

Hydrosilylation Reactions of Bioorganic Products

Darejan Iremashvili^{*}, Lali Tabatadze^{*}, Ketevan Ebraliidze^{**},
Nana Pirtskheliani^{*}, Irine Botchorishvili^{*}, Natia Shengelia^{*}

^{*} Faculty of Natural Sciences, Mathematics, Technologies and Pharmacy, Sokhumi State University, Tbilisi, Georgia

^{**} P. Melikishvili Institute of Physical and Organic Chemistry, Ivane Javakhishvili Tbilisi State University, Georgia

(Presented by Academy Member Koba Amirkhanashvili)

Abstract. The use of hydrosilylation products of allyl carbohydrate derivatives has become extremely relevant in food pharmaceutical and industrial technologies. Among the various methods available for creating C–Si bonds, catalytic hydrosilylations allow the direct addition of silanes (Si–H) to olefins. These reactions are used not only at the laboratory scale but also in the chemical industry for the production of functional organosilicon compounds. Hydrosilylation reactions, which allow the addition of Si–H to C=C/C≡C bonds, are typically catalyzed by homogeneous noble metal catalysts (Pt, Rh, Ir, and Ru). Organosilicon compounds are characterized by their stable and inert carbon-silicon bonds. The paper discusses the synthesis of a modified linear polysiloxane (functionalized and acetyl-protected allyl glucoside) by a simple high yield method using a platinum catalyst. The chemical structure of the carbohydrate-modified poly [methyl-3-(*tetraacetyl glucoside*) propyl]siloxane was studied using infrared (FTIR) spectroscopy. The spectrum does not show characteristic peaks of Si–H in the region of 2100–2300 cm^{−1} and characteristic peaks of the –CH=CH₂ bond in the region of 3095 cm^{−1}, but absorption peaks appear in the region of the 1010 cm^{−1} characteristic for the group of (Si–C). © 2025 Bull. Georg. Natl. Acad. Sci.

Keywords: allyl derivatives of carbohydrates, poly (methylhydro) siloxane, allylation, hydrosilylation

Introduction

Allyl glycoside products of mono-, di-, and polysaccharides of plant origin are intermediate compounds in organic synthesis [1–4]. Many natural saccharides undergo chemical modification or build blocks in hybrid substances of biological or synthetic origin. The use of carbohydrate macromolecules is important for improving the quality and quantity of food products, agricultural crops, as well as in pharmaceutical and environmental technologies. The chemical composition of cellulose-containing renewable plant raw materials and their practically inexhaustible resources, unique properties (high mechanical strength, water insolubility, chemical inertness, thermal plasticity, biodegradability) are of constant interest to researchers, which in the future allows industrial polymeric materials to be processed into materials with biodegradable properties [5].

Hydrosilylation is used to obtain and modify both low-molecular and high-molecular compounds. The reactions of allyl derivatives of hydrosilylation

rocarbons with synthetic polymers allow, depending on the conditions, to obtain a wide range of different substances. Hydrosilylation reactions of unsaturated carbohydrate products are of great practical importance. They are the most effective and convenient methods for obtaining linear polysiloxanes modified with carbohydrates. Modified polysiloxanes with a low degree of substitution are soluble in non-polar media. As the carbohydrate content increases, the polymers become increasingly soluble in polar solvents (methanol, isopropanol). The outcome of hydrosilylation of carbohydrate products depends on the structure of unsaturated compounds and silanes, as well as the nature of the catalyst and the reaction conditions [6-8].

The paper discusses the stepwise hydrosilylation reaction of allyl-tetra-O-acetyl- β -D-glucopyranoside with poly(*methylhydro*)siloxane using dichloro(*dicyclo pentadienyl*)platinum (II) as a catalyst.

Experimental Materials

The chemical structure was studied using a SHIMADZU IRSpirit-x Fourier transform infrared spectrometer (FTIR). All allylation and hydrosilylation reactions were carried out in the azot region. All reagents for the synthesis (1,2,3,4,6-Penta-O-acetyl- β -D-glucopyranose, $C_2H_4Cl_2$, allyl alcohol, ethyl acetate, dichloro(*dicyclo pentadienyl*)platinum (II), poly(*methylhydro*)siloxane and $BF_3[(C_2H_5)_2]$), purchased from Aldrich, were used as received or distilled prior to use. Solvents (toluene, methanol) were purified and evaporated under the appropriate temperature and pressure conditions.

Synthesis of allyl-2,3,4,6-Tetra-O-acetyl- β -D-glucopyranose (2) [9]. To a solution of 2.34 g (0.006 mol) of β -pentaacetate and 2 ml (0.03 mol) of allyl alcohol in 40 ml (0.4 mol) of CH_2Cl_2 add 7.4 ml (0.05 mol) of $BF_3 \cdot Et_2O$, stir for 5 h at $0^\circ C$. Dilute with ethyl acetate and wash with $NaHCO_3$.

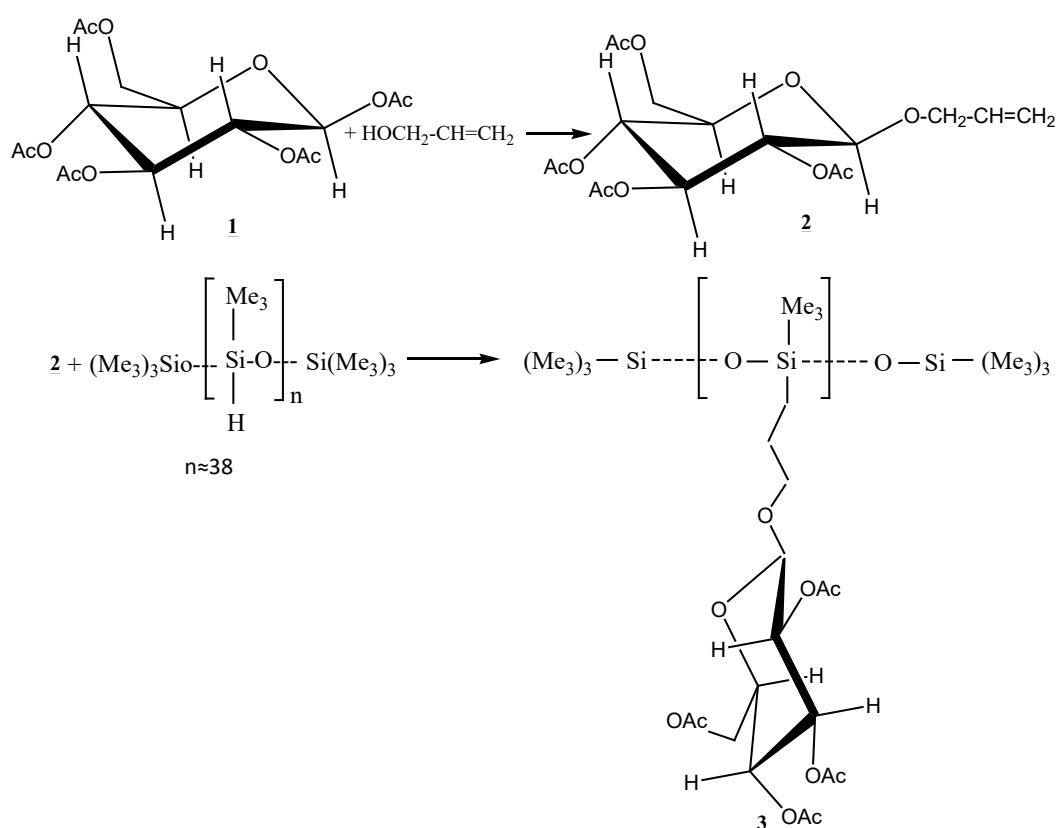
Leave the filtrate overnight over Na_2SO_4 . Concentrate the solution under vacuum. A colored syrup is obtained. The product crystallizes from a mixture of ethanol and hexane. Yield 1.4 g (60.3%). T_{melt} $87^\circ C$.

Synthesis of poly[methyl-3-(*tetraacetyl glucosidyl*)propyl]siloxane (3). 1.12 g (0.0004 mol) of poly(methylhydro)siloxane was placed in a reaction flask and 1.4 g (0.003 mol) of allyl-2,3,4,6-tetra-O-acetyl- β -D-glucopyranose (20% molar excess) was added. The reaction was carried out under nitrogen atmosphere. 1-2 drops of dichloro(*dicyclo pentadienyl*)platinum(II) catalyst were added to 15 ml of freshly distilled toluene. The reaction solution was heated to $70^\circ C$ with constant stirring. After 60 minutes, 5 ml of methanol was added dropwise with vigorous stirring. The precipitated polymer was dissolved in toluene and freeze-dried. 2.1 g (106.0%) of poly[methyl-3-(*tetraacetyl glucosidyl*)propyl]siloxane are obtained (Scheme).

Results and Discussion

Carbohydrates are easily esterified to form esters (acetates, benzoates). Esters are mainly used as intermediates, for temporary protection of hydroxyl groups, and for identification of individual sugars. In the first step of the reaction, the monosaccharide was protected by acetyl groups, so sodium acetate had to be used as a catalyst to obtain the β -acetylated product. Allyl-2,3,4,6-tetra-O-acetyl- β -D-glucopyranose (2) was synthesized by the action of dichloroethane and allyl alcohol on the β -acetylated product (1) in the presence of $BF_3[(C_2H_5)_2]$ catalyst under continuous stirring. The reaction progress was monitored by thin-layer chromatography (toluene/acetone 4/1). The reducing carbohydrate was converted into allyl glycoside containing acetyl protecting groups, which allowed the obtained product (2) to be used in the hydrosilylation reaction.

In organic chemistry, allylation of carbohydrates is used for stereospecific glycosylation as a



Scheme. Synthesis of poly[methyl-3-(tetraacetyl glucosidyl)propyl]siloxane.

protecting group method in the preparation of synthetic oligosaccharide products [8]. The allyl group is easily cleaved under mild conditions either by oxidative cleavage with selenium dioxide or by isomerization and subsequent acid hydrolysis. The nature of the double bond makes the allyl group suitable for hydrosilylation reactions. No side reactions occurred during the hydrosilylation process, as the acetyl protecting groups are inert under the conditions of the hydrosilylation reaction.

FTIR (ν , cm^{-1}): the spectrum does not show characteristic absorption peaks of Si-H in the region of $2100\text{-}2300\text{ cm}^{-1}$; characteristic absorption peaks of the -CH=CH_2 bond in the region of 3095 cm^{-1} are also not visible, but absorption peaks appear in the region of 2800 cm^{-1} , which is typical for the $\nu(\text{CH}_2)$ group; $2900\text{-}2920\text{ cm}^{-1}$ $\nu(\text{CH}_3)$; 1370 cm^{-1} $\delta(\text{CH}_2)$; 1730 cm^{-1} (C=O); $1260\text{-}1300\text{ cm}^{-1}$ (C-O-C); 1010 cm^{-1} (Si-C); $756, 641$ [$\text{Si}(\text{Me}_3)$].

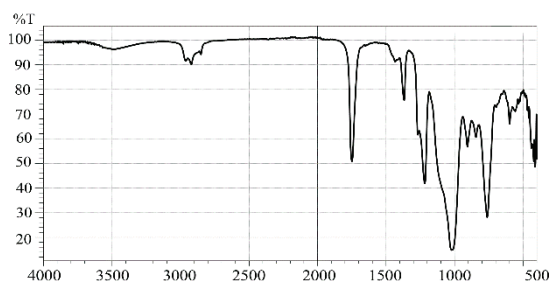


Fig. FTIR spectrum poly [methyl-3-(tetraacetyl glucosidyl)propyl]siloxane.

Conclusion

Carbohydrates are important representatives of natural macromolecules and have various functions, which are determined by the structural arrangement and the interaction of hydroxyl groups (inter- and intramolecular hydrogen bonds). The unique properties of poly(methylhydro)siloxane (high oxygen conductivity, low toxicity, bioactivity, low moisture and strong hydrophobicity) are advantageously combined with the hydrophilicity

of carbohydrate groups. By introducing a carbohydrate component into a non-polar polymer matrix, a polymer with amphiphilic properties is obtained, which has a strong tendency to self-assembly (coagulation). The hydrophilic carbohydrate blocks increase the interaction with more hydrophilic substances – solvents. With the catalyst selected by us and a simple method, via condensation of allyl glycoside protected by acetyl groups with poly(methylhydro)siloxane ($n=38$), poly[methyl-3-(tetraacetyl glucosidyl)propyl]siloxane was synthesized in high yield. This polymer will be

used in industry as a coating material, which allows it to be used as a surfactant. Additionally, its good bioavailability, makes it suitable for the use in biochemical and biological processes.

Acknowledgements

This research was carried out within the framework of the project by the Ministry of Education, Science and Youth of Georgia, „Competition Innovation Fund (CIF)“, 2nd grant project No. CIF-2-2024-08 agreement.

ორგანული ქიმია

ბიოორგანულ პროდუქტთა ჰიდროსილილირების რეაქციები

დ. ირემაშვილი*, ლ. ტაბატაძე*, ქ. ებრალიძე**, ნ. ფირცხელიანი*,
ი. ბოჭორიშვილი*, ნ. შენგელია*

* სოხუმის სახელმწიფო უნივერსიტეტი, საბუნებისმეტყველო მეცნიერებათა, მათემატიკის, ტექნოლოგიებისა და ფარმაციის ფაკულტეტი, თბილისი, საქართველო

** ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პ. მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი, საქართველო

(წარმოდგენილია აკადემიის წევრის კ. ამირხანაშვილის მიერ)

ნაშრომში აღნიშნულია ჰიდროსილილირების რეაქციების პრაქტიკული მნიშვნელობა, როგორც ყველაზე ეფექტური და მოსახერხებელი მეთოდი შესაბამისი სილიციუმორგანული ნაერთების მისაღებად. მათ ფართოდ იყენებენ, როგორც შესაბამისი სილილირებული დაბალმოლეკულური ნაერთების, ასევე მაღალმოლეკულური ნაერთების მისაღებად და მათი მოდიფიკაციისათვის. მოცემული ტიპის რეაქციებისადმი დიდი ინტერესი გამოწვეულია მეთოდის სიმარტივით, მოხერხებულობით, თანამდე პროდუქტების არარსებობით და შესაძლო სინთეზების ფართო სპექტრით, რომლებიც გამოიყენება სხვადასხვა პრაქტიკული მიზნებისთვის. ოლეფინების ჰიდროსილილირება არის მნიშვნელოვანი რეაქცია სხვადასხვა სილიციუმის ორგანული ნაერთების წარმოებისთვის, როგორცაა ინდუსტრიულად მნიშვნელოვანი სილიკონის პროდუქტები. პლატინის კატალიზატორების, Speyer და Karstedt კატალიზატორების

სარგებლობა ფართოდ არის აღიარებული ამ სფეროში და სასურველია უმაღლესი თვისებების მქონე ორგანოსილიციუმის მასალების უფრო ეკონომიური წარმოებისთვის. მნიშვნელოვანია ჰიდროსილირების აღნიშნულ კვლევებში გარდამავალი მეტალების როლი. კვლევის შედეგები დამოკიდებულია უჯერი ნაერთებისა და სილანების სტრუქტურაზე, ასევე კატალიზატორის ბუნებასა და რეაქციის ჩატარების პირობებზე. ორგანოსილიციუმის ნაერთები ხასიათდება მათი სტაბილური და ინერტული ნახშირბად-სილიციუმის ბმებით. ნაშრომში განხილულია მოდიფიცირებული ხაზოვანი პოლისილოქსანის (ფუნქციონალიზებული და აცეტილის ჯგუფებით დაცული ალილგლუკოზიდის) სინთეზი მარტივი მეთოდით და მაღალი გამოსავლიანობით პლატინის კატალიზატორის გამოყენებით. ნახშირწყლებით მოდიფიცირებული ხაზოვანი პოლისილოქსანის პოლი(მეთილ-3-(ტეტრააცეტილ გლუკოზიდ)პროპილ)სილოქსანის ქიმიური სტრუქტურა შესწავლილია ინფრაწითელი სპექტროსკოპიით (FTIR). სპექტრში არ აღინიშნება ალილის ჯგუფისათვის დამახასიათებელი პიკი 3095 cm^{-1} უბანსა და Si-H-ის დამახასიათებელი პიკები 2100-2300 cm^{-1} უბნებში. სპექტრში აღინიშნება აცეტილის (C=O) ჯგუფისთვის დამახასიათებელი პიკი 1730 cm^{-1} უბანსა და Si-C ჯგუფისათვის დამახასიათებელი პიკი 1010 cm^{-1} უბანში.

REFERENCES

1. Tabatadze L. V., Sidamonidze N. N., Pirveli N. O., Gakhokidze, R. A. (2005) Synthesis of certain S-containing disaccharide derivatives. *J. Chemical Natural Compounds*, **41**(5):592-593. <https://doi.org/10.1007/s10600-005-0215-7>.
2. Pachulia, Z., Shengelia, N., Tabatadze, L., Gakhokidze, R. (2016) Modeling of the synthesis of sulfanilamide monoglucoside by quantum-chemical method. *Bull. Georg. Natl. Acad. Sci.*, **10**(4): 33-36. <http://science.org.ge/bnas/t10-n4/05-Pachulia.pdf>.
3. Sidamonidze N.N., Tabatadze L.V., Vardiashvili R.O. (2022) Condensation reactions of 1-chloro-2,3,4-tri-O-acetyl- α -l-arabinopyranose and 1-Chloro-2,3,4-tri-O-acetyl- α -L-rhamnopyranose with α -pyrrolidone and ϵ -caprolactam. *Oxidation Communications*, **45**(4): 628-634. <https://scibulcom.net/en/article/iDO5QngHP0kPfatsbXE1>.
4. Sidamonidze N.N., Gakhokidze R.A., Vardiashvili R.O., Gelovani T.D., Tabatadze L.V. (2023) Synthesis and biological activity of some derivatives of N-glycosylamines. *Oxidation Communications*, **46**(1): 87-95. <https://scibulcom.net/en/article/68tkrjXr3gCY4TLLSZhI>.
5. Mtchedlishvili M.Sh., Tabatadze L.V., Gventsade D.I., Lezhava T.G., Gventsadze L.D., Iremashvili D.J., Shonia T.M. (2024) Technological aspects of biopolymers based on Yucca Gloriosa fiber. *Bull. Georg. Natl. Acad. Sci.*, **18**(4): 138-144. <http://science.org.ge/bnas/vol-18-4.html>.
6. Jonas G., Stadler R. (1994) Carbohydrate modified polysiloxane II. Synthesis via hydrosilylation of mono-, di- and oligosaccharide allylglycosides. *Acta Polymer*, **45**(1): 14-20. <https://doi.org/10.1002/actp.1994.010450104>.
7. Hofmann R.J., Vlatković M., Wiesbrock F. (2017) Fifty years of hydrosilylation in polymer science: a review of current trends of low-cost transition-metal and metal-free catalysts, non-thermally triggered hydrosilylation reactions, and industrial applications. *Polymers*, **9**(10):534. <https://pmc.ncbi.nlm.nih.gov/articles/PMC6418815/>.
8. Kitov P.I., Bundle D.R. (2001) Mild oxidative one-pot allyl group cleavage. *National Librane of Medicine*, **3**(18): 2835-8. DOI:10.1021/ol016278t.
9. Tabatadze L. V., Gakhokidze R. A., Lomtadze Z. Sh., Sidamonidze N. N., Sabauri N. A. (2007) Synthesis and antimicrobial activity of sulfur-containing glycosides. *J. Pharmaceutical Chemistry*, **41**(8): 407-408. <https://link.springer.com/article/10.1007/s11094-007-0088-0>.

Received March, 2025