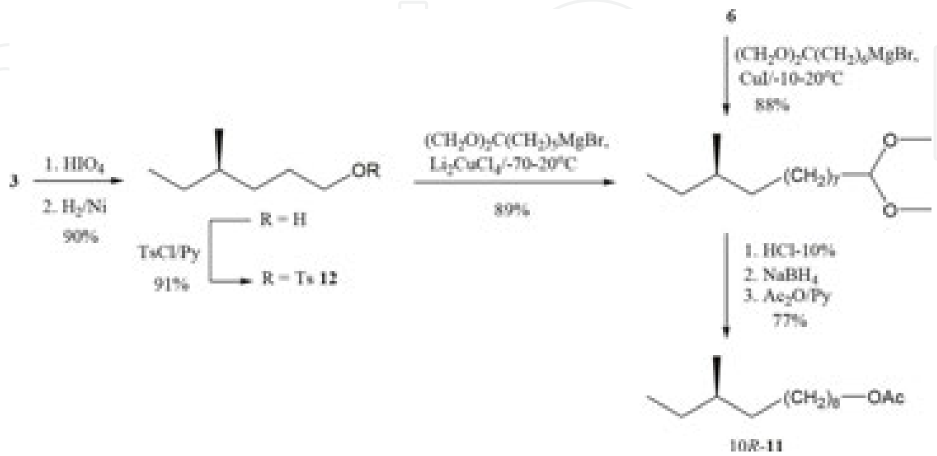
(4*S*, 6*S*, 7*S*)-7-hydroxy-4,6-dimethylnonan-3-one (**7**) named Serricornin is the female-produced sex pheromone of the small tobacco beetle, *Lasioderma serricorne*, that has been isolated and identified by Chuman *et al*. [48, 49] The key step in synthesis of this pheromone was reaction between **8** with ethyl triisopropoxytitanium according to Cram's rule to obtain a ratio of isomer (3*S*,4*S*)-**9** with ee 85% [50]. In order to isolate individual optical isomers, (*S*)-1-phenylethylamine (S-PEA) was treated with acid **10** to afford a mixture of diastereomeric salts [51]. After repeated crystallization, the (3*S*, 4*S*)-**10** exhibited ee 92%. The compound **10** was converted into the lactone by a two-step procedure, followed by Grignard coupling that completed synthesis of the target pheromone (**Scheme 2**).



Scheme 2. Synthetic route of Serricornin.

3.1.3. (10R)-methyldodecyl acetate (10R-11)

The smaller tea tortrix moth, *Adoxophyes* sp., is a widespread and economically important pest of the tea plant. It has been demonstrated that the male-produced sex pheromone consists of four components, in which 10*R*-**11** was identified as the minor component [52]. Tamaki *et al.* [53] showed that the 10*R*-**11** was more bioactive than the *S*-isomer in field test. The synthesis of *R*-**11** has been reported through two approaches which employed the Grignard coupling



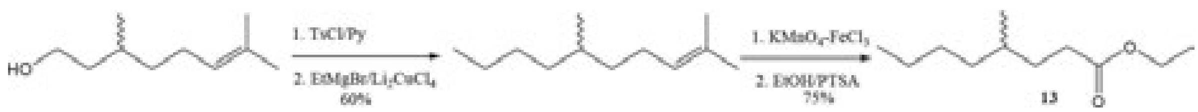
Scheme 3. Synthetic route of (10R)-methyldodecyl acetate.

between the achiral and chiral units as a key step [54]. The latter unit was obtained from the chiral diol **3** converted into the tosylate **12** or the above bromide **6**. Coupling of these compounds with the corresponding Grignard reagents of protected aldehydes and subsequent esterification completed synthesis of the pheromone 10*R*-**11** (**Scheme 3**).

3.2. Racemic pheromones

3.2.1. Ethyl 4-methyloctanoate (13)

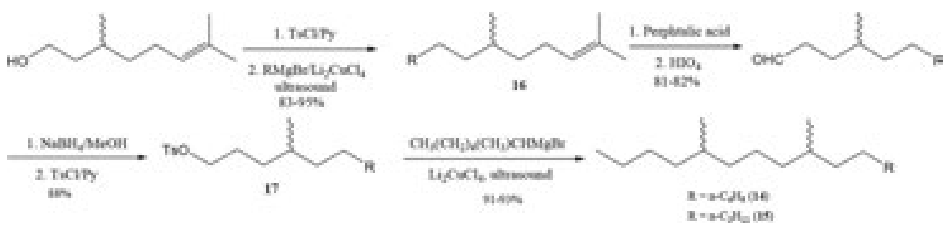
Hallett *et al*. [30] described identification of the aggregation pheromone of Rhinoceros beetles, *Oryctes rhinoceros* L., the most important destructive pest of coconut, oil, and other palms in tropical Southern Asia, Pacific islands, and Indian islands as ethyl 4-methyloctanoate (**13**). The racemic pheromone [55, 56] has been straightforwardly synthesized from natural citronellol with one-step oxidation of 2,6-dimethyl-2-decene by $KMnO_4$-$FeCl_3$ as the key step, followed by esterification in overall yield of 45% (**Scheme 4**).



Scheme 4. Synthetic route of ethyl 4-methyloctanoate.

3.2.2. 5,9-Dimethylpentadecane (14) and 5,9-dimethylhexadecane (15)

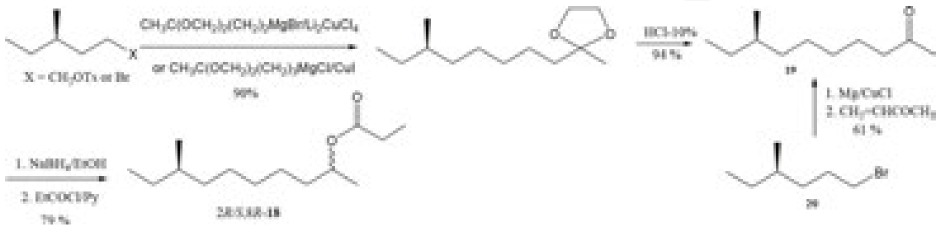
Francke *et al.* [57] identified and synthesized the major and minor components of sex pheromone of female leaf miner moths, *Leucoptera coffeella*, a pest of coffee trees as 5,9-dimethylpentadecane (**14**) and 5,9-dimethylhexadecane (**15**), respectively. Synthesis of these racemic components has been described from citronellol by Doan *et al.* [58]. Grignard coupling reactions with tosylated intermediates under ultrasound irradiation, which has been efficiently employed in literature [59], were the key steps in the synthetic strategy. The alkene derivatives **16** were oxidized and then reduced to afford the important tosylated synthon **17**. Grignard reaction of the corresponding tosylates **17** with 2-methylhexylmagiesium bromide furnished the racemic pheromones, **14** and **15**, under accelerating ultrasound irradiation in yields over 90% (**Scheme 5**).



Scheme 5. Synthetic route of 5,9-dimethylpentadecane and 5,9-dimethylhexadecane.

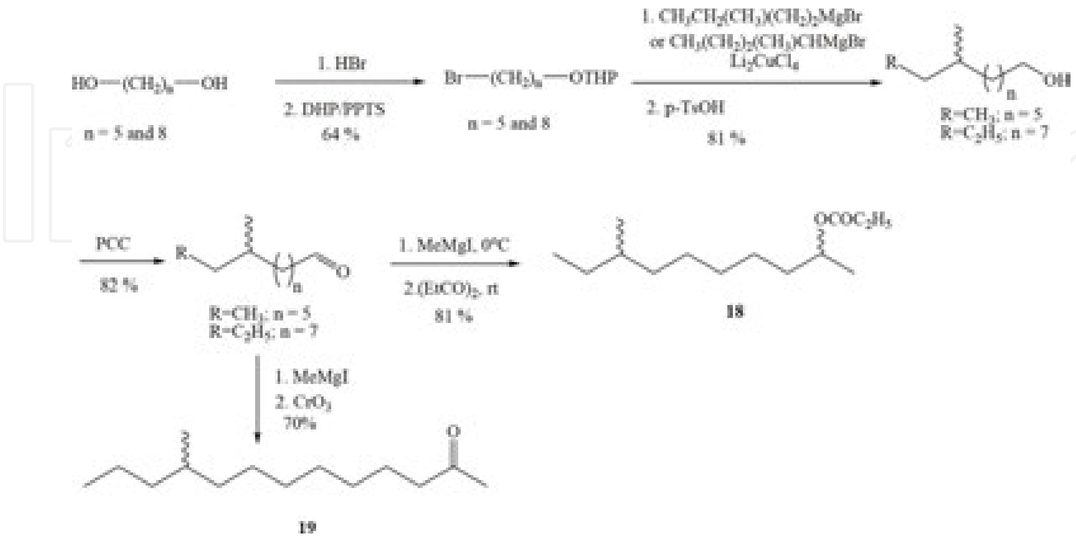
3.2.3. *8-Methyldec-2-yl propanoate (18) and 10-methyl-2-tridecanone (19)*

8-Methyldec-2-yl propanoate (**18**) was identified as sex pheromone of northern corn rootworm, *Diabrotica longicornis* Say [60] and western corn rootworm, *Diabrotica virgifera virgifera* Le Conte [61] while the sex pheromone of southern corn rootworm, *Diabrotica undecimpunctata howardi* Barber, was isolated and identified as 10-methyl-2-tridecanone (**19**) by Guss *et al.* [62]. A method for the synthesis of mixture (2*R*/*S*,8*R*)-**18** with a chiral centre at C-8 was performed using three chiral substrates using Grignard coupling as a key step [63]. The important ketone synthon was reduced with $NaBH_4$, followed by esterification to obtain the pheromone in total yield over 50% (**Scheme 6**).



Scheme 6. Synthetic route of 8-methyldec-2-yl propanoate.

In a similar fashion, synthesis of the sex pheromone 10*R*-**19** from the chiral material was based on the successive reaction of 1-tosyloxy-4R-methylheptane and the Grignard reagent of 1-bromo-5,5-ethylenedioxyhexane [64]. A straightforward approach to the synthesis of racemic mixtures of **18** and **19** has been recently reported from diol derivatives using the Grignard coupling of protected bromohydrins as a key step [65]. The important intermediate aldehydes, which have a similar structure in both pheromones, were synthesized by oxidation reaction of corresponding alcohols using PCC as an oxidation reagent. Pheromones **18** and **19** were obtained in overall yields of 35% and 29%, respectively (**Scheme 7**).



Scheme 7. Synthetic route of 8-methyldec-2-yl propanoate and 10-methyl-2-tridecanone.

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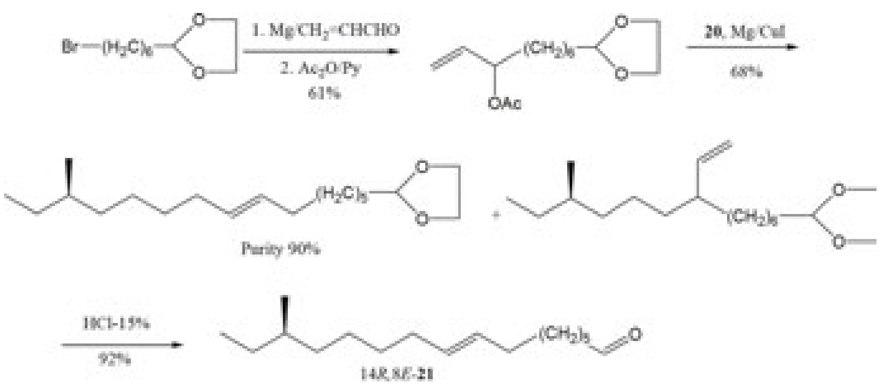
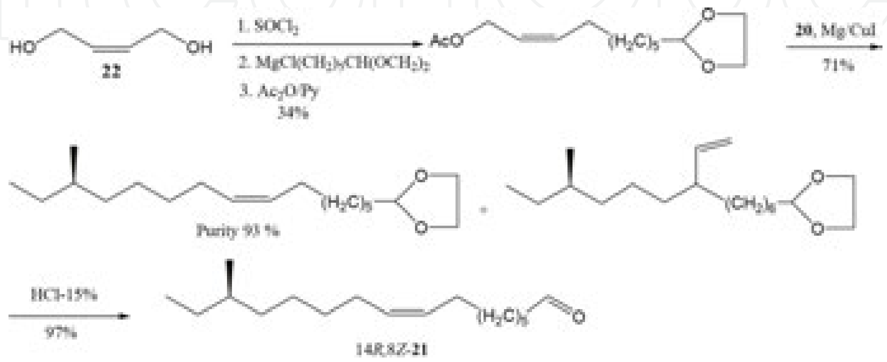
3.3. Olefinic pheromones

3.3.1. (14R)-Methyl-8-hexadecenal (14R-21)

The geometrical isomers of (14*R*)-methyl-8-hexadecenal (14*R*-**21**) were identified as major components of the pheromone of Khapra beetle, *Trogoderma granarium*. Both pheromone isomers were found in a *Z*: *E* ratio of 92 : 8 and named (*Z*) and (*E*)-trogodermal [66]. Mori and coworkers [67, 68] demonstrated that the *R*-enantiomers, 14*R*,8*Z*-**21** and 14*R*,8*E*-**21**, revealed bioactivity on male dermestid beetles, *T. glabrum*, *T. inclusum* and *T. variabile*. Nguyen *et al.* [69, 70] described synthesis of the both *R*-isomers based on the chiral bromide substrate **20** and employed substitution coupling as a key step. **Scheme 8** shows synthetic route of the *E*-isomer from acrolein using S_N2' substitution of Grignard reagent of **20** to acyclic allyl acetate to afford the *E*-isomer with purity of 90%, containing a small amount of branched product. At the same time, the Z-isomer was efficiently prepared *via* three steps in overall yield 24% from commercially available *Z*-2-buten-1,4-diol. The key step was condensation of *Z*-disubstituted primary allyl acetate with Grignard reagent according to the nucleophilic substitution mechanism (S_N2) to furnish the pheromone 14*R*,8*Z*-**21** as a major product (**Scheme 9**).



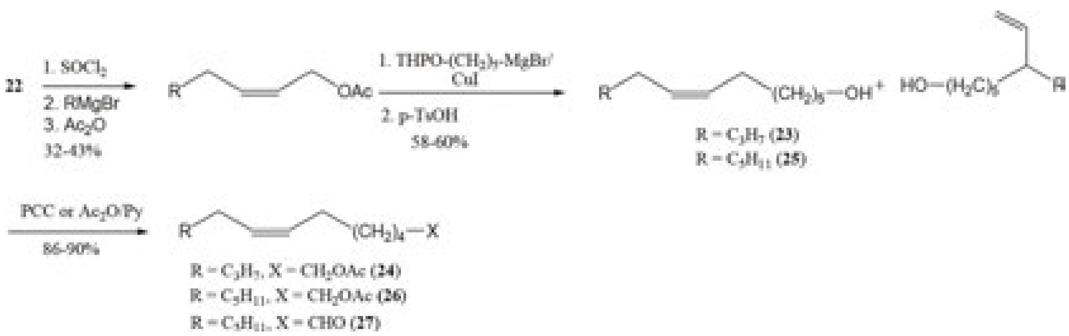
Scheme 8. Synthetic route of (14R, 8E)-14-methyl-8-hexadecenal.



Scheme 9. Synthetic route of (14R, 8Z)-14-methyl-8-hexadecenal.

3.3.2. *(Z)-7-Dodecenol (23), (Z)-7-dodecen-1-yl acetate (24), (Z)-7-tetradecenol (25), (Z)-7-tetradecen-1-yl acetate (26), (Z)-7-tetradecenal (27)*

Berger *et al.* [71] isolated and identified (*Z*)-7-dodecen-1-yl acetate (**24**) as the male-produced pheromone of cabbage loopers, *Trichoplusia ni* Hubner, a destructive pest of peas and weed plants in Asia while the precursor of this pheromone, (*Z*)-7-dodecen-1-ol (**23**) was reported as an inhibitor of this sex pheromone by Tumlinson *et al.* [72]. Vang *et al.* [25] described the identification of three compounds, (*Z*)-7-tetradecenol (**25**), (*Z*)-7-tetradecen-1-yl acetate (**26**), and (*Z*)-7-tetradecenal (**27**) as the sex pheromone of the citrus pock caterpillar, *Prays endocarpa*. The compound **26** has also been found as sex pheromone of other species such as the citrus flower moth (*P. citri* and *P. nephelomina*) [73, 74] and the olive moth (*P. oleae Bern*) [75, 76]. These pheromones have been synthesized from the available commercial diol **22** *via* the S_N2 mechanism between Grignard reagent prepared from protected bromohydrins with *Z*-allyl acetate derivatives in presence of CuI catalyst as a key step [77]. The *Z*-isomers were purified by column chromatography using Silica gel impregnated with $AgNO_3$ as the stationary phase (**Scheme 10**).

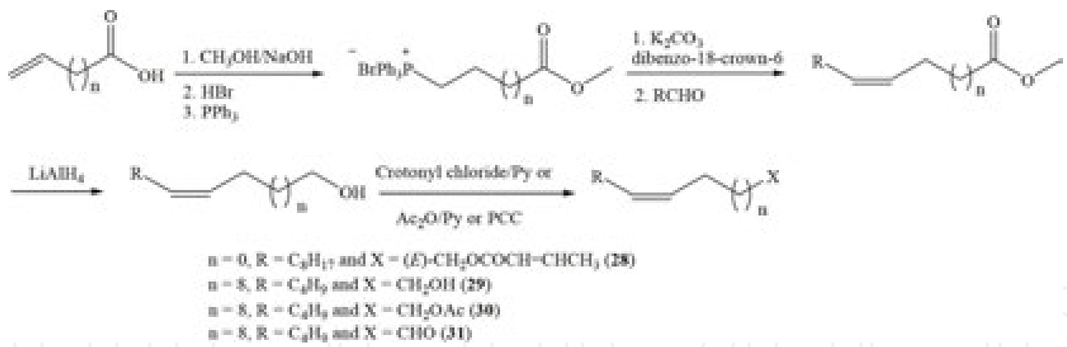


Scheme 10. Synthetic route of derivatives of (Z)-7-dodecenol and (Z)-7-tetradecenol.

3.3.3. *(Z)-3-Dodecen-1-yl (E)-2-butenoate (28), (Z)-11-hexadecenol (29), (Z)-11-hexadecenyl acetate (30), (Z)-11-hexadecenal (31)*

The sweet potato weevil, *Cylas formicarius elegantulus* S., and Diamondback moth, *Plutella xylostella* L., are prevalently serious insects in Vietnam. Heath *et al.* [27] identified and first synthesized (*Z*)-3-dodecen-1-yl (*E*)-2-butenoate (**28**) as the female-produced sex pheromone of the sweet potato weevil. The female of Diamondback moth secretes the pheromone to attract the males identified as (*Z*)-11-hexadecenyl acetate (**30**) and (*Z*)-11-hexadecenal (**31**) in a ratio of 1:1 to 3:1 [78]. Yamada and Koshihara [79] found (*Z*)-11-hexadecen-1-ol (**29**) synergizing the attractiveness of the pheromone mixtures of **30** and **31**.

The efficient synthetic pathway of these pheromones from commercially unsaturated acid derivatives has been described [80]. Acrylic acid or 1-undecenic acid was straightforwardly converted into the corresponding triphenylphosphonium salt of methyl esters which reacted with 1-alkanal in presence of dibenzo-18-crown-6 to afford (*Z*)-ester derivatives. Reduction of these derivatives with $LiAlH_4$ was done to obtain the corresponding alcohols which were

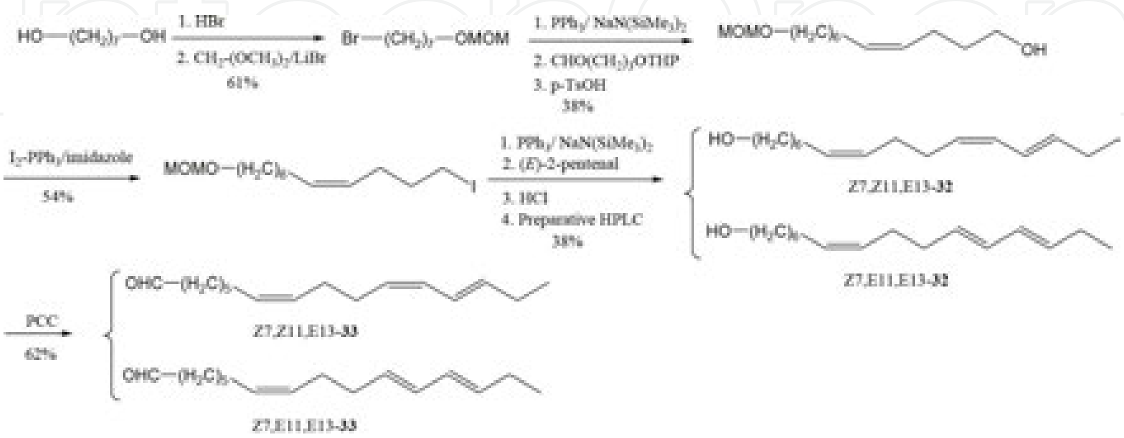


Scheme 11. Synthetic route of (Z)-3-dodecen-1-yl (E)-2-butenoate and derivatives of (Z)-11-hexadecenol.

subsequently oxidized with PCC into the aldehyde pheromone (**31**) or esterified with crotonyl chloride and anhydride acetic into pheromones **28** and **30**, respectively (**Scheme 11**). Another way for synthesis of **29–31** based on (*Z*)-2-buten-1,4-diol similar to the description in **Scheme 10** has also been reported by Nguyen [81].

3.3.4. 7,11,13-Hexadecatrien-1-ol (32) and 7,11,13-hexadecatrienal (33)

Ando *et al.* [82] have identified (*Z*7,*Z*11)-hexadecatrienal (*Z*7,*Z*11-**34**) as an sex attractant of the citrus leaf miner females, *Phyllocnistis citrella* Stainton, a harmful citrus pest in Asia. However, two other research groups [83, 84] demonstrated that a mixture of (*Z*7,*Z*11,*E*13)-hexadecatrienal (*Z*7,*Z*11,*E*13-**33**) and *Z*7,*Z*11-**34** at a ratio of 3:1 strongly attracted the citrus leaf miner in Brazil and California. Vang *et al.* [19] have described synthesis and comparison of biological test of two geometrical isomers, *Z*7,*Z*11,*E*13-**33** and *Z*7,*E*11,*E*13-**34**. The isomers were synthesized, the key steps being Wittig reaction of the protected ylides using a base $NaN(SiMe_3)_2$ to furnish (*Z*)-isomer as the major products in overall yield of 3%. The pure individual isomers, (*Z*7,*Z*11,*E*13)-**33** and (*Z*7,*E*11,*E*13)-**33,** were obtained by isolation from a mixture of corresponding alcohols **32** (2:1) using preparative HPLC methodology, followed by oxidation with PCC (**Scheme 12**).



Scheme 12. Synthetic route of isomers of 7,11,13-hexadecatrien-1-ol and 7,11,13-hexadecatrienal.

4. Pheromone trap

Pheromone trap is a useful tool for management of insects. Numerous trap types are being used efficiently for IPM such as board trap, tube trap, and pitfall trap (**Figure 1**). The board traps are most commonly used for trapping moths damaging vegetables or forest trees, while the tube traps are used efficiently for trapping fruit fly. These traps are either hung from branches or nailed to infested trees. Pitfall trap is usually employed to collect beetles and weevils. This trap consists of a container with a lot of small windows buried in the ground where its windows are at surface level [85]. The use of trap generally baited with a lure containing the corresponding pheromone is significantly dependent on individual insect characteristics. The pheromone is dissolved in a suitable solvent, usually hexane and then placed on a rubber septum or septa to protect the compounds from degradation. After evaporation of the solvent, the lure is pinned at centre of the traps which would be put on the field at suitable intervals. Lures are designed to release pheromones at a constant or near-constant rate during the course of the experiment. Release rate is dependent on the molecular, physical and chemical properties of the lure matrix and environmental conditions such as temperature and local weather. Traps are checked and insects are recorded over time, usually for several days or weeks.

Figure 1. Examples of trap types.

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5. Control of harmful insects in Vietnam

5.1. Diamondback moth, *Plutella xylostella*

- Lure type: synthesized pheromone, **29** (>98%, GC), **30** (99.2%, GC) and **31** (95.5%, GC) in a ratio of 1:10:1 and lures provided from AgriSense Co.
- Trap type: sticky board traps (**Figure 2**).
- Areas: vegetable fields in Tu Liem (HaNoi, north of Vietnam), Da Lat (Lam Dong province, central highland region of Vietnam), Cu Chi and Hoc Mon District (Ho Chi Minh City, South of Vietnam).

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Figure 2. Sticky board trap and captured Diamondback moths, *P. xylostella* [86].

Diamondback moth attacks only cruciferous vegetable crops in the family Cruciferae including cabbage, broccoli, cauliflower, collard, etc. Plant damage is caused by larvae feeding on foliar tissue and this is particularly damaging to the seedlings, resulting in disrupted head formation. A comparison study of field test using the synthesized pheromones and commercial lures was carried out between years 1994 and 1995 in many areas of Vietnam [80]. The summary of the results is presented in **Table 2**. It reveals that distributing density of Diamondback moths is clearly different among geographic areas in Vietnam. For example, the mean males captured by all lures in Da Lat and Cu Chi are significantly higher than the pests in Tu Liem and Hoc Mon district. The authors also demonstrated stronger male response when dosage of the pheromone mixture steadily increases and the captured males by lures containing 5 mg of the synthesized pheromone are similar to the commercial lures.

Lure (mg)	Captured mean males/trap/night±S.E.					
	Tu Liem (Jan. 2 to Feb. 2, 1994)	Da Lat (Apr. 20 to May 20, 1994)	Cu Chi (Mar. 1 to Apr. 1, 1994)	Hoc Mon (Jan. 4 to Feb. 4, 1994)	Cu Chi (Mar. 1 to Apr. 1, 1995)	Hoc Mon (Jan. 4 to Feb. 4,1995)
1[a]	51.9±11.3	95.9±19.9	68.3±15.2	–	–	–
3[a]	95.5±19.2	183.9±25.6	112.2±21.3	–	–	–
5[a]	116.3±21.3	258.3±30.8	204.9±32.5	126.5±16.2	212.4±32.1	116.4±17.1
Com.[b]	117.9±22.6	286.4±35.5	214.6±35.1	131.2±19.7	216.1±33.7	124.8±18.3
Control	1.5	2.1	1.2	–	–	–

[a] Loaded with synthesised pheromone.
[b] Lure of AgriSense Co.

Table 2. Pheromone trap catches of *P. xylostella* males testing different dosages in different areas for one month in years 1994 and 1995 [80].

5.2. Sweet potato weevils, *Cylas formicarius elegantulus*

- Lure type: lures baited with the synthesized pheromone **28** (96%, GC) and products provided by Department of Entomology, CIP Aptartodo 5969, Lima 1, Peru.
- Trap type: tube trap made from plastic flask with six windows (**Figure 3**).

- Area: sweet potato fields in Hoc Mon district (Ho Chi Minh City).

Figure 3. Tube traps and captured sweet potato weevils, *C. formicarius elegantulus* [86].

Sweet potato weevil, *C. formicarius* is the most serious pest of sweet potato which mainly causes damage to fields not only in Vietnam but also around the world. The adult female deposits a single egg near the juncture of stem and tuber and the hatched larvae burrow directly into the tuber of plant. Management of this pest is particularly important in agriculture and storage. Nguyen *et al.* [80] carried out field tests of the weevils in sweet potato fields of Hoc Mon district of Ho Chi Minh City. The results revealed that the weevil capture increased with an increase of pheromone dosage and two pheromone sources, synthesized and commercial, are comparable in their attractiveness to this weevil (**Table 3**).

Cultivation season	**Captured mean males/trap/night±S.E**				
	Lure (mg)				
	0.01[a]	0.1[a]	1.0[a]	1.0[b]	Control
1	124.6±30.5	215.3±86.4	486.8±183.4	541.2±202.3	0
2	108.9±26.2	202.6±39.1	455.9±121.5	501.6±136.2	0

[a] Loaded with synthesised pheromone.
[b] Pheromone provided from Department of Entomology, CIP Apartado 5969, Lima 1, Peru.

Table 3. Trap catches of *C. formicarius* males testing different dosages of the pheromone for one week in 1995 [86].

5.3. Screening sex attractants for moths in Mekong Delta of Vietnam

- Lure type: synthesized and commercial compounds
  - Monoenyl alcohols: Z7-12:OH (**23**), Z11-14:OH and E11-14:OH
  - Monoenyl acetates: Z5-10:Ac, Z5-12:Ac, Z7-12:Ac (**24**), Z9-12:Ac, Z9-14:Ac, Z11-14:Ac, E11-14:Ac
  - Dienyl acetates: Z9,E11-14:Ac and Z9,E12-14:Ac
  - Monoenyl aldehyde: Z11-14:Ald
  - Trienes: Z3,Z6,Z9-18:H, Z3,Z6,Z9-19:H, Z3,Z6,Z9-20:H and Z3,Z6,Z9-21:H

- ◦ Epoxydienes: racemic mixtures of epoxy3,Z6,Z9-18:H, Z3,epoxy6,Z9-18:H, Z3,Z6,epoxy9-18:H and their C_{19}-C_{21} homologs
- Trap type: sticky board trap (30 × 27 cm)
- Area: orchards of Chinese apple, guava and longan in Can Tho City from December 1998 to November 1999 and orchards of plum and guava from January to December in 2000

Hai *et al.* [18] screened six typical attractants to obtain evaluation of the harmful pest population in Mekong Delta of Vietnam. The field tests found male attraction of nineteen Lepidopteran species including nine taxonomically identified species and ten other taxonomically unidentified species. Compound Z11-14:Ac and its mixture were identified as important attractants of Tortricid species such as *A. privatana*, *A. atrolucens*, *M. furtive*, while numerous Noctuid species such as *A. signata, C. eriosoma, C. agnate, C. albostriata, A. ochreata, and S. pectinicornis* were attracted by lures baited with Z7-12:Ac (**24**) as a major component. In addition, the seasonal effect clue for male catch of Noctuid species was also observed. For example, the flights were primarily captured in the dry season, from January to March, and in the latter half of the rainy season, September to December whereas the male catch was rarely observed from April to July. These results could help to depict effective ecological behaviour of the pests in these areas.

5.4. Rhinoceros beetle, *Oryctes rhinoceros*

- Lure Type: synthesized compound **13** and the host material, kairomone, which was extracted from fresh coconut tissue in solvents mixture (ethanol (68%), ethyl acetate (27%) and pentane (5%)).
- Trap type: pitfall traps made from 20-liter plastic buckets with window size about 3 × 8 cm (**Figure 4**).
- Area: coconut fields with the 3–10 years old trees in Hau Giang and Ben Tre province (Mekong Delta).

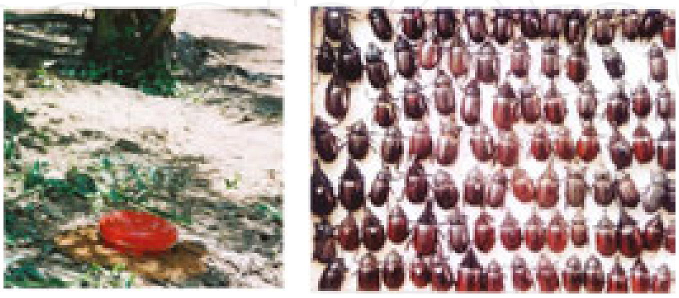

Figure 4. Pitfall trap and captured rhinoceros beetles, *O. rhinoceros* [77].

The coconut rhinoceros beetle causes extensive damage to economically important wild and plantation palms in Vietnam and Southeast Asia region. The adults eat the leaves and burrow into the crown leading to stunted plant development. Dang *et al.* [55] investigated the beetles in two provinces of Mekong Delta between two seasons, dry and rainy, in years 2004 and 2005 using lures baited with pheromone and kairomone. The authors showed that synergism of kairomone leads to an increased beetle response to their pheromone in all trials and the beetle catches were not too different between the two provinces at the same time. The result revealed that the insect density in the rainy season was higher than in the dry season in both areas (**Table 4**). In addition, steady increase of the beetle catches with increasing release rate of the pheromone was also observed (**Table 5**).

Lure (50 mg)	**Captured mean pests/trap/2 weeks±S.E.**			
	Hau Giang		**Ben Tre**	
	Dry season[a]	**Rainy season**[b]	**Dry season**[c]	**Rainy Seasond**[d]
Kairomone (K)	0	0	0	0
Pheromone (P)	1.33±0.33	1.67±0.33	1.67±0.33	1.67±0.33
P+K	2.67±0.27	6.67±0.27	3.33±0.43	8.67±0.27

[a] Jan. 25, 2014 to Feb. 27, 2004.
[b] June 5, 2014 to June 19, 2004.
[c] Feb. 4, 2005 to Feb. 19, 2005.
[d] June 15, 2004 to June 29, 2004.

Table 4. Trap catches of rhinoceros beetles testing in different areas in dry and rainy reasons of years, 2004 and 2005 [55].

Lure (mg)	30	40	50	60	Control
Pests[a]	0.33±0.33	0.33±0.33	2.33±0.88	3.00±0.58	0

[a]Mean number/trap/2 weeks±S.E.

Table 5. Trap catches of *O. rhinoceros* pests testing different dosages of the pheromone combining with kairomone in Ben Tre province from Apr. 1 to Apr. 15, 2005 [55].

5.5. Citrus leaf miners, *Phyllocnistis citrella*

- Pheromone: two geometrical isomers of synthesized compounds **32** and **33** and commercial isomers of **34**.
- Trap type: sticky board trap (30 × 27 cm).
- Area: citrus orchards in Can Tho City from November 21, 2005 to March 12, 2006 and in Ogasawara Islands, Japan from November 17, 2005 to April 5, 2006.

The citrus leaf miner, a widespread Asian species, is found to be dangerous to all citrus in many areas around the world such as, in East and South Africa. The larvae make serpentine mines on young leaves or shoots, resulting in leaf curling and inducing a serious plant disease. Vang *et al*. [19] described field trials of the moths in citrus orchards in Vietnam and Japan using isomeric mixture of compounds **44–46**. The data in Vietnam revealed that the citrus leaf miner males were not captured by a lure baited only with *Z*7,*Z*11-**46** but were efficiently attracted with a mixture of *Z*7,*Z*11,*E*13-**45** and *Z*7,*Z*11-**46** in a ratio of 3:1, whereas similar synergistic effect on moth catches was not observed in Japan. The authors, therefore, concluded that the sex pheromone of Vietnamese citrus leaf miners is different from their pheromone in Japan.

5.6. Citrus Pock Caterpillar, *Prays endocarpa*

- Pheromone: synthesized compounds **25**, **26** and **27**.
- Trap type: sticky board trap (30 × 27 cm).
- Area: pomelo orchards of villages in Vinh Long province in 2007 and from April 4 to June 10, 2008.

The citrus pock caterpillar is an economically serious pest of the pomelo (*Citrus grandis* L.) orchard in Vietnam and Southeast Asia. The larvae attack and mine into the peel of the fruit which would either develop into tumours or even drop if the attack is in the early stage of development. Vang *et al*. [25] reported the analysis of gas chromatography-mass (GC-MS) from pheromone gland extract of female moths finding three monoenyl-C_{14} derivatives, **25–27** in a ratio of 10:3:10. Field data showed that the male moth was attracted by only aldehyde **27**, while both other compounds were not attractive as well as no synergism with this aldehyde in the adult catches was found. The authors also demonstrated that achieving efficiency with mass trapping experiment was similar to use of a pesticide in suppression of the pest in pomelo orchard.

5.7. Citrus leaf rollers (*Archips atrolucens*, *Adoxophyes privatana* and *Homona* sp.)

- Pheromone: synthetic and commercial compounds Z11-14:Ac, *E*11-14:Ac, *Z*9-14:Ac, Z9-12:Ac and 14:Ac.
- Trap type: sticky board trap (30 × 27 cm).
- Area: orange orchards in Hau Giang province and Can Tho City in 2011 and 2012.

Recently, the natural pheromones of three citrus leaf rollers, *Archips atrolucens*, *Adoxophyes privatana* and *Homona* sp., which have been known as serious defoliators of citrus trees in Vietnam, were identified using analysis techniques GC-EAD and GC-MS [23]. The results showed that three components Z11-14:Ac, *E*11-14:Ac and 14:Ac in a ratio of 64:32:4 were identified as the sex pheromone of *A. atrolucens* while two other couples Z11-14:Ac and Z9-14:Ac (92:8); Z11-14:Ac and Z9-12:Ac (96:4) as the sex pheromones of *A. privatana* and *Homona* sp., respectively. However, their field test revealed that amount of the minor components in tested pheromones of all three species was slightly greater than those in the natural pheromones. For instance, the best male catches were found for *A. atrolucens,* a blending mixture of Z11-14:Ac, E11-14:Ac and 14:Ac at a ratio of 2:1:1; for *A. privatana,* a blending mixture of Z11-14:Ac and Z9-14:Ac at a ratio of 9:1 and similarly for *Homona* sp., a blending mixture of Z11-14:Ac and Z9-12:Ac at a ratio of 9:1.

6. Conclusions

In this chapter, we review the researches related to synthesis and field evaluation of insect pheromones which have been done by Vietnamese researchers or collaborators since 1980s. Pest control by the use of attractant traps promises to obtain an accurately quantitative estimation of insect population. This important information would help farmers to get more effective protection of the plants in Vietnam. In some cases, using the pheromones could reduce damage to the plants. In addition, pheromones were made possible by advances in synthetic organic chemistry and most of the synthetic approaches mentioned earlier are novel and employable to prepare at a large scale. Some schemes of the synthetic routes have become a standard methodology for synthesis of the similarly structured molecules such as synthesis of enantiomers from (*S*)-3,7-dimethylocta-1,6-diene or synthesis of *Z* and *E*-monoenyl from (*Z*)-2-buten-1,4-diol and acrolein, respectively. Moreover, this study is motivated by the prospect of gaining better understanding of ecological relationships to develop IPM in Vietnam. Also, it helps organic chemists, entomologists and authorities to get sharp orients for further projects in developing an efficient environmentally benign tool. We believe that pheromones are going to become essential materials for the durable development of a green agriculture in the near future.

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