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Synthesis of N-Glycosyl Amides via Hydrolysis of Protected Glycosyl Oxazolines and Ritter-like Reactions of Native Carbohydrates

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Abstract

A stereoselective synthesis of *N*-glycosyl amides was studied from available *N*-glycosyl oxazolines prepared by Ritter-like reactions of protected sugar acetonides. Hydrolysis reactions of the protected pentofuranosyl and hexafuranosyl oxazolines, as precursors of glycosyl amine derivatives, were carried out in the presence of silica gel in chloroform to give *N*-α- and β-glycosyl amides in good yields after column chromatography on silica gel. Access to selectively blocked *N*-α-xylo-, -ribo-, β-arabino-furanosyl, α-glyco-, α-allo-furanosyl, α- and β-galactopyranosyl amides (twelve examples) useful for preparing modified *N*-glycosides was accomplished through a mild hydrolysis of sugar oxazolines with 2-alkyl substituents in acidic and neutral conditions. To further explore the scope of the $BF_3{\cdot}Et_2O$-mediated approach developed for *N*-furanosyl oxazolines, a stereoselective synthesis of protected N-α-hexopyranosyl oxazoline was fulfilled in a high yield from D-galactopyranose diacetonide derivative. The Ritter-like promoted reaction between D-arabinose and benzonitrile afforded 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline as the main product. In acetonitrile the $BF_3{\cdot}Et_2O$-KHF_2-assisted reactions of unprotected native sugars were found to result in the formation of mixtures of *N*-furanosyl and pyranosyl acetamides.

Introduction

Chemical modification of carbohydrates by introduction of different functional groups at an anomeric carbon to form glycosides is essential for the understanding of their biological functions [1]. *N*-functionalization of sugars leading to *N*-glycosides with enhanced stability towards hydrolytic enzymes play a remarkable role in the field of glycobiological studies [2]. The development of sugar mimetics with the C-N glycosidic linkage is interesting for medicinal chemistry, and designing effective therapeutic agents [3]. The amide bond is an important connection found in natural compounds which can be used for attaching other biologically active molecules [4-5] to carbohydrates. *N*-Glycosyl amides are stable under basic as well as acidic conditions and synthetic studies towards formation of the glycosyl amide linkage, approaches to structurally modified *N*-glycosides are of interest for carbohydrate chemistry.

N-Glycosyl amides and glycopeptides are known to take part in a variety of

biological processes, and demonstrate a wide range of bioactivities, mainly because these types of carbohydrate derivatives can bind efficiently to specific sites of proteins, may be involved in numerous cell recognition processes [6], and can serve as glycomimetics. A series of glycosyl amides have been investigated as inhibitors of glycogen phosphorylase and the results of such studies provide evidence for interesting inhibitory properties of various *N*-β-glucopyranosyl amides (Fig.1, e.g., compounds **I-II**) [7, 8]. *N*-Glycosyl amides as modulators of the activity of this enzyme may be used for developing a treatment for type 2 diabetes [8,9]. Furthermore, *N*-glycosyl amides **III** and **IV** were synthesized for evaluation of their potential antibacterial activities [10, 11]. *N*-β- and α-fucosyl amides were identified as high-affinity ligands for lectin LecB [10] and it has also been reported that galacto-furanosyl or -pyranosyl amides may act as inhibitors of galactosidases or galactofuranosyltransferases [11, 12]. Recently, *N*-sulfonyl amide derivatives of galaltopyranose **V** and glycopyranose **VI** as inhibitors of carbonic anhydrase II have been shown to exhibit antiglaucoma activities [13]. Protected 2-chloro-1-acetamido sugar derivatives with *gluco*, *galacto* configuration (e.g., compound **VII a**) prepared from glycals and free amines (compound **VII b**) were found to be potently cytotoxic against the U-87 malignant glyoma (a brain tumor) cell line with IC-50 = 1 nm −22 μM [14]. The glycoconjugate of the galactose with quinolinic acid derivative **VIII** involving amido linkage between sugar and a quinoline moiety exhibits cytotoxicity against cancer cells at the micromolar level [15] (Figure 1). In this context, it is worth noting interesting biological properties of bicyclic compound assigning to tetrahydropyrimidinone derivatives (6M3NP, the full title in ref.16) with an aromatic fragment and amide bond in pyrimidone moiety, and a new catalytic approach for its production. The compound showed antimicrobial and antioxidant activities. The anticancer activity of a phenyl acrylamide urea derivative was witnessed against various cell lines such as MCF7, MDA-MB-231, and T47D (breast cancer) [16].

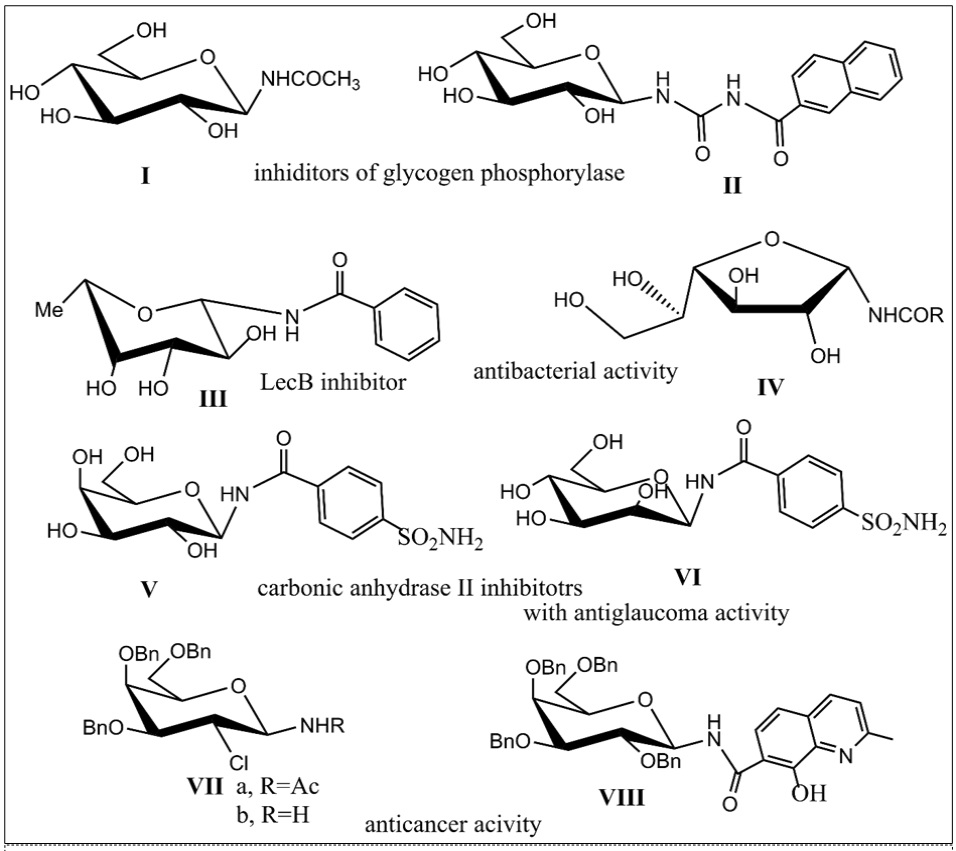
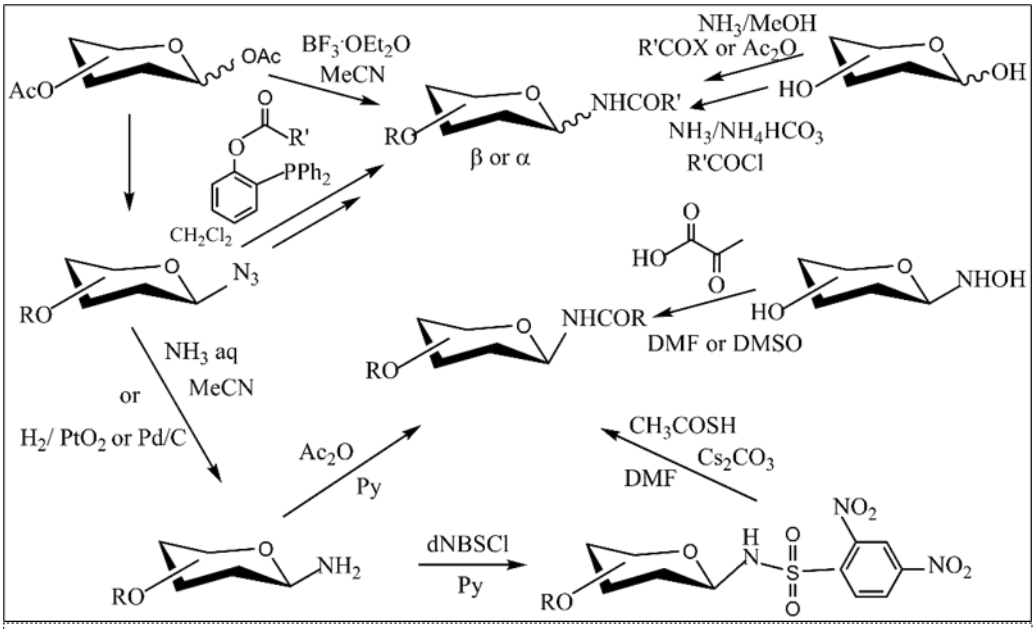


Figure 1. Biologically active N-glycosyl amides

The obvious potential of *N*-glycosyl amides in medicinal chemistry has driven the search for stereoselective and efficient routes to produce these monosaccharide derivatives. Various approaches to access modified *N*-glycosides in different carbohydrate derivatives have been developed [1, 2, 4]. Stereoselective synthetic methods to *N*-α- and β-glycosyl amides were earlier studied from protected and native carbohydrate precursors, and the most known of them are summarized in Scheme 1. The formation of *N*-glycosyl amides can be realized by preparation of intermediate aminosugars from blocked or unprotected sugars followed by their acylation with the acylating agent or via direct coupling of amides to glycosyl halides [2, 12, 17]. The main drawback of a simple approach is the anomerization of glycosyl amines which leads to a mixture β- and α-amides after the acylation reaction. A facile and efficient synthesis to various β-glycosyl amines and amides was recently described from benzoylated α-glycosyl bromides by the ammonolysis reaction with aqueous ammonia [18]. The method for preparing β- or a mixture of β-and α-glycosyl amides has been reported by decarboxylative reaction of unprotected sugar oximes with α-ketoacids in dimethylsulfoxide [19]. Synthesis of protected β-glycosyl acetamides was also developed by treating 2,4-dinitrobenzenesulfonyl β-glycosyl amides derived from from glycosyl azides with thioacetic acid and cesium carbonate [20]. Protected *N*-glycosyl acetamides as a mixture of *N*-β- and α-glycosides were obtained via a Ritter-type reaction of peracetylated D-hexopyranoses with acetonitrile in the presence of boron trifluoride etherate at room temperature [21].

Glycosyl azides are used as valuable precursors for stereoselective synthesis of β-glycosyl amides because they possess chemical stability without anomerization at their anomeric centre and can be reduced by various methods prior to acylation reaction with the acyl derivatives. A common method, that is the most studied in carbohydrate chemistry, is based upon the Staudinger reactions including reduction-acylation process in which unprotected/blocked α- or β-glycosyl azide reacts with diphenyl phospanyl-phenyl esters [22-24]. The diastereoselectivity of these reactions proves dependent on sugar protecting group and the configuration of the starting azide.



Scheme 1. The known synthetic routes to N-glycosyl amides

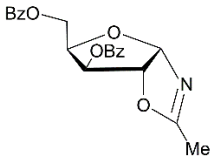
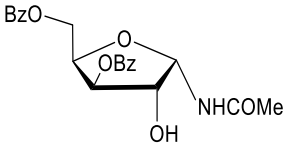
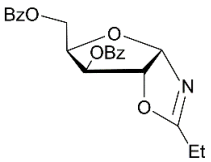
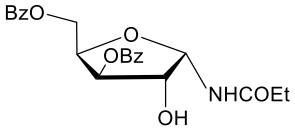
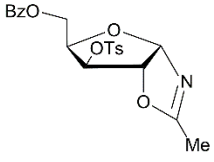
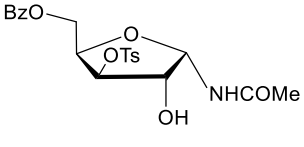
A limited number of synthetic routes was developed for the synthesis of α-glycosyl amides. Most of them include two steps and have been described for several hexo- and pentofuranose derivatives [11,24]. The method investigated by the Bernardi goup is founded on the traceless Staudinger ligation of various glycosyl azides of pyranose and furanose series with functionalized phosphines for stereoselective synthesis of α- or β-glycopyranosyl, α- or β-ribo- and arabinofuranosyl amides [23].

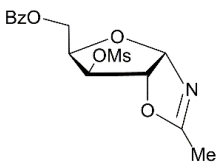
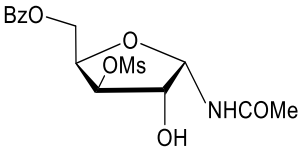
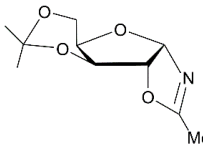
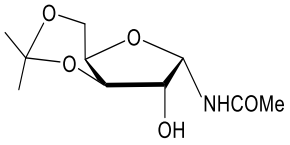
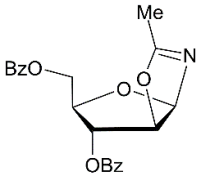
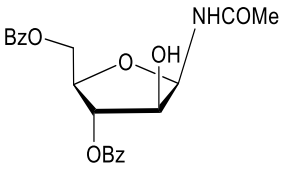
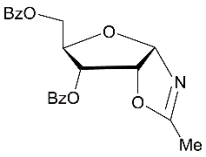
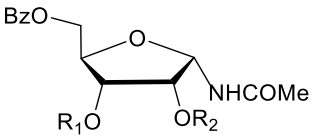
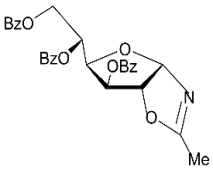
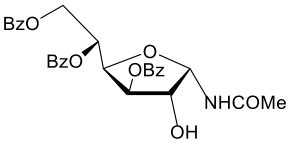
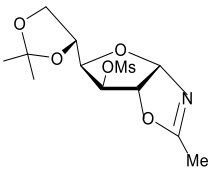
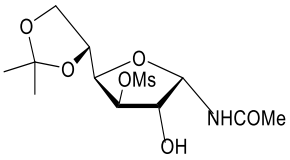
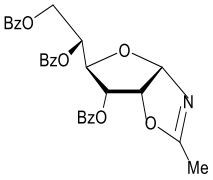
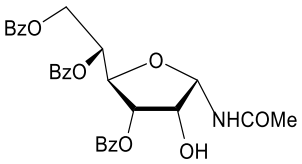
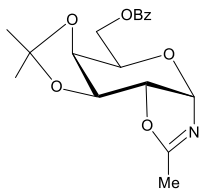
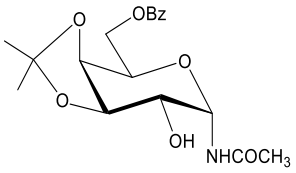
In extension of our previous study of the Ritter-like reaction in field of carbohydrates this paper reports exploration of synthetic routes to a series of novel and known *N*-glycosyl amides from available sugar oxazolines or native carbohydrates for further preparation and biological evaluation of modified *N*-glycosides and glycoconjugates with nucleosides.

Results and Discussion

Synthesis study of a series of *N*-glycosyl amides has been undertaken starting from a new approach developed for preparing *N*-glycosyl oxazolines [25] from the sugar acetonide derivatives. It was earlier shown that $BF_3{\cdot}Et_2O$-mediated reactions of the 3,5-di-*O*-benzoylated D-xylofuranose-1,2-*O*-acetonide with nitriles followed by column chromatography on silica gel gave target 2-alkyl substituted oxazolines along with *N*-α-xylofuranosyl amides isolated in low yields. In the course of the present research, hydrolysis reactions of protected *N*-xylofuranosyl, ribofuranosyl and arabinofuranosyl oxazolines were studied on silica gel to prepare *N*-glycosyl amides. Formation of *N*-glycosyl amides from protected sugar oxazolines was found to proceed on silica gel under mild conditions in chloroform. Hydrolysis reactions of the protected oxazolines in the presence of silica gel gave *N*-α- and β-glycosyl acetamides in good yields after column chromatography. Results on synthesis of a set of protected *N*-glycosyl amides are summarized in Table 1.

Table 1. Synthesis of selectively protected N-glycosyl amides via hydrolysis reactions of N-glycosyl oxazolines on silica gel

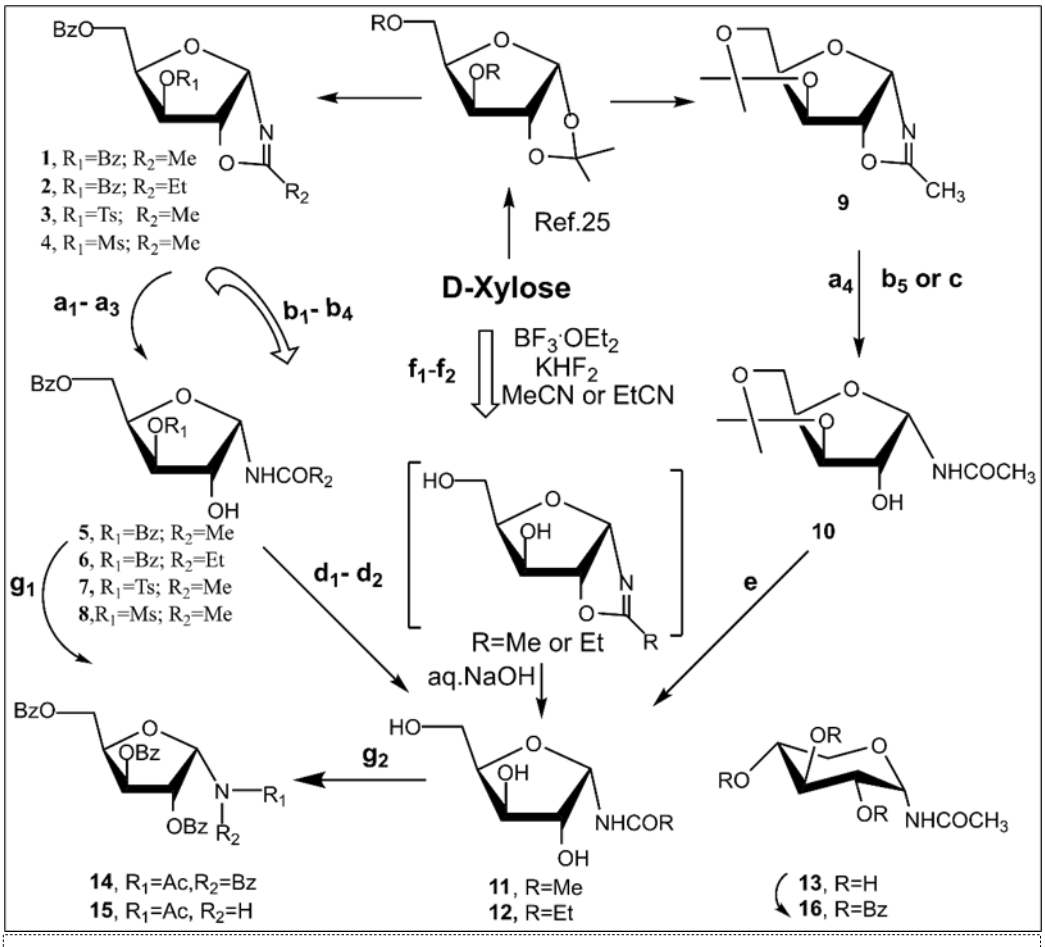
Entry	Protected D-furanosyl and pyranosyl oxazolines	Silica gel 60 H (70-230 mesh, Merck)	Time for hydrolysis reaction	N-glycosyl amide	(Yield, %) [a]
1	 **1**	$CHCl_3$	22	 **2**	**2** (84%)
2	 **3**	$CHCl_3$	18	 **4**	**4** (85%)
3	 **5**	$CHCl_3$	18	 **6**	**6** (85%)

4	 **7**	$CHCl_3$	18	 **8**	**8** (86%)
5	 **9**	$CHCl_3$	22	 **10**	**9** (78%)
6	 **11**	$CHCl_3$	48	 **12**	**12** (84%)
7	 **13**	$CHCl_3$	48	 **14**, R_1=Bz; R_2=H **15**, R_1=H; R_2=Bz	**14** (45%) and **15** (11%) [b]
8	 **16**	$CHCl_3$	22	 **17**	**17** (78%)
9	 **18**	$CHCl_3$	18	 **19**	**19** (80%)
10	 **20**	$CHCl_3$	18	 **21**	**21** (70%)
11	 **22**	$CHCl_3$	18	 **23**	**23** (78%)

[a]Isolated yield after keeping oxazoline on silica gel and subsequent column chromatography on silica gel using chloroform-methanol

[b]Yields of individual N-ribofuranosides isolated after additional chromatography of a mixture isomeric products on silica gel using ethyl acetate-petroleum ether

In the first place, with oxazolines in hands, syntheses of a series of selectively protected *N*-α-xylofuranosyl amides were investigated from the oxazolines under various conditions (Scheme 2). $BF_3{\cdot}Et_2O$-mediated reactions of benzoylated D-xylofuranose 1,2-*O*-acetonide derivative with acetonitrile and propionitrile gave oxazolines in high yields after work-up of the reaction mixtures [25], but the formation of glycosyl amides was observed in 8-19% yields after chromatography using for elution mixtures of ethylacetate-petrolium ether. Partial hydrolysis of *N*-α-xylofuranosyl oxazolines took place during chromatography on silica gel. These findings may be attributable to moderate stability of the intermediate hemiorthoamidate derivatives forming after the nucleophilic addition of water to oxazolines **1** or **2** during chromatographic isolation, and their ability to undergo the regioselective cleavage into the α-glycosyl amides on silica gel. Further, the hydrolysis of oxazolines of *xylo* series was also studied under storing. Protected xylofuranosyl oxazoline **1** under a long storing (conditions a_1) gave a mixture of products from which the benzoylated *N*-α-glycoside **4** was isolated in

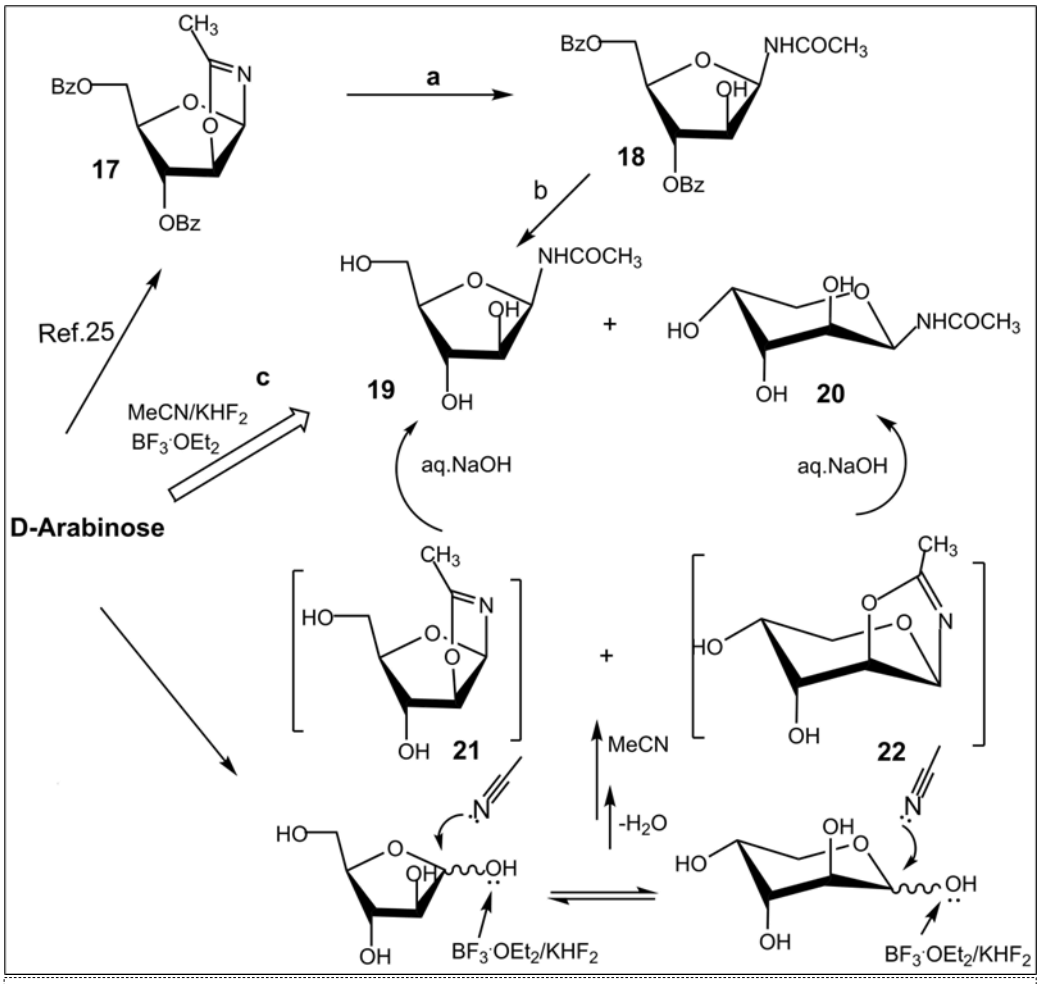


Scheme 2. Synthetic study of N-α-glycosyl amides with *xylo* configuration from D-xylose. Reagents and conditions: a1) **1**, long storing at 5-8 ^{0}C, CC, **4**, 67%; a2) **2**, long storing at 5-8 ^{0}C, CC, **6**, 86%; a3) **3**, long storing at 5-8 ^{0}C, CC, 6, 60%; a4) **7**, long storing at 5-8 ^{0}C, CC, 8, 90%; b1) **1**, $CHCl_3$, silica gel (entry1, table 1), 5, 84%; b2) **2**, $CHCl_3$, silica gel (entry 2, table 1), **6**, 85%; b3) **3**, $CHCl_3$, silica gel (entry 3, table 1), 7, 85%; b4) **4**, (entry 4, table 1), **8**, 86%; b5) **9**, $CHCl_3$, silica gel (entry 5, table 1), **10**, 78%; c) **9**, 75% aq AcOH, rt, 20 h, CC, **11**, 90%; d1) **5**, NH_3/MeOH, rt, 18 h, CC, **11**, 77%; d2) **6**, NH_3/MeOH, rt, 18 h, CC, **12**, 81%; f1) D-xylose CH_3CN, KHF_2, $BF_3.Et_2O$, rt, 4 h, CC, **11**, 37%, **13**, 5-6%; f2) D-xylose, EtCN, KHF_2, $BF_3{\cdot}Et_2O$, rt, 4 h, CC, **12**, 28%; g1) **5**, BzCl/Py, rt, **14**, 42%, **15**, 42%; g2) a mixture of **11** and **13**, BzCl/Py, Et_3N, rt, **14** (15%), and **15**/**16**, 70%.

67% yield. The oxazolines **2** and **3** (conditions a_2-a_3) also yielded N-α-xylofuranosyl acetamides **6-7** in 67-86% yields after a long storing and chromatograpy or crystallization. Protected *N*-α-xylofuranosyl acetamide **10** was prepared from the 3,5-*O*-isopropylidene derivative of xylofuranosyl oxazoline **9** in a high 90% yield using mild conditions for the hydrolysis reaction (Scheme 2, conditions a_4). We failed to carry out a direct synthesis of *N*-α-glycoside **10** by treatment of **9** with 73% aq. acetic acid at room temperature due to acidic hydrolysis of the oxazoline **9** is likely accompanied by the formation of acyclic by-products.

It was found that hydrolysis reactions of the protected N-α-xylofuranosyl oxazolines **1-4** and **9** proceeded on silica gel to give selectively protected *N*-α-glycosyl acetamides in good yields (Scheme 2, Table 1, enties 1-5) after column chromatography on silica gel using chloroform and chloroform-methanol as eluents. Deacylation of *N*-α-xylofuranosyl amide derivatives **5** and **6** with cold saturated NH_3/MeOH gave *N*-α-glycosides **11** and **12** in 77% and 81% yields, respectively (Scheme 2). Removing the isopropylidene protecting group in N-α-glycosyl amide **10** with 75% aq. CH_3COOH furnished the target *N*-α-xylofuranosyl acetamide (**11**, 90%).

The Ritter-like $BF_3{\cdot}Et_2O$-promoted reaction of D-xylose in acetonitrile afforded *N*-α-xylofuranosyl acetamide **11** as the main product in 37% yield along with formation of *N*-α-xylopyranosyl acetamide **13** (about 5-6%) and acyclic glycosyl amides as by-products (Scheme 2, conditions f_1). The spectral data of *N*-α-xylofuranosyl acetamide prepared by the one-pot synthesis from D-xylose were identical to those of *N*-α-glycosyl acetamide **11** synthesized via protected *N*-α-xylofuranosyl acetamide **5** in five steps. However, efforts to separate *N*-α-glycosides **11** and **13** by column chromatograpy on silica gel were unsuccessful. Benzoylation of selectively protected *N*-acetyl D-xylofuranosyl amide **5** with benzoyl chloride in pyridine followed by column chromatography afforded individual perbenzoylated *N*-α-D-xylofuranosyl acetamide **14** (42%) and tri-*O*-benzoylated derivative **15** (42%). Treatment of a mixture of isomeric N-glycosides **11** and **13** (a separate fraction isolated by column chromatography on silica gel after the Ritter-like reaction), with benzoyl chloride in pyridine in the presence of triethylamine gave individual tetra-O-benzoylated N-α-xylofuranosyl acetamide **14** (15%) and a mixture of tri-*O*-benzoylated N-glycosides **15** and **16** (70%) (a ratio 3:1 according to ^1H and ^{13}C NMR spectral data), which were inseparable by chromatography on silica gel. The formation of N-α-xylofuranosyl and pyranosyl acetamides may proceed via generation of corresponding intermediate oxazolines forming during Ritter-like reactions of furanose and pyranose forms of D-xylose with acetonitrile in the presence of the Lewis acid. The $BF_3{\cdot}Et_2O$-mediated reaction of D-xylose in propionitrile at room temperature afforded N-propionyl-α-D-xylofuranosylamide (**12**) which was isolated in 28% yield after column chromatography on silica gel. The structure of the N-α-glycoside was supported by comparison of NMR spectral data with those of **12** prepared by the multi-step approach from D-xylose through 3,5-di-*O*-benzoylated *N*-α-xylofuranosyl oxazoline **2** (Scheme 2). The magnitudes of $^3J_{H\text{-}1,H\text{-}2}$ vicinal couplings [26] for protected *N*-acetyl-α-D-xylofuaranosyl amides **8** ($J_{1,2}$ = 3.5 Hz), **7** ($J_{1,2}$ = 3.8 Hz), **6** ($J_{1,2}$ = 4.1 Hz) and **5** ($J_{1,2}$ = 4.2 Hz) confirm their α-anomeric configurations and the *cis*-arrangement of H-1 and H-2 protons in the furanose rings, resonance signals of H-1 protons being displayed as doublet of doublets ($J_{NH,H\text{-}1}$ = 9-10 Hz) for synthesized *N*-α-xylofuranosyl amides in their NMR spectra measured in $CDCl_3$. Absorption bands of the amide bond were revealed in the range of 1680-1505 cm^{-1} in IR-spectra of *N*-α-xylofuranosylamide derivatives. Furthermore, the downfield chemical shifts for C-1 signals (80-84 ppm) were observed in a series of *N*-α-xylofuranosyl amides **5-8** and **10** in comparison with the anomeric carbons of *N*-α-xylofuranosyl oxazolines **1-4** and **9** [25], which appeared at 100-101 ppm in the ^{13}C NMR spectra, indicating



Scheme 3. Synthesis of N-β-D-glycosyl acetamides with *arabino* configuration from D-arabinose. Reagents and conditions: a) **17**, $CHCl_3$, silica gel (entry 6, table 1), **18**, 84%; b) **18**, NH_3/MeOH, rt, 18 h, **19**, 68%; c) D-arabinose, CH_3CN, KHF_2, $BF_3{\cdot}Et_2O$, rt, 4 h 10 min, CC, **19**, 21%, **20**, 18%.

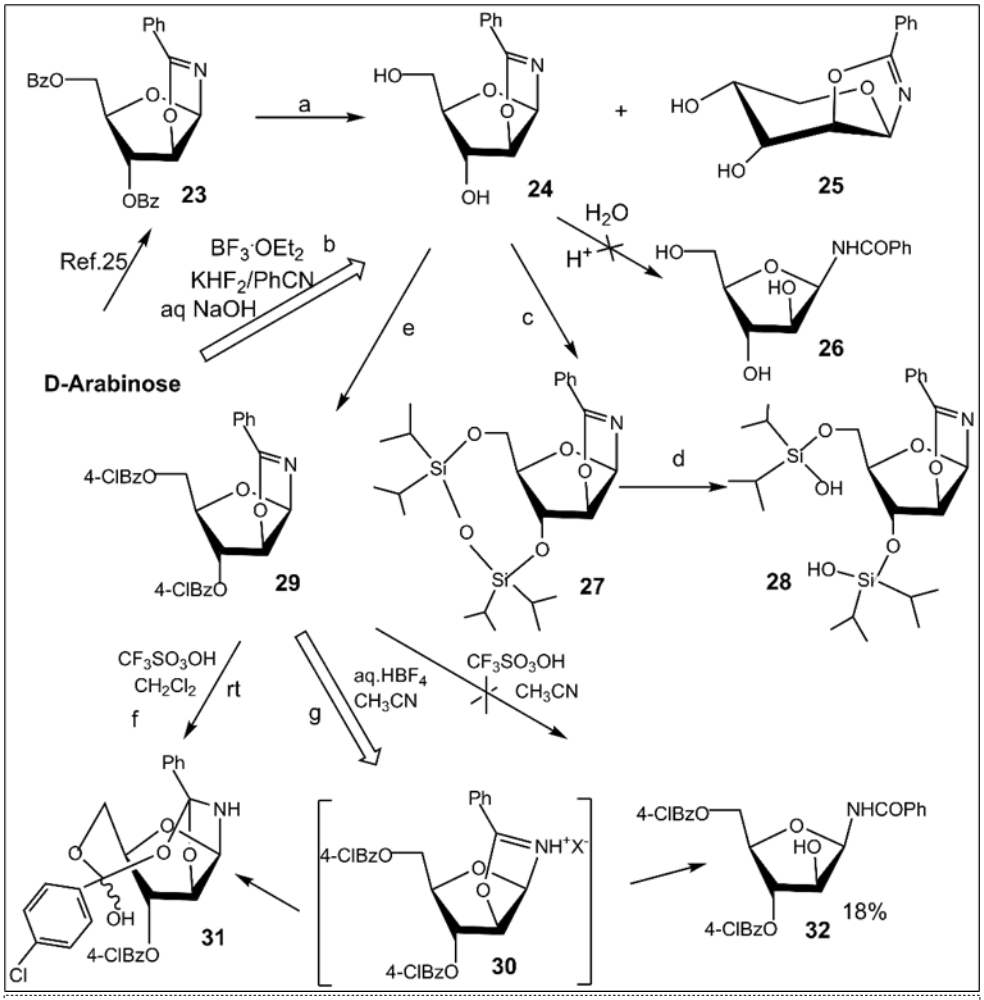
attachment of acetamide group at the anomeric carbon in synthesized *N*-glycosides deriving from oxazolines. Resonance signals of H-1 protons for deprotected *N*-xylofuranosyl amides **11** and **12** as well *N*-xylopyranosyl amide **13** displayed as doublets for synthesized *N*-α-glycosyl amides in their NMR spectra measured in D_2O or CD_3OD. The low value of $^3J_{H\text{-}1,H\text{-}2}$ vicinal coupling for *N*-acetyl-α-D-xylopyranosyl amide **13** ($J_{1,2}$ = 3.1 Hz) is in good accordance with α configuration [12] at the anomeric centre of known xylopyranosyl amide derivatives. Further, synthetic approaches to N-β-arabinofuranosyl amides were studied from D-arabinose using the $BF_3{\cdot}Et_2O$-mediated reactions. The Ritter-like reaction of D-arabinose in acetonitrile in the presence KHF_2 and $BF_3{\cdot}Et_2O$ afforded *N*-β-arabinofuranosyl acetamide (**19**) in 21% yield along with of *N*-β-arabinopyranosyl acetamide **20** (18%) which were separated by column chromatography on silica gel (Scheme 3). The spectral data of *N*-β-arabinofuranosyl acetamide **19** prepared by the one-pot synthesis from D-arabinose were identical to those of the same *N*-β-glycosyl acetamide obtained in six steps through the hydrolysis reaction of the benzoylated oxazoline **17** on silica gel (entry 6, Table 1) followed by the deacylation of the protected *N*-glycoside **18** with ammonia in methanol (Scheme 3, conditions b).

The structure of *N*-β-arabinopyranoside **20** was supported by NMR spectral data and mass-spectroscopy. The formation of isomeric *N*-β-glycosides **19** and **20** with acetamide group can be explained by generation of intermediate oxazolines (Scheme 3) during reactions of furanose and

pyranose forms of D-arabinose in acetonitrile in the presence of $BF_3{\cdot}Et_2O$ [16] and KHF_2 as promoters, and a subsequent stereoselective cleavage of oxazolines **21** and **22** under basic work-up of the reaction mixture.

The $BF_3{\cdot}Et_2O$-mediated reaction of D-arabinose in benzonitrile, unlike that of in acetonitrile, gave rise to 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline (**24**) and 2-phenyl-β-D-arabinopyrano-[1,2-d]-2-oxazoline (**25**) at room temperature in 56% and 10% yields, respectively (Scheme 4, conditions b). After basic treatment of the reaction mixture isomeric 2-phenyl substituted glycosyl oxazolines were isolated by column chromatography on silica gel. The structure of **24** was supported by comparison of its spectral data with those of 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline prepared by removing benzoyl protecting groups (NH_3/MeOH) (Scheme 4, conditions a) in the oxazoline **23** ealier synthesized in six steps starting from D-arabinose [25]. The assignment of structure for 2-phenyl-β-D-arabinopyrano-[1,2-d]-2-oxazoline **25** was made on the basis of its ^1H and ^{13}C NMR, mass spectral data. The benzoylated β-arabinofuranosyl oxazoline **23** as well as the unprotected oxazoline **24** with 2-phenyl substituent did not afford corresponding *N*-glycosyl amides under hydrolysis reactions in neutral or acidic conditions (on silica gel in chloroform), and they possess more stability in comparison with *cis*-fused benzoylated β-arabino- and α-xylofuranosyl oxazolines with 2-aliphatic alkyl substituents (Table 1, entries 1-4). Unlike 2-methyl-α-D-xylofurano-[1,2-d]-2-oxazoline and its derivatives, 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline (**24**) was stable under a long storing, and formation of *N*-β-arabinofuranosyl amide **26** has not been found in the neutral conditions. Exploration of hydrolysis of oxazoline **24** was performed under various acidic conditions (aqueous trifluoroacetic acid, 6N aq. hydrocloric acid), but formation of *N*-glycosyl amide **26** was not observed due to to acidic hydrolysis of the oxazoline ring has been accompanied by the formation of acyclic by-products via cleavage of the furanose ring.

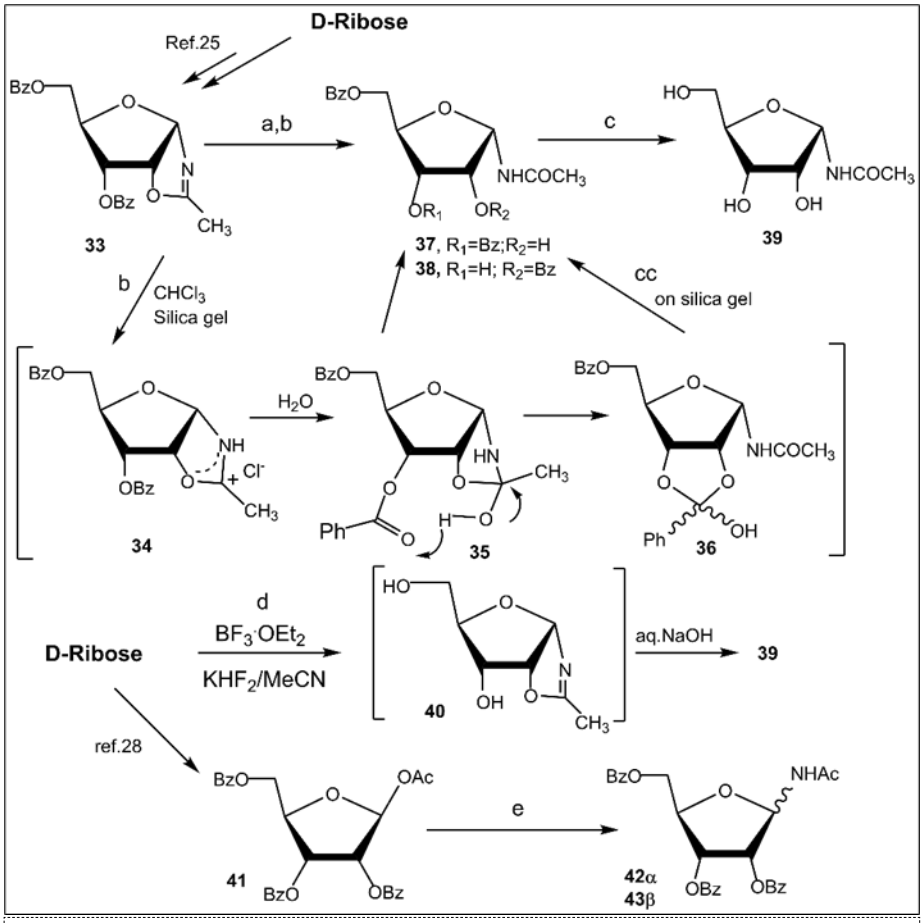
Further, to solve a challenge of a selective cleavage of 2-phenyl substituted glycosyl oxazolines, investigation of hydrolysis reactions of 3,5-di-*O*-protected 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazolines was performed to prepare N-β-arabinofuranosyl benzamide derivatives (Scheme 4). Silylated derivative of oxazoline **27** was prepared by treatment of the oxazoline **24** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in pyridine in 98% yield. The hydrolysis reaction of the oxazoline ring in **27** was studied under acidic conditions (aq.HCl/CH_2Cl_2) at room temperature. The cleavage of silyl protective group in **27** proceeded instead of selective transformations on 2-phenyl substituted oxazoline ring and silylated oxazoline derivative **28** was prepared in 88% yield. Benzoylation of the oxazoline **24** with 4-chlorobenzoyl chloride in pyridine at room temperature afforded 3,5-di-*O*-4-clorobenzoylated oxazoline **29** in 89% yield. The search for reaction conditions for selective hydrolysis of 2-phenyl substituted oxazoline ring in 3,5-di-O-acylated N-β-arabinofuranosyl oxazoline deivatives has been undertaken. Hydrolysis of benzoylated oxazoline **29** was studied in the presence 2-3 equiv. CF_3SO_3OH in acetonitrile, but no formation of protected N-β-arabinofuranosyl amide **32** was detected under tested conditions. Treatment of oxazoline **29** with 2-3 equiv. CF_3SO_3OH in CH_2Cl_2 at room temperature gave only adduct **31** in 25% yield. Conversions of by-product **31** was explored under mild acidic (on silica gel in chloroform) or basic conditions (aq. $NaHCO_3$ in CH_3CN/CH_2Cl_2), but no formation of target N-glycoside **32** was observed, only the starting arabinofuranose derivative was isolated in the both cases. Selective cleavage of the oxazoline ring in **29** was explored in the presence of a strong acid such as aqueous HBF_4. The hydrolysis reaction of oxazoline **26** was investigated in acetonitrile with various access of aqueous HBF_4. It was found that cleavage of oxazoline ring in **26** took place in the presence of a small access of the acid promoter to afford a mixture of products after column chromatography.



Scheme 4. Synthesis of 2-phenyl substituted *N*-β-D-glycosyl oxazolines of *arabino* configuration and acylated *N*-benzoyl-β-D-arabinofuranosylamide from D-arabinose. Reagents and conditions: a) **23**, NH_3/MeOH, rt, 18 h, **24**, 74%; b) D-arabinose, PhCN, KHF_2, $BF_3{\cdot}Et_2O$, rt, 4 h 10 min, CC, **24**, 56%, **25**, 10%; c) **24**, $(iPr_2SiCl)_2O$, Py, rt, **27**, 98%; d) **27**, CH_2Cl_2, aq. 33% HCl, **27**, 88%; e) **24**, 4ClBzCl, Py, rt, **29**, 89%; f) **29**, CF_3SO_3OH, CH_2Cl_2, rt, **31**, 25%; g) **29**, aq. HBF_4, CH_3CN, $0^0\rightarrow$ rt, 20 h, 20 h, **31**, 19%, **32**, 32%, recovery 23% of **29**.

N-β-arabinofuranosyl amide **32** (32%) was isolated after the hydrolysis reaction of the oxazoline under tested conditions followed by column chromatography on silica gel. It should be noted that cleavage of the oxazoline ring in **29** also results in formation of by-product **31** (14% yield) likely through coparticipation of 5-*O*-4-chlorobenzoyl group in the oxazolinium intermediate **30**, and presumably 1-β-amino arabinose derivative (according to NMR data) as a result of acid-catalyzed hydrolysis of the 1,2-oxazoline ring of sugar in the presence of aqueous acid [27]. ^{1}H NMR analysis of the reaction mixture after the mild basic treatment showed absence of N-β-glycosyl amide **32**, but the formation of the latter along with by-sugar derivaives was found to take place during chromatography on silica gel likely through transformations of the oxazolinium intermediate. The structures of synthesized N-β-arabinofuranosyl benzamide derivative **32** as well by-product **31** were supported by ^{1}H, ^{13}C NMR and mass spectra.

Next, synthesis of protected *N*-ribofuranosyl acetamide derivatives was studied starting from D-ribose (Scheme 5). Hydrolysis reaction of the acylated α-D-ribofuranosyl oxazoline **33**, prepared ealier from D



Scheme 5. Synthesis of *N*-D-ribofuranosyl acetamide derivatives from D-ribose. Reagents and conditions: a) **33**, a long storing at 5-8 ^{0}C, **37**, 62%; b) **33**, $CHCl_3$, silica gel (entry 7, table 1), **37**, 45% and **38**, 15%; c) **37**, NH_3/MeOH, rt, 18 h, **39**, 72%; d) D-ribose, CH_3CN, KHF_2, $BF_3{\cdot}Et_2O$, 0^0C→rt, 3 h, **39**, 9%; e) peracylated D-ribofuranose **41**, CH_3CN, KHF_2, $BF_3{\cdot}Et_2O$, 0^0C→rt, 2 h, 1N aq. NaOH, **42α**, 10%, **43β**, 10%.

-ribose by Ritter-like reaction of benzoylated 1,2-*O*-isopropylidene-D-ribofuranose derivative [25], gave in neutral conditions (a long storing at 5-8 ^{0}C) 3,5-di-*O*-benzoylated *N*-α-ribofuranosyl acetamide **37** (70% of conversion of the oxazoline to the N-α-glycoside was determined according to ^{1}H NMR data of a mixture of products), which was isolated in 62% yield after column chromatography on silica gel.

O-Deprotection of *N*-α-riboside derivative **37** with cold saturated NH_3/MeOH at room temperature gave *N*-acetyl-α-D-ribofuranosyl amide (**39**) in 72% yield. Protected *N*-α-ribofuranosyl acetamide **37** (45%) along with 2,5-di-*O*-benzoylated *N*-α-ribofuranosyl acetamide **38** (15%) was also obtained using the hydrolysis reaction of the benzoylated oxazoline **33** on silica gel (entry 7, Table 1). In this case a mixture of isomeric protected *N*-ribofuranosyl acetamides **37** and **38** was prepared as a result of the hydrolysis reaction accompanied by migration of the 3-*O*-benzoyl group which led to 2,5-di-*O*-benzoyl *N*-α-ribofuranosyl acetamide **38** (Scheme 5). The plausible mechanism of the studied reaction leading to selectively di-*O*-acylated N-α-ribofuranosides from the oxazoline **33** is likely to include the formation of the oxazolinium itermediate **34** and a subsequent generation intermediates **35** and **36**, which afford isomeric benzoylated *N*-α-ribofuranosyl acetamides during column chromatography on

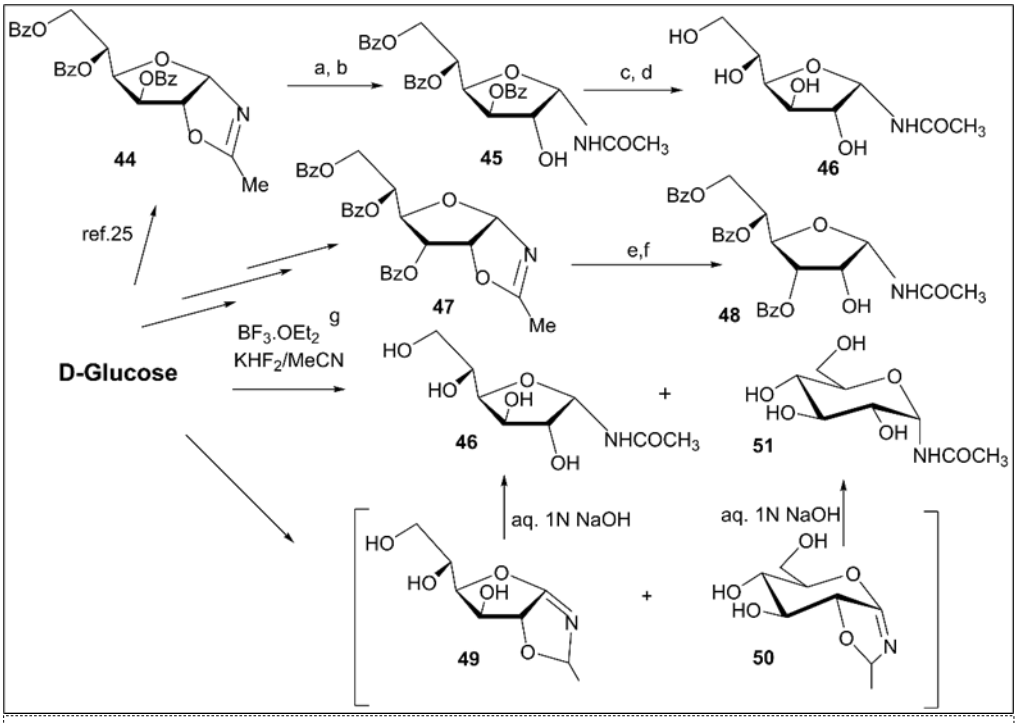
silica gel using chloroform, chloroform-methanol as eluents. The Ritter-like reaction of D-ribose promoted with $BF_3{\cdot}Et_2O$ in the presence of KHF_2 in acetonitrile at room temperature afforded *N*-α-ribofuranosyl acetamide (**39**) which was isolated by column chromatography on silica gel in a low 9% yield (Scheme 5, conditions e). The formation of **39** is likely to proceed through intermediate unstable oxazoline **40** forming as a result of $BF_3{\cdot}Et_2O$ promoted reaction of D-ribose with acetonitrile. Main products of the Ritter-like reaction were acyclic D-ribose derivatives with acetamide group, but their structures have not been established.

Further, the Ritter-like reaction of peracylated D-ribofuranose **41**, prepared from D-ribose according to the known method [28], was studied in acetonitrile. Treatment of fully *O*-acylated D-ribose derivative **41** with KHF_2-$BF_3{\cdot}Et_2O$ in CH_3CN (conditions b_3), unlike 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose [25], afforded a mixture of products from which individual benzoylated *N*-α- and β-ribofuranosylacetamides **42α** (10%) and **43β** (10%) were isolated by column chromatography on silica gel. In this case the oxazoline was not obtained by the Ritter reactions in acetonitrile in the presence of a strong Lewis acid such as $BF_3{\cdot}OEt_2$. Notably, in previous study on synthesis of nucleosides described earlier in the work [29], the only benzoylated *N*-β-ribofuranosyl acetamide **42β** has been prepared in 44% yield after the reaction of acetate **41** with acetonitrile under refluxing in the presence of trimethylsilyl triflate as a mild catalyst. Besides, Song and Hollingsworth [21] have reported a stereoselective synthesis of *N*-β-glycosyl amides from peracylated D-monosaccharides with *gluco*-, *galacto*- and *manno*-configurations using Ritter-type reactions with acetonitrile in the presence of methanesulfonic acid or $BF_3{\cdot}Et_2O$. The stereoselectivity of studied anomeric Ritter-like reactions of D-glucose and mannose peracetates was explained by the anomerization via open-chain intermediates forming under acidic conditions.

Exploring synthetic routes to *N*-hexofuranosyl amides, the hydrolysis reactions of protected *N*-α-glucofuranosyl and -allofuranosyl oxazolines prepared from D-glucose [25] were tested under conditions similar to *N*-xylofuranosyl oxazolines (Scheme 3). Hydrolysis of benzoylated *N*-α-glucofuranosyl oxazoline **44** as well as benzoylated *N*-α-xylofuranosyl oxazoline **1** proceeded under storing in the presence of traces of water (Scheme 6, conditions a) to afford the *N*-α-glucofuranosyl acetamide derivative **45** (80% of conversion into the *N*-glycoside according to ^{1}H NMR data), which was isolated in 66% yield after chromatography on silica gel.

The hydrolysis reaction of the benzoylated oxazoline **44** on silica gel in chloroform (entry 6, Table 1) gave *N*-α-glucoside **45** in 58% yield after column chromatography. The deprotection of the latter with NH_3/MeOH or 1 M MeONa in methanol, using the Zemplén-deacylation conditions, gave *N*-α-glucofuranosyl acetamide **46** in 65% and 72% yields, respectively. The benzoylated allofuranosyl oxazoline **47** prepared by Ritter-like reaction of protected 1,2-*O*-isopropylidene-α-D-allofuranose, which was synthesized in two steps from available D-glucose diacetonide according to the known method [30], afforded acylated *N*-α-allofuranosyl acetamide **48** (80%) under stereoselective hydrolysis on silica gel (Scheme 6). After a long storing the oxazoline **47** gave 3,5,6-tri-*O*-benzoylated *N*-α-allofuranosyl acetamide **48** in a high 85% yield (Scheme 6, conditions f). The Ritter-like reaction of D-glucose in acetonitrile at room temperature gave rise to N-α-D-glucofuranosyl acetamide (**46**) and isomeric α-D-glucopyranosyl acetamide (**51**) in 13% and 37% yields, respectively, which were isolated by column chromatography on silica gel.

The formation of N-glycoside **46** was supported by comparison of its spectral data with those of N-α-D-glucofuranosyl acetamide prepared by removing benzoyl protecting groups (NH_3/MeOH) in the acylated *N*-α-glucofuranosyl acetamide **45** ealier synthesized via the intermediate oxazoline **44**.

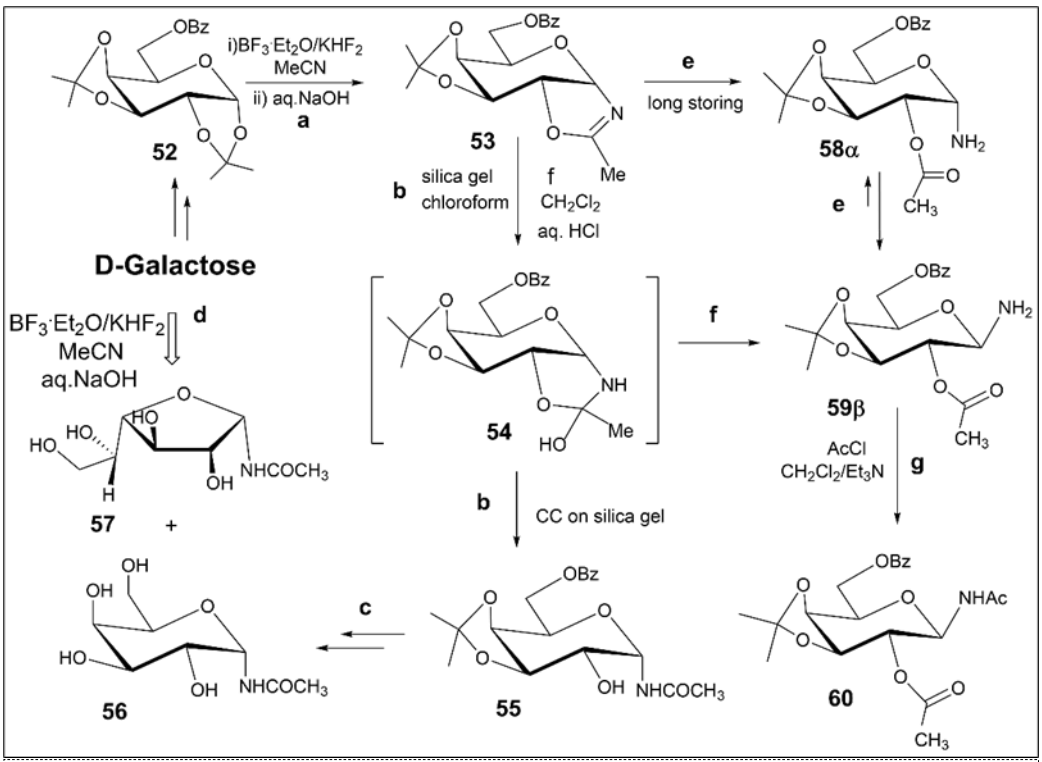


Scheme 6. Synthesis of N-α-D-glycosyl acetamides of *glyco* and *allo* configuration from D-glucose. Reagents and conditions: a) **44**, a long storing at 5-8 ^{0}C, **45**, CC, 66%; b) **44**, $CHCl_3$, silica gel (entry 8, table 1), **45**, 78%; c) **45**, NH_3/MeOH, rt, 18 h, **46**; 65%; d) **45**, 1 M MeONa/MeOH, rt, 14 h, **46**, 72%; e) **47**, (entry 9, table 1), **48**, 80%; f) **47**, a long storing at 5-8 ^{0}C, **48**, 85%; g) D-glucose, CH_3CN, KHF_2, $BF_3{\cdot}Et_2O$, rt, 4 h, CC, **46**, 13%, **51**, 37%.

Besides, the structure of N-glycopyranoside **51** was confirmed by NMR spectral data as in the case of the preparation of N-α-D-glucopyranosyl acetamide described earlier via azidosugar [22]. The most probable mechanistic pathway of the $BF_3{\cdot}Et_2O$-mediated Ritter-like reaction leading to isomeric N-glyco-furanosyl and -pyranosyl acetamides includes the formation of intermediate 2-methyl-β-D-glucofurano-[1,2-d]-2-oxazoline (**49**) and 2-methyl-β-D-glucopyrano-[1,2-d]-2-oxazoline (**50**) from D-glucose in the presence the Lewis acid followed by hydrolysis reactions under basic work-up the reaction mixture (Scheme 6).

In extension of this study, synthesis of protected *N*-α-galactopyranosyl acetamides was investigated using benzoylated *N*-α-galactopyranosyl oxazoline **53** which was prepared by the $BF_3{\cdot}Et_2O$-KHF_2-promoted reaction of the 6-*O*-benzoyl D-galactopyranose 1,2;3,4-diacetonide derivative **52** with acetonitrile in a high 93% yield without chromatography on silica gel (Scheme 7, conditions a). A selective hydrolysis of the protected N-α-galactopyranosyl oxazoline **53** proceeded on silica gel in chloroform to give the *N*-α-galactopyranosyl acetamide derivative **55** (78%) likely through the formation of the intermediate hemiorthoamidate derivative **54** in mild acidic conditions (Scheme 7, conditions b). Full *O*-deprotection of intermediate *N*-glycoside **55**, isolated by column chromatography on silica gel, afforded the target *N*-α-galactopyranosyl acetamide **56** (58% yield over two steps, Scheme 7, conditions c). N-Acetyl-α-D-galactopyranosyl amine **56** has earlier been synthesized by acetylation of α-D-glycopyranosyl amine with acetic anhydride and studied along with a number of N-acyl-α-galactopyranosyl amines as potential competitive inhibitors of α-D-galactosidase [31]. Compound **56** displayed inhibiting properties towards α-D-galactosidase from *Trichoderma reesei*. The Ritter-like reaction of D-galactose in acetonitrile at room temperature gave rise to N-α-D-galactofuranosyl

acetamide (**57**) and isomeric α-D-galactopyranosyl acetamide (**56**) in 18% and 15% yields, respectively, after column chromatography on silica gel. Notably, as opposed to benzoylated *N*-α-pentofuranosyl oxazolines **1** and **33** or *N*-α-glucofuranosyl oxazoline **44** (Schemes 2, 5 and 6), the protected *N*-α-galactopyranosyl oxazoline **53** did not result in *N*-α-galactopyranosyl acetamide **55** under the mild conditions for the hydrolysis reaction (conditions e). In this case, after a long-term storing of the individual *N*-α-galactopyranosyl oxazoline **53** in the presence of traces of H_2O, the formation of *N*-β-galactopyranosylamine derivative **59β** was established from ^1H and ^{13}C NMR spectra taken in $CDCl_3$ (82% yield, conditions e). The structure of **59β** was confirmed from 2D NMR spectroscopy and mass spectrum (Experimental part). Hydrolysis reaction of the oxazoline **53** in the presence of aq. HCl in methylene chloride gave β-amine **59β** in 34% yield according to ^1H NMR spectrum of the reaction mixture (Scheme 7, conditions f). Besides, full *O*- and *N*-acetylation of the β-amine **59β** (conditions g) gave the only 2-*O*-acetylated *N*-β-galactopyranosyl acetamide derivative **60** in 75% yield after chromatography on silica gel. The chemical shifts and large magnitudes of $^3J_{1,2}$ vicinal couplings for H-1 protons observed in ^1H NMR spectra of the β-amine **59β** (4.03 ppm, d, $J_{1,2}$ = 8.7 Hz) and the β-amide **60** (5.12 ppm, t, $J_{1,2} = J_{H\text{-}1,\,NH}$ = 9.3 Hz) are indicative of the β-anomeric configuration of amino and acetamido groups at the anomeric centers. It is necessary to note that the values of H-1 coupling constants for **59β** and **60** are in good accordance with those (8.3-9.8 Hz), which are characteristic for the known acylated *N*-β-galactosyl amides described earlier by Pleuss and Kunz [32].



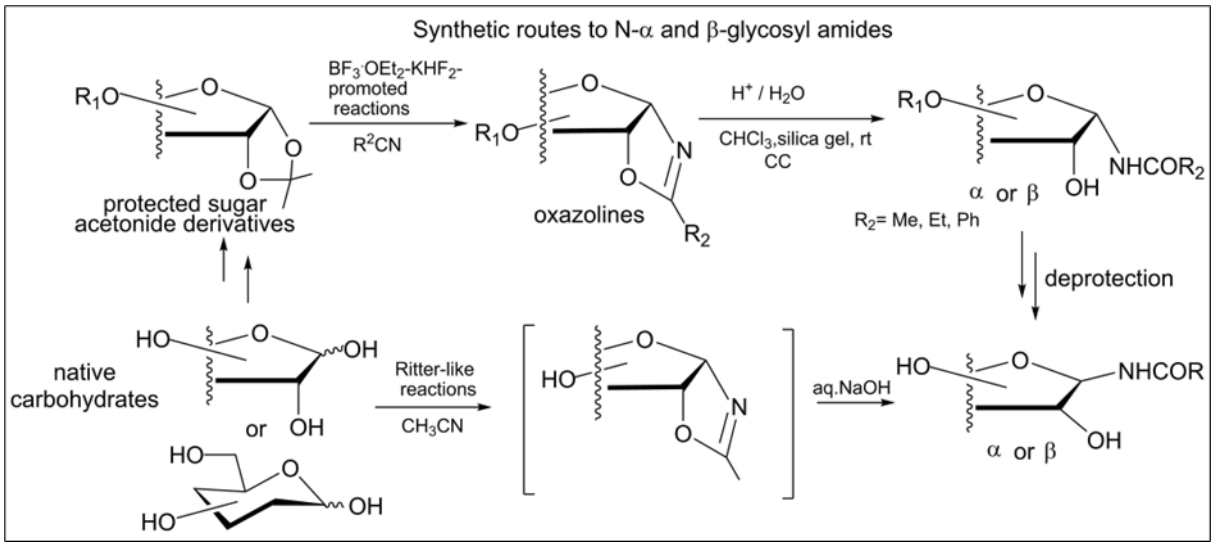
Scheme 7. Synthesis of protected *N*-α-D-galactopyranosyl oxazoline and *N*-α- and β-D-galactosyl acetamides from D-galactose. Reagents and conditions: a) **52**, CH_3CN, KHF_2, $BF_3{\cdot}Et_2O$, rt, 18 h, 1N aq NaOH; **53**, 93%; b) **53**, CC on silica gel, (entry 11, table 1), **55**, 78%; c) i) **55**, 80% aq CH_3COOH, 50-55^{0}C, 18 h, ii) NH_3/MeOH, rt, 18 h, **56**, 58% over two steps; d) D-galactose, CH_3CN, KHF_2, $BF_3{\cdot}Et_2O$, rt, 4 h 10 min, CC, **56**, 15%, **57**, 18%; e) **53**, a long-term storing at 5-8 ^{0}C, 82%, **59β**; f) **53**, CH_2Cl_2, aq.HCl, **59β**, 34%; g) **59β,** AcCl, CH_2Cl_2, Et_3N**,** rt, **60**, 75%.

The formation of the *N*-β-galactosylamine derivative **59β** arises from the anomerization [27, 33] of the intermediate α-glycosyl amine **58α** which produces under a long-term storage of *N*-α-galactopyranosyl oxazoline **53**. Selectively protected *N*-β-galactopyranosylamine **59β** may be used for preparing N-sulfonyl amide derivatives of galactopyranose with antiglaucoma activity.

The structures of synthesized *N*-α- and β-galactosyl amides were confirmed by NMR and mass spectra. New synthetic approaches to N-glycosyl amine derivatives were studied from D-galactose via the Ritter-like reaction of D-galactopyranose 1,2;3,4-diacetonide derivative for preparation of intermediate N-α-D-galactopyranosyl oxazoline followed by hydrolysis reactions with the formation of N-α- and β-galactopyranosyl amines or α-amide. It was shown that the efficient method developed for N-furanosyl oxazolines [25] from sugar acetonides can be utilized for stereoselective synthesis of protected N-hexopyranosyl oxazoline from D-galactopyranose diacetonide derivative. A series of synthesized protected *N*-glycosyl amides as well as N-glycopyranosyl oxazoline(s) can be used as potential glycosyl donors in carbohydrate chemistry for the preparation of *O*- and *N*-glycosides [32].

Conclusion

In summary, two synthetic routes to *N*-glycosyl amides were investigated from D-pentose and hexose sugars. Hydrolysis reactions of *N*-α-furanosyl oxazolines, prepared from protected D-pentofuranose and hexafuranose 1,2-*O*-acetonides, have been studied in neutral and acidic conditions to prepare *N*-α-furanosyl amides. Protected glycosyl 1,2-oxazolines with 2-aliphatic alkyl substituents were found to undergo gradual conversions to *N*-glycosyl amides in neutral conditions in the presence of traces of water. It has been shown that hydrolysis reactions of blocked 2-methyl substituted *N*-glycosyl oxazolines proceeded on silica gel in chloroform to give selectively protected *N*-α- or β-glycosyl amides in good yields. *N*-Glycosyl oxazolines with 2-phenyl substituent e.g., 3,5-di-*O*-benzoylated 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline as well as the unprotected arabinofuranosyl oxazoline did not afford corresponding *N*-glycosyl amides in neutral or acidic conditions due to they possess more stability in comparison with *cis*-fused β-arabino- and α-xylofuranosyl oxazolines with 2-alkyl substituents.



Reaction conditions for selective cleavage of 2-phenyl substituted β-arabinofuranosyl oxazolines were explored and the hydrolysis of the protected oxazoline in the presence of HBF_4 in acetonitrile gave rise to benzoylated β-arabinofuranosyl benzamide in a moderate yield after chromatography on silica gel. In addition, syntheses of *N*-α-gluco-, allofuranosyl, and *N*-α- or β-galactopyranosyl amides of biological interest were accomplished through a mild hydrolysis of protected *N*-α-glycosyl oxazolines. In the second direct approach, *N*-furanosyl and pyranosyl acetamides were obtained through the $BF_3{\cdot}OEt_2$-KHF_2-mediated reactions of a series of native sugars in acetonitrile at room temperature. The synthesized *N*-glycosyl amides will be used for preparation and future biological evaluation of modified *N*-glycosides and glycoconjugates with anticancer nucleosides.

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Experimental part.

General information. Column chromatography was performed on silica gel 60 H (70-230 mesh; Merck, Darmstadt, Germany), and thin-layer chromatography (TLC) on Merck silica gel aluminum 60 F_{254} precoated plates. All commercially available reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and CD_3OD with a Bruker Avance-500-DRX spectrometer at 500.13 and 126.76, respectively. ^1H and ^{13}C NMR chemical shifts (δ, ppm) are relative to internal chloroform peak (7.26 ppm for ^1H and 77.0 for ^{13}C NMR). Splitting patterns were reported as following: s: singlet, d: doublet, t: triplet, m: multiplet. *J* values are reported in Hz. Optical rotations were measured with Autopol III automatic polarimeter. IR spectra were measured with on PerkinElmer Spectrum 100FT-IR spectrometer. Melting points were determined on a Boetius apparatus and were uncorrected. High resolution mass spectra (HRMS) were recorded on an Agilent Q-TOF 6550 Instrument (USA) using ESI (electrospray ionization).

General procedure for preparation of protected N-glycosyl amides by hydrolysis reactions of N-glycosyl oxazolines on silica gel (Table 1).

The oxazoline (0.5 – 1.6 mmol) prepared from corresponding protected D-pentofuranose or -hexafuranose acetonide was dissolved in chloroform and placed to the top of a silica gel column (60 H, 70-230 mesh; Merck, Darmstadt, Germany) prepared in chloroform, which was washed with a small volume of chloroform. After 18-48 h a silica gel column was washed with chloroform and further column chromatography gave N-glycosyl amides in 70-86% yields using mixtures of chloroform-methanol for gradual elution.

*3,5-Di-O-benzoyl-N-acetyl-α-D-xylofuranosylamide (**5**) from the oxazoline **1***:

a_1. The *N*-xylofuranosyl oxazoline derivative **1** (0.04 g, 0.1 mmol) was kept at 5-8 °C for 6 weeks. The oily residue was chromatographed on a silica gel, using for elution chloroform, chloroform–methanol 10:1 and 5:1 to give (0.028 g, 67%) *N*-α-D xylofuranosylacetamide **5**.

b_1.The 3,5-di-O-benzoyl-protected oxazoline **1** (310 mg, 0.78 mmol) was dissolved in chloroform and placed to the top of a silica gel column which was prepared in chloroform. After 24 h at room

temperature a silica gel column was washed chloroform and then further gradual elution with chloroform-methanol 30:1, 15:1 and 10:1 gave (0.275 g, 85%) of 3,5-di-O-benzoyl-N-acetyl-α-D-xylofuranosylamide (**5**) as oil.

$[\alpha]_D^{20}$ +15.8 (c 1.0, $CHCl_3$). IR (KBr): ν 3388, 1722, 1656, 1526, 1271, 1180, 1106 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.51-7.99 (m, 10H, 2 x COC_6H_5), 6.86 (d, 1H, *J* = 9.0 Hz, NHCOMe), 6.07 (dd, 1H, $J_{1,2}$ = 4,2 Hz, H-1), 5.52 (dd, 1H, $J_{3,4}$ = 4.0, $J_{3,2}$ = 1.5 Hz, H-3), 4.76-4.80 (m, 1H, H-4), 4.59 (dd, 1H, H-5), 4.57 (dd, 1H, H-5′), 4.37 (dd, 1H, $J_{2,1}$ = 4.2, $J_{2,3}$ = 1.5 Hz, H-2), 2.07 (s, 3H, $NHCOCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.9 ($NHCOMe$), 166.3 и 166.1 (C=O, 2xCOC_6H_5), 133.9, 133.1, 129.8, 129.63, 129.62, 128.7, 128.6, 128.3 (2xCOC_6H_5), 80.7 (C-1), 79.1 (C-4), 75.8, 74.1 (C-2, C-3), 62.85 (C-5), 23.5 ($NHCOCH_3$). HRMS (ESI^+): m/z calcd for $C_{21}H_{21}NO_7$ $[M+Na]^+$: 422.1216, found 422.1208.

*3,5-Di-O-benzoyl-N-propionyl-α-D-xylofuranosylamide (**6**) from the oxazoline **2***:

a_2. The *N*-xylofuranosyl oxazoline derivative **2** (0.08 mg, 0.2 mmol) was kept at 5-8 °C for 5 weeks. The oily residue was chromatographed on a silica gel, using for elution chloroform, chloroform–methanol 11:1 and 5:1 to give (0.072 g, 86%) benzoyl-protected *N*-propionyl-α-D-xylofuranosyl amide **6**.

b_2. The oxazoline **2** (0.167 g, 0.42 mmol) after the hydrolysis reaction on silica gel gave 3,5-di-*O*-benzoyl-*N*-propionyl-α-D-xylofuranosylamide (**6**) (0.148 g, 85%) as white solid. M.p. 144-145 °C. $[\alpha]_D^{20}$ +15.1 (c 0.57, $CHCl_3$) IR (KBr): ν 3387, 2924, 1727, 1653, 1525, 1275 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.43-8.03 (m, 10H, 2 x COC_6H_5), 6.91 (d, 1H, *J* = 9.0 Hz, NHCOEt), 6.13 (dd, 1H, $J_{1,2}$ = 4.1 Hz, H-1), 5.57 (dd, 1H, $J_{3,4}$ = 3.8, $J_{3,2}$ = 1.0 Hz, H-3), 4.77-4.82 (m, 1H, H-4), 4.62 (dd, 1H, H-5), 4.61 (dd, 1H, H-5′), 4.42 (dd, 1H, H-2), 2.34 (q, 2H, $NHCOCH_2CH_3$). 1.21 (t, 3H, $NHCOCH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.7 (CN), 166.3 and 166.1 (C=O, 2xCOC_6H_5), 133.9, 133.2, 129.8, 129.7, 129.6, 128.76, 128.7, 128.4 (2xCOC_6H_5), 80.8 (C-1), 79.1 (C-4), 75.8, 74.1 (C-2, C-3), 62.9 (C-5), 29.8 ($NHCOCH_2CH_3$), 9.4 ($NHCOCH_2CH_3$). HRMS (ESI^+): m/z calcd for $C_{22}H_{23}NO_7$ $[M+Na]^+$: 436.1367, found 436.1366.

*5-O-Benzoyl-3-O-p-toluenesulfonyl-N-acetyl-α-D-xylofuranosylamide (**7**) from the oxazoline **3***:

a_3.The oxazoline **3** (0.6 g, 1.31 mmol) was coevaporated with chloroform and kept at 5-8 °C for 4 weeks. The residue was treated with methanol under heating and prepared solution was left under cooling. Crystalline product was filtred off and dried on air. 5-O-Benzoyl-3-O-*p*-toluenesulfonyl-N-acetyl-α-D-xylofuranosylamide (**7**) (0.375 g, 60%) was prepared as yellow crystals. M.p. 161-163 °C (MeOH). $[\alpha]_D^{20}$ +4.8 (c 0.5, $CHCl_3$). IR (KBr): ν 3394, 1725, 1672, 1516, 1367, 1275, 1182 $см^{-1}$. ^1H NMR (500 MHz, DMSO-d_6) δ: 8.16 (d, 1H, *J* 9.5 Hz, NHCOMe), 7.42-7.89 (m, 9H, COC_6H_5 and $OSO_2C_6H_4CH_3$), 6.26 (d, 2-OH), 5.73 (dd, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.99 (br.s, 1H, H-3), 4.47-4.49 (m, 1H, H-4), 4.26 (dd, 1H, H-5), 4.17 (dd, 1H, H-5′), 4.10 (br.s, 1H, H-2), 2.33 (s, 3H, $OSO_2C_6H_4CH_3$), 1.90 (s, 3H, NHCOMe). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 170.54 ($NHCOMe$), 165.68 (C=O, COC_6H_5), 145.94, 138.98, 132.82, 130.78, 129.71, 129.65, 129.21, 128.04 (COC_6H_5 и $OSO_2C_6H_4CH_3$), 84.63 (C-1), 80.63 (C-4), 74.78, 73.04 (C-2, C-3), 62.54 (C-5), 23.27 (NHCOMe), 21.57 ($OSO_2C_6H_4CH_3$). HRMS (ESI^+): m/z calcd for $C_{21}H_{23}NO_8S$ $[M+Na]^+$: 472.1042, found 472.1035.

b_3. The oxazoline **3** (0.554 g, 1.28 mmol) was dissolved in chloroform and placed to the top of a silica gel column which was prepared in chloroform. After 18 h at room temperature a silica gel column was washed chloroform and then further gradual elution with chloroform-methanol 20:1, 15:1 and 9:1 gave

(0.490 g, 85%) of 5-O-benzoyl-3-O-tosyl-N-acetyl-α-D-xylofuranosylamide (**7**).

*5-O-Benzoyl-3-O-methanesulfonyl-N-acetyl-α-D-xylofuranosylamide (**8**) from the oxazoline **4***:

b_4.The oxazoline **4** (0.354 g, 0.99 mmol) was dissolved in chloroform and placed to the top of a silica gel column which was prepared in chloroform. After 18 h at room temperature a silica gel column was washed chloroform and then further gradual elution with chloroform-methanol 15:1 and 10:1 gave (0.32 g, 86%) of 5-O-benzoyl-3-O-mesyl-N-acetyl-α-D-xylofuranosyamide (**8**) as oil. $[\alpha]_D^{20}$ +5.6 (c 1.0, $CHCl_3$). IR (solution in $CHCl_3$): ν 3430, 1725, 1687, 1506, 1358, 1178 см$^{-1}$. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-8.05 (m, 5H, COC_6H_5), 7.18 (br.d, 1H, *J* = 9.0 Hz, NHCOMe), 6.0 (dd, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.20 (d, 1H, H-3), 4.69-4.73 (m, 1H, H-4), 4.49-4.55 (m, 3H, H-2 and 2H-5), 3.11 (s, 3H, OSO_2CH_3), 2.09 (s, 3H, NHCOMe). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 172.1 (NHCOMe), 166.4 (C=O, COC_6H_5), 133.4, 129.8, 129.65, 129.5, 128.5 (COC_6H_5), 82.9 (C-1), 80.6 (C-4), 75.3, 73.7 (C-2, C-3), 62.2 (C-5), 38.3 (OSO_2CH_3). 23.5 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_{15}H_{19}NO_8S$ $[M-H_2O]^+$: 355.0726, found 375.0699.

*3,5-O-Isopropylidene-N-acetyl-α-D-xylofuranosylamide (**10**) from the oxazoline **9**:*

a_4. The oxazoline **9** (0.35 g, 1.64 mmol) was coevaporated with chloroform and kept at 5-8 °C for 6 weeks. The oily residue was chromatographed on a silica gel, using for elution mixtures of ethylacetate: petroleum ether, and chloroform-methanol 10:1 to give (0.342 g, 90%) of 3,5-*O*-isopropylidene-*N*-acetyl-α-D-xylofuranosylamide (**10**) as oil. $[\alpha]_D^{20}$ +15.7 (c 1.0, $CHCl_3$). IR (solution in $CHCl_3$): ν 3425, 3019, 2932, 1680, 1505, 1377 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.26 (br.d, 1H, NH), 5.95 (dd, 1H, $J_{1,2}$ = 3.5, $J_{1,NH}$ = 9.7 Hz, H-1), 4.32 (br.s, 1H, H-3), 4.05 (d, 1H, H-2), 3.98-4.02 (m, 1H, H-4), 3.92 (dd, 1H, $J_{5,4}$ = 2.3, $J_{5,5'}$ = 13.6 Hz, H-5), 3.84 (d, 1H, H-5′), 2.07 (s, 3H, NHCOCH_3), 1.45 and 1.38 [2s, 6H, $(CH_3)_2$C-]. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.7 (NH$COCH_3$), 97.3 *C*-$(CH_3)_2$, 81.5 (C-1), 75.0 (C-4), 74.9, 71.3 (C-2, C-3), 60.8 (C-5), 23.4 and 19.3 (CH_3)$_2$C-, 28.7 (NHCOCH_3). HRMS (ESI$^+$): m/z calcd for $C_{10}H_{17}NO_5$ $[M+Na]^+$: 254.1004, found 254.1008.

b_5. The oxazoline **9** (0.3 g, 1.4 mmol) was dissolved in chloroform and placed to the top of a silica gel column which was prepared in chloroform. After 22 h a silica gel column was washed chloroform and then further gradual elution with chloroform-methanol 30:1, 15:1 and 8:1 gave (0.254 g, 78%) of 3,5-*O* -isopropylidene-*N*-acetyl-α-D-xylofuranosylamide (**10**).

N-Acetyl-α-D-xylofuranosylamide (***11***) *from protected N-xylofuranosyl acetamides*

c. 3,5-*O*-isopropylidene-*N*-acetyl-α-D-xylofuranosylamide (**10**) (0.250 g, 0.12 mmol) was dissolved in 5 ml 75% aq acetic acid and reaction mixture was stirred for 20 h, then it was coevaporated with toluene (2x10 ml). The residue was chromatographed on a silica gel, using for elution chloroform, chloroform–methanol 10:1, 5:1 to give (0.202 g, 90%) of *N*-α-D- xylofuranosylacetamide **11**.

d_1.3,5-Di-*O*-benzoyl-*N*-acetyl-α-D-xylofuranosylamide (**5**) (0.136 g, 0.34 mmol) was dissolved in 14 ml methanol saturated at 0 °C with ammonia, then reaction mixture was stirred for 17 h at room temperature and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform–methanol 15:1, 5:1 to give (0.05 g, 77%) of *N*-α-D-xylofuranosylacetamide (**11**). M.p. 148-149 °C. $[\alpha]_D^{20}$ +48.8 (c 0.72, MeOH). IR (KBr): ν 3411, 3368, 1656, 1510, 1301, 1083 cm^{-1}. ^{1}H NMR (500 MHz, CD_3OD) δ = 5,84 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.18-4.21 (m, 1H, H-4), 4.16 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{3,2}$ = 1.7 Hz, H-3), 4,02 (dd, 1H, $J_{2,1}$ = 1.7 Hz, H-2), 3.77 (dd, 1H, $J_{5,4}$ = 4.9 Hz, $J_{5,5'}$ = 11.5 Hz, H-5), 3.73 (dd, 1H, $J_{5',4}$ = 5.2 Hz, H-5′), 2.03 (s, 3H, NHCO$\underline{CH_3}$). ^{13}C NMR (126 MHz, CD_3OD) δ = 173.8 (NH$\underline{CO}$Me), 82.0 (C-1), 81.3 (C-4), 77.8, 77.2

(C-2, C-3), 61.9 (C-5), 22.9 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_7H_{13}NO_5$ [M+Na]$^+$: 214.0691, found 214.0686.

N-Propionyl-α-D-xylofuranosylamide (***12***)

d_2.3,5-Di-*O*-benzoyl-*N*-propionyl-α-D-xylofuranosylamide (**6**) (0.055 g, 0.13 mmol) was dissolved in 3 ml methanol and 7 ml methanol saturated at 0 °C with ammonia was added to prepared solution, then reaction mixture was stirred for 18 h at room temperature and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform –methanol 20:1, 6:1 to give (0.022 g, 81%) of *N*-propionyl-α-D-xylofuranosylamide (**12**) as oil. $[\alpha]_D^{20}$ +44.8 (c 0.53, MeOH). IR (KBr): ν 3400, 3365, 1657, 1505, 1308, 1083 см$^{-1}$. ^{1}H NMR (500 MHz, CD_3OD) δ: 5.85 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.18-4.21 (m, 1H, H-4), 4.16 (dd, 1H, $J_{2,3}$ = 1.6 Hz, $J_{3,4}$ = 3.6 Hz, H-3), 4.02 (dd, 1H, $J_{2,3}$ = 1.6 Hz, $J_{2,1}$ = 3.9 Hz, H-2), 3.77 (dd, 1H, $J_{5,4}$ = 5.0 Hz, $J_{5,\ 5'}$ = 11.5 Hz, H-5), 3.73 (dd, 1H, $J_{5',4}$ = 6.2 Hz, H-5′), 2.31 (q, 2H, -N=C-$\underline{CH_2}CH_3$), 1.15 (t, 3H, -N=C-$CH_2\underline{CH_3}$). ^{13}C NMR (126 MHz, CD_3OD) δ**:** 175.9 (NH$\underline{CO}$Et), 80.5 (C-1), 79.9 (C-4), 76.4, 75.8 (C-2, C-3), 60.4 (C-5), 28.8 (-NHCO$\underline{CH_2}CH_3$), 8.6 (-NHCO$CH_2\underline{CH_3}$). HRMS (ESI$^+$): m/z calcd for $C_8H_{15}NO_5$ [M+Na]$^+$: 228.0842, found 228.0843.

Synthesis of N-acyl-α-D-xylofuranosylamides from D-xylose:

*N-Acetyl-α-D-xylofuranosylamide (**11**) from D-xylose*

f_1. To a stirred solution of D-xylose (0.211 g, 1.4 mmol) in anhydrous acetonitrile (6 ml), KHF_2 (0.411 g, 5.24 mmol), boron trifluoride diethyl etherate (1.4 ml, 11.0 mmol) were added at rt. The reaction mixture was stirred at room temperature for 3 h 30 min, and then poured into cooled 25.5 ml aq 1N NaOH and evaporated to dryness, coevaporated with ethanol. The residue was chromatographed on a silica gel, using for elution mixtures of chloroform-methanol 7:1, 6:1 and 4:1 to give 0.027 g of a mixture of **11** and **13** (about 6% yield of **13** according to ^{1}H NMR data) as oil. ^{1}H NMR (500 MHz, CD_3OD) a separate fraction containing a mixture of N-xylosides **11** and **13** (a ratio-2:3.2). ^{1}H NMR (500 MHz, CD_3OD) N-α-D-xylopyranosyl acetamide **13**, δ = 5.38 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 3,84 (d, 1H, $J_{2,1}$ = 3.1 Hz, H-2), 3.78-3.81 (m, 1H, H-3), 3.58 (dd, 1H, $J_{5,4}$ = 5.4 Hz, $J_{5,5'}$ = 11.8 Hz, H-5), 3.53 (dd, 1H, $J_{5',4}$ = 3.2 Hz, H-5′), 3.49-3.51 (m, 1H, H-4), 2.0 (s, 3H, NHCO$\underline{CH_3}$). ^{13}C NMR (126 MHz, CD_3OD) δ: 174.2 (NH$\underline{CO}$Me), 81.3 (C-1), 77.5, 71.7, 70.3 (C-4, C-2, C-3), 66.4 (C-5), 22.7 (NHCO$\underline{Me}$).

^{1}H NMR (500 MHz, CD_3OD) N-α-D-xylofuranosyl acetamide **11**, δ = 5,84 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.18-4.21 (m, 1H, H-4), 4.16 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{3,2}$ = 1.7 Hz, H-3), 4,02 (dd, 1H, $J_{2,1}$ = 1.7 Hz, H-2), 3.77 (dd, 1H, $J_{5,4}$ = 4.9 Hz, $J_{5,5'}$ = 11.5 Hz, H-5), 3.73 (dd, 1H, $J_{5',4}$ = 5.2 Hz, H-5′), 2.03 (s, 3H, NHCO$\underline{CH_3}$). ^{13}C NMR (126 MHz, CD_3OD) δ = 173.8 (NH$\underline{CO}$Me), 82.0 (C-1), 81.3 (C-4), 77.8, 77.2 (C-2, C-3), 61.9 (C-5), 22.9 (NHCO$\underline{Me}$). HRMS (ESI$^+$): m/z calcd for $C_7H_{13}NO_5$ [M+Na]$^+$: 214.0691, found 214.0686.

and 0.099 g (37%) of *N*-acetyl-α-D-xylofuranosylamide (**11**) as crystalline product.

*N-Propionyl-α-D-xylofuranosylamide (**12**) from D-xylose*

f_2. To a stirred suspension of dried D-xylose (0.218 g, 1.45 mmol) in anhydrous propionitrile (6 ml), KHF_2 (424 mg, 5.4 mmol) boron trifluoride diethyl etherate (1.4 ml, 11.0 mmol) were added at rt. The reaction mixture was stirred at room temperature for 4 h, and then poured into cooled 25 ml aq. 1N NaOH and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution mixtures of chloroform-methanol 6:1, 5:1 and 3:1 to give (0.082 g, 28%) of N-propionyl-α-D-xylofuranosylamide (**12**) as oil.

*Benzoylation of 3,5-di-O-benzoyl-N-α-D-xylofuranosyl acetamide **5***

g1. To a stirred solution of selectively protected N-xylofuranosyl amide **5** (0.034 g, 0.085 mmol) in anhydrous pyridine (3 ml) benzoyl chloride (0.08 ml, 0.69 mmol) was added at 0 °C and then the reaction mixture was stirred for 48 h at room temperature, diluted with CH_2Cl_2 and poured into cold 5% aq $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (3x50 ml), the combined organic extracts were washed cooled 5% aq $NaHCO_3$, water, dried and evaporated. The residue was chromatographed on a silica gel, using for elution mixtures of hexane-ethylacetate 6:1, 5:1, and 2:1 to give (0.022 g, 42%) of perbenzoylated N-α-xylofuranosyl amide **14**. M.p. 89-92 °C. $[\alpha]_D^{20}$ +78.4 (c 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34-8.13 (m, 25H, 4 x COC_6H_5), 6.52 (dd, 1H, $J_{3,2}$ = 6.0, $J_{3,4}$ = 7.1 Hz, H-3), 6.39 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 5.69 (dd, 1H, $J_{2,1}$ = 7.6, $J_{2,3}$ = 6.0 Hz, H-2), 5.11-5.22 (m, 1H, H-4), 4.49 (dd, 1H, H-5), 4.60 (dd, 1H, H-5′), 2.07 (s, 3H, $NHCO(C_6H_5)CH_3$. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.5, 172.8, 171.4, 166.0 and 165.6 (C=O, $CON(C_6H_5)(CH_3$, 4xCOC_6H_5), 133.8, 133.7, 133.5, 133.29, 133.22, 130.2, 129.9, 129.8, 129.5, 129.4, 128.8, 128.5, (5x$CO\underline{C_6H_5}$), 85.4 (C-1), 77.6 (C-4), 77.0, 76.5 (C-2, C-3), 63.4 (C-5), 26.2 ($NHCO(C_6H_5)CH_3$. HRMS (ESI^+): m/z calcd for $C_{35}H_{29}NO_9$ $[M+Na]^+$: 630.1735, found 630.1742.

and (0.018 g, 42%) of tri-O-benzoyl derivative **15**. M.p. 54-55 °C. $[\alpha]_D^{20}$ +31.8 (c 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 - 8.1 (m, 15H, 3xCOC_6H_5),6.41 (dd, 1H, $J_{1,2}$= 4.1, $J_{NH,H-1}$= 9.7 Hz, H-1), 6.23 (d, 1H, $NHCOCH_3$), 5.87 (dd, 1H, $J_{3,4}$ = 4.3, $J_{3,2}$ = 2.0 Hz, H-3), 5.67 (dd, 1H, $J_{2,3}$ = 2.0, $J_{2,1}$ = 4.1 Hz, H-2), 4.85-4.88 (m, 1H, H-4), 4.59 (dd, 1H, H-5), 4.54 (dd, 1H, H-5′), 2.01 (s, 3H, $NHCOCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.1, 166.2, 164.9, 164.4 (C=O, $CONHCH_3$, 3xCOC_6H_5), 134.2, 133.9, 133.3, 130.0, 129.9, 129.7, 128.9, 128.7, 128.8, 128.5, 128.4 (3x$CO\underline{C_6H_5}$), 79.8 (C-1), 76.4 (C-4), 75.57, 75.55 (C-2, C-3), 62.6 (C-5), 23.6 ($NHCOCH_3$). HRMS (ESI^+): m/z calcd for $C_{28}H_{25}NO_8$ $[M+Na]^+$: 526.1473, found 526.1478.

N-Acetyl-β-D-arabinofuranosylamide (**19**) *from benzoylated N-arabinofuranosyl oxazoline* **17**:

*Preparation of 3,5-di-O-benzoyl-N-acetyl-β-D-arabinofuranosylamide (**18**) from oxazoline* **17**

a.The benzoylated N-β-D-arabinofuranosyl oxazoline **17** (0.13 g, 0.95 mmol) gave (0.114 g, 84%) 3,5-di-*O*-benzoyl-*N*-acetyl-α-D-arabinofuranosylamide (**18**) as oil after the hydrolysis reaction on silica gel. $[\alpha]_D^{20}$ +15.8 (c 1.0, $CHCl_3$). IR (KBr): ν 3388, 1722, 1656, 1526, 1271, 1180, 1106 см$^{-1}$. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36-8.04 (m, 10H, 2 x COC_6H_5), 6.90 (br.d, 1H, J = 9.1 Hz, NHCOMe), 5.91 (dd, 1H, $J_{1,2}$ = 4,0 Hz, H-1), 5.52 (d, 1H, $J_{3,2}$ = 2.8 Hz, H-3), 4.61 (dd, 1H, H-5), 4.58 (dd, 1H, H-5′), 4.34-4.38 (m, 1H, H-4), 4.31 (br.d, 1H, H-2), 2.04 (s, 3H, $NHCO\underline{CH_3}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.9 ($NH\underline{CO}Me$), 166.3 and 166.3 (C=O, 2xCOC_6H_5), 133.7, 133.2, 129.8, 129.7, 128.5, 128.6, 128.4 (2x$CO\underline{C_6H_5}$), 81.0 (C-1), 80.5 (C-4), 78.45, 78.42 (C-2, C-3), 64.4 (C-5), 23.4 ($NHCO\underline{CH_3}$). HRMS (ESI^+): m/z calcd for $C_{21}H_{21}NO_7$ $[M+Na]^+$: 422.1216, found 422.1208.

N-Acetyl-β-D-arabinofuranosylamide (**19**)

b.3,5-Di-*O*-benzoyl-*N*-acetyl-α-D-arabinofuranosylamide (**18**) (0.17 g, 0.42 mmol) was dissolved in 8 ml methanol saturated at 0 °C with ammonia, then reaction mixture was stirred for 18 h at room temperature and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform –methanol 15:1, 6:1 to give (0.028 g, 68%) of *N*-α-arabinofuranosylacetamide **19**. M.p. 148-149 °C. $[\alpha]_D^{20}$ +34.4 (c 0.75, MeOH). IR (KBr): ν 3411, 3368, 1656, 1510, 1301, 1083 см$^{-1}$. ^{1}H NMR (500 MHz, CD_3OD) δ: 5.73 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.0 (t, 1H, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 3.1 Hz, H-3), 3.92 (dd, 1H, $J_{2,1}$ = 4.2 Hz, H-2), 3.76-3.79 (m, 1H, H-4), 3.71

(dd, 1H, $J_{5,4}$ = 4.5 Hz, $J_{5,5'}$ = 11.2 Hz, H-5), 3.66 (dd, 1H, $J_{5',4}$ 4.7 Hz, H-5′), 2.03 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, CD_3OD) δ: 172.3(NHCOMe), 83.9 (C-1), 80.7 (C-4), 76.7, 76.6 (C-2, C-3), 62.0 (C-5), 21.5 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_7H_{13}NO_5$ [M+Na]$^+$: 214.0691, found 214.0686.

*Synthesis of N-acetyl-β-D-arabinofuranosylamide **19** and N-acetyl-β-D-arabinopyranosylamide **20** from D-arabinose*

c.To a stirred suspension of dried D-arabinose (0.257 g, 1.7 mmol) in anhydrous acetonitrile (8 ml), KHF_2 (0.485 g, 6.2 mmol) and boron trifluoride diethyl etherate (1.6 ml, 12.6 mmol) were added at rt. The reaction mixture was stirred at room temperature for 4 h 10 min, and then poured into cooled 28 ml aq. 1N NaOH and evaporated, coevaporated with ethanol to dryness. The residue was dissolved in methanol, chloroform-methanol- 4:1 under mild heating, inorganic salts were filtered off and filtrate was evaporated. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform –methanol 6:1, 5:1 and 4:1, 3:1 to give 0.07 g (21%) of *N*-acetyl-β-D-arabinofuranosylamide (**19**) as crystalline product. Spectral data of the latter were identical to those for **19** (CD_3OD) prepared from the protected oxazoline **17**.

^{1}H NMR (500 MHz, D_2O) δ: 5.59 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1), 4.1 (t, 1H, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 3.1 Hz, H-3), 3.98 (dd, 1H, $J_{2,1}$ = 4.9 Hz, H-2), 3.70-3.81 (m, 1H, H-4), 3.64 (dd, 1H, $J_{5,4}$ = 4.5 Hz, $J_{5,5'}$ = 11.2 Hz, H-5), 3.60 (dd, 1H, $J_{5',4}$ 4.7 Hz, H-5′), 1.99 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, D_2O) δ: 175.0 (NHCOMe), 82.4 (C-1), 80.0(C-4), 75.7, 75.0 (C-2, C-3), 61.4 (C-5), 22.1 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_7H_{13}NO_5$ [M+Na]$^+$: 214.0691, found 214.0686.

0.058 g (18%) of *N*-acetyl-β-D-arabinopyranosylamide (**20**) as white solid. M.p. 167-170 °C. $[\alpha]_D^{20}$ -14.8 (c 0.32, MeOH). ^{1}H NMR (500 MHz, D_2O) δ = 5.23 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 3.82-3.84 (m, 1H, H-4), 3.77 (dd, 1H, J = 3.2 Hz, $J_{3,2}$ = 6.8 Hz, H-3), 3.73 (dd, 1H, $J_{2,1}$ = 3.2 Hz, H-2), 3.57 (dd, 1H, $J_{5,4}$ = 3.7 Hz, $J_{5,5'}$ = 12.1 Hz, H-5), 3.49 (dd, 1H, $J_{5',4}$ = 7.0 Hz, H-5′), 1.88 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, CD_3OD) δ = 175.4 (NHCOMe), 75.9 (C-1), 69.2, 68.1, 65.5, (C-4, C-2, C-3), 63.6 (C -5), 21.8 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_7H_{13}NO_5$ [M+Na]$^+$: 214.0691, found 214.0692.

*Preparation of 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline (**24**) and 2-phenyl-β-D-arabinopyrano -[1,2-d]-2-oxazoline (**25**) from D-arabinose*

b. To a suspension of dried D-arabinose (0.317 g, 2.11 mmol) in anhydrous benzonitrile (4.5 ml), KHF_2 (0.598 g, 7.65 mmol) boron trifluoride diethyl etherate (1.6 ml, 15.6 mmol) were added at rt. The reaction mixture was stirred at room temperature for 5 h 30 min, and poured into cooled 36 ml aq.1N NaOH, prepared solution left at 5-8 ^{0}C for 18 h, then coevaporated with ethanol at mild heating to dryness. The residue was dissolved in methanol, chloroform-methanol- 4:1 under mild heating, inorganic salts were filtered off and filtrate was coevaporated with silica gel and placed to the top of a silica gel column which was washed chloroform (60 ml) and then further gradual elution with chloroform-methanol 30:1, 15:1 and 10:1, 5:1 gave 0.338 g of a mixture of products. Additional chromatography on silica gel prepared in chloroform using for elution chloroform and chloroform-petroleum ether-methanol 15:6:0.5 → 15:6:1.5 gave (0.276 g, 56%) of 2-phenyl-β-D-arabinofurano-[1,2-d]-2-oxazoline (**24**) as oil. Spectral data of the latter were identical to those for **24** prepared from the protected oxazoline **22**.

^{1}H NMR (500 MHz, D_2O) δ = 7.42-7.99 (m, 5H, -N=C-C_6H_5), 6.11 (d, 1H, $J_{1,2}$ = 6.2 Hz, H-1), 5.05 (dd, 1H, $J_{2,3}$ = 1.3 Hz, H-2), 4.33 (br.d, 1H, H-3), 3.98-4.0 (m, 1H, H-4), 3.48 (dd, 1H, $J_{5,4}$ = 6.0, $J_{5,5'}$ = 11.8 Hz, H-5), 3.44 (dd, 1H, $J_{5',4}$ = 6.1 Hz, H-5′). ^{13}C NMR (126 MHz, D_2O) δ = 168.7 (CN), 134.0,

130.0 and 128.0 (N-C_6H_5), 102.0 (C-1), 90.8 (C-4), 87.3, 77.8 (C-2, C-3), 62.9 (C-5). HRMS (ESI^+): m/z calcd for $C_{12}H_{13}NO_4$ $[M+H]^+$: 236.0923, found 236.0927.

and (0.050 g, 10 %) 2-phenyl-β-D-arabinopyrano-[1,2-d]-2-oxazoline (**25**) as foam. $[\alpha]_D^{20}$ -21.0 (c 0.5, MeOH). ^1H NMR (500 MHz, D_2O) δ =7.37-7.78 (m, 5H, -N=C-C_6H_5), 5.67 (d, 1H, $J_{1,2}$ = 6.8 Hz, H-1), 4.55 (t, 1H, $J_{2,3}$ = 6.7 Hz, H-2), 3.86-3.88 (m, 1H, H-4), 3.76-3.81 (m, 1H, H-3 and H-5), 3.61 (dd, 1H, $J_{5',4}$ = 3.2 Hz, $J_{5,5'}$ = 12.5 Hz, H-5′). ^{13}C NMR (126 MHz, D_2O) δ = 168.5 (CN), 133.2, 129.5, 128.7, 128.4 (N-C_6H_5), 92.5 (C-1), 90.8, 69.2, 66.4 (C-4, C-2, C-3), 66.0 (C-5). LC-MS (ESI^+): m/z calcd for $C_{12}H_{13}NO_4$ $[M+H]^+$: 236.1, found 236.1.

2-Phenyl-(3,5-O-1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-arabinofurano)-[1,2-d]-2-oxazoline (**27**)

c.To a stirred solution of the oxazoline **24** (0.049 g, 0.21 mmol) in anhydrous pyridine (2.6 ml) 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (0.132 ml, 4.16 mmol) was added and then the reaction mixture was stirred for 48 h at room temperature. Water was added to prepared solution, the aqueous phase was extracted with CH_2Cl_2 (3x40 ml), the combined organic extracts were washed with 1N aq. HCl (2x6 ml), cooled 5% aq $NaHCO_3$, water, dried over anh. Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution a mixture of hexane-ethylacetate 9:1, 8:1, and 5:1 to give (0.097 g, 98%) of oxazoline derivative **27** as oil. $[\alpha]_D^{20}$ -31.3 (c 0.8, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: = 8.0 (d, 2H, N=C-C_6H_5), 7.51-7.54 *(t, 1H,* N=C-C_6H_5*), 7.42* (*t, 2H,* N=C-C_6H_5), 6.05 (d, 1H, $J_{1,2}$ =6.6 Hz, H-1), 5.0 (dd, 1H, $J_{2,3}$ = 4.1 Hz, H-2), 4.31 (dd, 1H, $J_{3,4}$ = 8.0 Hz, H-3), 4.05 (dd, 1H, $J_{5,4}$ = 3.2, $J_{5,5'}$ = 12.2 Hz, H-5), 3.91 (dd, 1H, $J_{5',4}$ = 5.9 Hz, H-5′), 3.23-3.75 (m, 1H, H-4), 0.97-1.20 (m, 28H, 4x $(CH_3)_2CH$]. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.2 (CN), 132.2, 128.9, 128.4, 127.1 (-N=C-C_6H_5), 99.6.1 (C-1), 88.9 (C-4), 80.0, 79.9 (C-2, C-3), 62.8 (C-5), 17.5, 17.3, 17.2, 16.89, 17.1 [4x$(CH_3)_2CH$], 13.3, 13.2, 12.69, 12.66 [4x$(CH_3)_2CH$]. HRMS (ESI^+): m/z calcd for $C_{24}H_{39}N_1Si_2O_5$ $[M+H]^+$: 477.2367, found 478.2380**.**

2-Phenyl-(3,5-di-O-diisopropylsilylhydroxy-β-D-arabinofurano)-[1,2-d]-2-oxazoline (***28***)

d.To the oxazoline **27** (0.022 g, 0.045 mmol) was added CH_2Cl_2 (0.5 ml) containing aq.33% HCl (0.027 ml) and then the reaction mixture was stirred for 24 h at room temperature. Water was added to prepared solution, the aqueous phase was extracted with CH_2Cl_2 (3x40 ml), the combined organic extracts were washed with cooled 5% aq $NaHCO_3$, water, dried over anh. Na_2SO_4 and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution a mixture of hexane-ethylacetate 9:1, 8:1, and 4:1 to give (0.02 g, 88%) of oxazoline derivative **28** as oil. ^1H NMR (500 MHz, $CDCl_3$), δ = 7.96 *(*dd, 2H, N=C-C_6H_5), 7.50 *(t,* 1H, N=C-C_6H_5*), 7.43* (*t,* 2H, N=C-C_6H_5), 6.17 (d, 1H, $J_{1,2}$ =6.3 Hz, H-1), 4.96 (dd, 1H, $J_{2,3}$ = 2.1, $J_{2,1}$ = 6.3 Hz, H-2), 4.68 (dd, 1H, $J_{3,4}$ = 4.8 Hz, H-3), 3.93-3.96 (m, 1H, H-4), 3.82 (dd, 1H, $J_{5,4}$ = 8.0, $J_{5,5'}$ = 11.5 Hz, H-5), 3.7 (dd, 1H, $J_{5',4}$ = 3.7 Hz, H-5′), 0.97-1.12 (m, 28H, 4x $(CH_3)_2CH$]. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.4 (CN), 132.4, 129.0, 128.4, 126.5 (-N=C-C_6H_5), 100.4 (C-1), 89.5 (C-4), 84.4, 76.4 (C-2, C-3), 60.8 (C-5), 17.4, 17.2, 17.1, 17.0, 16.9 [4x$(CH_3)_2CH$], 13.5, 13.4, 13.1, 12.6 [4x$(CH_3)_2CH$]. LC-MS (ESI^+): m/z calcd for $C_{24}H_{41}N_1Si_2O_6$[M-OH]$^+$: 478.24**,** found 478.3.

2-Phenyl-(3,5-di-O-4-chlorobenzoyl)-β-D-arabinofurano)-[1,2-d]-2-oxazoline ***(29)***

e. To a stirred solution of the oxazoline **24** (0.076 g, 0.32 mmol) in anhydrous pyridine (4 ml) 4-chlorobenzoyl chloride (0.17 ml, 1.27 mmol) was added at 0 °C and then the reaction mixture was stirred for 18 h at room temperature, diluted with CH_2Cl_2 and poured into cold 5% aq $NaHCO_3$. The

aqueous phase was extracted with CH_2Cl_2 (3x50 ml), the combined organic extracts were washed with 1N aq. HCl, cooled 5% aq $NaHCO_3$, water, dried and evaporated. The residue was chromatographed on a silica gel, using for elution a mixture of hexane-ethylacetate 6:1, 5:1, and 3:1 to give (0.147 g, 89%) of benzoylated oxazoline derivative **29** as white solid. M.p. 49-52 ºC. $[\alpha]_D^{20}$ -124.9 (c 0.67, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$), δ = 7.99 (d, 4H, 4ClC_6H_5CO and N=C-C_6H_5), 7.86 (d, 2H, 4ClC_6H_5CO), 7.56 (t, 1H, N=C-C_6H_5), 7.42-7.46 (m, 4H, 4ClC_6H_5CO and N=C-C_6H_5), 7.22 (d, 2H, 4-ClCOC_6H_5), 6.4 (d, 1H, $J_{1,2}$ = 6.2 Hz, H-1), 5.67 (br.d, 1H, $J_{3,4}$ = 2.3 Hz, H-3), 5.22 (dd, 1H, $J_{2,3}$ = 0.9 Hz, H-2), 4.56-4.59 (m, 1H, H-4). 4.41 (dd, 1H, $J_{5,4}$ = 5.5, $J_{5,5'}$ = 11.7 Hz, H-5), 4.35 (dd, 1H, $J_{5',4}$ = 6.2 Hz, H-5′). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.7 (CN), 165.2 and 164.7 (C=O, 2x4-ClCOC_6H_5), 140.4, 139.6, 132.7, 131.3, 131.1, 129.1, 129.0, 128.7, 128.6 (2x4-ClCOC_6H_5, -N=C-C_6H_5), 102.1 (C-1), 86.3 (C-4), 81.4, 79.5 (C-2, C-3), 63.8 (C-5). HRMS (ESI$^+$): m/z calcd for $C_{26}H_{19}NCl_2O_6$ $[M+H]^+$: 512.0663, found 512.0693

3,*5-Di-O-4-chlorobenzoyl-N-benzoyl-β-D-arabinofuranosylamide (**32**)*

g. To a stirred solution of benzoylated oxazoline derivative **29** (0.047 mg, 0.09 mmol) in anhydrous acetonitrile (4 ml) 46% aq. HBF_4 (0.047 ml, 0.246 mmol) was added at at 0ºC. The reaction mixture was stirred under cooling for 30 min and at room temperature for 20 h, and then diluted with CH_2Cl_2 (5 ml), cold 5% aq $NaHCO_3$ was added to prepared solution under stirring. The aqueous phase was extracted with CH_2Cl_2 (3x30 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution mixtures of hexane-ethylacetate 6:1, 4:1, 1:1 and ethylacetate to give 0.007 g (19%) of cyclic product **31** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 7.22 – 8.02 (4m, 15H, Ph, 4ClPh), 5.82-5.87 (m, 0.7H, NH), 5.69 (s, 1H, H-3), 5.51-5.56 (m, 2.3H, H-2 and H-1), 4.82 (dd, 1H, $J_{5,4}$ = 3.4, $J_{5,5'}$ = 11.8 Hz, H-5), 4.72-4.75 (m, 1.4H, H-4), 4.64 (dd, 1H, $J_{5',4}$ = 5.2 Hz, H-5′), 3.2 (br.s, 1H, OH). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 165.5, 165.4 and 165.0 (C=O, 4ClPhCO, CO(NH)-), 140.2, 139.6, 133.7, 131.3, 131.2, 131.14, 131.2, 130.0, 129.9, 128.8, 128.7, 128.5 (4ClC_6H_5CO, -NH-C-C_6H_5), 100.9 (C-1), 82.3, 81.5, 70.0 (C-4, C-2 and C-3), 63.9 (C-5). LC-MS (ESI$^+$): m/z calcd for C26H21O7N1Cl2 $[M+Na]^+$: 552.1, found 553.1.

0.011 g (23%) of the starting oxazoline **29** and 3,5-di-O-4-chlorobenzoyl-N-benzoyl-β-D-arabinofuranosylamide (**32**) (0.012 g, 32%) as oil. $[\alpha]_D^{20}$ -12.5 (c 0.2, $CHCl_3$).^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, 2H, 4-ClCOC_6H_5), 7.96(d, 2H, 4-ClCOC_6H_5), 7.84 (d, 2H, COC_6H_5), 7.84 (d, 2H, COC_6H_5), 7.54 (t, 1H, COC_6H_5), 7.36-7.45 (2m, 6H, 4-ClCOC_6H_5 and COC_6H_5), 6.11 (dd, 1H, $J_{NH,\,H-1}$ = 8.7 Hz, J = 4.4 Hz, H-1), 5.22 (dd, 1H, $J_{3,2}$ = 1,9 Hz, $J_{3,4}$ = 4,1 Hz, H-3), 5.52 (d, 1H, $J_{3,2}$ = 2.8 Hz, H-3), 4.64 (d, 2H, H-5 and H-5′), 4.44 (dd, 1H, $J_{2,1}$ = 4.4 Hz, H-2), 4.36-4.41 (m, 1H, H-4), 3.4 (br.s., 1H, 2-OH). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 167.6, 165.7 and 165.6 (NHCOBz), 2xCO-4-ClC_6H_5), 131.28, 131.26, 131.17, 129.1, 129.0, 128.9, 128.6, 127.4 (2xCO4-ClC_6H_5), 81.5 (C-1), 81.0 (C-4), 78.2, 74.8 (C-2, C-3), 64.4 (C-5), 31.0 (NHCOBz). LS-MS (ESI$^+$): m/z calcd for $C_{26}H_{21}O_7NCl_2$[M+H]$^+$: 530.1, found 530.1.

*3,5-Di-O-benzoyl-N-acetyl-α-D-ribofuranosylamide (**37**) from the oxazoline 33:*

a. The oxazoline **33** (0.3 g, 0.75 mmol) was coevaporated with chloroform and kept at 5-8 ºC for 6 weeks. The oily residue was chromatographed on a silica gel, using for elution mixtures of ethylacetate: petroleum ether, and ethylacetate-methanol 6:1 to give (0.188 g, 62%) of 3,5-di-*O*-benzoyl-*N*-acetyl-α-D-ribofuranosylamide (**37**). M.p. 155-156 ^{0}C. $[\alpha]_D^{20}$ +62.2 (c 0.45, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-8.06(m, 10H, 2 x COC_6H_5), 6.84 (d, 1H, *J* 8.9 Hz, NHCOMe), 5.97

(dd, 1H, $J_{1,2}$ 4.4 Hz, H-1), 5.38 (dd, 1H, $J_{3,4}$ 4.9 Hz, $J_{3,2}$ 6.5 Hz, H-3), 4.61-4.65 (m, 2H, H-2 and H-4), 4.56 (dd, 1H, H-5), 4.51 (dd, 1H, H-5′), 2.06 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.83 (NHCOMe), 166.31 and 166.80 (C=O, 2xCOC_6H_5), 133.77, 133.24, 129.80, 129.73, 128.58, 128.96, 128.65, 128.44 (2xCOC_6H_5), 80.32 (C-1), 76.81 (C-4), 74.76, 69.67 (C-3, C-2), 64.28 (C-5), 23.49 (NHCOCH$_3$). HRMS (ESI$^+$): m/z calcd for $C_{21}H_{21}NO_7$ $[M+Na]^+$: 422.1216, found 422.1208.

*3,5-Di-O-benzoyl-N-acetyl-α-D-ribofuranosylamide (**37**) and 2,5-di-O-benzoyl-N-acetyl-α-D-ribofuranosylamide (**38**)*

b. The oxazoline **33** (0.207 g, 0.54 mmol) was dissolved in chloroform and placed to the top of a silica gel column which was prepared in chloroform. After 48 h at room temperature a silica gel column was washed chloroform and then further gradual elution with chloroform-methanol 30:1, 15:1 and 8:1 gave 0.16 g of a mixture of protected N-ribofuranosides, The prepared mixture of isomeric N-ribosides was chromatographed on silica gel using using for elution a mixture of hexane-ethylacetate 1:1, 1.5:1 and 1:2 to give (0.032 g,15%) of 2,5-di-O-benzoyl-N-acetyl-α-D-ribofuranosylamide (**38**). M.p. 160-161^{0}C. $[\alpha]_D^{20}$ +18.0 (c 0.13, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49-8.1 (m, 10H, 2 x COC_6H_5), 6.79 (d, 1H, J = 9.5 Hz, NHCOMe), 6.18 (dd, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 5.46 (t, 1H, $J_{2,3}$ = 5.2 Hz, $J_{2,1}$ = 5.4 Hz, H -2), 4.66 (m, 1H, H-4), 4.54 (dd, 1H, $J_{5,4}$ = 4.9 Hz, $J_{5,5'}$ = 12.9 Hz, H-5), 4.47-4.52 (m, 2H, H-5′ and H -3), 2.06 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.5 (NHCOMe), 166.5 and 165.6 (C=O, 2xCOC_6H_5), 133.9, 133.4, 129.8, 129.7, 129.5, 128.9, 128.7, 128.6 (2xCOC_6H_5), 81.3 (C-1), 79.0 (C-4), 72.5, 71.6 (C-3, C-2), 64.4 (C-5), 23.6 (NHCOCH$_3$). HRMS (ESI$^+$): m/z calcd for $C_{21}H_{21}NO_7$ $[M+Na]^+$: 422.1216, found 422.1211.

(0.097 g, 45%) of 3,5-di-O-benzoyl-N-acetyl-α-D-ribofuranosylamide (**37**).

M.p. 155-156 ^{0}C. $[\alpha]_D^{20}$ +62.2 (c 0.45, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-8.06 (m, 10H, 2 x COC_6H_5), 6.84 (d, 1H, J = 8.9 Hz, NHCOMe), 5.97 (dd, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 5.38 (dd, 1H, $J_{3,4}$ = 4.9 Hz, $J_{3,2}$ = 6.5 Hz, H-3), 4.61-4.65 (m, 2H, H-2 and H-4), 4.56 (dd, 1H, H-5), 4.51 (dd, 1H, H-5′), 2.06 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.8 (NHCOMe), 166.3 and 166.8 (C=O, 2xCOC_6H_5), 133.7, 133.2, 129.8, 129.7, 128.6, 128.96, 128.6, 128.4 (2xCOC_6H_5), 80.3 (C-1), 76.8 (C-4), 74.8, 69.7 (C-3, C-2), 64.3 (C-5), 23.5 (NHCOCH$_3$). HRMS (ESI$^+$): m/z calcd for $C_{21}H_{21}NO_7$ $[M+Na]^+$: 422.1216, found 422.1208.

*N-Acetyl-α-D-ribofuranosylamide (**39**)*

c. 3,5-Di-*O*-benzoyl-*N*-acetyl-α-D-ribofuranosylamide (**37**) (0.170 g, 0.43 mmol) was dissolved in 15 ml methanol saturated at 0^{o}C with ammonia, then reaction mixture was stirred for 10 h at room temperature and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform –methanol 15:1, 5:1 and 2:1 to give (0.061 g, 72%) of *N*-α-ribofuranosylacetamide **39** as oil. $[\alpha]_D^{20}$ +61.4 (c 0.33, MeOH). ^{1}H NMR (500 MHz, CD_3OD) **δ:** 5.68 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1), 4.09-4.13 (m, 2H, H-2 and H-3), 3.91-3.94 (m, 1H, H-4), 3.71 (dd, 1H, $J_{5,4}$ 3.1 Hz, $J_{5,5'}$ 12.1 Hz, H-5), 3.57 (dd, 1H, $J_{5',4}$ 4.2 Hz, H-5′), 2.04 (s, 3H, NHCOCH$_3$). ^{13}C NMR (126 MHz, CD_3OD) δ: 173.86 (NHCOMe), 84.18 (C-1), 81.64 (C-4), 72.54, 71.92 (C-2, C-3), 62.96 (C-5), 22.95 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_7H_{13}NO_5$ $[M+Na]^+$: 214.0691, found 214.0684.

d. To a stirred suspension of dried D-ribose (0.210 g, 1.39 mmol) in anhydrous acetonitrile (4.5 ml), KHF_2 (0.328 g, 4.2 mmol) and boron trifluoride diethyl etherate (1.15 ml, 9.0 mmol) were added 0^{0}C. The reaction mixture was stirred under cooling for 30 min and then for 3 h at room temperature, and then poured into cooled 25 ml aq. 1N NaOH and evaporated, coevaporated with ethanol to dryness.

The residue was dissolved in methanol, chloroform-methanol- 4:1 under mild heating, inorganic salts were filtered off and filtrate was evaporated. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform –methanol 6:1, 5:1 and 3:1, 1:1 to give 0.024 g (9%) of *N*-acetyl-α-D-ribofuranosylamide (**39**) as oil. Spectral data of the latter were identical to those for **39** prepared from the protected oxazoline **37**.

*Synthesis of 3,5-di-O-benzoyl-N-acetyl-α-and β-D-ribofuranosylamides **42α** and **43β** from peracylated D-ribose **41***

e. To a stirred solution of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**41**) (0.250 g, 0.495 mmol) in anhydrous acetonitrile (10 ml) KHF_2 (0.116 g, 1.48 mmol) and boron trifluoride diethyl etherate (0.36 ml, 2.84 mmol) were added at 0^0C. Then, the reaction mixture was stirred at room temperature for 2 h, and then poured into cooled 6.5 ml 1N aq NaOH. The aqueous phase was extracted with CH_2Cl_2 (3x40 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution mixtures of hexane-ethylacetate 6:1, 4:1 and 1:1 to give 2,3,5-tri-*O*-benzoyl-*N*-acetyl-β-D-ribofuranosylamide (**43β**) (0. 025 g, 10%). $[\alpha]_D^{20}$ -4.1 (c 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41-8.15 (m, 15H, 3 x COC_6H_5), 6.47 (d, 1H, *J* 8.9 Hz, NHCOMe), 6.07 (dd, 1H, $J_{1,2}$ 6.5 Hz, H-1), 5.84 (dd, 1H, $J_{3,2}$ 5.1 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.62 (t, 1H, H-3), 4.75 (dd, 1H, H-5), 4.62-4.65 (m, 1H, H-4), 4.61 (dd, 1H, H-5′), 2.03 (s, 3H, NHCOCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.80 (NHCOMe), 166.23, 165.64 and 165.56 (C=O, 3xCOC_6H_5), 133.71, 133.66, 133.45, 129.92, 129.86, 129.76, 128.67, 128.55, 128.52 (3xCOC_6H_5), 82.16 (C-1), 79.28 (C-4), 76.81, 73.88 (C-3, C-2), 64.20 (C-5), 23.45 (NHCOCH_3). HRMS (ESI^+): m/z calcd for $C_{28}H_{25}NO_8$ $[M+Na]^+$:526.1472, found 526.1423.

and 2,3,5-tri-*O*-benzoyl-*N*-acetyl-α-D-ribofuranosylamide (**42α**) (0.025 g, 10%). $[\alpha]_D^{20}$ +23.8 (c 0.76, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40-8.12 (m, 15H, 3 x COC_6H_5), 6.45 (d, 1H, *J* 9.6 Hz, NHCOMe), 6.38 (dd, 1H, $J_{1,2}$ 4.5 Hz, H-1), 5. 85-5.88 (m, 2H, H-2 and H-3), 4.72-4.74 (m, 1H, H-4), 4.67 (dd, 1H, H-5), 4.60 (dd, 1H, H-5′), 2.08 (s, 3H, NHCOCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 169.93 (NHCOMe), 166.22, 165.08 and 164.80 (C=O, 3xCOC_6H_5), 133.88, 133.77, 133.34, 129.79, 129.57, 128.71, 128.67, 128.56 (3xCOC_6H_5), 79.08 (C-1), 78.62 (C-4), 72.91, 71.02 (C-3, C-2), 64.25 (C-5), 23.64 (NHCOCH_3). HRMS (ESI^+): m/z calcd for $C_{28}H_{25}NO_8$ $[M+Na]^+$:526.1472, found 526.1434.

3,5,6-Tri-O-benzoyl-N-acetyl-α-D-glucofuranosylamide (**45**) *from the oxazoline* **44**:

a_1. The oxazoline **44** (0.3g, 0.75 mmol) [24] was coevaporated with chloroform and kept at 5-8 °C for 7 weeks. The oily residue was chromatographed on a silica gel, using for elution mixtures of ethylacetate -petroleum ether, and chloroform-methanol 9:1 to give 0.202 g (66%) of benzoylated *N*-acetyl-α-D-glucofuranosylamide (**45**) as oil. $[\alpha]_D^{20}$ -57.3 (c 1.0, $CHCl_3$). IR (KBr): ν 3358, 2927, 1727, 1656, 1519, 1281, 1267, 1109 $см^{-1}$. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31-7.99 (m, 15H, 3 x COC_6H_5), 6.85 (br.d, 1H, *J* = 8.8 Hz, NHCOMe), 6.11 (dd, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.74-5.78 (m, 1H, H-5), 5.56 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 4.92 (dd, 1H, $J_{6,5}$ = 2.5, $J_{6,6'}$ = 12.3 Hz, H-6), 4.84 (dd, 1H, H-4), 4.64 (dd, 1H, $J_{6,5}$ = 5.5 Hz, H-6′), 4.32 (d, 1H, $J_{2,1}$ = 3.7 Hz, H-2). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.9 (CONHCH$_3$), 166.2, 166.0 and 165.1 (C=O, 3xCOC_6H_5), 133.8, 133.2, 132.06, 129.9, 129.7, 129.6, 128.6, 128.4, 128.3 (3xCOC_6H_5), 81.1 (C-1), 78.4, 76.0, 74.1, 68.3 (C-5, C-4, C-2, C-3), 64.1 (C-6), 29.7 (NHCOCH_3). HRMS (ESI^+): m/z calcd for $C_{29}H_{27}NO_9$ $[M+Na]^+$: 556.1578, found 556.1554.

a2. The oxazoline **44** (250 mg) was kept at 5-8 °C for a week. The oily residue was chromatographed

on a silica gel, using for elution mixtures of ethylacetate: petroleum ether 3:1, 1:1 and ethylacetate-methanol 9:1 to give (0.133 g, 53%) of the oxazoline **44** and 0.085 g (33%) of 3,5,6-tri-*O*-benzoyl-*N*-acetyl-α-D-glucofuranosylamide (**45**) as oil.

b.The oxazoline **44** (0.100 g, 0.25 mmol) was dissolved in chloroform and placed to the top of silica gel column which was prepared in chloroform. After 24 h a silica gel column was washed chloroform and further chromatography gave 0.08 g (78%) of benzoylated *N*-acetyl-α-D-glucofuranosylamide (**45**) as oil, using for elution mixtures of chloroform-methanol 20:1, 15:1 and 10:1.

N-Acetyl-α-D-glucofuranosylamide (**46**):

c. 3,5,6-Tri-*O*-benzoyl-*N*-acetyl-α-D-glucofuranosylamide (**45**) (0.17 g, 0.32 mmol) was dissolved in 7 ml methanol and 11 ml methanol saturated at 0°C with ammonia was added to prepared solution, then reaction mixture was stirred for 18 h at room temperature and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform–methanol 15:1, 6:1 and 2:1 to give (0.046 g, 65%) of *N*-acetyl-α-D-glucofuranosylamide (**46**). m.p. 189-190 °C. $[\alpha]_D^{20}$ +91.4 (c 0.65, MeOH). ^{1}H NMR (500 MHz, CD_3OD) δ = 5.85 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.24 (dd, 1H, H-3), 4.05 (dd, 1H, H-4), 4.01 (dd, 1H, $J_{2,1}$ = 3.6, $J_{2,3}$ = 1.1 Hz, H-2), 3.86-3.90 (m, 1H, H-5), 3.78 (dd, 1H, $J_{6,5}$ = 3.1, $J_{6,6'}$ = 11.5 Hz, H-6), 3.59 (dd, 1H, $J_{6',5}$ = 6.2, H-6′), 2.03 (s, 3H, NHCO$\underline{CH_3}$). ^{13}C NMR (126 MHz, CD_3OD) δ = 172.3 (NH$\underline{CO}$Me), 81.0 (C-1), 79.2, 76.3, 75.5, 69.6 (C-4, C-2, C-3, C-5), 64.0 (C-6), 21.5 (NHCO$\underline{CH_3}$). HRMS (ESI^+): m/z calcd for $C_8H_{15}NO_6$ $[M+Na]^+$: 244.0797, found 244.0794.

d. To solution 3,5,6-tri-*O*-benzoyl-*N*-acetyl-α-D-glucofuranosylamide (**45**) (0.16 g, 0.30 mmol) in 2 ml anhydrous methanol and 0.36 ml 1 M methanolic NaOMe solution was added and then the reaction mixture was kept at rt for 14 h. Amberlyt 15 (H^+ form) was added to remove sodium ions, the resin was filtered off, and washed with methanol, solvent was removed under diminished pressure. The residue was chromatographed on a silica gel, using conditons described above, to give (0.048 g, 72%) of *N*-acetyl-α-D-glucofuranosylamide (**46**).

N-Acetyl-α-D-glucofuranosylamide (**46**) *and N-acetyl-α-D-glucopyranosylamide* (**51**) *from D-glucose:*

To a stirred suspension of dried D-glucose (0.25 g, 1.38 mmol) in anhydrous acetonitrile (7.5 ml), KHF_2 (0.445 g, 5.7 mmol) boron trifluoride diethyl etherate (1.4 ml, 11.0 mmol) were added at rt. The reaction mixture was stirred at room tempera ture for 4 h, and then poured into cooled 25 ml 1N aq NaOH and evaporated to dryness, coevaporated with ethanol. The residue was chromatographed on a silica gel, using for elution mixtures of chloroform-methanol 4:1 3:1 and 1:1 to give 0.115 g (36%) of N-acetyl-α-D-glucopyranosylamide (**51**) as oil. ^{1}H NMR (500 MHz, D_2O) δ = 5.38 (d, 1H, $J_{1,2}$ = 5.6 Hz, H-1), 3.6 (dd, 1H, H-2), 3.48-3.59 (m, 3H, H-6 and H-6', H-3), 3.32 (ddd, 1H, J = 2.3, J = 4.9, J = 10.2 Hz, H-5), 3.24 (dd, 1H, H-4), 1.9 (s, 3H, $NHCOCH_3$). ^{13}C NMR (126 MHz, CD_3OD) δ = 175.9 (NHCOMe), 76.4 (C-1), 72.9, 72.5, 69.23, 69.21, 60.8 (C-4, C-2, C-3, C-5), 60.3 (C-6), 21.9 (NHCOMe). $[\alpha]_D^{20}$ +105.4 (c 0.35, MeOH). HRMS (ESI^+): m/z calcd for $C_8H_{15}NO_6$ $[M+Na]^+$: 244.0797, found 244.0793.

The further elution with a mixture of chloroform: methanol: water - 20:5:1 gave 0.040 g (13%) of N-acetyl-α-D-glucofuranosylamide (**46**). Spectral data of the latter were identical to those for **46** (CD_3OD) prepared from the protected oxazoline **44**.

3,5,6-Tri-O-benzoyl-N-acetyl-α-D-allofuranosylamide (**48**) *from benzoyl-protected N-α-D-allo-furanosyl oxazoline* **47**:

2-Methyl-(3,5,6-tri-O-benzoyl-α-D-allofurano)-[1,2-d]-2-oxazoline (**47**):

To a stirred solution of intermediate 2,3,5-tri-O-benzoylated allofuranose-1,2-acetonide (0.1 g, 0.34 mmol) in anhydrous benzonitrile (3.2 ml) KHF_2 (0.050 g, 1.66 mmol) and boron trifluoride diethyl etherate (0.2 ml, 2.83 mmol) were added successively. The reaction mixture was stirred at room temperature for 18 h, and then poured into cooled 3.47 ml 1N aq NaOH. The aqueous phase was extracted with $CHCl_3$ (3x30 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to give the oxazoline **47** (0.09 g, 93%) as a colorless oil. $[\alpha]_D^{20}$ +68.1 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31-8.01 (m, 20H, 2 x COC_6H_5, -N=C-C_6H_5), 6.14 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 5.85-5.89 (m, 1H, H-5), 5.34 (d, 1H, $J_{3,2}$ = 5.8 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 5.25 (d, 1H, $J_{2,1}$ = 4.5 Hz, H-2), 4.84 (dd, 1H, $J_{6,5}$ = 3.5, $J_{6,6'}$ = 12.1 Hz, H-6), 4.67 (dd, 1H, $J_{6,5}$ = 7.0 Hz, H-6′), 4.20 (dd, 1H, H-4). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 166.8 (CN), 166.1, 165.6 and 165.4 (C=O, 3xCOC_6H_5), 133.4, 133.3, 133.2, 132.7, 129.8, 129.7, 128.4, 128.37 (3x$CO\underline{C_6H_5}$, -N=C-C_6H_5), 100.6 (C-1), 78.6, 74.9, 74.7, 71.1 (C-5, C-4, C-2, C-3), 63.3 (C-6). HRMS (ESI$^+$): m/z calcd for $C_{29}H_{25}NO_8$ $[M+Na]^+$: 538.1478, found 538.1455.

3,5,6-Tri-O-benzoyl-N-acetyl-α-D-allofuranosylamide (**48**) *by hydrolysis of the oxazoline* **47**

e. The oxazoline **47** (0.07 g, 0.17 mmol) was dissolved in chloroform and placed to the top of silica gel column which was prepared in chloroform. After 18 h a silica gel column was washed chloroform and further chromatography gave 0.051 g (70%) of benzoylated *N*-acetyl-α-D-allofuranosylamide (**48**) as oil using for elution mixtures of chloroform-methanol 20:1, 15:1 and 10:1. $[\alpha]_D^{20}$ +38.8 (c 0.33 $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33-7.95 (m, 15H, 3 x COC_6H_5), 6.68 (br.d, 1H, *J* = 9.0 Hz, NHCOMe), 6.11 (dd, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.62-5.68 (m, 1H, H-5), 5.53 (dd, 1H, $J_{3,4}$ = 4.9 Hz, $J_{3,2}$ = 6.5 Hz, H-3), 4.92 (dd, 1H, $J_{6,5}$ = 3.6, $J_{6,6'}$ = 12.2 Hz, H-6), 4.50-4.64 (m, 3H, H-4, H-6′, H-2). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.6 ($CONHCH_3$), 166.1 and 165.6 (C=O, 3xCOC_6H_5), 133.7, 133.3, 133.2, 129.9, 129.7, 128.6, 128.5, 128.4, 128.3 (3x$CO\underline{C_6H_5}$), 80.2 (C-1), 75.2, 71.8, 69.8 (C-5, C-4, C-2, C-3), 64. 63.2 (C-6), 23.6 ($NHCO\underline{CH_3}$). HRMS (ESI$^+$): m/z calcd for $C_{29}H_{27}NO_9$ $[M+Na]^+$: 556.1578, found 556.1559.

f. The oxazoline **47** (0.045 g) was kept at 5-8 °C for six weeks. The oily residue was chromatographed on a silica gel, using for elution mixtures of ethylacetate-petroleum ether 3:1, chloroform-methanol 15:1 and 9:1 to give (0.039 g, 85%) 3,5,6-tri-*O*-benzoyl-*N*-acetyl-α-D-allofuranosylamide (**48**) as oil.

*6-O-benzoyl-3,4-O-isopropylidene-α-D-galactopyranosylamine (**55**) from the oxazoline **53**:*

2-Methyl-(6-O-benzoyl-3,4-O-isopropylidene-α-D-galactopyrano)-[1,2-d]-2-oxazoline (**53**)

a. To a stirred solution of 6-*O*-benzoyl D-galactopyranose diacetonide **52** (0.44 g, 1.23 mmol) in anhydrous acetonitrile (10 ml) KHF_2 (0.226 g, 2.35 mmol) and boron trifluoride diethyl etherate (1.1 ml, 8.75 mmol) were added successively. The reaction mixture was stirred at room temperature for 18 h, and then poured into cooled 21.5 ml 1N aq NaOH. The aqueous phase was extracted with $CHCl_3$ (3x50 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to give the oxazoline **53** (0.41 g, 93%) as a colorless oil. $[\alpha]_D^{20}$ - 66.2 (c 1.0, $CHCl_3$). IR (in $CHCl_3$): ν 2994, 2931, 1722, 1665, 1373, 1273, 1240 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46-8.1 (m, 5H, COC_6H_5), 5.83 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.76 (dd, 1H, $J_{2,1}$ = 7.7, $J_{2,3}$ = 2.1 Hz, H-2), 4.52-4.60 (m, 2H, H-6 and H-3), 4.45 (dd, 1H, $J_{6,5}$ = 7.2, $J_{6,6'}$ = 11.4 Hz H-6′), 4.34 (dd, 1H, H-4), 3.57-3.61 (m, 1H, H-5), 2.13 (s, 3H, NCH_3), 1.55 and 1.41 (2s, 3H, $(CH_3)_2$C-). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.0 (CN), 166.4 (C=O, COC_6H_5), 133.0, 130.0, 129.8, 128.4 (COC_6H_5), 110.0 [C-$CH_3)_2$], 91.5 (C-1), 73.0, 70.7, 70.2, 65.8 (C-5, C-4, C-2, C-3), 63.5 (C-6), 26.7 and 24.7 [(CH_3)$_2$C-], 13.9 (NMe).

HRMS (ESI$^+$): m/z calcd for $C_{18}H_{21}NO_6$ $[M+H]^+$: 348.1442, found 348.1443, and $C_{18}H_{21}NO_6$ $[M+Na]^+$: 370.1261, found 370.1263.

*Preparation of 6-O-benzoyl-N-acetyl-3,4-O-isopropylidene-α-D-galactopyranosylamide (**55**) by hydrolysis of the oxazoline **53***

b.The oxazoline **53** (0.32 g, 0.89 mmol) was dissolved in chloroform and placed to the top of silica gel column which was prepared in chloroform. After 24 h a silica gel column was washed chloroform and then further gradual elution with chloroform-methanol 30:1, 15:1 and 8:1 chloroform-methanol gave (0.275 g, 82%) of protected *N*-α-D-galactopyranosylamide (**55**) as oil. $[\alpha]_D^{20}$ +70.1 (c 0.67, $CHCl_3$). IR (solution in $CHCl_3$): ν 2953, 2928, 1721, 1686, 1492, 1378, 1263 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.46-8.1 (m, 5H, COC_6H_5), 7.17 (br.d, 1H, NH), 5.67 (dd, 1H, $J_{1,2}$ = 3.5, $J_{1,NH}$ = 9.7 Hz, H-1), 4.48-4.52 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 4.09 (t, 1H, H-2), 2.04 (s, 3H, NHCO*CH*$_3$), 1.54 and 1.37 [2s, 3H, $(CH_3)_2C$-]. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.0 (NH*CO*CH_3), 166.4 (C=O, COC_6H_5), 133.1, 129.8, 129.6, 128.3 (COC_6H_5), 110.3 [*C*-$CH_3)_2$], 74.2 (C-1), 73.5, 72.1, 68.7, 66.8 (C-4, C-2, C-3, C-5), 64.2 (C-6), 26.4 and 24.6 [(*CH*$_3)_2$C-], 23.4 (NHCO*CH*$_3$). HRMS (ESI$^+$): m/z calcd for $C_{18}H_{23}NO_7$ $[M+Na]^+$: 388.1372, found 318.1368.

*N-Acetyl-α-D-galactopyranosylamide (**56**) from protected N-acetyl-3,4-O-isopropylidene-α-D-galactopyranosylamide (**55**)*

c.The *N*-acetyl D-galactopyranosylamide deivative **55** (0.25 mg, 0.67 mmol) was dissolved in 4 ml 80% aq acetic acid and reaction mixture was stirred at 50-55 °C for 18 h, then coevaporated with toluene (2x10 ml). Then residue was dissolved in 4 ml methanol and 12 ml methanol saturated at 0 °C with ammonia was added to prepared solution, then reaction mixture was stirred for 18 h at room temperature and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform–methanol 6:1, 3:1 and 2:1, then chloroform–methanol-water 20:5:1 to give (0.085 g, 58%) of *N*-acetyl-α-D-galactopyranosylamide (**56**). M.p. 168-170 °C (crystallization under storing). $[\alpha]_D^{20}$ +86.56 (c 1, MeOH). ^1H NMR (500 MHz, D_2O) δ = 5.52 (d, 1H, $J_{1,2}$ = 5.7 Hz, H-1), 3.96 (dd, 1H, H-2), 3.89 (br.d, 1H, H4), 3.75 (dd, 1H, H-3), 3.69 (m, 1H, H-5), 3.61 (dd, 2H, H-6 and H-6′), 2.09 (s, 3H, $NHCOCH_3$). ^{13}C NMR (126 MHz D_2O) δ = 175.9 (NHCOMe), 76.7 (C-1), 71.8, 69.3, 68.8, 66.1 (C-4, C-2, C-3, C-5), 61.0 (C-6), 21.9 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_8H_{15}NO_6$ $[M+Na]^+$: 244.0797, found 244.0793.

*Preparation of N-Acetyl-α-D-galactopyranosylamide (**56**) and N-acetyl-α-D-galactofurano-sylamide (**57**) from D-galactose*

d.To a stirred suspension of dried D-galactose (0.27 g, 1.49 mmol) in anhydrous acetonitrile (8 ml), KHF_2 (0.47 g, 6.0 mmol) boron trifluoride diethyl etherate (1.5 ml, 11.8 mmol) were added at rt. The reaction mixture was stirred at room temperature for 3 h 30 min, and then poured into cooled 27 ml 1N q NaOH and evaporated to dryness, coevaporated with ethanol. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform-petroleum ether: methanol 4:2:1 3:1, chloroform–methanol 1:1, and methanol to give 0.05 mg (18%) of N-acetyl-α-D-galactofuranosylamide (**57**) as oil. $[\alpha]_D^{20}$ +24.8 (c 0.56, MeOH).^1H NMR (500 MHz, D_2O)δ=5.46 (d, 1H,$J_{1,2}$=4.5Hz, H-1), 3.96-4.0 (m, 2H, H-4, H-5), 3.63 (dt, 1H, J = 4.4, J = 3.3, J = 7.0, Hz, H-3), 3.58 (dd, 1H, $J_{2,1}$ = 4.4, $J_{2,3}$ = 4.1Hz, H-2), 3.49 (dd, 1H, $J_{6,5}$ = 4.6 Hz, $J_{6,6'}$ = 11.7 Hz, H-6), 3.42 (dd, 1H, $J_{6,5'}$ = 7.3 Hz, H-6′), 1.9 (s, 3H, $NHCOCH_3$). ^{13}C NMR (126 MHz, D_2O) δ = 174.9 (NHCOMe), 81.4 (C-1), 79.7, 75.7, 74.8, 70.8 (C-4, C-2, C-3, C-5), 62.4 (C-6), 21.9 (NHCOMe). HRMS (ESI$^+$): m/z calcd for $C_8H_{15}NO_6$ $[M+Na]^+$:

244.0797, found 244.0792.

and 0.048 g (15%) of N-acetyl-α-D-galactopyranosylamide as oil. Spectral data of the latter were identical to those for **56** (^{1}H and ^{13}C NMR in D_2O) prepared from the protected oxazoline **53**.

Preparation of 6-O-benzoyl-3,4-O-isopropylidene-β-D-galactopyranosylamine (***59β***) *from the oxazoline **53***

e.The oxazoline **53** (0.062 g) was stored at 5-8 ^{0}C for 3 months and β-D-galactopyranosylamine derivative **59β** was prepared as white solid (according to ^{1}H, ^{13}C NMR and ^{13}C/ DEPT NMR data of a mixture in $CDCl_3$, 85% yield of amine **59β** was determined from ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43-8.07 (m, 10H, COC_6H_5), 4.87 (dd, 1H, $J_{2,1}$ = 8.7, $J_{2,3}$ = 7.7 Hz, H-2), 4.61 (dd, 1H, $J_{6a,5}$ = 4.7, $J_{6a,6b}$= 12.3 Hz, H-6a), 4.53 (dd, 1H, $J_{6b,5}$ = 7.3 Hz, H-6b), 4.26 (dd, 1H, $J_{4,5}$ = 2.1, $J_{4,3}$ = 5.4 Hz, H-4), 4.21 (dd, 1H, H-3), 4.10-4.14 (m, 1H, H-5), 4.03 (d, 1H, J = 8.7 Hz, H-1), 2.12 (s, 3H, CH_3CO), 1.96 (br.s, 2H, NH_2), 1.55 and 1.35 [2s, 3H, $(CH_3)_2C$-]. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.8 ($COCH_3$), 166.5 (C=O, COC_6H_5), 133.2, 129.9, 129.8, 128.4 (COC_6H_5), 110.6 [C-$CH_3)_2$], 84.2 (C-1), 79.8, 74.0, 73.8, 71.5 (C-2, C-4, C-3, C-5), 64.1 (C-6), 27.8 and 26.3 [($CH_3)_2$C-], 21.2 ($COCH_3$). HRMS (ESI$^+$): m/z calcd for $C_{18}H_{23}NO_7$ $[M+H]^+$: 366.1548, found 366.1539, $[M+Na]^+$: 388.1372, found 388.1368. LS-MS (ESI$^+$): m/z calcd for $C_{18}H_{23}NO_7$ $[M-NH_2]^+$: 349.12, found 349.1, $[M+Na]^+$: 388.13, found 388.1.

The structure of β-D-galactopyranosylamine derivative **59β** was confirmed by^{1}H and ^{13}C NMR spectral data, ^{1}H-^{1}H COSY and 2D NOESY spectrum Figure 2). An evident cross-peak between H-1 and H-5 protons observed in the NOESY spectra (Figure 2) provides support of the β-anomeric configuration of **59β**. There are cross-peaks between the protons H-1 and H-3, and the protons H-4 and H-5. Besides, a weak NOE effect was observed for H-1 and H-2.

f. The oxazoline **53** (0.1 g, 0.29 mmol) was dissolved in CH_2Cl_2 (4.0 ml) and then 0.015 ml 33% aq. HCl was added to prepared solution. The reaction mixture was stirred at rt for 48 h, diluted CH_2Cl_2 and then was washed with cooled 5% aq $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (2x10 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to dryness to give (0.095 g) of oil product containing the starting oxazoline and galactopyranosylamine derivative. The formation of *N*-β-galactopyranosylamine derivative **59β** (34%) was determined from ^{1}H NMR spectra of the reaction mixture taken in $CDCl_3$.

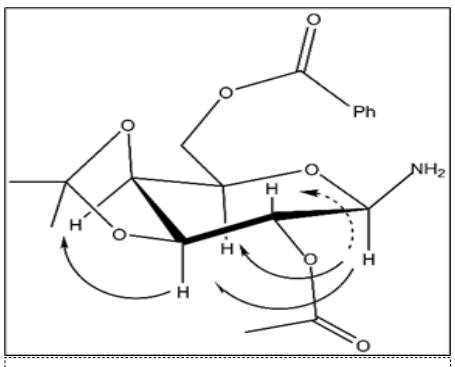

Figure 2. 1D NOE correlations for β-d-galactopyranosylamine derivative 59β

6-O-Benzoyl-N-acetyl-3,4-O-isopropylidene-2-O-acetyl-β-D-galactopyranosylamide (***60***)

To a stirred solution of protected β-D-galactopyranosylamine **59β** (0.018 g, 0.049 mmol) and Et_3N (0.01 ml, 0.07 mmol) in anhydrous CH_2Cl_2 (2.0 ml), acetyl chloride (0.02 ml, 0.28 mmol) was added at 0^0C. The reaction mixture solution was stirred at room temperature for 18 h, diluted CH_2Cl_2 and then was washed cooled with 5% aq $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (2x10 ml). The combined organic extracts were washed with water, dried over anh. Na_2SO_4, and evaporated to dryness. The residue was chromatographed on a silica gel, using for elution chloroform, chloroform–ehylacetate 1:1 to give (0.014 g, 75%) of *N*-β-D-galactopyranosylamide derivative (**60**) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42-8.05 (m, 5H, COC_6H_5), 6.30 (br.d, 1H, $J_{1,NH}$ = 9.3 Hz, NH), 5.11 (t, 1H, $J_{1,2} = J_{1,NH}$ = 9.3 Hz, H-1), 4.90 (dd, 1H, $J_{2,3}$ = 6.7 Hz, H-2), 4.61 (dd, 1H, $J_{6a,5}$ = 5.8, $J_{6a,6b}$= 11.7 Hz, H-6a), 4.53 (dd, 1H, $J_{6b,5}$ = 7.2 Hz, H-6b), 4.28-4.31 (m, 3H, H-3, H-4, H-5), 2.12 (s, 3H, CH_3CO), 1.98 (s, 3H, NHCOCH_3), 1.53 and 1.35 [2s, 3H, $(CH_3)_2$C-]. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.0 (NHCOCH$_3$), 170.3 and 166.4 (2 C=O, $COCH_3$ and COC_6H_5), 133.2, 129.8, 128.4 (COC_6H_5), 110.8 [C-$CH_3)_2$], 76.8 (C-1), 76.2, 73.7, 72.4 (C-4, C-2, C-3, C-5), 63.7 (C-6), 27.8 and 26.2 [(CH_3)$_2$C-], 23.5 and 21.0 (COCH_3 and NHCOCH_3). LC-MS (ESI$^+$): m/z calcd for $C_{20}H_{25}NO_8$ $[M+Na]^+$: 430.1, found 430.1.

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