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SYNTHESIS AND STRUCTURAL CHARACTERISTICS OF TOSYL FUNCTIONALIZED GALACTOMANNANS

© ***D.M. Amonova*, A.A. Boydedaev, M.Sh. Karimov, M.O. Kalonova, B.I. Muhitdinov, A.S. Turaev***

Institute of Bioorganic Chemistry named after A.S. Sadykov, Academy of Sciences of the Republic of Uzbekistan, st. Mirzo Ulugbeka, 83, Tashkent, 100125, Uzbekistan, amonovadilnoza@gmail.com

In this study, tosylation reactions of low-molecular-weight galactomannan samples (DP = 19, Mw = 9.1 kDa, Man/Gal = 1.79) were investigated in the presence of tosyl chloride. The tosylation reactions were carried out in different reaction media, including dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF) and water environments. In the reactions performed in dimethyl sulfoxide and water media, no tosyl groups were detected in the products. However, when the reaction was conducted under the same conditions in N,N-dimethylformamide medium, galactomannan tosyl derivatives with degrees of substitution (DS) ranging from 0.37 to 0.71 were obtained. Tosylated galactomannan samples with a degree of substitution (DS) of 0.65 were obtained at 5 °C by using 3.0 mol of tosylating reagent per mol of GMU in N,N-dimethylformamide, achieving a yield of 77.1%. The structures of the low-molecular-weight galactomannan tosyl derivatives were investigated using UV, FTIR, and ^{13}C NMR spectroscopy techniques. A characteristic absorption of the aromatic ring of the tosyl group was observed at 222 nm in the UV spectrum. FTIR spectroscopy confirmed the successful tosylation process through the characteristic -C=C- absorption bands of the tosyl aromatic ring in the range of 1590–1640 cm^{-1}. Additionally, the symmetric and asymmetric stretching vibrations corresponding to the C-O-S and C-S bonds in the tosylated galactomannans were observed at 812 cm^{-1} and 667 cm^{-1}, respectively. In the ^{13}C NMR spectra of the obtained galactomannan tosyl derivatives, signals corresponding to the carbon atoms of the tosyl group were observed at 20.53; 125.42; 127.99; 129.51; and 142.54 ppm for TsC5, TsC3, TsC2, TsC4, and TsC1, respectively. Moreover, signals corresponding to the tosylated ManC2 and ManC3 carbon atoms were identified at 81.07 and 81.63 ppm. The spectroscopic analysis results indicated that the tosyl groups in the galactomannan tosyl derivatives were attached to the polysaccharide backbone via the ManC2 and ManC3 carbon atoms.

Keywords: low-molecular-weight galactomannan, tosyl chloride, modification, tosylation reactions, tosyl derivatives of galactomannan.

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Introduction

Chemical modification of polysaccharides is an important tool to alter their physicochemical, biological, and functional properties. This approach is particularly significant for biopolymers derived from renewable sources, offering broad possibilities for developing environmentally safe materials [1, 2]. Among the most studied reactions in the modification process is tosylation using p-toluenesulfonyl chloride (TsCl), known for its high selectivity and efficient reaction yield [3]. The degree of tosylation largely depends on reaction conditions, solvent choice, and the excess amount of reagents used. Many polysaccharides are insoluble in water or common organic solvents [4–6]. Therefore, special solvents or solvent mixtures are required, such as DMA/LiCl, DMSO/LiCl, DMSO/TBAF, or DMF/LiCl. These mixtures are especially effective for dissolving cellulose, enabling homogeneous modification reactions [7–12]. In this study, we investigate the reaction conditions for the tosylation of galactomannan samples using TsCl.

Galactomannans are natural, water-soluble heteropolysaccharides obtained mainly from seed endosperms, consisting of a main chain of β-(1→4)-D-mannopyranose with α-(1→6)-D-galactopyranose side chains [13]. The galactose-to-mannose ratio is a key factor that determines their branching degree and physicochemical and biological properties [14, 15]. Galactomannans are widely used in the food industry as fillers, stabilizers, and emulsifiers, and in pharmaceuticals and medicine as drug delivery carriers [16, 17]. To improve their bioavailability, galactomannans can be treated physically, chemically, or enzymatically. In chemical modifications, the hydroxyl groups

* Corresponding author.

of galactomannans act as reactive centers. These groups can react with various functional agents such as acetic anhydride, halogen anhydrides, chlorides, and isocyanates [18–20]. Low-molecular-weight fractions of galactomannans exhibit higher bioavailability, biological activity, and chemical reactivity. Modification with tosyl chloride enables the introduction of functional groups, preparation of bioconjugates, and synthesis of complex biomaterials. However, the water solubility, amorphous structure, and high hydrophilicity of polysaccharides may pose challenges for tosylation reactions [21, 22]. Thus, optimization of tosylation conditions requires considering factors such as low temperature, anhydrous media, and use of acid neutralizers (e.g., pyridine, triethylamine). Galactomannan polysaccharides chemically modified with tosyl groups exhibit a high degree of chemical reactivity. This property makes them effective platforms for the formation of covalently bound conjugates with various biologically or pharmaceutically active components. The presence of functional groups in such modified polysaccharides enables further chemical interactions with different biomolecules, positioning them as highly promising materials for the development of targeted drug delivery systems.

Materials and Methods

Synthesis of Galactomannan Tosyl Derivatives. The object of the study is low molecular weight galactomannan (LMG-20 DP=19, Mw=9.12), obtained by radical depolymerization (4.5%H_2O_2, 60 °C, $Cu(CH_3COO)_2$ 0.32 mg/ml) of guar gum (DP=1158, Mw=563 kDa, Sigma-Aldrich Chemie GmbH, Germany). Low-molecular-weight galactomannan samples (PD=19) were dissolved in N,N-dimethylformamide (or dimethyl sulfoxide or distilled water), followed by the addition of a 10% solution of tosyl chloride (p-toluenesulfonyl chloride) in N,N-dimethylformamide. The molar ratio of galactomannan to tosyl chloride ranged from 1.0 : 1.0 to 1.0 : 9.0. Subsequently, triethylamine (TEA : TsCl = 1 : 3 mol : mol) was added. The tosylation reactions were conducted at 5–20 °C for 24 hours under an inert nitrogen atmosphere. After the reaction, the mixture was dialyzed and lyophilized.

Determination of Molecular Weight. Molecular weights and distributions were measured using gel permeation chromatography (GPC) on an Agilent 1260 Infinity II system (Germany) equipped with various detectors and columns (Germany), at 40 °C using aqueous 0.1 M $NaNO_3$ and 8.0 mM NaN_3 as eluents. Columns were calibrated with pullulan standards.

Structural Analysis. FTIR spectra were obtained using a Thermo Nicolet AVATAR 370 (USA) or Shimadzu IR Tracer-100 (Japan) in the range 400–4000 cm^{-1}.

^{13}C NMR spectra of the polysaccharides and their tosyl derivatives were recorded using Varian Unity Plus 400 MHz, Bruker Avance 400/600 MHz, and JNM-ECZ600R instruments at 20–50 °C in D_2O/CD_3COCD_3.

UV spectra were recorded using a Shimadzu UV-1280 (China) spectrophotometer. The tosyl group content (%) in the products was calculated using UV absorbance at 225 nm and a calibration curve:

$$C = \frac{D \cdot V}{K \cdot m} \cdot 100\% \quad (1)$$

where D – absorbance at 225 nm; V – volume of solution (mL); K – calibration constant (KTs = 0.0418); m – sample mass (mg).

The degree of substitution of the tosylated galactomannan samples was determined using the following formula.

$$DS = \frac{155x \cdot (100 - Ts\%)}{(504 - x + 155x) \cdot Ts\%} \cdot 100\%$$

Ts% – The content of tosyl groups in the tosylated galactomannan samples, determined by UV spectrophotometry.

Results and Discussion

The studies were conducted with a sample of low molecular weight galactomannan LMG-20 (MW=9.1 kDa, Man/Gal=1.79). The tosylation reactions of low molecular weight galactomannan were investigated in DMSO, DMF and water (Fig. 1).

The reactions were carried out using varying amounts of tosyl chloride (TsCl) (1.0–9.0 mol/mol of GMU) at different temperatures (5–20 °C). The tosylation reactions were conducted in an inert nitrogen atmosphere in the presence of triethylamine (TEA), taken at a molar ratio of 1 : 3 (TsCl : TEA). The changes in the molecular weight (Mw), polydispersity index (PDI), degree of substitution (DS), and overall yield of the obtained product during the reaction were investigated (Table 1).

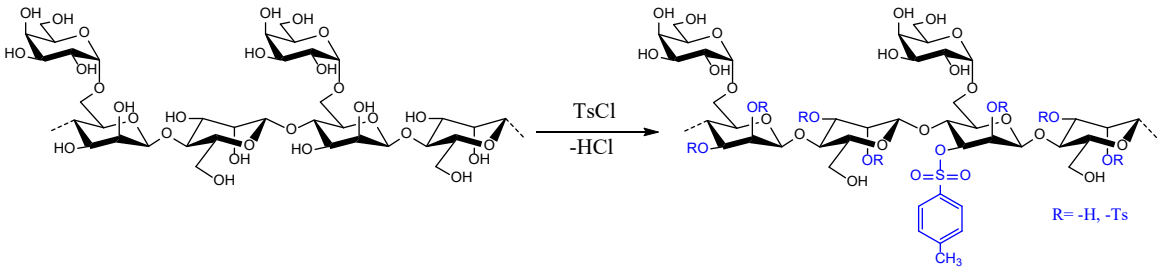

Fig. 1. Tosylation Reaction of Low-Molecular-Weight Galactomannan Samples

Table 1. Reaction Conditions and Molecular Weights of Products from Tosylation of Low Molecular Weight Galactomannan Samples (Conditions: TsCl : TEA = 1 : 3 mol/mol, 24 hours reaction time)

Sample	Medium	TsCl (mol/mol GMU)	T (°C)	Mw (kDa)	DP	DS	Yield (%)
LMG-20	–	–	–	9.12	19	–	–
LMG-Ts-DMSO	DMSO	1.0	5	–	–	–	–
LMG-Ts-W	H_2O	1.0	5	–	–	–	–
LMG-Ts-DMF1	DMF	1.0	5	9.44	19	0.37	52.11
LMG-Ts-DMF2	DMF	3.0	5	10.63	18	0.65	77.18
LMG-Ts-DMF3	DMF	6.0	5	11.08	17	0.69	78.56
LMG-Ts-DMF4	DMF	9.0	5	10.14	16	0.71	74.64
LMG-Ts-DMF5	DMF	3.0	8	10.26	13	0.52	73.75
LMG-Ts-DMF6	DMF	3.0	10	9.82	18	0.49	69.26
LMG-Ts-DMF7	DMF	3.0	15	8.43	17	0.41	51.82
LMG-Ts-DMF8	DMF	3.0	20	6.57	15	0.38	34.57

T – Temperature, Mw – Molecular Weight, DP – degree of polymerization, DS – degree of substitution

In reactions carried out in a DMSO and water medium (TsCl 1.0 mol/mol GMU, 1 hour, 5 °C), tosyl groups were not detected in the resulting products. When the reaction was carried out under the same conditions in a DMF medium, low-molecular-weight galactomannan tosyl derivatives were obtained. The difficulty in tosylating low-molecular-weight galactomannan samples in DMSO and aqueous media may be due, on one hand, to the freezing of solvents at low temperatures, which hinders the progress of the reaction, and on the other hand, to the strong hydrogen bonding between DMSO and water molecules with the galactomannan chains, which may prevent the substitution of hydroxyl groups with tosyl groups.

Under conditions where time and temperature remained unchanged (24 hours, 5 °C), reactions carried out with varying amounts of tosyl chloride (1.0–9.0 mol/mol GMU) yielded products with degrees of substitution (DS) ranging from 0.37 to 0.71. It was observed that increasing the amount of tosylating reagent up to 3.0 mol/mol GMG led to a sharp increase in the DS value of the product up to 0,65. Further increases in the amount of tosyl chloride did not result in significant changes in the DS values of the obtained products. This negative effect of excess tosylating reagent on tosylation efficiency corresponds with findings from other studies on polysaccharide tosylation [4]. Additionally, reactions conducted with varying amounts of tosyl chloride (1.0–9.0 mol/mol GMU) yielded samples with a degree of polymerization (DP) ranging from 18 to 16, and a slight decrease in DP was observed with increasing tosyl chloride concentration. Tosylated galactomannan samples were obtained with yields ranging from 34.57 to 78.56%.

The influence of temperature on the molecular size of the reaction products was examined in further studies. Reactions were carried out at temperatures ranging from 0–20 °C, while keeping the tosyl chloride amount and reaction time constant (TsCl 3.0 mol/mol GMU, 24 hours). The results showed that temperature plays a significant role in the reaction course. An increase in temperature led to a noticeable decrease in the molecular size of the obtained products. In particular, raising the temperature from 5 to 20 °C caused the DS value of the resulting product to drop from 0.65 to 0.38 and the yield to decrease from 77.18 to 34.57%. This phenomenon may be explained by the thermal instability and partial decomposition of triethylamine hydrochloride (TEA·HCl) formed during the reaction. Furthermore, the tosylation reactions of polysaccharides involving tosyl chloride are considered exothermic and increasing the temperature enhances the hydrolysis of tosyl chloride. Therefore, it is recommended to conduct these reactions at low temperatures.

The structures of low-molecular-weight galactomannan tosyl derivatives were studied using UV, IR, and ^{13}C NMR spectroscopy. The UV spectra of the low-molecular-weight galactomannan tosyl derivatives are presented in

Figure 2. The absorption band characteristic of the aromatic ring of the tosyl group was identified at 222 nm in the UV spectrum of the samples (LMG-Ts-DMF2), confirming the presence of the tosyl group in the studied samples.

The IR spectra of tosyl chloride and galactomannan tosyl derivatives are presented in Figure 3. Absorption bands characteristic of symmetric and asymmetric stretching vibrations of O-H bonds in the monosaccharide residues of the samples were observed in the 3200–3600 cm^{-1} region of the IR spectra. In the 2900 cm^{-1} region, absorption bands corresponding to the symmetric and asymmetric stretching vibrations of N-C-H bonds in the monosaccharide residues were identified. These bands correspond to the N-C6-H bonds in the hexose units (galactose and mannose) of galactomannans.

Absorptions corresponding to the symmetric and asymmetric stretching vibrations of the -C=C- bonds in the aromatic ring of the tosyl group were detected in the 1590–1640 cm^{-1} region. In the spectra of galactomannan tosyl derivatives, characteristic absorption bands of symmetric and asymmetric stretching vibrations of O=S=O bonds were observed at 1343 and 1174 cm^{-1}, respectively. Absorption bands in the 1060 cm^{-1} region correspond to the symmetric and asymmetric stretching vibrations of C-O-C bonds in the glucopyranose ring, while the bands in the 894 cm^{-1} region are characteristic of symmetric and asymmetric stretching vibrations of β-(ManC1-O-ManC4) glycosidic bonds in the polymannan chain.

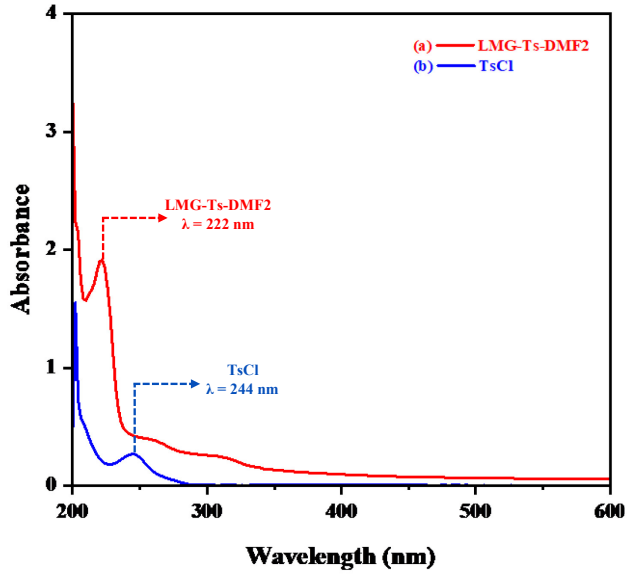

Fig 2. The UV spectra of (a) galactomannan tosyl derivatives LMG-Ts-DMF2 sample (PD = 18, DS = 0.65) and (b) tosyl chloride

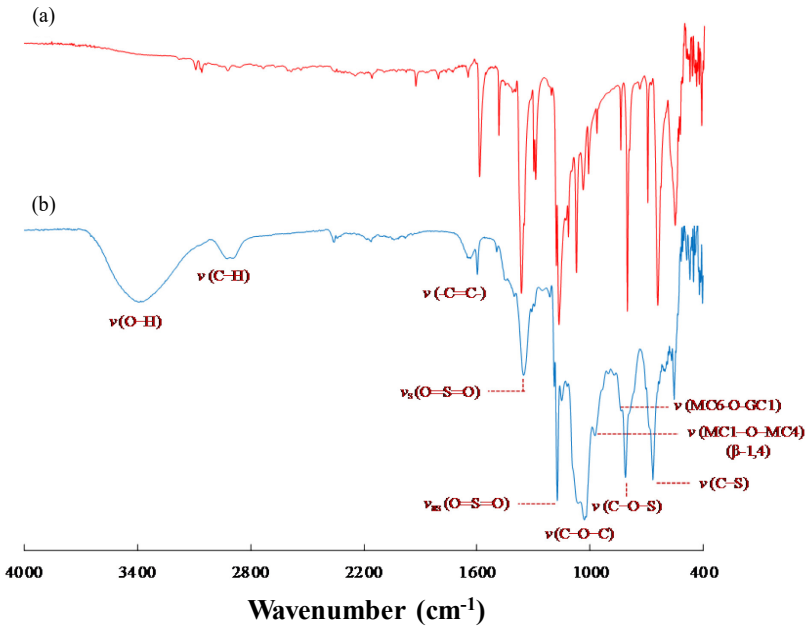

Fig 3. The IR spectra of (a) tosyl chloride and (b) LMG-Ts-DMF2 (PD = 18, DS = 0.65) samples

Absorptions in the 870 cm^{-1} region were attributed to the Man(C6)-O-Gal(C1) glycosidic bonds between mannose and galactose residues [23]. Additionally, absorption bands corresponding to the symmetric and asymmetric stretching vibrations of C-O-S and C-S bonds in the galactomannan tosyl derivatives were observed at 812 cm^{-1} and 667 cm^{-1}, respectively. In the IR spectra of the synthesized galactomannan tosyl derivatives, new absorption bands characteristic of the tosyl group were detected: -C=C- (aromatic ring, 1590–1640 cm^{-1}), O=S=O (symmetric 1343 cm^{-1}, asymmetric 1174 cm^{-1}), C-O-S (812 cm^{-1}), and C-S (667 cm^{-1}). These findings confirm that the obtained samples structurally correspond to galactomannan tosyl derivatives.

The ^{13}C NMR spectra of galactomannan tosyl derivatives are presented in Figure 4. In the studies, signals characteristic of the methyl group carbon atoms (TsC5) of the tosyl group in galactomannan tosyl derivatives were observed at 20.53 ppm. Signals at 60.57; 61.30 and 66.47 ppm corresponded to the ManC6, GalC6, and galactosylated ManC6' carbon atoms, respectively. By analyzing the signal integrals corresponding to ManC6 (60.57 ppm) and ManC6' (66.47 ppm) carbon atoms in the tosyl derivatives, it was determined that the Man/Gal ratio in the polysaccharide chain did not change during the tosylation reaction, indicating that no degalactosylation occurred.

Signals corresponding to GalC2, GalC4, and GalC3 carbon atoms were observed at 68.47; 69.34 and 69.92 ppm, respectively. In the regions of 75.07; 73.34 and 71.36 ppm, signals were attributed to ManC2, GalC5, and ManC3 carbon atoms, respectively. Signals corresponding to galactosylated ManC5' and non-galactosylated ManC5 carbon atoms were observed at 77.03 ppm and 77.55 ppm, respectively.

Characteristic signals for the ManC4 carbon atoms were identified in the range of 78.90–79.70 ppm in the spectrum. Signals specific to the tosylated ManC2 ((Ts)MC2) and ManC3 ((Ts)MC3) carbon atoms were observed at 81.07 and 81.63 ppm, respectively. This indicates that in the obtained galactomannan tosyl derivatives, the tosyl groups are attached to the polysaccharide chain through the C2 and C3 carbon atoms of mannose residues. Signals characteristic of GalC1, galactosylated ManC1', and non-galactosylated ManC1 carbon atoms were observed at 100.15; 102.51 and 102.72 ppm, respectively. Analysis of these signals also confirmed that the Man/Gal ratio remained unchanged in the obtained tosylated derivatives.

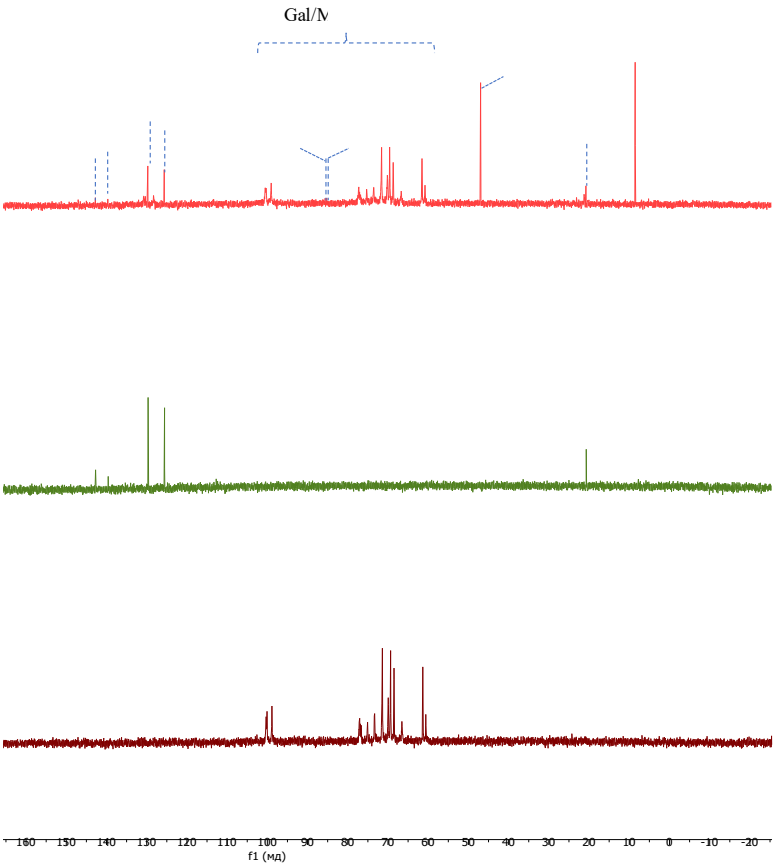

Fig 4. The ^{13}C NMR spectrum of (a) galactomannan tosyl derivatives LMG-Ts-DMF2 (DP = 18, DS = 0.65), (b) tosyl chloride and (c) low molecular weight galactomannan LMG-20 (MW=9.1 kDa, Man/Gal=1.79)

Additionally, the spectra showed signals characteristic of the tosyl group carbon atoms TsC3, TsC2, TsC4, and TsC1 at 125.42; 127.99; 129.51 and 142.54 ppm, respectively.

In the ^{13}C NMR spectra of the obtained galactomannan tosyl derivatives, signals at 20.53; 125.42; 127.99; 129.51 and 142.54 ppm corresponded to the TsC5, TsC3, TsC2, TsC4 and TsC1 carbon atoms of the tosyl groups, respectively. Signals at 81.07 and 81.63 ppm corresponded to the tosylated ManC2 and ManC3 carbon atoms. The spectroscopic analysis confirms that in the galactomannan tosyl derivatives, the tosyl groups are linked to the polysaccharide chain through the ManC2 and ManC3 carbon atoms.

Conclusion

In this study, low-molecular-weight galactomannan samples were chemically modified in the presence of tosyl chloride. The reactions were carried out in dimethyl sulfoxide (DMSO), water, and dimethylformamide (DMF) media using various amounts of tosyl chloride (1.0–9.0 mol/mol GMU) and at different temperatures (5–20 °C). As a result of the research, the optimal reaction conditions were determined to be 3.0 mol of tosyl chloride at 5 °C in DMF medium. Spectroscopic studies showed that the tosyl groups were linked to the polysaccharide chain via ether bonds. The galactomannan samples modified with tosyl groups exhibited high reactivity and can be used as platforms for the synthesis of further covalent conjugates. Such modified polysaccharides are considered promising candidates for loading biologically active substances and developing drug delivery systems.

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Conflict of Interest
The authors of this work declare that they have no conflicts of interest.

References

1. Li Z. W. et al. *Polymers*, 2022, vol. 14, no. 19, 4161. https://doi.org/10.3390/polym14194161.
2. Singh S. et al. *Current Materials Science: Formerly: Recent Patents on Materials Science*, 2023, vol. 16, no. 3, pp. 316–351. https://doi.org/10.2174/2666145416666221208150926.
3. Devadoss T. *Journal of Molecular Structure*, 2023, vol. 1289, 135850. https://doi.org/10.1016/j.molstruc.2023.135850.
4. Gericke M. et al. *Carbohydrate Polymers*, 2015, vol. 127, pp. 236–245. https://doi.org/10.1016/j.carbpol.2015.03.025.
5. Namnouad P. et al. *New Journal of Chemistry*, 2023, vol. 47, no. 30, pp. 14134–14141. https://doi.org/10.1039/D3NJ00830D.
6. Koschella A. et al. *Molecules*, 2020, vol. 25, no. 22, 5382. https://doi.org/10.3390/molecules25225382.
7. Potthast A. et al. *Cellulose*, 2002, vol. 9, pp. 41–53. https://doi.org/10.1023/A:1015811712657.
8. Zhang C. et al. *The Journal of Physical Chemistry B*, 2014, vol. 118, no. 31, pp. 9507–9514. https://doi.org/10.1021/jp506013c.
9. Ostlund A. et al. *Biomacromolecules*, 2009, vol. 10, no. 9, pp. 2401–2407. https://doi.org/10.1021/bm900667q.
10. Liebert T. *American Chemical Society*, 2010, pp. 3–54. https://doi.org/10.1021/bk-2010-1033.ch001.
11. Muhitdinov B. et al. *Carbohydrate Polymers*, 2017, vol. 173, pp. 631–637. https://doi.org/10.1016/j.carbpol.2017.06.033.
12. Muhitdinov B., Heinze T., Turaev A., Koschella A., Normakhamatov N. *European Polymer Journal*, 2019, vol. 119, pp. 181–188. https://doi.org/10.1016/j.eurpolymj.2019.07.030.
13. Heinze T., Koschella A. *Polímeros*, 2005, vol. 15(2), pp. 84–90. https://doi.org/10.1590/S0104-14282005000200005.
14. Amonova D.M. et al. *Khimiya rastitel'nogo syr'ya*, 2022, no. 2, pp. 51–60. https://doi.org/10.14258/jcprm.2022029551. (in Russ.).
15. Azimova L.B. et al. *Russ. J. Bioorganic Chem*., 2020, vol. 46, no. 7, 13. https://doi.org/10.1134/S106816202007002X.
16. Nunes C.A. et al. *Food research international*, 2015, vol. 75, pp. 270–280. https://doi.org/10.1016/j.foodres.2015.06.011.

17. Flores García Y. et al. *Foods*, 2025, vol. 14(9), 1587. https://doi.org/10.3390/foods14091587.
18. Tahmouzi S. et al. *Food science & nutrition*, 2023, vol. 11(9), pp. 4869–4897. https://doi.org/10.1002/fsn3.3383.
19. Gómez-Rodríguez G.N. et al. *Biotecnia*, 2023, vol. 25(2), pp. 126–135. https://doi.org/10.18633/biotecnia.v25i2.1883.
20. Shenoy M.A. et al. *Journal of Applied Polymer Science*, 2010, vol. 117(1), pp. 148–154. https://doi.org/10.1002/app.31872.
21. Wang J. et al. *Carbohydrate polymers*, 2014, vol. 113, pp. 325–335. https://doi.org/10.1016/j.carbpol.2014.07.028.
22. Cumpstey I. *International scholarly research notices*, 2013, vol. 1, 417672. https://doi.org/10.1155/2013/417672.
23. Heinze T. et al. *Macromolecular Bioscience*, 2016, vol. 16(1), pp. 10–42. https://doi.org/10.1002/mabi.201500184.

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Information about authors

Amonova Dilnoza Muxtarovna – PhD, Senior Researcher, amonovadilnoza@gmail.com

Boydedaev Azizbek Anvarjon ugli – PhD, Junior Researcher, azizbek.boydedaev@gmail.com

Karimov Mukhiddin Shokirjon ugli – Doctoral Student, mkarimov1996@mail.ru

Kalonova Mukhabbat Oqilkhan kizi – Junior Researcher, abbashanovamuhabbathon@gmail.com

Muhitdinov Bahtiyor Ikromovich – DSc, Leading Researcher, muhitdinov.bahtiyor@gmail.com

Turaev Abbaskhan Sabirkhanovich – Doctor of Chemical Sciences, Academician, Director, abbaskhan@mail.ru