Synthesis And Characterization Of Sex Pheromones In Lepidoptera (Order: Lepidoptera)

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ABSTRACT

The intensive development of agricultural production currently requires the expansion of the use of chemical plant protection products against insect pests, which in turn leads to environmental pollution and irreparable losses in the biocenosis. Therefore, the development of fundamentally new plant protection products, characterized by safety in relation to the environment and high selectivity of action, becomes more and more relevant. The use of sex pheromones in integrated plant protection systems leads to the need to develop convenient synthesis schemes that make it possible to obtain pheromones of various pest species with good yield and high isomeric purity from the same initial compounds - synthons.

Keywords: pheromone, pest, gamma bollworm, honeybee uterus, odoriferous wood borer, melon fly, synthesis of pheromones.

Pheromones of Lepidoptera and their components, in terms of chemical structure, are represented by long-chain acetates, alcohols, aldehydes, epoxides, and other hydrocarbons. They may contain one or two unsaturated fragments or branching [1].

The identification of the precursor may, in some cases, be significantly easier than the identification of the final product. Table 1 presents the proposed precursors with various functional groups.

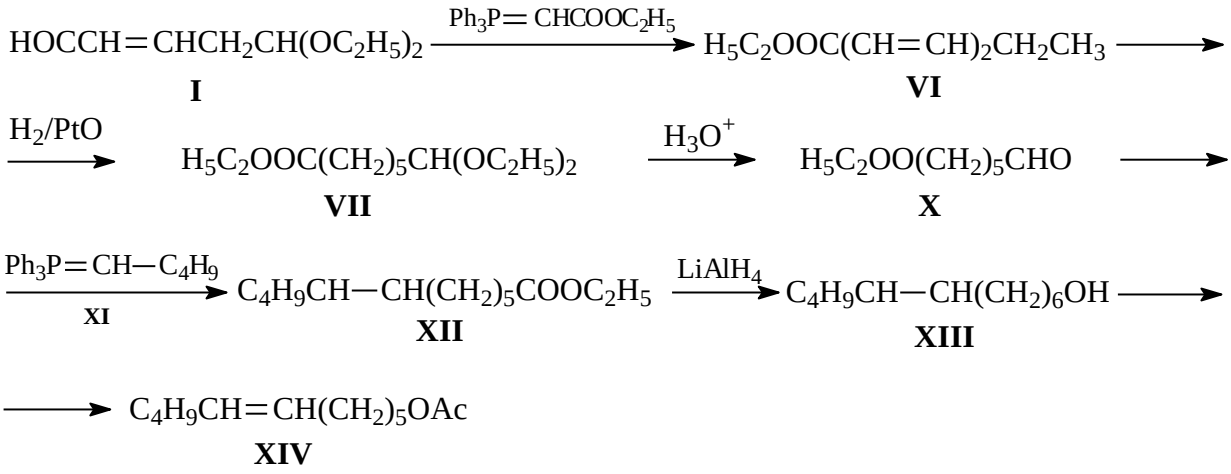
If the functional group in the active compound is identified, it is not difficult to infer the nature of the precursor.

Synthesis of the Gamma Moth Component

The harmful impact of the gamma moth Autographa gamma on cotton is observed during the development of the first generation. The second and third generations develop on vegetable and melon crops, as well as on grain-legume crops. The development of methods for synthesizing the sex pheromone of the gamma moth and determining the biological activity of the sex attractant depending on its composition and dosage, as well as the formulation of recommendations for creating preparative forms of the pheromone for practical use in plant protection, are presented in studies [2,3].Цис-7- додеценилацетат является компонентом феромона совки гамма (*Autographa gamma*).

The synthesis of its synthetic analog is based on the reaction of carbethoxymethylenetriphenylphosphorane (V) with monodiethylacetal pimelic aldehyde (I), proceeding with the formation of a diene ester acetal (VI) in good yield. Hydrogenation of this compound over platinum oxide yields the product—ester acetal (IV). Acidic hydrolysis of this acetal under mild conditions leads, with high efficiency, to the ethyl ester of 7-oxoheptanoic acid. Subsequently, condensation of the aldehyde (VII) with pentylidenetriphenylphosphorane (VIII) is carried out under "cis-olefination" conditions (VIII). The resulting product is reduced by lithium aluminum hydride to the corresponding cis-7-dodecen-1-ol (XVI), which is then oxidized using pyridinium

chlorochromate to cis-7-dodecenal and acetylated to yield the final product (XIV).



Component of the pheromone of the goat moth Cossus cossus

cis-7-Dodecen-1-yl acetate is the main component of the sex pheromone of the goat moth Cossus cossus. It was synthesized via a Wittig reaction. High stereoselectivity in the formation of the cis-isomer was achieved by condensing the monoacetal of pimelic aldehyde with pentamethylenetriphenylphosphorane, followed by hydrolysis of the resulting acetal to yield cis-7-dodecenol. Subsequent reduction of the secondary alcohol led to the synthesis of the main component of the sex pheromone of Cossus cossus.

$$C_4H_9—CH=CH—(CH_2)_6OAc$$

The isomeric purity of the synthesized compounds was determined by gas-liquid chromatography using a capillary column with a moderately polar phase (Carbowax, 20 m) and a packed column with the stereospecific phase UF-275. The purity of the cis-isomer was found to be 96–98%.

Mass spectra of the samples were recorded using the TIC (Total Ion Current) method in the range of 50–110 m/z. The MS conditions were as follows: Drying gas flow rate: 4 L/min, Drying gas temperature: 320 °C, Nebulizer gas pressure: 20 psi, Evaporator temperature: 250 °C, Capillary voltage: 4500 V.

Queen pheromone of the honey bee *Apis mellifera*

Honey bees play a crucial role in maintaining natural ecosystems by pollinating 85% of flowering plants—approximately 300,000 species worldwide. Their activity directly influences the biodiversity of natural ecosystems [25].

The queen honey bee (Apis mellifera) conserves honey reserves efficiently: she reduces brood production when nectar flow declines and flies long distances to forage. The biology and behavior of honey bees are fully adapted to cold climates—they can forage even in cold, cloudy, or hot weather, and queen mating occurs at low temperatures.

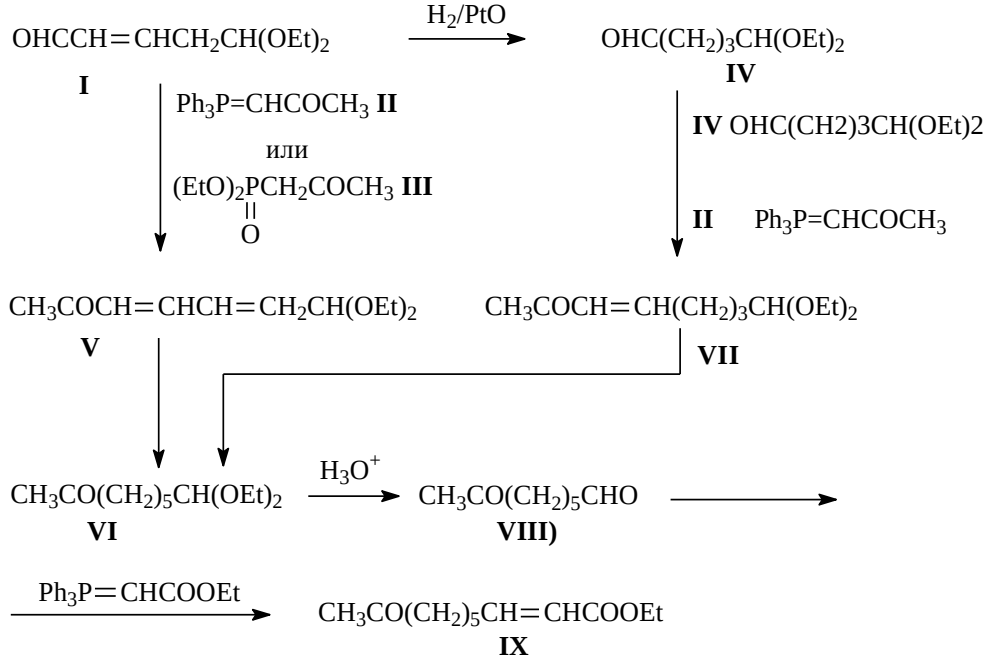
The pheromone of the honey bee (Apis mellifera) queen has been found to contain cis- and trans-monoolefinic alcohols and their acetates. A wide range of cis-monoolefinic alcohols and their acetates can be synthesized via the Wittig reaction.

The conventional approach involves the reaction of alkylidenetriphenylphosphoranes with carbonyl compounds, yielding olefins as mixtures of cis- and trans-isomers. However, high stereospecificity toward the cis-isomer can be achieved by using: Aliphatic phosphoranes, Aliphatic aldehydes, Nonpolar solvents, No lithium salts [4] An alternative method involves generating phosphorus ylides from the corresponding phosphonium salts using an alkali metal bis(trimethylsilyl)amide, followed by reaction with aldehydes. This approach produces cis-alkenes with 98% stereochemical purity.

The most efficient synthetic routes for 9-oxo-trans-2-decenoic acid—a key component of the queen honey bee (Apis mellifera) pheromone—and its esters are based on: Condensation of 7-oxooctanal (XII) with malonic acid, Wittig reaction with

ethoxycarbonylmethylenetriphenylphosphoran e, followed by hydrolysis to the final product, Given these pathways, there is a clear need to develop simplified synthetic methods for 7-oxooctanal (XII) or its derivatives to facilitate large-scale production.

The synthesis of ethyl 9-oxo-trans-2-decenoate, a key derivative of the queen honey bee pheromone, was achieved using readily available monoacetals of glutaric and glutaconic aldehydes [3]. Monodiethylacetal of glutaconic aldehyde (I) reacts with acetylmethylenetriphenylphosphorane (II) in ether, yielding dienic ketoacetal (V) with 45% and 28% yields, respectively. Alternatively, monodiethylacetal of glutaraldehyde (IV) with phosphorane (II) produces monounsaturated ketoacetal (VIII) in 65% yield. The dienic ketoacetal (V) was hydrogenated over platinum oxide to form the saturated ketoacetal (V). Hydrolysis of (VIII) with dilute hydrochloric acid yielded the ketoaldehyde (XIV). The ketoaldehyde (XIV) selectively reacts with ethoxycarbonylmethylene-triphenylphosphorane at the aldehyde group, forming ethyl 9-oxo-trans-2-decenoate (IX) in 61% yield [2,3]. The route via glutaconaldehyde monoacetal (I) provides moderate yields but demonstrates synthetic flexibility. The glutaraldehyde (IV) pathway offers higher efficiency (65%) for intermediate (VIII). The final Wittig reaction ensures selective formation of the trans-ester (IX), crucial for pheromone activity.



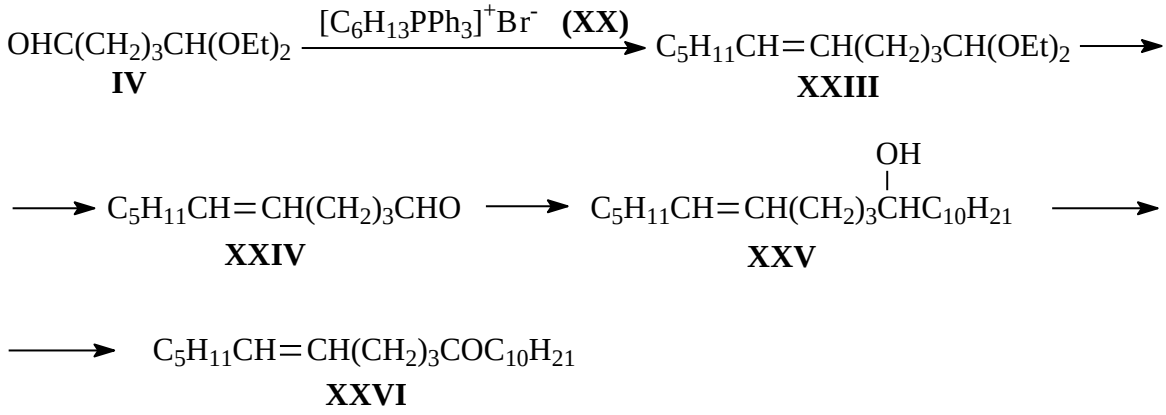
Pheromone component of the douglas-fir tussock moth *(Orgyia pseudotsugata)*

The monoacetal (IV) serves as a versatile synthon for the synthesis of various δ,ε-unsaturated ketones, particularly cis-6-heneicosen-11-one (XIV)—the major sex pheromone component of both the North American Douglas-fir tussock moth (Orgyia pseudotsugata) and the common Eurasian tussock moth (Orgyia antiqua).

Synthetic routes to ketone (XIV): Eschenmoser Fragmentation Cleavage of cyclic epoxy-p-toluenesulfonylhydrazides [8]. Via alkyl aryl sulfoxides or dithiane derivatives of undecanal. Condensation of 5-oxopentadecanal with appropriate ylides [26]. Through the nitrile of 6-undecynoic acid. The monoacetal (IV) route enables efficient access to the cis-alkenone (XIV) with high stereoselectivity. The Wittig method (using 5-oxopentadecanal) is particularly effective for constructing the C11 ketone backbone. Dithiane chemistry offers an alternative for introducing the aliphatic chain.

The reaction of monoacetal (IV) with a phosphorane generated from phosphonium salt (X) under cis-olefination conditions yielded diethylacetal of cis-5-undecenal (XI) with an 84% yield. Acidic hydrolysis of this compound led to cis-5-undecenal (XII) with a 77% yield. Aldehyde (XXIV), when reacted with magnesium bromide decyl, gave the unsaturated alcohol (XVIII) with a moderate

yield, which was then oxidized with pyridinium chlorochromate to the final ketone (XXV). The overall yield of the ketone, starting from the monoacetal, was 28.7%.



Melon fly *Myiopardalis pardalina Big.*

The melon fly (Myiopardalis pardalina) is widely distributed in Asia and several European countries, including Azerbaijan, Armenia, Georgia, Cyprus, Turkey, and Ukraine, as well as Afghanistan, Israel, India, Jordan, Iraq, Iran, Kazakhstan, Kyrgyzstan, Lebanon, Pakistan, Saudi Arabia, Syria, Tajikistan, Turkmenistan, and Uzbekistan. It primarily damages wild and cultivated plants from the Cucurbitaceae family: melon, watermelon, and less frequently – pumpkin and cucumber, with a preference for melon (Cucumis melo).

It produces 3–4 generations per year. The flies emerge during the flowering period of the melon. Female flies lay their eggs in the skin of the ovaries and young fruits, as well as on the leaves. The larvae penetrate the fruit flesh, where they feed on the seeds, then leave the fruit and go into the soil to pupate.

The spring flight coincides with the fruit formation period of host plants. At this time, the soil temperature, where the insects overwinter, reaches +20°C. The pest's flight is observed from early June to mid-October. They feed on the juice of the fruits. The lifespan of the imago is about 2 months. The puncture sites in the fruit flesh can serve as an environment for the development of viral and fungal diseases. The first signs of melon fly infestation are the appearance of small bumpy spots or simple bumps at the puncture sites on the fruit. Later, as the larvae develop, internal rotting of the fruits begins. The damaged fruits eventually rot and become unsuitable for further use.

To prevent further spread of the pest, strict quarantine measures are in place. One of the key elements of pest population management programs is the elimination of male flies, but capturing female flies is equally important for reducing fruit damage.

At the Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan (ICPS AS RUz), research was conducted on the identification of attractive substances from the biomaterial of the melon fly Myiopardalis pardalina Bigot [9]. For this purpose, entomological biomaterial of the melon fly Myiopardalis pardalina Bigot was collected. The insect biomass was kept in glass containers covered with moistened gauze fabric, with small pieces of melon attached to maintain the insects' viability, and kept at room temperature for 72 hours. During this time, the covering fabric was regularly moistened with a sugar solution. Then, the adult melon flies were transferred to a cylindrical structure with removable lids for the staining process using diethyl ether (Fig 2).

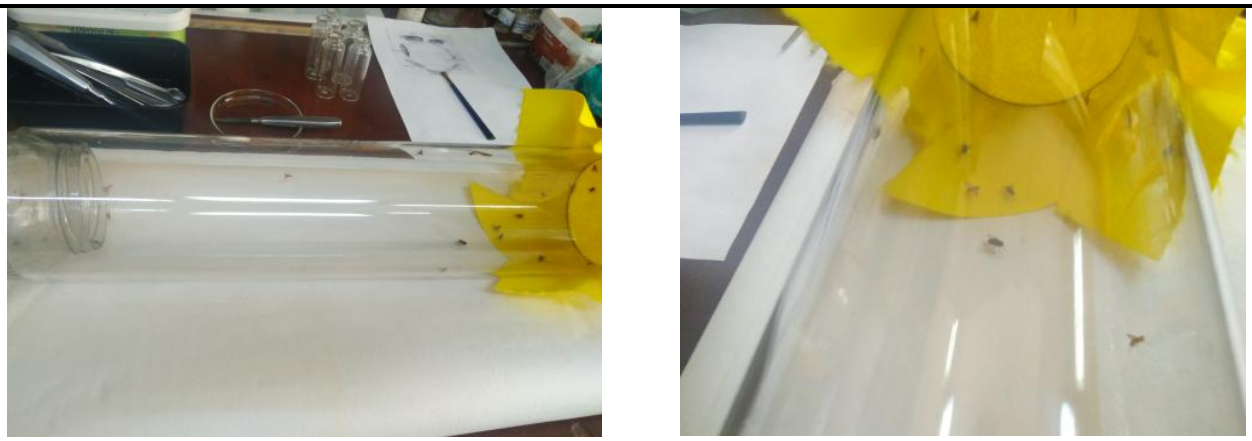


Figure 2. Cylindrical apparatus for conducting the staining process of the melon fly.

Figure 3. Melon fly dissection procedure.

Staining of the insects was carried out using small doses of diethyl ether (Figure 3). Initially, the insects exhibited an excited state—individuals spun around on their backs, sharply twitching their wings. This was followed by a temporary paralysis of the insects. The abdomens of the paralyzed female Myiopardalis pardalina were dissected and placed in a vial containing 5 ml of methylene chloride (Figure 4). The extract was kept in a refrigerator for several days.

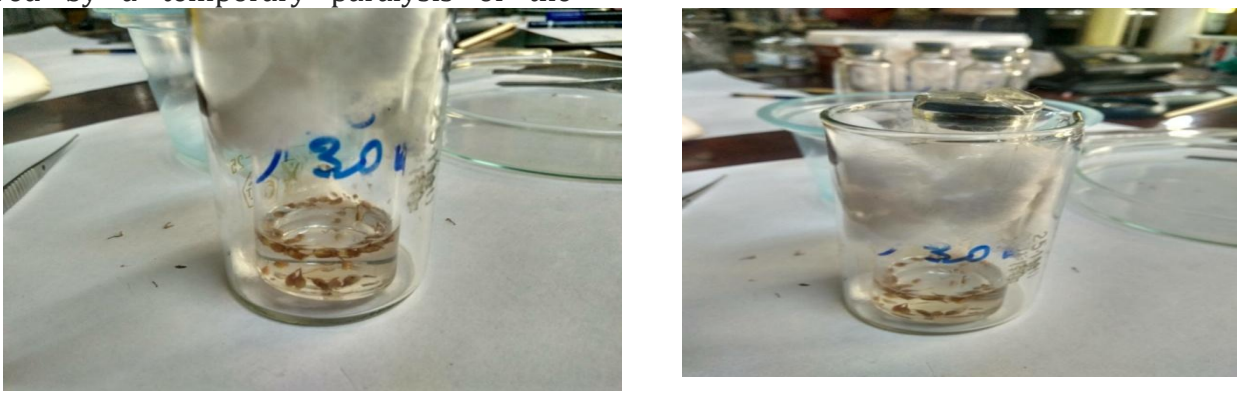
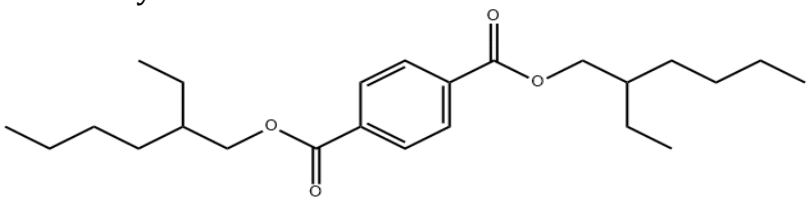


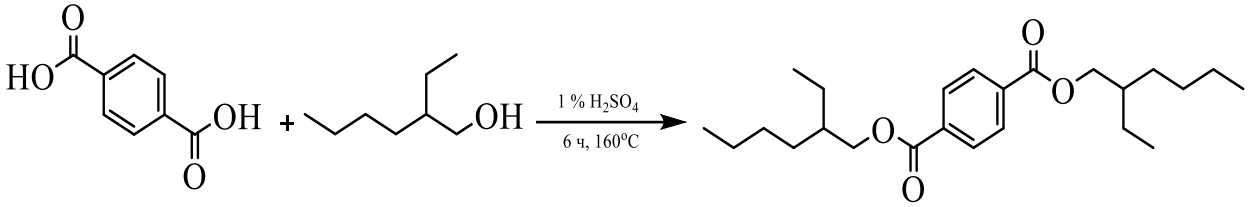
Figure 4. Prepared extracts of dissected melon fly specimens.

GC-MS Analysis of (*Myiopardalis pardalina)* Melon fly pheromone components, combined extracts from dissected Myiopardalis pardalina specimens were analyzed using GC-MS (MassHunter). Key Finding: A pheromone component with retention time (RT) = 23.147 min was identified as bis(2-ethylhexyl) 1,4-benzenedicarboxylate (a diester derivative of terephthalic acid). This compound represents a newly characterized potential pheromonal or semiochemical signal in M. pardalina. Structural Note: The symmetrical 2-ethylhexyl ester groups suggest volatility optimization for aerial dispersal. Instrumentation: Agilent MassHunter GC-MS system. Ionization mode: Electron impact (EI). Spectral Match:

Confirmed via NIST library and synthetic standards. Behavioral assays are needed to validate the pheromonal activity of this diester. Comparative analysis with other Bactrocera spp. may reveal evolutionary conservation.



Synthetic Route for the Identified Pheromone Component. Based on the structural features of the identified compound (bis(2-ethylhexyl) terephthalate), the following synthetic pathway was developed:



Conclusione

The development of practical applications for various pheromones is of great importance because: insects remain the primary pests on most agricultural crops (cotton, cereals, vegetables – including melons, and others), against which extensive control efforts are carried out year after year over large areas; with the widespread introduction of pheromones into production, it is possible to significantly reduce the amount of chemical plant protection used, which will lead both to savings in the costs of crop cultivation and to a reduction in the pesticide pressure on the environment.

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