Baku State University Journal of Chemistry and Material Sciences, 2024, v. 1 (4), p.1-5

journal homepage: http://bsuj.bsu.edu.az/en
https://doi.org/10.30546/209501.201.2024.1.04.057

OBTAINING ALKENE DERIVATIVES OF CHITIN

Gunay Mammadova, Zarnishan Bayramova, Eldar Akhmedov
Baku State University, Baku, Azerbaijan

Received: 13 november 2024
Accepted: 04 december 2024
Published: 24 december 2024

This article presents the results of obtaining an alkene derivative of chitin from a chitin biopolymer. Chitin from a crab shell was used for the reaction in the work. The reaction was carried out in the presence of EDC, NHS, and DMAP. Acrylic acid was first used to introduce a double bond into the chitin molecule. It was found that at 20-40°C the reaction does not occur, and at 50°C the reaction follows the Michael reaction path. Then, using the same method, a reaction was carried out with but-3-enoic acid. Using a less electrophilic acid, the expected compound was obtained

The article concludes that to obtain an alkene derivative of chitin, it is necessary to use a less electrophilically activated acid to ensure the reaction proceeds in the desired direction.

The structure of the compound was identified using nuclear magnetic resonance.

Keywords: Chitin, derivatives of chitin, Michael reaction, acrylic acid, but-3-enoic acid

INTRODUCTION

Recently, the practical application of natural polysaccharides has been steadily growing. One of the most common polysaccharides in nature is chitin (second place among biopolymers after cellulose). Billions of tons of chitin are formed and decomposed in living organisms every year [10]. This biopolymer is the main component of the exoskeleton (cuticle) of arthropods and a number of other invertebrates. It is contained in the shells of crustaceans and the cell walls of fungi, a number of bacteria and blue-green algae. Chitin not only has unique physical and chemical properties, but also opens up amazing prospects for us in the field of biomedical and environmental research [1-3, 5-7] It is used in various fields, from medicine to the food industry, and is the main component of invertebrate exoskeletons and fungal cell walls. Chitin is an insoluble polysaccharide composed of N-acetylglucosamine. Its unique structure and properties make chitin and its derivatives important materials for the development of new technologies. For many years, it has attracted the attention of scientists and researchers due to its unique chemical properties and application possibilities [11-16]. Chitin has high strength and resistance to microorganisms, which makes it an ideal material for protection.

Recently, chitin has been actively explored for use in biomaterials and bioplastics. Chitin derivatives show significantly higher reactivity and better chemical versatility. Chitin derivatives show their potential as natural polymers with low toxicity and high biocompatibility. In recent years, the study of chitin and its derivatives has attracted increasing attention in the field of organic chemistry. One of the most promising areas in organic chemistry is the creation of alkene derivatives of chitin (electrophilic olefins), from which cationic derivatives of chitin can be obtained in the future. Cationic derivatives of chitin are known for their significant antibacterial activity and are an alternative to traditional antibiotics [14,16]. These derivatives expand the functional capabilities of chitin and allow the development of new materials with improved characteristics. This opens up new

E-mail address: gunaymammadova0987@gmail.com

horizons for the use of these compounds in various industries, including medicine, pharmaceuticals, and materials science.

In this article we will consider in detail the processes of obtaining chitin derivatives and reaction conditions, as well as the identification of the resulting compound using NMR spectroscopy methods.

EXPERIMENTAL

The reaction was carried out in a sealed vessel loaded with a magnetic stirrer in the presence of EDC, NHS, DMAP, DMAA and lithium chloride

Below are the weight values of the reagents taken:

- chitin with an acetylation degree of about 100% and an average viscosity molecular weight (MW) of 3.4 × 104, 7.2 × 104, 18.8 × 104 Da - 0.5 g
- lithium chloride - 1.4 g
- DMAA (dimethylacetamide) - 30 ml
- NHS (N-hydroxysuccinimide) - 0.7 equiv
- EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) – 1 equiv
- DMAP (N,N,-dimethylaminopyridine) - 0.1 equiv
- Acrylic acid 0.2 equiv
- but-3-enoic acid 0.2 equiv

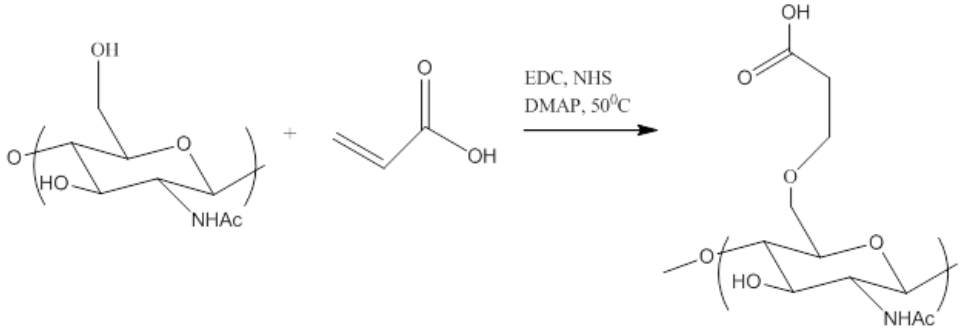
1H NMR spectra were recorded on a Bruker Avance II spectrometer operating at 400 MHz in 1% CF3CO2H in D2O with proton signal suppression by DOH.

RESULTS AND DISCUSSION

For our studies, we used chitin from crab shells. As is known, chitin is a solid translucent substance that is insoluble in water and polar organic solvents [2,15]. It dissolves in a solution of lithium chloride in dimethylacetamide, in ionic liquids, and in concentrated solutions of some salts. To introduce a double bond into the chitin macromolecule and form an ester bond using the classical carbodiimide method, we used acrylic acid. For this, chitin was treated with acrylic acid in the presence of EDC, NHS, and DMAP. Chitin and lithium chloride were placed in a test tube loaded with a magnetic stirrer. The test tube was hermetically sealed. Then dry DMAA was added to the test tube. The mixture was purged with dry nitrogen. The mixture was stirred for 3 h at 20^0C. A pale yellow transparent viscous solution of chitin was obtained. The tube was opened using a decapper. In the next step, NHS, EDC, DMAP and acrylic acid were added to the chitin solution.

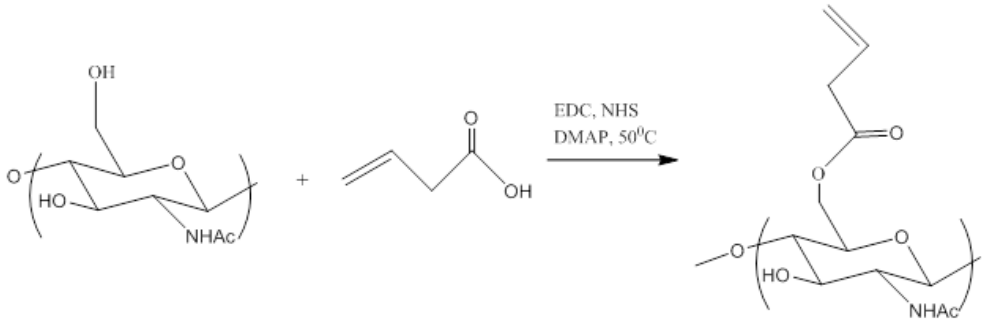
We hoped to achieve a chemical reaction of the carboxyl group of acrylic acid with the hydroxyl group of chitin at position6 [4]. However, it was found that in the temperature range of 20–40^0C such interaction does not occur. The temperature was then increased to 500C and the reaction mixture was stirred for 3 hours.

However, increasing the temperature resulted in a Michael reaction [14] and the formation of carboxyethyl derivatives of chitin, rather than the interaction of the carboxyl group with the hydroxyl functionality (Scheme 1)



Scheme 1.

Apparently, the high electrophilicity of the double bond in the acrylic acid molecule was the reason for the process to proceed along the Michael reaction pathway [23]. For this reason, we decided to use an alkenoic acid containing a significantly less electrophilically activated C=C double bond and took but-3-enoic acid as a reagent. The reaction was carried out using the same method in the presence of EDC, NHS and DMAP at a temperature of 500C. The interaction of chitin with but-3-enoic acid leads to the formation of alkene derivatives of chitin containing a double bond (Scheme 2). The resulting polymers were precipitated with acetone. They were washed with acetone and ethanol and dried under vacuum.



Scheme 2.

The reaction was repeated with chitin of different molecular weights and it was found that the reaction proceeds almost identically for chitin of high, medium and low molecular weights. By changing the molar ratio of but-3-enoic acid/chitin, it is easy to regulate the degree of substitution of the resulting chitin derivatives.

Thus, we synthesized chitin derivatives of different (low, medium and high) molecular weights with different (low, moderate and high) degrees of substitution.

The obtained compounds were characterized by physical methods, which confirmed the proposed structure. The most informative method was 1H NMR spectroscopy, which confirmed the proposed formula of the polymers.

On the figure 1 shows the 1H NMR spectrum with signal assignment

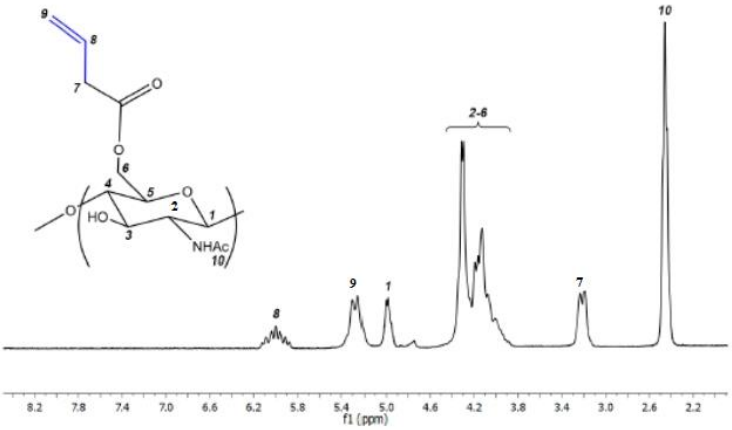


Fig. 1. 1H NMR spectrum of obtained compound

As can be seen from the spectrum, the signal of the acetyl group is observed as a doublet at 2.45 ppm. The signal from the methylene group (H7) is observed as a doublet at 3.2 ppm. The signal from the carbohydrate part of chitin (2-6) isobserved as a multiplet at 3.9-4.4 ppm. The signal from the methyl group of carbohydrate 1 is observed as a multiplet at 4.9-5.1 ppm. The signal from hydrogen at C9 of the H2C=CH- group is observed as a doublet at5.2-5.4 ppm. The signal from hydrogen at C8 of the H2C=CH- group is observed as a multiplet at 5.8-6.2 ppm.

CONCLUSION

In this article, we have examined in detail the process of obtaining chitin derivatives, which is an important component not only in biomedicine, but also in various industries such as the food industry and ecology.

The use of chitin and its derivatives opens up new horizons for the development of innovative materials and technologies that contribute to sustainable development.

Promising research directions in this area could lead to more efficient and environmentally friendly products. It is important to continue to study the properties of these compounds and their potential applications to make the most of the opportunities that chitin offers.

Thus, chitin derivatives have great potential and can play a key role in the future of science and industry. We hope that the ideas and results presented in the article will inspire further research and practical application of chitin derivatives.

Thus, we can come to the following conclusions:

The an alkene derivative of chitin was synthesized, that is, a double bond was introduced into the chitin macromolecule by chemical interaction of the carboxyl group of the acid with the hydroxyl group of chitin in position 6. It was found that the reaction proceeds at temperatures above 40° and when using an alkenoic acid containing a less electrophilically activated C=C double bond.

By changing the acid/chitin molar ratio, chitin derivatives with different degrees of substitution were obtained.

The structure and spectrum of the synthesized compound are proposed.

REFERENCES

[1] Egorov, A.R.; Khubiev, O.; V.V. Rubanik, Jr.; Lobanov, N.N.; Savilov, S.V.; Kirichuk, A.A.; Kritchenkov,I.S; Tskhovrebov, A.G. and Kritchenkov, A.S. The first selenium containing chitin and chitosan derivatives: combined synthetic, catalytic and biological studies, Int. J. Biol. Macromol. 209 (2022) 2175–2187, https://doi.org/10.1016/j.ijbiomac.2022.04.199.

[2] Kertmen, A.; Ehrlich, H.; Patentology of chitinous biomaterials. Part I: Chitin. Carbohydrate Polymers 2022, 282, 11910. https://doi.org/10.1016/j.carbpol.2022.119102

[3] Ding, F.Y.; Shi, X.W.; Li, X.X.; Cai, J.; Duan, B.; and Du, Y.M. Homogeneous synthesis and characterization of quaternized chitin in NaOH/urea aqueous solution. Carbohydr. Polym. 2012, 87, 422–426. https://doi.org/10.1016/j.carbpol.2011.07.069

[4] Gürer, F.; Kargl, R.; Bracˇicˇ, M.; Makuc, D.; Thonhofer, M.; Plavec, J.; Mohan, T.; and Kleinschek, K.S. Water-based carbodiimide mediated synthesis of polysaccharide-amino acid conjugates: Deprotection, charge and structural analysis. Carbohydr. Polym. 2021, 267, 118226 https://doi.org/10.1016/j.carbpol.2021.118226

[5] Zhuang, Li,S.; Antibacterial activity of chitosan and its derivatives and their interaction mechanism with bacteria: current state and perspectives, Eur. Polym. J. 138 (2020) 109984,https://doi.org/10.1016/j.eurpolymj.2020.109984

[6] Kou, S.G.; Peters, L.; and Mucalo, M. Chitosan: A review of molecular structure, bioactivities and interactions with the human body and micro-organisms. Carbohydr. Polym. 2022, 282, 119132 https://doi.org/10.1016/j.carbpol.2022.119132

[7] Kritchenkov, A.S.; Egorov, A.R.; Abramovich, R.A.; Kurliuk, A.V.; Shakola, T.V.; Kultyshkina, E.K.; Ballesteros, Meza, M.J.; Pavlova, A.V.; Suchkova, E.P.; Le Nhat Thuy, G.; et al. Water-soluble triazole chitin derivative and its based nanoparticles: Synthesis, characterization, catalytic and antibacterial properties. Carbohydr. Polym. 2021, 257, 117593. https://doi.org/10.1016/j.carbpol.2020.117593

[8] Kritchenkov, A.S.; and Skorik, Y.A. Click reactions in chitosan chemistry. Russ. Chem. Bull. 2017, 66, 769–781. https://doi.org/10.1007/s11172-017-1809-5

[9] Liu, Y.; Li, B.; Xu, C.; Shi, Z.; Liu, L.; Fan, Y.; and Yu, J. Efficient preparation of fluorescent nanomaterials derived from chitin via a modification-first strategy assisted by click chemistry. Green Chem. 2024, 26, 7176–7187 https://doi.org/10.1016/j.carbpol.2022.120142

[10] Wang, M.; Yin, G.-Z.; Yang, Y.; Fu, W.; Díaz Palencia, J.L.; Zhao, J.; N. Wang, Y. Jiang, D. and Wang Y., Bio-based flame retardants to polymers: a review, Adv. Ind. Eng. Polym. Res. 6 (2) (2023) 132–155, https://doi.org/10.1016/j.aiepr.2022.07.003.

[11] Peng, N.; Ai, Z.; Fang, Z.;Wang, Y.; Xia, Z.; Zhong, Z.; Fan, X.; and Ye, Q. Homogeneous synthesis of quaternized chitin in NaOH/ureaaqueous solution as a potential gene vector. Carbohydr. Polym. 2016, 150, 180–186 https://doi.org/10.1016/j.carbpol.2016.04.110

[12] Re, N. Pellegrini, A. Proteggente, A. Pannala, M. Yang, C. and Rice-Evans, Antioxidant activity applying an improved ABTS radical cation decolorization assay, Free Radic. Biol. Med. 26 (9–10) (1999) 1231–1237, https://doi.org/10.1016/s0891-5849(98)00315-3.

[13] Kou, S.; Peters, L.; and Mucalo, M. Chitosan: a review of molecular structure, bioactivities and interactions with the human body and micro-organisms, Carbohydr. Polym. 282 (2022) 119132, https://doi.org/10.1016/j. carbpol.2022.119132.

[14] Sashiwa, H.; Yamamori, N.; Ichinose, Y.; Sunamoto, J.; and Aiba, S.I. Michael reaction of chitosan with various acryl reagents in water. Biomacromolecules 2003, 4, 1250–1254 https://doi.org/10.1021/bm030022o

[15] Varlamov, V.P.; Il'ina, A.V.; Shagdarova, B.T.; Lunkov, A.P.; and Mysyakina, I.S. Chitin/Chitosan and Its Derivatives: Fundamental Problems and Practical Approaches. Biochemistry 2020, 85, 154–176. https://doi.org/10.1134/S0006297920140084

[16] Mohammadi, Z.; Eini, M.; Rastegari, A.; and Tehrani, M.R. Chitosan as a machine for biomolecule delivery: a review, Carbohydr. Polym. 256 (2021) 117414, https:// doi.org/10.1016/j.carbpol.2020.117414.