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SYNTHESIS AND STRUCTURAL CHARACTERISTICS OF THE ASCORBAT CHITOSAN BOMBYX MORI

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Abstract: Ascorbate chitosan samples were synthesized and studied the interaction of chitosan with ascorbic acid by using elemental analysis UV, NMR - spectroscopic methods. The results of investigation were shown that the interaction of chitosan and ascorbic acid in water leads to the formation of a donor-acceptor bond between the amino group of chitosan and the enolic group of ascorbic acid.

Keywords: ascorbatechitosan, ascorbic acid, donor-acceptor bond, interaction, UV and NMR spectroscopy

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Introduction

A wide possibility of chitosan (CS) modification allows to obtain its water-soluble derivatives, among which chitosan ascorbate is of special interest, which exhibits pronounced bioactivity in the growth and development of plants, possessing antimicrobial and immune active properties. One of the economically justified methods of obtaining water-soluble chitosan derivatives is the synthesis of chitosan ascorbate (CSA), since CSA is used in agriculture [1, p. 1075; 2, p. 182].

It is known from the scientific literature that the optimal conditions and mechanisms for obtaining ascorbate chitosan are not sufficiently studied. The sources contain contradictory data on the mechanisms of interaction of chitosan with ascorbic acid and structural characteristics of this compound [1, p. 1076; 3, p. 373; 4, p. 20; 5, p. 1976].

The purpose of this work is to determine the optimal conditions for the synthesis of chitosan ascorbates, as well as to study their physico-chemical and structural characteristics using NMR, UV-spectroscopic methods.

Research methodology

The interaction of the initial components is based on the interaction of the third (C3-OH) enolar hydroxyl group of ascorbic acid (AA) with the chitosan amino group with the formation of a donor-acceptor bond [3, p. 373; 6, p. 253].

Within the framework of this work, chitosan ascorbate Bombyxmori was synthesized for the first time, structural characteristics were studied using NMR and UV spectroscopy methods.

The sample of chitosan was characterized by extent of deacetylation of 75% and size of molecular mass of M = 130000. For experiments it is used l-ascorbic acid of the brand x. h. Keeping of the general in chitosan is determined by Dumas's method [7, page 33] by burning of a hinge plate in a quartz tube at the expense of oxygen of solid oxidizers in the atmosphere of carbon dioxide. Content of the general nitrogen of chitosan is 8.1%. Ascorbate chitosan study is carried out by a suspension method at ratios of CS and AA components 2:1, 3:1; 4:1; 5:1; 6:1, 8:1; pHinitial. = 2.5, t = 50 ° C. The experiment duration is 60 min. At the same time, chitosan ascorbate formation was controlled by pH changes in the mixture of CS and AA.The formed samples were isolated by deposition in ethanol, as the obtained chitosan ascorbate is not dissolved in alcohol. The amount of AA in the samples (MAA) was determined by iodometric titration. The binding degree (BD) of chitosan (CS) to ascorbic acid (AA) was estimated by the ratio (MAA)experience / (MAA) calc.

Study results and their discussion

The highest binding degree (BD) in the range from 78.0 to 83.3% are the CSA samples obtained at a ratio of CS: AA [4:1]. Data on the BD change from molar ratio of CS: AA are given in Table 1.

Table 1

Dependence of the degree of binding of AA on the ratio of CS:AA, t=50^{0}C, τ=1 h

Mole ratio (CS: AA)	N,%	[AA], %	[$AA_{exper.}$], %	BD	Exit, %
2:1	5,25	35,3	20,8	58,0	60,0
3:1	5,65	19,1	12,0	63,0	62,6
4:1	6,22	15,0	12,5	83,3	92,4
5:1	6,40	12,4	9,3	75,0	89,5
6:1	6,63	10,6	8,9	83,9	87,0
8:1	7,49	8,15	6,5	80,4	89,2

On the basis of the obtained results, it is revealed that with the increase in the content of AA in the reaction system there are changes in nitrogen (N, %) from 5.25 to 7.49% and yield of CSA 60-92.4%. From the data obtained it is clear that with the increase in the molar ratio of ascorbic acid there is a natural increase in its content in the ascorbate chitosan. With the increase in the ratio of CS: AAcomponents it is established more than 4:1, the degree of ascorbic acid binding and the yield of final products change insignificantly. Thus, the optimal ratio of CS: AA, which has the highest degree of ascorbic acid binding to CS - 4:1. This is due to the fact that functional groups are filled with reactive AA groups.

To identify water-soluble derivatives, NMR - 1H-13C spectroscopic studies using VARIAN-400 (USA) spectrophotometer were carried out. D_2O and CD_3OD solvents were used in all experiments. It is known that chitosan is characterized by resonances in the range of 4.6-4.9, which coincide with proton H-1, which indicates glucose bonds. Further, protons N-2, N-3-N-6 are relaxed in the range of 3.7-4.0 ppm. There are also resonances in the 3.2 ppm. range. - 2.1 ppm., which correspond to amino groups and acetamide groups of this polysaccharide. In the 1HNMR - chitosan ascorbate spectrum a shift of absorption

bands in the range from 3.15 to 3.04 m.d. and a change of band intensity in the resonance range of 3.7-3.8 ppm. were detected, which indicate the interaction of chitosan amino groups with ascorbic acid (Fig. 1. and Fig. 2.).

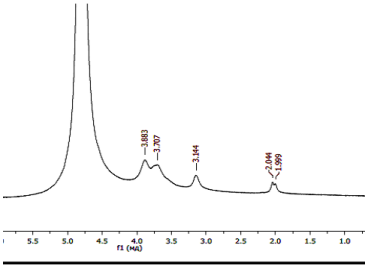


Fig.1. 1H -NMR chitosan spectrum

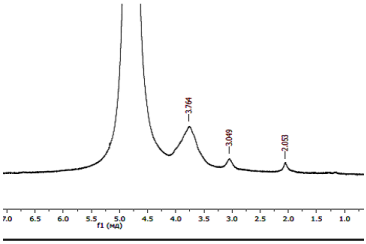


Fig. 2. 1H-NMR spectrum of ascorbate chitosan.

In the chitosan 13C NMR spectra there are resonances of C-1 atoms in the region of 102-101 ppm., located in the glucose ring of monomeric links of chitosan. There are also peaks in the range of 70-76 ppm., corresponding to C-3, C-4, C-5; in the region of 60 ppm. - due to resonances of C-6 groups. In the range of 56.3 m.d. there is a peak corresponding to P-2 chitosan amino groups. As can be seen from the experimental data, chemical shifts of the solvent at 178.53 ppm., typical for acetic acid carboxylic group, are observed in 13C chitosan NMR spectra, and the signal for acetamide group is 175 ppm., which is 25% in the chitosan sample. In ascorbate chitosan, new signals in the range from 174 to 176 ppm. are observed, which confirm the formation of donor-acceptor bonds between chitosan amino groups and carbonyl groups of ascorbic acid (Fig. 3., 4.).

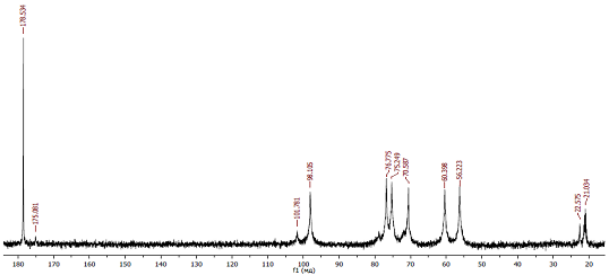
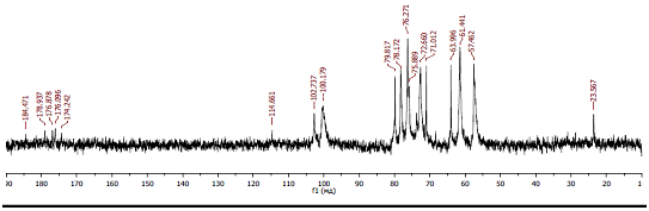


Fig. 3. 13C - NMR - chitosan spectrum

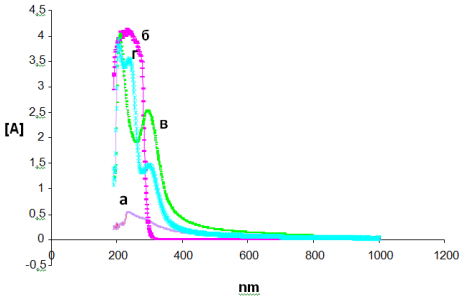
In the range from 56.2 to 57.5 ppm. peaks of chitosan amino groups are observed in the region of 61.4 and 63.9 m.d. - C-6 of ascorbic acid carbon. The peaks in the region of 71, 72,6 and 75,9, 76,3, 79 ppm., related to the carbon associated with C4, C5 and C3 atoms of chitosan piranous ring and ascorbic acid molecules, respectively, were also revealed. Thus, a shift of resonances in the range from 118 to 114 ppm. compared to ascorbic acid is found in the NMR - CSA spectra, and this shift is associated with the formation of donor-acceptor bonds [5, p. 1976-



1977].

Fig. 4.13C - NMR - spectrum of chitosan ascorbate.

UV-spectroscopic studies were carried out on the Specord 210 in the absorption range from 190 nm to 1000 nm, respectively. The results of UV-spectroscopic studies of the samples showed the presence of characteristic absorption bands at 206, 238 and 299 nm (Fig.5.). It should be noted that aqueous solutions of ascorbic acid have characteristic absorption bands in the range of 250-265 nm [6, p. 252]. When chitosan interacts with ascorbic acid, the absorption band shift is observed, because the amine group of chitosan, interacting with



the enolar group of ascorbic acid, forms donor-acceptor bonds.

Fig.5. UV spectra of chitosan (a), ascorbic acid (b),

CSA (1:1) (c) and CSA (2:1) (d).

The obtained results of UV-spectroscopic studies show that in comparison with the initial components an increase in the absorption band in the region of 200-250 nm is detected, and with an increase in the share of ascorbic acid in the composition of CSA an increase in intensity and new bands in the region of 200-220 nm are detected, which indicates the formation of a connection with the help of donor-acceptor mechanism of CS with AA .

Thus, the results of NMR and UV-spectroscopy indicate the formation of chitosan ascorbate as a result of interaction of the chitosan amine group with the ascorbic acid enolar group on the basis of the donor-acceptor mechanism.

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