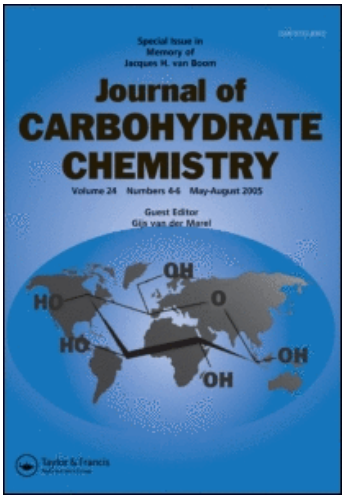

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Synthesis of *C*-Disaccharides An Unusual Ring Closure Reaction

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To cite this Article Khan, Abu T. , Sharma, Parijat and Schmidt, Richard R.(1995) 'Synthesis of *C*-Disaccharides An Unusual Ring Closure Reaction', Journal of Carbohydrate Chemistry, 14: 9, 1353 — 1367
To link to this Article: DOI: 10.1080/07328309508005416
URL: http://dx.doi.org/10.1080/07328309508005416

J. CARBOHYDRATE CHEMISTRY, 14(9), 1353-1367 (1995)

SYNTHESIS OF *C*-DISACCHARIDES
AN UNUSUAL RING CLOSURE REACTION

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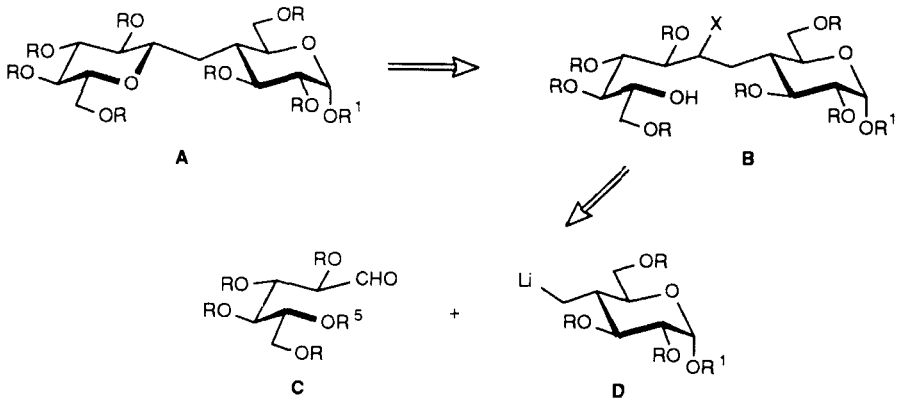
Received November 21, 1994 - Final Form July 27, 1995

ABSTRACT

Reaction of the 4-*C*-lithiomethyl intermediates, obtained from 4-deoxy-4-*C*-iodomethylglucopyranosides **5a,b**, with open-chain glucose derivative **8** afforded 4-deoxy-4-*C*-heptitylglucopyranosides **9a,b**. Mesylation of the newly generated hydroxy group and then desilylation gave **11a,b** which were subjected to ring closure under basic conditions. Surprisingly, no *C*-bridged cellobiosides **12a,b** (or, alternatively the corresponding maltosides) were obtained as major products; with loss of one benzyl alcohol residue the furanosides **13a,b** were preferentially formed. Their generation and structural assignment is discussed.

INTRODUCTION

C-Disaccharides (for instance **A** in Scheme 1) are interesting non-natural compounds.[1] They are close analogues of disaccharides in which the interglycosidic oxygen atom has been replaced by a methylene or a substituted methylene group. The conformations of methylene-bridged *C*-disaccharides seem to be similar to those of the corresponding *O*-disaccharides.[2] Therefore, as some of these types of compounds are thought to be able to affect the activity of glycosidases, mainly via competitive inhibition,[3,4] thus, their availability is highly desirable. A general interest in carbon-bridged disaccharides and modified derivatives has recently led to various methods for their synthesis.[1,2,5-15] Based on the ready access of heteroatom-stabilized 1-*C*-lithiated

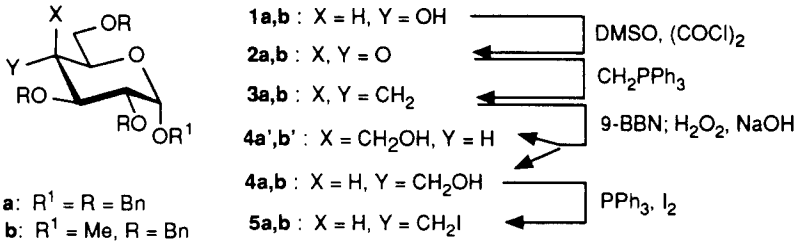


Scheme 1

glycals as C_6-nucleophiles[16] and *C*-formyl derivatives of sugars as C_7-electrophiles,[5] we have reported the diastereocontrolled synthesis of β(1-3)- and β(1-4)-connected *C*-disaccharides.[5] In a second approach we have employed a C_6-electrophile + C_7-nucleophile route.[17] A rigid $^1C_4$ conformer was selected as the C_7-nucleophile because the corresponding $^4C_1$-derived conformer exhibited interactions between the 6-oxygen and the newly formed anomeric center of the ketose moiety which was generated from gluconolactone as the C_6-electrophile.[17] We would like to report our strategy designed to circumvent this problem, i.e. employing open-chain sugar aldehydes (for instance **C**, Scheme 1) as C_6-electrophiles and *C*-lithiomethyl-branched sugars (**D**) as C_7-nucleophiles. Their reaction to give **B** and ensuing tetrahydropyran ring closure should provide the target molecules (for instance **A**, a cellobioside analog).

RESULTS AND DISCUSSION

For the generation of the required 4-*C* lithiomethylglucose derivative **D** we have chosen the 4-*C*-iodomethylglucose derivatives **5a,b** (Scheme 2) as starting materials. They can be easily prepared by slight modifications of procedures previously reported.[5] Thus, benzyl and methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranosides (**1a**,[18] and **1b**[18]) were converted to the corresponding 4-uloses **2a,b** by Swern oxidation.[19] Wittig reaction with methylene triphenylphosphorane furnished exocyclic methylene derivatives **3a,b**. Since hydroxylation of **3a,b** via addition of borane with the $BH_3 \cdot SMe_2$ complex proved to be



Scheme 2

neither regio- nor diastereoselective,[5] we used 9-borabicylo[3.3.1]nonane (9-BBN) for the hydroboration;[1] this reaction afforded after oxidation with H_2O_2 in the presence of NaOH a 3:1 and a 3:2 mixture of hydroxymethyl derivatives **4a/4a'**[5] and **4b/4b'**, respectively, in high overall yields and with high regioselectivity. These epimers were readily separated and the *gluco* isomers **4a,b** were converted into iodo derivatives **5a,b** by using triphenylphosphine/iodine.[11] The *galacto* isomers **4a',b'** can be also transformed into **4a,b** via oxidation, isomerisation, and then reduction, as previously reported.[5]

The required open-chain C_6-electrophile **8** (Scheme 2) was readily obtained from 2,3,4,6-tetra-*O*-benzyl-D-glucose diethyldithioacetal (**6**).[20] Reaction of **6** with *tert*-butyldimethylchlorosilane (TBDMS-Cl) in the presence of imidazole afforded 5-*O*-silyl protected **7** which was transformed into **8** by treatment with $HgCl_2/CdCO_3$ in an acetone-water mixture.

For the ligation of **5** and **8**, **5a,b** were first transformed into the *C*-lithiomethyl derivatives by treatment with *n*-butyllithium in THF at -90 °C; then addition of **8** and

raising the temperature to -50 °C afforded the desired compounds **9a,b** as single diastereoisomers (of unknown configuration). If excess *n*-butyllithium is employed elimination within **8** becomes an important side reaction. Reaction of **9a,b** with methanesulfonyl chloride (MsCl) in the presence of pyridine afforded 2b-*O*-mesyl derivatives **10a,b** and then treatment with tetra-*n*-butylammonium fluoride (TBAF) furnished 6b-*O*-deprotected compounds **11a,b**, which are ready for tetrahydropyran ring closure.

Compounds **11a,b** were treated with NaH in THF at 0 °C for cyclization (Table 1) providing 4-*C*-(3-heptulos-1-yl)glycopyranoside derivatives **13a,b** of unknown configuration at the anomeric 3b-center as the major products and the expected methylene-bridged *C*-disaccharides **12a,b** as the minor compounds. With potassium *tert*-butoxide as base, **11b** could be exclusively converted to **13b** (Table 1). Cyclization attempts with **11b** under different basic conditions finally led to a 2:3 ratio of **12b/13b** (Table 1). After chromatographic separation, hydrogenolytic *O*-debenzylation of **12b** was carried out affording known methylene bridged cellobiose analog **14b**[2] and, after *O*-acetylation, derivative **16b**, thus proving the structural assignments for **12a,b**. Hydrogenolytic debenzylation of **13a,b** afforded compounds **15a,b** which upon treatment with acetic anhydride in pyridine afforded the spirocyclic ketosides **17a,b**. The structural assignment of **13a,b** rests on their NMR data and the transformations into **15a,b** and **17a,b**. **13a,b** exhibits four protons originating from two vicinal methylene groups at δ_H 2.42-2.48 and at δ_H 1.62-1.66 for **15b** along with two methylene carbon atoms at δ_C 29.39 and 21.79. The structure of the spiro compound **17b** was determined by normal ^1H NMR, 2D-COSY, and HMBC experiments. We could prove the existence of the central 6-membered ring by a coupling of C-3b (quaternary) and H-3a measured by HMBC technique. H-3a appeared as a doublet of a doublet ($J_{3a,4a} = J_{2a,3a} = 10.0$ Hz) showing that ring closure occurred without affecting the conformation of the a-ring.

The preferred formation of **13a,b** over **12a,b** is presumably due to a conformational proximity effect in $\mathbf{B}^-$. The 6b-oxide oxygen is close to the 3b-hydrogen, thus favoring β-elimination to **E** and ensuing ring closure to a furanoside instead of the expected direct nucleophilic displacement of the 2b-mesylate group. Thus, interesting new types of complex branched sugars become accessible.

EXPERIMENTAL

General procedures. Melting points were determined in a metal block and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 250 MHz and 62.5 MHz, respectively, on a Bruker AC-250 spectrometer. Chloroform-d was used as the solvent

Table 1. Transformation of **11a,b** into **12a,b** and **13a,b** [a]

	Reaction conditions	12 + 13	12/13
11a	NaH, THF, 0 °C, 15 h	77%	1 : 10
11b	NaH, THF, 0 °C, 12 h	72%	1 : 14
11b	t-BuOK, C_6H_6, RT, 2 h	70%	only **13b**
11b	NaH, DMF, -40 °C, 10 h	65%	2 : 3

[a] For details, see experimental

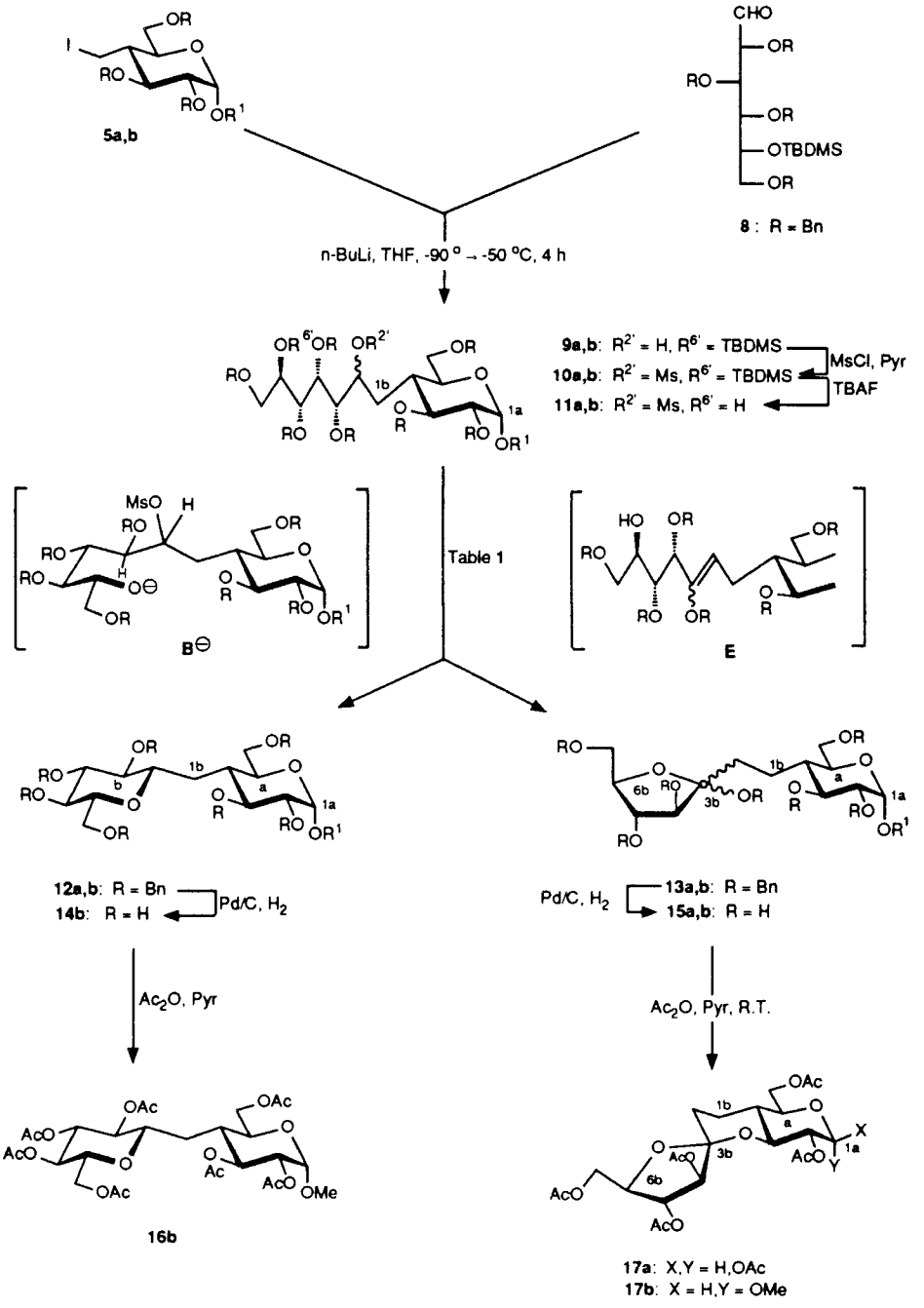
with tetramethylsilane as the internal standard (δ = 0.00 ppm), unless otherwise stated. Specific rotations were determined with a Perkin Elmer 241 MC polarimeter. Flash chromatography: silica gel 60 (J.T. Baker, 230-400 mesh ASTM) and TLC: DC-Plastikfolien, silica gel 60 F_{254} (Merck, layer thickness 0.2 mm), detection by UV light (254 nm) or by spraying with 5% $(NH_4)_2MoO_4$ and 0.1% $Ce(SO_4)_2$ in 10% H_2SO_4 and heating to 120 °C. Elemental analyses were performed by Heraeus Elementaranalysator (CHN-O-RAPID). All solvents were distilled before using.

Compounds **1a-5a** were synthesized as previously reported.[5] Compounds **1b-5b** were also prepared in the same manner.[5]

2,3,4,6-Tetra-*O*-benzyl-5-*tert*-butyldimethylsilyl-D-glucose Diethyldithioacetal (7). A mixture of 2,3,4,6-tetra-*O*-benzyl-D-glucose-diethyldithioacetal (**6**)[20] (6.7 g, 10.3 mmol), *tert*-butyldimethylchlorosilane (4.6 g, 30 mmol) and imidazole (2.8 g, 40 mmol) in dry dichloromethane (60 mL) was refluxed for 14 h. After the reaction was complete (TLC monitoring), the mixture was extracted with dichloromethane (100 mL) and the extract washed with water (2 x 50 mL). The extract was dried over $MgSO_4$, concentrated *in vacuo*, and the crude residue purified by flash column chromatography (ethyl acetate/petroleum ether, 1:9). Compound **7** was obtained after purification as a colourless oil (4.5 g, 58%), TLC [petroleum ether/ethyl acetate 9:1]: R_F 0.55; ^1H NMR (250 MHz, $CDCl_3$): δ 0.08 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.94 [s, 9H, $SiC(CH_3)_3$], 1.17, 1.26 (2t, 6H, SCH_2CH_3), 2.53-2.75 (2m, 4H, SCH_2CH_3), 3.63 (dd, 1H, H-5), 3.84-4.22 (m, 6H, H-1, H-2, H-3, H-4, H-6, H-6'), 4.50 (s, 2H, OCH_2Ph), 4.62-4.92 (m 6H, OCH_2Ph), 7.27-7.42 (m, 20H, PhH).

Anal. Calcd for $C_{44}H_{60}O_5S_2Si$ (761.2): C, 69.43; H, 7.95. Found: C, 69.22; H, 7.98.

2,3,4,6-Tetra-*O*-benzyl-5-*O*-*tert*-butyldimethylsilyl-D-glucose (8). To a mixture of **7** (2.5 g, 3.3 mmol), cadmium carbonate (3.5 g) in an acetone/water mixture (5:1, 60 mL) was added dropwise mercury (II) chloride (3.5 g) in acetone solution (10 mL). The



Scheme 3

resultant mixture was stirred for 1 h and then filtered through a bed of Celite followed by removal of the solvents under reduced pressure. The residue was extracted with chloroform (3 x 100 mL) and the organic phase washed several times with lukewarm water, dried ($MgSO_4$), concentrated *in vacuo*, and finally purified by flash chromatography. The compound was eluted with ethyl acetate/petroleum ether (1:6) to give **8** as a colourless syrupy liquid (1.6 g, 75%): R_F 0.35, ^1H NMR (250 MHz, $CDCl_3$): 0.05 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.90 [s, 9H, $SiC(CH_3)_3$], 3.55 (dd, 1H, H-6), 3.79 (dd, 1H, H-6'), 3.91-4.09 (m, 4H, H-2, H-3, H-4, H-5), 4.46-4.80 (m, 8H, OCH_2Ph), 7.17-7.31 (m, 20H, PhH), 9.63 (s, 1H, CHO).

Anal. Calcd for $C_{40}H_{50}O_6Si$ (654.9): C, 73.36; H, 7.70. Found: C, 72.93; H, 7.84.

Benzyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(3,4,5,7-tetra-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-D-*glycero*-D-*ido*- or -D-*gulo*-heptit-1-yl)-α-D-glucopyranoside (9a). A solution of benzyl 2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-(iodomethyl)-α-D-glucopyranoside **5a** (0.5 g, 0.75 mmol) in dry THF (20 mL) was taken into a 50 mL double jacketed low temperature flask under N_2 atmosphere and cooled to -90 °C. To this solution was added a solution of *n*-butyllithium (1.6 M, 0.450 mL, 0.72 mmol) at -90 °C. After 20 min a solution of **8** (0.492 g, 0.75 mmol) in dry THF (5 mL) was added dropwise at the same temperature and stirring was continued for another 3 h. Then the temperature was raised to -50 °C and stirred for 1 h. The reaction mixture was quenched by adding saturated ammonium chloride solution (10 mL) and extracted with diethyl ether (2 x 100 mL), washed with water (50 mL), and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residual crude mass was purified by flash chromatography (petroleum ether/ethyl acetate, 8.7:1.3) to give **9a** as a colourless oily liquid (0.359 g, 40%): R_F 0.45, $[\alpha]_D$ +38.8 ° (*c* 1.1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ - 0.02 (s, 3H, $SiCH_3$), 0.027 (s, 3H, $SiCH_3$), 0.848 [s, 9H, $SiC(CH_3)_3$], 1.22-1.25 (m, 1H, H-1'a), 1.65-1.75 (m, 1H, H-1'b), 1.90-2.05 (m, 1H, H-4), 2.84 (d, 1H, J = 5.4 Hz, OH, D_2O-exchangeable), 3.42 (dd, 1H, J = 2.5, J = 5.9 Hz, H-3'), 3.49-3.56 (m, 4H, H-2, H-6a, H-6b and H-7'b), 3.65 (ddd, 1H, J = 10.9 Hz, H-5), 3.77-3.87 (m, 4H, H-3, H-4', H-5', H-7'a), 3.91 (dd, 1H, J = 5.5, J = 5.6 Hz, H-2'), 4.18 (ddd, 1H, J = 3.1, J = 3.2, J = 9.4 Hz, H-6'), 4.40-4.77 (m, 15 H, OCH_2Ph), 4.88 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.00 (d, 1H, J = 11.3 Hz, CHPh), 7.12-7.43 (m, 40 H, PhH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 139.00, 138.89, 138.70, 138.48, 138.39, 138.17, 138.12, 137.49, 128.22, 128.15, 128.12, 127.83, 127.68, 127.57, 127.52, 127.43, 127.36, 127.32, 127.25, 127.16, 95.32, 82.65, 81.79, 81.56, 79.63, 79.52, 74.74, 74.42, 74.34, 73.90, 73.64, 73.33, 73.26, 73.16, 72.46, 72.20, 71.42, 70.39, 69.27, 68.72, 39.34, 33.69, 25.93, 18.06.

Anal. Calcd for $C_{75}H_{88}O_{11}Si$ (1193.5): C, 75.47; H, 7.43. Found: C, 75.05; H, 7.61.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(3,4,5,7-tetra-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-D-*glycero*-D-*ido*- or -D-*gulo*-heptit-1-yl)-α-D-glucopyranoside (9b). To a solution of methyl 2,3,6-tri-*O*-benzyl-4-deoxy-4-*C*-(iodomethyl)-α-D-glucopyranoside **5b** (0.294 g, 0.5 mmol) in dry THF (15 mL) was added a solution of *n*-butyllithium (1.6 M in hexane, 0.3 mL, 0.48 mmol) dropwise at -90 °C under N_2 atmosphere. After stirring for 20 min a solution of **8** (0.321 g, 0.5 mmol) in dry THF (5 mL) was added slowly. The reaction mixture was stirred for 3 h at -90 °C and then the temperature was raised to -50 °C. Stirring was continued for 1 h, then the reaction was quenched by adding saturated ammonium chloride solution (10 mL) and extracted with diethyl ether (2 x 75 mL). The organic layer was washed with water (40 mL) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue purified by flash chromatography with petroleum ether/ethyl acetate (8.5:1.5) to yield 0.290 g (52%) of **9b** as a colourless oil. R_F 0.42, $[\alpha]_D$ +13.2 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ -0.015 (s, 3H, $SiCH_3$), 0.029 (s, 3H, $SiCH_3$), 0.854 [s, 9H, $SiC(CH_3)_3$], 1.20-1.30 (m, 1H, H-1'a), 1.65-1.80 (m, 1H, H-1'b), 1.90-2.10 (m, 1H, H-4), 2.82 (d, 1H, J = 5.4 Hz, OH, D_2O exchangeable), 3.36 (s, 3H, OCH_3), 3.42 (dd, 1H, J = 2.4, J = 5.9 Hz, H-3'), 3.48-3.58 (m, 4H, H-2, H-6a, H-6b, H-7'b), 3.60 (ddd, 1H, H-5), 3.72-3.82 (m, 4H, H-3, H-4', H-5', H-7'a), 3.89 (dd, 1H, J = 5.3, J = 5.5 Hz, H-2'), 4.17 (ddd, 1H, J = 3.0, J = 3.2, J = 9.2 Hz, H-6'), 4.37-4.77 (m, 14H, OCH_2Ph, H-1), 4.98 (d, 1H, J = 11.4 Hz, -CHPh), 7.12-7.33 (m, 35 H, PhH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 139.01, 138.88, 138.68, 138.45, 138.40, 138.20, 138.08, 128.31, 128.22, 128.15, 128.11, 128.02, 127.85, 127.77, 127.71, 127.66, 127.58, 127.51, 127.40, 127.35, 127.31, 127.23, 127.18, 98.15, 82.67, 81.91, 81.60, 79.66, 79.50, 74.71, 74.56, 74.37, 73.90, 73.63, 73.35, 73.16, 72.70, 72.45, 71.00, 70.44, 69.30, 55.09, 39.47, 33.55, 25.93, 18.07.

Anal. Calcd for $C_{69}H_{84}O_{11}Si$ (1117.5): C, 74.15; H, 7.58. Found: C, 74.14; H, 7.70.

Benzyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(3,4,5,7-tetra-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-mesyl-D-*glycero*-D-*ido*- or -D-*gulo*-heptit-1-yl)-α-D-glucopyranoside (10a). To a solution of alcohol **9a** (0.378 g, 0.317 mmol) in dry dichloromethane (10 mL) at ice-bath temperature was added dry pyridine (1 mL) and distilled mesyl chloride (0.2 mL, 2.6 mmol). After removing the ice-bath the reaction mixture was stirred for 12 h at room temperature. Then it was extracted with dichloromethane (2 x 50 mL), washed with 1.5 N hydrochloric acid solution (2 x 20 mL) to remove pyridine and finally washed with water (50 mL). The organic extract was dried over $MgSO_4$ and concentrated *in vacuo* to give 0.380 g (95%) of the crude residue of **10a** which was used directly for the

next step. Only a small amount of the crude residue was purified for characterization because it undergoes decomposition during chromatography. The desired compound **10a** was eluted with petroleum ether/ethyl acetate (3:1). R_F 0.5, $[\alpha]_D$ +39.6 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ -0.005 (s, 3H, $SiCH_3$), 0.033 (s, 3H, $SiCH_3$), 0.857 [s, 9H, $SiC(CH_3)_3$], 1.90-2.05 (m, 3H, H-1'a, H-1'b, H-4), 2.84 (s, 3H, OSO_2CH_3), 3.42-3.60 (m, 5H, H-2, H-5, H-6a, H-7'a, H-7'b), 3.67 (dd, 1H, J = 4.9, J = 9.9 Hz, H-6'a), 3.78-3.92 (m, 4H, H-3, H-6b, H-4', H-5'), 4.08-4.15 (m, 1H, H-3'), 4.37-4.70 (m, 15H, OCH_2Ph), 4.90 (d, 1H, J = 3.4 Hz, H-1), 5.05 (d, 1H, J = 11.8 Hz, CHPh), 5.20-5.30 (m, 1H, H-2'), 7.05-7.42 (m, 40H, PhH).

Anal. Calcd for $C_{76}H_{90}O_{13}SSi$ (1271.6): C, 71.78; H, 7.13. Found: C, 71.62; H, 7.27.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(3,4,5,7-tetra-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-mesyl-D-*glycero*-D-*ido*- or -D-*gulo*-heptit-1-yl)-α-D-glucopyranoside (10b). To a solution of **9b** (0.430 g, 0.385 mmol) in dry dichloromethane (10 mL) was added dry pyridine (1 mL) and distilled mesyl chloride (0.2 mL, 2.6 mmol) at 0 °C. The mixture was stirred for 12 h at room temperature, extracted with dichloromethane (2 x 50 mL), the extract washed with 1.5 N HCl solution (2 x 20 mL), then with water (2 x 20 mL), and dried ($MgSO_4$). Removal of solvents gave the crude product **10b** (0.450 g, 98%) which was used directly in the next step. ^1H NMR (250 MHz, $CDCl_3$): δ -0.007 (s, 3H, $SiCH_3$), 0.028 (s, 3H, $SiCH_3$), 0.855 [s, 9H, $SiC(CH_3)_3$], 1.90-2.05 (m, 3H, H-1'a, H-1'b, H-4), 3.43-3.60 (m, 5H, H-2, H-5, H-6a, H-7'a, H-7'b), 3.68 (dd, 1H, J = 4.6, J = 10.4 Hz, H-6'a), 3.75-3.95 (m, 4H, H-3, H-6b, H-4', H-5'), 4.08-4.15 (m, 1H, H-3'), 4.35-4.72 (m, 14H, OCH_2Ph, H-1), 5.04 (d, 1H, J = 11.8 Hz, CHPh), 5.20-5.30 (m, 1H, H-2'), 7.05-7.32 (m, 35H, PhH).

Benzyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(3,4,5,7-tetra-*O*-benzyl-2-*O*-mesyl-D-*glycero*-D-*ido*- or -D-*gulo*-heptit-1-yl)-α-D-glucopyranoside (11a). A solution of **10a** (0.180 g, 0.148 mmol) in dry THF (10 mL) was treated with tetra-*n*-butylammonium fluoride (0.187 g, 0.595 mmol) and stirred for 3 h at room temperature. The reaction mixture was extracted with diethyl ether (2 x 50 mL), washed with water (20 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue purified by flash chromatography with petroleum ether/ethyl acetate (2:1) to afford 0.120 g (70%) of **11a** as a colourless oil. R_F 0.4, $[\alpha]_D$ 48.9 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 1.80-2.10 (m, 3H, H-1'a, H-1'b, H-4), 2.89 (s, 3H, OSO_2CH_3), 2.95 (d, 1H, J = 4.1 Hz, OH, D_2O exchangeable), 3.49-3.51 (4H, H-5, H-6a, H-7'a, H-7'b), 3.60 (dd, 1H, $J_{1,2}$ = 3.3, $J_{2,3}$ = 9.7 Hz, H-2), 3.67 (dd, 1H, $J_{5',6'}$ = 4.1, $J_{6',7'}$ = 7.6 Hz, H-6'), 3.78 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, H-3), 3.86-3.90 (m, 3H, H-6b, H-4', H-5'), 3.98 (dd, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 3.8 Hz, H-3'), 4.28-4.71 (m, 15H, OCH_2Ph), 4.90 (d, 1H, J = 3.5 Hz, H-1), 5.10 (d, 1H, J = 11.9 Hz, CHPh), 5.25-5.29 (m, 1H, H-2'), 7.06-7.41 (m, 40H, PhH).

Anal. Calcd for $C_{70}H_{76}O_{13}S$ (1157.3): C, 72.64; H, 6.62. Found: C, 72.31; H, 6.78.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-4-*C*-(3,4,5,7-tetra-*O*-benzyl-2-*O*-mesyl-D-*glycero*-D-*ido*- or -D-*gulo*-heptit-1-yl)-α-D-glucopyranoside (11b). The compound **10b** (0.450 g) which was obtained after mesylation was dissolved in dry THF (10 mL) and tetra-*n*-butylammonium fluoride (0.350 g, 1.1 mmol). The mixture was stirred for 3 h at room temperature, extracted with diethyl ether (2 x 50 mL), and the extract washed with water (20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the crude residue was purified by flash chromatography (petroleum ether/ethyl acetate 2:1) to provide 0.295 g (70%) of compound **11b** as a colourless oil. R_F 0.41, $[\alpha]_D$ 38.1 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 1.80-2.10 (m, 3H, H-1'a, H-1'b, H-4), 2.90 (s, 3H, OSO_2CH_3), 2.95 (brs, 1H, OH, D_2O exchangeable), 3.35 (s, 3H, OCH_3), 3.47-3.60 (m, 5H, H-2, H-5, H-6a, H-7'a, H-7'b), 3.60-3.87 (m, 3H, H-6b, H-4', H-5'), 3.88-3.96 (m, 2H, H-6', H-3), 3.99 (dd, 1H, $J_{2',3'} = J_{3',4'} = 3.8$ Hz, H-3'), 4.28-4.70 (m, 14H, OCH_2Ph, H-1), 5.08 (d, 1H, J = 11.8 Hz, -CHPh), 5.25-5.29 (m, 1H, H-2'), 7.09-7.34 (m, 35H, PhH).

Anal. Calcd for $C_{64}H_{72}O_{13}S$ (1081.2): C, 71.09; H, 6.71. Found: 71.03; H, 6.89.

Benzyl 4-*C*-(2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-D-*glycero*-D-*gulo*-heptit-1-yl)-2,3,6-tri-*O*-benzyl-4-deoxy-α-D-glucopyranoside (12a) and Benzyl 4-*C*-(benzyl 4,5,7-tri-*O*-benzyl-1,2-dideoxy-α- or -β-D-*arabino*-3-heptulofuranosid-1-yl)-2,3,6-tri-*O*-benzyl-4-deoxy-α-D-glucopyranoside (13a). To a solution of **11a** (0.120 g, 0.104 mmol) in dry THF (10 mL) was added sodium hydride (50% in oil, 0.006 g, 0.125 mmol) at 0 °C and stirred for 12 h. The reaction was quenched by adding a piece of ice and extracted with diethyl ether (2 x 50 mL); the extract was washed with brine (25 mL) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography (petroleum ether/ethyl acetate 3:1). First **12a** (0.010 g, ~ 9%) and then **13a** (0.075 g, 68%) were eluted. **12a**, R_F 0.50, $[\alpha]_D$ +39.9 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 1.35-1.44 (m, 1H, H-1b), 2.1-2.3 (m, 2H, H-1'b, H-4a), 3.09 (dd, 1H, $J_{2b,3b} = J_{3b,4b} = 8.8$ Hz, H-3b), 3.21 (dd, 1H, H-5b), 3.38 (dd, 1H, $J_{1b,2b} = 9.0$, $J_{2b,3b} = 9.9$ Hz, H-2b), 3.45-3.60 (m, 6H, H-2a, H-6'a, H-4b, H-6b, H-7b, H-7'b), 3.72 (dd, 1H, $J_{5a,6a} = 3.6$, $J_{6a,6a'} = 10.8$ Hz, H-6a), 3.85 (dd, 1H, $J_{2a,3a} = 9.6$, $J_{3a,4a} = 9.9$ Hz, H-3a), 4.08 (dd, 1H, $J_{5a,6a} = 10$ Hz, H-5a), 4.40-4.45 (m, 12H, OCH_2Ph), 4.80-5.00 (m, 5H, OCH_2Ph, H-1a), 7.09-7.39 (m, 40H, PhH). ^{13}C NMR (62.5 Hz, $CDCl_3$): δ 138.96, 138.62, 138.47, 138.37, 138.32, 138.24, 137.44, 128,53, 128.33, 128.27, 128.21, 128.13, 127.95, 127.77, 127.76, 127.69, 127.66, 127.61, 127.48, 127.43,

127.14, 95.15, 87.35, 82.71, 81.78, 78.70, 78.45, 77.18, 75.48, 75.11, 74.76, 74.65, 73.43, 73.23, 72.32, 70.79, 70.00, 69.20, 68.23, 40.38, 28.14.

Anal. Calcd for $C_{69}H_{72}O_{11}$ (1061.3): C, 78.08; H, 6.84. Found: C, 78.07; H, 7.23.

13a: R_F 0.40, $[\alpha]_D$ +29.6 ° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.99-2.07 (m, 1H, H-4a), 2.42-2.48 (m, 3H), 3.48-3.58 (m, 5H, H-2a, H-6a, H-6'a), 3.71 (dd, 1H, J = 4.6, J = 6.5 Hz), 3.80-3.94 (m, 3H, H-3a, H-5a), 4.04 (dd, 1H, J ≈ 1, J = 4.5 Hz), 4.30-4.80 (m, 15H, OCH_2Ph), 4.89 (d, 1H, $J_{1a,2a}$ = 3.5 Hz, H-1a), 5.00 (m, 1H, J = 11.1 Hz, CHPh), 5.17 (ddd, 1H, J ≈ 1, J = 6.5, J = 7.0 Hz), 7.19-7.39 (m, 40 H, PhH).

Anal. Calcd for $C_{69}H_{72}O_{11}$(1061.3): C, 78.08; H, 6.83. Found: C, 78.31; H, 6.82.

Methyl 4-*C*-(2,6-Anhydro-3,4,5,7-tetra-*O*-benzyl-1-deoxy-D-*glycero*-D-*gulo*-heptit-1-yl)-2,3,6-tri-*O*-benzyl-4-deoxy-α-D-glucopyranoside (12b) and Methyl 4-*C*-(benzyl 4,5,7-tri-*O*-benzyl-1,2-dideoxy-α- or β-D-*arabino*-3-heptulofuranosid-1-yl)-2,3,6-tri-*O*-benzyl-4-deoxy-α-D-glucopyranoside (13b). To a solution of **11b** (0.215 g, 0.199 mmol) in dry THF (15 mL) was added sodium hydride (50% in oil, 0.012 g, 0.239 mmol) at 0 °C and stirred for 15 h. Excess sodium hydride was destroyed by adding a piece of ice and extracted with diethyl ether (2 x 75 mL). The organic layer was washed with brine (20 mL) and dried ($MgSO_4$). Removal of the solvent gave an oily liquid which was purified by flash chromatography (petroleum ether/ethyl acetate 3:1). First **12b** (0.009 g, ~ 5%) and then **13b** (0.130 g, 67%) were eluted. **12b**: R_F 0.669, $[\alpha]_D$ +19.2 ° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.32-1.42 (m, 1H, H-1b), 2.16-2.24 (m, 2H, H-1'b, H-4a), 3.10 (dd, 1H, $J_{2b,3b} = J_{3b,4b}$ = 8.8 Hz, H-3b), 3.26 (s, 3H, OCH_3), 3.35 (dd, 1H, $J_{1b,2b}$ = 9.4, $J_{2b,3b}$ = 8.9 Hz, H-2b), 3.55-3.65 (m, 7H, H-2a, H-6a, H-4b, H-5b, H-6b, H-7b, H-7'b), 3.70 (dd, 1H, $J_{5a,6a}$ = 3.3, $J_{6a,6'a}$ = 10.5 Hz, H-6'a), 3.77 (dd, 1H, $J_{2a,3a}$ = 9.3, $J_{3a,4a}$ = 9.8 Hz, H-3a), 4.02 (d, 1H, J = 11.8 Hz, H-5a), 4.40-4.80 (m, 14H, OCH_2Ph, H-1a), 4.95 (d, 1H, J = 11.8 Hz, CHPh), 7.10-7.32 (m, 35H, PhH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 138.94, 138.66, 138.47, 138.36, 138.31, 138.28, 128.36, 128.29, 128.23, 128.18, 128.14, 127.86, 127.81, 127.69, 127.63, 127.49, 127.21, 98.25, 87.37, 82.89, 82.09, 78.79, 78.57, 77.20, 75.50, 75.14, 74.83, 73.48, 73.27, 72.83, 70.45, 70.05, 69.32, 54.78, 40.40, 28.20. MS (FAB): 984 (M^+), 953 (M^+ - OCH_3)

13b: R_F 0.365, $[\alpha]_D$ -3.2 ° (*c* 1, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.95-2.07 (m, 1H, H-4a), 2.46-2.48 (m, 3H), 3.30 (s, 3H, OCH_3), 3.50-3.61 (m, 5H, H-2a, H-6a, H-6'a), 3.71-3.94 (m, 3H, H-3a, H-5a), 4.04 (dd, 1H, J ≈ 1, J = 4.5 Hz), 4.30-4.80 (m, 13H, OCH_2Ph), 4.61 (d, 1H, $J_{1a,2a}$ = 3.7 Hz, H-1a), 5.00 (d, 1H, J = 11.1 Hz, CHPh), 5.14 (ddd, 1H, J ≈ 1, J = 6.7, J = 7.3 Hz), 7.19-7.35 (m, 35H, PhH).

Anal. Calcd for $C_{63}H_{68}O_{11}$ (985.2): C, 76.80; H, 6.96. Found: C, 76.42; H, 7.07.

Methyl 4-*C*-(2,6-Anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptit-1-yl)-4-deoxy-α-D-glucopyranoside (14b). A mixture of compound **12b** (0.035 g, 0.030 mmol) and 10% palladium on charcoal (10 mg) in dioxane/methanol (1:1, 8 mL) was stirred vigorously under hydrogen at normal pressure. The reaction was over after 8 h and the catalyst was filtered off. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (chloroform/methanol 1:1) to provide **14b** (0.011 g, 88%) as a colourless oil. R_F 0.30, $[\alpha]_D$ +57.2 ° (*c* 1, methanol) [Ref.:[2] $[\alpha]_D$ +63.2 ° (*c* 0.5, methanol)]; ^{1}H NMR (250 MHz, MeOH-d^4): δ 1.58 (ddd, 1H, J = 3.4, 9.2, 14.9 Hz, H-1b), 1.72 (m, 1H, H-4a), 2.07 (dd, 1H, J = 4.6, 14.9 Hz, H-1'b), 3.05 (dd, 1H, $J_1 = J_2 = 9$ Hz), 3.21 (dd, 1H, J = 4.7, 8.2 Hz), 3.30 (s, 3H, OCH_3), 3.34-3.41 (m, 4H), 3.51-3.73 (m, 4H), 3.80-3.85 (m, 2H), 4.69 (d, 1H, $J_{1a,2a}$ = 3.6 Hz, H-1a); the ^{1}H NMR data are in agreement with those reported.[2] ^{13}C NMR (62.5 MHz, MeOH-d^4): δ 101.42, 81.79, 79.62, 78.95, 75.40, 74.94, 74.20, 72.42, 72.09, 63.69, 63.21, 55.36, 41.44, 30.25. MS (FAB + NaCl): 377 (M + Na), 355 (MH^+), 323 $(M\text{-}OCH_3)^+$.

Methyl 2,3,6-Tri-*O*-acetyl-4-*C*-(2,6-anhydro-3,4,5,7-tetra-*O*-acetyl-1-deoxy-D-*glycero*-D-*gulo*-heptit-1-yl)-4-deoxy-α-D-glucopyranoside (16b). To a solution of **14b** (0.008 g, 0.02 mmol) in dry pyridine (1 mL) was added acetic anhydride (0.5 mL). After 12 h at room temperature, the reaction mixture was concentrated with toluene (3 x 15 mL) to remove excess pyridine and acetic anhydride. The crude residue was purified by flash chromatography with petroleum ether/ethyl acetate (2:3) to provide 12 mg (78%) of **16b** as a colourless oil. R_F 0.5, $[\alpha]_D$ +34.8 ° (*c* 0.9, chloroform); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.54 (dd, 2H, J = 4.3, 7.2 Hz, H-1b, H-1'b), 1.95-2.08 (m, 1H, H-4a), 1.95 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.99 (s, 6H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 3.37 (s, 3H, OCH_3), 3.52 (ddd, 1H, $J_{1b,2b}$ = 4.7, $J_{2b,3b}$ = 9.4 Hz, H-2b), 3.60 (ddd, 1H, $J_{6b,7b}$ = 4.5, $J_{7b,7'b}$ = 12.2, $J_{5b,6b}$ = 9.8 Hz, H-6b), 4.05-4.20 (m, 4H, H-5a, H-6a, H-6'a, H-7b), 4.30 (dd, 1H, $J_{6b,7'b}$ = 2, $J_{7b,7'b}$ = 12.1 Hz, H-7b), 4.75 (dd, 1H, $J_{2b,3b} = J_{3b,4b}$ = 9.3 Hz, H-3b), 4.80 (dd, 1H, $J_{1a,2a}$ = 3.65, $J_{2a,3a}$ = 9.6 Hz, H-2a), 4.88 (d, 1H, $J_{1a,2a}$ = 3.65 Hz, H-1a), 4.98 (dd, 1H, $J_{4b,5b} = J_{5b,6b}$ = 9.8 Hz, H-5b), 5.12 (dd, 1H, $J_{3b,4b} = J_{4b,5b}$ = 9.3 Hz, H-4b), 5.35 (dd, 1H, $J_{2a,3a}$ = 9.7 Hz, $J_{3a,4a}$ = 11.1 Hz, H-3a). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 170.60, 170.45, 170.31, 170.14, 169.88, 169.56, 169.43, 97.20, 75.52, 74.95, 74.16, 72.79, 72.22, 68.80, 68.33, 68.48, 63.83, 62.13, 55.25, 39.58, 27.94, 20.76, 20.61, 20.58, 20.55. MS: m/e 648 (M^+), m/e 617 (M^+, -OMe), m/e 529 (base peak)

4-*C*-(1,2-Dideoxy-D-*arabino*-3-heptulofuranos-1-yl)-4-deoxy-D-glucopyranose (15a) and 4-*C*-(1,4,5,7-Tetra-*O*-acetyl-1,2-dideoxy-α- or -β-D-*arabino*-3-

heptulofuranos-1-yl)-1,2,3,6-tetra-*O*-acetyl-4-deoxy-D-glucopyranose (17a). A mixture of **13a** (0.075 g, 0.071 mmol) and 10% palladium on carbon (40 mg) in dioxane/methanol (1:1, 8 mL) was stirred vigorously under hydrogen at normal pressure. The reaction was monitored by TLC. After 16 h the catalyst was filtered off and the solvent was evaporated *in vacuo*. The crude product (**15a**) [TLC (chloroform/methanol, 5:1) R_F = 0.47] was dissolved in acetic anhydride (5 mL) and pyridine (5 mL). The reaction mixture was stirred for 12 h. After evaporation of the solvents, flash chromatography with petroleum ether/ethyl acetate (1:2) gave 35 mg (88%) of **17a** as a colourless oil, (α:β, 1:1), R_F 0.5, $[\alpha]_D$ +65.9 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 1.55-1.87 (m, 10H, H-1b, H-1'b, H-2b, H-2'b, H-4a), 2.03 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.09 (s, 6H, $COCH_3$), 2.10 (s, 6H, $COCH_3$), 2.11 (s, 6H, $COCH_3$), 2.12 (s, 6H, $COCH_3$), 2.17 (s, 3H, $COCH_3$), 3.54-3.86 (m, 4H, H-5a, H-3a), 4.00-4.29 (m, 8H, H-6b, H-7'b, H-6a, H-6'a), 4.40 (dd, 2H, $J_{6b,7b}$ = 3.8, $J_{7b,7'b}$ = 12 Hz, H-7b), 4.88-5.00 (m, 4H, H-5b, H-2a), 5.15 (d, 2H, $J_{4b,5b}$ = 1.4 Hz, H-4b), 5.68 (d, 1H, $J_{1a,2a}$ = 8.2 Hz, H-1aβ), 6.32 (d, 1H, $J_{1a,2a}$ = 3.7 Hz, H-1aα). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 170.71, 170.46, 170.44, 169.92, 169.49, 169.19, 169.11, 169.03, 168.99, 168.97, 105.66, 105.41, 92.38, 90.22, 81.39, 81.21, 79.12, 79.05, 78.41, 78.37, 77.20, 74.87, 72.40, 71.74, 70.71, 69.59, 68.52, 63.24, 62.99, 62.79, 38.94, 38.66, 27.31, 26.98, 20.95, 20.86, 20.71, 20.58. MS: m/e 574 (M^+), m/e 515, m/e 170 (base peak).

Methyl 4-*C*-(1,2-Dideoxy-D-*arabino*-3-heptulofuranos-1-yl)-4-deoxy-α-D-glucopyranoside (15b). A mixture of **13b** (0.120 g, 0.122 mmol) and 10% palladium on carbon (40 mg) in dioxane/methanol (1:1, 8 mL) was stirred vigorously under hydrogen at normal pressure. The reaction was over after 20 h, the catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography with chloroform/methanol (8.5:1.5) to furnish **15b** (0.040 g, 93%) as an amorphous solid, mp 132-133 °C. R_F 0.416, $[\alpha]_D$ +109.3 ° (*c* 1, methanol); ^1H NMR (400 MHz, MeOH-d^4): δ 1.52-1.58 (m, 2H, $-CH_2$), 1.62-1.66 (m, 2H, $-CH_2$), 1.84-1.87 (m, 1H, H-4a), 3.39 (s, 3H, OCH_3), 3.46-3.47 (m, 1H), 3.53-3.59 (m, 2H), 3.63-3.68 (m, 2H), 3.73-3.84 (m, 3H), 3.86-3.94 (m, 2H), 4.74 (d, 1H, $J_{1a,2a}$ = 3.6 Hz, H-1a). ^{13}C NMR (62.5 MHz, MeOH-d^4): δ 107.77, 101.57, 84.90, 84.67, 80.74, 73.53, 72.68, 72.33, 63.14, 62.59, 55.44, 40.51, 29.34, 21.79.

Anal. Calcd for $C_{14}H_{26}O_{10}$ (354.3): C, 47.45; H, 7.40. Found: C, 47.30; H, 7.08.

Methyl 4-*C*-(3,4,5,7-Tetra-*O*-acetyl-1,2-dideoxy-α- or -β-D-*arabino*-3-heptulofuranos-1-yl)-2,3,6-tri-*O*-acetyl-4-deoxy-α-D-glucopyranoside (17b). To a solution of **15b** (0.035 g, 0.099 mmol) in dry pyridine (3 mL) was added acetic anhydride (3 mL). The reaction mixture was stirred for 12 h at room temperature. Evaporation and then flash chromatography (petroleum ether/ethyl acetate 1:2) afforded

16b (0.058 g, 94%) as an amorphous powder, mp 55-56 °C, R_F 0.35, $[\alpha]_D$ +121.1 ° (*c* 1, chloroform); ^1H NMR (250 MHz, $CDCl_3$): δ 1.54-1.70 (m, 4H, H-1b, H-1'b, H-2b, H-2'b), 1.75-1.81 (m, 1H, H-4a), 2.03 (s, 3H, $COCH_3$), 2.06 (s, 9H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 3.37 (s, 3H, OCH_3), 3.67 (ddd, 1H, $J_{5a,6a}$ = 4.2, $J_{4a,5a}$ = 8.6, $J_{5a,6'a}$ = 10 Hz, H-5a), 4.02 (dd, 1H, $J_{2a,3a}$ = 8.3, $J_{3a,4a}$ = 9.4 Hz, H-3a), 4.06 (ddd, 1H, $J_{6b,7b}$ = 3.6, $J_{5b,6b}$ = 5.0 Hz, H-6b), 4.14-4.21 (m, 3H, H-6a, H-6'a, H-7'b), 4.37 (dd, 1H, $J_{6b,7b}$ = 3.5, $J_{7b,7'b}$ = 11.9 Hz, H-7b), 4.86 (dd, 1H, $J_{4b,5b}$ = 1Hz, H-5b), 4.89 (dd, 1H, $J_{1a,2a}$ = 3.6, $J_{2a,3a}$ = 8.1 Hz, H-2a), 4.92 (d, 1H, $J_{1a,2a}$ = 3.6 Hz, H-1a), 5.04 (d, 1H, $J_{4b,5b}$ = 1 Hz, H-4b). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 170.75, 170.48, 169.93, 169.90, 169.15, 105.37, 97.65, 81.55, 78.85, 78.42, 71.22, 69.00, 68.74, 63.15 (CH_2), 63.07 (CH_2), 55.16, 39.61, 27.36 (CH_2), 20.89, 20.74, 20.70 (CH_2), 20.61.

Anal. Calcd for $C_{24}H_{34}O_{14}$ (546.5): C, 52.74; H, 6.27. Found: C, 52.89; H 6.34.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. A.T.K. and P.S. are grateful for stipends from the Alexander von Humboldt Foundation. We would like to thank Dr. A. Geyer and Dr. K.-H. Jung for their help in the structural assignments.

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