Study Of The Synthesis Of The Sex Pheromone Of The European Corn Borer (Ostrinia Nubilalis)

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ABSTRACT

The European corn borer (*Ostrinia nubilalis*) is one of the key phytophagous pests in the agroecosystems of Europe and North America. One of the promising methods of its control is the use of sex pheromones for monitoring and communication disruption strategies. This paper examines the biochemical and molecular mechanisms of sex pheromone synthesis in *O. nubilalis*, as well as the analytical methods used. The data obtained contribute to improving the effectiveness of pheromone traps and developing genetically grounded approaches for population control. The use of sex pheromones in integrated pest management systems necessitates the development of practical synthesis schemes, enabling the production of corn borer pheromones (*Ostrinia nubilalis* Hbn.) from common precursor compounds—synthons.

Keywords: pheromones, pest, caterpillar, European corn borer, pheromone synthesis, cis-11-tetradecen-1-ol acetate.

Introduction

The European corn borer (*Ostrinia nubilalis* Hübner) is a dangerous pest of corn and several other crops. The primary damage is caused by larvae developing inside the stalks, leading to reduced yield and quality of the harvest. Traditional control methods based on chemical insecticides are associated with a number of environmental and economic challenges. Therefore, the use of pheromone-based technologies as part of integrated pest management has become increasingly relevant.

In Uzbekistan, corn crops suffer significant damage from *Ostrinia nubilalis*, which develops in two generations per season, infesting 10–35% of corn fields with a density of 1–2 larvae per plant. Yield losses can reach 18–20% [1–2]. Protecting the crop often requires 1–2 insecticide treatments per generation. However, due to the concealed lifestyle of the larvae, such treatments do not always produce the desired results. Improving the efficiency of protective measures depends significantly on accurate timing of treatments, which is based on in-depth knowledge of pest biology and phenological development in the observed region.

Pheromone traps facilitate regular monitoring. Methods for their use have been developed for pest monitoring, short-term forecasting, and population regulation through mass trapping, sterilization, or male disorientation. The degree of corn infestation by the borer is assessed visually in corn fields and

adjacent crops, starting from the emergence of adult moths until cob ripening, at intervals of every 7–10 days. Detailed inspections focus on tassels, young cob silks, and leaf axils. As visual inspection is labor-intensive, in recent years sticky traps baited with synthetic sex pheromones—*cis*-11-tetradecenyl acetate—or food attractants such as cucurbitacins have become widely used [3].

Female *O. nubilalis* synthesize and release a specific blend of sex pheromones that attract males. The main components of this pheromone blend include (Z)-11-tetradecenyl acetate and (E)-11-tetradecenyl acetate. The biosynthesis of these compounds involves a complex fatty acid transformation pathway with the participation of specific enzymes.

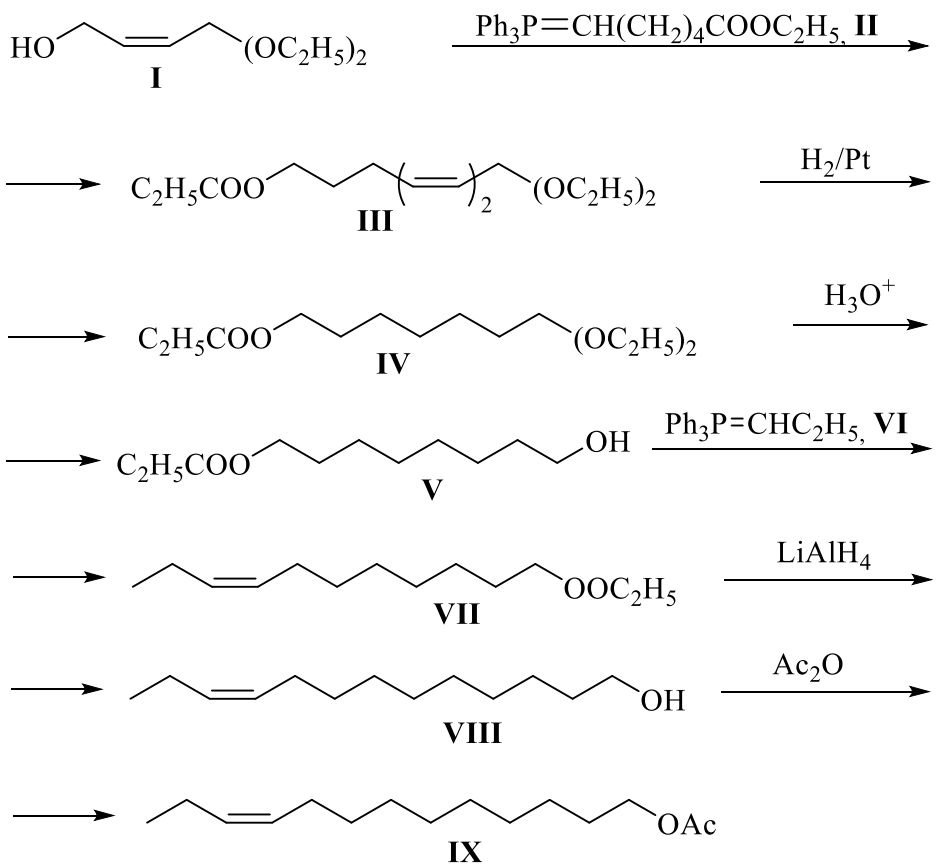
Discussion And Results

Field testing of pheromones is the final stage of many laboratory studies and, together with sex screening, serves as a foundation for their practical use in corn protection.

It is highly relevant to develop methods for the synthesis of these compounds for the European corn borer (*Ostrinia nubilalis*). In general, insect pheromones are relatively volatile, non-toxic organic compounds that act over distances of up to several hundred meters from the source of the odor [5].

The most common methods for synthesizing pheromones involve the use of *cis*-monoolefinic alcohols and their acetates as key intermediates. These compounds are typically synthesized using the Wittig reaction [4].

The objective of this study is the synthesis of compounds based on monoacetal of glutaraldehyde. High stereospecificity — particularly for obtaining the *cis*-isomer — is achieved through the use of aliphatic phosphoranes and aliphatic aldehydes in non-polar solvents. The generation of ylides from the corresponding phosphonium salts using bis(trimethylsilyl)amide of an alkali metal, followed by reaction with aldehydes, leads to *cis*-alkenes with up to 95% stereochemical purity. This method has been applied for the synthesis of attractants containing a single unsaturated bond, specifically *cis*-11-tetradecenyl acetate — a synthetic pheromone of the European corn borer (*Ostrinia nubilalis* Hbn.).



The reaction between carboethoxybutylene triphenylphosphorane (II) and mono-diethylacetal of pimelic aldehyde (I) proceeds smoothly, yielding the ester acetal (III) in good yield. Hydrogenation of this intermediate over platinum oxide gives the same product — ester acetal (IV). Acidic hydrolysis of this acetal under mild conditions (in acetone solution at 20 °C) produces the ethyl ester of 11-oxoundecenoic acid (V) in high yield. Subsequent reaction with propylidene triphenylphosphorane (VI) under *cis*-olefination conditions yields compound (VII). This is then reduced with lithium aluminum hydride to the corresponding *cis*-11-tetradecen-1-ol (VIII), which is oxidized using pyridinium chlorochromate to produce *cis*-11-tetradecenyl acetate (IX).

The isomeric purity of the synthesized compounds was determined using gas-liquid chromatography on a capillary column with a moderately polar phase (Carbowax, 20 m) and a packed column with the stereospecific UF-275 phase. The *cis*-isomer content was found to be 95–96% (IX).

Mass spectra of the samples were recorded using the TLC (Total Ion Current) method in the range of 50–1100 mass units under the following conditions: gas flow temperature – 320 °C, nebulizer gas pressure – 20 psi, temperature – 250 °C, capillary voltage – 4500 V.

Table 1. Yields, Physicochemical, and Spectral Analyses

№	Compound	Compound	Boiling Point (mm Hg)	Elemental Analysis		IR Spectrum (cm^{-1})	^{1}H NMR Spectrum (δ, ppm), number of protons
				Found %	Found %		
1	1,1-Diethoxy-cis-11-tetradecene	52	120-123(2)	C_{14} $H_{26}O$ C 74,94 H 12,58	C 75,21 H12,74	1100 1120 3010	0,90t(3H,CH_3) 0,15t(6H, CH_3) 1,25m(10H,CH_2) 2,00m(1H,OCHO) 5,40m(2H,CHCH)
2	cis-11-Tetradecene	95	95-97(2)	C_{14} $H_{24}O$ C 78,61 H 12,71	C 79,06 H12,80	1720 2710 3000	1,31c(3H,CH_3) 2,5m(10H, CH_3) 0,90m (4H,CH_2 CCH_2) 2,45m(2H,CH_2O) 5,45m(2H,CHCH) 9,85t(1H,CHO) 0,85t(3H,CH_3)
3	cis-11-Tetradecen-1-yl acetate	37	94-95 (0,5)	C_{14} $H_{22}O$ C 78,11 H 13,22	C 78,19 H13,22	1050 3005 3620	1,25m.c(12H,CH_2) 2,05m(4H, CH_2 $COCH_2$) 3,50t(2H,CH_2 O) 5,25m(2H,CH_2 O)

The obtained results confirm that the ratio of cis- and trans-isomers may vary between populations, which is important for adapting traps to local conditions. The genetic characteristics of the enzymatic systems involved in synthesis are of interest for biotechnological solutions in pest control, including the development of transgenic bait plants or genetically engineered microbial biofactories.

Conclusion

Pheromones are chemical substances released by insects that trigger specific behavioral and physiological responses in receiving insects, particularly those belonging to the order Lepidoptera. One component of the

European corn borer *Ostrinia nubilalis* Hbn pheromone, cis-11-tetradecenyl acetate, was synthesized using the Wittig reaction. The study of the biosynthetic pathways of sex pheromones in the corn borer enables the development of more precise and environmentally friendly pest control methods. Genetic and biochemical characterization of key enzymes opens up prospects for creating innovative plant protection tools based on the natural communication mechanisms of insects.

The Delta-type sticky trap consisted of a laminated cardboard structure with a replaceable sticky insert, in the center of which a dispenser was placed on the adhesive surface. The studies used a pheromone preparation composed of cis-11-tetradecenyl acetate (Z-11-C14Ac).

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