**Synthesis of Polyacid Derivatives of Inulin**

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**Abstract.** Among the numerous natural polymer compounds, inulin holds a special place. Its unique monosaccharide composition and widespread use in plants make inulin a promising raw material for creating new polymer materials. For this purpose, in this study, new polymeric acids were synthesized by chemical modification of inulin. The influence of reaction parameters on the composition and chemical structure of inulin derivatives has been established. It has been proven that the introduction of acid groups into the inulin structure leads to a decrease in the molecular weight of the synthesized compounds.

**Keywords**: polysaccharides, inulin, modification, structure, molecular weight, composition, inulin derivatives.

**INTRODUCTION**

The field of application of high-molecular-weight compounds covers a wide range of polymer materials intended for use in various branches of practical activity. The results achieved to date show the possibility of obtaining polymer materials with specified physicochemical, mechanical, operational, and medical-biological properties [1-3]. In particular, research aimed at modifying the structure of macromolecules to give them new functional characteristics is of interest. In particular, methods for introducing reactive groups that provide the possibility of subsequent application are being actively studied. Among various classes of polymers, polysaccharides occupy a special place, containing special functional groups in their structure, which ultimately determine a whole range of properties of the synthesized polymer [4-6]. One such class of polymer compounds is macromolecular systems containing acidic groups in their structure.

When acid groups are chemically introduced into the polysaccharide structure, changes occur in the supramolecular structure, molecular mass, and reactivity, and the field of practical application expands [7-8]. Such chemical modification allows for the regulation of physicochemical characteristics such as solubility, swelling, and sorption characteristics of the obtained derivatives. The chemical introduction of acid groups contributes to the formation of new centers capable of electrostatic interactions with various compounds. In addition, the mechanical properties of the synthesized natural polymer change, making it possible to use it in various chemical-technological processes. For example, it is known that heparin has anticoagulant properties due to its sulfate groups, oxidized cellulose is considered a hemostatic material, pectin compounds have long been used as adsorbents for toxic substances, and carboxymethylcellulose as an effective thickener [9-10].

Based on the above, in this study, it was interesting to conduct chemical modification of inulin and obtain samples containing acidic carboxyl functional groups. Therefore, the main goal of this work was to establish the relationship between the degree of modification of inulin and the change in its physicochemical and functional properties of the synthesized derivatives.

**METHODS**

For the synthesis, inulin with a molecular weight of 5600±400 Da was used, which was dried to constant weight for 24 hours at a temperature of 50-60°C. After drying, inulin was placed in a 250 ml flask. Then, 100 ml of tetrachloromethane was added and left to stir for 3 hours at a temperature of 25°C. After thorough mechanical mixing, a mixture of nitric and orthophosphoric acid was added in various proportions. The synthesis continued for 1-12 hours at a temperature of 25-50°C. The obtained samples were separated on a special ceramic filter, washed with distilled water, and dried at a temperature of 50-60°C. The presence and quantitative content of -COOH groups were determined by titrating calcium by the acetate method.

To substantiate the structure of the obtained compounds, the spectroscopy method was used. For this purpose, the IR spectra of the synthesized compounds were recorded on a Vector-22 FTIR spectrometer. The morphological structure of the modified inulin was studied using XRD-6100 diffractometer (Shimadzu, Japan).

To assess the molecular changes occurring during the chemical modification process, the average molecular weight of the obtained inulin derivatives was determined. All molecular-mass characteristics were calculated by chromatography using Yedrogel 100-1000 columns at 25°C, equipped with a detector. The chosen physical method made it possible to assess the change in the molecular-mass distribution of macromolecules after the introduction of functional groups. A 0.25 N sodium chloride solution was used as the mobile phase at a flow rate of 0.05 ml/min. The calibration dependence was constructed using standard samples with a narrow molecular weight distribution.

**RESULTS AND DISCUSSION**

The presence of a large number of hydroxyl groups in the monomer units of inulin allows for various types of chemical or physical modifications. In this case, the initial physicochemical properties of inulin change. To establish the relationship between the properties of inulin derivatives and reaction conditions, a series of experiments were conducted under various reaction conditions. In particular, the influence of time, temperature, and the ratio of modifying reagents on the structure of the synthesized inulin derivatives was studied. The following data from the obtained results are presented in Table 1.

**TABLE 1.** Influence of modification conditions on the composition and yield of inulin derivatives

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **№** | **Ratio HNO3/H3PO4** | **Time, hour** | **T, oC** | **Content –СООН, %** | **Yield, %** |
| **1** | 1,0:0,5 | 1 | 25 | 1,6 | 91,0 |
| **2** | 1,0:1,0 | 1 | 25 | 2,5 | 85,0 |
| **3** | 1,0:1,5 | 3 | 35 | 3,8 | 82,3 |
| **4** | 2,0:1,0 | 3 | 50 | 4,1 | 79,0 |
| **5** | 2,0:1,0 | 5 | 50 | 5,0 | 76,5 |
| **6** | 2,0:1,0 | 8 | 50 | 6,4 | 74,0 |
| **7** | 2,0:1,0 | 10 | 50 | 8,0 | 70,5 |
| **8** | 2,0:1,0 | 12 | 50 | 8,2 | 68,0 |

The obtained data in Table 1 characterize the influence of the weight ratio of nitric and phosphoric acids, temperature, and reaction time on the degree of properties of inulin derivatives. From the obtained results, it can be seen that with an increase in the proportion of phosphoric acid in the mixture from 1.0:0.5 to a ratio of 1.0:1.0, the content of -COOH groups increases from 1.6 to 2.5%. This proves that the oxidation process proceeds more effectively with optimal combination of the modifying mixture. Further increase in the content of phosphoric acid and reaction time leads to an increase in the content of -COOH to 3.8%. With an increase in temperature from 25-35 to 50°C, an increase in the degree of carboxylation is observed. Thus, at an acid ratio of 2.0:1.0 and an increase in reaction time from 3 to 5 hours, the number of -COOH groups increases from 4.1 to 5.0%. Increasing the reaction duration to 8 hours also contributes to the growth of -COOH. The limiting content of acid groups (8.2%) is reached at 12 hours of reaction. However, along with this, substitution is also noted.

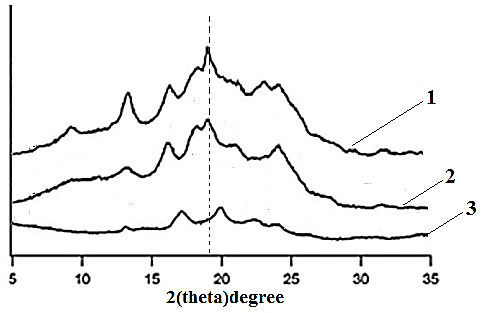
Further, we studied the molecular parameters of the synthesized inulin derivatives with different content of acid groups (see Table 2).

The data in Table 2 show the dependence of the molecular-mass characteristics of inulin derivatives on the content of -COOH groups. With an increase in the number of acid groups, a gradual decrease in both the average molecular mass Mw and the average numerical mass Mn is observed. This indicates that the modification process is accompanied by partial destruction of inulin. With a low content of -COOH groups (1.6%), the Mw and Mn values are 5280 and 2390 Da, which is close to the initial inulin values. However, already at a -COOH content of 3.8%, molecular masses decrease, reflecting the beginning of noticeable hydrolysis. With a further increase in the degree of modification to 5.0-8.2%, the destruction process becomes more pronounced (Mw decreases to 3200 Da, and Mn to 1030 Da) s.

**TABLE 2. Influence of the degree of modification on the molecular weight of inulin derivatives**

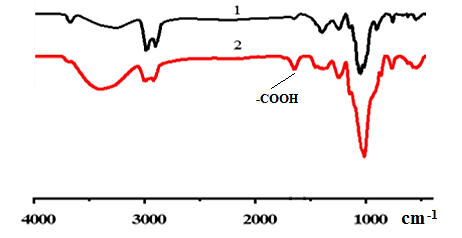
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **№** | **Content – СООН, %** | **Мw, Da** | **Мn, Da** | **Polydispersity coefficient** |
| 1 | 1,6 | 5280 | 2390 | 2,20 |
| 2 | 2,5 | 4850 | 2160 | 2,25 |
| 3 | 3,8 | 4460 | 1880 | 2,37 |
| 4 | 4,1 | 4130 | 1545 | 2,68 |
| 5 | 5,0 | 3810 | 1345 | 2,83 |
| 6 | 6,4 | 3430 | 1160 | 2,95 |
| 7 | 8,0 | 3230 | 1050 | 3,07 |
| 8 | 8,2 | 3200 | 1030 | 3,10 |

Simultaneously, the polydispersity coefficient increases, changing from 2.20 to 3.10. The increase in this indicator proves an increase in the heterogeneity of molecular mass, which is typical for biopolymer destruction. Increasing the polydispersity coefficient indicates presence in the system of macromolecules of different sizes. The most significant changes are observed at -COOH levels above 4.0%, which can be considered the limit of inulin structure stability under these conditions.



**FIGURE 1.** X-ray diffraction patterns of inulin (1) and modified inulin containing 2.5 (2) and 8.0 (3) % acid residues (-COOH).

The presented diffractogram shows samples of inulin and its synthesized derivatives in the 5°-35° region. All samples exhibit an amorphous profile with several wide diffraction peaks, indicating the absence of pronounced crystallinity. The most intense peak in all samples is observed around 19°, which is likely related to regularly ordered inulin fragments. After modification, the intensity significantly decreases and the destruction of the initial supramolecular structure of inulin occurs.



**FIGURE 2.** FTIR spectrum of inulin (1) and its derivative (2).

Figure 2 shows the IR spectra of inulin (1) and its modified derivative (2). In the initial inulin spectrum, characteristic absorption bands are observed at 3392 cm-1, corresponding to the valence vibrations of the hydroxyl groups (-OH), as well as a band at 2914 cm-1, caused by vibrations of the C-H bond. After chemical modification, a new wide band at 1695 cm-1 relating to the valence vibrations of the C=O (-COOH) bond. The appearance of this band, along with a decrease in the intensity of -OH-group absorption, confirms the introduction of acid groups into the inulin structure. The obtained spectral data correspond to the proposed method of functionalization and confirm the formation of inulin derivatives containing new acid residues.

**CONCLUSION**

Thus, in the presented work, the possibility of introducing acid groups into the monomer units of inulin through chemical modification has been proven. Optimal reaction conditions have been found that allow for controlling the structure, composition, and molecular mass of inulin derivatives. It was also shown that the degree of substitution can be adjusted by adjusting those. The main indicators of the synthesized compounds were established by titration, FTIR spectroscopy, chromatography, and X-ray structural analysis. The presence of acid groups in the structure of inulin and its physicochemical properties opens up new ways for the technical purpose of inulin. Currently, we are continuing research on developing new approaches to the synthesis of inulin derivatives that exhibit the properties of polymeric acids and determining their use.

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