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METHOD OF OBTAINING AND PHYSICO-CHEMICAL PROPERTIES OF CARBOXYMETHYL ETHERS OF CHITOSAN FROM BEES INANIMATE

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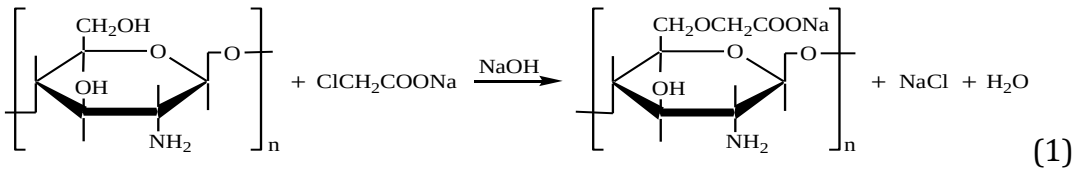
ABSTRACT

This article presents the results of obtaining biopolymers of carboxymethyl esters of chitosan from a new promising source - dry dead bees. Dried and crushed deadwood, collected during the spring renewal of the bee colony, was used. The process was carried out under general conditions according to the general method of alkylation. The solubility of the products obtained was compared, UV spectroscopy was performed, and conductometric analysis was studied. The resulting biopolymers were identified by taking infrared spectra with an IR Fourier spectrometer "IRTracer-100" (SHIMADZU CORP., Japan 2017)

Chitosan and its derivative, carboxymethylchitosan, are the most common biologically active polymers. Due to their high biological activity, these biopolymers are actively introduced into various spheres of human life.

Carboxymethylchitosan CMCHS is prepared by adding a carboxymethyl group to the chitosan structure. This modification increases its solubility in neutral and basic solutions without affecting other important characteristics [1]. CMCHS is obtained by carboxymethylation of hydroxyl and amine groups of chitosan [2]. Various template substitutions can be obtained depending on the reaction temperature used (Figure-1).



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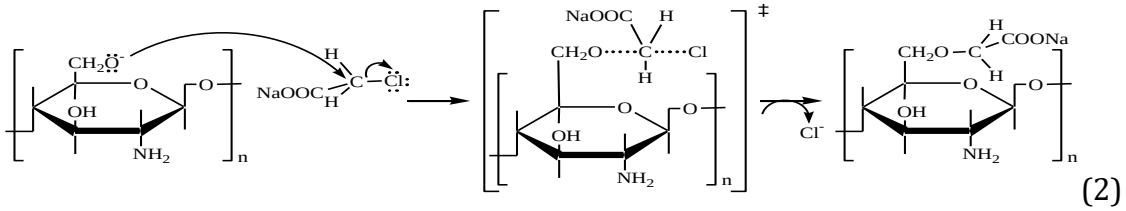
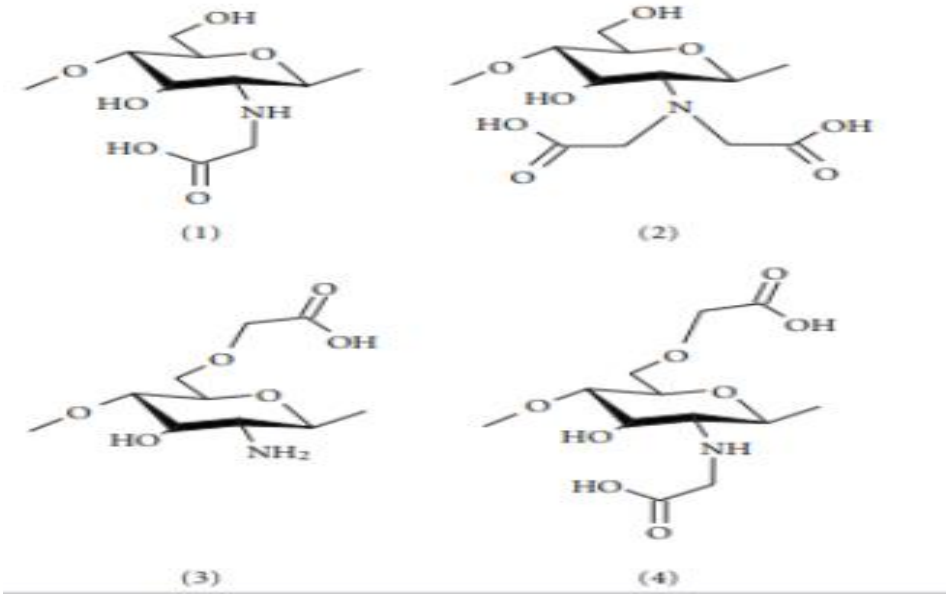


Fig.1. Synthesis (1) and mechanism synthesis (2) of O-carboxymethylchitosan

At room temperature, O-substitution is preferred, while at higher temperatures, N-substitution is an efficient route. Taking into account the reaction conditions and reagents, various derivatives can be produced, i.e. N-, O-, N, O- or N, N-dicarboxymethyl chitosan (Figure-2) [3].

Recently, there has been an increase in interest in chitosan and its derivatives. In addition, they have good biological activity, radiation resistance, film formation ability.

The above requirements are fully met by these polymers, since they undergo biological degradation without the formation of harmful substances, are not scarce, and are relatively inexpensive in relation to medical products.



2-Figure. Chemical structure of various types of carboxymethyl chitosan (CMCHS): (1) N- CMCHS, (2) N,N-CMCHS, (3) O- CMCHS, and (3) N,O- CMCHS (showing modification in the D-glucosamine unit).

In this regard, this gives us researchers the opportunity to consider honey bees, that is, dead bees, as a new promising method for obtaining chitin and chitosan [4]. The strength of the bee family (the mass of worker bees in the bee family, measured in kg) is, on average, 7.5 -8 kg. In summer, during the period of active honey collection and in spring after wintering, the bee colony is renewed by almost 60-80% [5]. Synthesis of CMCHS has been carried out on the basis of the methodology presented in [6] literature.

Particular attention should be paid to the fact that the samples after the reaction of carboxymethylation of chitosan dissolve in water, while the original chitosan is

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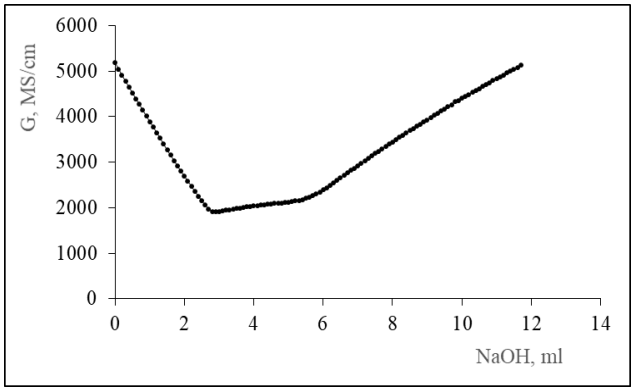
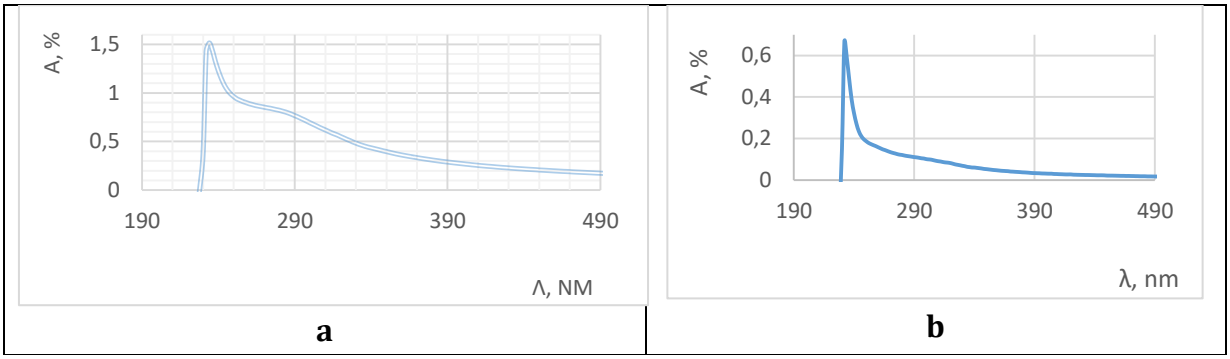
insoluble in water. This is a consequence of the introduction of hydrophilic carboxymethyl groups, which once again confirms the formation of CMCHS [7–8].

0.05 g of CMCHS has been dissolved in 25 ml of 0.02 N. NaOH. The conductivity values have been then determined by titration with 0.1 N NaOH. According to the graph, it is possible to determine the degree of its exchange by the volume of alkali consumed for the titration of the carboxyl group in the CMCHS molecule. The curve of the conductometric titration of carboxymethylchitosan, obtained at a temperature of 650 °C, reaction time 4 hours and a ratio of CZ/MAA 1:1, is described as a broken line corresponding to a certain range of titrant consumption (Figure-3). In the initial step of the NaOH titration, the CMCHS samples correspond to the volume of base added to neutralize the strong acid (H_3O^+) present in the intermediate solution from 0 to V1. The following (V1-V2) cross sections are observed, which are typical for the titration of carboxymethyl groups (CH_2COOH). As the titration continues, the base volume (V2-V3) used to neutralize the ions (NH_3^+; NH_2R; NHR_2; where R is CH_2COOH) is displayed. Subsequent titration shows an increase in the electrical conductivity G, which indicates an excess volume of a strong electrolyte (NaOH) [9].



3-Figure. Conductometric titration line with CMCHS solution.

The difference in the structure of the polymer chains of chitosan and carboxymethylchitosan is also reflected in their UV spectroscopy values (Figure-4).



a **b**

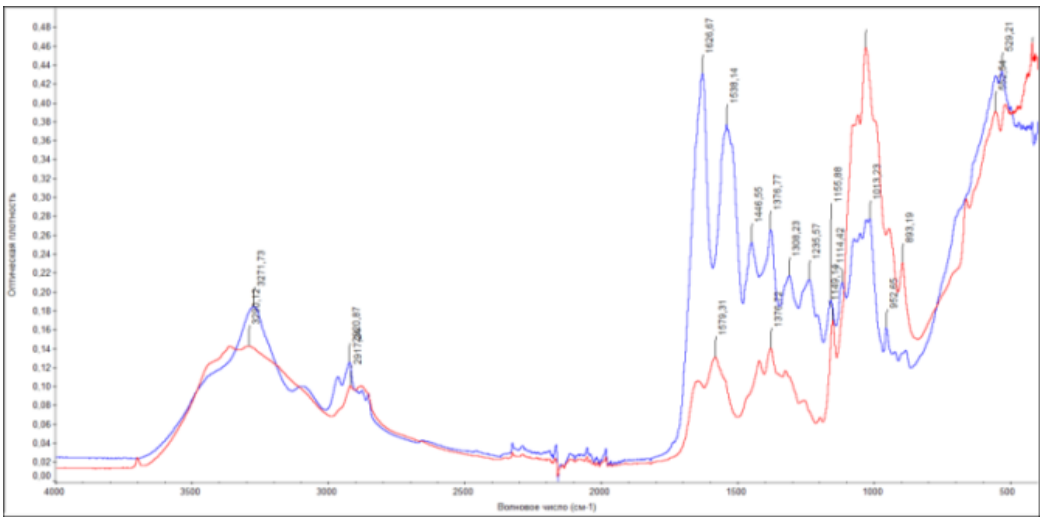
4- Figure. UV spectroscopy of chitosan and carboxymethylcytosan
a - chitosan b- CMCHS

In the process of carboxymethylation of chitosan, the concentration of the alkaline solution, the temperature, the duration of the carboxymethylation reaction, and the

amount of monochloroacetic acid (MAA) were controlled by selecting the ratio of ChS: MAA. With an increase in the NaOH concentration from 20% to 30%, the solubility of the chitosan sample obtained by alkaline treatment increased from 70–75% to 85% [9–10].

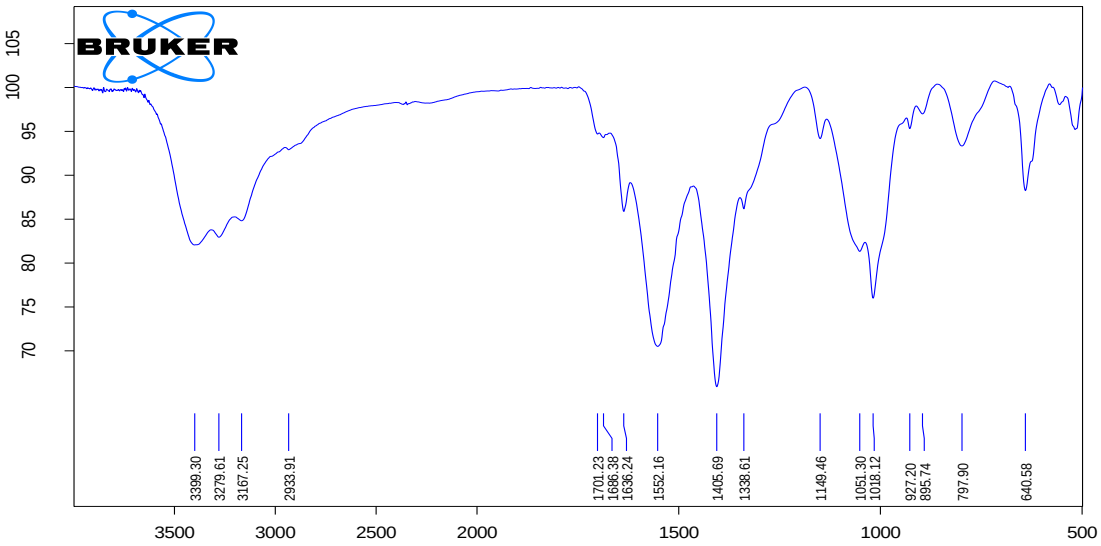
The difference in the molecular structure of chitosan and CMCHS has been studied using IR spectroscopy. It was found that in the IR spectrum of chitin, characteristic absorption bands are observed in the 3270 regions related to the vibration of the -N–H- bond, as well as absorption bands at 1375 cm^{-1}, which indicate the presence of the $-CH_3$ group and absorption in the region of 1625 cm^{-1} is characteristic of C= About the group. The IR spectrum of chitosan shows peaks at 3300 cm^{-1} and 1390–1000 cm^{-1}, which indicate the presence of an NH_2 group.

In this case, absorption in the range of 1360–1000 cm^{-1} for all types of amines, absorption bands appear, caused by the participation of the C–N bond in the skeletal vibrations of the molecule. In a sample of chitin and chitosan, bands were also recorded with maxima at 1433 cm^{-1} of the bending vibration of the CH_2 group and 1373 cm^{-1} (inflection) of the bending vibration of the OH bond. In a sample of chitosan, a wide band of medium intensity is observed in the region of 1320–1387 cm^{-1}, corresponding to the vibration of the OH bond (Figure-5). The IR spectra of CMCHS show an absorption peak in the region of 3399.30-3167.25 cm^{-1}, which is characteristic of hydroxyl groups. The absorption band in the region of 1552 cm^{-1} is typical for C=O groups (Figure -6).



5-Figure. IR spectra of chitosan obtained from the dead bees

Thus, in O-CMCHS, substitution occurs only in the –OH group without affecting the $–NH_2$ groups. In addition, –COOH groups can interact with $–NH_2$ groups by intermolecular and intramolecular bonds and charge $–NH_3^+$ groups into O-CMCHS. In this regard, under the same conditions, the amount of $–NH_3^+$ of the O-CMCHS group is greater than in chitosan. Which explains the superior antibacterial properties of O-CMCHS.



6-Figure. IR spectra of O-carboxymethylchitosan obtained from the dead bees

With an increase in the molecular weight (MW) of the polymer, the content of $-NH_2$ groups in chitosan and O-CMCHS increases, the flexibility of the chain increases, which leads to an increase in antibacterial activity. The presence of carboxyl groups in the CMCHS structure imparts viscosity, good water-retaining, membrane-forming, flocculating, chelating and sorption properties.

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