SYNTHESIS OF NEW AZOMETHINE DERIVATIVES OF CHITOSAN *APIS MELLIFERA* BASED ON AROMATIC ALDEHYDE

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Abstract: Chitin and chitosan should be considered cellulose derivatives. The basis of this approach to these polysaccharides is their chemical structure. The macromolecular chains of these polymers are formed by glucopyranose rings, which, when connected by β-(1→4) glucosidic bonds, form linear polymer chains. The biological functions and mechanical properties of these polysaccharides are largely determined by the conformation of macromolecules and the distribution of reactive groups in them. Due to their unique properties, chitin and chitosan are becoming increasingly important in practical and especially in the medical and biological activities of mankind. Using methods of chemical modification of chitosan, a number of new biologically active materials have been created. The main interest in these products is due to the preservation of the basic physicochemical and biological properties of the original polymer and the acquisition of new properties depending on the nature of the introduced groups. Modified chitosan can be used in various fields such as drug delivery, textiles, wastewater treatment and a number of biomedical applications.

The purpose of this work is to obtain chitin from the dead Apis Mellifera, to obtain chitosan from chitin, as well as to synthesize a Schiff base based on chitosan with some aldehydes; the physicochemical properties of the resulting compounds have been studied.

Keywords: dead bees, *Apis Mellifera*, chitin, chitosan, biopolymer, aldehydes, Schiff bases, azomethines.

Аннотация: Хитин и хитозан следует рассматривать как производные целлюлозы. Основой такого подхода к данным полисахаридам является их химическое строение. Макромолекулярные цепи этих полимеров образованы глюкопиранозными циклами, которые, соединяясь β-(1→4) глюкозидными связями, образуют линейные полимерные цепи. Биологические функции и механические свойства этих полисахаридов во многом определяются конформацией макромолекул и распределением в них реакционноспособных групп. Благодаря своим уникальным свойствам, хитин и хитозан приобретают все большее значение в практической и особенно в медико-биологической

деятельности человечества. С использованием методов химической модификации хитозана создан ряд новых биологически активных материалов. Основной интерес к этим продуктам обусловлен сохранением основных физико-химических и биологических свойств исходного полимера и приобретением новых свойств в зависимости от природы введенных групп. Модифицированный хитозан можно использовать в различных областях, таких как доставка лекарств, текстильная промышленность, очистка сточных вод и ряд биомедицинских применений.

Целью данной работы является получение хитина из подмора *Apis Mellifera*, получение хитозана из хитина, а также синтез основания Шиффа на основе хитозана с некоторыми альдегидами, изучены физико-химические свойства полученных соединений.

Ключевые слова: подмор пчел, *Apis Mellifera*, хитин, хитозан, биополимер, альдегиды, основания Шиффа, азометины.

INTRODUCTION. Scientists' constant interest in azomethine compounds is due to their wide range of useful properties. Representatives of this class of compounds, their analogs and derivatives are included in a number of drugs, such as local anesthetics, antiarrhythmics, antiallergics, antiasthmatics, etc.

Schiff bases (azomethines) are also very interesting from the point of view of the chemical properties they exhibit. They are characterized by specific reactions: reactions with electrophilic and nucleophilic reagents, coupling reactions with the formation of a cyclic ring, and other reactions.

RELEVANCE. Related azomethine compounds play a very important role in a number of important processes, including enzymatic, synthetic reactions, in the synthesis of primary and secondary alkylamines, as intermediates by general methods, in the reduction of nitrile salts of triethylsilane, and also in the effective synthesis of aldehydes o in [1, p.347; 2, p.147].

The comparative simplicity of synthesis and the widespread occurrence of substances containing -HC=N- groups in living nature have always attracted the attention of researchers. The presence of a double bond in molecules determines the characteristics of the formation reactions and affects the spatial structure and chemical properties of these compounds [3, pp. 24-29].

Some compounds of this class are used in technology as monomers, components of lubricating and cooling liquids for cutting metals, biocidal and antioxidant additives to fuels and oils, components of polymer compositions, and radioprotective substances.

In addition, azomethine compounds are part of a number of pesticides, including fungicides, bactericides and herbicides. Their high biological activity and

structural similarity to some natural compounds make them very promising substances for use as plant protection products [4, 181-189].

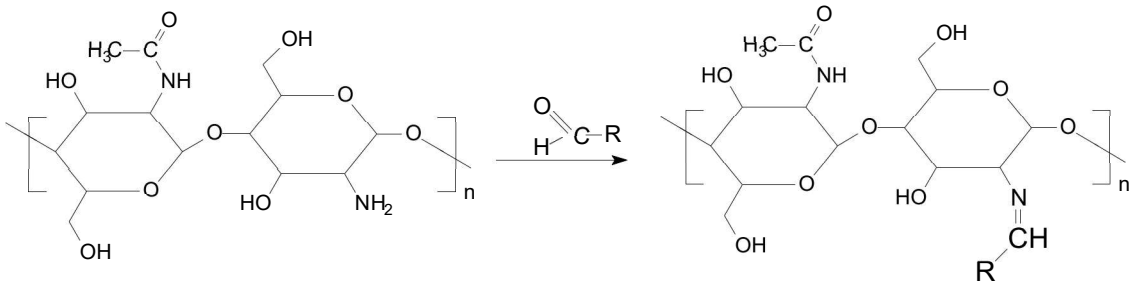
The presence of various aliphatic and aromatic fragments in the molecule of Schiff bases, which are part of many natural compounds, is an important promising direction in the search for biological activity of compounds of such a structure . Among azomethine compounds containing aromatic groups, a number of highly effective plant growth stimulants and medicinal products (antiseptics, coronary activators, antiviral drugs) have been discovered, and they are also widely used in the synthesis of aromatic substances and dyes [5, p.1331-1337].

MATERIALS AND METHODS. In Uzbekistan, due to the widespread use of beekeeping, the possibility of obtaining chitin raw materials on a large scale (from dead bees) has been considered. As of 2022, there are about 1 million bee families in farms of various categories. The strength of a bee family (measured in kg, the weight of worker bees in a bee family) is on average 3.5 - 4 kg. According to observations, a honey family is renewed by almost 80% twice a year. Thus, the annual raw material base of dead bees can be from 6 to 10 thousand tons, this makes it possible to consider dead bees as a new alternative source of obtaining chitosan, along with traditionally used types of raw materials.

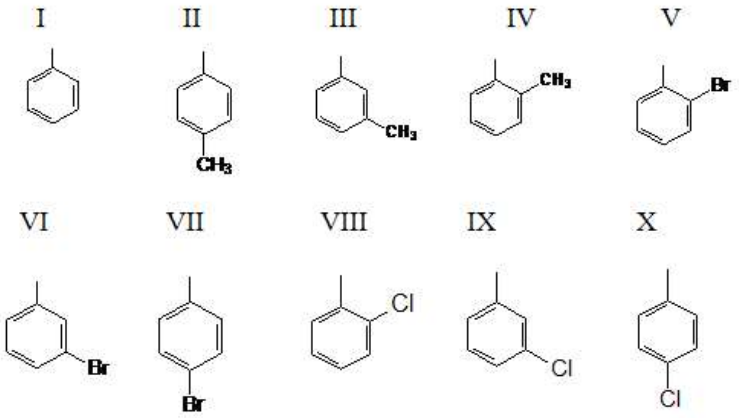
The aim of this work is to obtain chitosan from dead bees *Apis Mellifera* and its basis to synthesize azomethine derivatives with aromatic aldehydes.

We isolated chitin from the dead bees of Apis Mellifera. The process was carried out using a well-known method, which includes the stages of deproteinization and demineralization [6, p.96].

RESULTS AND DISCUSSION. The reaction scheme of chitosan with aromatic aldehydes of the benzene ring is presented below:

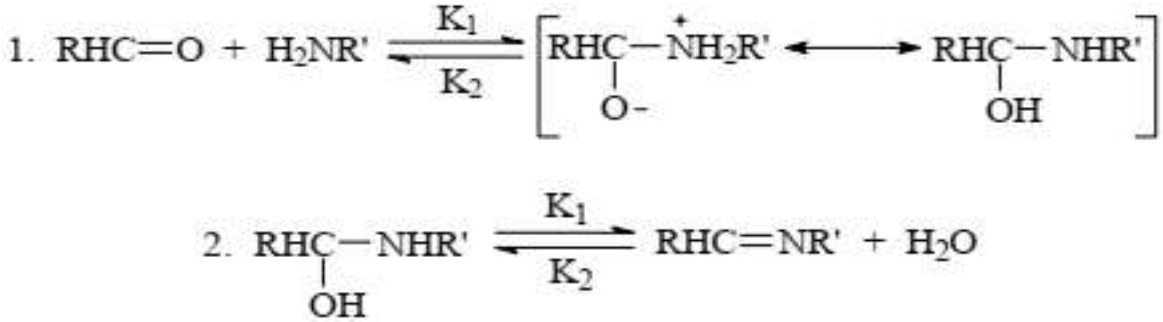


Where R:



Scheme 1. Obtaining azomethine derivatives of chitosan with aromatic aldehydes

According to modern concepts, the formation of azomethines (Schiff bases) from aldehydes and amines occurs in two stages, each of which is a reversible reaction. It is assumed that the mechanism of the reaction of chitosan with aldehydes is as follows: in the first stage, an amine is added to the aldehyde to form an intermediate carbinolamine (Scheme 2). In the second stage, the amino alcohol is dehydrated. Dehydration is facilitated by electron-donating substituents of the CHO group.



Scheme 2. Formation of Schiff base

When studying the IR spectrum of the synthesized Schiff base of chitosan with different aldehydes, the following characteristic absorption signals are observed, cm^{-1} : the decrease and shift in the intensity of the absorption signals in the regions of 3000 – 3601 cm^{-1} indicated the formation of Schiff due to free amino groups. The stretching vibrations of the -OH groups forming an intramolecular hydrogen bond were manifested in the region of 3435.99 cm^{-1}, the absorption signal in the regions of 2918.77 and 1626.9 cm^{-1} are due to symmetrical vibrations of the C=O bond in CH and amides (amide bond I) in the methylene group. The IR spectrum also contains the following characteristic absorption signals, cm^{-1}: 1460.1 and 892.86 - deformation vibrations of the -OH group; 1150.97 deformation

vibrations of the C- H bond in CH_3; 1050.16 C-O-C bonds, 1274.69 vibrations of the C = C bonds of the aromatic rings. An intense absorption signal in the region of 1603.02-1681.27 cm -1 indicates the formation of azomethine bonds C = N of the synthesized Schiff bases [7, pp. 90-97].

The physicochemical properties of the obtained compounds are presented in the table below.

Table. Physicochemical properties of azomethine compounds

Number connections	Melting point, °C	R_f	Solvent	IR spectrum, -HC=N-, cm^{-1}	Exit, %
I	125-127	0.72 water: methanol (2:8)	Acetone	1678,12	86
II	210-212	0.56 water: methanol (2:8)	Acetone, benzene	1603,02	78
III	243-245	0.57 water: methanol (2:8)	DMSO: Acetone	1623,10	80
IV	215-217	0.49 water: methanol (2:8)	Acetone, benzene	1623,00	81
V	196-198	0.74 water: methanol (2:8)	Acetone	1574.19	90
VI	183-185	0.67 water: methanol (2:8)	Acetone	1681.27	92
VII	210-212	0.65 water: methanol (2:8)	Acetone	1623,04	89
VIII	146-148	0.54 water: methanol (2:8)	Acetone	1521,56	91
IX	195-197	0.68 water: methanol (2:8)	Acetone, benzene	1640,12	92

X	**238-240**	**0.63 water: methanol (2:8)**	**Acetone, benzene**	**1660,13**	**90**

SUMMARY. The main source of raw materials for obtaining chitin and chitosan in our republic are the dead bees *Apis Mellifera*. The expansion of the areas of application of these biopolymers leads to the search for new promising sources of the studied polysaccharides. Thus, from the dead bees A biopolymer of chitin was isolated from *Apis Mellifera* bees; chitosan was obtained from chitin using appropriate chemical processes; new azomethine derivatives of chitosan with various aromatic aldehydes were synthesized. The obtained compounds can be used in the textile, cosmetic and pharmaceutical industries, as well as in the agricultural sector.

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