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Convenient preparation of 3,5-anhydro- and 2,5-anhydropentofuranosides, and 5,6-anhydro-D-glucofuranose by use of the Mitsunobu reaction

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Abstract—Methyl 3,5-anhydro-α-D-xylofuranosides are obtained by use of the Mitsunobu reaction from 2-*O*-protected methyl α-D-xylofuranosides, which are easily prepared from D-xylose. The Mitsunobu reaction of methyl 3-*N*-benzylamino-3-deoxy- and 3-azido-3-deoxyarabinofuranosides, which are prepared from the conveniently available methyl 2,3-anhydro-α-D- and 2,3-anhydro-α-L-lyxofuranosides by nucleophilic ring opening, yields the corresponding methyl 2,5-anhydro-α-D- and 2,5-anhydro-α-L-arabinofuranosides. Ring opening of 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose with azide yields the corresponding 5-azido derivative. The structure and configuration of the products is confirmed by NMR spectroscopy. 5,6-Anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose is formed by the Mitsunobu reaction of 1,2-*O*-isopropylidene-α-D-glucofuranose. Its structure is verified by single-crystal X-ray diffraction analysis.

Keywords: Mitsunobu reaction; 2,5-Anhydro-arabinofuranosides; 3,5-Anhydro-xylofuranosides; 5,6-Anhydro-α-D-glucofuranose; Single-crystal X-ray structural analysis

1. Introduction

Bicyclic 2,5-anhydro- and 3,5-anhydrofuranosides are versatile building blocks for syntheses. The fixed conformation and the steric repulsion by the bridge will favour the stereoselectivity of their reactions. As they exhibit more or less ring strain, they are reactive compounds. The anhydro bridges can, for instance, be opened by nucleophiles to yield interesting products. Acid-catalyzed hydrolysis and subsequent reduction should lead to oligohydroxyoxetanes or -oxolanes. Furthermore, they represent precursors for anhydro nucleosides, which can be used for the synthesis of locked nucleic acids ('LNAs').

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2. Results and discussion

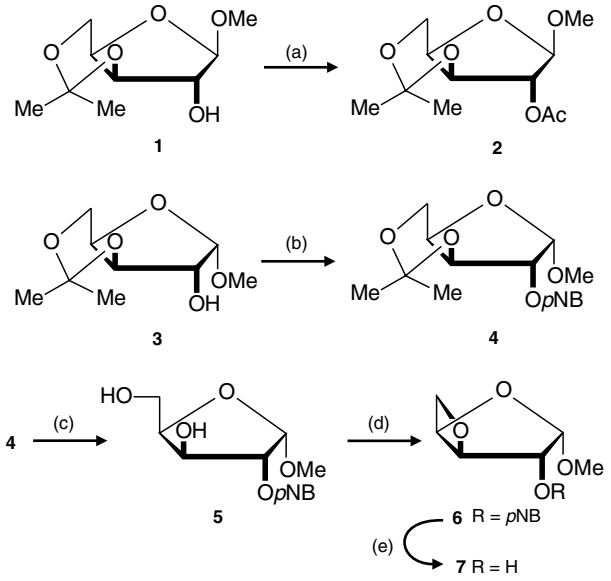
In the course of our investigations on thio-,[1] seleno-[2] and telluroanhydrofuranosides,[2] we became interested in new methods for the synthesis of the corresponding oxygen analogues. Unexpectedly, attempts to apply the Mitsunobu reaction to unprotected methyl pentofuranosides did not lead to the desired methyl 2,5-anhydro- or 3,5-anhydrofuranosides. Instead, methyl 2,3-anhydrofuranosides (epoxysugars) were formed.[3] Therefore, a different synthetic strategy had to be developed that would enforce an intramolecular attack of the hydroxy group in the 2- or 3-position upon the 5-position of the furanosides.

Derivatives of inexpensive D-xylose with a blocked hydroxy group in the 2-position should be suitable starting compounds for the synthesis of methyl 3,5-anhydrofuranosides. For instance, 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (**17**) has been prepared from the

corresponding 3,5-diol.[4] Arabinose derivatives with a protected hydroxy group in the 3-position, on the other hand, could lead to methyl 2,5-anhydrofuranosides. In principle, the corresponding D-lyxose derivatives are as well suitable, but they are not as easily available. Furthermore, they would yield highly strained products. D-Ribose derivatives are ruled out on account of stereochemical reasons.

D-Xylose can be transformed into the methyl 3,5-*O*-isopropylidene-D-xylofuranosides **1** and **3** on a large scale in two steps[5] (Scheme 1). The anomers are easy to separate by vacuum distillation.[6] The free hydroxy group in the 2-position of **1** and **3** can be protected with a variety of electrophilic reagents to prevent the formation of 2,3-anhydrosugars under the conditions of the Mitsunobu reaction. The 2-mesylates, which we have prepared earlier,[1] seemed not to be a good choice since a mesylate substituent represents a good leaving group. This could again give rise to the formation of 2,3-anhydro instead of the desired 3,5-anhydro derivative. The 2-*O*-(2-fluorobenzyl) derivative, on the other hand, can be readily cyclised to the corresponding oxetano furanoside.[7] We have used it to prepare isonucleosides.[7] It is, however, not useful for the synthesis of free 3,5-anhydrofuranosides since the fluorobenzyl substituent cannot easily be removed. Therefore, we have prepared the 2-acetate **2** and the 2-(4-nitrobenzoate) **4** as a compromise, which should allow one to perform a straightforward Mitsunobu reaction and, on the other hand, a facile deprotection. The acetate **2** turned out to be not suitable as precursor because the acid-catalysed cleavage of the *O*-isopropylidene protecting group led to anomerisation and also to the formation of undesired pyranosides. But **4** was very suitable as a starting compound. It was cleanly deprotected to methyl 2-*O*-(4-nitrobenzoyl)-α-D-xylofuranoside (**5**) without any rearrangement as established by single-crystal X-ray structural analysis of **5** (Fig. 1). The Mitsunobu reaction of the diol **5** gave the 3,5-anhydrofuranoside **6** in good yield. Debenzoylation of **6** with sodium methoxide, finally, led to unprotected methyl 3,5-anhydro-α-D-xylofuranoside (**7**). The corresponding β-anomer has been obtained by Buchanan in a multi-step synthesis.[8] The structure and configuration of **7** follows from its NMR spectra. In particular, the chemical shifts δ 4.78 for H-3 and δ 74.9 for C-3 as well as the coupling constants $J_{1,2}$ 4.4 Hz, $J_{2,3}$ 6.2 Hz, $J_{3,4}$ 4.3 Hz, $J_{4,5endo}$ 2.4 Hz and $J_{4,5exo}$ 4.5 Hz in **7** as compared with δ 3.83 (H-3), δ 62.1 (C-3), $J_{1,2} \sim 0$ Hz, $J_{2,3}$ 2.3 Hz, $J_{3,4} \sim 0$ Hz, $J_{4,5endo}$ 1.2 Hz and $J_{4,5exo} \sim 0$ Hz in the 2,5-anhydro derivative **13** (see below) are indicative of the oxetane structure and the α-D-*xylo* configuration of **7**.

The epoxide **8** is conveniently available in two steps from D-xylose or D-arabinose.[3] Reaction of **8** with benzylamine according to a literature procedure for the preparation of aziridines from oxiranes in the carbohydrate series[9] gave methyl 3-*N*-benzylamino-3-deoxy-α-D-arabinofuranoside (**9**) as the only product of the ring-opening reaction (Scheme 2). The nucleophilic attack upon the epoxide ring exclusively occurred at the 3-position of **8**. The structure of **9** follows from its NMR spectra. The chemical shifts δ(H-2) 4.06 and δ(C-2) 76.7 are higher than δ(H-3) 3.03 and δ(C-3) 65.9, as one would expect on account of the substituent effects of oxygen and nitrogen. Subsequent Mitsunobu reaction of **9** did, however, not yield the aziridine **10**. Instead, we obtained methyl 2,5-anhydro-3-*N*-benzylamino-3-deoxy-α-D-arabinofuranoside (**11**). The reac-



Scheme 1. Reagents: (a) AcCl, pyridine; (b) 4-nitrobenzoyl chloride, pyridine; (c) AcOH–H_2O; (d) DIAD, PPh_3, pyridine; (e) NaOMe, MeOH. *p*NB = 4-nitrobenzoyl.

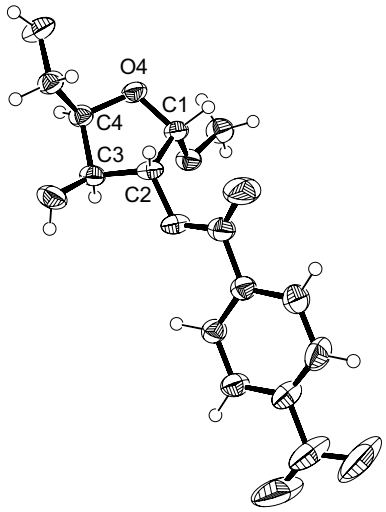
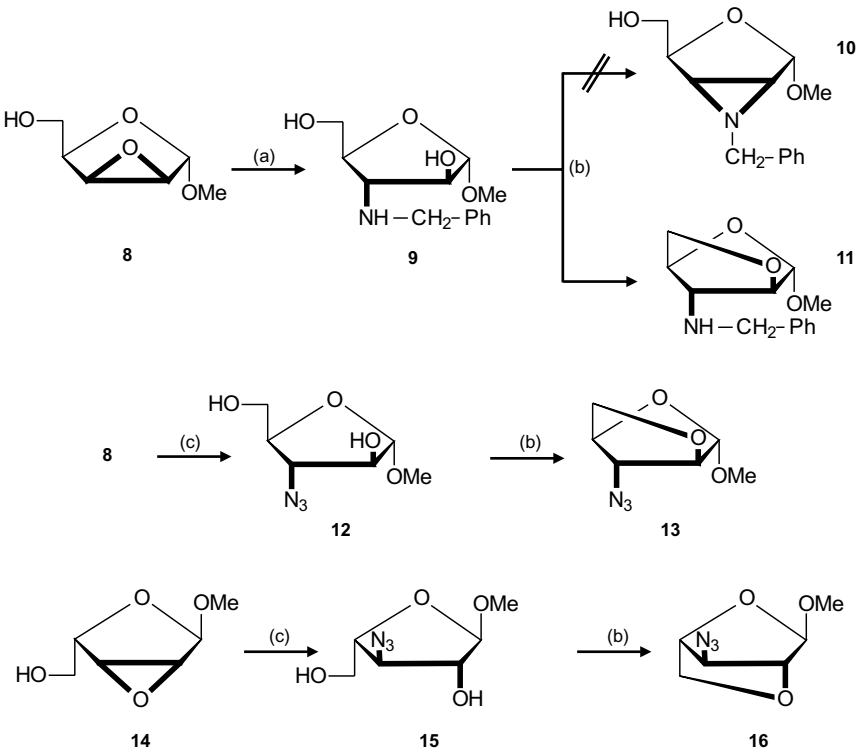


Figure 1. ORTEP view of the single-crystal X-ray diffraction structure of methyl 2-*O*-(4-nitrobenzoyl)-α-D-xylofuranoside (**5**) with atomic numbering. Thermal ellipsoids are drawn on the 50% probability level.



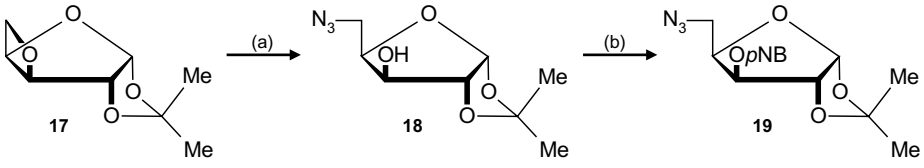
Scheme 2. Reagents: (a) $PhCH_2NH_2$; (b) DIAD, PPh_3, pyridine; (c) NaN_3/NH_4Cl, aq EtOH.

tion of the epoxide **8** with sodium azide gave methyl 3-azido-3-deoxy-α-D-arabinofuranoside (**12**).[10] It was again the only product. The corresponding 2-azido derivative was not formed. The position of the nitrogen substituent at C-3 in **11** and **12** is once more obvious from the NMR spectra. As in the case of **9**, δ(H-2) > δ(H-3) and δ(C-2) > δ(C-3) for the benzylamino **11** and the azido derivative **12** (see Experimental). The Mitsunobu reaction of **12** led to the expected methyl 2,5-anhydro-3-azido-3-deoxy-α-D-arabinofuranoside (**13**).

Methyl 2,3-anhydro-α-L-lyxofuranoside (**14**) is the enantiomer of **8**. It can be prepared in two steps from inexpensive L-arabinose.[3] In an identical reaction sequence as for **13**, **14** was transformed into methyl 2,5-anhydro-3-azido-3-deoxy-α-L-arabinofuranoside (**16**) via methyl 3-azido-3-deoxy-α-L-arabinofuranoside (**15**). The anhydro-azido sugars **13** and **16** represent another pair of enantiomers. Their NMR spectroscopic data agree, therefore, within the limits of experimental deviations.

Although oxetanes are not as highly strained compounds as oxiranes, ring opening with nucleophiles is possible. We have studied the reaction of the 3,5-anhydrofuranose **17**[4] with sodium azide hoping to obtain a 3-azido derivative by nucleophilic attack at the 3-position. But the displacement reaction took place at C-5, and 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**18**) was formed (Scheme 3). The determination of its structure by NMR techniques was not quite straightforward since hydroxy and azido groups exhibit very similar effects on the chemical shifts. Fortunately, however, the corresponding 3-(4-nitrobenzoate) **19** was a crystalline compound, and its single-crystal X-ray diffraction analysis answered the structural question (cf. Fig. 2).

Since we had been able to prepare the desired 2,5-anhydro- and 3,5-anhydropentofuranosides from methyl pentofuranosides with two free hydroxy groups we focused our interest on the synthesis of more complex



Scheme 3. Reagents: (a) NaN_3/NH_4Cl, aq EtOH; (b) 4-nitrobenzoyl chloride, pyridine. *p*NB = 4-nitrobenzoyl.

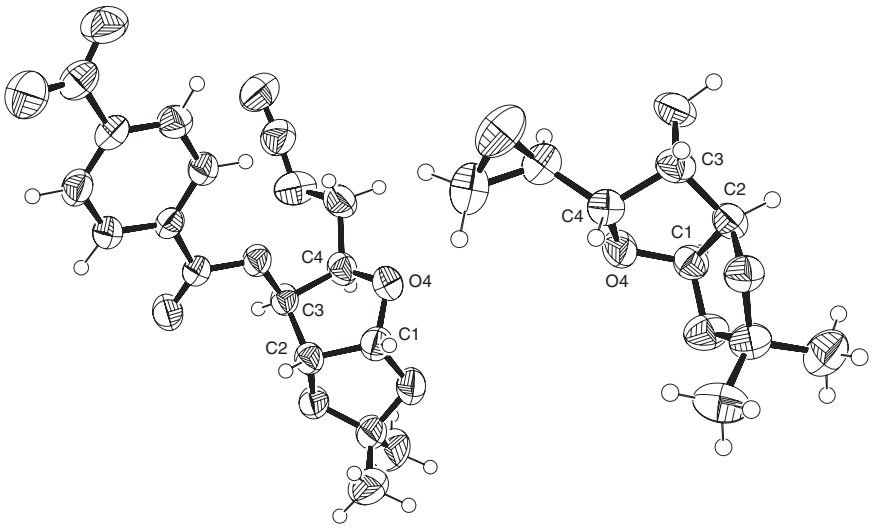
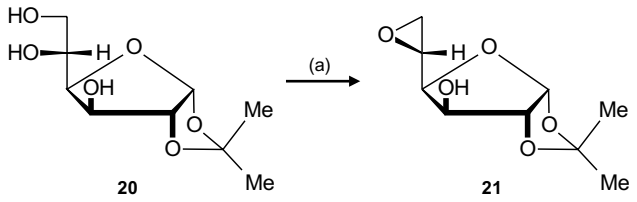


Figure 2. ORTEP views of the single-crystal X-ray diffraction structures of 5-azido-5-deoxy-1,2-*O*-isopropylidene-3-*O*-(4-nitrobenzoyl)-α-D-xylofuranose (**19**) and 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose **21** with atomic numbering. Thermal ellipsoids are drawn on the 50% probability level.

monosaccharides with three free hydroxy groups. In particular, cheap 1,2-*O*-isopropylidene-α-D-glucofuranose **20** seemed to be an interesting starting compound for the synthesis of anhydro derivatives. Several possibilities are thinkable for the intramolecular Mitsunobu reaction of **20**:

- Attack of the hydroxy group in the 3-position upon C-5 under inversion of the configuration should give an oxetane derivative with the L-*ido* configuration.
- Attack of the hydroxy group in the 3-position upon C-6 should give an oxolane derivative with the D-*gluco* configuration.
- Attack of the hydroxy group in the 6-position upon C-5 under inversion of the configuration should give an oxirane derivative with the L-*ido* configuration.
- Attack of the hydroxy group in the 3-position upon an intermediately formed oxirane under ring opening/ring closure should give the corresponding oxetanes or oxolanes.
- Attack of the hydroxy group in the 5-position upon C-6 should give an oxirane with the D-*gluco* configuration.

We obtained one single product from the Mitsunobu reaction of **20**. According to its NMR spectra (see Experimental) and especially upon an X-ray structural analysis (cf. Fig. 2) this product was determined to be the oxirane, 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (**21**) (Scheme 4). Thus, our method provides a 5,6-anhydrohexofuranose in one step, whereas known syntheses for this type of compounds require substantially more steps. The 5,6-anhydrohexofuranoses are valuable starting compounds for further syntheses. They



Scheme 4. Reagents: (a) DIAD, PPh_3, pyridine.

are, for instance, useful for the preparation of 5-thiohexoses.[11]

3. Experimental

3.1. General methods

Melting points (corrected) were determined by use of an electrothermal apparatus. IR spectra (KBr pellets or films) were measured with an ATI Mattson Genesis spectrometer. NMR spectra were recorded with Bruker AMX 400 and DRX 500 spectrometers in $CDCl_3$ if not stated otherwise. Chemical shifts δ (ppm) are related to Me_4Si (^1H and ^{13}C). Standard correlation techniques were used for assignments. Mass spectra were measured on a Varian CH 7 (EI, 70 eV) and a VG Analytical 70–250 S (HRMS) apparatus. Optical rotations were measured on a Perkin–Elmer 341 polarimeter. Thin-layer chromatography (TLC) was carried out on E. Merck PF_{254} foils (detection: UV light, EtOH–H_2SO_4 spray/200 °C), and column chromatography on E. Merck Kie-

selgel 60 (70–230 mesh). Solvents were purified and dried according to standard laboratory procedures.[12]

3.2. Single-crystal X-ray structural analyses

The crystal data and a summary of experimental details for **5**, **19** and **21** are given in Table 1. Data collection was performed on a Kappa CCD Nonius diffractometer, with graphite-monochromated Mo Kα radiation (wavelength 0.71073 Å) in the rotation Φ scan mode. The refinement method was full-matrix-block least-squares on F^2. Hydrogen positions were obtained by difference Fourier synthesis. The H-atom refinement method was difmap and geometrical in case of **5**, and mixed in case of **19** and **21**. The absolute structure parameters (flack values) were in accordance with the expected structure. The structures were solved by direct methods using the SIR-97 program[13] and the SHELXL-97 program.[14] The Cremer–Pople puckering parameters (Table 2) were calculated with the PLATON program.[15]

3.3. Starting materials

Methyl 3,5-*O*-isopropylidene-β-D-xylofuranoside (**1**) and -α-D-xylofuranoside (**3**) were prepared according to a literature procedure.[5] The anomers were separated by vacuum distillation.[6] Methyl 3-azido-3-deoxy-α-D-arabinofuranoside (**12**)[10] and 3,5-anhydro-1,2-*O*-isopropylidene-α-D-xylofuranose (**17**)[4] were prepared as described in the literature. Methyl 2,3-anhydro-α-*O*-lyxofuranoside (**8**) and methyl 2,3-anhydro-α-*O*-lyxofuranoside (**14**) were prepared as described earlier.[3]

Table 1. Crystal data and structure refinement for **5**, **19** and **21**

	5	**19**	**21**
Molecular formula	$C_{13}H_{15}NO_8$	$C_{15}H_{16}N_4O_7$	$C_9H_{14}O_5$
Molecular weight ($g\,mol^{-1}$)	313.26	364.32	202.20
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$
a (pm)	974.9(1)	677.6(1)	543.0(1)
b (pm)	731.0(1)	698.3(1)	928.8(1)
c (pm)	1065.5(1)	1829.9(1)	1997.2(1)
β (°)	113.34(1)	90.23(1)	90.00
V (Å^3)	697.19(14)	865.84(18)	1007.3(2)
Z (molecules per cell)	2	2	4
D_{calcd} ($g\,cm^{-3}$)	1.492	1.397	1.333
Absorption coefficient (mm^{-1})	0.126	0.113	0.109
$F(0\,0\,0)$	328	380	432
Crystal size (mm)	$0.33 \times 0.26 \times 0.21$	0.51×0.41 0.33	0.45×0.22 0.09
θ Range for data collection (°)	2.08–27.49	3.01–27.53	2.04–27.48
Index ranges	$0 \leqslant h \leqslant 12$	$0 \leqslant h \leqslant 8$	$0 \leqslant h \leqslant 7$
	$-9 \leqslant k \leqslant 9$	$-8 \leqslant k \leqslant 7$	$0 \leqslant l \leqslant 12$
	$-13 \leqslant l \leqslant 12$	$-23 \leqslant l \leqslant 23$	$-25 \leqslant l \leqslant 25$
Reflections collected	13,343	5988	11,694
Independent reflections	3191	3026	2297
Reflections with $[I \geqslant 2\sigma(I)]$	3072	2533	1771
Function minimised[a]	$x = 0.0735$	$x = 0.0676$	$x = 0.0975$
	$y = 0.0822$	$y = 0.0735$	$y = 0.0866$
Data/restraints/parameters	3191/1/248	3026/1/273	2297/0/160
Goodness-of-fit on F^2	0.985	1.106	1.015
Final R indices $[I \geqslant 2\sigma(I)]$	$R_1 = 0.0341$	$R_1 = 0.0452$	$R_1 = 0.0491$
	$wR_2 = 0.0992$	$wR_2 = 0.1135$	$wR_2 = 0.1153$
R Indices (all data)	$R_1 = 0.0357$	$R_1 = 0.0581$	$R_1 = 0.0739$
	$wR_2 = 0.1014$	$wR_2 = 0.1240$	$wR_2 = 0.1475$
Largest difference peak and hole (e Å^{-3})	0.213 and −0.162	0.216 and −0.224	0.455 and −0.445

[a] $\sum w(F_o^2 - F_c^2)^2, w = 1/[\sigma^2(F_o^2) + x^2 + yP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Cremer–Pople puckering parameters

Compound	Atom sequence	Puckering parameters		Closest pucker descriptor
		Q(2) (Å)	Φ (2) (°)	
5	O(4)–C(1)–C(2)–C(3)–C(4)	0.432(2)	76.9(2)	Envelope C(2)-*endo*
19	O(4)–C(1)–C(2)–C(3)–C(4)	0.339(3)	317.3(5)	Envelope C(4)-*exo*
21	O(4)–C(1)–C(2)–C(3)–C(4)	0.362(2)	295.9(4)	Twist C(3)-*endo*, C(4)-*exo*

1,2-*O*-isopropylidene-α-D-glucofuranose (**20**) was obtained from Lancaster synthesis.

3.4. Methyl 2-*O*-acetyl-3,5-*O*-isopropylidene-β-D-xylofuranoside (2)

Acetyl chloride (15.0 mL, 210.2 mmol) was dropped into a solution of **1** (24.0 g, 117.4 mmol) in dry pyridine (250 mL) at 0 °C within 30 min. After stirring for 1 h, the reaction mixture was poured onto ice-water (1000 mL) and extracted with $CHCl_3$ (2×200 mL, 3×100 mL). The combined organic extracts were washed with water (100 mL) and brine (6×100 mL each). After drying over $MgSO_4$ and evaporation of the solvent, the residue was purified by vacuum distillation to yield **2** (26.2 g, 106.3 mmol, 90.5%) as a pale-yellow syrup: bp 99 °C (0.4 mm); $[\alpha]_D^{20}$ −56.2 (*c* 1.1, $CHCl_3$); R_f 0.64 (2:1 EtOAc–petroleum ether); IR: *v* 1750 (C=O) cm^{-1}; ^1H NMR (400 MHz): δ 1.38 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 2.10 (s, 3H, $COCH_3$), 3.42 (s, 3H, OCH_3), 3.83 (dd, 1H, H-5), 3.97 (dd, 1H, H-5′), 4.20–4.25 (m, 2H, H-3, H-4), 4.92 (s, 1H, H-1), 5.06 (s, 1H, H-2). $J_{4,5}$ 4.9, $J_{4,5'}$ 4.5, $J_{5,5'}$ 12.0 Hz; ^{13}C NMR (101 MHz): 20.8 ($CO\mathit{C}H_3$), 21.1 (CH_3), 26.9 (CH_3), 55.2 (OCH_3), 60.7 (C-5), 73.1 (C-4), 75.4 (C-3), 81.5 (C-2), 98.6 ($\mathit{C}Me_2$), 108.1 (C-1), 169.5 (C=O). Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.25; H, 7.52.

3.5. Methyl 3,5-anhydro-α-D-xylofuranoside (7)

3.5.1. Methyl 3,5-*O*-isopropylidene-2-*O*-(4-nitrobenzoyl)-α-D-xylofuranoside (4). A solution of 4-nitrobenzoyl chloride (49.2 g, 265.1 mmol) in dry pyridine (490 mL) was dropped into a solution of **3** (49.2 g, 240.9 mmol) in dry pyridine (170 mL) at 0 °C. The solution was stirred overnight at room temp. Water (16 mL) was added. The solvent was evaporated in a vacuum, and the residue was dissolved in $CHCl_3$ (340 mL). The solution was washed with water (3×300 mL), with $NaHSO_4$ solution (3 M, 3×300 mL) and again with satd $NaHCO_3$ solution (3×300 mL each). After drying over $MgSO_4$, filtration and evaporation of the solvent **4** (81.7 g, 231.3 mmol, 96%) was obtained as a brown syrup that was used in the next step without further purification. R_f 0.21 (10:1 toluene–EtOAc); IR: *v* 1733 (C=O), 1530 (NO_2), 1318 (NO_2) cm^{-1}; ^1H NMR (400 MHz): δ 1.42 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 3.39 (s, 3H, OCH_3), 3.93 (dd, 1H, H-5), 4.10 (dd, 1H, H-5′), 4.22 (ddd, 1H, H-4), 4.57 (dd, 1H, H-3), 5.28 (dd, 1H, H-2), 5.37 (d, 1H, H-1), 8.23 (ddd, 2H, ArH), 8.29 (ddd, 2H, ArH). $J_{1,2}$ 4.4, $J_{2,3}$ 2.0, $J_{3,4}$ 4.0, $J_{4,5}$ 4.2, $J_{4,5'}$ 4.2, $J_{5,5'}$ 12.6, $^3J_{ArH,\ ArH}$ 8.8, $^4J_{ArH,\ ArH}$ 2.0, $^5J_{ArH,\ ArH}$ 2.0, $^4J_{ArH,\ ArH}$ 2.1 Hz; ^{13}C NMR (101 MHz): δ 20.8 (CH_3), 27.6 (CH_3), 56.2 (OCH_3), 60.2 (C-5), 71.1 (C-4), 73.6 (C-3), 80.1 (C-2), 98.8 ($\mathit{C}Me_2$), 101.8 (C-1), 123.6 ($2CH_{Ar}$), 131.0 ($2CH_{Ar}$), 135.0 (C-1_{Ar}), 150.8 (C-4_{Ar}), 163.8 (C=O).

3.5.2. Methyl 2-*O*-(4-nitrobenzoyl)-α-D-xylofuranoside (5). A solution of **4** (81.7 g, 231.3 mmol) in water (75 mL) and HOAc (145 mL) was stirred at 50 °C for 4 h. After stirring overnight at room temperature, the solvent was evaporated. After repeated co-distillation with toluene **5** (74.1 g, ~100%, contaminated with traces of toluene) was obtained as yellow crystals: mp 112 °C (MeOH). $[\alpha]_D^{20}$ +154.8 (*c* 1.0, $CHCl_3$); R_f 0.62 (5:5:1 toluene–EtOAc–EtOH); IR: *v* 3453 (OH), 1729 (C=O), 1530 (NO_2), 1351 (NO_2) cm^{-1} ; ^1H NMR (400 MHz): δ 2.67 (t, 1H, OH-5), 3.40 (s, 3H, OCH_3), 3.65 (d, 1H, OH-3), 3.98 (dd, 2H, H-5, H-5′), 4.32 (dt, 1H, H-4), 4.78 (ddd, 1H, H-3), 5.07 (dd, 1H, H-2), 5.25 (d, 1H, H-1), 8.25 (ddd, 2H, ArH), 8.30 (ddd, 2H, ArH). $J_{1,2}$ 4.4, $J_{2,3}$ 6.2, $J_{3,4}$ 7.4, $J_{3,\ OH\text{-}3}$ 7.2, $J_{4,5}$ 3.1, $J_{4,5'}$ 3.1, $J_{5,\ OH\text{-}5}$ 6.2, $J_{5',\ OH\text{-}5}$ 6.2, $^3J_{ArH,\ ArH}$ 9.1, $^4J_{ArH,\ ArH}$ 2.0, $^5J_{ArH,\ ArH}$ 2.1, $^4J_{ArH,\ ArH}$ 2.1 Hz; ^{13}C NMR (101 MHz): δ 55.4 (OCH_3), 61.8 (C-5), 74.9 (C-3), 76.6 (C-4), 82.4 (C-2), 100.0 (C-1), 123.6 ($2CH_{Ar}$), 131.1 ($2CH_{Ar}$), 137.8 (C-1_{Ar}), 150.9 (C-4_{Ar}), 165.0 (C=O).

3.5.3. Methyl 3,5-anhydro-2-*O*-(4-nitrobenzoyl)-α-D-xylofuranoside (6). The reaction was carried out under N_2. Diisopropyl azodicarboxylate (0.3 mL, 1.53 mmol) and subsequently a solution of **5** (0.23 g, 0.75 mmol) in dry pyridine (0.5 mL) were added to a solution of triphenylphosphine (0.40 g, 1.53 mmol) in dry pyridine (4 mL). After 5 h at 80 °C the solvent was evaporated, and the residue was filtered through silica gel (50 g, EtOAc). Column chromatography (50 g silica gel, 1:2 petroleum ether–EtOAc) yielded **6** as a yellow solid (containing traces of diisopropyl hydrazodicarboxylate according to the NMR spectra). The product was debenzoylated by use of the Zemplén procedure without further purification. R_f 0.75 (EtOAc); ^1H NMR (400 MHz): δ 3.45 (s, 3H, OCH_3), 4.41 (dd, 1H, H-5_{endo}), 4.81 (dd, 1H, H-5_{exo}), 5.05 (ddd, 1H, H-4), 5.38 (dd, 1H, H-3), 5.46 (dd, 1H, H-2), 5.61 (d, 1H, H-1), 8.22 (ddd, 2 H, ArH), 8.29 (ddd, 2H, ArH). $J_{1,2}$ 4.0, $J_{2,3}$ 1.6, $J_{3,4}$ 4.5, $J_{4,5\text{-}\mathit{endo}}$ 2.6, $J_{4,5\text{-}\mathit{exo}}$ 4.5, $J_{5\text{-}\mathit{endo},5\text{-}\mathit{exo}}$ 7.9, $^3J_{ArH,\ ArH}$ 8.9, $^4J_{ArH,\ ArH}$ 2.1, $^5J_{ArH,\ ArH}$ 2.1, $^4J_{ArH,\ ArH}$ 2.0 Hz; ^{13}C NMR (101 MHz): 56.4 (OCH_3), 75.4 (C-4), 76.6 (C-5), 79.5 (C-2), 87.5 (C-3), 104.7 (C-1), 123.6 ($2CH_{Ar}$), 131.0 ($2CH_{Ar}$), 134.8 (C-1_{Ar}), 150.8 (C-4_{Ar}), 163.8 (C=O).

3.5.4. Methyl 3,5-anhydro-α-D-xylofuranoside (7). Compound **6** was dissolved in a mixture of benzene and MeOH (1:1, 20 mL). A solution of NaOMe in MeOH (1 mL) prepared from Na (0.05 g, 2.17 mmol) was added. After 2 h at 40 °C the reaction mixture was allowed to reach room temperature. Then the mixture was neutralised with HOAc in MeOH, and the sol-

vent was evaporated. Chromatographic workup (50 g silica gel, EtOAc) and distillation yielded **7** (0.05 g, 0.34 mmol, 45% total yield for this and the previous step) as a colourless oil: bp 64 °C (0.5 mm); $[\alpha]_D^{20}$ +92.8 (*c* 1.0, $CHCl_3$); R_f 0.46 (EtOAc); IR: *v* 3441 (OH) cm^{-1}; ^1H NMR (500 MHz): δ 2.91 (s, 1H, OH), 3.54 (s, 3H, OCH_3), 4.22 (d, 1H, H-2), 4.24 (dd, 1H, H-5_{endo}), 4.70 (dd, 1H, H-5_{exo}), 4.90 (ddd, 1H, H-4), 5.03 (d, 1H, H-3), 5.34 (d, 1H, H-1). $J_{1,2}$ 3.8, $J_{3,4}$ 4.3, $J_{4,5\text{-}endo}$ 2.4, $J_{4,5\text{-}exo}$ 4.5, $J_{5\text{-}endo,5\text{-}exo}$ 7.9 Hz; ^{13}C NMR (101 MHz): δ 56.9 (OCH_3), 75.7 (C-2), 75.8 (C-4), 77.2 (C-5), 89.9 (C-3), 105.8 (C-3); EIMS: *m*/*z* (%) 129 (1), 117 (6), 116 (21) [$M^{+\cdot}-CH_2O$], 115 (10) [$M^{+\cdot}-OCH_3$], 101 (7), 88 (6), 87 (100), 86 (10), 85 (20), 84 (8), 83 (2), 75 (10), 74 (16), 73 (7), 72 (5), 71 (32), 69 (24), 68 (15), 61 (56), 60 (10), 59 (28), 58 (17), 57 (56), 56 (24), 55 (46), 54 (8), 45 (22). Anal. Calcd for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 48.88; H 7.06.

3.6. Methyl 2,5-anhydro-3-benzylamino-3-deoxy-α-D-arabinofuranoside

3.6.1. Methyl 3-benzylamino-3-deoxy-α-D-arabinofuranoside (9). A solution of **8**[3] (1.57 g, 10.74 mmol) in benzylamine (10 mL) was stirred at 150 °C for 5 h. After vacuum evaporation of the solvent (0.8 mm), the residue was chromatographed (silica gel, 370 g, 3:1 EtOAc–EtOH) to yield **9** (2.15 g, 8.49 mmol, 79%) as a pale-yellow syrup that was used for the Mitsunobu reaction without further purification. R_f 0.56 (3:1 EtOAc–EtOH); ^1H NMR (500 MHz): δ 3.03 (d, 1H, H-3), 3.31 (s, 3H, OCH_3), 3.59 (dd, 1H, H-5), 3.74 (dd, 1H, H-5′), 3.75 (d, 1H, PhC*H*), 3.85 (d, 1H, PhC*H*), 4.04 (ddd, 1H, H-4), 4.06 (s, 1H, H-2), 4.83 (s, 1H, H-1), 7.22–7.33 (m, 5H, ArH). $J_{3,4}$ 3.4, $J_{4,5}$ 2.7, $J_{4,5'}$ 1.9, $J_{5,5'}$ 11.7, $^2J_{CH2}$ 12.9 Hz; ^{13}C NMR (126 MHz): δ 52.0 (Ph*C*H_2), 54.7 (OCH_3), 62.2 (C-5), 65.9 (C-3), 76.7 (C-2), 85.2 (C-4), 109.7 (C-1), 127.2 (CH_{Ar}), 128.2 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 139.3 (C-1_{Ar}).

3.6.2. Methyl 2,5-anhydro-3-benzylamino-3-deoxy-α-D-arabinofuranoside (11). A solution of **9** (0.80 g, 3.16 mmol) in dry toluene (5 mL) was added to a solution of triphenylphosphine (0.85 g, 3.24 mmol) and diisopropyl azodicarboxylate (0.6 mL, 3.07 mmol) in dry toluene (35 mL) at 0 °C. After 2 h the reaction was finished (TLC monitoring). The solvent was evaporated. The residue was purified by column chromatography (100 g silica gel, 3:1 EtOAc–EtOH) to yield **11** (0.64 g, 2.72 mmol, 86%) as a yellow oil: $[\alpha]_D^{20}$ +83.9 (*c* 1.0, $CHCl_3$); R_f 0.63 (3:1 EtOAc–EtOH); IR: *v* 3345 (NH) cm^{-1} ; ^1H NMR (400 MHz): δ 2.70 (s, 1H, NH), 3.24 (d, 1H, H-3), 3.39 (s, 3H, OCH_3), 3.60 (d, 1H, H-5_{endo}), 3.71 (dd, 1H, H-5_{exo}), 3.79 (s, 2H, PhCH_2), 4.16 (d, 1H, H-2), 4.39 (d, 1H, H-4), 4.79 (s, 1H, H-1), 7.20–7.35 (m, 5H, ArH). $J_{2,3}$ 2.1, $J_{4,5\text{-}exo}$ 1.0, $J_{5\text{-}endo,5\text{-}exo}$ 8.2 Hz; ^{13}C NMR (101 MHz): δ 52.3 (Ph*C*H_2), 55.8 (OCH_3), 63.1 (C-3), 72.0 (C-5), 75.6 (C-2), 77.8 (C-4), 106.6 (C-1), 127.0 (CH_{Ar}), 128.1 ($2CH_{Ar}$), 128.4 ($2CH_{Ar}$), 140.0 (C-1_{Ar}); EIMS: *m*/*z* (%) 235 (1) [$M^{+\cdot}$], 204 (2) [$M^{+\cdot}-OCH_3$], 174 (36), 144 (5) [$M^{+\cdot}-C_7H_7$], 118 (5), 105 (4), 92 (16), 91 (100, $C_7H_7^+$), 97 (20), 69 (13), 65 (22), 51 (6), 45 (12), 43 (12), 41 (9), 39 (10); HRMS Calcd for $C_{13}H_{17}NO_3$: 235.1185. Found: 235.1208. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 65.17; H, 7.34; N, 5.85.

3.7. Methyl 2,5-anhydro-3-azido-3-deoxy-α-D-arabinofuranoside (13)

Compound **12**[10] {0.47 g, 2.48 mmol; IR: *v* 3399 (OH), 2107 (N_3) cm^{-1}; ^1H NMR (400 MHz, D_2O): δ 3.25 (s, 3H, OCH_3), 3.59 (dd, 1H, H-5), 3.66 (dd, 1H, H-5′), 3.68 (dd, 1H, H-3), 3.89 (ddd, 1H, H-4), 4.03 (dd, 1H, H-2), 4.80 (d, 1H, H-1). $J_{1,2}$ 1.5, $J_{2,3}$ 3.6, $J_{3,4}$ 6.5, $J_{4,5}$ 5.2, $J_{4,5'}$ 3.8, $J_{5,5'}$ 12.3 Hz; ^{13}C NMR (101 MHz, D_2O): δ 55.4 (OCH_3), 61.5 (C-5), 66.6 (C-3), 80.0 (C-2), 82.2 (C-4), 108.6 (C-1); EIMS: *m*/*z* (%) 158 (17) [$M^{+\cdot}-OCH_3$], 151 (4), 115 (9), 87 (50), 74 (100), 69 (43); CIMS: *m*/*z* (%) 207 (100) [M^++NH_4], 175 (63), 164 (31), 162 (84)}, triphenylphosphine (1.29 g, 4.92 mmol) and diisopropyl azodicarboxylate (0.95 mL, 4.86 mmol) were refluxed (3 h) in dry pyridine (14 mL). The solvent was evaporated, and the residue was chromatographed twice (100 g silica gel each; (1) 1:1 EtOAc–hexane; (2) 1:2 EtOAc–pentane, R_f 0.35) to yield **13** (0.28 g, 1.63 mmol, 66%) as a pale yellow oil. Traces of diisopropyl hydrazodicarboxylate could not be completely removed. Thus no correct elemental analysis was obtained. ^1H NMR (500 MHz): δ 3.48 (s, 3H, OCH_3), 3.73 (d, 1H, H-5_{endo}), 3.83 (d, 1H, H-3), 3.86 (dd, 1H, H-5_{exo}), 4.26 (d, 1H, H-2), 4.60 (d, 1H, H-4), 4.92 (s, 1H, H-1). $J_{2,3}$ 2.3, $J_{4,5\text{-}exo}$ 1.2, $J_{5\text{-}endo,5\text{-}exo}$ 8.4 Hz; ^{13}C NMR (101 MHz): δ 56.8 (OMe), 62.1 (C-3), 72.5 (C-5), 77.7 (C-2 or C-4), 77.8 (C-2 or C-4), 106.4 (C-1).

3.8. Methyl 3-azido-3-deoxy-α-L-arabinofuranoside (15)

A solution of **14**[3] (0.93 g, 6.36 mmol), NaN_3 (0.84 g, 12.9 mmol) and NH_4Cl (0.82 g, 15.3 mmol) in EtOH (19 mL) and water (4.5 mL) was refluxed for 76 h. After evaporation of the solvent the residue was co-distilled four times with toluene (20 mL each) and twice with $CHCl_3$ (20 mL each). Chromatography (50 g silica gel, EtOAc, R_f 0.64) yielded **15** (1.16 g, 6.13 mmol, 96%) as a colourless syrup: $[\alpha]_D^{20}$ −165.5 (*c* 1.04, $CHCl_3$); IR: *v* 3408 (OH), 2108 (N_3) cm^{-1}; ^1H NMR (400 MHz, D_2O): δ 3.46 (s, 3H, OCH_3), 3.79 (dd, 1H, H-5), 3.87 (dd, 1H, H-5′), 3.89 (dd, 1H, H-3), 4.10 (ddd, 1H, H-4), 4.23 (dd, 1H, H-2), 5.01 (d, 1H, H-1). $J_{1,2}$ 1.6, $J_{2,3}$ 3.7, $J_{3,4}$ 6.4, $J_{4,5}$ 5.2, $J_{4,5'}$ 3.9, $J_{5,5'}$ 12.3 Hz; ^{13}C NMR

(101 MHz, D_2O): δ 55.4 (OCH_3), 61.5 (C-5), 66.6 (C-3), 80.0 (C-2), 82.2 (C-4), 108.6 (C-1); EIMS: *m/z* (%) 158 (6) [$M^{+\cdot}-OCH_3$], 115 (12), 87 (62), 74 (100), 69 (47); CIMS: *m/z* (%) 207 (100) [$M^+ + NH_4$], 175 (65), 164 (35), 162 (87); Anal. Calcd for $C_6H_{11}N_3O_4$: C, 38.10; H, 5.86; N, 22.21. Found: C, 37.14; H, 6.02; N, 20.52.

3.9. Methyl 2,5-anhydro-3-azido-3-deoxy-α-L-arabino-furanoside (16)

Compound **16** was prepared as described for **13** from **15** (0.93 g, 4.92 mmol), triphenylphosphine (2.56 g, 9.76 mmol) and diisopropyl azodicarboxylate (1.90 mL, 9.72 mmol). Chromatography (twice, 100 g silica gel each, 1:1 EtOAc–petroleum ether, R_f 0.61) yielded **16** (0.60 g, 3.50 mmol, 71%) as a pale-yellow oil, that contained traces of diisopropyl hydrazodicarboxylate. $[\alpha]_D^{20}$ −106.1 (*c* 0.97, $CHCl_3$); 1H NMR (500 MHz): δ 3.47 (s, 3H, OCH_3), 3.71 (d, 1H, H-5_{endo}), 3.81 (d, 1H, H-3), 3.84 (dd, 1H, H-5_{exo}), 4.25 (d, 1H, H-2), 4.59 (d, 1H, H-4), 4.91 (s, 1H, H-1). $J_{2,3}$ 2.3, $J_{4,5\text{-}exo}$ 1.1, $J_{5\text{-}endo,5\text{-}exo}$ 8.4 Hz; ^{13}C NMR (126 MHz): δ 56.3 (OCH_3), 61.8 (C-3), 72.1 (C-5), 77.38 (C-2 or C-4), 77.43 (C-2 or C-4), 106.1 (C-1); EIMS: *m/z* (%) 116 (14), 112 (9), 98 (4), 87 (22), 83 (42), 73 (24), 69 (100), 58 (58), 54 (72), 45 (95).

3.10. 5-Azido-5-deoxy-1,2-*O*-isopropylidene-3-*O*-(4-nitrobenzoyl)-α-D-xylofuranose (19)

3.10.1. 5-Azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (18). A solution of **17**,[4] (2.73 g, 15.9 mmol), NaN_3 (2.73 g, 42.0 mmol) and NH_4Cl (2.24 g, 41.9 mmol) in EtOH (22 mL) and water (14 mL) was refluxed for 230 h. After evaporation of the solvent EtOAc was added. After filtration, the residue was purified by chromatography (200 g silica gel, 1:1 EtOAc–petroleum ether 1:1, R_f 0.51) to yield **18** (2.76 g, 12.8 mmol, 81%) as a yellow oil that was benzoylated in the next step without further purification. IR: *v* 3396 (OH), 2104 (N_3) cm^{-1}; 1H NMR (400 MHz): δ 1.32 (s, 3H, Me), 1.50 (s, 3H, Me′), 3.54 (d, 1H, OH), 3.58 (virtual d, 2H, H-5, H-5′), 4.22 (dd, 1H, H-3), 4.28 (virtual dt, 1H, H-4), 4.54 (d, 1H, H-2), 5.95 (d, 1H, H-1). $J_{1,2}$ 3.5, $J_{3,OH}$ 4.8, $J_{3,4}$ 2.9, $J_{4,5/5'}$ 6.3 Hz; ^{13}C NMR (101 MHz): δ 26.2 (Me), 26.8 (Me′), 49.3 (C-5), 74.8 (C-3), 78.9 (C-4), 85.4 (C-2), 104.9 (C-1), 111.9 (*C*Me_2).

3.10.2. 5-Azido-5-deoxy-1,2-*O*-isopropylidene-3-*O*-(4-nitrobenzoyl)-α-D-xylofuranose (19). A concentrated solution of 4-nitrobenzoyl chloride (1.50 g. 8.1 mmol) in dry pyridine was added to a cooled (−18 °C) solution of **18** (1.43 g, 6.6 mmol) in dry pyridine (40 mL). After 3 h the reaction mixture was poured onto ice (300 g) and extracted with $CHCl_3$ (4 × 80 mL each). After drying over $MgSO_4$, filtration and evaporation of the solvent, the residue was purified by chromatography (100 g silica gel, 4:1 petroleum ether–EtOAc, R_f 0.31) yielding **19** as a yellow syrup. Recrystallisation from EtOH–ether yielded **19** (1.16 g, 3.18 mmol, 48%) as yellow needles: mp 71 °C (ether–EtOH); $[\alpha]_D^{20}$ +11.9 (*c* 1.0, $CHCl_3$); IR: *v* 2141 (N_3), 1724 (C=O), 1525 (NO_2), 1345 (NO_2) cm^{-1}; 1H NMR (400 MHz): δ 1.36 (s, 3H, Me), 1.58 (s, 3 H, Me′), 3.57 (dd, 1H, H-5), 3.62 (dd, 1H, H-5′), 4.55 (ddd, 1H, H-4), 4.71 (d, 1H, H-2), 5.50 (d, 1H, H-3), 6.06 (d, 1H, H-1), 8.21 (ddd, 2H, ArH), 8.32 (ddd, 2H, ArH). $J_{1,2}$ 3.8, $J_{3,4}$ 3.0, $J_{4,5}$ 5.7, $J_{4,5'}$ 6.6, $J_{5,5'}$ 12.9, $^3J_{ArH,\ ArH}$ 9.0, $^4J_{ArH,\ ArH}$ 2.1, $^5J_{ArH,\ ArH}$ 2.1, $^4J_{ArH,\ ArH}$ 2.1 Hz; ^{13}C NMR (101 MHz): δ 21.2 (Me), 26.7 (Me′), 49.1 (C-5), 77.65 (C-3 or C-4), 77.68 (C-3 or C-4), 83.4 (C-2), 104.8 (C-1), 112.6 (*C*Me_2), 123.8 ($2CH_{Ar}$), 130.9 ($2CH_{Ar}$), 134.3 (C-1_{Ar}), 151.0 (C-4_{Ar}), 163.5 (C=O); EIMS: *m/z* (%) 349 (4) [$M^{+\cdot}-CH_3$], 308 (8), 279 (5), 250 (36), 151 (10), 150 (100) [O_2N-C_6H_4-C=O], 141 (7), 140 (7), 134 (5), 120 (7), 104 (35) [C_6H_4-C=O], 92 (10), 85 (13), 84 (11), 76 (16); FABMS: *m/z* 365 [M^++1], 349 [M^+-CH_3]; HRFABMS: Calcd for $C_{15}H_{17}N_4O_7$: 365.1097. Found: 365.1073. Anal. Calcd for $C_{15}H_{16}N_4O_7$: C, 49.45; H, 4.43; N, 15.38. Found: C, 49.42; H, 4.34; N, 15.26.

3.11. Preparation of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (21)

The reaction was carried out under N_2. Diisopropyl azodicarboxylate (1.1 mL, 5.56 mmol) and subsequently **20** (0.63 g, 2.86 mmol) were added to a solution of triphenylphosphine (1.49 g, 5.68 mmol) in dry pyridine (16 mL). After 90 min at 90 °C the solvent was evaporated, and the residue was filtered twice through silica gel (50 g each, EtOAc; R_f 0.68) to yield **21** (0.25 g, 1.23 mmol, 43%) as a colourless solid: mp 132 °C (EtOAc–petroleum ether), lit. mp 131 °C[16]. $[\alpha]_D^{20}$ −26.2 (*c* 1.0, $CHCl_3$); 1H NMR (500 MHz): δ 1.32 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 2.87 (dd, 1H, H-6), 2.99 (dd, 1H, H-6′), 3.28 (s, 1H, OH), 3.41 (ddd, 1H, H-5), 4.02 (dd, 1H, H-4), 4.27 (d, 1H, H-3), 4.52 (d, 1H, H-2), 5.98 (d, 1H, H-1). $J_{1,2}$ 3.7, $J_{3,4}$ 2.5, $J_{4,5}$ 4.8, $J_{5,6}$ 2.8, $J_{5,6'}$ 4.5, $J_{6,6'}$ 4.7 Hz; ^{13}C NMR (101 MHz): δ 26.1 (CH_3), 26.7 (CH_3), 46.1 (C-6), 50.1 (C-5), 75.1 (C-3), 79.6 (C-4), 85.1 (C-2), 105.0 (C-1), 111.9 (*C*Me_2); EIMS: *m/z* (%) 188 (7), 187 (73) [$M^{+\cdot}-CH_3$], 169 (2), 159 (2), 127 (16), 85 (15), 59 (100), 43 (82).

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 1223 336408; fax: +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk. Deposition numbers CCDC 142688 (**5**), 142685 (**19**), 227215 (**21**).

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References

1. (a) Voss, J.; Schulze, O.; Olbrich, F.; Adiwidjaja, G. *Phosphorus, Sulfur, Silicon* **1997**, *120–121*, 389–390; (b) Schulze, O.; Voss, J.; Adiwidjaja, G.; Olbrich, F. *Carbohydr. Res.* **2004**, *339*, 1787–1802.
2. Adiwidjaja, G.; Schulze, G.; Voss, J.; Wirsching, J. *Carbohydr. Res.* **2000**, *325*, 107–119.
3. Schulze, O.; Voss, J.; Adiwidjaja, G. *Synthesis* **2001**, 229–234.
4. Moravcová, J.; Rollin, P.; Lorin, C.; Gardon, V.; Čapková, J.; Mazáč, J. *J. Carbohydr. Chem.* **1997**, *16*, 113–127.
5. Thomé, M. A.; Giudicelli, M. B.; Picq, D.; Anker, D. *J. Carbohydr. Chem.* **1991**, *10*, 923–926.
6. Baker, B. R.; Schaub, R. E.; Williams, J. H. *J. Am. Chem. Soc.* **1955**, *77*, 7–12.
7. Wirsching, J.; Schulze, O.; Voss, J.; Giesler, A.; Kopf, J.; Adiwidjaja, G.; Balzarini, J.; De Clercq, E. *Nucleos. Nucleot. Nucl.* **2002**, *21*, 257–274.
8. Buchanan, J. G. *Methods Carbohydr. Chem.* **1972**, *6*, 135–141.
9. Kroutil, J.; Trnka, T.; Budesinsky, M.; Cerny, M. *Collect. Czech. Chem. Commun.* **1998**, *63*, 813–825.
10. (a) Unger, F. M.; Christian, R.; Waldstätten, P. *Tetrahedron Lett.* **1977**, *50*, 4383–4384; (b) Unger, F. M.; Christian, R.; Waldstätten, P. *Carbohydr. Res.* **1979**, *69*, 71–77.
11. (a) Paulsen, H.; Todt, K. *Adv. Carbohydr. Chem.* **1968**, *23*, 206–232; (b) Bozó, É.; Boros, S.; Kuczmann, J.; Gács-Baitz, E. *Carbohydr. Res.* **1996**, *290*, 159–173.
12. Becker, H. G. O. *Organikum*, 19th ed.; Johann Ambrosius Barth: Leipzig, 1993.
13. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. SIR-97*; A Package for Crystal Structure Solution by Direct Methods and Refinement*; Bari, Perugia: Rome, 1997.
14. Sheldrick, G. M. SHELXL-97*; Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, 1997.
15. Spek, A. L. PLATON*; A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, 1999.
16. Horita, K.; Yoshioka, T.; Tanaka, T.; Oikawa, Y.; Yonemitsu, O. *Tetrahedron* **1986**, *42*, 3021–3028.