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PREPARATION OF AZOMETHINE DERIVATIVES (SCHIF BASES) CHITOSAN APIS MELLIFERA

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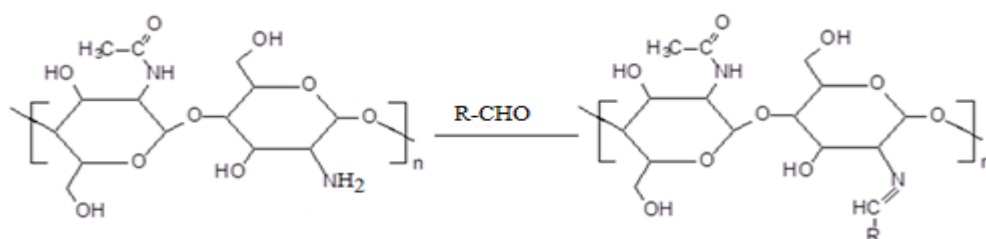
Abstract: Chitin and chitosan should be considered as derivatives of cellulose. The basis for such an approach to these polysaccharides is their chemical structure. The macromolecular chains of these polymers are formed by glucopyranose cycles, which, being connected by β -(1 \rightarrow 4) glucosidic 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 the unique properties of chitin and chitosan, they are becoming increasingly important in the practical and especially in the medical and biological activities of mankind. The aim of this work is to obtain chitin from *Apis Mellifera*, obtaining chitosan from chitin, synthesis of the Schiff base chitosan with acetic, salicylic, *o*-methoxy-*p*-hydroxy benzaldehyde and dialdehyde gossypol, study of the composition and individuality of the obtained products using IR spectroscopy methods.

Keywords: Chitin, chitosan, biopolymer, aldehydes, gossypol, Schiff bases, IR spectroscopy.

INTRODUCTION. Chitosan is a linear aminopolysaccharide. The biopolymer macromolecule consists of alternating 2-amino-2-deoxy- β -D- glucopyranose units linked by a β -(1 \rightarrow 4) -glycosidic bond. The presence and amount of primary amino groups, primary and secondary hydroxyl groups in chitosan, at which various transformations are possible, as well as N-Acetyl-D-glucosamine units, depend on the degree of deacetylation chitosan [1, 2]. Number of new biologically active materials has been created by the methods of chemical modification of chitosan. The priority interest in these products is due to the fact that the basic physicochemical and biological properties of the initial polymer are preserved and, depending on the nature of the introduced groups, it acquires new properties. The use of modified chitosan is possible in various fields, such as drug delivery, tissue engineering, wastewater treatment, and in a number of biomedical areas [3].

Schiff bases are widely used in organic synthesis and industrial technology as pigments, dyes, catalysts, intermediate products as polymer stabilizers. They have a wide range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic activity [4]. Some complexes of Schiff bases have a catalytic effect. The antioxidant activity of Schiff bases, thermal decomposition and catalytic activity of their complexes with metals have been studied [5].

MATERIAL AND METODS. We have synthesized a number of azomethines - Schiff bases with chitosan *Apis Mellifera*. The reaction of the amino group of chitosan with the aldehyde group proceeds according to the scheme shown in Figure 1.



where R:

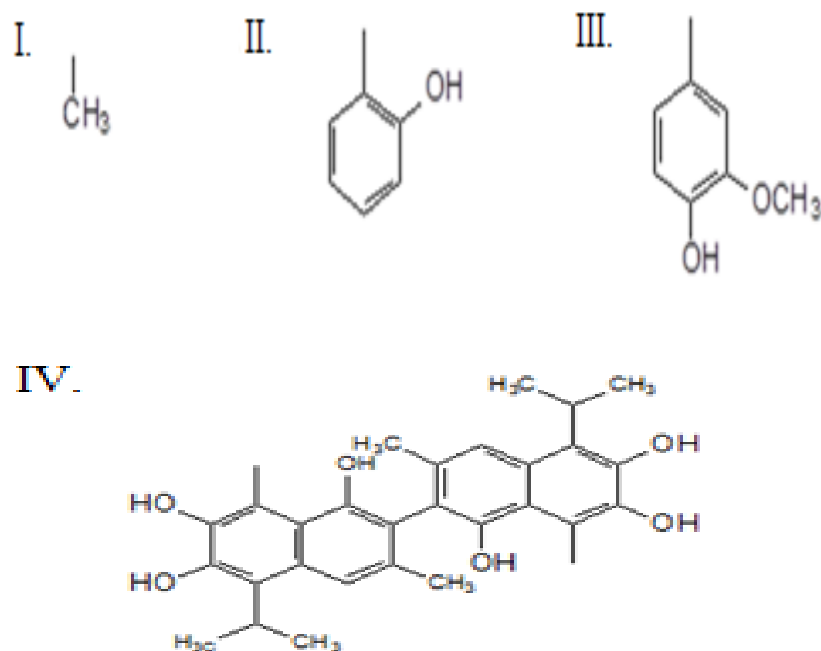


Fig 1. Schiff base formation scheme based on chitosan *Apis Mellifera*

According to modern concepts [6-9], the formation of azomethines (Schiff bases) from aldehydes and amines proceeds in two steps, each of which is reversible. Mechanism of reaction of interaction of chitosan with aldehydes expected next. In the first step, the amine is added to the aldehyde to form the intermediate carbinolamine (Fig. 2).

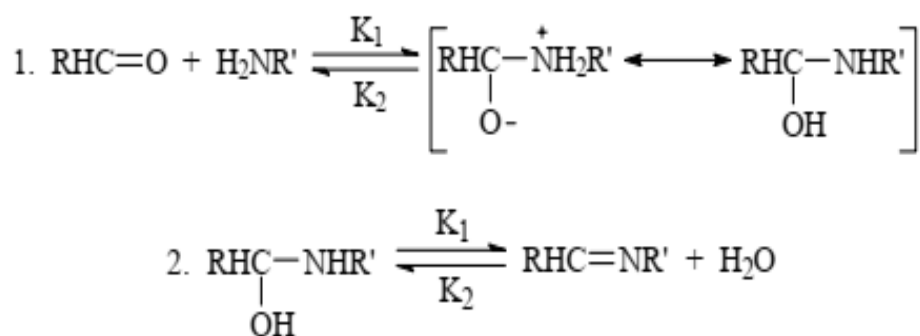


Fig 2. Schemes of chemical equations for the formation of Schiff bases from the amino groups of chitosan with aldehydes

The speed of this step depends on the nature of the substituents. Electron - withdrawing substituents, which increase the charge on the carbon atom of the aldehyde, accelerate the addition of the amine. Electrodonating substituents in an amine that increase basicity amine nitrogen increase and electron-withdrawing ones decrease K_1 constant. Bulky substituents in the - position to NH_2 - group, as well as in aldehydes, significantly complicate this reaction [10]. In the second stage, the amino alcohol dehydrated.

Dehydration is facilitated by electron donor substituents from the -CHO group. As a result, substituents have an opposite effect on the rate of the two main stages of the process, and the resulting effect depends on which of the stages is decisive [7]. Limiting stages can be different and at different pH environment [6]. In a neutral and slightly acidic solution, the

slowest stage is dehydration, and in an acidic one, addition of an amine. In an acidic environment, on the one hand, as a result of the addition of a hydrogen ion to aldehyde oxygen, the positive charge on the carbon of the -CHO group increases, on the other hand, dehydration proceeds faster.

With pH change environment, the rate of formation of azomethine can pass through the maximum pK reactive amine. At low pH dehydration proceeds at a faster rate and the addition step becomes the determining step. An excess of acid significantly lowers the basicity of the amine, reducing its nucleophilic properties to a minimum, which leads to a slowdown in the process as a whole [6].

The given mechanism of the reaction of -CHO groups with amines can apparently be transferred to the interaction of NH₂ - groups of chitosan with -CHO groups from aliphatic, aromatic and dialdehydes. However, in this case, the reaction should take place in multiple stages, and the structure of the final product should ultimately be determined by such factors as the different reactivity of the NH₂ groups located at the bulky substituent in the elementary unit of chitosan, the nucleophilicity of the -CHO groups conjugated with the aliphatic, aromatic aldehydes and pH value reaction environment due to the acid - base properties in solution of each of the aldehydes.

To identify the listed above factors on the passage of the condensation reaction of chitosan with each of the selected aldehydes seems to be a rather difficult task, requiring additional research and generalization of the material. The concentration of chitosan, pH and reaction temperature are significant for the physico - chemical properties of the polymer, such as: modulus of elasticity, efficiency in the adsorption of heavy metal ions, solubility, immobilization ability, gelation rate. On the other hand, different degrees of deacetylation chitosan also have an effect on the crosslinking of chitosan.

A Schiff base is accompanied by a change in the color of the sample, which is possibly due to the appearance of a chromophore group. Another explanation for this phenomenon is the formation of cross-links with the formation of a three-dimensional network structure. Chemically crosslinked structures are formed through the formation of a covalent bond between chitosan and gossypol. The crosslinking of a polymer strongly affects its rheological properties, especially at a low degree of crosslinking [11, 12, 13].

RESULTS AND DISCUSSION. The degree of crosslinking of chitosan is controlled by changing the stoichiometric ratio of aldehyde and amine. The crosslinking density directly depends on the concentration of gossypol and does not depend on other parameters. Also, the degree of crosslinking can be controlled by changing the ratio of charged and uncharged reactive primary amino groups of chitosan. The biological activity of the chitosan-gossypol structure can manifest itself in various media and increases when chitosan is combined with ions of various metals or cross-linked with other organic compounds. The conditions for the synthesis of new chitosan derivatives with aldehydes are given in the table.

Table 1

Synthesis conditions and properties of azomethine derivatives chitosan *Apis Mellifera*

No.	Connection	pH	Temperature, C	Time, min	Connection color	Exit. %
1.	I	4.5-5.0	50	150	brown	92
2.	II	4.5-5.0	60	180	yellow	95
3.	III	4.5-5.0	60	180	light brown	90
4.	IV	4.5-5.0	60	240	dark brown	51

In the IR spectrum of compound, I, in contrast to the structure of the starting substances, an absorption band appears - C = N - groups at $1653,57 \text{ cm}^{-1}$. In the region of $1027,28 \text{ cm}^{-1}$, an absorption band is observed - C - O - C - bonds of glucoperanose. The IR spectrum also contains the following characteristic absorption signals, cm^{-1} : 1417,9 and 896,74 - bending vibrations of the -OH group; 1149,51 bending vibrations of the C - H bond in -CH₃; 1062,3 C-O- C bonds. An intense absorption signal at 1653,57 indicates the formation of an azomethine bond C= N of the synthesized Schiff base (fig.3.)

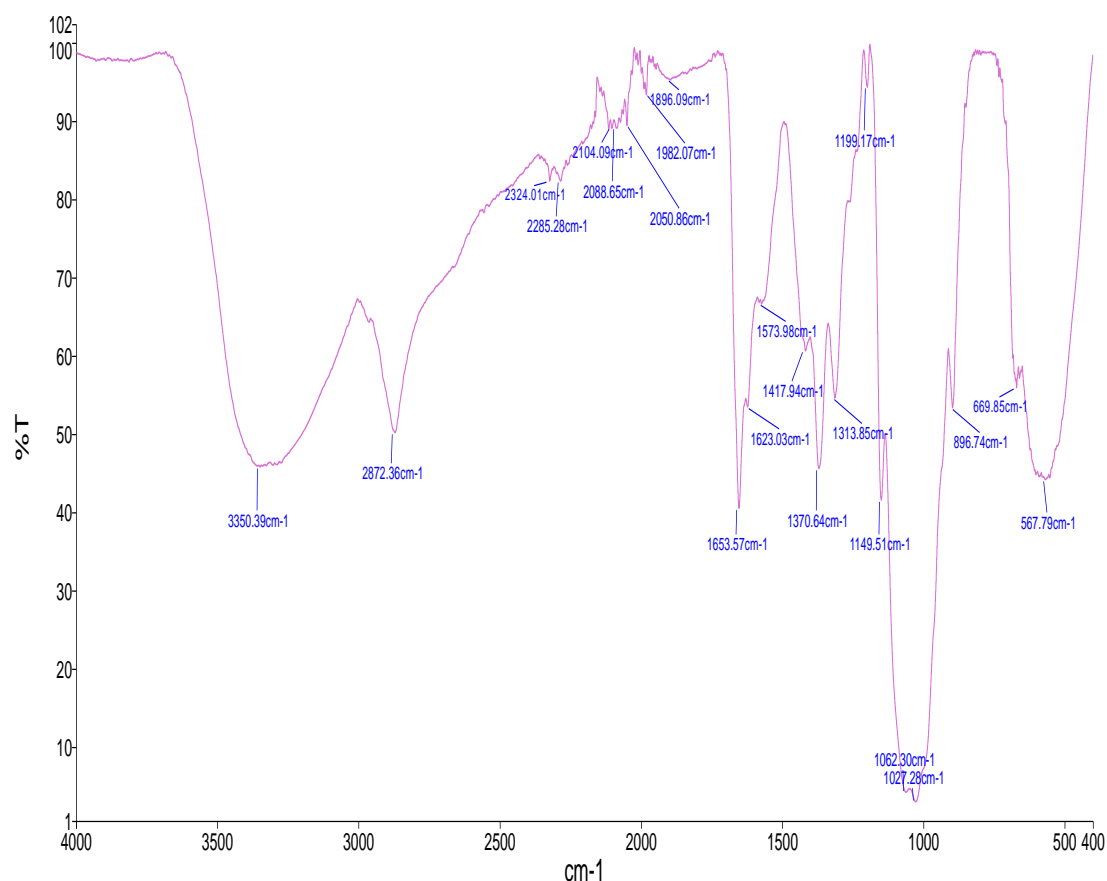


Fig 3. IR spectrum of the Schiff base of chitosan with acetaldehyde (I)

When studying the IR spectrum of the synthesized Schiff base chitosan with salicylaldehyde II (fig.4.), a decrease and a shift in the intensity of absorption signals in the regions of $3000 - 3601 \text{ cm}^{-1}$ testified to the formation of Schiff due to free amino groups. The stretching vibrations of the -OH groups forming an intramolecular hydrogen bond appeared in the region of $3435,99 \text{ cm}^{-1}$, the absorption signal in the regions of $2918,77$ and $1626,9 \text{ cm}^{-1}$ is 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 - bending vibrations of the -OH group; 1150,97 bending vibrations of the C - H bond in CH₃; 1050,16 C-O- C bonds, 1274,69 vibrations of C = C bonds of aromatic rings. An intense absorption signal at 1626, 99 indicates the formation of an azomethine bond C= N of the synthesized Schiff base [14, 15, 16]. The structure of compound III is confirmed by the presence of a - C = N - bond in the region of 1636.01 cm^{-1} . In the region of $1062,83 \text{ cm}^{-1}$, an absorption band is observed - C - O - C - bonds of glucoperanose

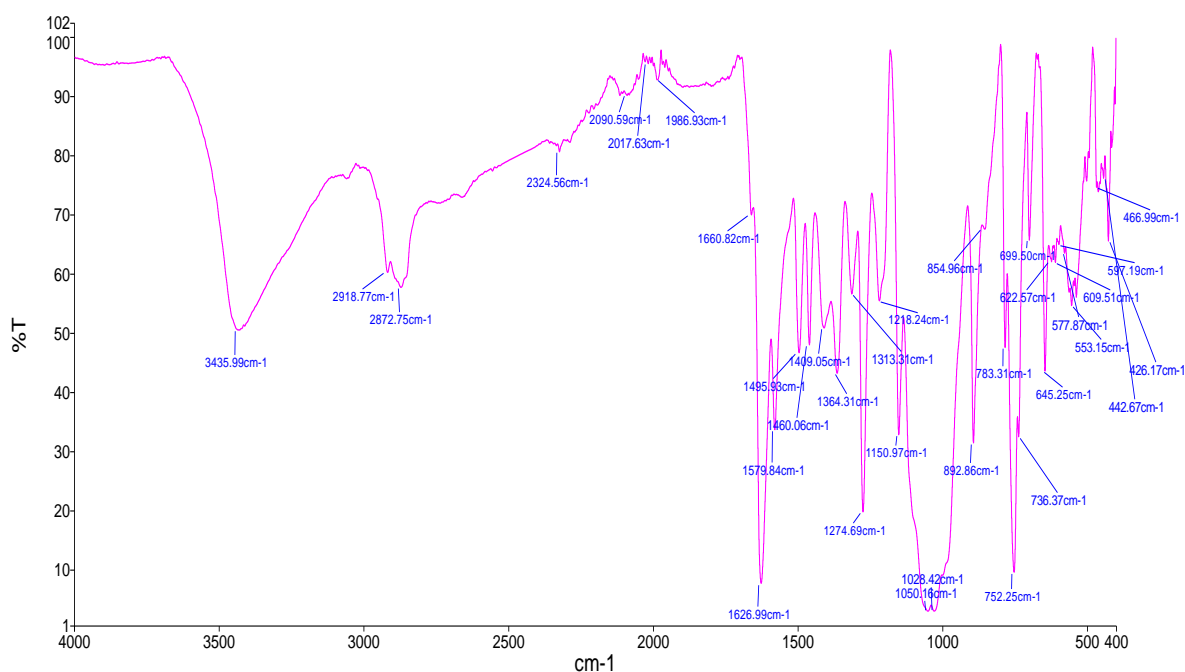


Fig 4. IR spectrum of the Schiff base of chitosan with salicylaldehyde (II)

The IR spectrum also contains the following characteristic absorption signals, cm^{-1} ; 1151,9 and 897,25 - bending vibrations of the -OH group; 1285,28 deformation vibrations of the C - H bond in - OCH_3 . An intense absorption signal in the region of 1636,01 indicates the formation of an azomethine bond $\text{C}=\text{N}$ of the synthesized Schiff base (fig.5.).

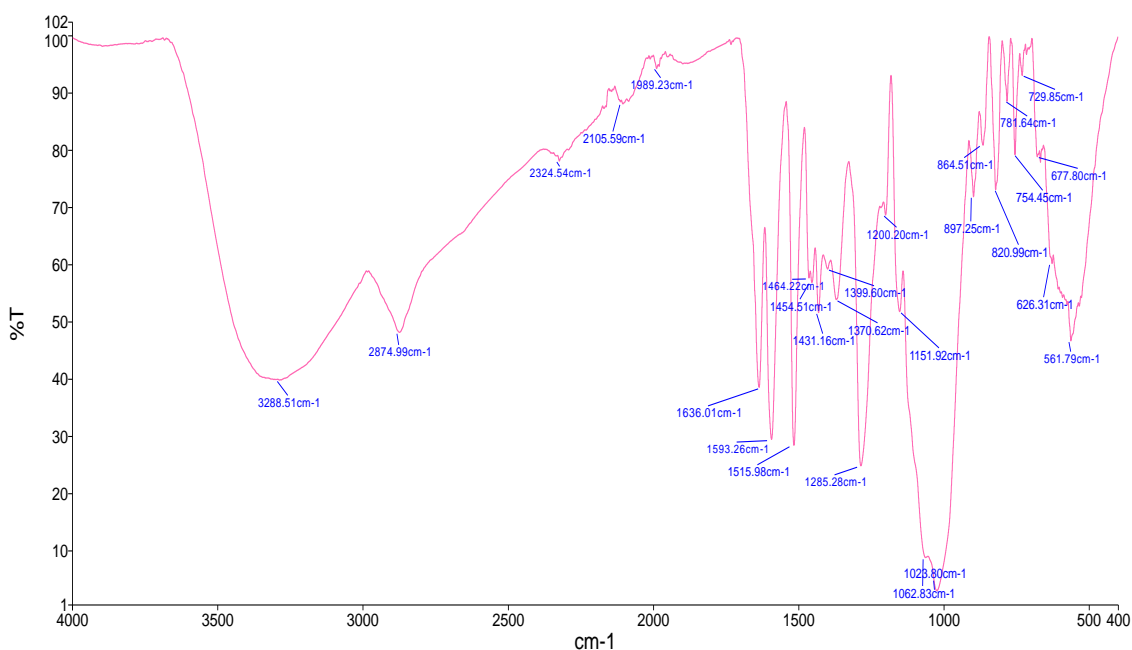


Fig 5. IR spectrum of the Schiff base of chitosan with o-methoxy-p-hydroxy benzaldehyde (III)

The structure of compound IV, in the region of $1062,74 \text{ cm}^{-1}$; an absorption band is observed - C - O - C - bonds of glucoperanose. The IR spectrum also contains the following characteristic absorption signals, cm^{-1} ; 1151,59 and 896,31 - bending vibrations of the -OH group; An intense absorption signal at 1606,12 points to the formation of a $\text{C}=\text{N}$ azomethine bond of the synthesized compound.

CONCLUSION. Polysaccharides chitin and chitosan are promising biomaterials of the future. Chitin, due to its structure and the presence of reactive groups, is able to form complexes with organic substances: cholesterol, proteins, peptides, and also has a high sorption capacity for heavy metals and radionuclides. The unique structure of the chitosan macromolecule and the presence of a positive charge determine the manifestation of antioxidant, radioprotective, fiber- and film-forming, immunomodulating, antitumor properties, as well as its low toxicity and biodegradability.

To date, in our Republic, the source for obtaining chitin and chitosan is the death of *Apis Mellifera* bees. The expansion of the areas of application of these biopolymers leads to the search for new promising sources of the studied polysaccharides. Thus, the biopolymer chitin was obtained from *Apis Mellifera*; chitosan was obtained from chitin using appropriate chemical processes; synthesized base Schiff chitosan with various aldehydes. The resulting compounds can be used in the textile, leather, cosmetic and pharmaceutical industries, biotechnology, and agriculture.

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