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Synthesis, Structure, and Properties of Allylamino Glycosides

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Abstract—Glycosylation of allylamine with D-glucose, D-galactose, and D-mannose in dry primary aliphatic alcohols was studied. The structures of the resulting *N*-allyl glycosylamines were established, and their reactivities were studied. It was found that *N*-allyl glycosylamines tend to structural isomerization involving a change in ring size and do not tend to radical polymerization in the presence of azo initiators.

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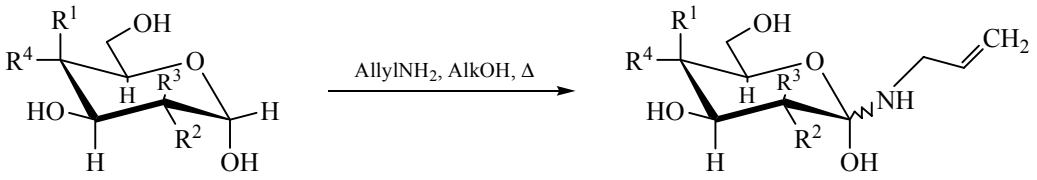
At present much attention is paid to the synthesis of novel hydrophilic polymers with mono-saccharide residues in the side chain. In the over-whelming majority of cases such polymers are pre-pared from carbohydrate monomers. However, the synthesis of monomers representing glycosylamines with unsaturated substituent has scarcely been reported in the literature, except for a number of short communications [1–3].

The aim of the present work was to study glycolsylation of allylamine with α-D-glucopyranose, α-D-galactopyranose, and D-galactose (an anomeric mixture of five- and six-membered tautomers), as well as α,β-D-mannopyranose in the media of dry methanol, ethanol, and propan-1-ol, to determine the structure and configuration of the anomeric center, and to study the reactivity of the synthesized allylamino glycosides.

The glycosylation of allylamine with D-aldohexoses was performed at 53–58°C. Such temperature ensured fairly fast glycosylation and, at the same time, a minimum overal rate of side reactions.



I, $R^1 = R^3 = H$, $R^2 = R^4 = OH$; **II**, $R^1 = R^2 = OH$, $R^3 = R^4 = H$; **III**, $R^1 = R^2 = H$, $R^3 = R^4 = OH$.

The reaction in an alcohol medium occurs at the interface, and the reaction time is limited by the rate of elimination of the formed glycosylamine from the monosaccharide crystal surface.

The rate of formation of *N*-allyl glycosylamine is strongly dependent not only on the properties of the dispersion medium, but also on the nature of the monosaccharide (see table). Thus, D-aldohexoses which have a D-arabino configuration react easier than aldoses which have a D-lyxo configuration. The following reactivity order of monosaccharides toward allylamine was observed: D-galactose > D-glucose > D-mannose. Thus, D-galactose, especially its furanose forms, is the least active. For example, the yield of the corresponding *N*-galactopyranoside **II** in the glycolsylation of allylamine in ethanol with a mixture of α,β-D-galactopyranose and α,β-D-galactofuranose is 18.6%, and, therewith, part of the starting monosaccharide is consumed for by-product formation. The yield of glycosylamine in the reaction with α-D-galactopyranose in the same solvent is 25.9%. The reaction has a longer time, and the contribution of oxidative processes is smaller.

Effect of the nature of the monosaccharide and solvent on allylamine glycosylation

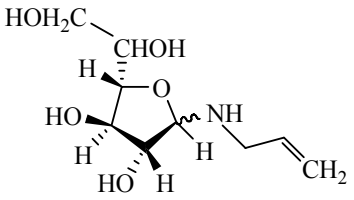
Monosaccharide	Alcohol	Reaction time, h	Conversion,[a] %	Configuration[b] glycosylamine
α-D-Glucopyranose	Methanol	1	100	β
α-D-Glucopyranose	Ethanol	1.5	100	β
α-D-Glucopyranose	Propan-1-ol	2.5	79.8	β
α-D-Galactopyranose	Methanol	3.5	77.8	β
α-D-Galactopyranose	Ethanol	3.5	41.6	β
α,β-Galactose, f + p	Ethanol	2.5	45.4	β
α,β-Mannopyranose	Methanol	0.17	100	α
α,β-Mannopyranose	Ethanol	0.25	100	α

[a] The proper solubilities of monosaccharides in alcohols were neglected in view of their low values. [b] Configuration of the anomeric center of pyranose which is the main part of the product.

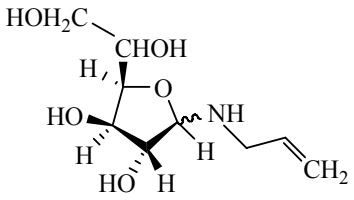
With α-D-glucopyranose and D-galactose as carbohydrate components, the main reaction products are the β-anomers of glycosylamines in all the solvents used.

The structure of the synthesized allylamino glycosides was assessed by high-resolution NMR spectroscopy in various solvents, as well as by solid-phase NMR spectroscopy. The configuration of the anomeric centers in products **I–III** was assessed on the basis H^1–C^1 coupling constants in the ^{1}H NMR spectra. The signal of the anomeric proton (H^1) was identified, and its chemical shift was assigned from a HSQC heteronuclear correlation experiment by the cross peak between C^1 (whose ^{13}C NMR signal is easily identified) with H^1, using a direct $^1J_{CH}$ constant. For example, Fig. 1 shows the assignment of signals in the ^{1}H and ^{13}C NMR spectrum of *N*-allyl-D-galactosamine. As seen, the spectrum corresponds to the cyclic pyranose form of the glycosylamine. Moreover, the ^{1}H NMR spectrum, too, contains signals of the aglycone of the minor form of the compound.

The chemical instability and the tendency of glycosylamines to isomerization makes them difficult to study in solutions. Thus, in DMSO-d_6 these compounds undergo oxidation, lysis, as well as tautomeric transformations to form the furanose forms. The latter phenomenon is also observed in CD_3OD and D_2O and the least expressed in DMF-d_7; most typical for 1-(allylamino)-1-deoxy-β-D-galactose. The structures of the minor tautomers of glycosylamines **I** and **II**, specifically 1-(allylamino)-1-deoxy-D-glucofuranose (**IV**) and 1-(allylamino)-1-deoxy-D-galactofuranose (**V**), are shown below.



IV



V

It should be noted that in the research on the allylamino glycosides, as also in their synthesis and recrystallization we did not observe formation of Amadori rearrangement products. The solid-phase NMR spectra of glycosylamines **I–III** contain well-resolved signals and contain no signals of minor isomers; however, we have to take into account the low sensitivity of this technique.

1-(Allylamino)-1-deoxy-β-D-glucopyranose usually forms fine crystals but sometimes it forms a little of long silky needles melting at a higher temperature than the bulk product (117–117.5 and 113°C, respectively). However, the differently melting samples of glycosylamine **I** have identical spectra data, which gives us grounds to state that this compound exists in two crystal modifications. Figure 2 shows the spectral

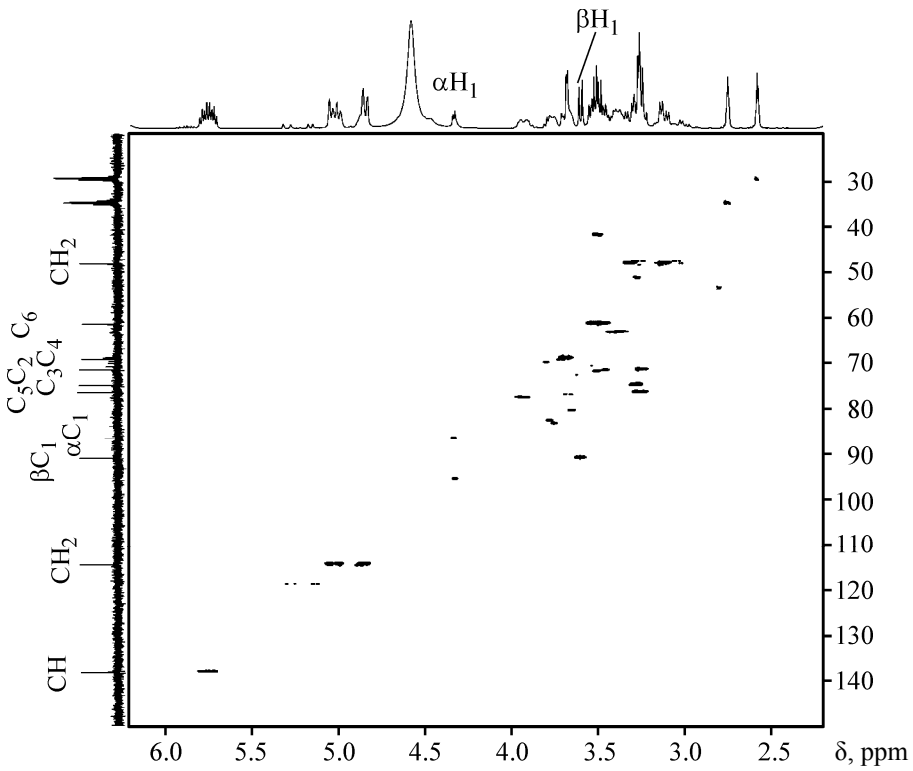


Fig. 1. HSQC NMR spectrum of glycosylamine **II** in DMF-d_7.

data providing evidence for the structure of 1-(allylamino)-1-deoxy-β-D-glucopyranose.

The ^{1}H NMR spectrum contains, in the range δ 3.0–4.0 ppm, carbohydrate ring proton signals, including a triplet characteristic of amino-D-glucopyranosides (δ 3.05, 3.07, and 3.09 ppm), which is lacking in the spectrum of D-glucopyranose and belongs to H^2. The H^1 doublet with components at δ 3.81 and 3.83 ppm has a large coupling constant of 8.6 Hz, implying that the compound in hand is a β-anomer. The doublet at δ 4.47 ppm (*J* 4.8 Hz) has a cross-peak at δ_C 86.45 ppm in the ^{13}C NMR spectrum. The aglycone signals appear over the entire spectral range, but the most illustrative are the downfield signals belonging to the double bond: a doublet from the cis and trans protons of the $=CH_2$ group and a multiplet from the =CH proton.

The ^{13}C NMR spectrum of a purified sample of glycosylamine **I** (Fig. 3) was measured so that the CH_2 signals were observed below the base line; therewith, the spectrum also contains weak signals of the minor isomer. However, the signal at δ 49.08 ppm was found not to belong to the allyl methylene group. At the same time, a weak signal of similar intensity is present at δ 48.34 ppm.

It should be noted that recrystallization of *N*-galactopyranoside **II** free of the parent monosaccharide from alcohols gave samples melting at different temperatures. This phenomenon is probably due to the samples having different crystal modifications or containing different fractions of isomer admixtures, specifically the α-anomer or cyclic tautomer **V**. Thus, for example, in one case we could measure ^{13}C NMR spectra in DMSO-d_6 for samples with mp 111.5–112 and 118–118.5°C. The spectra contained similar sets of signals of the major isomer and one of the two minor isomers, and one of the spectra lacked several signals, for example, the signal at δ 86.5 ppm. In all other cases, the spectral patterns were fully identical. Attempted isolation of individual isomers by column chromatography on silica failed: We obtained a series of fractions containing glycosylamine with the melting point gradually changing from fraction to fraction, so that the difference in the melting points of the compounds isolated from the first and last fractions proved to be substantial.

Glycosylation of allylamine with α,β-D-mannopyranose in methanol or ethanol results in exclusive formation of the α-anomer. The product did not crystallize from the reaction solution and could be crystallized only after removal of the solvent. The formation of the α-anomer of *N*-mannopyranoside **III**

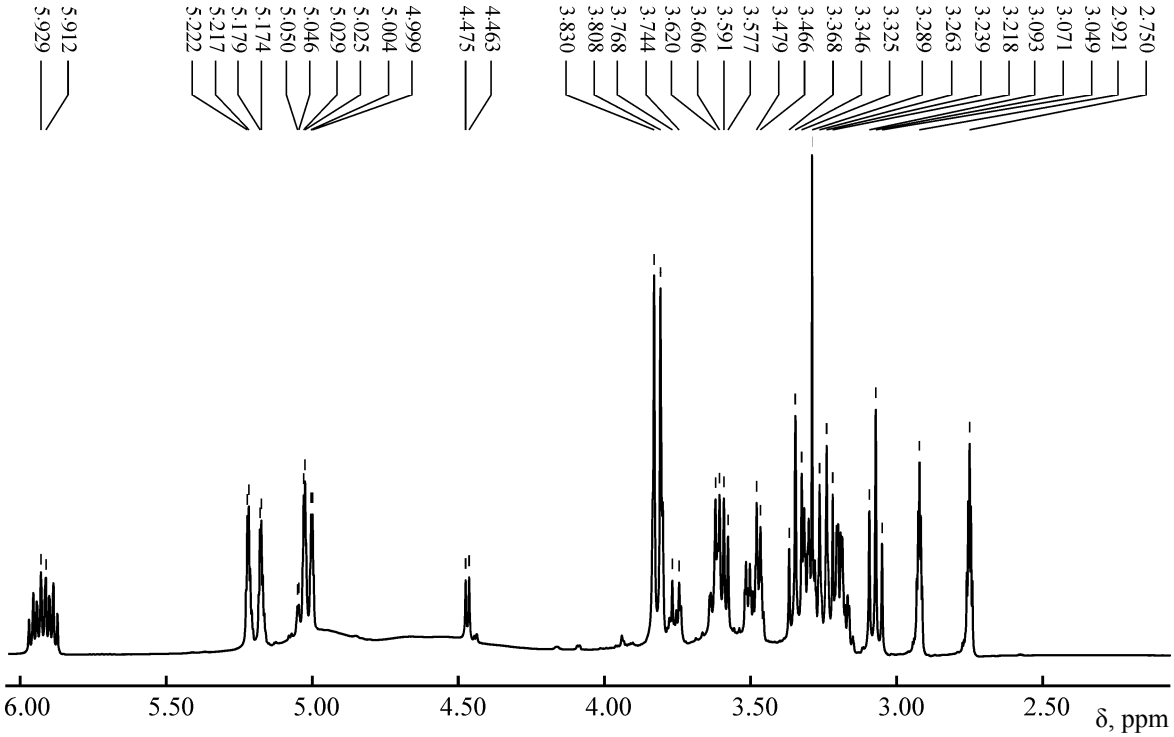


Fig. 2. ^{1}H NMR spectrum of glycosylamine **I** in DMF-d_7.

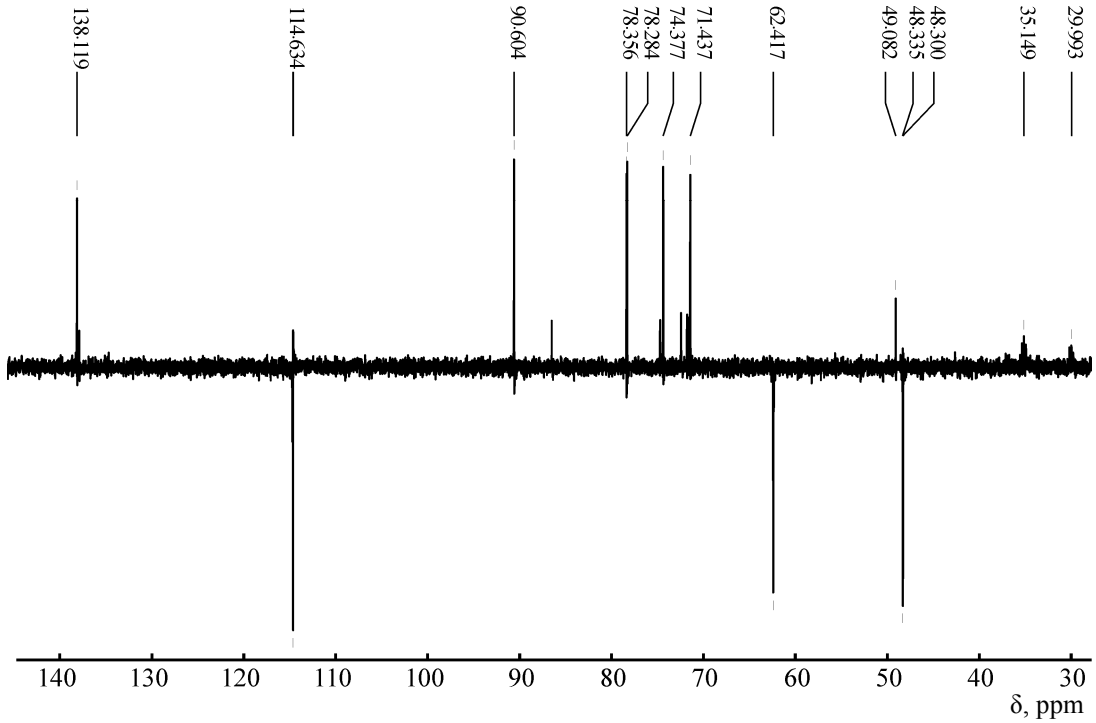


Fig. 3. DEPT ^{13}C NMR spectrum of glycosylamine **I** in DMF-d_7.

as a single product is probably explained by the Δ^2-effect, in view of the fact that the pyranose ring contains an axial hydroxyl in the 2 position.

The spectral data presented in Fig. 4 were obtained for the 1-(allylamino)-1-deoxy-α-D-mannopyranose sample which was not subjected to additional purifica-

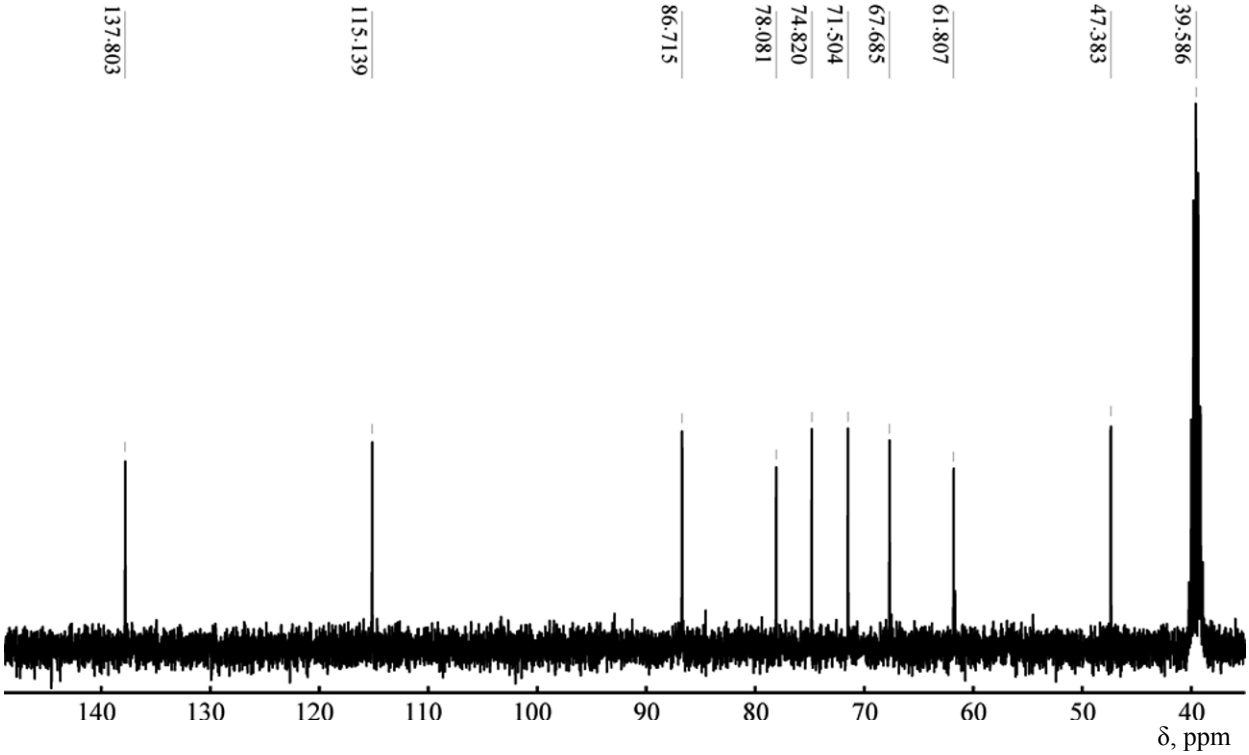


Fig. 4. ^{13}C NMR spectrum of glycosylamine **III** (synthesis in MeOH) in DMSO-d_6.

tion. According to these data, the product is sufficiently pure, which points to a high degree of conversion of D-mannose during glycosylation.

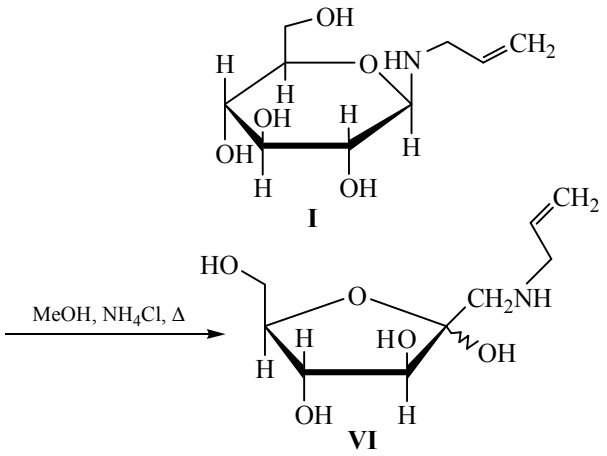
However, alcohols, in particular, ethanol, can be used for recrystallization of this compound, and the recrystallization is accompanied by partial anomerization. The latter is evidenced by the appearance in the ^{13}C NMR spectrum (DMF-d_7, δ 29.54, 34.88 ppm) of a set of weak signals both for the aglycone, for example, δ, ppm: 47.59 (CH_2), 114.78 (=CH_2), and 137.89 (=CH), and for the carbohydrate part of the molecule in the range 62–89 ppm.

The chemical properties of glycosylamines are largely dependent on the properties of their parent amines, in particular, on their basicity and the structure of the N-substituent in the amino group. Since allylamine ihas a fairly high basicity (pK_a 9.42), its glycosides are readily hydrolyzed already at normal conditions, and this process is autocatalytic. These compounds decompose in air, undergoing oxidation, hydrolysis, and isomerization to finally form viscous dark brown or almost black mixtures. The highest tendency to such transformations is characteristic of 1-(allylamino)-1-deoxy-β-D-galactopyranose, the second least stable compound is the corresponding D-glucopyranoside **I**, and the third is *N*-mannoside **III**. In the case of compound **I**, its needle-like crystal modification is the most stable. According to NMR data, such products were assigned the structure of 1-(allylamino)-1-deoxy-D-ketofuranoses. In Fig. 5 we present the spectral data providing evidence for the formation of several cyclic allyl-containing isomers.

The range 110–140 ppm, characteristic of CH=CH_2 carbon signal, shows, along with signals belonging to allylamino-D-mannopyranoside (δ, ppm: 115.38, 115.46 and 138.34, 138.62), two sets of well-resolved signals assignable to compounds containing a five-membered heterocycle, and, at the same time, allylamine and allylamonium signals are lacking.

When heated in dry alcohol solutions in the presence of weak acids, for example, NH_4Cl, glycosylamines undergo the Amadori rearrangement to form 1-(allylamino)-1-deoxy-D-ketofuranoses, but their yields are low.

Compounds like saccharide **VI** are fairly difficult to isolate pure from the saccharide mixtures isolated from the reaction mixtures, because the rearrangement products are highly prone to hydrolysis and oxidation. Figure 6 shows the NMR spectrum of the isolated mixture of saccharides obtained as the result of isomerization of compound **I**.



The spectral data show that ring contraction stronger affects the chemical shifts of double bond carbon atoms than tautomerization. In particular, the change of the ring size in compound **I**, associated with the expulsion of the anomeric C^1 atom from the ring, results in that the chemical shifts of the CH= and $=CH_2$ carbons in 1-(allylamino)-1-deoxy-D-fructofuranose are quite different from those in the parent compound.

Like allylamine, its *N*-glycosyl derivatives do not enter radical polymerization in the presence of azo initiators and scarcely enter copolymerization with other vinyl monomers, in particular, 1-vinylpyrrolidin-2-one. For example, on heating of 1-(allylamino)-1-deoxy-β-D-glucopyranose with 2.0 wt % of AIBN at 57°C in dry ethanol for 44 h no polymerization was observed, 54.5% of the starting compound was recovered, and the rest were by-products. On attempted copolymerization with 50 and 75 mol % of 1-vinylpyrrolidin-2-one under the same conditions we obtained 1-vinylpyrrolidin-2-one contaminated with the comonomer and its decomposition products, which crystallized on cooling. Of the allylamino glycosides we considered 1-(allylamino)-1-deoxy-α-D-mannopyranose as the most convenient monomer, since it is the most stable and best soluble compound. Thus, heating at 60°C of a dry methanol solution of 10 mol % of this glycoside, 1-vinylpyrrolidin-2-one, and 1.8 wt % of AIBN for 25 h gave 80.1% of a copolymer containing, according to NMR data, an admixture of the carbohydrate monomer. However, further purification against dry methanol involved substantial losses (44.4%), implying formation of oligomers containing D-mannopyranole residues.

The copolymer was studied by one- and two-dimensional NMR spectroscopy, but the information contained in the resulting data proved insufficient. The ^{1}H NMR spectra of the copolymer before and after purification were identical, except for residual monomer signals, and differed from the ^{1}H NMR spectrum of pure polyvinylpyrrolydone by that they contained several weak signals, for example, a doublet

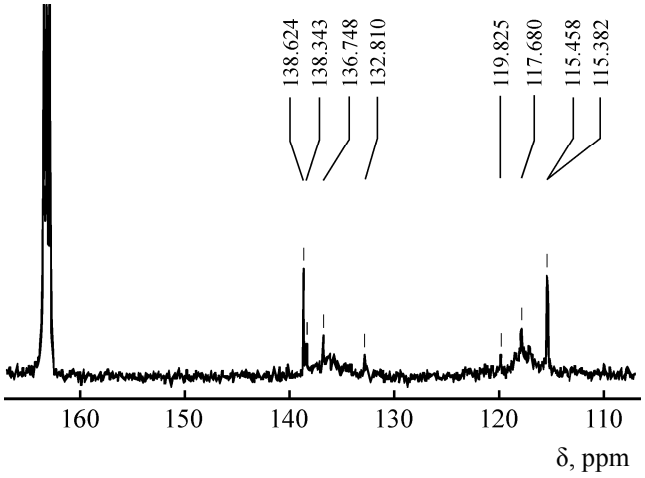


Fig. 5. ^{13}C NMR spectrum of the transformation products of glycosylamine **III**, DMF-d_7 (δ 163.15 ppm).

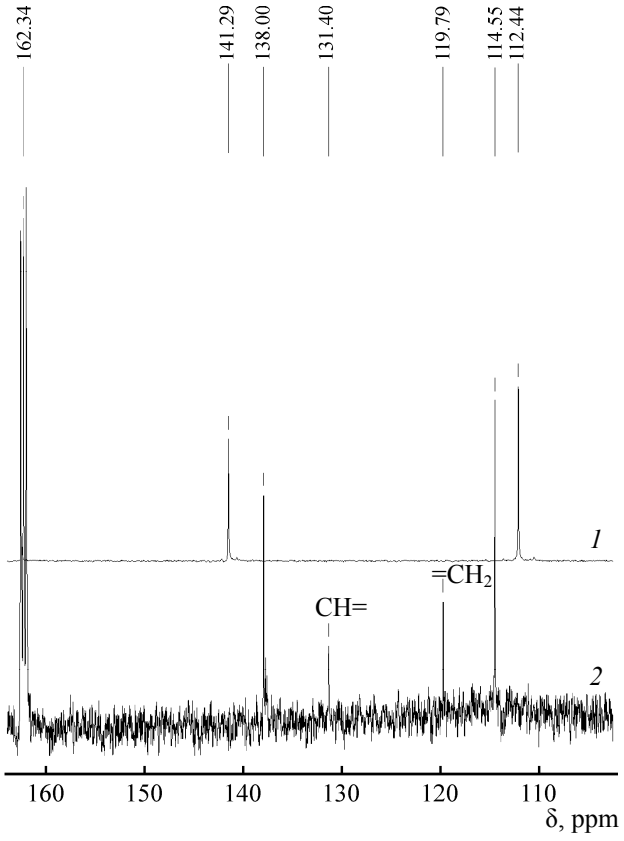


Fig. 6. ^{13}C NMR spectra of (*1*) allylamine and (*2*) a mixture of saccharides in the range of allyl double bond signals.

at δ 5.07 ppm (*J* 0.97 Hz) [for glycosylamine **III**: δ 5.07 ppm, *J* 1.1 Hz]. The signals corresponding to D-mannose residues are overlapped by broad signals of polyvinylpyrrolydone blocks, and, in view of the low content of these residues, their concentration was impossible to estimate with reasonable accuracy. In the range 1.2–2.5 ppm, there are lactam ring signals and in the range 3.1–4.1 ppm, hydrocarbon chain signals: 3.21, 3.29 (CH_2), and 3.75 ppm (CH).

EXPERIMENTAL

The reactions were performed with predistilled allylamine, bp 52.7–53°C (760 mm). Methanol, ethanol, and propan-1-ol were dried by prolonged boiling with excess CaH_2 followed by distillation. D-Glucose, D-galactose, and D-mannose were preliminarily studied by ^1H and ^{13}C NMR spectroscopy to obtain information about their anomeric composition, ring size, tendency to tautomerism, and inversion of substituent at C^1 in various solvents and at various temperatures, which was then used in structural characterization of the synthesized glycosylamines. All glycosylamine samples were dried in a vacuum over P_4O_{10}.

Dialysis was performed using Cellu SepH1 membranes with the following characteristics: width 45± 2 mm, thickness 27±2 μm, molecular weight cut-off up 1 kDa. The molecular weight of polymers M_η were estimated roughly by viscometry at 25°C, using methanol, the Ubbelohde viscometer, and the Mark–Kuhn–Houwink equation for polyvinylpyrrolidone [4].

The NMR spectra were obtained on Bruker WM-400 and Avance II 400 spectrometers (^1H, 400.1 MHz; ^{13}C, 100.6 MHz) for solutions and on Avance III 500 (^1H, 500 MHz; ^{13}C, 125.76 MHz) for solid sample (external reference glycine). The IR spectra were measured on a Shimadzu FTIR-8400S spectrometer. Elemental analysis was performed on C,H,N,S Leco-932 and Vario Elemental analyzers.

Synthesis of 1-(allylamino)-1-deoxy-β-D-glucopyranose. *a*. Allylamine, 5.71 g (0.10 mol), was added to a suspension of 18.0 g (0.10 mol) of ground α-D-glucopyranose in 35 ml of dry ethanol. The thick material was ground to uniform consistency, after which it was heated on a water bath at 60°C for 1.5 h with stirring at 0.5-h intervals. Therewith, the temperature of the mixture was 53–54°C. After 1-h heating about 50% of D-glucose dissolved, and after an additional 0.5 h the precipitate dissolved almost completely. The material that crystallized was cooled to 0–10°C, the product was filtered off, and the filtrate was left for crystallization at 22°C. The crystalline material that formed was washed with a little cold ethanol and combined with bulk products, after which the mixture was recrystallized from isopropanol or dry ethanol at a temperature below 55°C. For recrystallization should be taken such solvent volume which would allow to dissolve the precipitate as soon as possible. Yield 17.65 g (80.5%), white fine crystals, mp 113°C (ethanol, propan-2-ol). IR spectrum, ν, cm^{-1}: 465.78, 513.03, 583.43, 633.57, 674.07, 1276.79, 874.66, 895.87, 925.77, 980.74, 1008.70, 1027.02, 1089.71, 1164.92, 1193.85, 1257.50, 1315.36, 1348.15, 1362.61, 1380.94, 1400.22, 1417.58, 1451.33, 1469.66, 1510.16, 1644.20 (>C=C<). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 47.66 (allyl CH_2), 61.38 (C^6), 70.52 (C^4), 73.48 (C^2), 77.42 (C^3), 77.58 (C^5), 85.69 (α-C^1), 89.89 (β-C^1), 114.85 (=CH_2), 137.63 (CH=). White silky needles (not always formed), mp 117–117.5°C (ethanol). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 47.63 (allyl CH_2,), 61.38 (C^6), 70.52 (C^4), 73.48 (C^2), 77.42 (C^3), 77.58 (C^5), 89.89 (β-C^1), 114.85 (=CH_2), 137.63 (CH=).

b. Allylamine, 5.71 g (0.10 mol), was added to a suspension of 18.0 g (0.10 mol) of ground α-D-glucopyranose in 35 ml of dry ethanol. After mixing and purging with argon, the mixture was heated at 60±0.5°C (the mixture temperature was 53°C) for 1 h with stirring at 0.5-h intervals. After 0.5-h heating about 50 vol % of D-glucose dissolved. When the reaction was complete, the solution was decanted from a scanty precipitate, the latter was washed with a little cold methanol, and the washings were combined with bulk solution.

After standing at 20–22°C for 2 h the solution crystallized completely, the crystals were triturated with cold methanol, filtered off, and dried at 22°C in air. The filtrate was evaporated on a rotary evaporator in 3–4 portions, and the residue was left for crystallization. The crystalline material that formed was filtered off, washed with ethanol on the filter, dried, and combined with bulk product. The filtrate was left for crystallization, and the crystals were filtered off and combined with bulk product. Yield 17.83 g (81.4%), mp 107–109°C. 1-(Allylamino)-1-deoxy-β-D-glucopyranose was recrystallized 1–2 times from dry methanol, mp 113–113.5°C (fine crystals, prisms), mp 115–116.5°C (needles). ^1H NMR spectrum (DMF-d_7), δ, ppm: 3.07 t (1H, H_2), 3.29 s

(2H, allyl CH_2), 3.13–3.78 m (9H, H^{3-5}, CH_2, 4OH), 3.82 d (β-H^1, *J* 8.6 Hz), 4.46 d (α-H^1, *J* 4.8 Hz), 5.01 d.d (1H, *cis*-H, *J* 4.839 Hz), 5.04 d (1H, NH, *J* 1.617 Hz), 5.19 d.d (1H, *trans*-H, *J* 17.25 Hz), 5.87–5.97 m (1H, *cis*-H). ^{13}C NMR spectrum (DMF-d_7), δ_C, ppm: 48.30 (CH_2, allyl), 62.41 (C^6), 71.43 (C^4), 74.37 (C^2), 78.28 (C^3), 78.35 (C^5), 90.60 (β-C^1), 114.63 (=CH_2), 138.11 (CH=). Found, %: C 49.39; H 8.22; N 7.01; C 49.63; H 8.35; N 6.69. $C_9H_{17}NO_5$. Calculated, %: C 49.31; H 7.82; N 6.39.

c. Allylamine, 5.71 g (0.10 mol), was added to a hot (60°C) suspension of 18.0 g (0.10 mol) of a finely ground α-D-glucopyranose in 40 ml of dry propan-1-ol. After mixing and purging with argon, the mixture was heated at 60±0.5°C with stirring at 0.5-h intervals. After 2.5-h heating, 80 ml of dry propan-1-ol was added to the reaction mixture which crystallized, the mixture was ground and then heated with stirring at 75–80°C until the precipitate no longer dissolved. The solution was let to settle, and then the most part of the solution was decanted from the precipitate; the decanted solution soon crystallized. The product was filtered off and dried in air at 22°C. The filtrate was combined with the solution over the precipitate, and the mixture was heated for some time with stirring. The warm solid material was filtered off, washed with a little ethanol, and dried to obtain 3.63 g of the starting D-glucose. The filtrate was reduced to 60 ml in a vacuum on a rotary evaporator, left for crystallization, cooled to 0°C, the crystals that formed were filtered off, washed with a little propan-1-ol, dried, and combined with bulk product. Yield 14.07 g (64.2%, including the conversion of 80.5%).

Synthesis of 1-(allylamino)-1-deoxy-β-D-galactopyranose. *a*. Allylamine, 5.71 g (0.10 mol), was added to a suspension of 18.0 g (0.10 mol) of a finely ground α-D-glucopyranose in 50 ml of dry ethanol. After mixing and purging with argon, the mixture was heated on a water bath successively at 60°C (1 h), 65°C (1 h), and 80°C (1.5 h) with stirring at 0.5-h intervals. The yellow solution was decanted from the precipitate, after which the decanted solution crystallized. The precipitate was triturated with dry ethanol, filtered off, and dried in air to isolate 10.51 g of D-galactose. The crystallized 1-(allylamino)-1-deoxy-D-galactopyranose was filtered off, washed with two portions of cold ethanol, and dried to obtain 5.48 g of a white substance. The filtrate was poured into 60 ml of dry diethyl ether. A few minutes after mixing, a suspension of needle-like crystals formed. The crystals were filtered off, washed with ethanol, and dried to obtain 0.19 g of a white silky material. Yield 5.67 g (25.9 %, including the conversion of 62%), mp 109° C (ethanol), 108–109°C (finely crystalline precipitate obtained by mixing diethyl ether with the mother liquor after crystallization), 117°C (from propan-2-ol), 118.0°C (from methanol), and 111.0–112°C (fine crystals precipitated into diethyl ether from the mother methanol solution). ^1H NMR spectrum (DMF-d_7), δ, ppm: 3.07–4.16 m (12H, H^{2-5}, CH_2OH, 3OH, CH_2), 3.76 d (β-H^1, *J* 7.5 Hz), 4.49 d (α-H^1, *J* 4.9 Hz), 5.01 d.d (1H, *cis*-H, *J* 10.3 Hz), 5.18 d (1H, *J* 17.2 Hz), 5.20 d.d (1H, *trans*-H, *J* 17.2 Hz), 5.32 d.d (1H, *cis*-H, *J* 10.5 Hz, minor), 5.45 d.d (1H, *trans*-H, *J* 17.3 Hz, minor), 5.91–5.92 m (1H, vic. H), 6.04 m (1H, vic. H, minor). ^{13}C NMR spectrum (DMF-d_7), δ_C, ppm: 48.32 (allyl CH_2), 61.59 (C^6), 69.40 (C^4), 71.72 (C^2), 72.05 (C^3), 76.74 (C^5), 91.12 (β-C^1), 114.62 (=CH_2), 138.13 (CH=). Solid-phase ^{13}C NMR spectrum, δ_C, ppm: 47.18 (allyl CH_2), 63.08 (C^6), 70.74 (C^4), 71.78 (C^2, C^3), 76.64 (C^5), 87.05 (β-C^1), 118.52 (=CH_2), 136.79 (CH=).

b. Allylamine, 5.71 g (0.10 mol), was added to a suspension of 18.0 g (0.10 mol) of a mixture of cyclic tautomers of α,β-D-galactose in 5 ml of dry ethanol. After mixing, the mixture was heated at 77°C for 0.5 h, stirred, and further heated first at 65°C for 1.5 h with stirring at 0.5-h intervals and then at 60°C for 0.5 h. About 50 vol % of the solid phase dissolved in 1.5 h after reaction start. However, the amount of D-galactose no longer decreased, but the reaction mixture got dark. It was left for crystallization, and the crystals were filtered off and washed with dry ethanol. The filtrate was left for crystallyzation, and the product was extracted from the resulting crystalline material by stirring with isopropanol at 60–80°C. The extract was partially evaporated in a vacuum and left for crystallization. The subsequent filtration and work-up of the filtrate gave 2.91 g of glycosylamine, mp 116–117°C, which was combined with glycosylamine isolated by fractional crystallization from propan-2-ol of a mixture of substances, isolated from the filtrate obtained by treatment of the reaction mixture. Yield 4.08 g (18.6%). Recrystallization from dry ethanol gave spherical polycrystals formed by needles with the face length of 3 mm. Found, %: C 49.32; H 7.79. $C_9H_{17}NO_5$. Calculated, %: C 49.31; H 7.82.

c. Allylamine, 5.71 g (0.10 mol), was added to a hot (60°C) mixture of 18.0 g (0.10 mol) of ground α-D-galactopyranose and 45 ml of dry methanol. The

components were mixed, and the mixture was heated under argon for 3.5 h, maintaining the mixture temperature at 53–55°C and stirring at 0.5-h intervals. About 50 vol % of D-galactose reacted already in 1 h after the reaction start, after which glycosylation slowed down, and the solution started to get colored. The hot solution was decanted from a scanty precipitate and left for crystallization, the precipitate was washed with two small portions of methanol, filtered off, and dried to obtain 4.0 g of the starting monosaccharide. The latter filtrate, too, was left for crystallization. After crystallization the filtrates were cooled to 0–5°C, the precipitates were filtered off, washed with ethanol, and dried. The combined filtrate was left to stand in air, in a few days crystals formed and were filtered off, dried, and combined with main bulk of the product. Yield 13.87 g (63.9%, accounting for the conversion of 81.4%). IR spectrum, ν, cm^{-1}: 521.71, 568.96, 670.22, 707.83, 781.12, 803.30, 873.69, 891.05, 919.02, 949.88, 1013.52, 1077.17, 1089.71, 1115.74, 1154.32, 1169.75, 1214.11, 1258.47, 1289.43, 1311.50, 1327.90, 1351.04, 1385.76, 1412.76, 1452.30, 1493.77, 1529.45, 1643.24 (>C=C<).

Synthesis of 1-(allylamino)-1-deoxy-α-D-mannopyranose. *a*. Allylamine, 5.71 g (0.10 mol), was added to a hot (60°C) mixture of 18.0 g (0.10 mol) of ground α-D-mannopyranose and 45 ml of dry methanol. Therewith, the reaction accompanied by monosaccharide dissolution started immediately. The reaction mixture was stirred and heated at 60°C for 10 min. Over this time D-mannose has reacted completely. Methanol was removed by vacuum distillation from the resulting colorless solution to leave a viscous transparent syrup which started to crystallize in 2–3 h. A little dry crystals obtained previously by trituration of the syrup on a glass surface followed by washing with dry diethyl ether was added to the obtained material, after which it was left at 20°C for crystallization. The resulting thick crystalline material was thoroughly ground and dried first in air and then in a vacuum over P_4O_{10}. Yield 21.60 g (98.6%), white fine crystals, mp 107–110°C. IR spectrum, ν, cm^{-1}: 655.75, 675.04, 718.43, 771.47, 786.90, 829.33, 845.73, 861.16, 896.84, 908.41, 930.59, 937.34, 950.84, 967.23, 1001.95, 1013.52, 1033.77, 1055.95, 1075.24, 1092.60, 1115.74, 1127.32, 1149.50, 1260.39, 1312.47, 1331.76, 1362.61, 1415.65, 1454.23, 1644.20 (>C=C<). ^{1}H NMR spectrum (DMF-d_7), δ, ppm: 3.11 s (1H, H^5), 3.73 d.d (1H, H_3, *J* 3.3 Hz), 3.15–3.86 m (10H, $H^{2,4}$, CH_2OH, 3OH, CH_2), 4.06 s (1H, α-H^1, *J* 1.1 Hz), 5.01 d.d (1H, *cis*-H, *J* 10.2 Hz), 5.06 d (1H, *J* 1.1 Hz), 5.15 d.d (1H, *trans*-H, *J* 17.2 Hz), 5.83–5.99 m (1H, vic. H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 47.38 (allyl CH_2), 61.80 (C^6), 67.68 (C^4), 71.50 (C^3), 74.82 (C^2), 78.08 (C^5), 86.71 (α-C^1), 115.13 (=CH_2), 137.80 (CH=). ^{13}C NMR spectrum (DMF-d_7), δ, ppm: 47.59 (allyl CH_2, minor), 47.83 (allyl CH_2), 62.58 (C^6, minor), 62.62 (C^6), 68.52 (C^4), 68.87 (C^4, minor), 72.17 (minor), 72.24 (minor), 72.28 (C^3), 72.60 (minor), 75.71 (C^2), 78.11 (minor), 78.43 (C^5), 83.70 (minor), 87.40 (α-C^1), 88.01 (β-C^1), 114.66 (=CH_2), 114.78 (=CH_2, minor), 137.88 (CH=, minor), 138.19 (CH=). Found, %: C 50.19; H 8.27; N 6.38; C 51.72; H 7.83; N 6.41. $C_9H_{17}NO_5$. Calculated, %: C 49.31; H 7.82; N 6.39.

b. Analogously, 2.86 g (0.05 mol) of allylamine was glycosylated with 9.0 g (0.05 mol) of α,β-D-mannopyranose in 22.5 ml of dry ethanol. The reaction time was 15 min. The product started to crystallize in 3 h after removal of the solvent. Yield 10.82 g (98.8%).

Copolymerization of (1-allylamino)-1-deoxy-α-D-mannopyranose with 1-vinylpyrrolidin-2-one. A solution of 0.1096 g (0.0005 mol) of 1-(allylamino)-1-deoxy-α-D-mannopyranose, 0.50 g (0.0045 mol) of 1-vinylpyrrolidin-2-one and 0.011 g (1.8 wt %) of AIBN in 1.18 ml of dry methanol was heated under argon at 60°C for 25 h. Anhydrous methanol, 15 ml, was added to the resulting colored solution, and then the solution was added dropwise with stirring to two 225-ml portions of dry diethyl ether. After the polymer precipitated, the turbid liquid was decanted from the flaky white precipitate, and the precipitate was filtered off, washed with dry diethyl ether, and dried first in air and then in a vacuum over P_4O_{10} to obtain 0.42 g of a cream-coloured copolymer powder. The decanted fine dispersion was filtered, and the precipitate which was filtered off was dried to obtain 0.07 g of a white substance. Yield 0.49 g (80.1%). The copolymer was purified from the 1-(allylamino)-1-deoxy-D-mannopyranose admixture by dialysis. To this end, 0.36 g of the copolymer in 45 ml of dry methanol was placed into a cylindrical membrane shell, after which the membrane was kept in 750 ml of dry methanol under stirring for 50 h. The solution was reduced in a vacuum to 20 ml, the polymer was isolated as described above and dried over P_4O_{10} to obtain 0.20 g of the product (55.6% of the quantity taken for purification), cream-colored powder, $[\eta]^{25}$ 0.275 dl/g (methanol), $M_\eta \approx 54.297$ kDa, assuming that poly(1-vinylpyrrolidin-2-one) was obtained.

Isomerization of 1-(allylamino)-1-deoxy-β-D-glucopyranose. A mixture of 1.0 g (0.00456 mol) of 1-(allylamino)-1-deoxy-β-D-glucopyranose, 0.05 g (0.00093 mol) of NH_4Cl, and 15 ml of dry methanol was heated at the bath temperature of 65°C for 1.5 h. The resulting colorless transparent solution was heated at 70°C for 1 h, after which the dark colored solution was reduced by half. The catalyst and saccharide fractions were isolated by treatment with dry diethyl ether. Therewith, white mixtures were filtered off and washed with ether on the filter not removing the solvent completely. Then the solvent was quickly removed, and the quickly deliquescing and colored fractions were stored in a vacuum over P_4O_{10}. The saccharide fractions were identified mostly as a contaminated glycosylamine, but 1-(allylamino)-1-deoxy-D-fructofuranose was also identified in a mixture. ^{13}C NMR spectrum (DMF-d_7), δ, ppm: 41.98 (C^1, CH_2, minor), 61–100 (minor signals of D-glucose isomers and the rearrangement product), 119.78 (=CH_2, minor), 131.39 (CH=, minor).

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