Pheromons and the influence of ecological factors on them

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Abstract. *Pheromones help alter the behavior, physiological and emotional state or metabolism of other individuals of the same species. Pheromones have found their application in agriculture. When combined with various types of traps, pheromones that lure insects can kill a significant number of pests.*

This article shows the concept of pheromones, their specific significance, as well as their significance for biological species, ways of their possible use for human needs, as well as the influence of external physical environmental factors on pheromones. In modern environmental conditions, this issue is most acute, and research in this area is very promising. Pheromones are one of the types of external stimuli that affect the behavior and physiological state of humans and animals, a complex of special olfactory signals.

Key words*: physical factors of the environment, environment, pheromones, highly volatile substances, releasers, primers, stimulants, pesticides, chemicalization of agriculture, agrocenosis, environmental problems, chemical pollution of the environment, research perspective, synthetic pheromones, pheromone signals, pheromone traps, methods quantum theory, adsorption, temperature, energy, chemical formula of pheromones, atomic structure of pheromone, disparlyure.*

Introduction.

In foreign countries of the 20th and 21st centuries, "the problem of environmental safety has gone beyond the national and regional and has become a global problem for all mankind ... Mankind really felt what kind of threat it faces, resulting in an anthropogenic impact on the environment." Intensive human economic activity has brought the world to the brink of environmental disaster. Human impact on the environment is multifaceted. The main anthropogenic factors destroying the habitat are: urban growth, mining, road transport, industry and agricultural chemicals.

In the deterioration of the environment, chemical exposure is in the first place. The role of chemical objects in human life can hardly be overestimated. They are given one of the important places in the fight against pests, diseases and weeds of agricultural crops, but the effects of pesticides are never unambiguous. Pesticides used in agriculture are organic compounds that are toxic not only to pests, but also to humans and animals. Man uses pesticides to destroy a limited number of organisms, which make up no more than 0.5% of the total number of species inhabiting the biosphere, while pesticides, when used, affect all living organisms. When carrying out protective measures, pesticides are always directed against the population [2].

President of the Republic of Uzbekistan Sh.M. Mirziyoyev, speaking at the meeting of the heads of states - founders of the International Fund for Saving the Aral Sea, noted that it is necessary to start introducing environmentally friendly technologies, lay the foundations for the comprehensive introduction of a green economy, environmentally friendly, energy and water saving technologies. The head of state also initiated the organization of a conference next year with the support of the UN, the World Bank, the Asian Development Bank and the Global Environment Facility, at which negotiations on practical issues of creating a zone of environmental innovations and technologies in environmentally disadvantaged regions of the world will be held. This is provided for in the strategy of actions for five priority areas of development of the Republic of Uzbekistan for 2017-2021 in subparagraph 3.3 [1]. Modernization and intensive development of agriculture is understood as the implementation of investment projects for the construction of new, reconstruction and modernization of existing processing enterprises, the widespread introduction of intensive methods in agricultural production, primarily modern water and resource-saving agricultural technologies, the use of high-performance agricultural machinery; expansion of research work on the creation and introduction into production of new breeding varieties of agricultural crops resistant to diseases and pests, adapted to local soil, climatic and environmental conditions, and animal breeds with high productivity[4].

Insect pheromones, discovered more than fifty years ago, can now become a safe and harmless substitute for pesticides and other harmful chemicals that are currently used in the fight against harmful insects that cause huge damage to agriculture.

Pheromones are biologically active substances, products of external secretion, secreted into the external environment by insects, fish, animals and humans. Pheromones, providing chemical communication between organisms of the same species, are some kind of volatile chemosignals capable of controlling neuroendocrine behavioral responses, developmental processes, social behavior and reproduction. Pheromones alter the behavior, physiological and emotional state, and even the metabolism of different individuals of the same species. These substances, are means of regulation, play an important role in the communication of many species of insects, for example, ensuring the rapprochement of males and females during the breeding season, the concentration of insects on forage plants and in wintering places, or controlling the behavior and physiological processes of working individuals of social insects. Pheromones are found in animals of various taxonomic groups, from invertebrates to mammals. At present, insect pheromones are considered the most studied.

There are two main types of pheromones that differ in their effects: releasers and primers. The first type - releasers, are able to induce an individual to take immediate action, for example, pheromones that transmit danger signals between individuals of the same species. Typically, releasers are highly volatile airborne substances. The second type - primers, are designed to form a special behavior and influence on other individuals, an example is the pheromones secreted by the queen bee, in order to suppress the sexual development of female bees, turning them into ordinary working bees. Primers are most commonly distributed by contact. At this time, releasers have been studied better than primers; by their example, several subtypes of pheromones can be distinguished, such as: attractants - these include sex pheromones and aggregation pheromones that stimulate the accumulation of insects; repellents - repelling pheromones; stimulants - pheromones that cause activity, for example, pheromones, anxiety; deterrents - inhibiting the reaction, etc[5].

The source of pheromone in insects can be individual secretory cells scattered throughout the body or groups of them, which form a special organ - the pheromone gland. The ducts of the pheromone glands open on the surface of the body or in cavities that communicate with the external environment. Insects secrete pheromone in trace amounts: for example, a female codling moth (Cydiapomonella) releases only 9 nanograms of pheromone per hour. However, even this amount is enough for the male moth to smell and find the female in the crown of the tree. Insects perceive the smell of pheromones with the help of chemoreceptor sensilla - special receptors in the form of hairs, bristles or tubercles located on the antennae; their number on one antenna can reach 15 thousand. A very small amount of pheromone in the air is sufficient for an insect's response. [4]

Usually, pheromones are not one substance, but a mixture of the main, predominant by weight component with small additives (minor components): they can contain more than 10 components. One substance can have several different functions. Pheromone molecules are highly volatile, quickly decompose under the action of atmospheric oxygen, moisture and light. In terms of chemical composition, insect pheromones belong to various classes of organic compounds, such as alcohols, ethers, terpenoids, steroids, aldehydes, heterocyclic compounds, and others.

Knowing the chemical composition of the insect pheromone, it is possible to synthesize it in laboratory conditions. It is these synthetic analogs of sex and aggregation pheromones that can be used to protect plants from pests. The advantage of synthetic pheromones, which are used in micro doses, is their high species specificity and attractiveness. They are completely harmless to humans and the environment, and also act directly on the target species of insect pest.

There are two main areas of application of synthetic pheromones against harmful insects: The first is monitoring. This suggests that the use of pheromones provides an opportunity to record such processes as the flight of pests, to obtain data on their numbers, or even the ability to determine the area of quarantine pests. The second is pest control. By saturating the air with synthetic pheromone, it is possible to prevent males from finding females, attract insects and catch or destroy them before they can find a natural source of pheromone. In both cases, the reproduction of pests is blocked.

However, in addition to the effect of pheromones on pests, it is necessary to consider the influence of environmental factors on the pheromones themselves. Taking into account the huge species diversity of insect pests and the complexity of the composition of pheromones, an urgent task is to develop universal methods for studying pheromone communication, which will save material, labor and time resources.

It is important to pay attention to another aspect of the possible use of pheromones - the establishment of the species composition of insects in a particular area. This is most clearly seen in the example of a scoop. Analogs of sex pheromones of many species of scoops were synthesized .. Observations were carried out in cotton crop rotation of three farms in Yangiyul district, as well as in the fields of the Research Institute of Vegetable, Melons and Gourds in Tashkent District, Tashkent Region. We used two- and three-component pheromone moths (Agrotissegetum) (OTs-77 and OTs-8), exclamation moth (Agrotisexclamationis) (BK-23 and BK-137), C-black scoop (Xestia c-nigrum) (SCh-72), bindworm (Emmeliatrabealis) (Minus-21), cotton moth (Helicoverpaarmigera) (KS), meadow moth (Mythimnaunipuncta) (MC).

Dispensers with pheromones were placed in triangular traps made of laminated paper, which were placed in the fields at the rate of 1 trap per hectare at a height of 25 cm above the plants. The pipettes were renewed every 10 days. Observations were carried out over three years in the fields of cotton, kenaf, corn, alfalfa, red pepper, tomato and pumpkin. Based on the number of males of each species caught in pheromone traps, we calculated the indicators of the relative abundance of the species [4].

In the surveyed fields of cotton crop rotation (cotton, kenaf, corn, alfalfa), the scoop complex, determined by the presence of pheromones, is usually of the same type. However, in some years differences were observed, which mainly concerned small species. Thus, in all regions, the bindweed was the dominant species.

(Emmeliatrabealis), subdominant - exclamation (Agrotisexclamationis) and winter (Agrotissegetum). There were no caradrina scoops (Spodopteraexigua) and corn scoops (Spodopterafrugiperda) in the corn and cotton fields. In a cotton field, bindweed (Emmeliatrabealis), winter moth (Agrotissegetum), exclamation moth (Agrotisexclamationis), cotton moth (Helicoverpaarmigera), meadow moth (Mythimnaunipuncta), as well as gamma moth (Autographagamma),

black (Xestia c-nigrum), upsilon scoop (Agrotisipsilon). The species diversity of moths in the corn field was somewhat less: there was no cotton moth (Helicoverpaarmigera) and no upsilon moth (Agrotisipsilon).

In the alfalfa field, all types of scoops were identified, the pheromones of which were used. All kinds of scoops, feromonos which were used during observations, with the exception of caradrins (Spodopteraexigua) and leaf moths (Spodopterafrugiperda). On vegetable crops in Tashkent region, the number of scoops was generally higher than in cotton crop rotation fields in Yangiyul region. In vegetable crops, like In the agrocenoses of the cotton crop rotation, the dominant species was the bindweed (Emmeliatrabealis), the subdominant was the exclamation moth (Agrotisexclamationis) and the winter (Agrotissegetum) moth. So, a day after the installation of pheromone traps, 14.7 individuals were caught on red peppers, and 11 individuals on tomatoes and alfalfa. At the same time, in the fields of alfalfa, tomatoes and red pepper, it was found on traps with winter pheromones of 6, 7.7 and 10.7 individuals, respectively. According to available data, the generalized economic threshold of harmfulness is considered to be the capture, on average, for one trap per day (night) of 5 or more butterflies of winter moths (Agrotissegetum), which corresponds to a caterpillar density of 2.6 - 4.0 individuals per 1 m^2.

In the fields of vegetable crops studied by us, the number of butterflies of the winter moth (Agrotissegetum) exceeded the aforementioned EVP. With the help of pheromones from other moths, a large number of other species have been identified, which are not inferior to the winter moth (Agrotissegetum); the total number of identified moths was significantly higher than the generalized damage threshold established for only one species.

Thus, the use of gender (sex) analogs of pheromones makes it possible to establish the specific composition of moths in the fields of various crops, as well as to reveal the total number of pests in a separate field and give a signal about the need for protective measures to regulate their number[3].

Modeling of photo-excitation processes has shown that the presence, number and mutual arrangement of multiple bonds in a molecule affects the absorption wavelengths. For pheromones that do not contain multiple bonds, the absorption maximum lies in the range 136-144 nm, for unsaturated hydrocarbons and unsaturated oxygen-containing pheromones - in the range 157-204 nm, for oxygen-containing pheromones with conjugated double bonds - in the range 226-230 nm. The intensity of the pheromone signal will decrease when exposed to light radiation, since the excited state is unstable, the molecule goes into the main state, losing energy due to radiation, vibrations or collision with other molecules.

Exposure to electromagnetic radiation leads to a change in the electronic and atomic structure of pheromones. Most pheromones of lepidoptera insects belong to unsaturated compounds containing up to three double bonds in the structure. Analysis of the electronic structure of pheromone molecules shows that, regardless of the presence and type of the oxygen-containing functional group, the redistribution of the electron density upon absorption of light occurs in the region of the arrangement of double bonds and corresponds to the transition of an electron from π-bonding to π * - brobing orbitals. The change in bond lengths occurs only in the region of the location of multiple bonds and does not affect the oxygen-containing functional groups. Such a change in the bond length is unlikely to lead to the destruction of the initial atomic structure of molecules only under the action of electromagnetic radiation, but will increase their reactivity and promote chemical reactions when interacting with components For bicyclic pheromones, upon transition to an excited state, an increase in the length of one of the bonds included in both cycles is observed, which can lead to the opening of one of the cycles of the molecule and the destruction of the pheromone molecule.

An assessment of the resistance of pheromones to thermal exposure using the results of ab initio calculations showed that thermal exposure in noncyclic and monocyclic molecules is most likely to change the lengths of single bonds, while light radiation primarily affects multiple bonds, leading to an increase in their lengths. For bicyclic unsaturated pheromones, exposure to light radiation and thermal exposure lead to similar structural changes - an increase in the length of a single bond included in both cycles, which can lead to its rupture and the opening of one of the cycles in the structure of the molecule.

The factors that can deactivate pheromone molecules can be adsorption on the surface of plants, exposure to temperature, light and chemical interaction with substances-components of the air. Water molecules that are present in the air can interact with polar pheromone molecules, which will lead to a decrease in their concentration. Exposure to light radiation of the ultraviolet part of the spectrum transforms pheromone molecules into an excited state, while the bond lengths and bond angles in the molecules change. Connecting the considered process of excitation of a molecule with communication of insects, it can be assumed that a pheromone molecule in an excited state may not be captured by insect sensors, since the efficiency of binding of a pheromone inside a receptor depends on its atomic structure, that is, the intensity of the pheromone signal will decrease.

Pheromone molecules must have certain physical characteristics in order to remain in the air flow for some time, sufficient for the propagation of the signal, but they must not accumulate in the territory in order to carry the actual information about the position of the signal source. The huge species diversity of insect pests, the multicomponent composition of pheromones, and complex multistage processes for obtaining pheromones from insects under laboratory conditions necessitate the development of alternative non-experimental methods for studying the properties of pheromones and mechanisms of chemical communication. We can examine the properties of pheromone molecules of insect pests by examining them using the methods of the quantum theory of condensed matter.

The aim of the study was to theoretically study the physical properties of disordered organic systems, namely the atomic and electronic structure of pheromone molecules in the ground and excited states, to identify their photophysical characteristics, and to assess their stability under light and thermal exposure.

The application of the methods of quantum theory makes it possible to obtain the basic physical characteristics of pheromone molecules and assess their resistance to such external factors as thermal and light exposure without the use of expensive experimental techniques. This approach is universal for different types of pheromone molecules of various insect species, which is very important, given the multicomponent composition of pheromones and the species diversity of insect pests.

Establishing the relationship between the search behavior of insects and the physical characteristics of pheromone molecules can be used to obtain information about the search behavior of insects, based on data on the chemical composition of pheromone. The data on the resistance of pheromone molecules to the action of environmental factors, obtained using ab initio methods of quantum theory, can be used to modernize and increase the efficiency of methods for controlling the number of insects based on the use of pheromone drugs.

Research methods. Theoretical modeling and calculation of the physical characteristics of pheromone molecules were carried out within the framework of the density functional theory using the B3LYP functional, using the 6-31G ** and cc-pVDZ basic packages implemented in the GAMESS-US program. The absorption spectra were calculated and the molecules were optimized in the excited state by the Time Dependent method. The assessment of the effect of thermal action on pheromone molecules was carried out using a method based on the calculation of normal vibration modes.

The influence of the geometry of molecules on the value of the electric dipole moment and the absorption spectra of pheromones was considered. [5] For oxygen-containing pheromones, a change in conformation leads to a change in the dipole moment by an average of 30% relative to the linear structure; for hydrocarbons, an increase in the dipole moment upon passing from a linear to a maximally twisted conformation is up to 50%.

For oxygen-containing pheromones, the values of the electric dipole moment are in the range of 1.23-2.71 D, for unsaturated hydrocarbons, in the range from 0.29 to 0.49. Pheromones, in which partial positive and partial negative charges are located on different parts of the molecule, are mutually oriented in space so that other polar molecules are nearby - air components, for example, water molecules, whose dipole moment is 1.85 D. Coulomb interaction between polar fragments of molecules can create favorable conditions for their mutual orientation, the occurrence of a chemical reaction and, as a consequence, for the destruction of pheromone. Considering the high polarity of molecules as a factor contributing to the chemical interaction of pheromones with polar components of the medium, it can be concluded that for oxygen-containing pheromones the probability of destruction as a result of chemical reactions will be higher than for pheromones-hydrocarbons, whose dipole moment is significantly less than 1 D, in all possible conformations.

All calculated pheromones of Lepidoptera absorb radiation corresponding to the ultraviolet part of the spectrum, in the range from 130 to 230 nm. Changing the geometry for some pheromones leads to a shift in the absorption maximum, but by no more than 8 nm, that is, no more than 6%. Analysis of the spectral characteristics showed that the maximum absorption of pheromones depends primarily on the presence and mutual arrangement of multiple bonds and practically does not depend on the type of oxygen-containing functional group. The greatest energy is required for the excitation of the limiting epoxide, the minimum - for pheromones with conjugated double bonds. As noted earlier, a change in the conformation of the molecule does not lead to a significant shift in the absorption maximum.

Exposure to electromagnetic radiation leads to a change in the electronic and atomic structure of pheromones. For disparlura, a pheromone of the gypsy moth (Lymantriadispar), which does not have multiple bonds in the structure, the change in the electron density upon absorption of radiation occurs in the region of the epoxy ring for all conformers. Calculation of the geometry of the disparlyur in the excited state shows similar structural changes for all conformations: the bond angles change in the epoxy ring, one of the C-O bonds increases on average to 0.9 Å, which can further lead to its rupture and, as a consequence, to the opening of the cycle and the destruction of the pheromone. Most pheromones of lepidoptera insects belong to unsaturated compounds containing up to three double bonds in their structure. Analysis of the electronic structure of pheromone molecules shows that regardless of the presence and type of oxygen-containing functional group, the redistribution of the electron density upon absorption of light occurs in the region of the arrangement of double bonds and corresponds to the transition of an electron from π-bonding to π *-brobing orbitals (Figure 3). bonds are indicated in angstroms (Å).

Similar structural changes occur in all unsaturated pheromones of Lepidoptera. The increase in the lengths of double bonds occurs on average by 0.1 Å. Such a change in the bond length is unlikely to lead to the destruction of the initial atomic structure of molecules only under the influence of electromagnetic radiation, but will increase their reactivity and promote chemical reactions when interacting with air components. The interaction of the pheromone with the protein of the insect's olfactory receptor occurs according to the "key-lock" principle, that is, in addition to the chemical composition of the pheromone, its geometric correspondence with the protein plays an important role. Therefore, the course of chemical reactions or a significant change in the initial geometry of the molecule will lead to the deactivation of the pheromone as a carrier of information.

The calculated characteristics of lepidoptera pheromones were compared with the data on the search activity of insects. For example, the pheromone of the gypsy moth (Lymantriadispar) consists of one component - disparlura, the a heromone of the pine silkworm (Dendrolimuspini) includes four components. One can see clear differences in the intensity and wavelength of absorption of pheromones of these two types. It is known that the gypsy moth (Lymantriadispar), whose pheromone absorbs in the 130 nm region with a very low intensity, is characterized by searching behavior throughout the day, while the pine silkworm (Dendrolimuspini) is characterized by activity in the evening and night hours, in the absence of solar radiation. For pheromones of the Siberian silkworm (Dendrolimussibiricus) and moths (Geometridae) - moths, the absorption spectra lie in the same range as for the pine silkworm (Dendrolimuspini) and have similar values of the intensity of electronic transitions. The traced relationship between the spectral characteristics of molecules and data on the time of flight suggests that the physical properties of pheromones to some extent determine the time of search activity of insects.

CONCLUSION

The efficiency of information transfer using pheromone molecules is determined by a number of factors, for example, such as the resistance of pheromones to the effects of the external environment on them, that is, to their physicochemical characteristics. The purpose of pheromones and the principle of their action is based on their preservation of their composition and structure, for a certain time, which should be sufficient for spreading in the air, and reaching individuals that must receive a chemical signal. And the use of highly resistant molecules as pheromones can lead to clogging of the information channel and disorientation of individuals receiving signals.

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