Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbohydrate Research 339 (2004) 1293–1300
Carbohydrate RESEARCH

Synthesis of *cis*-(1 → 3)-glycosides of allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside

Janusz Madaj,* Magdalena Jankowska and Andrzej Wiśniewski

Department of Chemistry, Sugar Chemistry Group, University of Gdańsk, ul. Sobieskiego 18, PL-80-952 Gdańsk, Poland

Received 27 November 2003; accepted 25 January 2004

Available online 24 March 2004

Abstract—Syntheses of allyl 2,3,4-tri-*O*-benzyl-α-D-gluco- and D-galactopyranosyluronate-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside via oxidation of the hydroxymethyl group of allyl 2,3,4-tri-*O*-benzyl-α-D-gluco- and D-galactopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside under Jones conditions are described. Structures of the title compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy.

Keywords: Uronic acid; 2-Acetamido-2-deoxy-D-glucopyranose; Jones oxidation; ^{1}H and ^{13}C NMR spectroscopy

1. Introduction

Uronic acids are of important biological significance and have attracted the attention of many chemists. Their glycosides are found in many polysaccharides of microbes, plants, and animals.[1,2] They play important roles in biological recognition and cellular communication.[3] Linked to uronic acids (of the D-gluco-, D-galacto-, or D-ido- configurations) they are lipopolysaccharide components of bacteria cell walls. Glycoproteins and lipopolysaccharides with this type of sugar moiety are not easily available from natural sources because of their microheterogeneity. In this paper we describe syntheses of disaccharide fragments of lipopolysaccharides (LPS) isolated from Gram-negative bacterial cell walls: α-D-Glc*p*A-(1 → 3)-D-Glc*p*NAc from *Shigella boydii* 5[4] and *Hafnia alvei* PCM 1185[5] and *Proteus mirabilis* 010;[6] α-D-Gal*p*A-(1 → 3)-D-Glc*p*NAc from *Escherichia coli* O65[7] and *Vibrio cholerae* O22[8] and *Proteus vulgaris* O46.[9]

2. Results and discussion

Reaction of the *O*-allyl group with cysteamine[10] forms a commonly used linker to BSA (*bovine serum albumin*) or HSA (*human serum albumin*). Allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**2**), prepared from allyl 2-acetamido-2-deoxy-α-D-glucopyranoside[11] (**1**), was used as a glycosyl acceptor. Direct reaction between **2** and methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranosyluronate bromide[12] (**3**) led to the intermolecular *O*-acetyl group migration.[13] This type of side reaction is well known in the literature[14,15] and may be the result of low reactivity of uronic acid derivatives.[16,17] Because the direct reaction of **2** and **3** was ineffective, we decided to change the strategy of synthesis. In some cases an alternative method of preparation of oligosaccharides containing uronic acid units via oxidation of the hydroxymethyl group in appropriately prepared substrate oligosaccharides, was used.[18–20] Based on our previous results,[21] we chose the method of Kong and co-workers[22] to obtain a free terminal hydroxyl group. The reaction of **2** and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate [**5**, obtained from 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**4**)] carried out in

* Corresponding author. Fax: +48-58-345-04-72; e-mail: januszm@chemik.chem.univ.gda.pl

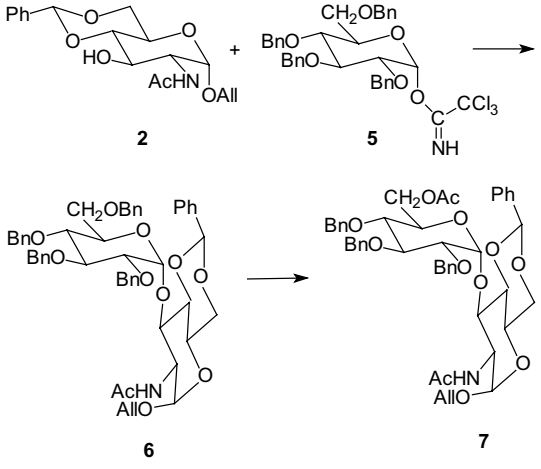
0008-6215/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2004.01.014

DMF gave the expected allyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**6**) in 71% yield. Selective replacement of the 6-*O*-benzyl group with *O*-acetyl in **6** led to allyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**7**) in only 11% yield (Scheme 1).

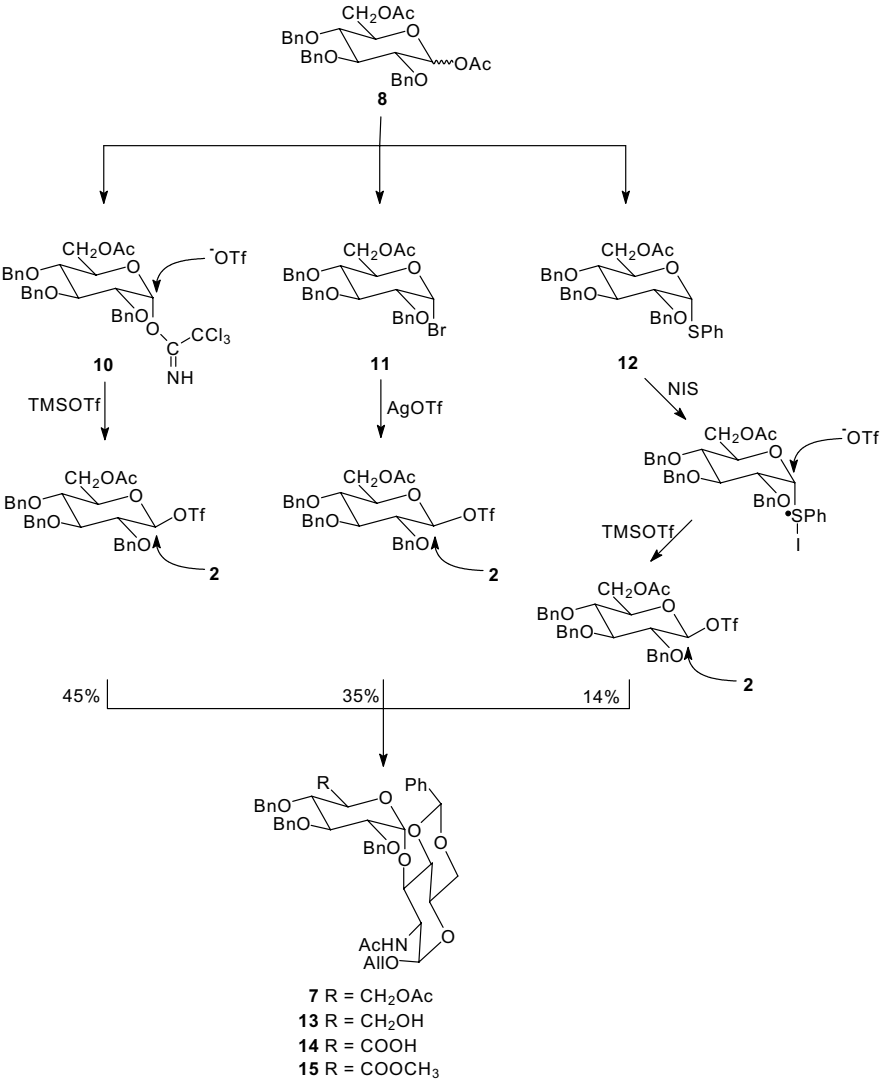
The low yield of the reaction was the result of the cleavage of the benzylidene ring with zinc chloride. So we decided to make a similar replacement in **4** before formation of the disaccharide and 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranose (**8**) was obtained in good yield. Compound **8** was used as a substrate for synthesis of three new glycosyl donors **10**–**12**. Selective 1-O-deacetylation of **8** and reaction with trichloroacetonitrile gave the trichloroacetimidate **10**. Reaction of **8** with titanium tetrabromide gave 6-*O*-acetyl-2,3,4-tri-*O*-benzyl–D-glucopyranosyl bromide (**11**). Phenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-α-D-glucopyranoside (**12**) was obtained in the reaction of **8** with thiophenol in the presence of BF_3 ethyl etherate. Condensation of **2** with **10** or **11** or **12** led to **7** in yield of 45%, 35%, and 14%, respectively. The results of the reaction of **2** with trichloroimidate **10** indicate that the replacement of the *O*-benzyl group with *O*-acetyl causes lower yield but does not change the configuration of formed glycosylic bond. Allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**13**) was obtained as the result of O-deacetylation of **7**. Oxidation of **13** under Jones conditions[23–26] gave allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**14**). Its structure was confirmed by NMR spectroscopy. Additionally a small portion of **14** was transformed into the methyl ester with iodomethane, and allyl [methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside] (**15**) was obtained. Signals of the *O*-methyl group at δ 3.68 in the ^{1}H NMR spectrum and of the carboxyl carbon atom at δ 170.5 in the ^{13}C NMR spectrum confirm the presence of a carboxyl group in the studied compound.

The results of the reaction shown in Scheme 2 clearly indicate that in the reaction studied the reactivity of glycosyl donor has an effect on yield. In all these reactions, the 1,2-*cis* glycoside is formed. These results seem to be interesting because the synthesis of 1,2-*cis* glycosides (especially oligosaccharides) is more difficult than 1,2-*trans* ones. A similar 1,2-*cis* glycoside, allyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**17**), was obtained when the glycosyl donor had the D-*galacto* configuration as shown in Scheme 3. The glycosyl donor, 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl bromide (**16**), was obtained from the appropriate 1,6-di-*O*-acetyl derivative. It is worthwhile to mention, that in the preparation of this compound, better results than those of the method of Kong and coworkers gave direct transformation (without hydrolysis) of methyl per-*O*-benzyl-D-galactoside in a mixture of acetic anhydride and acetic acid in the presence of concentrated sulfuric acid.[27] Further O-deacetylation of **17** gave the compound with a free hydroxyl group at C-6 (**18**), which was oxidized to the uronic acid derivative **19**. Purification of **19** was not effective, so the product was transformed into the methyl ester **20** and purified by column chromatography.

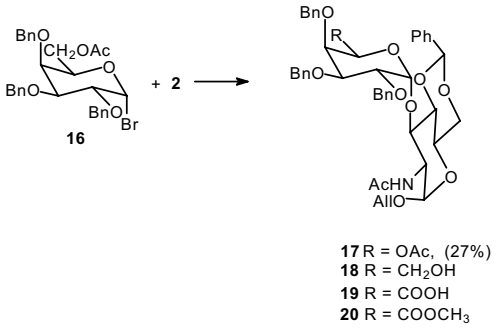
There are many elements that influence the configuration of a formed glycosyl bond. The most important is neighboring group participation. A similar disaccharide to the title compound, but with the β configuration, β-D-Glc*p*-(1 → 3)-D-Glc*p*NPhth, was obtained[28] when 6-*O*-levulinoyl-2,3,4-tri-*O*-*p*-toluoyl-D-glucopyranosyl trichl-oroacetimidate was used as the glycosyl donor and 4-methoxyphenyl 2-deoxy-4,6-*O*-benzylidene-2-phtha-



Scheme 1.



Scheme 2.



Scheme 3.

limido-α-D-glucopyranoside was the glycosyl acceptor. Because the 2-*O*-toluoyl group of the donor can participate in the reaction, the 1,2-*trans* glycoside was obtained. Another element that can influence the configuration of a formed glycosyl bond is the solvent effect. It was difficult to state the influence of the solvent on the reaction because compound **2** is not soluble in most common organic solvents used in the synthesis of glycosides. Compound **2** is very soluble in DMF, and we carried out our reactions in a mixture of DMF and dichloromethane when used in the reactions as a solvent only, DMF did not change the configuration of the formed products. In our opinion the presence of the *O*-benzylidene group is responsible for poor solubility of **2**. This observation seems to confirm the solubility of allyl 2-acetamido-3,5-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside [A compound obtained to prepare a $(1\rightarrow4)$-disaccharide; results will be prepared for publication] in dichloromethane.

Besides poor solubility, compound **2** is rather unreactive as a glycosyl acceptor (formation of desired disaccharides requires relatively long time). In our opinion this low reactivity of **2** is the main reason of the stereoselectivity of the reactions. In Scheme 2 we proposed possible explanation for α glycoside formation. In all

these cases substrate α donors in reactions with promoters are transformed into more reactive β byproducts. The role of an *O*-triflate anion in formation of glycosylic bond is known in the literature.[29] Nucleophilic substitution of the anomeric OTf group with **2** under an S_N2 mechanism gave possibility to formation of the 1,2-*cis* glycosides. The influence of the 6-*O*-acetyl group on the configuration of a formed glycoside is proposed in the literature.[30] In our opinion, in the reactions described in this paper, this effect is not the most important. This conclusion could confirm our results of condensation of **2** with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate (**5**) or 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl bromide (results in preparation for publication). The presence of a 6-*O*-benzyl or 6-*O*-*tert*-butyldimethylsilyl group in the molecule of the glycosyl donor does not change the product configuration.

In summary, allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**2**), even if it is difficultly soluble and unreactive, is interesting as the glycosyl acceptor because it affords possibilities for preparation of 1,2-*cis* glycosides found in nature.

3. Experimental

3.1. General methods

All reactions were carried out in commercially available dry solvents (Fluka, water <0.005%). Thin-layer chromatography was performed with E. Merck pre-coated Silica Gel 60 F-254 plates, and detection of compounds was achieved by charring after spraying with 5% H_2SO_4 in EtOH. Column chromatography was carried out with Kieselgel 60 Silica Gel (E. Merck, <200 mesh). ^1H and ^{13}C NMR spectra were recorded at 25 °C with a Varian Mercury spectrometer at 400 and 100 MHz, respectively, with Me_4Si as internal standard. Assignments were based on homonuclear decoupling experiments and homo- and heteronuclear correlation. Mass spectra were measured using MALDI-TOF with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. Optical rotations were measured with a JASCO J-20 polarimeter. Elemental analyses were carried out with a Carlo Erba apparatus.

3.2. Allyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (6)

Allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside **2** (0.2 g, 0.58 mmol, prepared per the Warren and Jeanloz procedure[11]) in dry DMF (17 mL) was stirred at −60 °C under dry nitrogen, and trimethylsilyl triflate (125 μL) was added. After 10 min 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate[31] **5** (0.5 g, 0.73 mmol) in dry CH_2Cl_2 (17 mL) was added dropwise, and the mixture was stirred for 1 h at −60 °C and then 16 h at rt. Next Pr_2EtN (0.1 mL) was added. The solution was concentrated and co-concentrated with toluene to dryness. The mixture was dissolved in CH_2Cl_2, washed with aq $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated. The residue was eluted from a column of silica gel with 1:3 EtOAc–toluene to give **6** (0.36 g, 71%) as an oil: $[\alpha]_D^{20}$ +50 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.4–7.24 (m, 25H, Ph), 6.25 (d, 1H, NH), 5.77 (m, 1H, =CH), 5.44 (d, 1H, $J_{1,2}$ 4.0, H-$1^{II\dagger}$), 5.42 (s, 1H, CHPh), 5.21 (m, 2H, $=CH_2$), 4.94 (d, 1H, OCH_2Ph), 4.87 (d, 1H, $J_{1,2}$ 3.2, H-1^{I}), 4.81 (d, 1H, OCH_2Ph), 4.70 (d, 1H, OCH_2Ph), 4.5 (m, 3H, OCH_2Ph), 4.39 (m, 1H, H-2^{I}), 4.24 (m, 3H, H-3^{I}, H-$6^{II'}$, OCH_2Ph), 4.20 (m, 2H, H-$6^{I'}$, OCH_2), 3.85 (m, 4H, H-3^{II}, H-4^{I}, H-5^{II}, OCH_2), 3.77 (m, 2H, H-6^{I}, H-6^{II}), 3.5 (m, 2H, H-2^{II}, H-5^{I}), 3.19 (dd, 1H, $J_{3,4}$ 10.0, $J_{4,5}$ 10.4, H-4^{II}), 1.86 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 170.69 ($NCOCH_3$), 138.89 (=CH), 138.4–126.64 (Ph), 118.07 ($=CH_2$), 102.44 (CHPh), 97.24 (C-1^{I}), 96.36 (C-1^{II}), 83.10 (C-3^{II}), 81.88 (C-4^{I}), 78.73 (C-2^{II}), 77.99 (C-4^{II}), 75.97 (OCH_2Ph), 74.75 (OCH_2Ph), 74.17 (OCH_2Ph), 72.45 (C-3^{I}), 71.03 (OCH_2Ph), 70.49 (C-6^{II}), 70.31 (C-5^{I}), 69.26 (C-6^{I}), 68.7 (OCH_2), 62.92 (C-5^{II}), 52.27 (C-2^{I}), 23.26 ($NHCOCH_3$). Anal. Calcd for $C_{52}H_{57}NO_{11}$: C, 71.64; H, 6.54; N, 1.6. Found: C, 70.95; H, 6.87; N, 1.01.

3.3. Phenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-α-D-glucopyranoside (11)

Boron trifluoride-diethyl ether (0.3 mL) was added to a solution of 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranose[22] **8** (0.87 g, 1.6 mmol) and PhSH (0.3 mL, 2.94 mmol) in dry CH_2Cl_2 (15 mL), and the mixture was stirred for 20 h at rt. Next the mixture was diluted with CH_2Cl_2, washed with aq $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated. The residue was crystallized from MeOH to give compound **11** (0.31 g, 32%), mp 112.6–113.0 °C; anomer β was not isolated. ^1H NMR ($CDCl_3$): δ 7.47–7.26 (m, 20H, Ph), 5.60 (d, 1H, $J_{1,2}$ 5.0, H-1), 5.02 (d, 1H, OCH_2Ph), 4.88 (d, 1H, OCH_2Ph), 4.82 (d, 1H, OCH_2Ph), 4.78 (d, 1H, OCH_2Ph), 4.69 (d, 1H, OCH_2Ph), 4.57 (d, 1H, OCH_2Ph), 4.03 (m, 1H, H-5), 4.28 (dd, 1H, $J_{5,6}$ 5.2, $J_{6,6'}$ 11.6, H-6), 4.07 (dd, 1H, $J_{5,6'}$ 2.0, H-6′), 3.93 (t, 1H, $J_{3,4}$ 10.0, H-3), 3.87 (dd, 1H, $J_{2,3}$ 9.6, H-2), 3.51 (dd, 1H, $J_{4,5}$ 8.8, H-4) 1.96 (s, 3H, $COOCH_3$). ^{13}C NMR δ 170.86 ($COOCH_3$), 138.68–127.54 (Ph), 86.93 (C-1), 82.63 (C-3), 79.93 (C-2), 77.34 (C-4), 76.05 (OCH_2Ph), 75.31 (OCH_2Ph), 72.74

† Indices according to Nomenclature of Carbohydrates (Recommendations 1996), *Carbohydr. Res.* **1997**, *297*, 1–92.

(OCH_2Ph), 69.78 (C-5), 63.31 (C-6), 20.10 ($COOCH_3$). Anal. Calcd for $C_{35}H_{36}O_6S$: C, 71.92; H, 6.16; S, 5.48. Found: C, 71.93; H, 6.36; S, 5.24.

3.4. 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl bromide (12)

To a solution of **8** (0.6 g, 1.1 mmol) in a mixture of EtOAc (1.1 mL), and CH_2Cl_2 (11 mL), $TiBr_4$ (1.2 g, 3.3 mmol) was added, and the mixture was stirred for 2 h at rt. The mixture was diluted with CH_2Cl_2, washed with iced-cold water, dried with $MgSO_4$, and concentrated. The syrupy residue (0.48 g) was immediately used for next reaction.

3.5. Allyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (7)

3.5.1. Procedure (a). A mixture of allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranoside (**2**) (0.2 g, 0.58 mmol), 2,4,6-collidine (0.2 mL, 1.6 mmol), and molecular sieves 4 Å (1 g) in dry DMF (15 mL) was stirred at rt under dry nitrogen, and silver triflate (0.4 g, 1.6 mmol) was added. After 10 min, 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl bromide **12** (0.48 g) in dry CH_2Cl_2 (17 mL) was added dropwise, and the mixture was stirred for 20 h at rt. Next Pr_2EtN (0.1 mL) was added. The mixture was concentrated and co-concentrated with toluene to dryness. The residue was dissolved in CH_2Cl_2, filtrated through Celite, washed with aq $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated. The residue was eluted from a column of silica gel with 1:1.5 EtOAc–toluene to give **7** (0.165 g, 35%) as an oil.

3.5.2. Procedure (b). A mixture of **2** (0.17 g, 0.49 mmol), 6-*O*-acetyl-2,3,4,-tri-*O*-benzyl-α-D-glucopyranosyl trichloroacetimidate[32] **10** (0.39 g, 0.61 mmol), and trimethylsilyl triflate (160 μL) was stirred in dry DMF (20 mL), and CH_2Cl_2 (20 mL) at −60 °C for 1 h, and then at rt for 16 h as described above for preparation from **6**. Subsequent chromatography (1:2 EtOAc–toluene) afforded **7** (0.18 g, 45%) as an oil.

3.5.3. Procedure (c). The mixture of **2** (0.15 g, 0.42 mmol), phenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-α-D-glucopyranoside **11** (0.3 g, 0.51 mmol), NIS (0.12 g, 0.51 mmol), and MS 4 Å (1 g) in a mixture of DMF (7 mL)–CH_2Cl_2 (5 mL)–EtOAc (5 mL) was stirred at 0 °C under dry nitrogen. After 5 min trimethylsilyl triflate (30 μL) was added, and the mixture was stirred for 0.5 h at 0 °C and then for 16 h at rt. The mixture was concentrated and co-concentrated with toluene to dryness. The residue was dissolved in CH_2Cl_2, filtered, washed with aq $NaHCO_3$ and water, dried with $MgSO_4$, and concentrated. The residue was eluted from a column of silica gel with 1:1 EtOAc–toluene to give **7** (49 mg, 14%) as an oil: $[\alpha]_D^{20}$ +65.9 (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.4–7.1 (m, 20H, Ph), 6.0 (d, 1H, NH), 5.89 (m, 1H, =CH), 5.49 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{II}), 5.44 (s, 1H, CHPh), 5.32 (m, 2H, $=CH_2$), 4.97 (d, 1H, OCH_2Ph), 4.89 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{I}), 4.87 (d, 1H, OCH_2Ph), 4.77 (d, 1H, OCH_2Ph), 4.53 (m, 2H, OCH_2Ph), 4.48 (m, 1H, H-2^{I}), 4.3 (d, 1H, OCH_2Ph), 4.27–4.16 (m, 4H, H-3^{I}, H-5^{II}, H-6^{II}, OCH_2), 4.12 (m, 2H, H-4^{I}, H-$6^{II,}$), 4.04 (m, 1H, OCH_2), 3.95 (m, 3H, H-3^{II}, H-6^{I}, H-$6^{I,}$), 3.77 (m, 1H, $J_{4,5}$ 9.6 Hz, $J_{5,6}$ 10.4 Hz, H-5^{I}), 3.38 (dd, 1H, $J_{2,3}$ 9.2, H-2^{II}), 3.25 (t, 1H, $J_{3,4}$ 9.2 Hz, $J_{4,5}$ 9.6 Hz, H-4^{II}), 2.08 (s, 3H,$COCH_3$), 2.02 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 171.18 ($COCH_3$), 170.35 ($NCOCH_3$), 138.86 (=CH), 138.27–126.61 (Ph), 118.72 ($=CH_2$), 102.41 (CHPh), 97.66 (C-1^{I}), 96.09 (C-1^{II}), 83.22 (C-3^{II}), 81.48 (C-4^{I}), 79.32 (C-2^{II}), 78.64 (C-4^{II}), 75.9 (OCH_2Ph), 74.77 (OCH_2Ph), 72.06 (C-5^{II}), 71.15 (OCH_2Ph), 69.2 (C-5^{I}), 68.91 (OCH_2), 68.31 (C-3^{I}), 64.58 (C-6^{II}), 62.99 (C-6^{I}), 5.86 (C-2^{I}), 23.31 ($CO\underline{C}H_3$), 21.15 ($NHCO\underline{C}H_3$); MALDITOF-MS: calcd for $C_{47}H_{53}NO_{12}$: 823.92 [M]. Found: 846.3 $[M+Na]^+$.

3.6. Allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (13)

The solution of **7** (0.364 g, 0.44 mmol) in saturated methanolic ammonia was stirred for 1 day at rt. Next the solution was concentrated to dryness to give **13** (0.33 g, 95%) as an oil: $[\alpha]_D^{20}$ +75.5 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.4–7.1 (m, 20H, Ph), 6.23 (d, 1H, NH), 5.9 (m, 1H, =CH), 5.43 (m, 2H, H-1^{II}, CHPh), 5.37 (m, 2H, $=CH_2$), 4.96 (d, 1H, OCH_2Ph), 4.89 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.68 (d, 2H, OCH_2Ph), 4.51 (m, 2H, OCH_2Ph), 4.45 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2^{I}), 4.29 (d, 1H, OCH_2Ph), 4.25–4.15 (m, 3H, H-3^{I}, H-$6^{II,}$, OCH_2), 4.02–3.73 (m, 7H, H-3^{II}, H-4^{I}, H-5^{II}, H-6^{I}, H-$6^{I,}$, H-6^{II}, OCH_2), 3.39 (dd, 1H, $J_{1,2}$ 4.0 Hz, $J_{2,3}$ 9.6 Hz, H-2^{II}), 3.22 (dd, 1H, $J_{3,4}$ 8.8 Hz, H-4^{II}), 2.02 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 170.65 ($NCOCH_3$), 138.95 (=CH), 138.45–126.6 (Ph), 118.31 ($=CH_2$), 102.41 (CHPh), 97.55 (C-1^{I}), 96.39 (C-1^{II}), 83.11 (C-3^{II}), 81.68 (C-4^{I}), 79.03 (C-2^{II}), 78.21 (C-4^{II}), 75.87 (OCH_2Ph), 74.77 (OCH_2Ph), 72.78 (C-3^{I}), 71.28 (C-5^{II}), 71.02 (OCH_2Ph), 69.23 (C-6^{II}), 68.87 (OCH_2), 62.98 (C-5^{I}), 62.94 (C-6^{I}), 52.11 (C-2^{I}), 23.26 ($NHCO\underline{C}H_3$). Anal. Calcd or $C_{45}H_{51}NO_{11}$: C, 69.14; H, 6.53; N, 1.79. Found: C, 69.0; H, 6.64; N, 2.07.

3.7. Allyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (14)

The mixture containing CrO_3 (0.47 g, 4.7 mmol), concd H_2SO_4 (0.39 mL) and water (1.9 mL) was added dropwise to a solution of **13** (0.41 g, 0.53 mmol) in acetone

(15 mL). Then the reaction mixture was poured into ice-water and extracted with EtOAc. The EtOAc solution was washed with water, dried with $MgSO_4$, and concentrated. The residue was eluted from a column of silica gel with 10:9:1 CH_2Cl_2–EtOAc–AcOH to give **14** (0.3 g, 72%) as an oil: $[\alpha]_D^{20}$ +64.5 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.38–7.08 (m, 20H, Ph), 6.37 (d, 1H, NH), 5.89 (m, 1H, =CH), 5.56 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1^{II}), 5.43 (s, 1H, CHPh), 5.29 (m, 2H, $=CH_2$), 4.92 (d, 1H, OCH_2Ph), 4.84 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{I}), 4.74 (m, 2H, OCH_2Ph), 4.55 (m, 3H, H-2^{I}, OCH_2Ph), 4.35 (d, 1H, $J_{4,5}$ 10 Hz, H-5^{II}), 4.49 (d, 1H, OCH_2Ph), 4.29 (d, 1H, OCH_2Ph), 4.24 (m, 1H, H-3^{I}), 4.17 (m, 1H, OCH_2), 3.99 (m, 1H, OCH_2), 3.90 (m, 4H, H-3^{II}, H-4^{I}, H-6^{I}, H-6$^{I'}$), 3.74 (m, 1H, $J_{4,5}$ 9.6 Hz, $J_{5,6}$ 10.4 Hz, H-5^{I}), 3.64 (dd, 1H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.6, H-4^{II}), 3.44 (dd, 1H, $J_{2,3}$ 10, H-2^{II}), 2.09 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 173.57 (COOH), 171.49 (N*C*OCH_3), 138.77 (=CH), 138.17–126.54 (Ph), 118.66 ($=CH_2$), 102.22 (CHPh), 97.45 (C-1^{I}), 96.88 (C-1^{II}), 82.78 (C-3^{II}), 80.78 (C-4^{I}), 78.99 (C-4^{II}), 78.37 (C-2^{II}), 75.97 (OCH_2Ph), 74.94 (OCH_2Ph), 73.37 (C-3^{I}), 71.55 (OCH_2Ph), 70.54 (C-5^{II}), 69.12 (C-5^{I}), 68.75 (OCH_2), 62.74 (C-6^{I}), 51.86 (C-2^{I}), 23.39 (NCO*C*H_3); MALDITOF-MS: Calcd for $C_{45}H_{49}O_{12}N$: 795.87 [M]. Found: 818.2 $[M+Na]^+$.

3.8. Allyl (methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside) (15)

To a solution of **14** (50 mg, 0.07 mmol) in dry DMF (1.5 mL) was added $KHCO_3$ (50 mg, 0.5 mmol) and CH_3I (40 μL, 0.64 mmol). The mixture was stirred 1 h at 0 °C. After evaporation, the residue was dissolved in CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated gave **15** (35 mg, 62%) as an oil: $[\alpha]_D^{20}$ +63.2 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.4–7.1 (m, 20H, Ph), 5.93 (m,1H, =CH), 5.85 (d, 1H, NH), 5.54 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{II}), 5.39 (s, 1H, CHPh), 5.29 (m, 2H, $=CH_2$), 4.92 (d, 1H, OCH_2Ph), 4.88 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.76 (d, 1H, OCH_2Ph), 4.62 (m, 2H, OCH_2Ph), 4.55–4.48 (m, 2H, H-2^{I}, OCH_2Ph), 4.38 (d,1H, $J_{4,5}$ 10.4 Hz, H-5^{II}), 4.27 (d, 1H, OCH_2Ph), 4.18 (m, 2H, H-3^{I}, OCH_2), 4.02 (m, 1H, OCH_2), 3.88 (m, 4H, H-3^{II}, H-4^{I}, H-6^{I}, H-6$^{I'}$), 3.74 (dd, 1H, $J_{4,5}$ 10.0 Hz, $J_{5,6}$ 10.4 Hz, H-5^{I}), 3.68 (s, 3H, $COOCH_3$), 3.63 (t, 1H, $J_{3,4}$ 9.2 Hz, H-4^{II}), 3.43 (dd, 1H, $J_{2,3}$ 10 Hz, H-2^{II}), 2.08 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 170.5 (*C*OOCH_3), 170.08 (N*C*OCH_3), 138.8 (=CH), 138.2–126.5 (Ph), 118.49 ($=CH_2$), 102.29 (CHPh), 97.45 (C-1^{I}), 96.99 (C-1^{II}), 82.99 (C-3^{II}), 80.9 (C-4^{I}), 78.99 (C-4^{II}), 78.37 (C-2^{II}), 75.98 (OCH_2Ph), 74.77 (OCH_2Ph), 73.17 (C-3^{I}), 71.42 (OCH_2Ph), 70.92 (C-5^{II}), 69.17 (C-5^{I}), 68.83 (OCH_2), 62.74 (C-6^{I}), 52.65 (COO*C*H_3), 51.79 (C-2^{I}), 23.51 (NCO*C*H_3); MALDITOF-MS: Calcd for $C_{46}H_{51}NO_{12}$: 809.9 [M]. Found: 832.4 $[M+Na]^+$.

3.9. 1,6-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-galactopyranose[33] (16)

Concd H_2SO_4 (1.53 mL) was added dropwise to a stirred solution of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranoside (8.2 g, 14.8 mmol) in a mixture of AcOH (39 mL) and Ac_2O (39 mL) at 0 °C. After 1 h water (100 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with aq $NaHCO_3$ water, dried with $MgSO_4$, and concentrated to give **16** (6.5, 82%) as an oil: ^1H NMR ($CDCl_3$): δ 7.4–7.25 (m, 15H, Ph), 6.39 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.98 (d, 1H, OCH_2Ph), 4.88 (d, 1H, OCH_2Ph), 4.76 (d, 1H, OCH_2Ph), 4.71 (m, 2H, OCH_2Ph), 4.62 (d, 1H, OCH_2Ph), 4.18 (dd, 1H, $J_{1,2}$ 10.0 Hz, $J_{2,3}$ 10.0 Hz, H-2), 4.13 (dd, 1H, $J_{5,6}$ 6.4 Hz, $J_{6,6'}$ 10.8 Hz, H-6), 4.07 (dd, 1H, $J_{5,6'}$ 6.0 Hz, H-6′), 4.02 (m, 1H, H-5) 3.92 (bd, 1H, H-4), 3.88 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3), 2.12 (s, 3H, COOCH_3), 1.98 (s, 3H, $COOCH_3$). ^{13}C NMR δ 170.78 (*C*OOCH_3), 169.63 (*CO*OCH_3), 138.68–127.63 (Ph), 90.84 (C-1), 78.78 (C-3), 75.55 (C-2), 74.89 (OCH_2Ph), 74.37 (C-4), 73.62 (OCH_2Ph), 73.61 (OCH_2Ph), 71.01 (C-5), 63.27 (C-6), 21.35 (COO*C*H_3), 21.02 (COO*C*H_3).

3.10. 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl bromide[33] (17)

Compound **17** was prepared from **16** (1.09 g, 2.03 mmol) as described for the preparation of **12**, yielding (0.93 g). The syrupy product was immediately used for next reaction.

3.11. Allyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (18)

Glycosylation of **2** (0.36 g, 1.03 mmol) with bromide **17** (0.9 g) in dry DMF (15 mL) and CH_2Cl_2 (15 mL) promoted by silver triflate (0.75 g, 2.9 mmol) was carried out as described above for preparation of **7** (procedure b). Subsequent purification of the product by column chromatography (1:1.5 EtOAc–toluene) afforded **18** (0.23 g, 27%) as an oil: $[\alpha]_D^{20}$ +66.7 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.4–7.1 (m, 20H, Ph), 5.98 (d, 1H, NH), 5.9 (m, 1H, =CH), 5.43 (d, 1H, $J_{1,2}$ 4.0, H-1^{II}), 5.44 (s, 1H, CHPh), 5.3 (m, 2H, $=CH_2$), 4.97 (d, 1H, OCH_2Ph), 4.87 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{I}), 4.85 (d, 1H, OCH_2Ph), 4.74 (d, 1H, OCH_2Ph), 4.53 (m, 2H, OCH_2Ph), 4.48 (m, 1H, H-2^{I}), 4.29 (d, 1H, OCH_2Ph), 4.26–4.22 (m, 2H, H-6^{I}, H-6^{II}), 4.19 (m, 1H, OCH_2), 4.16–4.07 (m, 3H, H-3^{I}, H-5^{II}, H-6^{II,}), 4.03 (m, 1H, OCH_2), 3.91 (m, 3H, H-3^{II}, H-4^{II}, H-5^{I}), 3.76 (m, 1H, $J_{6,6'}$ 10.0 Hz, H-6$^{II'}$), 3.38 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2^{II}), 3.25 (t, 1H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.6, H-4^{II}), 2.08 (s, 3H,$COCH_3$), 2.02 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 171.19 (*C*OCH_3), 170.33 (N*C*OCH_3), 138.89 (=CH), 138.29–125.51 (Ph),

118.74 (=CH_2), 102.44 (CHPh), 97.71 (C-1^I), 96.08 (C-1^{II}), 83.28 (C-5^I), 81.49 (C-3^{II}), 78.68 (C-2^{II}), 77.99 (C-4^{II}), 75.93 (OCH_2Ph), 74.8 (OCH_2Ph), 72.08 (C-3^I), 71.19 (OCH_2Ph), 69.23 (C-6^I), 68.93 (OCH_2), 68.33 (C-5^{II}), 64.61 (C-6^{II}), 62.99 (C-4^{II}), 5.88 (C-2^I), 23.35 ($CO\mathit{C}H_3$), 21.16 ($NHCO\mathit{C}H_3$); MALDITOF-MS: Calcd for $C_{47}H_{53}NO_{12}$: 823.92 [M]. Found: 846.3 $[M+Na]^+$.

3.12. Allyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (19)

Compound **19** was prepared from **18** (0.2 g, 0.19 mmol) as described for the preparation of **13**, yielding (0.16 g, 85%) as a syrup: $[\alpha]_D^{20}$ +74.2 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.38–7.1 (m, 20H, Ph), 6.26 (d, 1H, NH), 5.87 (m, 1H, =CH), 5.55 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{II}), 5.38 (s, 1H, CHPh), 5.22 (m, 2H, =CH_2), 4.87 (m, 2H, OCH_2Ph, H-1^I), 4.69 (d, 1H, OCH_2Ph), 4.52 (m, 2H, OCH_2Ph), 4.39 (dd, 1H, $J_{1,2}$ 4.0 Hz, $J_{2,3}$ 9.6 Hz, H-2^I), 4.31 (d, 1H, OCH_2Ph), 4.22–4.11 (m, 4H, H-3^I, H-$6^{I'}$, H-$6^{II,}$, OCH_2Ph), 4.01–3.93 (m, 3H, H-2^{II}, H-5^{II}, OCH_2), 3.89–3.79 (m, 4H, H-3^{II}, H-5^I, H-6^I, OCH_2), 3.65 (m, 2H, H-4^I, H-6^{II}), 3.35 (dd, 1H, $J_{3,4}$ 11.6 Hz, $J_{4,5}$ 2.8 Hz, H-4^{II}), 1.98 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 170.63 ($N\mathit{C}OCH_3$), 138.89 (=CH), 138.4–126.47 (Ph), 118.27 (=CH_2), 102.07 (CHPh), 97.39 (C-1^I), 96.31 (C-1^{II}), 82.81 (C-5^I), 78.88 (C-3^{II}), 75.76 (C-5^{II}), 75.09 (C-4^I), 75.46 (OCH_2Ph), 75.02 (OCH_2Ph), 73.04 (C-3^I), 71.53 (OCH_2Ph), 70.82 (C-2^{II}), 69.16 (C-6^I), 68.83 (OCH_2), 63.2 (C-6^{II}), 62.76 (C-4^{II}), 52.23 (C-2^I), 23.18 ($NHCO\mathit{C}H_3$); MALDITOF-MS: Calcd for $C_{45}H_{51}NO_{11}$: 781.89 [M]. Found: 804.2 $[M+Na]^+$.

3.13. Allyl (methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyluronate-(1 → 3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside) (20)

Compound **20** was prepared from **19** (0.16 g, 0.2 mmol) as described for the preparation of **14**. After oxidation the oil was converted to the methyl ester as described above for preparation of **15** and subsequently purified by column chromatography (2:1 EtOAc–toluene) afforded **20** (81 mg, 50%) as an oil: $[\alpha]_D^{20}$ 113.8 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.35–7.08 (m, 20H, Ph), 5.88 (m,1H, =CH), 5.81 (d, 1H, NH), 5.63 (s, 1H, H-1^{II}), 5.35 (s, 1H, CHPh), 5.23 (m, 2H, =CH_2), 4.85 (m, 3H, H-1^I, OCH_2Ph), 4.73 (d, 1H, OCH_2Ph), 4.47 (m, 3H, H-5^{II}, OCH_2Ph), 4.4 (dd, $J_{1,2}$ 4.0, $J_{2,3}$ 10.4 Hz, 1H, H-2^I), 4.32 (d, 1H, OCH_2Ph), 4.22–4.1 (m, 4H, H-3^I, H-3^{II}, H-6^I, OCH_2), 3.98 (m, 3H, H-2^{II}, H-$6''$, OCH_2), 3.85 (m, 2H, H-4^I, H-4^{II}), 3.72 (dd, 1H, $J_{4,5}$ 9.2 Hz, $J_{5,6}$ 10.4 Hz, H-5^I), 3.59 (s, 3H, $COOCH_3$), 1.91 (s, 3H, $NCOCH_3$). ^{13}C NMR δ 169.98 ($\mathit{C}OOCH_3$), 169.53 ($N\mathit{C}OCH_3$), 138.79 (=CH), 138.41–126.44 (Ph), 118.83 (=CH_2), 102.94 (CHPh), 97.89 (C-1^I), 97.16 (C-1^{II}), 82.41 (C-4^I), 77.98 (C-2^{II}), 78.99 (C-4^{II}), 76.54 (C-3^I), 74.97 (C-6^I), 74.91 (C-3^{II}), 74.82 (OCH_2Ph), 73.88 (OCH_2Ph), 71.87 (OCH_2Ph), 71.27 (C-5^{II}), 69.06 (C-5^I), 68.76 (OCH_2), 62.51 (C-4^{II}), 52.36 ($COO\mathit{C}H_3$), 51.79 (C-2^I), 23.38 ($NCO\mathit{C}H_3$); MALDITOF-MS: Calcd for $C_{46}H_{51}NO_{12}$: 809.9 [M]. Found: 832.2 $[M+Na]^+$.

Acknowledgements

This work was supported by a research grants BW/8000-5-0237-3 and DS/8361-4-0134-3 from the Polish State Committee for Scientific Research (KBN).

References

1. Chernyak, A. Ya.; Komarov, L. O.; Kochetkov, N. K. *Carbohydr. Res.* **1991**, *216*, 381–398.
2. Cedzyński, M.; Knirel, Y. A.; Różalski, A.; Shaskov, A. S.; Vinogradov, E. V.; Kaca, W. *Eur. J. Biochem.* **1995**, *232*, 558–562.
3. Furnsinn, C.; Sanderson, A. L.; Radda, G. K.; Leighton, B. *Int. J. Biochem. Cell Biol.* **1995**, *27*, 805–814.
4. L'vov, V. L.; Shaskov, A. S.; Knirel, Y. A.; Arifulina, A. E.; Senchenkova, S. N.; Yakovlev, A. V.; Dimitriev, B. *Carbohydr. Res.* **1995**, *279*, 183–192.
5. Katzenellenbogen, E.; Kübler, J.; Gamian, A.; Kocharova, N. A.; Knirel, Y. A.; Kochetkov, N. K. *Carbohydr. Res.* **1996**, *293*, 61–70.
6. Swierzeko, A. St.; Shaskov, A. S.; Senchenkova, S. N.; Toukach, F. V.; Paramonov, N. A.; Kaca, W.; Knirel, Y. A. *FEBS Letters* **1995**, *398*, 297–302.
7. Perry, M. B.; MacLean, L. L. *Carbohydr. Res.* **1999**, *322*, 57–66.
8. Cox, A. D.; Brisson, J. R.; Thibault, P.; Perry, M. B. *Carbohydr. Res.* **1997**, *304*, 191–208.
9. Perpelov, A. V.; Senchenkova, S. N.; Torzewska, A.; Bartodziejska, B.; Shaskov, A. S.; Rozalski, A.; Knirel, Y. A. *Carbohydr. Res.* **2000**, *328*, 229–234.
10. Holst, O.; Brade, L.; Kosma, P.; Brade, H. *J. Bacteriol.* **1991**, *173*, 1862–7866.
11. Warren, Ch. D.; Jeanloz, R. W. *Carbohydr. Res.* **1977**, *53*, 67–84.
12. Bowering, W. D.; Timell, T. E. *J. Am. Chem. Soc.* **1960**, *82*, 2827–2830.
13. Madaj, J.; Trynda, A.; Jankowska, M.; Wiśniewski, A. *Carbohyr. Res.* **2002**, *337*, 1495–1498.
14. Urban, F. J.; Moore, B. S.; Breitenbach, R. *Tetrahedron Lett.* **1990**, *16*, 4421–4424.
15. Ziegler, T.; Kovač, P.; Glaudemans, C. P. J. *Liebigs Ann.. Chem.* **1990**, 613–616.
16. Nakahara, Y.; Ogawa, T. *Tetrahedron Lett.* **1987**, *28*, 2731–2734.
17. Lonn, H.; Lonngren, J. *Carbohydr. Res.* **1984**, *132*, 39–44.
18. Sajtos, F.; Hajko, J.; Köver, K. E.; Liptak, A. *Carbohydr. Res.* **2001**, *341*, 253–259.
19. Carter, M. B.; Petillo, P. A.; Anderson, L.; Lerner, L. E. *Carbohydr. Res.* **1994**, *258*, 299–306.
20. Halkes, K. M.; Vermeer, H. J.; Slaghek, T. M.; Hooft, P. A. V.; Loof, A.; Kamerling, J. P.; Vliegenthart, J. F. G. *Carbohydr. Res.* **1998**, *309*, 15–188.

21. Oxidation of primary alcohol group of allyl 2-acetamido-2-deoxy-α-D-glucopyranoside derivative, 3rd International Conference of Ph.D Students, Miskolc, 2001.
22. Yang, G.; Ding; Kong, F. *Tetrahedron Lett.* **1987**, *38*, 6725–6728.
23. Bowden, K.; Heilbron, I. M.; Jones, E. R. H. *J. Chem. Soc.* **1946**, 39–45.
24. Heilbron, I. M.; Jones, E. R. H.; Sondheimer, F. *J. Chem. Soc.* **1949**, 604–607.
25. Haynes, L. J.; Heilbron, I. M.; Jones, E. R. H.; Sondheimer, F. *J. Chem. Soc.* **1947**, 1583–1586.
26. Heilbron, I. M.; Jones, E. R. H.; Sondheimer, F. *J. Chem. Soc.* **1947**, 1583–1590.
27. Ponpipom, M. M. *Carbohydr. Res.* **1977**, *59*, 311–318.
28. Slaghek, T. M.; Nakahara, Y.; Ogawa, T.; Kamerling, J. P.; Vliegenthart, J. F. G. *Carbohydr. Res.* **1994**, *255*, 61–85.
29. Zeng, Y.; Ning, J.; Kong, F. *Tetrahedron Lett.* **2002**, *43*, 3729–3733.
30. Cheng, Y. P.; Chen, H. T.; Lin, Ch. *Tetrahedron Lett.* **2002**, *43*, 7721–7723.
31. Schmidt, R. R.; Michel, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 731–732.
32. Hoch, M.; Heinz, E.; Schmidt, R. R. *Carbohydr. Res.* **1989**, 21–28.
33. Nashed, M. A.; Anderson, L. *Carbohydr. Res.* **1976**, *51*, 65–72.