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Carbohydrate Research 324 (2000) 149–160

CARBOHYDRATE RESEARCH

Studies on the origin of stereoselectivity in the synthesis of 1,2-trans glycofuranosyl azides

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Received 5 August 1999; accepted 24 October 1999

Abstract

The stereoselectivity of the 1,2-trans directed, Lewis acid-catalysed azidation of peracylated furanoses was found to depend on the reactivity of the azide donor (azide nucleophilicity) and the configuration at the anomeric centre relative to the neighbouring 2-*O*-acyl group. Reactions of 1,2-trans glycosyl esters with highly nucleophilic azide donors, generated from $SnCl_4$ and Me_3SiN_3, were stereospecific. The results are interpreted in terms of the rapid reaction of the azide species with bicyclic 1,2-acyloxonium (1,2-*O*-alkyliumdiyl-D-glycofuranose) ions, which were the primarily formed reactive intermediates. When using 1,2-cis glycosyl esters as starting materials the selectivity was reduced (90–94% de); the same is true with 1,2-trans counterparts if less nucleophilic Me_3SiN_3 in combination with Me_3SiOTf catalyst was used. This occurred due to the appearance of the more reactive but less selective oxocarbenium (glycofuranoxonium) ions either as primarily formed reactive intermediates in the former case or after equilibration with acyloxonium ions in the latter case. Protected 1,2-trans β-D-glycofuranosyl azides with ribo, xylo and 3-deoxy-erythro-pento configurations were best prepared from the corresponding glycosyl esters using 0.05 equivalents of $SnCl_4$, i.e., under anomerization-free conditions. Azidation of methyl glycofuranosides proceeds with inferior (80–90% de) and less predictable selectivity irrespective of the starting anomeric configuration.

Keywords: 1,2-trans Glycofuranosyl azides, synthesis; Azidation, stereoselective; Anomerization; Oxonium ions; Stannic chloride catalysis; Trimethylsilyl triflate catalysis

1. Introduction

Glycosyl azides [1] serve as valuable carbohydrate building blocks, especially as precursors to glycosylamines and heterocyclic derivatives such as 1,2,3-triazoles. Accordingly, several methods for their synthesis were developed, which proved to be quite general with respect to the desired relative configuration at C-1 and C-2 of the sugar. As a part of our programme towards a linear synthesis of 1,2,3-triazolo[4,5-*c*]pyridine nucleoside analogues [2] via the 1,2,3-triazole nucleosides, several β-D-pentofuranosyl azides were required, of which only those with the 1,2-trans configuration will be considered in this article. The Lewis acid-catalysed reaction of trimethylsilyl azide (Me_3SiN_3) with glycosyl esters possessing a participating 2-*O*-acyl group proved to be the most efficient and reliable method for the preparation of 1,2-trans glycosyl azides [1]. In fact, the azidation of pyranosyl esters [1,3,4] was consistently reported to be stereospecific regardless of the

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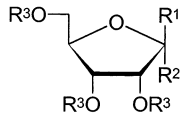
0008-6215/00/$ - see front matter
PII: S0008-6215(99)00293-1

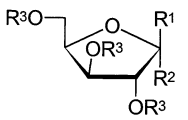
anomeric configuration of the starting ester, while the selectivity of aldofuranosyl counterparts was reduced in several cases [5,6]. The efficiency of this azidation approach in terms of the chemical yield and selectivity makes it undoubtedly the method of choice; however, a rather wide selection of catalysts and their amounts used (usually nearly equimolar) were not so clearly evident. Recently, Matsubara and Mukaiyama [4] reported for the first time a truly catalyst-aided synthesis of pyranosyl azides by taking advantage of $SnCl_4$–$AgClO_4$ systems in dichloromethane or ytterbium(III) triflate in nitromethane (0.05–0.2 equivalents). In addition, we [6] and others [5,7] have pointed out that the azidation of furanosyl esters could be carried out conveniently using only catalytic amounts of selected Lewis acids like $SnCl_4$ or Me_3SiOTf. Thus, of several catalysts tested in substoichiometric amounts, the azidation of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**1β**) with Me_3SiN_3 in dichloromethane at ambient temperature was completed only with $SnCl_4$ (0.05 equivalents, 12 h) and Me_3SiOTf (0.1 equivalents, 9 days) [6]. These experiments revealed another rather unexpected observation that, contrary to other catalysts which gave the 1,2-trans azide **2β** exclusively, the Me_3SiOTf reaction is much less selective (β:α = 17:3). In continuation of the previous work [6], a more detailed mechanism of azidation in non-nucleophilic solvents, like dichloromethane, is proposed herein, which provides a reasonable explanation for the exclusive formation of the β-azide **2β** in the $SnCl_4$-catalysed reaction as well as the reduced selectivity in the case of the Me_3SiOTf reaction. Showing advantages over other catalysts, $SnCl_4$ was employed for the highly stereoselective synthesis of 1,2-trans azides with β-D-ribofuranosyl-, β-D-xylofuranosyl-, 3-deoxy-β-D-*erythro*-pentofuranosyl-, and β-D-galactopyranosyl configurations.

2. Results and discussion

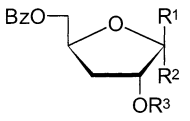
Stereochemistry of the reaction of **1β** *with* Me_3SiN_3. *Mechanistic considerations.*—A set of azidation experiments of **1β** with Me_3SiN_3 in the presence of $SnCl_4$ or Me_3SiOTf was carried out under various reaction conditions



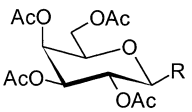
	R^1	R^2	R^3
1α	H	OAc	Bz
1β	OAc	H	Bz
2α	H	N_3	Bz
2β	N_3	H	Bz
3α	H	OH	Bz
3β	OH	H	Bz
5α	H	OMe	Bz
5β	OMe	H	Bz
6β	OAc	H	Ac
7β	N_3	H	Ac



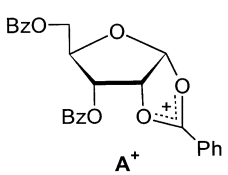
	R^1	R^2	R^3
8α	H	OBz	Bz
8β	OBz	H	Bz
9α	H	N_3	Bz
9β	N_3	H	Bz
10α	H	OAc	Ac
10β	OAc	H	Ac
11α	H	N_3	Ac
11β	N_3	H	Ac



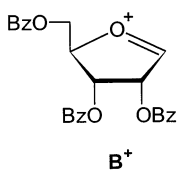
	R^1	R^2	R^3
12α	H	OAc	Ac
12β	OAc	H	Ac
13α	H	N_3	Ac
13β	N_3	H	Ac
14β	OMe	H	Bz
15α	H	N_3	Bz
15β	N_3	H	Bz



16 R = OAc
17 R = N_3



A^+



B^+

(Table 1). It is evident from Table 1 that the former is a considerably more efficient catalyst for any comparable set of reaction conditions. In view of the superior 1,2-trans selectivity observed in $SnCl_4$-catalysed reactions [1,3,4,6] (formation of 1,2-cis azides from peracylated aldoses has never been reported), it was rather surprising to find that the initially formed β-azide **2β** underwent slow anomerization in the presence of this Lewis acid, if the reaction was continued after consumption of **1β**. This effect was particularly noticeable at higher catalyst loadings (entries 2 and 3), but was completely absent with our optimized reaction conditions (0.05 equivalents, entry 1). Anomerization of the initially formed β-azide **2β** during the reaction may also give both anomers in the Me_3SiOTf-catalysed azidation. However, this hypothesis was disproved after several control anomerizations of **2β** were carried out by means of Me_3SiOTf and $SnCl_4$ in

Table 1
Catalysed azidation of **1β** with Me_3SiN_3 in CH_2Cl_2 at 23 °C

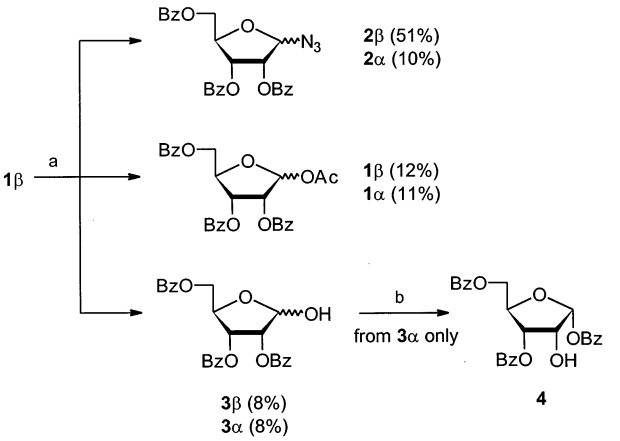
Entry	Catalyst (equiv.)	Time	Yield of **2β**+**2α** (%) [a]	**2β**:**2α**
1 [b]	$SnCl_4$ (0.05)	12 h	quant	100:0
2	$SnCl_4$ (1)	10 min	98	93:7
3	$SnCl_4$ (1)	7 days	90.5	64:36
4 [b]	Me_3SiOTf (0.1)	9 days	quant	85:15
5	Me_3SiOTf (0.5)	6 days	quant	86:14
6	Me_3SiOTf (1)	33 h	98	86:14
7	Me_3SiOTf (1)	21 days	96	85:15
8 [c]	Me_3SiOTf (1)	128 h [d]	95.5 [e]	80:20

[a] Crude product.
[b] Data from Ref. [6].
[c] Reaction carried out in a 1:1 mixture of CH_2Cl_2–Me_3SiOAc.
[d] Reaction proceeded to ~95% conversion.
[e] Contaminated with ~5% of acetates **1β** and **1α** (3:2).

the presence or absence of trimethylsilyl acetate (Me_3SiOAc), a side product of the glycosylation of **1β** with silylated nucleophiles [8]. The anomerization of **2α** [6] as well as **2β** (see Table 2 and entry 3 of Table 1) indicates the equilibrium composition of 64:36 ± 2 in favour of **2β** at 23 °C in dichloromethane. This value is quite different from that (β:α = 86:14 ± 1) consistently found in the Me_3SiOTf-catalysed azidation of **1β**, as well as the anomerization of **2β**, in the presence of Me_3SiOTf and Me_3SiOAc (1 equivalent each). Under conditions where the azidation of **1β** is complete within 1–1.5 days (Table 1, entry 6), only ~2% of the pure **2β** would anomerize within this time interval. Moreover, unlike the $SnCl_4$-catalysed reaction under optimized conditions (entry 1, Table 1), which revealed only

Table 2
Anomerization of **2β** in CH_2Cl_2 at 23 °C

Entry	Catalyst (equiv)	Additive (equiv)	Time (days)	**2β**:**2a**
1	$SnCl_4$ (0.5)	none	8	64:36
2	$SnCl_4$ (0.5)	Me_3SiOAc (1)	8	62:38
3	Me_3SiOTf (1)	none	1.5	67:33
4	Me_3SiOTf (1)	none	5.5	61:39
5	Me_3SiOTf (1)	none	11.3	62:38
6	Me_3SiOTf (1)	Me_3SiOAc (1)	5.5	92:8
7	Me_3SiOTf (1)	Me_3SiOAc (1)	11.3	90:10
8	Me_3SiOTf (1)	Me_3SiOAc (1)	21	86:14
9	Me_3SiOTf (1)	Me_3SiOAc (1)	40	87:13



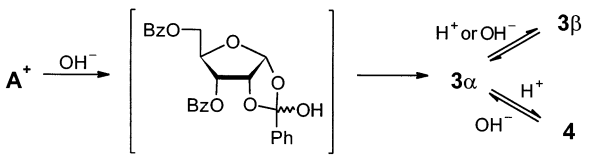
Scheme 1. Reagents and conditions: (a) Me_3SiN_3 (1.1 equiv), Me_3SiOTf (0.5 equiv), CH_2Cl_2, 3 h; then HCO_3^-, H_2O; (b) silica gel chromatography.

the presence of the unreacted starting material **1β** and the product **2β**, the Me_3SiOTf reaction appeared more complex (TLC data). When the latter reaction in the presence of 0.5 equivalents of Me_3SiOTf was quenched at the initial stage (after 3 h) and worked up, the crude reaction mixture contained six components (from ^1H NMR data) in fractions given in Scheme 1.

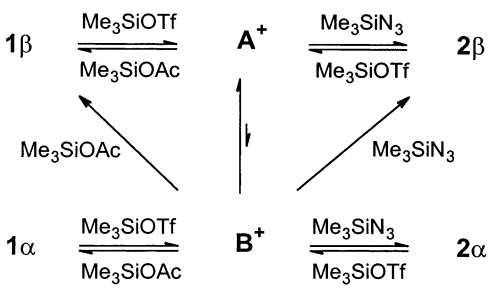
In Scheme 1, the **2β**:**2α** ratio of 84:16 was estimated to be almost identical (within an experimental error) to the ratio observed after complete consumption of the starting material (86:14; entry 5, Table 1). Virtually constant ratios throughout the progress of azidation suggests the existence of common intermediates for the unselective formation of both azides with the anomerization of **1β** taking place as a side reaction. By analogy to the anomerization of peracylated aldoses, e.g., β-glucose pentaacetate [9], these data clearly point to the intermediacy of the oxocarbenium ion $\mathbf{B}^+$ (2,3,5-tri-*O*-benzoyl-D-ribofuranoxonium cation) formed from the more stable 1,2-benzoxonium ion $\mathbf{A}^+$ (3,5-di-*O*-benzoyl-1,2-*O*-phenylmethyliumdiyl-α-D-ribofuranose cation) [8,10].

After chromatography on silica gel, the third anomeric pair of products, 2,3,5-tri-*O*-benzoyl-D-ribofuranose (**3αβ**) [11] was isolated as an inseparable mixture accompanied by a small amount of 1,3,5-tri-*O*-benzoyl-α-D-ribofuranose (**4**) [12] in 11% combined yield. Compound **4** is an artefact, which originated from

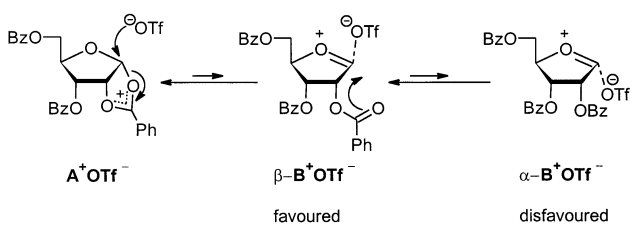
3α through 2→1 migration of the benzoyl group during chromatographic separation. The structures of these compounds were determined by comparison of ^{1}H and ^{13}C NMR data with those reported [11,12b,c], as well as by transformation of a mixture of **3β**, **3α**, and **4** into a mixture of known derivatives **1β**, **1α** [11a,13], and 2-*O*-acetyl-1,3,5-tri-*O*-benzoyl-α-D-ribofuranose [12b] by acetylation. The identification of compounds **3β** and **3α** provides indirect evidence for the existence of a relatively stable, long-lived 1,2-benzoxonium ion $\mathbf{A}^+$ (for an indirect ^{1}H NMR evidence of this cation, see Ref. [14]). Cyclic acyloxonium (1,3-dioxolan-2-ylium) ions [15] like $\mathbf{A}^+$ are ambident electrophiles [16], which can react with nucleophiles to give products of either kinetic or thermodynamic control. Unlike the azide nucleophile, which reacts at the anomeric centre (thermodynamic product), water [15,16] always reacts in a kinetic sense (at C-2 of the 1,3-dioxolan-2-ylium ring). In the case of the $\mathbf{A}^+$ ion a cyclic hemiorthoester [12a,17] is formed, which decomposes spontaneously to furnish **3α**, a product with retained stereochemistry of the benzoxonium ion $\mathbf{A}^+$. Although only **3α** would be expected to appear in the crude product mixture, the anomeric hydroxy group is inevitably subjected to the anomerization process during mildly alkaline workup manipulations, resulting in the mixture of anomers and, eventually, the rearranged product **4** (Scheme 2). Since the oxocarbenium ion $\mathbf{B}^+$ is apparently much more reactive (less stable) and, consequently, would be present in a negligible concentration, it is of interest that the concentration of $\mathbf{A}^+$ amounted to ~16% of the total product composition at the moment of trapping with water.



Scheme 2.



Scheme 3.



Scheme 4.

Based on the fact that Me_3SiN_3 is a relatively weak nucleophile and reacts with the ion $\mathbf{A}^+$ very slowly or not at all, the mechanism of the Me_3SiOTf-catalysed azidation of **1β** can now be rationalized, as shown in Scheme 3.

The stereochemical course of azidation will depend on the equilibrium composition of $\mathbf{A}^+$ and $\mathbf{B}^+$, their relative reactivities towards Me_3SiN_3 and Me_3SiOAc, and the concentration of both nucleophiles. The presence of Me_3SiOAc obviously triggers additional equilibria that are responsible for the observed ratio of azides (β:α = 43:7), which is substantially shifted from the intrinsic equilibrium value (β:α = 16:9).

Stereochemistry of the oxocarbenium triflate ion pair $\mathbf{B^+OTf^-}$.—The outcome of the stereochemistry attributed to $\mathbf{B^+OTf^-}$ should reside in the neighbouring group effect, which favours the β-triflate ion pair **β-B$^+$OTf$^-$**. This could be formed by the approach of the triflate anion to the anomeric position of $\mathbf{A}^+$ from the β-face, while the C–O bond of the 1,3-dioxolan-2-ylium ring is being cleaved. Since its lifetime is very short, the ion pair **β-B$^+$OTf$^-$** reverts either to the bicyclic ion $\mathbf{A^+OTf^-}$ or reacts with an external nucleophile almost instantaneously with predominant α-selectivity, before efficient equilibration between β- and α-triflate ion pairs could take place (Scheme 4).

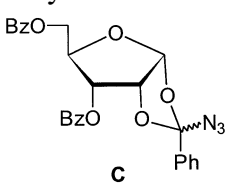
The above explanation may find support in the allylation of our model substrate **1β** with allyltrimethylsilane [18], which was reported

to be markedly α-selective under any conditions. This fact may reflect the inability of the cyclic ion $\mathbf{A}^+$ to react with weak carbon nucleophiles; that is why the oxocarbenium ion $\mathbf{B}^+$ could be responsible for the final product distribution. A general trend of α-selectivity deriving from oxocarbenium triflate ion pairs indicates that the bulk of **2β** should arise from the attack of Me_3SiN_3 on the benzoxonium ion $\mathbf{A}^+$.

Mechanistic alternatives.—The formation of **2α** in the Me_3SiOTf-catalysed azidation could take place by at least three additional mechanistic pathways; however, no firm evidence exists in favour of any pathway.

Direct S_N2 substitution at C-1. Direct displacement of Me_3SiOAc on the complex of the substrate and Me_3SiOTf by Me_3SiN_3, assuming the absence of the anchimeric assistance by the 2-*O*-benzoate group, hardly seems to be a noticeable alternative to the more favourable anchimerically assisted intramolecular displacement. An efficient S_N2 substitution requires a powerful nucleophile, which is not the case with Me_3SiN_3. Besides, as shown below, stronger azide donors than Me_3SiN_3 drive the reaction towards the increased β-selectivity.

2-Azido-1,3-dioxolane intermediates. To the best of our knowledge, the isolation or detection of 2-azido-1,3-dioxolane intermediates has never been reported in the synthesis of glycosyl azides. The hypothetical kinetic diastereoisomeric intermediate **C** could transform thermally or in the presence of Lewis acids, via the ion $\mathbf{A}^+$, into the thermodynamic products **2β** and **2α**. However, its appearance does not seem to be very likely because the relatively high stability of some non-carbohydrate derived 2-azido-1,3-dioxolanes towards protic acids [19] and temperature [20] suggests comparable stability of **C**.



C

Ring-opening mechanism. The competitive complexation of Me_3SiOTf with the furanose ring oxygen results in the endocyclic cleavage of the C(1)–O(4) bond and the formation of either an acyclic oxocarbenium ion or a monocyclic benzoxonium ion. The azidation of both with Me_3SiN_3 and subsequent Lewis acid-promoted recyclization would occur with a low selectivity and co-formation of acyclic by-products [21]. It is of interest to point out that no acyclic intermediates or by-products were identified in any of the azidation reactions of **1β**. With the hope of trapping the acyclic 4-*O*-silylated derivative, being more resistant towards subsequent recyclization, Me_3SiOTf was replaced by *tert*-butyldimethylsilyl triflate (0.5 equivalents) in a particular experiment. This reaction, however, proceeded analogously and without major differences from that given in Table 1 (entry 5). For this reason, the endocyclic cleavage in the catalysed azidation of glycosyl esters is not to be expected.

Effect of the azide nucleophilicity.—In contrast to the poorly selective Me_3SiOTf-catalysed reaction mentioned above, the $SnCl_4$-catalysed azidation of **1β** is stereospecific and, therefore, must proceed exclusively through the benzoxonium ion $\mathbf{A}^+$; Me_3SiN_3 acts as a nucleophile in both cases. The reaction of Me_3SiN_3 with $SnCl_4$ in dichloromethane at ambient temperature is known to first result in a soluble dimer $[Me_3SiCl\cdot Cl_2Sn(N_3)_2]_2$, which was then slowly transformed into a final insoluble polymeric product $[Cl_2Sn(N_3)_2]_n$ [22]. The soluble dimer, some higher oligomer, and/or their complex with a leaving group comprise probable azide donors of increased nucleophilicity in the $SnCl_4$-catalysed reaction of **1β** with Me_3SiN_3. The benzoxonium ion $\mathbf{A}^+$ is intercepted by the highly reactive azide donor immediately after its formation, before the isomerization to the oxocarbenium ion $\mathbf{B}^+$ could take place. Since the cation $\mathbf{A}^+$ has only a momentary existence, it could never be detected in the form of its hydrolysis products **3β** and **3α** by TLC analysis of the azidation progress.

The observation that the highly nucleophilic tin–azido species are responsible for the specificity observed has been further confirmed by a set of experiments in which trimethyltin azide (Me_3SnN_3) and tributyltin azide (Bu_3SnN_3), with precisely defined structures, were employed as azidation agents (Table 3).

Table 3
Azidation of **1β** with trialkyltin azides

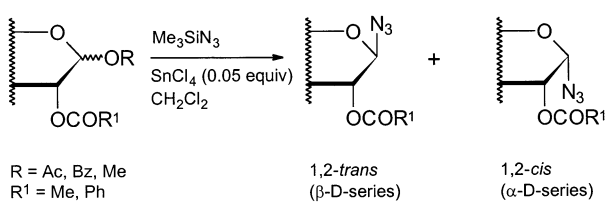
Entry	Catalyst (equiv)	Azide	Solvent	Time (days)	**2β**:**2α**
1	Me_3SiOTf (1)	Me_3SnN_3	CH_2Cl_2	5.5	96:4
2	Me_3SiOTf (1)	Bu_3SnN_3	CH_2Cl_2	8	97:3
3	none	Bu_3SnN_3	neat	8	100:0

The stereoselectivity of the Me_3SiOTf-catalysed azidation can be greatly improved simply by substituting more nucleophilic trialkyltin azides [23] for Me_3SiN_3. Bu_3SnN_3 as solvent (70 °C, 8 days, ~95% conversion) can function as an azide donor and a weak Lewis acid. Compound **2β** was isolated in about 70% yield along with a few unidentified side products. In this case, complete exclusion of either **1α** or **2α** was determined by ^1H NMR and TLC analyses.

Stereoselectivity of the $SnCl_4$-catalysed azidation. Substrate structure effect.—Superior selectivity and efficiency of the azidation of **1β** in comparison with other catalysts tested [6] suggested $SnCl_4$ (0.05 equivalents) for the 1,2-trans directed azidation of some other glycosyl substrates with Me_3SiN_3 (Scheme 5). In all cases examined (Table 4), reactions proceeded with 80–100% de selectivities in favour of 1,2-trans azides depending on the nature and configuration of the anomeric substituent relative to the 2-*O*-acyl group. The available 1,2-*cis* esters **1α** and **8α** displayed slightly reduced selectivities in comparison with their 1,2-trans counterparts **1β** and **8β**, because the corresponding oxocarbenium ions are formed as the first reactive intermediates after dissociation of the glycosidic bond. The highly nucleophilic azidation reagent intercepts the oxocarbenium ions, to a small extent, before they completely isomerize to the more stable acyloxonium ions. Trace amounts of α-azides **9α** and **13α** were detected in case of the azidation of **8β** and **12β**, presumably due to the contamination of starting materials with 1,2-*cis* esters **8α** (5%) and **12α** (~10%), respectively. For the same reason, a small amount of the α-azide **11α** could also be expected to form from α,β-D-xylofuranose tetraacetate (**10αβ**, 2:1 α:β mixture). The last example in Table 4 (entry 10) clearly demonstrates that the azidation of furanosyl and pyranosyl esters proceeds at comparable rates using much lower quantities of $SnCl_4$ than previously reported [1,3].

The azidation of methyl glycofuranosides **5β** and **14β** resulted in the predominant formation of the β-azides **2β** and **15β** with 90 and 80% de, respectively, being much inferior to those starting from the appropriate acetates **1β** and **12β**. The origin of minor quantities of 1,2-*cis* products **2α** and **15α** is not completely clear and points to the involvement of alternative mechanisms, e.g., the furanose ring opening.

Conclusions.—Furanose sugars turned out to be more useful probes for studying stereochemical effects of the azidation than their pyranose counterparts. The Lewis acid-catalysed reactions of pyranosyl esters with Me_3SiN_3 were reported [1,3,4] to be stereospecific without exception, while at least two properties affect the stereoselectivity in the furanosyl series, namely, the azide nucleophilicity and the nature of the substrate structure. When both effects are favourable, like in the case of 1,2-trans glycosyl esters and a Lewis acid capable of generating more nucleophilic azidating species after reaction with Me_3SiN_3 (e.g., $SnCl_4$), the azidation was stereospecific in all cases examined. This occurs because the 1,2-acyloxonium ion is primarily formed, which is rapidly captured by the nucleophile before isomerization to less selective reactive intermediates takes place. Glycosyl esters are also preferred starting materials over glycosides in the presence of the $SnCl_4$ catalyst.



Scheme 5.

Table 4
$SnCl_4$-catalysed azidation of various sugar derivatives with Me_3SiN_3 in CH_2Cl_2 at 23 °C [a]

Entry	Substrate	Time (h)	Product(s)	Yield (%) [b]	β:α [c]	$[\alpha]_D$ (*c*) [d] (°)
1 [e]	**1β**	12	**2β**	95	100:0	−45 (3.11)
2	**1α**	30	**2β** + **2α** [f]	100	95:5	
3	**5β**	30	**2β** + **2α** [g]	91	95:5	
4 [e]	**6β**	12	**7β**	97	1:0 [h]	−149 (1.0)
5	**8α**	4	**9β**	97	97:3	−73 (4.00)
			9α	2.4		+170 (0.99)
6	**8αβ** [i]	2	**9β**	94	>200:1	−72 (4.00) [m]
7	**10αβ** [j]	24	**11β**	88	nd [l]	−129 (2.20) [n]
8	**12αβ** [k]	12	**13β**	74	124:1	−171 (1.11) [m]
9	**14β**	12	**15β**	86	90:10	−150 (4.00)
			15α	7		+85 (4.00)
10	**16**	12	**17**	70	100:0	−14.6 (2.885) [o]

[a] Molar ratio of substrate:Me_3SiN_3:$SnCl_4$ = 1:1.1:0.05, except for entries 3 and 9, where 1.5 mol equiv of Me_3SiN_3 was used.
[b] Yields after chromatography and/or crystallization, crude yields are given for entries 2 and 3.
[c] Anomeric ratio determined from the ^{1}H NMR spectrum of the crude product mixture.
[d] Measured for solutions in $CHCl_3$ at 25 °C, unless stated otherwise.
[e] Data from Ref. [6].
[f] Contaminated with **1α** (8%), **1β** hardly detectable.
[g] Contaminated with a mixture of **5β** and **5α** (11%) in a 7:4 ratio.
[h] The corresponding α anomer was not identified.
[i] β:α = 19:1.
[j] α:β = 2:1.
[k] β:α = 9:1.
[l] Not determined, the corresponding α anomer was not identified.
[m] Measured at 26 °C.
[n] Measured in ethyl acetate at 24 °C.
[o] Measured at 20 °C; lit. $[\alpha]_D^{20}$ −16.2° (*c* 2.885) [33].

3. Experimental

General methods are those reported in Ref. [6]. NMR spectra were recorded for solutions in $CDCl_3$. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter. All reactions were carried out in a dry inert atmosphere.

Materials.—Dichloromethane (Fluka), kept over molecular sieves, was used as solvent. 1-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**1β**) and tetra-*O*-benzoyl-α-D-xylofuranose (**8α**) were supplied by Pfanstiehl under names that did not specify the anomeric configuration. Analysis of commercial samples (**1β**: ivory coloured powder with mp 127–128.5 °C; $[\alpha]_D^{26}$ +41.8° (*c* 1.32, $CHCl_3$); colourless needles after crystallization from isopropanol: mp 129–130 °C, lit. mp 131–132 °C [24]; $[\alpha]_D^{26}$ +42.3° (*c* 1.32), lit. $[\alpha]_D^{25}$ +42.2° (*c* 1.32) [24]; ^{1}H NMR [12b,13]. **8α**: mp 165–166.5 °C, lit. mp 164–165 °C [25]; $[\alpha]_D^{25}$ +167° (*c* 1.10, $CHCl_3$), lit. $[\alpha]_D^{20}$ +170° (*c* 1.1) [25]; ^{1}H NMR [12b,26]) revealed that both materials were configurationally homogeneous. Tetra-*O*-acetyl-α,β-D-xylofuranose (**10αβ**) was obtained from the same supplier and was bulb-to-bulb distilled before use at a bath temperature of 175 °C and ~0.01 mbar. The distillate contained mainly **10α** and **10β** in a 2:1 ratio. Methyl 3-deoxy-2,5-di-*O*-benzoyl-β-D-*erythro*-pentofuranoside (**14β**: mp 82–83 °C (hexane), lit. mp 80.5–81.5 °C [27b]) was conveniently prepared in five steps from 1,2-di-*O*-isopropylidene-5-*O*-methoxycarbonyl-3-*O*-tosyl-α-D-xylofuranose (Pfanstiehl), following the reported procedures [27].

Methyl 2,3,5-tri-O-*benzoyl-β*-D-*ribofuranoside* (**5β**).—This compound was prepared [28] from **7β** [6] after final purification by chromatography with CH_2Cl_2: $[\alpha]_D^{25}$ +58° (*c* 0.94, $CHCl_3$), lit. $[\alpha]_D$ +58° [29]; ^{1}H NMR: δ 3.42 (s, 3 H, OMe), 4.52 (dd, 1 H, H-5a),

4.70–4.76 (m, 2 H, H-4, 5b), 5.16 (s, 1 H, H-1), 5.68 (d, 1 H, H-2), 5.88 (dd, 1 H, H-3), 7.29–7.61, 7.87–7.91, and 8.0–8.10 (3 m, 15 H, Ar–H), $J_{2,3}$ 4.9, $J_{3,4}$ 6.6, $J_{4,5a}$ 6.3, $J_{5a,5b}$ 12.8 Hz.

Tetra-O-*benzoyl*-α,β-D-*xylofuranose* (**8αβ**). —The crude anomeric mixture (β:α = 7:10) was prepared from 1,2-*O*-isopropylidene-α-D-xylofuranose (Pfanstiehl) (30 g, 0.158 mol) by the method of Holy [26] and subsequently highly enriched in favour of the β anomer. This was first flash chromatographed with 10:1 petroleum ether–EtOAc, followed by CH_2Cl_2. A fraction, containing ~50% of the β anomer, was fractionally crystallized several times from EtOAc, then several times from acetone to remove the majority of **8α**. The concentrated mother liquor enriched with the β isomer was freed from unknown by-products by chromatography with a 10:1 → 2:1 gradient of petroleum ether–1% AcOH in EtOAc. After concentration, the appropriate fractions were crystallized twice, first from 5:1 MeOH–acetone, followed by MeOH to give **8β** (1.20 g, 1.3%), contaminated with ~5% of the α anomer. The crystalline material contained two kinds of crystals with a sharp melting range, for the most part plates with mp 111–113 °C along with some needles with mp 151–153 °C, lit. mp 108–109 °C [25]; $[\alpha]_D^{25}$ +18.2° (*c* 1.00, $CHCl_3$); lit. $[\alpha]_D^{20}$ +11.2° (*c* 1.0) [25]; ^{1}H NMR: δ 4.66–4.76 (m, 2 H, H-5a,5b), 5.11 (pseudo q, 1 H, *J* 5.7 Hz, H-4), 5.82 (d, 1 H, H-2), 5.96 (dd, 1 H, H-3), 6.67 (s, 1 H, H-1), 7.33–7.66 and 7.95–8.12 (2 m, 20 H, Ar–H), $J_{2,3}$ 1.0, $J_{3,4}$ 5.0 Hz; ^{1}H NMR [12b]; ^{13}C NMR: δ 62.84, 74.52, 80.03, 80.47, 99.49 (C-1 to C-5), 128.3–130.0 and 133.1–133.8 (Ar–C), 164.73 (2 CO), 164.96 and 166.04 (2 CO). This material was used for the azidation without further manipulations.

5-O-*Benzoyl*-*3*-*deoxy*-*1,2*-*di*-O-*acetyl*-α,β-D-erythro-*pentofuranose* (**12αβ**).—This compound was prepared [30] in five steps from 1,2-*O*-isopropylidene-α-D-xylofuranose and subsequently purified by chromatography (50:1 CH_2Cl_2–Et_2O): $[\alpha]_D^{25}$ −29.4° (*c* 1.25, $CHCl_3$), lit. $[\alpha]_D^{30}$ −27.2° [30b]. Although a single spot by TLC analysis, the ^{1}H NMR spectrum revealed the presence of **12β**, **12α**, and two unknown contaminants in a 81:10:5:4 ratio. ^{1}H NMR data for **12β**: δ 1.96 and 2.10 (2 s, each 3 H, 2 $OCOCH_3$), 2.17–2.33 (m, H-3α,3β), 4.34 (dd, 1 H, H-5a), 4.55 (dd, 1 H, H-5b), 4.73 (dddd, 1 H, H-4), 5.24 (dd, 1 H, H-2), 6.20 (s, 1 H, H-1), 7.42–7.49, 7.55–7.61, and 8.04–8.10 (3 m, 5 H, Ar–H), $J_{2,3\alpha}$ 1.1, $J_{2,3\beta}$ 4.6, $J_{3\alpha,4}$ 6.8, $J_{3\beta,4}$ 9.3, $J_{4,5a}$ 5.3, $J_{4,5b}$ 3.8, $J_{5a,5b}$ 11.9 Hz; ^{1}H NMR [30b]. ^{1}H NMR data for **12α**: δ 6.44 (d, $J_{1,2}$ 4.2 Hz, H-1).

Azidation of **1β** *with* Me_3SiN_3 *(Table 1).*—To a solution of **1β** (0.5–4 mmol scale) and Me_3SiN_3 (1.1 equiv) in the appropriate anhydrous solvent, was syringed the required amount of catalyst (neat Me_3SiOTf or 1 M solution of $SnCl_4$ in CH_2Cl_2) adjusting the final concentration to 3 mL of solvent per mmol of **1β**. After being stirred for the time specified, the reaction mixture was quenched with satd aq $NaHCO_3$ and worked-up as described previously [6] (see also the general procedure below), except for entry 8, which was first concentrated and rediluted with CH_2Cl_2. The **2β**:**2α** ratio was determined from the ^{1}H NMR spectrum of the crude mixture.

Anomerization of 2,3,5-tri-O-*benzoyl*-β-D-*ribofuranosyl azide* (**2β**) *(Table 2).*—To a solution of **2β** (244 mg, 0.5 mmol) and, when necessary, Me_3SiOAc (75 μL, 0.5 mmol) in CH_2Cl_2 was syringed either neat Me_3SiOTf (90 μL, 0.5 mmol) or 1 M solution of $SnCl_4$ in CH_2Cl_2 (0.25 mL, 0.25 mmol), adjusting the final concentration to 3 mL of CH_2Cl_2 per mmol of **2β**. After being stirred for the time specified, the reaction mixture (or 0.15 mL aliquot) was quenched and worked-up as usual. The **2β**:**2α** ratio was determined from the ^{1}H NMR spectrum of the crude mixture. Product mixtures from the anomerizations in the presence of Me_3SiOAc contained in addition ~2–5% of **1β** and **1α**.

Azidation of **1β** *with trialkyltin azides (Table 3)*

With Me_3SnN_3 *under* Me_3SiOTf *catalysis (entry 1).* To a suspension of **1β** (505 mg, 1 mmol) and Me_3SnN_3 (227 mg, 1.1 mmol) in CH_2Cl_2 (3 mL) was syringed Me_3SiOTf (180 μL, 1 mmol), whereby the azide dissolved almost instantaneously. The solution was stirred at room temperature (rt) for 5.5 days,

then quenched and worked-up as usual. The crude semisolid product mixture (589 mg) was directly analysed by ^{1}H NMR spectroscopy. Crystallization from MeOH afforded **2β** (184 mg, 38%) with mp 66.5–67.5 °C, lit. mp 66–67.5 °C [6]; ^{1}H and ^{13}C NMR [6].

With Bu_3SnN_3 under Me_3SiOTf catalysis (entry 2). A similar reaction on the same scale with Bu_3SnN_3 (365 mg, 1.1 mmol) took 8 days at rt. The crude product mixture consisted of two immiscible liquids and was further purified by dissolving in MeCN (10 mL) and washing with hexane (5 × 10 mL). Evaporation of MeCN left a colourless viscous oil (314 mg), which was analysed by ^{1}H NMR spectroscopy. Crystallization from MeOH gave **2β** (231 mg, 47%) with mp 67.5–68 °C.

With Bu_3SnN_3 only (entry 3). A suspension of **1β** (101 mg, 0.2 mmol) and Bu_3SnN_3 (0.4 mL) was heated in an oil bath at 70 °C for 8 days. The reaction mixture was allowed to cool, diluted with MeCN (2 mL) and washed with hexane (5 × 2 mL). Evaporation of MeCN left a brown viscous liquid (112 mg), which was analysed by ^{1}H NMR spectroscopy (~70% yield of **2β**).

Partial Me_3SiOTf-catalysed azidation of **1β** *with Me_3SiN_3.*—To a solution of **1β** (2.02 g, 4 mmol) and Me_3SiN_3 (0.58 mL, 4.4 mmol) in CH_2Cl_2 (12 mL) was syringed Me_3SiOTf (0.36 mL, 2 mmol). The mixture was stirred at rt for 3 h, then quenched with satd aq $NaHCO_3$ (12 mL) and the aqueous phase was extracted with CH_2Cl_2 (12 mL). The combined organic solutions were dried ($MgSO_4$) and concentrated to give a mixture of products in fractions, given in Scheme 1, as a colourless oil (2.02 g). A portion of this mixture (1.86 g) was chromatographed on silica gel (125 g) with CH_2Cl_2 (2 L) collecting 50–60 mL fractions, followed by CH_2Cl_2–Et_2O (19:1, 0.8 L and 10:1, 0.7 L) collecting 50 mL fractions. First eluted was the pure compound **2β** [717 mg, 40%; mp 67–69 °C (from MeOH)], followed by mixtures of **2β** and **2α** (68:32; 274 mg, 15%), **2β** and **2α** (5:95; 93 mg, 5%), **1β** and **1α** (96:4; 232 mg, 12.5%; crystallization from isopropanol gave pure **1β** with mp 128.5–130 °C; ^{1}H and ^{13}C NMR spectra were in agreement with those of the starting material), and pure 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-α-D-ribofuranose [**1α**: 179 mg, 9.5%; IR (film): *ν* 1726 (C=O), 1268 (benzoate C–O), 1227 (acetate C–O), 1134, 1110, 1024, and 708 cm^{-1} (benzoate); ^{1}H NMR: *δ* 2.15 (s, 3 H, $COCH_3$), 4.62 (dd, 1 H, H-5a), 4.73 (dd, 1 H, H-5b), 4.83 (ddd, 1 H, H-4), 5.64 (dd, 1 H, H-2), 5.84 (dd, 1 H, H-3), 6.72 (d, 1 H, H-1), 7.30–7.62, 7.86–7.91, and 8.04–8.12 (3 m, 15 H, 3 Ph), $J_{1,2}$ 4.6, $J_{2,3}$ 6.4, $J_{3,4}$ 2.5, $J_{4,5a}$ 3.6, $J_{4,5b}$ 3.4, $J_{5a,5b}$ 12.1 Hz; ^{13}C NMR: *δ* 21.02 (CH_3), 63.89 (C-5), 70.67 (C-3), 71.06 (C-2), 82.19 (C-4), 94.27 (C-1), 128.4–129.7, 133.34, 133.48, and 133.53 (Ar–C), 164.89, 165.56, and 166.02 (3 *C*OPh), 169.52 (*C*OCH_3); ^{1}H and ^{13}C NMR [11a,13]; EIMS: *m*/*z* 461 ([M–$COCH_3$]$^{+\bullet}$, 1.2%), 445 ([M–$OCOCH_3$]$^+$, 11), 105 ([PhCO]$^+$, 100)]. Last eluted was a mixture of **3β**, **3α**, and **4** in a 58:31:11 ratio (204 mg, 12%). Partial ^{1}H NMR data for **3β**: 3.87 (d, OH), 5.64 (br d, $J_{1,OH}$ 3.5 Hz, H-1), 5.69 (dd, $J_{1,2}$ 0.8 Hz, H-2), 5.91 (dd, $J_{3,4}$ 6.2, $J_{2,3}$ 5.0 Hz, H-3); for **3α**: 3.58 (d, OH), 5.49 (dd, $J_{2,3}$ 6.3 Hz, H-2), 5.79 (dd, $J_{3,4}$ 3.3 Hz, H-3), 5.82 (dd, $J_{1,OH}$ 7.5, $J_{1,2}$ 4.3 Hz, H-1); for **4**: 2.84 (d, $J_{2,OH}$ 10.5 Hz, OH), 5.60 (dd, *J* 6.5, 1.8 Hz, H-3), 6.69 (d, $J_{1,2}$ 4.5 Hz, H-1); ^{1}H and ^{13}C NMR spectra are in agreement with those reported [11,12b,c] for individual components. A further confirmation of identity was achieved by acetylation [31] of a portion (140 mg) of this mixture by acetic anhydride (1 mL) in the presence of 4-(*N*,*N*-dimethylamino)pyridine (2 mg) at rt for 1 day. Work-up as usual afforded a mixture of **1β**, **1α**, and 2-*O*-acetyl-1,3,5-tri-*O*-benzoyl-α-D-ribofuranose [12b] (109 mg) in an 8:1:1 ratio as determined on the basis of known ^{1}H NMR spectra of individual components and TLC analysis.

General procedure for the $SnCl_4$-catalysed azidation with Me_3SiN_3.—To a solution of sugar derivative and Me_3SiN_3 (1.1 equiv for glycosyl esters, 1.5 equiv for glycosides) in CH_2Cl_2 (2 mL/mmol) was added 50 mM $SnCl_4$ in CH_2Cl_2 (1 mL/mmol). The mixture was stirred at rt for the time specified in Table 4, the reaction was quenched with satd aq $NaHCO_3$ (1.5 mL/mmol) and the aq phase extracted with an equal vol of CH_2Cl_2 (three times for acetates **13β** and **17**). The combined organic solutions were dried ($MgSO_4$) and concentrated to give a crude product or a

mixture of anomers. Separation and purification was achieved as described for individual preparations.

Azidation of **1α**.—The crude product mixture, obtained from **1α** (36 mg, 71 μmol) in quantitative yield, contained compounds **2β**, **2α** and **1α** in a 88:4:8 ratio as shown by ^{1}H NMR analysis.

Azidation of **5β**.—The crude product mixture (444 mg), obtained from **5β** (477 mg, 1 mmol), contained compounds **2β**, **2α**, **5β**, and methyl 2,3,5-tri-*O*-benzoyl-α-D-ribofuranoside (**5α**) [32] in a 85:4:7:4 ratio as shown by ^{1}H NMR analysis.

2,3,5-Tri-O-*benzoyl*-β- (**9β**) *and* α-D-*xylofuranosyl azide* (**9α**)

From compound **8α**. Azidation of **8α** (5.66 g, 10 mmol) afforded the crude product mixture (β:α = 97:3), which was resolved by chromatography (CH_2Cl_2, H_2O content ≤ 0.01%). Both products were isolated as colourless viscous oils.

β-Azide **9β**: 4.73 g (97%); R_f 0.59 (CH_2Cl_2); IR (film): *ν* 2115 (N_3), 1727 (C=O), 1262 (benzoate C–O), 1098, and 710 cm^{-1} (benzoate); ^{1}H NMR: *δ* 4.71 (d, 2 H, H-5a,5b), 4.98 (dt, 1 H, H-4), 5.46 (br s, 1 H, H-2), 5.55 (s, 1 H, H-1), 5.88 (dd, 1 H, H-3), 7.37–7.63 and 8.00–8.10 (2 m, 15 H, Ar–H), $J_{2,3}$ 1.2, $J_{3,4}$ 4.9, $J_{4,5a} = J_{4,5b}$ 6.1 Hz; ^{13}C NMR: *δ* 62.42 (C-5), 74.82 (C-3), 80.13 (C-4), 80.91 (C-2), 93.73 (C-1), 128.3–129.9, 133.16, 133.76, and 133.84 (Ar–C), 164.78, 165.00, 166.02 (3 CO); EIMS: *m/z* 445 ($[M - N_3]^+$, 10%), 105 ($[PhCO]^+$, 100); CIMS (NH_3): *m/z* 505 ($[M + NH_4]^+$, 30), 445 ($[M - N_3]^+$, 33), 105 (100); IR, NMR and MS data are in agreement with the reported values [5a]. Anal. Calcd for $C_{26}H_{21}N_3O_7$ (487.47): C, 64.06; H, 4.34; N, 8.62. Found: C, 63.99; H, 4.45; N, 8.60.

α-Azide **9α**: 118 mg (2.4%); R_f 0.52; IR (film): *ν* 2116 (N_3), 1727 (C=O), 1268 (benzoate C–O), 1110, and 710 cm^{-1} (benzoate); ^{1}H NMR: *δ* 4.53–4.64 (2 m, 2 H, H-5a,5b), 4.96 (ddd, 1 H, H-4), 5.61 (pseudo t, 1 H, H-2), 5.96 (d, 1 H, H-1), 6.01 (dd, 1 H, H-3), 7.37–7.63 and 7.97–8.12 (2 m, 15 H, Ar–H), $J_{1,2}$ 5.0, $J_{2,3}$ 5.3, $J_{3,4}$ 6.2 Hz; ^{13}C NMR: *δ* 62.12 (C-5), 74.86 (C-3), 75.62 (C-4), 77.03 (C-2), 89.67 (C-1), 128.4–130.0, 133.22, and 133.73 (Ar–C), 165.42, 165.48, 165.96 (3 CO); CIMS (NH_3): *m/z* 505 ($[M + NH_4]^+$, 2.5%), 460 ($[M - N_2]^+$, 4.5), 445 ($[M - N_3]^+$, 22), 105 ($[PhCO]^+$, 100). Anal. Calcd for $C_{26}H_{21}N_3O_7$ (487.47): C, 64.06; H, 4.34; N, 8.62. Found: C, 64.01; H, 4.50; N, 8.47.

From compound **8αβ**. Azidation of **8αβ** (567 mg, 1 mmol) afforded the crude product mixture containing less than 0.5% of **9α**, which was purified by chromatography (CH_2Cl_2) to give **9β** (456 mg, 94%), identical to the compound obtained from pure **8α** above.

2,3,5-Tri-O-*acetyl*-β-D-*xylofuranosyl azide* (**11β**).—From the distilled compound **10αβ** (31.83 g, 0.1 mol), the reaction mixture was quenched by satd aq $NaHCO_3$ (120 mL) and the phases were allowed to separate overnight. The clear organic and the emulgated layers were treated with Celite (40 g) and, after 30 min, $MgSO_4$ (20 g). Stirring was continued for 1 h, the slurry was filtered through Celite and washed with CH_2Cl_2 (3 × 200 mL). The combined filtrate and washings were dried ($MgSO_4$) and concentrated to give the crude product (29.9 g) as a yellow liquid. This was purified by chromatography (50:1 CH_2Cl_2–EtOAc) to yield pure **11β** (26.56 g, 88%) as a slightly yellow liquid: IR (film): *ν* 2117 (N_3), 1748 (C=O), 1373 (acetate CH_3), and 1226 cm^{-1} (acetate C–O); ^{1}H NMR: *δ* 2.10, 2.12, and 2.14 (3 s, each 3 H, 3 $OCOCH_3$), 4.26 (dd, 1 H, H-5a), 4.37 (dd, 1 H, H-5b), 4.59 (ddd, 1 H, H-4), 5.04 (br s, 1 H, H-2), 5.19 (s, 1 H, H-1), 5.33 (dd, 1 H, H-3), $J_{2,3}$ 1.5, $J_{3,4}$ 4.6, $J_{4,5a}$ 7.1, $J_{4,5b}$ 4.9, $J_{5a,5b}$ 11.7 Hz; ^{13}C NMR: *δ* 20.48, 20.57, and 20.67 (3 $OCOCH_3$), 61.76 (C-5), 74.05 (C-3), 79.49 (C-4), 80.32 (C-2), 93.31 (C-1), 169.07, 169.39, and 170.42 (3 $OCOCH_3$); EIMS: *m/z* 259 ($[M - N_3]^+$, 50%), 139 ($[M - N_3 - 2\ AcOH]^+$, 100), 128 (93). Anal. Calcd for $C_{11}H_{15}N_3O_7$ (301.26): C, 43.86; H, 5.02; N, 13.95. Found: C, 44.30; H, 4.95; N, 13.82.

2-O-*Acetyl-5*-O-*benzoyl-3-deoxy*-β-D-erythro-*pentofuranosyl azide* (**13β**).—Azidation of **12αβ** (322 mg, 1 mmol) afforded the crude product mixture (β:α = 124:1), which was purified by chromatography (CH_2Cl_2) to give pure **13β** (222 mg, 74%) as a colourless oil; IR (film): *ν* 2113 (N_3), 1748 (acetate C=O), 1723 (benzoate C=O), 1377 (acetate CH_3), 1275 (benzoate C–O), 1231 (acetate C–O), 1125

(PhCOO–C), 1093, 1071, 1054, 1026, and 713 cm^{-1} (benzoate); ^1H NMR: δ 2.09 (s, 3 H, $OCOCH_3$), 2.12–2.20 (m, 1 H, H-3α), 2.24 (ddd, 1 H, H-3β), 4.38 (dd, 1 H, H-5a), 4.58 (dd, 1 H, H-5b), 4.72 (dddd, 1 H, H-4), 5.05 (dd, 1 H, H-2), 5.44 (s, 1 H, H-1), 7.43–7.49, 7.55–7.61, and 8.07–8.12 (3 m, 5 H, Ar–H), $J_{2,3\alpha}$ 1.1, $J_{2,3\beta}$ 4.5, $J_{3\alpha,3\beta}$ 14.0, $J_{3\alpha,4}$ 6.6, $J_{3\beta,4}$ 9.5, $J_{4,5a}$ 5.5, $J_{4,5b}$ 3.5, $J_{5a,5b}$ 12.0 Hz; ^{13}C NMR: δ 20.84 (CH_3), 31.43 (C-3), 65.82 (C-5), 77.89 (C-2), 78.58 (C-4), 94.30 (C-1), 128.40 (C-3′,5′), 129.61 (C-2′,6′), 129.67 (C-1′), 133.18 (C-4′), 166.28 and 169.97 (2 CO); FABMS: m/z 306 ($[MH^+]$, 6%), 263 ($[M-N_3]^+$, 100), 105 ($[PhCO]^+$, 92). Anal. Calcd for $C_{14}H_{15}N_3O_5$ (305.29): C, 55.08; H, 4.95; N, 13.76. Found: C, 55.24; H, 4.79; N, 13.67.

α Anomer **13α** could not be isolated due to the paucity of this material. Nevertheless, its presence in the crude mixture was identified by the $SnCl_4$-induced anomerization of pure **13β** as described for **2β** (entry 1 from Table 2). Compound **13α** displayed a doublet ($J_{1,2}$ 4.5 Hz) for the anomeric proton, centered at δ 5.62 ppm.

3-Deoxy-2,5-di-O-*benzoyl-β*- (**15β**) *and* -*α*-D-erythro-*pentofuranosyl azide* (**15α**).—Azidation of **14β** (21.0 g, 59 mmol) afforded the crude product mixture (β:α = 9:1), which was crystallized from MeOH to give pure **15β** (16.75 g, 77%) as colourless crystals: mp 59–61 °C; IR (film): ν 2113 (N_3), 1723 (C=O), 1268 (benzoate C–O), 1109, and 711 cm^{-1} (benzoate); ^1H NMR: δ 2.27–2.40 (m, 2 H, H-3α,3β), 4.41 (dd, 1 H, H-5a), 4.62 (dd, 1 H, H-5b), 4.82 (m, 1 H, H-4), 5.30 (m, 1 H, H-2), 5.60 (s, 1 H, H-1), 7.41–7.61 and 8.01–8.13 (2 m, 10 H, Ar–H), $J_{4,5a}$ 5.6, $J_{4,5b}$ 3.7, $J_{5a,5b}$ 12.0 Hz; ^{13}C NMR: δ 31.54 (C-3), 65.76 (C-5), 78.30 (C-2), 78.62 (C-4), 94.31 (C-1), 128.3–129.6, 133.09, and 133.45 (Ph–C), 165.36 and 166.18 (2 CO); CIMS (NH_3): m/z 385 ($[M+NH_4]^+$, 3%), 340 ($[MH-N_2]^+$, 15), 325 ($[M-N_3]^+$, 53), 105 ($[PhCO]^+$, 100). Anal. Calcd for $C_{19}H_{17}N_3O_5$ (367.36): C, 62.12; H, 4.66; N, 11.44. Found: C, 61.90; H, 4.49; N, 11.33.

The residue, obtained after concentration of the mother liquor, was resolved by chromatography (CH_2Cl_2, H_2O content ≤ 0.01%) to give an additional amount of **15β** [1.88 g, 9%; R_f 0.39 (CH_2Cl_2); mp 59–60.5 °C (from MeOH)] and the α-azide **15α** as a colourless oil: 1.52 g (7%); R_f 0.30; IR (film): ν 2114 (N_3), 1724 (C=O), 1268 (benzoate C–O), 1116, and 711 cm^{-1} (benzoate); ^1H NMR: δ 2.37–2.42 (m, 2 H, H-3α,3β), 4.38 (dd, 1 H, H-5a), 4.52 (dd, 1 H, H-5b), 4.77 (m, 1 H, H-4), 5.45 (dt, 1 H, H-2), 5.74 (d, 1 H, H-1), 7.42–7.49, 7.55–7.62 and 8.06–8.10 (3 m, 10 H, Ar–H), $J_{1,2}$ 4.5, $J_{2,3\alpha}$ and $J_{2,3\beta}$ 7.6, $J_{4,5a}$ 4.9, $J_{4,5b}$ 3.4, $J_{5a,5b}$ 12.0 Hz; ^{13}C NMR: δ 30.78 (C-3), 65.80 (C-5), 73.42 (C-2), 75.39 (C-4), 90.94 (C-1), 128.4–129.8, 133.20, and 133.45 (Ph–C), 165.72 and 166.18 (2 CO); CIMS (NH_3): m/z 385 ($[M+NH_4]^+$, 2%), 340 ($[MH-N_2]^+$, 40), 325 ($[M-N_3]^+$, 100), 105 ($[PhCO]^+$, 70). Anal. Calcd for $C_{19}H_{17}N_3O_5$ (367.36): C, 62.12; H, 4.66; N, 11.44. Found: C, 61.98; H, 4.78; N, 11.47.

2,3,4,6-Tetra-O-*acetyl-β*-D-*galactopyranosyl azide* (**17**).—Azidation of **16** (1.95 g, 5 mmol) afforded the crude product (1.67 g, 90%), which was crystallized from MeOH to give **17** (1.31 g, 70%) as colourless cubes: mp 96.5 °C, lit. mp 96 °C [33]; IR (KBr): ν 2165 and 2127 (N_3), 1743 (C=O), 1379 (acetate CH_3), 1236 (acetate C–O), and 1216 cm^{-1}; ^1H NMR: δ 1.99, 2.07, 2.10, and 2.18 (4 s, each 3 H, 4 $OCOCH_3$), 4.03 (ddd, 1 H, H-5), 4.12–4.23 (2 m, 2 H, H-6a,6b), 4.61 (d, 1 H, H-1), 5.04 (dd, 1 H, H-3), 5.17 (dd, 1 H, H-2), 5.43 (dd, 1 H, H-4), $J_{1,2}$ 8.6, $J_{2,3}$ 10.4, $J_{3,4}$ 3.3, $J_{4,5}$ 1.1, $J_{5,6a}$ 6, $J_{5,6b}$ 7 Hz; ^{13}C NMR: δ 20.45 and 20.55 (2 $COCH_3$), 20.59 (2 $COCH_3$), 61.16 (C-6), 66.77 (C-4), 67.96 (C-2), 70.64 (C-3), 72.76 (C-5), 88.19 (C-1), 169.30, 169.93, 170.06, and 170.32 (4 CO); EIMS: m/z 331 ($[M-N_3]^{+\bullet}$, 28%), 115 (100); FABMS: 374 (MH^+, 1.2), 346 ($[MH-N_2]^+$, 3.7), 331 ($[M-N_3]^+$, 100).

Acknowledgements

This investigation was supported by the Ministry of Science and Technology of Slovenia (Grant Nos. 33-030 and CI-01513) and the EU (BIOMED1, Agreement No. ERB-CIPDCT 930194, PL 93-1112). We thank Dr Bogdan Kralj at the Mass Spectrometry Cen

tre at the Jožef Stefan Institute (Ljubljana) and Dr Janez Plavec at the Slovenian National NMR Centre.

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