ELSEVIER

Carbohydrate Research 337 (2002) 1803–1810

CARBOHYDRATE RESEARCH

www.elsevier.com/locate/carres

The use of tri-*O*-acetyl-D-glucal and -D-galactal in the synthesis of 3-acetamido-2,3-dideoxyhexopyranoses and -hexopyranosides

Beata Liberek, Aleksandra Dąbrowska, Ryszard Frankowski, Marlena Matuszewska, Zygfryd Smiatacz*

Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, PL-80-952 Gdańsk, Poland

Received 12 February 2002; received in revised form 11 July 2002; accepted 13 August 2002

Abstract

Addition of hydrazoic acid to α,β-unsaturated aldehydes derived from tri-*O*-acetyl-D-glucal and -D-galactal gave 3-azido-2,3-dideoxyhexopyranoses. These were converted into 1,4,6-tri-*O*-acetyl-3-azido-2,3-dideoxyhexopyranoses as well as methyl and ethyl glycosides. Hydrogenation of the proamine group in 3-azido-2,3-dideoxy derivatives provided different 3-amino and 3-acetamido sugars. The configuration and conformation of all products were established on the basis of the ^{1}H and ^{13}C NMR, IR and polarimetric data.

Keywords: Hydrazoic acid; 3-Azide-2,3-dideoxy sugar; Hydrogenation; 3-Amine-2,3-dideoxy saccharide; AZT

1. Introduction

3-Azido-2,3-dideoxy sugars are of great interest as they may be used as precursors of different bio-active substances. Among them are 3-amino-2,3,6-trideoxyhexopyranoses, an important class of compounds found as structural components of various glycosidic and polysaccharide antibiotics[1] and 3-nitrosoureido sugars, which are highly active antitumor agents.[2] In addition, 3′-azido-2′,3′-dideoxy nucleosides are promising agents against retrovirus infections, especially human immunodeficiency virus (HIV).[3,4] 3′-Azido-3′-deoxythymidyne (AZT) is one of the most active nucleosides against HIV. It has been shown that human liver microsomes metabolize AZT to a toxic metabolite 3′-amino-3′-deoxythymidine (AMT).[5]

Acetylated glycals, treated with 0.02 molar equivalents of mercuric sulfate in a solvent consisting of 5 mM sulfuric acid and 1,4-dioxane undergo the transformation into α,β-unsaturated aldehydes.[6] Literature data have shown that conjugate addition of hydrazoic acid to α,β-unsaturated aldehydes, derived from tri-*O*-acetyl-D-glucal,[7–11] di-*O*-acetyl-L-rhamnal,[12] and di-*O*-acetyl-L-arabinal[13] is a convenient method for preparation of 3-azido-2,3-dideoxy hexopyranoses and pentofuranoses.

This paper describes the use of tri-*O*-acetyl-D-glucal and -D-galactal in the synthesis of 3-azido-2,3-dideoxy-hexopyranoses (via 1,4-addition of HN_3 to corresponding pseudoglycals), methyl and ethyl hexopyranosides and their transformation into 3-amino or 3-acetamido analogues. Some of the methyl 3-azido-2,3-dideoxy-hexopyranosides were later converted into 3-azido-2,3,6-trideoxy-6-iodo-hexopyranosides, useful intermediates in the synthesis of 3-amino-2,3,6-trideoxy-hexopyranoses or aminocyclitoles.[14]

2. Results and discussion

As previously reported,[9] starting from tri-*O*-acetyl-D-glucal **1** the mixture of 4,6-di-*O*-acetyl-3-azido-2,3-dideoxy-hexopyranoses ($\mathbf{3_{a-d}}$) was synthesized, in one-pot reaction, without isolation of hex-2-enoses (Scheme 1). The mixture $\mathbf{3_{a-d}}$ obtained was not separated. A similar mixture of $\mathbf{4_{a-d}}$ was obtained from and tri-*O*-acetyl-D-galactal **2**. Acetylation of $\mathbf{3_{a-d}}$ with acetic

* Corresponding author. Tel.: +48-58-3450334; fax: +48-58-3410357

E-mail address: smiatacz@chemik.chem.univ.gda.pl (Z. Smiatacz).

0008-6215/02/$ - see front matter
PII: S0008-6215(02)00288-4

anhydride in pyridine gave four diastereoisomers of 1,4,6-tri-*O*-acetyl-3-azido-2,3-dideoxyhexopyranoses (**5**–**8**) in the ratio **5**:**6**:**7**:**8** ~ 13:26:7:1, separated by column chromatography. Next, four methyl (**13**–**16**) and four ethyl (**17**–**20**) 4,6-di-*O*-acetyl-3-azido-2,3-dideoxy-D-*arabino*- and -D-*ribo*-hexopyranosides were formed by treatment of $\mathbf{3}_{\mathbf{a-d}}$ with methanol or ethanol *plus* methanesulfonyl chloride and *s*-collidine. Analogous methyl glycosidation of $\mathbf{4}_{\mathbf{a-d}}$ gave four 4,6-di-*O*-acetyl-3-azido-2,3-dideoxy-D-*lyxo*- and -D-*xylo*-hexopyranosides (**21**–**24**) (Scheme 2).

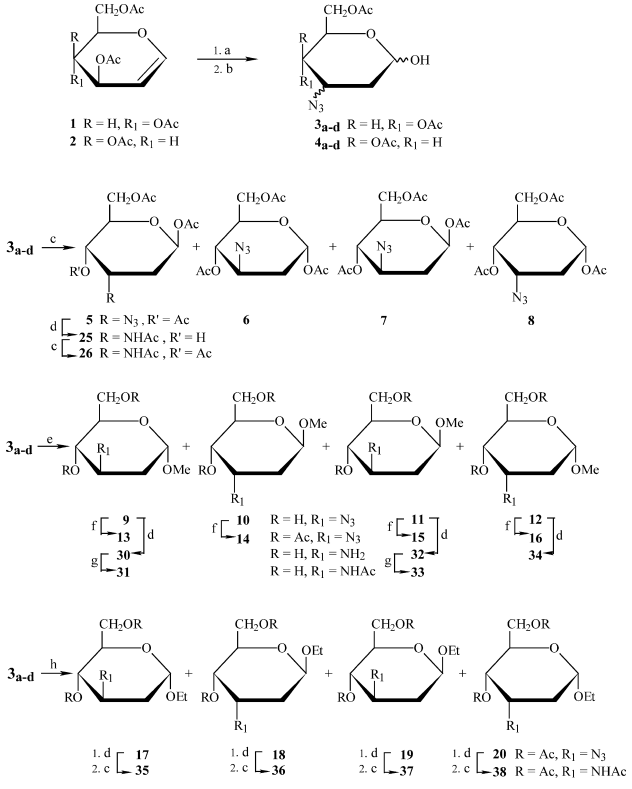
Separation of the crude mixture of the methyl glycosides **13**–**16** was possible only after column chromatography, deacetylation of two separated fractions, and repeated column chromatography,[8–10] which gave in turn: α-D-*arabino* (**9**), β-D-*ribo* (**10**), β-D-*arabino* (**11**), and α-D-*ribo* (**12**) isomers of deacetylated methyl glycosides. Respective acetylation of **9**–**12** allowed to obtain **13**–**16** in the ratio **13**:**14**:**15**:**16** ~ 2:1:2.5:1. Ethyl glycosides with -D-*arabino* (**17**, **19**) and -D-*ribo* (**18**, **20**) configurations were separated using analogous procedure as in methyl glycosides (**17**:**18**:**19**:**20** ~ 1:2.4:3.4:1). Isolation of pure methyl glycosides with -D-*lyxo*- (**21**, **24**) and -D-*xylo*- structures (**22**, **23**) was possible without additional deacetylation.

The configuration and conformation of **5**–**24** were established on the basis of the ^{1}H NMR spectra and polarimetric data. In the case of D-*arabino* and D-*lyxo* configurations, H-1 signals of the α anomers (**6**, **9**, **13**, **17**, **21**) appeared at higher δ values than those of the analogous protons of β anomers (**7**, **11**, **15**, **19**, **24**) ($\Delta\delta \sim 0.4$) owing to the respective equatorial and axial orientation of H-1. This regularity was disturbed in D-*ribo* (**5**, **8**, **10**, **12**, **14**, **16**, **18**, **20**) and D-*xylo* isomers (**22**, **23**) because of the axially oriented 3-azido group, which considerably deshielded H-1 proton in β anomers. However, the only one, weak coupling of the H-1 proton with axially oriented H-2 ($J_{1,2a}$ 2–4 Hz) left no doubt about the configuration of the anomeric center of all the α anomers (**6**, **8**, **9**, **12**, **13**, **16**, **17**, **20**, **21**, **23**). Respectively, two different coupling constants ($J_{1,2a}$ 9–10 and $J_{1,2e}$ 2–3 Hz) were diagnostic for all β anomers (**5**, **7**, **10**, **11**, **14**, **15**, **18**, **19**, **22**, **24**). Next, the strong coupling of H-3 and axially oriented H-2 ($J_{2a,3}$ 12–13 Hz) indicated axial orientation of H-3 proton and consequently D-*arabino* or D-*lyxo* structures of **6**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, **21**, **24**. Analogously, $J_{2a,3}$ 3–4 Hz was characteristic for equatorially oriented H-3 proton and D-*ribo* or D-*xylo* configurations of **5**, **8**, **10**, **12**, **14**, **16**, **18**, **20**, **22**, **23**. The coupling constants $J_{3,4} \sim J_{4,5}$ 9–10 Hz made us sure about D-*arabino* structure of **6**, **7**, **9**, **11**, **13**, **15**, **17**, **19** the same as $J_{3,4}$ 3–4 Hz together with $J_{4,5}$ 9–10 Hz implied D-*ribo* configuration of **5**, **8**, **10**, **12**, **14**, **16**, **18**, **20**. Likewise, $J_{4,5} \sim 1$ Hz is diagnostic for D-*lyxo* and D-*xylo* structures of **21**–**24**.[15]

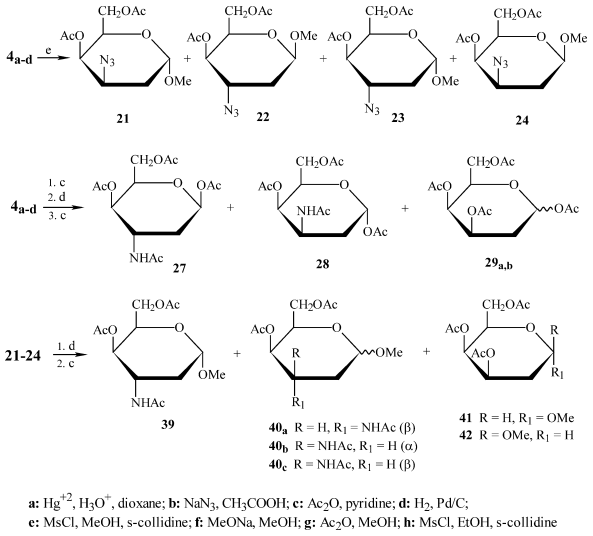
All the above findings were in accordance with the $^4C_1$ conformation of compounds **5**–**24**.

A good stereoselectivity of the 1,4-addition of hydrazoic acid to the hex-2-enopyranoses generated from tri-*O*-acetyl-D-glucal was in agreement with literature data[10] and provided compounds mainly with -D-*arabino* structure (*arabino*:*ribo* ~ 2.5:1), having the azido group equatorially oriented (**6**, **7**, **13**, **15**, **17**, **19**). This stereoselectivity was lost when addition of HN_3 occurred to di-*O*-acetylpseudogalactal. Our results showed the amounts of -D-*xylo*- glycosides (**22**, **23**), having the azido group axially oriented were higher than with -D-*lyxo*- ones (**21**, **24**). The ratio of the *xylo* versus *lyxo* isomers was difficult to estimate since there were always traces of the unseparated compounds **21**–**24** after column chromatography. Nevertheless, methyl glycosides with D-*xylo* configuration (**22**,**23**) were gained in 49% whereas with D-*lyxo* structure (**21**,**24**) in 22%. This lack of stereoselectivity may be due to the 4-OAc group which is a steric hindrance for an equatorial attack of azide anion on the hex-2-enopyranoses generated from D-galactal (**2**).

Catalytic hydrogenation of the azides was studied variously. *O*-Acetyl-3-azido (**4**, **5**, **17**–**20**, **21**–**24**) as well as 3-azido derivatives (**9**, **11**, **12**), single compounds (**5**, **9**, **11**, **12**, **17**–**20**) and unseparated mixtures of isomers (**4**, **21**–**24**) were hydrogenated. Three of the products of reduction were isolated as 3-amino derivatives (**30**, **32**, **34**) and the majority as 3-acetamido



Scheme 1.



Scheme 2.

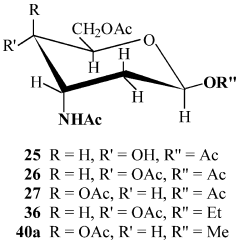


Fig. 1.

sugars (**26**–**28**, **31**, **33**, **35**–**40**$_{a-c}$). Compounds **25**, **29**$_{a,b}$, **41** and **42** were unexpected products of reactions.

Transformation of the deacetylated 3-azido glycosides (**9**, **11**, **12**) into 3-amino glycosides was achieved in good yield (85%). Reduction of the acetylated 3-azido compounds (**5**, **17**–**20**) was also efficient however $O \rightarrow N$ migration occurred during hydrogenation of **5**, causing acetylation of 3-amino group by the neighboring 4-OAc group and isolation of 3-acetamido derivative (**25**). This $O \rightarrow N$ migration was possible since 3-azido and 4-OAc groups in **5** had *cis* orientation. The proof that intramolecular acetylation of amine group occurred was provided by IR spectra, where two amide bands (1650, 1545 cm^{-1}) next to C=O vibrations (1730 cm^{-1}) as well as OH band (3240 cm^{-1}) were visible. Furthermore, the ^1H NMR spectra of **25** showed the 3-NHAc signal (δ 6.50) corresponding to one proton and 4-OH signal (δ 4.35) coupled with H-4 proton ($J_{4,OH}$ 4 Hz).

The idea to reduce unseparated mixtures **4a**–**d** and **21**–**24** was unprofitable since separation of the mixtures after hydrogenation (**27**–**29**, **39**–**42**) was complicated and inefficient. Hydrogenation of **4a**–**d** followed by acetylation afforded only two products of reduction (**27**, **28**) with overall yield 43% and traces of per-*O*-acetyl-2-deoxypyranoses (**29**$_{a,b}$, 5%). Similarly, reduction of the mixture **21**–**24** provided four products of hydrogenation: **39** (31%), not separated mixture **40**$_{a-c}$ (13%) and again small amounts of per-*O*-acetylated glycosides **41** and **42** (overall yield 4%).

The presence of the 3-OAc instead of 3-N_3 or 3-NHAc groups in **29**$_{a,b}$, **41** and **42** was demonstrated by ^1H NMR and IR spectra. The ^1H NMR of **29**$_{a,b}$, **41** and **42** revealed the additional singlet at $\delta \sim 2$, corresponding to three protons. Furthermore, the azide and amide bands were absent in the IR spectra.

The isolation of 3-OAc products (**29**$_{a,b}$, **41**, **42**) after the hydrogenation indicated that addition of the hydrazoic acid to α,β-unsaturated aldehyde derived from tri-*O*-acetyl-D-galactal was probably accompanied by addition of acetic acid present in the reaction medium. The last addition proceeded in traces so we did not find the responsive products on TLC. It seems less likely that 3-azide or 3-amine group could be substituted by acetoxy ion during hydrogenation followed by acetylation.

The configurations of the hydrogenation products had to be the same as their precursors. These were confirmed by ^1H NMR spectra and polarimetric data.

The coupling constant $J_{4,5}$ 9–10 Hz in the case of D-*arabino* (**30**–**33**, **35**, **37**) and α-D-*ribo* (**34**, **38**) products of reduction indicated $^4C_1$ conformation. Next, $J_{4,5} \sim 1$ Hz was diagnostic for $^4C_1$ form of α-D-*xylo* (**39**) and D-*lyxo* (**28**, **29**$_{a,b}$, **40**$_{b,c}$–**42**) isomers. The remaining coupling constants and chemical shifts were also in agreement with adoption of the $^4C_1$ form by above mentioned compounds.

Deviations from $^4C_1$ conformation were found for the hydrogenation products having β-D-*ribo* (**25**, **26**, **36**) and β-D-*xylo* (**27**, **40**$_a$) structures. These findings were supported by $J_{1,2a}$ coupling constants, which were not characteristic for the axial–axial orientation of H-1 and H-2a [$J_{1,2a}$: 5 (**25**), 4 (**26**, **36**), 6.8 (**27**), and 7.2 Hz (**40a**)]. The examination of $J_{4,5}$ coupling constants also called for a deformation of the $^4C_1$ chair form [$J_{4,5}$: 6 (**25**), 3.5 (**26**), 2.4 (**27**), 4 (**36**), and 2.8 Hz (**40a**)].

All of the compounds having a conformation other than $^4C_1$ form were β-glycosides with axially oriented 3-NHAc group (Fig. 1). This axial orientation of a bulky 3-NHAc group as well as anomeric effect were probably responsible for changes in $^4C_1$ conformation.

Noteworthy are the effects of substituents on the chemical shifts of H-3 protons in the ^1H NMR spectra. The comparison of these substituents showed that their deshielding influence on the H-3 proton changed in the order: -NH_2 (δ 2.8–3.4), -N_3 (δ 3.3–4.1), -NHAc (δ 4.2–4.7), and -OAc (δ 5.0–5.3). These findings are in accordance with stereoelectronic interactions crucial for ^1H NMR spectral position.

3. Experimental

General methods.—Melting points are uncorrected. Optical rotations were recorded at room temperature (20 °C) using a Hilger–Watt polarimeter for solutions in $CHCl_3$. TLC was performed on the Merck Kieselgel 60 F-254 plates with: A, 3:1 CCl_4–acetone; B, 2:1 CCl_4–Et_2O; C, 1:2 *n*-heptane–AcOEt; D, 4:1 petroleum ether–AcOEt; E, 1:3 toluene–AcOEt; F, 1:2 $CHCl_3$–MeOH; G, 5:1 $CHCl_3$–MeOH; H, 1:1 $CHCl_3$–Et_2O; I, 5:5:1 $CHCl_3$–Et_2O–MeOH. Column chromatography was performed on MN Kieselgel 60 (<0.08 mm). The ^1H NMR spectra ($CDCl_3$ or CD_3OD, internal Me_4Si) were recorded with a Varian Unity Plus 500 (500 MHz), Varian Mercury (400 MHz) or Varian XL-100 (100 MHz) instruments. The IR spectra were recorded as Nujol mulls with a Bruker IFS 66 spectrophotometer. Field desorption mass spectra (FD-MS) were recorded using a Varian Mat 711 mass spectrometer. Elemental analyses were conducted with a Carlo Erba EA1108 elemental analyzer.

4,6-Di-O-*acetyl-3-azido-2,3-dideoxy*-D-arabino- *and* -D-ribo-*hexopyranoses* ($\mathbf{3_{a-d}}$).—Starting from **1** prepared according to the procedure previously reported.[8,9]

4,6-Di-O-*acetyl-3-azido-2,3-dideoxy*-D-xylo- *and* -D-lyxo-*hexopyranoses* ($\mathbf{4_{a-d}}$).—Starting from **2** (3.964 g, 15 mmol) prepared analogously to $\mathbf{3_{a-d}}$. The reaction gave the mixture of $\mathbf{4_{a-d}}$ (3.672 g); IR: *v* 3300 (OH), 2100 (N_3), 1730 and 1250 (ester) cm^{-1}.

1,4,6-Tri-O-*acetyl-3-azido-2,3-dideoxy-β*-D-ribo- (**5**), -α-D-arabino- (**6**), -β-D-arabino- (**7**), *and* -α-D-ribo-*hexopyranoses* (**8**).—The mixture of hexopyranoses $\mathbf{3_{a-d}}$ (2.06 g, 7.5 mmol) was acetylated with Ac_2O (8 mL) and pyridine (8 mL). During 0.5 h the reaction was over (TLC, solvent A). After dilution with $CHCl_3$ (50 mL) the organic solution was washed with satd $NaHCO_3$ solution, with water and dried over Na_2SO_4. Concentration under reduced pressure led to 1.9 g of crude product, which was chromatographed (solvent B) to yield first **5** (21% in relation to **1**); mp 44–45 °C (CCl_4–Et_2O); $[\alpha]_D$ −7° (*c* 0.5, $CHCl_3$); R_f 0.40 (solvent B); IR: *v* 2090 (N_3), 1730 and 1225 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.25, 2.00 (2m, 2 H, 2 H-2), 2.08, 2.10, 2.12 (3 s, 9 H, 3 AcO), 4.10–4.50 (m, 4 H, H-3, H-5, 2 H-6), 5.00 (dd, 1 H, $J_{4,5}$ 10, $J_{3,4}$ 3.5 Hz, H-4), 5.95 (dd, 1 H, $J_{1,2a}$ 9, $J_{1,2e}$ 4 Hz, H-1); FDMS: *m*/*z* 315 (M^+). Anal. Calcd for $C_{12}H_{17}N_3O_7$: C, 45.72; H, 5.43; N, 13.33. Found: C, 45.01; H, 5.76; N, 12.70.

Eluted second was **6** (43%, syrup); $[\alpha]_D$ +79° (*c* 0.56, $CHCl_3$); R_f 0.32 (solvent B); IR: *v* 2080 (N_3), 1740 and 1230 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 2.10, 2.15 (2 s, 9 H, 3 AcO), 3.80–4.45 (m, 4 H, H-3, H-5, 2 H-6), 4.95 (t, 1 H, $J_{4,5} = J_{3,4}$ 10 Hz, H-4), 6.23 (bs, 1 H, H-1); FDMS: *m*/*z* 315 (M^+). Anal. Calcd for $C_{12}H_{17}N_3O_7$: C, 45.72; H, 5.43; N, 13.33. Found: C, 45.05; H, 5.55; N, 12.80.

Eluted third was **7** (11%, syrup); $[\alpha]_D$ +21° (*c* 0.6, $CHCl_3$); R_f 0.27 (solvent B); IR: *v* 2085 (N_3), 1735 and 1230 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.20–2.20 (m, 2 H, 2 H-2), 2.10, 2.15 (2 s, 9 H, 3 AcO), 3.50–4.50 (m, 4 H, H-3, H-5, 2 H-6), 4.87 (t, 1 H, $J_{4,5} = J_{3,4}$ 10 Hz, H-4), 5.70 (dd, 1 H, $J_{1,2a}$ 10, $J_{1,2e}$ 2 Hz, H-1); FDMS: *m*/*z* 315 (M^+). Anal. Calcd for $C_{12}H_{17}N_3O_7$: C, 45.72; H, 5.43; N, 13.33. Found: C, 45.08; H, 5.86; N, 12.70.

Eluted fourth was **8** (2%, syrup); $[\alpha]_D$ +94° (*c* 0.58, $CHCl_3$); R_f 0.19 (solvent B); ^1H NMR (100 MHz, $CDCl_3$): δ 2.06, 2.12 (2 s, 9 H, 3 AcO), 3.50–4.50 (m, 4 H, H-3, H-5, 2 H-6), 5.00 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.37 (bs, 1 H, H-1); FDMS: *m*/*z* 315 (M^+). Anal. Calcd for $C_{12}H_{17}N_3O_7$: C, 45.72; H, 5.43; N, 13.33. Found: C, 45.30; H, 5.31; N, 13.40.

General procedure for glycosidation.—To the crude syrupy mixture $\mathbf{3_{a-d}}$ or $\mathbf{4_{a-d}}$ (1 g) in CH_2Cl_2 (20 mL) dry *s*-collidine (3 mL) and MsCl (0.9 mL) were added. The reaction mixture was stirred for 10 min. at rt. After addition of MeOH (3 mL, 0.075 mol) or EtOH (4.2 mL, 0.075 mol), stirring was continued for an additional 3 h. Then the mixture was diluted with CH_2Cl_2 (15 mL), washed with 1 M aq HCl, followed by 1 M aq $NaHCO_3$ and cold water. After drying over $MgSO_4$ and evaporation to dryness, a syrupy mixture of four isomeric glycosides was obtained.

Methyl 3-azido-2,3-dideoxy-α-D-arabino- (**9**), -β-D-ribo- (**10**), -β-D-arabino- (**11**), *and* -α-D-ribo-*hexopyranosides* (**12**).—Prepared according to procedure previously reported.[8,9] Isolation of crystalline **9** followed by column chromatography (solvent C) yielded first **9** (overall yield 23% in relation to **1**).[9]

Eluted second was **10** (13%, syrup); $[\alpha]_D$ −27° (*c* 0.7, CH_3OH), lit.[10] +10°; R_f 0.23 (solvent C); IR: *v* 3402 (OH), 2098 (N_3) cm^{-1}; FDMS: *m*/*z* 203 (M^+). Anal. Calcd for $C_7H_{13}N_3O_4$: C, 41.38; H, 6.45; N, 20.68. Found: C, 41.60; H, 6.59; N, 20.17.

Similar treatment of second fraction, crystallization from EtOAc–*n*-hexane and silica gel chromatography (solvent C) gave first **11** (29%); mp 92–93 °C, lit.[10] 92–93 °C; $[\alpha]_D$ −14° (*c* 0.9, CH_3OH), lit.[10] −40°; R_f 0.24 (solvent C); IR: *v* 3360 (OH), 2091 (N_3) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.21 (td, 1 H, $J_{2a,3} \sim J_{2a,2e}$ 12.50 Hz, H-2_a), 1.94 (dq, 1 H, $J_{2e,3}$ 4.78 Hz, H-2_e), 3.10 (m, 1 H, $J_{5,6}$ 4.78, $J_{5,6'}$ 1.84 Hz, H-5), 3.14 (m, 1 H, $J_{4,5}$ 9.28 Hz, H-4), 3.31 (s, 3 H, OCH_3), 3.32 (m, 1 H, $J_{3,4}$ 9.28 Hz, H-3), 3.52 (dd, 1 H, $J_{6,6'}$ 11.76 Hz, H-6), 3.69 (dd, 1 H, H-6′), 4.32 (dd, 1 H, $J_{1,2a}$ 9.56, $J_{1,2e}$ 1.84 Hz, H-1); ^{13}C NMR (400 MHz, $CDCl_3$): δ 37.57 (C-2), 56.99 (OCH_3), 62.73 (C-6), 64.17 (C-3), 71.78 (C-5), 78.78 (C-4), 102.07 (C-1). FDMS: *m*/*z* 203 (M^+). Anal. Calcd for $C_7H_{13}N_3O_4$: C, 41.38; H, 6.45; N, 20.68. Found: C, 41.65; H, 6.52; N, 20.40.

Eluted second was **12** (14%, syrup); $[\alpha]_D + 210°$ (*c* 1.0, CH_3OH), lit.[10] + 252°; R_f 0.13 (solvent C); IR: *v* 3411 (OH), 2104 (N_3) cm^{-1}; FDMS: *m/z* 203 (M^+). Anal. Calcd for $C_7H_{13}N_3O_4$: C, 41.38; H, 6.45; N, 20.68. Found: C, 41.13; H, 6.57; N, 20.52.

Methyl 4,6-di-O-*acetyl-3-azido-2,3-dideoxy*-α-D-arabino- (**13**) -β-D-ribo- (**14**), -β-D-arabino- (**15**) *and* -α-D-ribo-*hexopyranosides* (**16**).—Acetylation of **9** with Ac_2O and pyridine led to **13** (86%, syrup).[9]

Acetylation of **10** gave **14** (93%, syrup); $[\alpha]_D - 69°$ (*c* 1.0, $CHCl_3$), lit.[10] − 11°; R_f 0.72 (solvent A); FDMS: *m/z* 287 (M^+). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 44.09; H, 5.83; N, 15.00.

Acetylation of **11** led to **15** (93%, syrup); $[\alpha]_D - 20°$ (*c* 0.86, $CHCl_3$); R_f 0.65 (solvent A); IR: *v* 2080 (N_3), 1735 and 1250 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.77 (m, 1 H, $J_{2a,2e}$ 13 Hz, H-2_a), 2.12, 2.15 (2 s, 6 H, 2 AcO), 2.30 (m, 1 H, H-2_e), 3.54 (s, 3 H, OCH_3), 4.13 (dd, 1 H, $J_{5,6'}$ 2.5 Hz, H-6′), 4.36 (dd, 1 H, $J_{6,6'}$ 12, $J_{5,6}$ 5 Hz, H-6), 4.52 (dd, 1 H, $J_{1,2a}$ 9.5, $J_{1,2e}$ 2 Hz, H-1); 4.97 (t, 1 H, $J_{4,5} = J_{3,4}$ 10 Hz, H-4); FDMS: *m/z* 287 (M^+). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 45.88; H, 7.10; N, 13.83.

Acetylation of **12** gave **16** (92%, syrup); $[\alpha]_D + 145°$ (*c* 1.0, $CHCl_3$), lit.[10] + 160°; R_f 0.65 (solvent A); FDMS: *m/z* 287 (M^+). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 45.82; H, 6.08; N, 14.75.

Ethyl 4,6-di-O-*acetyl-3-azido-2,3-dideoxy*-α-D-arabino- (**17**), -β-D-ribo- (**18**), -β-D-arabino- (**19**), *and* -α-D-ribo-*hexopyranosides* (**20**).—Separation of the crude syrupy mixture of **17**–**20** was analogous to isolation of **9**–**12**. Silica gel chromatography of first fraction (solvent C) followed by acetylation gave first **17** (20% in relation to **1**, syrup); $[\alpha]_D + 115°$ (*c* 1.0, $CHCl_3$); R_f 0.74 (solvent A); IR: *v* 2095 (N_3), 1745 and 1250 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.23 (t, 3 H, CH_2CH_3), 1.77 (t, 1 H, $J_{2a,2e} = J_{2a,3}$ 13.0 Hz, H-2_a), 2.11, 2.14 (2 s, 6 H, 2 AcO), 2.20 (m, 1 H, $J_{2e,3}$ 4 Hz, H-2_e), 3.61 (q, 2 H, CH_2CH_3), 3.80–4.00 (m, 2 H, H-3, H-5), 4.05 (dd, 1 H, $J_{5,6'}$ 3 Hz, H-6′), 4.30 (dd, 1 H, $J_{6,6'}$ 13, $J_{5,6}$ 5 Hz, H-6), 4.95 (t, 1 H, $J_{4,5} = J_{3,4}$ 10 Hz, H-4), 5.05 (d, 1 H, $J_{1,2a}$ 4, H-1); FDMS: *m/z* 301 (M^+). Anal. Calcd for $C_{12}H_{19}N_3O_6$: C, 47.84; H, 6.36; N, 13.95. Found: C, 46.40; H, 6.41; N, 13.55.

Eluted and acetylated second was **18** (8%, syrup); $[\alpha]_D - 4°$ (*c* 1.0, $CHCl_3$); R_f 0.74 (solvent A); IR: *v* 2080 (N_3), 1740 and 1240 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.24 (t, 3 H, CH_2CH_3), 1.80–2.30 (2 m, 2 H, 2 H-2), 2.10, 2.15 (2 s, 6 H, 2 AcO), 3.60 (q, 2 H, CH_2CH_3), 3.85–4.25 (m, 3 H, H-3, H-5, H-6′), 4.35 (dd, 1 H, $J_{6,6'}$ 13, $J_{5,6}$ 5 Hz, H-6), 4.81 (dd, 1 H, $J_{1,2a}$ 9, $J_{1,2e}$ 2.5 Hz, H-1), 5.00 (dd, 1 H, $J_{4,5}$ 9.5, $J_{3,4}$ 3.5 Hz, H-4), FDMS: *m/z* 301 (M^+). Anal. Calcd for $C_{12}H_{19}N_3O_6$: C, 47.84; H, 6.36; N, 13.95. Found: C, 47.19; H, 6.72; N, 13.3.

Silica gel chromatography of second fraction (solvent C) followed by acetylation gave first **19** (29%, syrup); $[\alpha]_D - 23°$ (*c* 1.0, $CHCl_3$); R_f 0.68 (solvent A); IR: *v* 2095 (N_3), 1745 and 1240 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.23 (t, 3 H, CH_2CH_3), 1.80 (td, 1 H, $J_{2a,2e} = J_{2a,3}$ 13 Hz, H-2_a), 2.10, 2.12 (2 s, 6 H, 2 AcO), 3.40–4.00 (m, 4 H, H-3, H-5, CH_2CH_3), 4.10 (dd, 1 H, $J_{5,6'}$ 2.5 Hz, H-6′), 4.30 (dd, 1 H, $J_{6,6'}$ 12, $J_{5,6}$ 5 Hz, H-6), 4.60 (dd, 1 H, $J_{1,2a}$ 9.5, $J_{1,2e}$ 2.5 Hz, H-1); 4.93 (t, 1 H, $J_{4,5} = J_{3,4}$ 10 Hz, H-4), FDMS: *m/z* 301 (M^+). Anal. Calcd for $C_{12}H_{19}N_3O_6$: C, 47.84; H, 6.36; N, 13.95. Found: C, 47.20; H, 6.31; N, 13.83.

Eluted and acetylated second was **20** (9%, syrup); $[\alpha]_D + 129°$ (*c* 1.0, $CHCl_3$); R_f 0.68 (solvent A); IR: *v* 2095 (N_3), 1740 and 1250 (ester) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.26 (t, 3 H, CH_2CH_3), 2.12, 2.15 (2 s, 6 H, 2 AcO), 3.66 (q, 2 H, CH_2CH_3), 4.10–4.50 (m, 4 H, H-3, H-5, 2 H-6), 4.92 (d, 1 H, $J_{1,2a}$ 3.5 Hz, H-1), 5.00 (dd, 1 H, $J_{4,5}$ 9, $J_{3,4}$ 4 Hz, H-4), FDMS: *m/z* 301 (M^+). Anal. Calcd for $C_{12}H_{19}N_3O_6$: C, 47.84; H, 6.36; N, 13.95. Found: C, 47.52; H, 6.52; N, 13.56.

Methyl 4,6-di-O-*acetyl-3-azido-2,3-dideoxy*-α-D-lyxo- (**21**), -β-D-xylo- (**22**), -α-D-xylo- (**23**), *and* -β-D-lyxo-*hexopyranosides* (**24**).—An obtained thick syrup was chromatographed (solvent D) to give first **21** (8% in relation to **2**, syrup); $[\alpha]_D + 107°$ (*c* 0.97, $CHCl_3$); R_f 0.38 (solvent D); IR: *v* 2104 (N_3), 1748 and 1230 (ester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.96 (dd, 1 H, $J_{2e,3}$ 4.8 Hz, H-2_e), 2.09 (td, 1 H, $J_{2a,3} = J_{2a,2e}$ 12.8 Hz, H-2_a), 2.08, 2.17 (2 s, 6 H, 2 AcO), 3.37 (s, 3 H, OCH_3), 3.85 (dq, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.06 (dd, 1 H, $J_{6,6'}$ 14.4 Hz, H-6), 4.07 (q, 1 H, $J_{5,6}$ 6.8, $J_{5,6'}$ 4.8 Hz, H-5), 4.11 (dd, 1 H, H-6′), 4.92 (d, 1 H, $J_{1,2a}$ 3.6, H-1); 5.30 (d, 1 H, $J_{4,5} \sim 0$ Hz, H-4), ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.12 (2 $COCH_3$), 30.00 (C-2), 54.51, 55.29 (C-3, OCH_3), 62.94 (C-6), 67.18 (C-4), 67.29 (C-5), 98.03 (C-1), 170.20, 170.55 (2 C=O). FDMS: *m/z* 287 (M^+). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 46.18; H, 6.10; N, 14.24.

Eluted second was **22** (16%, syrup); $[\alpha]_D + 6°$ (*c* 0.98, $CHCl_3$); R_f 0.34 (solvent D); IR: *v* 2105 (N_3), 1746 and 1231 (ester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.93 (q, 2 H, $J_{2e,3} = J_{2a,3}$ 3.6 Hz, H-2_e, H-2_a), 2.08, 2.13 (2 s, 6 H, 2 AcO), 3.52 (s, 3 H, OCH_3), 4.04 (q, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 4.14 (td, 1 H, H-5), 4.15–4.22 (m, 2 H, H-6, H-6′) 4.66 (t, 1 H, $J_{1,2a} = J_{1,2e}$ 5.6 Hz, H-1); 4.73 (dd, 1 H, $J_{4,5}$ 1.6 Hz, H-4), ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.13, 21.20 (2 $COCH_3$), 31.72 (C-2), 56.87 (OCH_3), 57.31 (C-3), 62.58 (C-6), 66.82 (C-4), 69.94 (C-5), 98.92 (C-1), 170.05, 170.55 (2 C=O). FDMS: *m/z* 286 ($M^+ - 1$). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 46.20; H, 6.10; N, 14.30.

Eluted third was **23** (33%, syrup); $[\alpha]_D + 146°$ (*c* 1.0, $CHCl_3$); R_f 0.28 (solvent D); IR: *v* 2111 (N_3), 1747 and 1231 (ester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.93 (dq, 1 H, $J_{2e,3}$ 3.2 Hz, H-2_e), 2.08, 2.13 (2 s, 6 H, 2

AcO), 2.15 (dt, 1 H, $J_{2a,3}$ 4.8, $J_{2a,2e}$ 15.2 Hz, H-2$_a$), 3.40 (s, 3 H, OCH_3), 3.88 (q, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.11 (dd, 1 H, H-6′), 4.15 (dd, 1 H, $J_{6,6'}$ 11.6 Hz, H-6), 4.34 (td, 1 H, $J_{5,6}$ 6.4, $J_{5,6'}$ 6.0 Hz, H-5), 4.73 (d, 1 H, $J_{4,5}$ 1.6 Hz, H-4), 4.81 (d, 1 H, $J_{1,2a}$ 3.6, H-1); ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.09, 21.16 (2 CO*CH*$_3$), 28.16 (C-2), 54.56 (C-3), 55.65 (OCH_3), 63.12 (C-6), 63.39 (C-5), 67.60 (C-4), 96.97 (C-1), 169.93, 170.52 (2 C=O). FDMS: m/z 286 ($M^+ - 1$). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 45.18; H, 5.50; N, 15.04.

Eluted forth was **24** (14%, syrup); $[\alpha]_D - 15°$ (c 1.0, $CHCl_3$); R_f 0.23 (solvent D); IR: ν 2102 (N_3), 1750 and 1229 (ester) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (m, 1 H, $J_{2a,3}$ 12.8 Hz, H-2$_a$), 2.08 (m, 1 H, $J_{2e,3}$ 4.8 Hz, H-2$_e$), 2.07, 2.17 (2 s, 6 H, 2 AcO), 3.52 (dq, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 3.54 (s, 3 H, OCH_3), 3.78 (td, 1 H, $J_{5,6} = J_{5,6'}$ 6.6 Hz, H-5), 4.16 (d, 2 H, H-6, H-6′), 4.47 (dd, 1 H, $J_{1,2a}$ 9.6, $J_{1,2e}$ 2.0 Hz, H-1), 5.27 (d, 1 H, $J_{4,5}$ 1.1 Hz, H-4); ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.05 (2 CO*CH*$_3$), 31.69 (C-2), 56.99 (OCH_3), 57.64 (C-3), 62.31 (C-6), 66.25 (C-4), 72.21 (C-5), 101.24 (C-1), 170.13, 170.47 (2 C=O). FDMS: m/z 287 (M^+). Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.96; N, 14.63. Found: C, 45.51; H, 6.09; N, 14.90.

The mixtures of **21**–**24** (0.48 g, 13%) were also eluted to make the total yield 84% (in relation to **2**).

General procedure for hydrogenation.—All 3-azido compounds (1 mM) were dissolved in abs. MeOH (15 mL) and hydrogenated in the presence of 10% Pd/C (5 mg) at atmospheric pressure for 2–4 h at 20 °C. The end of reduction was verified by TLC. Then, the catalyst was filtered off and the filtrate was evaporated in vacuo to give 3-aminosugars, which (0.2 g) were acetylated with Ac_2O (2 mL) and pyridine (2 mL) in solution of CH_2Cl_2 (10 mL) with catalytic amount of DMAP.

3-Acetamido-1,6-di-O-*acetyl-2,3-dideoxy-β*-D-ribo-*hexopyranose* (**25**).—Hydrogenation of **5** yielded **25** (89%, syrup); $[\alpha]_D$ −12° (c 0.5, $CHCl_3$); IR: ν 3240 (OH, NH), 1730 and 1250 (ester), 1650 and 1545 (amide) cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$): δ 2.05, 2.10 (2 s, 9 H, 2 AcO, *Ac*NH), 3.42 (dd, 1 H, $J_{5,6}$ 6 Hz, H-6), 3.80 (dd, 1 H, $J_{4,5}$ 6, $J_{3,4}$ 4 Hz, H-4), 4.05 (dd, 1 H, $J_{5,6'}$ 6 Hz, H-6′), 4.35 (d, 1 H, $J_{4,OH}$ 4 Hz, OH), 4.40 (m, 2 H, H-3, H-5), 6.10 (dd, 1 H, $J_{1,2a}$ 5, $J_{1,2e}$ 3 Hz, H-1), 6.50 (d, 1 H, $J_{3,NH}$ 7 Hz, NH). FDMS: m/z 289 (M^+). Anal. Calcd for $C_{12}H_{19}NO_7$: C, 49.82; H, 6.62; N, 4.84. Found: C, 50.01; H, 6.76; N, 5.01.

3-Acetamido-1,4,6-tri-O-*acetyl-2,3-dideoxy-β*-D-ribo-*hexopyranose* (**26**).—Acetylation of **25** gave **26** (44%, syrup); $[\alpha]_D - 4°$ (c 0.5, $CHCl_3$); R_f 0.60 (solvent B); IR: ν 3200 (NH), 1745 and 1240 (ester), 1650 and 1550 (amide) cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$): δ 2.03, 2.12, 2.14 (3 s, 9 H, 3 AcO), 2.37 (s, 3 H, *Ac*NH), 4.10–4.45 (m, 3 H, H-5, 2 H-6), 4.72 (m, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 5.02 (t, 1 H, $J_{4,5}$ 3.5 Hz, H-4), 6.18 (t, 1 H, $J_{1,2a} = J_{1,2e}$ 4 Hz, H-1), 6.32 (d, 1 H, $J_{3,NH}$ 8 Hz, NH). FDMS: m/z 331 (M^+). Anal. Calcd for $C_{14}H_{21}NO_8$: C, 50.75; H, 6.39; N, 4.23. Found: C, 50.50; H, 6.88; N, 4.06.

1,4,6-Tri-O-*acetyl-3-acetamido-2,3-dideoxy-β*-D-xylo- (**27**), -*α*-D-lyxo-*hexopyranose* (**28**) *and 1,3,4,6-tetra*-O-*acetyl-2-deoxy*-D-lyxo-*hexopyranoses* (**29$_{a,b}$**).—The mixture of **4$_{a-d}$** (1 g, 3.7 mM) was acetylated with Ac_2O in pyridine, next hydrogenated and again acetylated. Column chromatography of the crude product (solvent E) gave first was **27** (21% in relation to **2**); mp 136–139 °C (toluene–AcOEt); $[\alpha]_D + 4°$ (c 0.5, $CHCl_3$); R_f 0.20 (solvent E); IR: ν 3303 (NH), 1746 and 1229 (ester), 1656 and 1544 (amide) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (dk, 1 H, $J_{2e,3}$ 6.8 Hz, H-2$_e$), 2.01, 2.07, 2.12, 2.13 (4s, 12 H, *Ac*NH, 3 AcO), 2.20 (dk, 1 H, $J_{2a,2e}$ 14.0, $J_{2a,3}$ 4.8 Hz, H-2$_a$), 4.23–4.31 (m, 3 H, H-5, 2 H-6), 4.43 (m, 1 H, $J_{3,4}$ 6.4 Hz, H-3), 4.99 (dd, 1 H, $J_{4,5}$ 2.4 Hz, H-4), 5.75 (d, 1 H, $J_{3,NH}$ 7.6 Hz, NH), 6.02 (dd, 1 H, $J_{1,2a}$ 6.8, $J_{1,2e}$ 3.2 Hz, H-1); ^{13}C NMR (400, $CDCl_3$): δ 20.96, 21.04, 21.37, 23.35 (4 CO*CH*$_3$), 31.71 (C-2), 45.66 (C-3), 67.38 (C-4), 63.05, 71.42 (C-5, C-6), 90.73 (C-1), 169.30, 169.90, 170.13, 170.55 (4 C=O); FDMS: m/z 332 ($M + 1$)$^+$.

Eluted second was **28** (19%); mp 159–160 °C (toluene–AcOEt); $[\alpha]_D + 136°$ (c 0.5, $CHCl_3$); R_f 0.09 (solvent E); IR: ν 3293 (NH), 1747 and 1231 (ester), 1657 and 1545 (amide) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (dd, 1 H, $J_{2e,3}$ 5.2 Hz, H-2$_e$), 1.99 (td, 1 H, $J_{2a,2e}$ 13.2, $J_{2a,3}$ 12.8 Hz, H-2$_a$), 1.96, 2.05, 2.13, 2.18 (4s, 12 H, *Ac*NH, 3 AcO), 4.00 (dd, 1 H, $J_{6,6'}$ 11.2 Hz, H-6), 4.11 (dd, 1 H, H-6′), 4.28 (td, 1H, $J_{5,6} = J_{5,6'}$ 6.8 Hz, H-5), 4.59 (m, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 5.29 (d, 1 H, $J_{4,5}$ 0.6 Hz, H-4), 5.43 (d, 1 H, $J_{3,NH}$ 8.0 Hz, NH), 6.28 (d, 1 H, $J_{1,2a}$ 2.4, Hz, H-1); ^{13}C NMR (400, $CDCl_3$): δ 21.06, 21.14, 21.45, 23.58 (4 CO*CH*$_3$), 30.05 (C-2), 43.83 (C-3), 62.35 (C-6), 67.96 (C-4), 69.78 (C-5), 91.47 (C-1), 169.67, 170.49 (4 C=O); FDMS: m/z 332 ($M + 1$)$^+$.

The traces of the mixture of anomers **29$_{a,b}$** were eluted too (4%, syrup, α:β ~ 2:1); R_f 0.85 (solvent E); IR: ν 1747 and 1231 (ester) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): α anomer: δ 1.91 (dd, 1 H, $J_{2e,3}$ 4.8 Hz, H-2$_e$), 2.01, 2.05, 2.12, 2.15 (4s, 12 H, 4 AcO), 2.23 (td, 1 H, $J_{2a,2e}$ 12.8, $J_{2a,3}$ 12.4 Hz, H-2$_a$), 4.05-4.25 (m, 2 H, 2 H-6), 4.27 (td, 1 H, $J_{5,6} = J_{5,6'}$ 6.4 Hz, H-5), 5.31 (m, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 5.39 (bd, 1 H, $J_{4,5}$ 1.2 Hz, H-4), 6.32 (d, 1 H, $J_{1,2a}$ 2.4 Hz, H-1); β anomer: δ 1.91 (dd, 1 H, $J_{2e,3}$ 5.2 Hz, H-2$_e$), 2.02, 2.05, 2.14, 2.16 (4s, 12 H, 4 AcO), 2.08 (m, 1 H, $J_{2a,2e}$ 12.8, $J_{2a,3}$ 12.4 Hz, H-2$_a$), 3.95 (td, 1 H, $J_{5,6} = J_{5,6'}$ 6.8 Hz, H-5), 4.05–4.30 (m, 2 H, 2 H-6), 5.06 (dk, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 5.30 (dd, 1 H, $J_{4,5}$ 1.2 Hz, H-4), 5.79 (dd, 1 H, $J_{1,2a}$ 10.0, $J_{1,2e}$ 2.8 Hz, H-1); FDMS: m/z 333 ($M + 1$)$^+$, 331 ($M - 1$)$^+$.

Methyl 3-amino-2,3-dideoxy-α-D-arabino-*hexopyranoside* (**30**).—Reduction of 3-azido group in **9** (0.3 g, 1.5 mmol) gave **30** (0.22 g, 85%, syrup); $[\alpha]_D + 136°$ (c 0.4, CH_3OH), lit.[2] + 129°; R_f 0.25 (solvent F); IR: ν 3340 (OH, NH_2), 1595 (NH) cm^{-1}.

*Methyl 3-acetamido-2,3-dideoxy-α-*D-arabino-*hexopyranoside* (**31**).—Acetylation of **30** resulted in **31** (73%); mp 134–136 °C (EtOH – *n*-hexane); $[\alpha]_D + 132°$ (*c* 0.7, $CHCl_3$); R_f 0.47 (solvent G); IR: *v* 3296 (OH, NH), 1640 and 1555 (amide) cm^{-1}; ^1H NMR (500 MHz, CD_3Cl): δ 1.66 (td, 1 H, $J_{2a,2e} = J_{2a,3}$ 12.5 Hz, H-2_a), 2.02 (s, 3 H, *Ac*NH), 2.04 (dq, 1 H, $J_{2e,3}$ 4.8 Hz, H-2_e), 3.38 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.42 (s, 3 H, OCH_3), 3.59 (m, 1H, $J_{5,6}$ 7.5, $J_{5,6'}$ 2.8 Hz, H-5), 3.75 (dd, 1 H, $J_{6,6'}$ 12.0 Hz, H-6), 3.90 (dd, 1 H, H-6′), 4.23 (dq, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.83 (d, 1 H, $J_{1,2a}$ 3.0 Hz, H-1). Anal. Calcd for $C_9H_{17}NO_5$: C, 49.31; H, 7.82; N, 6.39. Found: C, 47.35; H, 7.88; N, 5.91.

*Methyl 3-amino-2,3-dideoxy-β-*D-arabino-*hexopyranoside* (**32**).—Reduction of 3-azido group in **11** yielded **32** (84%, syrup); $[\alpha]_D - 51°$ (*c* 0.7, CH_3OH), lit.[2] $-62°$; R_f 0.29 (solvent F); IR: *v* 3348 (OH, NH_2), 1591 (NH) cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 1.40 (td, 1 H, $J_{2a,2e}$ 12.7, $J_{2a,3}$ 12.2 Hz, H-2_a), 2.06 (dq, 1 H, $J_{2e,3}$ 4.4 Hz, H-2_e), 2.78 (dq, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 3.09 (t, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 3.25 (dq, 1H, $J_{5,6}$ 5.9, $J_{5,6'}$ 2.4 Hz, H-5), 3.50 (s, 3 H, OCH_3), 3.71 (dd, 1 H, $J_{6,6'}$ 12.21 Hz, H-6), 3.89 (dd, 1 H, H-6′), 4.51 (dd, 1 H, $J_{1,2a}$ 9.3, $J_{1,2e}$ 1.9 Hz, H-1); ^{13}C NMR (500, CD_3OD): δ 37.70 (C-2), 52.46 (C-6), 55.30 (OCH_3), 61.43 (C-3), 71.74 (C-5), 77.64 (C-4), 101.18 (C-1).

*Methyl 3-acetamido-2,3-dideoxy-β-*D-arabino-*hexopyranoside* (**33**).—Acetylation of **32** gave **33** (75%); mp 174–176 °C (EtOH – *n*-hexane); $[\alpha]_D - 17°$ (*c* 0.5, $CHCl_3$); R_f 0.49 (solvent G); IR: *v* 3273 (OH, NH), 1640 and 1553 (amide) cm^{-1}; ^1H NMR (500 MHz, CD_3Cl): δ 1.24 (td, 1 H, $J_{2a,2e} = J_{2a,3}$ 12.5 Hz, H-2_a), 1.79 (s, 3 H, *Ac*NH), 1.87 (dq, 1 H, $J_{2e,3}$ 4.5 Hz, H-2_e), 3.08 (t, 1 H, $J_{4,5}$ 9.4 Hz, H-4), 3.11 (m, 1H, $J_{5,6}$ 4.9, $J_{5,6'}$ 1.8 Hz, H-5), 3.31 (s, 3 H, OCH_3), 3.53 (dd, 1 H, $J_{6,6'}$ 11.6 Hz, H-6), 3.70 (dd, 1 H, H-6′), 3.72 (m, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 4.32 (dd, 1 H, $J_{1,2a}$ 9.8, $J_{1,2e}$ 1.8 Hz, H-1); ^{13}C NMR (500 MHz, CD_3Cl): δ 22.90 ($CO\mathit{CH}_3$), 38.17 (C-2), 52.74 (C-6), 56.96 (OCH_3), 62.93 (C-3), 70.72 (C-5), 79.40 (C-4), 102.50 (C-1), 173.57 (C=O). Anal. Calcd for $C_9H_{17}NO_5$: C, 49.31; H, 7.82; N, 6.39. Found: C, 49.27; H, 7.86; N, 6.17.

*Methyl 3-amino-2,3-dideoxy-α-*D-ribo-*hexopyranoside* (**34**).—Reduction of 3-azido group in **12** yielded **34** (78%, syrup); $[\alpha]_D + 71°$ (*c* 0.6, CH_3OH); R_f 0.22 (solvent F); IR: *v* 3335 (OH, NH_2), 1604 (NH) cm^{-1}; ^1H NMR (500 MHz, CD_3OD): δ 1.70 (dq, 1 H, $J_{2a,2e}$ 14.6, $J_{2a,3}$ 3.9 Hz, H-2_a), 2.40 (dd, 1 H, $J_{2e,3}$ 1.96 Hz, H-2_e), 2.62 (bs, 1 H, OH), 3.02 (dd, 1 H, $J_{6,6'}$ 12.21 Hz, H-6), 3.36 (m, 1 H, $J_{3,4}$ 2.93 Hz, H-3), 3.41 (m, 1 H, H-6′), 3.46 (s, 3 H, OCH_3), 4.02 (m, 1H, $J_{5,6}$ 5.86, $J_{5,6'}$ 3.42 Hz, H-5), 4.03 (dd, 1 H, $J_{4,5}$ 9.28 Hz, H-4), 4.77 (d, 1 H, $J_{1,2a}$ 5.86, H-1); ^{13}C NMR (500, CD_3OD): δ 32.12 (C-2), 46.54 (C-6), 52.96 (C-3), 55.58 (OCH_3), 69.71 (C-5), 74.73 (C-4), 97.89 (C-1).

*Ethyl 3-acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-*D-arabino-*hexopyranoside* (**35**).—Reduction of 3-azido group in **17** followed by acetylation resulted in **35** (67%, syrup); $[\alpha]_D + 97°$ (*c* 0.5, $CHCl_3$), R_f 0.50 (solvent A); IR: *v* 3220 (NH), 1745 and 1250 (ester), 1670 and 1550 (amide) cm^{-1}; ^1H NMR (100 MHz, CD_3Cl): δ 1.23 (t, 3 H, $CH_2\mathit{CH}_3$), 1.65 (td, 1 H, $J_{2a,2e} = J_{2a,3}$ 13.5 Hz, H-2_a), 1.94 (s, 3 H, *Ac*NH), 2.09, 2.11 (2 s, 6 H, 2 OAc), 2.25 (dd, 1 H, $J_{2e,3}$ 4 Hz, H-2_e), 3.63 (q, 2 H, CH_2CH_3), 4.07 (m, 2 H, $J_{5,6}$ 5, $J_{5,6'}$ 2 Hz, H-5, H-6′), 4.40 (dd, 1 H, $J_{6,6'}$ 13 Hz, H-6), 4.60 (m, 1 H, $J_{3,4}$ 10 Hz, H-3), 4.80 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.97 (d, 1 H, $J_{1,2a}$ 3.5 Hz, H-1), 5.67 (bd, 1 H, $J_{3,NH}$ 8 Hz, NH). FDMS: *m*/*z* 317 (M^+). Anal. Calcd for $C_{14}H_{23}NO_7$: C, 52.99; H, 7.31; N, 4.41. Found: C, 53.12; H, 7.15; N, 4.20.

*Ethyl 3-acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-β-*D-ribo-*hexopyranoside* (**36**).—Reduction of 3-azido group in **18** followed by acetylation yielded **36** (57%, syrup); $[\alpha]_D - 79°$ (*c* 0.4, $CHCl_3$); R_f 0.60 (solvent A); IR: *v* 3200 (NH), 1740 and 1240 (ester), 1660 and 1545 (amide) cm^{-1}; ^1H NMR (100 MHz, CD_3Cl): δ 1.21 (t, 3 H, $CH_2\mathit{CH}_3$), 1.75–2.20 (m, 2 H, 2 H-2), 2.03 (s, 3 H, *Ac*NH), 2.13 (s, 6 H, 2 AcO), 3.57 (q, 2 H, CH_2CH_3), 3.80–4.15 (m, 2 H, H-5, H-6′), 4.35 (dd, 1 H, H-6), 4.70 (m, 1 H, $J_{3,4} = J_{2a,3} = J_{2e,3}$ 4 Hz, H-3), 4.86 (t, 1 H, $J_{4,5} = J_{3,4}$ 4 Hz, H-4), 5.03 (t, 1 H, $J_{1,2a} = J_{1,2e}$ 4 Hz, H-1), 5.64 (bd, 1 H, $J_{3,NH}$ 8 Hz, NH). FDMS: *m*/*z* 317 (M^+). Anal. Calcd for $C_{14}H_{23}NO_7$: C, 52.99; H, 7.31; N, 4.41. Found: C, 53.08; H, 6.99; N, 4.11.

*Ethyl 3-acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-β-*D-arabino-*hexopyranoside* (**37**).—Reduction of 3-azido group in **19** followed by acetylation resulted in **37** (67%, syrup); $[\alpha]_D - 12°$ (*c* 0.9, $CHCl_3$); R_f 0.40 (solvent A); IR: *v* 3200 (NH), 1740 and 1250 (ester), 1660 and 1550 (amide) cm^{-1}; ^1H NMR (100 MHz, CD_3Cl): δ 1.24 (t, 3 H, $CH_2\mathit{CH}_3$), 1.64 (td, 1 H, $J_{2a,2e} = J_{2a,3}$ 13.5 Hz, H-2_a), 1.96 (s, 3 H, *Ac*NH), 2.10 (s, 6 H, 2 OAc), 2.30 (dq, 1 H, $J_{2e,3}$ 5 Hz, H-2_e), 3.60 (q, 2 H, CH_2CH_3), 3.70 (dq, 1 H, $J_{5,6}$ 5, $J_{5,6'}$ 2.5 Hz, H-5), 4.15 (dd, 1 H, H-6′), 4.35 (m, 1 H, $J_{3,4}$ 10 Hz, H-3), 4.40 (dd, 1 H, $J_{6,6'}$ 12.5 Hz, H-6), 4.65 (dd, 1 H, $J_{1,2a}$ 10, $J_{1,2e}$ 2 Hz, H-1), 4.80 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 6.10 (bd, 1 H, $J_{3,NH}$ 8 Hz, NH). FDMS: *m*/*z* 317 (M^+). Anal. Calcd for $C_{14}H_{23}NO_7$: C, 52.99; H, 7.31; N, 4.41. Found: C, 52.18; H, 7.10; N, 4.24.

*Ethyl 3-acetamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-*D-ribo-*hexopyranoside* (**38**).—Reduction of 3-azido group in **20** followed by acetylation gave **38** (48%, syrup); $[\alpha]_D + 45°$ (*c* 0.8, $CHCl_3$); R_f 0.27 (solvent A); IR: *v* 3300 (NH), 1735 and 1240 (ester), 1670 and 1520 (amide) cm^{-1}; ^1H NMR (100 MHz, CD_3Cl): δ 1.28 (t, 3 H, $CH_2\mathit{CH}_3$), 1.70–2.25 (m, 2 H, 2 H-2), 2.00 (s, 6 H, 2 OAc), 2.10 (s, 3 H, *Ac*NH), 3.60 (q, 2 H, CH_2CH_3), 4.05–4.30 (m, 3 H, H-5, 2 H-6), 4.73 (m, 1 H, $J_{3,4} = J_{2a,3} = J_{2e,3}$ 4 Hz, H-3), 4.90 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4),

5.00 (d, 1 H, $J_{1,2a}$ 3, H-1), 7.05 (bd, 1 H, $J_{3,NH}$ 8 Hz, NH). FDMS: m/z 317 (M^+). Anal. Calcd for $C_{14}H_{23}NO_7$: C, 52.99; H, 7.31; N, 4.41. Found: C, 53.01; H, 6.99; N, 4.40.

Methyl 3-acetamido-4,6-di-O-*acetyl-2,3-dideoxy*-α-D-xylo- (**39**), -β-D-xylo- (**40$_a$**), -α-D-lyxo- (**40$_b$**), -β-D-lyxo-*hexopyranoside* (**40$_c$**) *and methyl 3,4,6-tri*-O-*acetyl-2-deoxy*-α-D-lyxo- (**41**) *and* -β-D-lyxo-*hexopyranoside* (**42**).—Reduction of 3-azido group in the mixture of **21**–**24** and subsequent acetylation resulted in a few products, which were separated by column chromatography (solvent: first H, next I). Eluted first was **39** (31%, syrup); $[\alpha]_D + 56°$ (c 0.6, $CHCl_3$); R_f 0.10 (solvent I); IR: ν 3403 (NH), 1744 and 1231 (ester), 1679 and 1512 (amide) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (dt, 1 H, $J_{2e,3}$ 1.0 Hz, H-2$_e$), 2.00, 2.06, 2.11 (3s, 9 H, 3 AcO), 2.22 (dt, 1 H, $J_{2a,2e}$ 14.4, $J_{2a,3}$ 5.2 Hz, H-2$_a$), 3.42 (s, 3 H, OCH_3), 4.07 (dd, 1 H, $J_{6,6'}$ 11.2, H-6), 4.13 (dd, 1 H, H-6′), 4.19 (m, 2 H, $J_{3,4}$ 2.4, $J_{5,6}$ 8.2, $J_{5,6'}$ 5.2 Hz, H-3, H-5), 4.86 (d, 1 H, $J_{4,5}$ 0.8 Hz, H-4), 4.90 (d, 1 H, $J_{1,2a}$ 3.6, $J_{1,2e}$ 1.0 Hz, H-1), 6.76 (d, 1 H, $J_{3,NH}$ 7.2 Hz, NH); ^{13}C NMR (400, $CDCl_3$): δ 21.14, 21.20, 23.88 (3 COCH_3), 28.83 (C-2), 44.53 (C-3), 55.62 (OCH_3), 63.65 (C-6), 64.10 (C-5), 66.85 (C-4), 98.62 (C-1), 169.37, 170.58 (3 C=O); FDMS: m/z 304 $(M+1)^+$.

Eluted second was the mixture of isomers **40$_{a,b,c}$** (13%, syrup, **40$_a$**:**40$_b$**:**40$_c$** ~ 2:1:1); R_f 0.05 (solvent I); IR: ν 3294 (NH), 1745 and 1231 (ester), 1655 and 1545 (amide) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) **40$_a$**: δ 1.80 (dq, 1 H, $J_{2e,3}$ 5.6 Hz, H-2$_e$), 2.08 (1 H, $J_{2a,2e}$ 13.6 Hz, H-2$_a$), 3.49 (s, 3 H, OCH_3), 4.08 (1 H, $J_{5,6} = J_{5,6'}$ 6.0 Hz, H-5), 4.27 (d, 2 H, 2 H-6), 4.33 (m, 1 H, $J_{3,4}$ 5.6 Hz, H-3), 4.62 (dd, 1 H, $J_{1,2a}$ 7.2, $J_{1,2e}$ 2.4 Hz, H-1), 4.92 (q, 1 H, $J_{4,5}$ 2.8 Hz, H-4), 5.55 (bd, 1 H, $J_{3,NH}$ 7.6 Hz, NH); **40$_b$**: δ 1.67 (1 H, H-2$_a$), 2.00 (1 H, H-2$_e$), 3.52 (s, 3 H, OCH_3), 3.82 (t, 1 H, H-5), 4.26 (m, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 4.50 (dd, 1 H, $J_{1,2a}$ 9.6, $J_{1,2e}$ 2.0 Hz, H-1), 5.17 (d, 1 H, $J_{4,5}$ ~ 0 Hz, H-4), 5.50 (bd, 1 H, NH); **40$_c$**: δ 1.86 (1 H, H-2$_a$), 1.93 (1 H, H-2$_e$), 3.36 (s, 3 H, OCH_3), 4.54 (m, 1 H, $J_{3,4}$ 2.0, H-3), 4.86 (bs, 1 H, $J_{1,2a}$, $J_{1,2e}$ ~ 0 Hz, H-1), 5.22 (d, 1 H, $J_{4,5}$ ~ 0 Hz, H-4), 5.35 (bd, 1 H, $J_{3,NH}$ 7.2 Hz, NH); FDMS: m/z 272 $(M - OCH_3)^+$.

There were also eluted traces of **41** (2%, syrup); R_f 0.78 (solvent I); IR: ν 1748 and 1231 (ester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (dd, 1 H, $J_{2e,3}$ 5.2 Hz, H-2$_e$), 1.98, 2.06, 2.13 (3s, 9 H, 3 AcO), 2.06 (m, 1 H, $J_{2a,2e}$ 12.8, $J_{2a,3}$ 12.4 Hz, H-2$_a$), 3.36 (s, 3 H, OCH_3), 4.11 (m, 3 H, H-5, 2 H-6), 4.90 (d, 1 H, $J_{1,2a}$ 3.2 Hz, H-1), 5.28 (dq, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 5.33 (d, 1 H, H-4); ^{13}C NMR (400, $CDCl_3$): δ 21.07, 21.21 (3 COCH_3), 30.49 (C-2), 55.24 (OCH_3), 62.78, 66.87 (C-5, C-6), 66.43 (C-3), 66.98 (C-4), 98.72 (C-1), 169.98, 170.30 (3 C=O); FDMS: m/z 303 $(M-1)^+$, 305 $(M+1)^+$, and **42** (2%, syrup); R_f 0.66 (solvent I); IR: ν 1747 and 1231 (ester) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.95–2.12 (m, 2 H, $J_{2e,3}$ 5.6, $J_{2a,3}$ 12.0 Hz, H-2$_e$, H-2$_a$), 2.00, 2.05, 2.13 (3s, 9 H, 3 AcO), 3.53 (s, 3 H, OCH_3), 3.80 (td, 1 H, $J_{5,6} = J_{5,6'}$ 6.6 Hz, H-5), 4.14, 4.20 (2 dd, 2 H, $J_{6,6'}$ 11.2 Hz, 2 H-6), 4.48 (dd, 1 H, $J_{1,2a}$ 9.2, $J_{1,2e}$ 2.8 Hz, H-1), 5.00 (dq, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 5.26 (d, 1 H, H-4); ^{13}C NMR (400, $CDCl_3$): δ 21.05, 21.16 (3 COCH_3), 32.24 (C-2), 57.07 (OCH_3), 62.08 (C-6), 65.72 (C-4), 68.71 (C-3), 71.23 (C-5), 101.22 (C-1); FDMS: m/z 303 $(M-1)^+$, 305 $(M+1)^+$.

Acknowledgements

This research was supported by the Polish State Committee for Scientific Research under grants DS/8361-4-0134-2 and BW/8000-5-0313-1.

References

1. Hauser, F. M.; Ellenberger, S. R. *Chem. Rev.* **1986**, *86*, 35–67.
2. Roger, P.; Monneret, C.; Fournier, J.-P.; Choay, P.; Gagnet, R.; Gosse, C.; Letourneux, Y.; Attasi, G.; Gouyette, A. *J. Med. Chem.* **1989**, *32*, 16–23.
3. Ciuffo, G. M.; Santillan, M. B.; Estrada, M. R.; Yamin, L. J.; Jauregui, E. A. *J. Mol. Struct.-Theochem.* **1998**, *428*, 155–165.
4. Gauthier, Ch.; Ramondenc, Y.; Ple, G. *Tetrahedron* **2001**, *57*, 7513–7517.
5. Pan-Zhou, X-R.; Cretton-Scott, E.; Zhou, X-J.; Yang, M-X.; Lasker, J. M.; Sommadossi, J-P. *Biochem. Pharmacol.* **1998**, *55*, 757–766.
6. Gonzalez, F.; Lesage, S.; Perlin, A. S. *Carbohydr. Res.* **1975**, *42*, 267–274.
7. Hansen, P.; Lau, J.; Pedersen, E. B.; Nielsen, C. M. *Liebigs Ann. Chem.* **1990**, 1079–1082.
8. Dąbrowska, A.; Smiatacz, Z. *Book of Abstracts*, VIIth European Carbohydrate Symposium, Cracow, Poland, August 1993; A 015.
9. Dąbrowska, A.; Dokurno, P.; Konitz, A.; Smiatacz, Z. *Carbohydr. Res.* **2000**, *323*, 230–234.
10. Daley, L.; Roger, P.; Monneret, C. *J. Carbohydr. Chem.* **1997**, *16* (1), 25–48.
11. Pedersen, E. B.; Wengel, J. *Synthesis* **1991**, 451–454.
12. (a) Florent, J.-C.; Monneret, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1171–1172;
(b) Abbaci, B.; Florent, J.-C.; Monneret, C. *J. Chem. Soc. Chem. Commun.* **1989**, 1896–1897;
(c) Abbaci, B.; Florent, J.-C.; Monneret, C. *Carbohydr. Res.* **1992**, *228*, 171–190.
13. Wengel, J.; Lau, J.; Pedersen, E. B.; Nielsen, C. M. *J. Org. Chem.* **1991**, *56*, 3591–3594.
14. Dąbrowska, A.; Konitz, A.; Smiatacz, Z. *Carbohydr. Res.* **2002**, *337*, 3591–3594.
15. Liberek, B.; Konitz, A.; Frankowski, R.; Smiatacz, Z. *Carbohydr. Res.* **2000**, *326*, 151–158.