

Syntheses of β -C(1 $\rightarrow$ 3)-Glucopyranosides of 2- and 4-Deoxy-D-hexoses

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The *Oshima–Nozaki* (Et_2AlI) condensation of isolevoglucosenone (**4**) with 2,6-anhydro-3,4,5,7-tetra-*O*-benzyl-D-glycero-D-gulo-heptose (**5**) gave an enone **6** that was converted with high stereoselectivity to 3-*C*-[(1*R*)-2,6-anhydro-D-glycero-D-gulo-heptitol-1-*C*-yl]-2,3-dideoxy-D-arabino-hexose (**1**; 1:1 mixture of α - and β -D-pyranose), and to 3-*C*-[(1*R*)-2,6-anhydro-D-glycero-D-gulo-heptitol-1-*C*-yl]-2,3-dideoxy-D-lyxo-hexose (**2**; 2.7:1.4:1.0:1.4 mixture of α -D-furanose, β -D-furanose, α -D-pyranose, and β -D-pyranose). The *Oshima–Nozaki* (Et_2AlI) condensation of levoglucosenone (**17**) with aldehyde **5** gave an enone **18** that was converted with high stereoselectivity to 3-*C*-[(1*R*)-2,6-anhydro-D-glycero-D-gulo-heptitol-1-*C*-yl]-3,4-dideoxy- α -D-arabino-hexopyranose (**3**; single anomer).

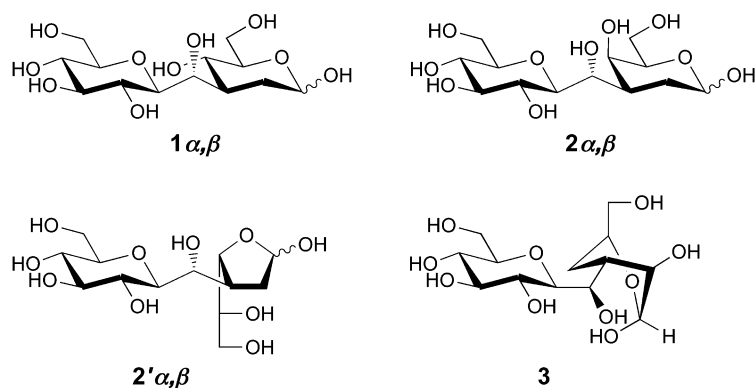
Introduction. – Carbohydrates regulate the sociology of cells and play a crucial role in the construction of multicellular organs and organisms [1]. Glycoproteins and glycolipids found at the surface of cells are the words and the phrases cells use to communicate with each other, and with viruses and bacteria [2]. With a growing understanding of the precise function that cell-surface carbohydrates play in disorders such as inflammation, viral and bacterial infections, to cancer, numerous carbohydrate analogs have now been developed and have entered into clinical studies [3]. Disaccharide mimetics such as C-linked disaccharides and oligosaccharides containing them offer the advantage of being resistant to acidic and enzymatic hydrolysis [4][5]. They are potential inhibitors of glycosidases and glycosyltransferases [6]. In this report, we apply our convergent synthetic method for the construction of C(1 $\rightarrow$ 3)-linked disaccharides [7] to the preparation of yet unknown β -C-glucopyranosides in which a hydroxymethano linker connects β -D-glucopyranose to C(3) of 2-deoxy-D-arabino-hexose (see **1**), 2-deoxy-D-lyxo-hexose (see **2**), and 4-deoxy-D-arabino-hexose (see **3**).

The oligosaccharide components of the glycolipid-type antigens isolated from *Mycobacterium smegmatis* contain the β -D-Glcp-(1 $\rightarrow$ 3)- β -D-Glcp moiety [8]. This motif, for which **1** is a mimetic, is also found in the glucan fragment responsible for triggering the defense of the soybean to infections by the mould *Phytophthora megasperma* [9]. The lipopolysaccharide *O*-antigens of *Actinobacillus pleuropneumonia* serotype 8 contains the β -D-Glcp-(1 $\rightarrow$ 3)- β -D-Galf motif [10] for which **2'** is a mimetic¹⁾²⁾.

A deoxy-carba-disaccharide differs in two respects from the original disaccharide. It is known that deoxysaccharides play a dominant role in many important intercellular

¹⁾ For rare examples of C-glycosides of deoxyhexoses, see [11].

²⁾ For the syntheses of (1 $\rightarrow$ 3)-disaccharides containing deoxyhexoses, see [12]. The α -D-Glcp-(1 $\rightarrow$ 3)-1,5-anhydro-2-deoxy-D-arabino-hexitol is an inhibitor of Golgi membrane *endo*- α -D-mannosidase [13].



adhesive reactions [14]. As a range of extremely interesting biological activities expressed by deoxysaccharides [15], we performed the synthesis of analogs of this class of saccharides.

Results and Discussion. – The *Oshima–Nozaki* coupling of enones and aldehydes with Me_2AlSPh allowed generation of C(1 $\rightarrow$ 3)-linked disaccharides in a few synthetic steps with high stereoselectivity [7]. Unfortunately, the method is not general yet, and the yield strongly depends on the nature of the aldehyde. Attempts to perform the coupling reaction of known **4** with **5**, promoted by Me_2AlSPh and followed by *in situ* reduction resulted in only poor yields (*ca.* 10–20%) of desired sulfide **7**. A new route involving a 1,4-addition of thiophenol to enone **6** was thus developed. In a precedent report [7], we had applied the *Oshima–Nozaki* condensation [16] to isolevoglucos-enone (**4**) and D-glucopyranose-derived carbaldehyde **5** to generate enone **6** in 80% yield. In the meantime, we have attempted to hydrogenate its alkene moiety but did not find conditions for stereoselective reactions. However, the addition of thiophenol in the presence of Et_3N gave a single adduct that was not isolated but treated directly with $\text{Me}_4\text{N}[\text{B}(\text{OAc})_3\text{H}]$ in MeCN/AcOH [17] to give **7** in 50% yield. Treatment of sulfide **7** with *Raney*-Ni in THF gave **8**. As the methanolysis of the anhydro-*arabino*-hexose moiety of **8** was unsuccessful, we exchanged the benzyl protective groups for acetates by hydrogenolysis ($\text{H}_2, \text{Pd}(\text{OH})_2/\text{C}, \text{MeOH}$) followed by peracetylation ($\text{Ac}_2\text{O}/\text{pyridine}$, *N,N*-dimethylpyridin-4-amine (DMAP) as catalyst). This produced **9** in 56% yield that was reacted with Ac_2O and CF_3COOH to furnish a mixture of anomeric pyranose peracetate **10**. Ammonolysis in MeOH provided pure C-disaccharide **1** in 76% yield (*Scheme 1*).

^1H -NMR Spectra of the new compounds **7–10** were consistent with the structures proposed. A confirmation for the D-*arabino* configuration of the 2-deoxyhexopyranose moiety of **1** was given by the spectral data collected for acetone **11** obtained by reaction of **8** with 2,2-dimethoxypropane and acetone in the presence of *p*-toluenesulfonic acid. The ^{13}C -NMR chemical shift of the two Me groups of acetone **11** ($\delta(\text{C})$ 20.1 and 30.1) confirmed a chair conformation of the 1,3-dioxane moiety with 1',4-*syn* disubstitution [18] (see *Fig. 1*).

4 + **5** $\xrightarrow[-95^\circ (80\%)]{\text{Et}_2\text{AlI, CH}_2\text{Cl}_2}$ **6 (1'R)**

6 (1'R) $\xrightarrow[2. \text{Ac}_2\text{O/pyr, DMAP (56\%)}]{1. \text{H}_2, \text{Pd(OH)}_2/\text{C, MeOH}}$ **7 X = SPh**
8 X = H

7 X = SPh
8 X = H $\xrightarrow{(69\%)} \text{Raney-Ni, THF}$ **9 X = SPh**
10 X = Ac
11 X = H

9 $\xrightarrow{(67\%)} \text{Ac}_2\text{O, CF}_3\text{COOH}$ **10 X = Ac**
11 X = H

10 X = Ac
11 X = H $\xrightarrow{(76\%)} \text{NH}_3/\text{MeOH}$ **12 X = H**

12 $\xrightarrow{(54\%)} \text{(MeO)}_2\text{CMe}_2, \text{TsOH}$ **13**

Fig. 1. *Conformation of acetonide 11*

The 2D-NOESY ^1H -NMR spectrum of **11** showed cross-peaks for signal pairs at $\delta(\text{H})$ 4.31/4.01 (H-C(4)/H-C(1')), 4.31/2.04 (H-C(4)/H-C(2)), 4.31/1.46 (H-C(4)/Me_{ax} of the acetonide), 4.01/2.04 (H-C(1')/H_{ax}-C(2)), 4.01/1.46 (H-C(1')/Me_{ax}), 3.23/1.97 (H-C(2')/H_{eq}-C(2)), and 2.09/1.97 (H-C(3)/H_{eq}-C(2)).

Furthermore, the following coupling constants between vicinal protons were measured $^3J(\text{H}-\text{C}(3), \text{H}_{\text{ax}}-\text{C}(2)) = 12.8 \text{ Hz (trans)}$, $^3J(\text{H}-\text{C}(3), \text{H}-\text{C}(4)) = 10.8 \text{ Hz (trans)}$, $^3J(\text{H}-\text{C}(1'), \text{H}-\text{C}(3)) = 10.3 \text{ Hz (trans)}$, $^3J(\text{H}_{\text{eq}}-\text{C}(2), \text{H}-\text{C}(3)) = 7.0 \text{ Hz}$, and $^3J(\text{H}-\text{C}(1'), \text{H}-\text{C}(2')) = 2.0 \text{ Hz}$ confirming the structure and conformation represented in Fig. 1.

The 600-MHz ^1H -NMR (CD_3OD , 25°) spectrum of **1** showed a 1:1 mixture of α - and β -D-pyranose and less than 3% of the corresponding furanoses. The coupling constants between vicinal protons as well as the 2D-NOESY ^1H -NMR spectra of these C-disaccharides were consistent with nearly 1:1 equilibria of the conformers **1A** and **1B** represented in Fig. 2 that can be inscribed in a diamond lattice [19].

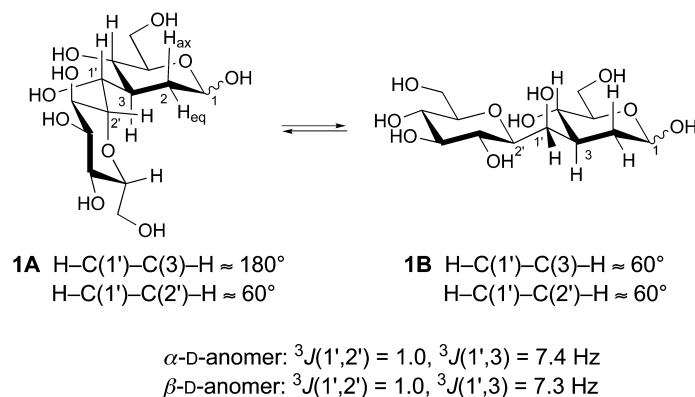
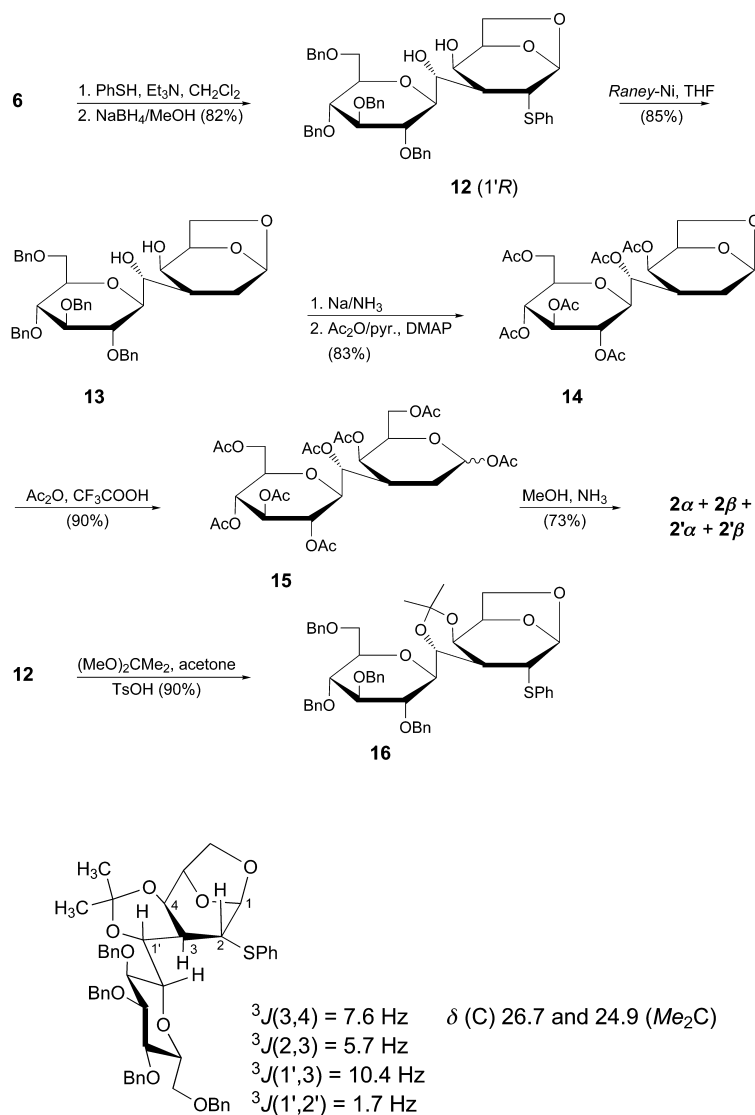


Fig. 2. Major conformers of **1a** and **1b**

When the addition of thiophenol to enone **6** was followed by reduction with NaBH_4 in MeOH instead of $\text{Me}_4\text{N}[\text{B}(\text{OAc})_3\text{H}]$, the D-galacto derivative **12** was formed in 82% yield, instead of the D-gluco system **7** (Scheme 2). Subsequent desulfurization with Raney-Ni in THF provided pure **13** in 85% yield. Exchange of the benzyl protective groups for acetates was realized in 83% yield applying the Birch conditions ($\text{Na}/\text{NH}_3, \text{THF}$) and then by peracetylation under standard conditions that gave **14**. Acid-catalyzed acetolysis of the 1,6-anhydro moiety of **14** yielded a peracetate **15** that was methanolized with NH_3/MeOH to furnish a 2.7:1.4:1.0:1.4 mixture of α -D-furanose **2'a**, β -D-furanose **2'b**, α -D-pyranose **2a**, and β -D-pyranose **2b**. The D-galacto configuration of **12** was confirmed by the NMR data (2D-NOESY ^1H -NMR, $^3J(\text{H},\text{H})$) of its acetonide **16** obtained in the usual way (Fig. 3). Conformational analysis of the C-disaccharides **2** and **2'** could not be carried out because of spectral complexities (mixture of four compounds).

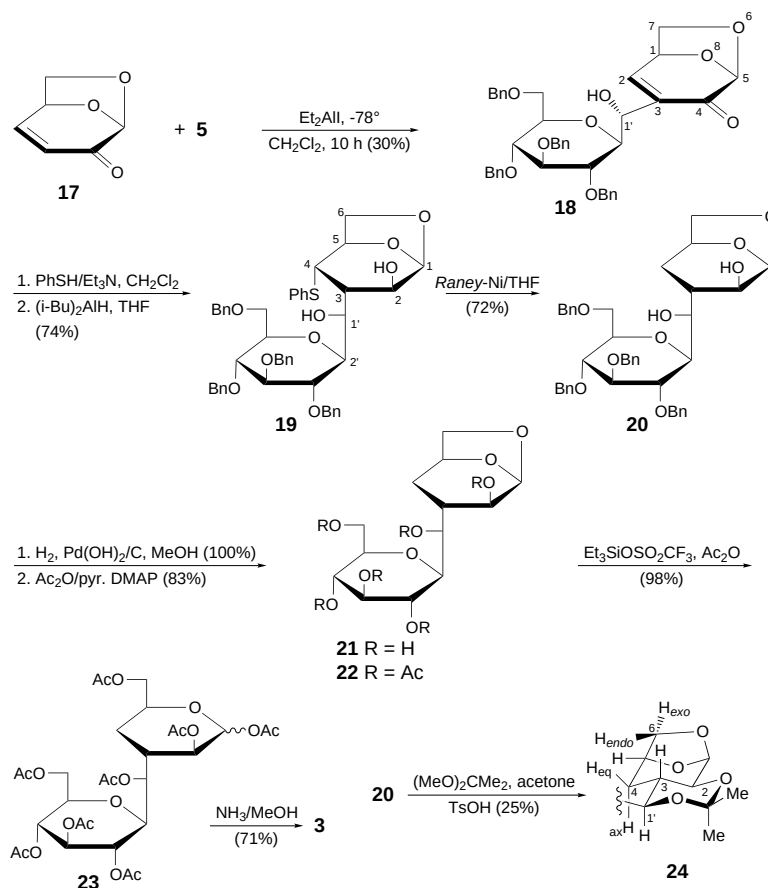
When applied to aldehyde **5** and levoglucosenone (**17**), the Oshima–Nozaki condensation induced with Et_2AlI in CH_2Cl_2 at -95° gave a single product **18** (30%) together with recovered aldehyde **5** (20%) and levoglucosenone (40%) (Scheme 3). No better conversion rate could be reached without concurrent decomposition on changing temperature and reaction time. This demonstrates that levoglucosenone **17** is much less reactive than isolevoglucosenone (**4**) in Oshima–Nozaki-type condensations. The (1'R) configuration of the alcoholic moiety of **18** will be established below. It is the same as that found for the product of the Oshima–Nozaki condensation of

Scheme 2

Fig. 3. Conformation of acetonide **16**

isolevoglucosenone, as expected for aldol reactions involving a closed-transition state (Zimmermann–Traxler model [20]). In the latter case, the face *syn* with respect to the oxa bridge (α -face of the pyranose) is preferred by the aldehyde. We assign this preference to a steric factor, *i.e.*, the attack of the enolate onto its β -face that would lead to (1'*S*) configuration is impeded because of the C–H of the C(6) center as already noticed in similar reactions [21].

Scheme 3



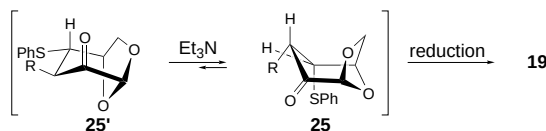
Addition of thiophenol to **18** catalyzed by Et_3N gave an unstable adduct, which was reduced *in situ* with diisobutylaluminium hydride to give diol **19** in 74% yield. Desulfurization of **19** with *Raney-Ni* in THF provided **20** in 72% yield, the relative configuration of which (*D-arabino*) was established by the NMR (2D-NOESY ^1H -NMR, $^3J(\text{H,H})$, ^{13}C -NMR) data of acetone **24** obtained in the usual way, see below. Hydrogenolysis of **20** gave polyol **21** that was peracetylated to **22** (83%, overall). Treatment of **22** with triethylsilyl trifluoromethanesulfonate in acetic anhydride produced a mixture of anomeric pyranose peracetates **23**, the ammonolysis of which in MeOH liberated C-disaccharide **3**.

The ^1H -NMR spectrum of **24** showed for H–C(3) three relatively large coupling constants $^3J(2,3) = 9.1$, $^3J(3,4_{\text{ax}}) = 12.3$, and $^3J(3,1') = 10.2$ Hz, establishing that the corresponding pairs of vicinal protons adopt *anti*-periplanar or nearly *anti*-periplanar relationships. This is consistent only with a chair conformation for the 1,3-dioxane moiety, what is confirmed by the ^{13}C -NMR chemical shifts of the Me groups of the acetone ($\delta(\text{C})$ 30.0 and 20.3). The 1,6-anhydrohexose moiety must adopt a chair conformation for its tetrahydropyran ring *trans*-annulated with the dioxane ring ($^3J(2,3) = 9.1$ Hz). This defines the structure shown in *Scheme 3* for **24**. It was

confirmed by the observation of cross-peaks in the 2D-NOESY ^1H -NMR spectrum for the proton pairs at $\delta(\text{H})$ 1.46/4.03 ($\text{Me}_{\text{ax}}/\text{H}-\text{C}(1')$), 1.46/3.73 ($\text{Me}_{\text{ax}}/\text{H}-\text{C}(2)$). The vicinity of the $\text{H}-\text{C}(3)$ proton to the $\text{H}_{\text{endo}}-\text{C}(6)$ proton was also confirmed by the 2D-NOESY ^1H -NMR spectrum.

These results can be interpreted in terms of the formation of intermediate **25** upon the addition of PhSH to enone **18** (Scheme 4). The substituent at C(3) resides in a thermodynamically preferred equatorial position. The carbonyl moiety of **25** is then reduced at its less sterically hindered face, the *exo* face of the bicyclo[3.2.1]octane system.

Scheme 4



The 600 MHz ^1H -NMR spectrum (CD_3OD , 25°) of the C-disaccharide **3** is not consistent with a chair pyranose moiety at the reductive end but with a major twist-boat conformer (see Fig. 4). Its α -D-pyranose form was established by the 2D-NOESY ^1H -NMR spectrum.

The coupling constants between vicinal protons $^3J(3,4_{\text{ax}})=10.7$ and $^3J(4_{\text{ax}},5)=3.3$ Hz on one hand and $^3J(3,4_{\text{eq}})=4.1$ and $^3J(2,3)=4.4$ Hz on the other hand are consistent with a twist-boat conformer for the D-arabinohexose moiety of **3** (Fig. 4). The relatively large $^3J(1',3)$ ($=10.0$ Hz) and the small $^3J(1',2')$ ($=0$ Hz) suggest the major rotamer shown in Fig. 4). The α -D-pyranose form of **3** was confirmed by the lack of cross-peaks in the 2D-NOESY for $\text{H}-\text{C}(1)$ ($\delta(\text{H})$ 6.12) with $\text{H}_{\text{ax}}-\text{C}(4)$ ($\delta(\text{H})$ 1.83) and $\text{H}-\text{C}(5)$ ($\delta(\text{H})$ 3.76).

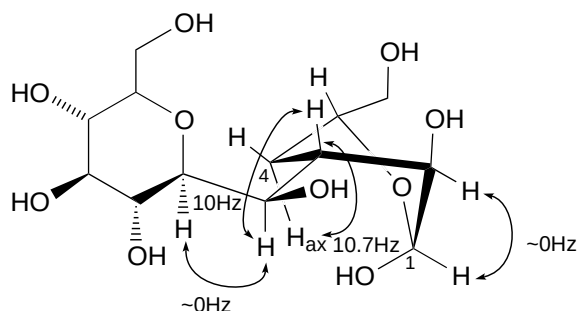


Fig. 4. Probably the most abundant conformer of C-disaccharide **3**

Conclusions. – Three new C(1 $\rightarrow$ 3)-linked disaccharides that connect β -D-glucopyranose and 2-deoxy- and 4-deoxyhexoses through a hydroxymethano linker were prepared via the Oshima–Nozaki condensation of 2,6-anhydro-3,4,5,7-tetra-*O*-benzyl-D-glycero-D-gulo-heptose (**5**) [22] to isolevoglucosenone (**4**) and to levoglucosenone (**17**). In both condensations the (1'*R*)-hydroxymethano linker was obtained exclusively. This observation opens the possibility to construct C(1 $\rightarrow$ 3)-disaccharides

with monosubstituted methano linkers (e.g., CH(F), CH(NH₂)) with predictable configuration and high stereoselectivity.

This work was supported by the Swiss National Science Foundation (Grants No. 20-55567.98 and No. 20-63667.00), the Office Fédéral de l'Éducation et de la Science (COSTD13/0001/99 and COSTD25/0001/02), and the Fonds Herbette (Lausanne). We are grateful also to Mr. Martial Rey and Francisco Sepúlveda for technical help.

Experimental Part

General. See [23].

3-C-[(1R)-2,6-Anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-D-arabino-hexopyranose (**1**). A mixture of **10** (102 mg, 0.15 mmol) and sat. NH₃ soln. in MeOH (5 ml) was stirred at 20° for 5.5 h. Solvent evaporation afforded **1** and acetamide (by ¹H-NMR). Chromatography (silica gel, CHCl₃/MeOH 1:1) gave 39 mg (76%) of **1**, α/β-D-anomers 1:1. Hygroscopic white solid. [α]_D²⁵ = +6.0, [α]_D²⁵ = +13, [α]_D²⁵ = +21, [α]_D²⁵ = +23 (c = 0.27, MeOH). UV (MeCN): 192 (500). IR (KBr): 3265, 2930, 1645, 1430, 1100, 905, 595. ¹H-NMR (600 MHz, CD₃OD): α-D-anomer: 5.27 (br. d, ³J = 2.7, H-C(1)); 3.96 (dd, ³J(1',3) = 7.4, ³J(1',2') = 1.0, H-C(1')); 3.83 (m, H-C(5)); 3.59 (dd, ³J(4,5) = 9.7, ³J(3,4) = 9.7, H-C(4)); 3.31 (dd, ³J(2',3') = 9.2, ³J(1',2') = 1.0, H-C(2')); 2.36 (dddd, ³J(2ax,3) = 13.2, ³J(3,4) = 9.7, ³J(1',3) = 7.4, ³J(2eq,3) = 4.1, H-C(3)); 1.80 (ddd, ²J = 13.2, ³J(2eq,3) = 4.1, ³J(1,2eq) = 1.0, H_{eq}-C(2)); 1.55 (ddd, ²J = 13.2, ³J(2ax,3) = 13.2, ³J(1,2ax) = 3.5, H_{ax}-C(2)); β-D-anomer: 4.84 (dd, ³J(1,2ax) = 9.5, ³J(1,2eq) = 2.0, H-C(1)); 4.01 (dd, ³J(1',3) = 7.3, ³J(1',2') = 1.0, H-C(1')); 3.49 (dd, ³J(4,5) = 9.6, ³J(3,4) = 9.6, H-C(4)); 3.37 (m, H-C(5)); 3.33 (dd, ³J(2',3') = 9.2, ³J(1',2') = 1.9, H-C(2')); 2.06 (dddd, ³J(2ax,3) = 12.9, ³J(3,4) = 9.6, ³J(1',3) = 7.3, ³J(2eq,3) = 4.1, H-C(3)); 1.90 (ddd, ²J = 12.9, ³J(2eq,3) = 4.1, ³J(1,2eq) = 2.0, H_{eq}-C(2)); 1.35 (ddd, ²J = 12.9, ³J(2ax,3) = 12.9, ³J(1,2ax) = 9.5, H_{ax}-C(2)); other signals: 3.90–3.70 (m, 8 H, CH₂-(6) (α- and β-D)), CH₂-(7') (α- and β-D)); 3.55 (2dd, ³J(3',4') = 9.2, ³J(2',3') = 9.2, 2 H, H-C(3') (α- and β-D)); 3.43–3.39 (m, 4 H, H-C(4') (α- and β-D), H-C(5') (α- and β-D)); 3.28 (m, 2 H, H-C(6') (α- and β-D)). ¹³C-NMR (150.9 MHz, CD₃OD): α-D-anomer: 91.7 (d, J = 168, C(1)); 79.8 (d, J = 143, C(4')); 74.3 (d, J = 139, C(1')); 73.6 (d, J = 146, C(5)); 71.3 (d, J = 143, C(4)); 70.9 (d, J = 143, C(5')); 70.6 (d, J = 144, C(3')); 39.4 (d, J = 132, C(3)); 33.3 (t, J = 127, C(2)); β-D-anomer: 96.5 (d, J = 158, C(1)); 80.5 (d, J = 143, C(5)); 79.8 (d, J = 143, C(4')); 73.8 (d, J = 141, C(1')); 70.9 (2d, J = 143, J = 143, C(4), C(5')); 70.6 (d, J = 144, C(3')); 44.0 (d, J = 130, C(3)); 35.4 (t, J = 130, C(2)); other signals: 81.5, 81.4 (2d, J = 147, J = 147, C(6') (α- and β-D)); 79.3, 79.2 (2d, J = 139, J = 139, C(2') (α- and β-D)); 63.0, 62.9, 62.4, 62.4 (4t, J = 142–143, C(6) (α- and β-D), C(7') (α- and β-D)). CI-MS (NH₃): 323 (3, [M – 17]⁺), 273 (8), 137 (20), 87 (100). Electrospray-MS (pos.; MeCN/H₂O/AcOH 50:50:1): 358.3 (100, [M + H₂O]⁺), 364.3 (70, [M + Na + H]⁺), 373.3 (40, [M + MeOH + H]⁺).

3-C-[(1R)-2,6-Anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-D-lyxo-hexose (**2**). As described for **1**, with **15** (58 mg, 0.09 mmol) and sat. NH₃ soln. in MeOH (4 ml) (for 5 h): 21 mg (73%) of **2**, 2.7:4:1:1.4 mixture of α-D-furanose **2'α**, β-D-furanose **2'β**, α-D-pyranose **2α**, and β-D-pyranose **2β**. White solid. M.p. 45–49°. [α]_D²⁵ = –1.6, [α]_D²⁵ = –3.7, [α]_D²⁵ = –4.8, [α]_D²⁵ = –6.9 (c = 0.19, MeOH). UV (MeCN): 194 (930). IR (KBr): 3385, 2930, 1655, 1420, 1090, 1025, 910. ¹H-NMR (400 MHz, CD₃OD): **2'α**: 5.41 (d, ³J(1,2β) = 4.8, H-C(1)); 4.33 (dd, ³J(3,4) = 6.9, ³J(4,5) = 1.5, H-C(4)); 2.90 (dddd, ³J(2β,3) = 10.5, ³J(1',3) = 8.5, ³J(2α,3) = 8.0, ³J(3,4) = 6.9, H-C(3)); 1.96 (dd, ²J = 12.6, ³J(2α,3) = 8.0, H_α-C(2)); 1.78 (ddd, ²J = 12.6, ³J(2β,3) = 10.5, ³J(1,2β) = 4.8, H_β-C(2)); **2'β**: 5.47 (dd, ³J(1,2α) = 5.1, ³J(1,2β) = 2.6, H-C(1)); 4.36 (dd, ³J(3,4) = 6.4, ³J(4,5) = 1.7, H-C(4)); 2.70 (dddd, ³J(2α,3) = 10.0, ³J(1',3) = 8.1, ³J(3,4) = 6.4, ³J(2β,3) = 5.7, H-C(3)); 2.26 (ddd, ²J = 13.2, ³J(2α,3) = 10.0, ³J(1,2α) = 5.1, H_α-C(2)); 1.63 (ddd, ²J = 13.2, ³J(2β,3) = 5.7, ³J(1,2β) = 2.6, H_β-C(2)); **2'α**: 5.31 (d, ³J(1,2β) = 3.2, H-C(1)); 2.33 (m, H-C(3)); 1.74 (ddd, ²J = 12.9, ³J(2β,3) = 12.8, ³J(1,2β) = 3.2, H_β-C(2)); 1.50 (dd, ²J = 12.9, ³J(2α,3) = 4.9, H_α-C(2)); **2'α**: 4.79 (dd, ³J(1,2β) = 9.5, ³J(1,2α) = 2.3, H-C(1)); 2.06 (m, H-C(3)); 1.61 (m, ²J = 12.8, H_α-C(2)); 1.45 (ddd, ²J = 12.8, ³J(2β,3) = 12.7, ³J(1,2β) = 9.5, H_β-C(2)); other signals: 4.08–3.16 (m, H-C(4) except for **2'α** and **2'β**, H-C(5), CH₂(6), H-C(1'), H-C(2'), H-C(3'), H-C(4'), H-C(5'), H-C(6'), CH₂(7')). ¹³C-NMR (100.6 MHz, CD₃OD): **2'α**: 98.5 (d, J = 170, C(1)); 84.7 (d, J = 146, C(4)); 41.7 (d, J = 134, C(3)); 38.8 (t, J = 131, C(2)); **2'β**: 99.5 (d, J = 171, C(1)); 82.0 (d, J = 146, C(4)); 43.1 (d, J = 130, C(3)); 38.8 (t, J = 131, C(2)); **2α**: 92.1 (d, J = 167, C(1)); 37.5 (d, J = 128, C(3)); 28.4 (t, J = 128, C(2)); **2β**: 97.1 (d, J = 160, C(1)); 43.0 (d, J = 130, C(3)); 31.1 (t, J = 126, C(2)); other signals: 81.4, 81.3, 81.2, 81.0, 80.2, 79.9, 79.8, 79.8, 79.1, 79.1, 74.4, 73.8, 73.0, 72.8, 72.7, 71.0, 70.8, 70.8, 70.6, 69.4, 69.1, 65.3, 64.7 (30 d, CH); 65.4, 65.2, 63.6, 63.3, 62.5, 62.4, 62.3, 62.2 (8t, CH₂). Electrospray-MS (pos.; MeCN/H₂O/AcOH 50:50:1): 358.3 (50, [M + 18]⁺), 363.3 (100, [M + Na]⁺).

3-*C*-[*(1R)*-2,6-Anhydro-D-glycero-D-gulo-heptitol-1-*C*-yl]-3,4-dideoxy- α -D-arabino-hexopyranose (**3**). As described for **1**, with **23** (50 mg, 0.07 mmol) and sat. NH_3 soln. in MeOH (5 ml) (for 4.5 h). Chromatography (silica gel, $\text{CHCl}_3/\text{MeOH}$ 1.7:1) afforded 18 mg (71%) of **3**, as a single anomer. Hygroscopic white solid. M.p. 43–45°. $[\alpha]_{\text{D}}^{25} = -33$, $[\alpha]_{\text{D}}^{25} = -44$, $[\alpha]_{\text{D}}^{25} = -72$, $[\alpha]_{\text{D}}^{25} = -84$ ($c = 0.14$, MeOH). UV (MeCN): 197 (1300). IR (KBr): 3390, 2930, 1655, 1535, 1430, 1090, 1010, 955. $^1\text{H-NMR}$ (600 MHz, CD_3OD): 5.12 (*s*, H-C(1)); 4.22 (*d*, $^3J(1',3) = 10.0$, H-C(1')); 4.07 (*d*, $^3J(2,3) = 4.4$, H-C(2)); 3.89 (*d*, $^2J = 11.8$, H_a-C(7')); 3.76 (*dddd*, $^3J(4\beta,5) = 9.4$, $^3J(5,6b) = 6.4$, $^3J(5,6a) = 4.6$, $^3J(4\alpha,5) = 3.3$, H-C(5)); 3.69 (*dd*, $^2J = 11.8$, $^3J(6',7'b) = 5.1$, H_b-C(7')); 3.58 (*dd*, $^3J(3',4') = 9.3$, $^3J(2',3') = 9.3$, H-C(3')); 3.56 (*dd*, $^2J = 11.2$, $^3J(5,6a) = 4.6$, H_a-C(6)); 3.50 (*dd*, $^2J = 11.2$, $^3J(5,6b) = 6.4$, H_b-C(6)); 3.39, 3.35 (H-C(4'), H-C(5')); 3.32 (*m*, H-C(6')); 3.20 (*d*, $^3J(2',3') = 9.3$, H-C(2')); 2.82 (*dddd*, $^3J(3,4\alpha) = 10.7$, $^3J(1',3) = 10.0$, $^3J(2,3) = 4.4$, $^3J(3,4\beta) = 4.1$, H-C(3)); 1.83 (*ddd*, $^2J = 14.0$, $^3J(3,4\alpha) = 10.7$, $^3J(4\alpha,5) = 3.3$, H_a-C(4)); 1.42 (*ddd*, $^2J = 14.0$, $^3J(4\beta,5) = 9.4$, $^3J(3,4\beta) = 4.1$, H_b-C(4)). $^{13}\text{C-NMR}$ (100.6 MHz, CD_3OD): 104.0 (*d*, $J = 172$, C(1)); 82.0 (*d*, $J = 141$, C(1')); 81.6 (*d*, $J = 142$, C(6')); 80.1 (*d*, $J = 140$, C(4')); 78.0 (*2d*, $J = 141$, $J = 141$, C(2), C(2')); 71.7 (*d*, $J = 142$, C(5)); 71.6 (*d*, $J = 142$, C(3')); 71.5 (*d*, $J = 142$, C(5')); 67.8 (*t*, $J = 140$, C(6)); 62.8 (*t*, $J = 142$, C(7')); 37.5 (*d*, $J = 129$, C(3)); 29.6 (*t*, $J = 125$, C(4)). Electrospray-MS (pos.; MeCN/ H_2O /AcOH 50:50:1): 340.3 (100, M^+), 363.3 (12, $[M + \text{Na}]^+$), 381.3 (12, $[M + \text{MeCN}]^+$), 404.3 (10, $[M + \text{MeCN} + \text{Na}]^+$).

1,6-Anhydro-3-*C*-[*(1R)*-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-*C*-yl]-2,3-dideoxy-2-(phenylthio)- β -D-glucopyranose (**7**). To a soln. of **6** [8] (1.49 g, 2.20 mmol) and thiophenol (240 μl , 2.34 mmol) in CH_2Cl_2 (6 ml) cooled to 0° was added Et_3N (62 μl , 0.44 mmol). The mixture was stirred at 0° for 90 min. To a soln. of tetramethylammonium triacetoxymethylborohydride [16] (4.72 g, 17.9 mmol) in anhyd. MeCN (10 ml) was added AcOH (10 ml), and the mixture was stirred at 20° for 1 h. The latter was cooled to -40°, and the previous mixture (containing the thiophenol adduct) was added *via* a cannula. After stirring at 20° for 5 h, the reaction was quenched with 0.5N aq. sodium potassium tartrate (20 ml), the mixture diluted with CH_2Cl_2 (25 ml) and washed with sat. aq. NaHCO_3 soln. (25 ml). The aq. layer was extracted with CH_2Cl_2 (3 $\times$ 20 ml), the combined org. phase dried (MgSO_4) and evaporated, and the residue submitted to FC (silica gel, light petroleum ether/AcOEt 3:2): 860 mg (50%) of **7**. White solid. M.p. 141–143°. $[\alpha]_{\text{D}}^{25} = -6.3$, $[\alpha]_{\text{D}}^{25} = -8.1$, $[\alpha]_{\text{D}}^{25} = -18$, $[\alpha]_{\text{D}}^{25} = -21$ ($c = 0.23$, CHCl_3). UV (MeCN): 252 (9600), 212 (25200). IR (KBr): 3505, 3030, 2900, 1580, 1455, 1360, 1125, 1065, 990, 895, 735, 700. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.42–7.13 (*m*, 25 arom. H); 5.60 (*s*, H-C(1)); 4.92–4.40 (*m*, 8 H, OCH_2Ph); 4.39 (*d*, $^3J(5,6\text{exo}) = 4.3$, H-C(5)); 4.07 (*d*, $^3J(1',3) = 6.3$, H-C(1')); 3.88 (*d*, $^3J(3,4) = 3.9$, H-C(4)); 3.70–3.66 (*m*, $\text{CH}_2(6)$); 3.63–3.59 (*m*, H-C(3'), H-C(4')); 3.50 (*dd*, $^2J = 10.2$, $^3J(6',7'a) = 2.1$, H_a-C(7')); 3.46 (*dd*, $^2J = 10.2$, $^3J(6',7'b) = 5.4$, H_b-C(7')); 3.45 (*dd*, $^3J(5',6') = 9.3$, $^3J(4',5') = 9.3$, H-C(5')); 3.16 (*ddd*, $^3J(5',6') = 9.3$, $^3J(6',7'b) = 5.4$, $^3J(6',7'a) = 2.1$, H-C(6')); 3.09 (*d*, $^3J(2',3') = 9.3$, H-C(2')); 2.94 (*d*, $^3J(2,3) = 6.0$, H-C(2)); 1.92 (*ddd*, $^3J(1',3) = 6.3$, $^3J(2,3) = 6.0$, $^3J(3,4) = 3.9$, H-C(3)). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 138.4, 137.8, 137.5, 137.4, 133.9 (5s, 5 arom. C); 131.9–127.4 (25d, arom. C); 102.9 (*d*, $J = 176$, C(1)); 87.1 (*d*, $J = 139$, C(4')); 78.7 (*d*, $J = 138$, C(2')); 78.2, 78.1, 78.0 (3d, C(5), C(5'), C(6')); 77.3 (*d*, C(3')); 75.6 (*t*, $J = 143$, OCH_2Ph); 75.4 (*t*, $J = 143$, OCH_2Ph); 75.0 (*t*, $J = 144$, OCH_2Ph); 73.5 (*t*, $J = 142$, OCH_2Ph); 69.0 (*t*, $J = 143$, C(7')); 68.2 (*d*, $J = 144$, C(4)); 67.7 (*d*, $J = 145$, C(1')); 66.0 (*t*, $J = 151$, C(6)); 48.6 (*d*, $J = 144$, C(2)); 45.7 (*d*, $J = 133$, C(3)). CI-MS (NH_3): 791 (2, M^+), 731 (1), 647 (47), 441 (15), 191 (14), 91 (100). Anal. calc. for $\text{C}_{47}\text{H}_{50}\text{O}_9\text{S}$ (790.97): C 71.37, H 6.37; found: C 71.24, H 6.23.

1,6-Anhydro-3-*C*-[*(1R)*-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-*C*-yl]-2,3-dideoxy- β -D-arabino-hexopyranose (**8**). A soln. of **7** (624 mg, 0.79 mmol) in THF (30 ml) was treated with Raney-Ni (*ca.* 6 g), and the suspension was stirred for 2 h at 20°. When the reaction was complete (TLC with light petroleum ether/AcOEt 1:2), the solid was filtered off and washed with AcOEt. The combined filtrate and washings were dried (MgSO_4) and evaporated. FC (silica gel, light petroleum ether/AcOEt 1:2) afforded 372 mg (69%) of **8**. White solid. M.p. 133–135°.

$[\alpha]_{\text{D}}^{25} = -16$, $[\alpha]_{\text{D}}^{25} = -21$, $[\alpha]_{\text{D}}^{25} = -32$, $[\alpha]_{\text{D}}^{25} = -38$ ($c = 0.25$, CHCl_3). UV (MeCN): 212 (27000). IR (KBr): 3510, 3430, 3030, 2930, 2885, 1455, 1365, 1125, 1065, 995, 900, 880, 740, 700. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.37–7.20 (*m*, 20 arom. H); 5.55 (*d*, $^3J = 3.9$, H-C(1)); 4.94–4.49 (*m*, 8 H, OCH_2Ph); 4.41 (*d*, $^3J(5,6\text{exo}) = 5.3$, H-C(5)); 3.84 (*m*, H-C(4)); 3.78–3.69 (*m*, H-C(1'), H-C(3'), H-C(4'), $\text{CH}_2(6)$, H_a-C(7'), OH-C(4)); 3.65 (*dd*, $^2J = 10.5$, $^3J(6,7'b) = 5.1$, H_b-C(7')); 3.58 (*dd*, $^3J(5',6') = 9.6$, $^3J(4',5') = 9.6$, H-C(5')); 3.49 (*ddd*, $^3J(5',6') = 9.6$, $^3J(6',7'b) = 5.1$, $^3J(6',7'a) = 1.7$, H-C(6')); 3.31 (*d*, $^3J(2',3') = 9.6$, H-C(2')); 2.47 (*d*, $^3J(1',\text{OH}) = 10.2$, OH-C(1')); 2.04–1.95 (*m*, H_a-C(2), H-C(3)); 1.29 (*m*, H_b-C(2)). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 138.4, 137.9, 137.8, 137.6 (4s, 4 arom. C); 128.6–127.5 (20d, arom. C); 99.4 (*d*, $J = 172$, C(1)); 87.0 (*d*, $J = 145$, C(4')); 78.5 (*d*, $J = 145$, C(6')); 78.2 (*d*, $J = 140$, C(2')); 78.0 (*d*, $J = 146$, C(5')); 77.5 (*d*, $J = 156$, C(5)); 77.4 (*d*, $J = 151$, C(3')); 75.6 (*t*, $J = 142$, OCH_2Ph); 75.1 (*t*, $J = 146$, OCH_2Ph); 75.0 (*t*, $J = 143$, OCH_2Ph); 73.4 (*t*, $J = 142$, OCH_2Ph); 72.0 (*d*, $J = 144$, C(4)); 71.3 (*d*, $J = 143$, C(1')); 69.0 (*t*, $J = 143$, C(7')); 66.0

(*t*, *J* = 150, C(6)); 38.6 (*d*, *J* = 133, C(3)); 30.6 (*t*, *J* = 129, C(2)). CI-MS (NH₃): 683 (2, *M*⁺), 633 (1), 486 (1), 271 (1), 181 (4), 149 (2), 91 (100). Anal. calc. for C₄₁H₄₆O₉ (682.81): C 72.11, H 6.79; found: C 72.19, H 6.79.

4-O-Acetyl-1,6-anhydro-2,3-dideoxy-3-C-[(1*R*)-1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-β-D-arabino-hexopyranose (9). A degassed mixture of **8** (293 mg, 0.43 mmol), 10% Pd(OH)₂ C (290 mg), and MeOH (60 ml) was stirred under H₂ at 20° for 60 h. The catalyst was filtered off, the solvent evaporated, and the product purified by FC (silica gel, CH₂Cl₂/MeOH 2 : 1): white solid. The latter was mixed with Ac₂O (2.5 ml), pyridine (3 ml), and DMAP (0.5 mg) and stirred at 20° for 15 h. Evaporation gave a residue that was taken up in toluene (10 ml), and the solvent was evaporated again. The latter operation was repeated twice and the residue purified by FC (silica gel, light petroleum ether/AcOEt 1 : 2): 138 mg of **9** (56%, 2 steps). White solid. M.p. 162–163°. [α]₅₈₉²⁵ = –27, [α]₅₄₆²⁵ = –18, [α]₄₃₅²⁵ = –41, [α]₄₀₅²⁵ = –46 (*c* = 0.26, CHCl₃). UV (MeCN): 194 (4800). IR (KBr): 3450, 2970, 1755, 1735, 1450, 1370, 1240, 1145, 1065, 1020, 910. ¹H-NMR (400 MHz, CDCl₃): 5.58 (*s*, H–C(1)); 5.30 (*d*, ³*J*(1',3) = 10.4, H–C(1')); 5.18 (*dd*, ³*J*(4',5') = 9.3, ³*J*(3',4') = 9.3, H–C(4')); 5.05 (*ddd*, ³*J*(5',6') = 9.3, ³*J*(4',5') = 9.3, ³*J*(3',4') = 9.3, ³*J*(2',3') = 9.3, H–C(3'), H–C(5')); 4.65 (*s*, H–C(4)); 4.43 (*d*, ³*J*(5,6*exo*) = 4.7, H–C(5)); 4.29 (*d*, ²*J* = 7.6, H_{endo}–C(6)); 4.21 (*dd*, ²*J* = 12.3, ³*J*(6',7'a) = 6.0, H_a–C(7)); 4.09 (*d*, ²*J* = 12.3, H_b–C(7)); 3.77 (*dd*, ³*J*(2',3') = 9.3, ³*J*(1',2') = 1.7, H–C(2')); 3.69 (*dd*, ²*J* = 7.6, ³*J*(5,6*exo*) = 4.7, H_{exo}–C(6)); 3.60 (*m*, H–C(6')); 2.24 (*m*, H–C(3)); 2.13–1.99 (19 H, H_{eq}–C(2), 6 Ac); 1.53 (*dd*, ²*J* = 14.8, H_{ax}–C(2)). ¹³C-NMR (100.6 MHz, CDCl₃): 171.6, 170.4, 170.1, 169.9, 169.5, 169.3 (6s, COO); 99.7 (*d*, *J* = 171, C(1)); 76.4 (*d*, *J* = 146, C(6')); 75.9 (*d*, *J* = 141, C(2')); 74.8 (*d*, *J* = 154, C(5)); 74.4 (*d*, *J* = 152, C(4')); 69.6 (*d*, *J* = 149, C(1')); 69.0 (*d*, *J* = 148, C(4)); 68.3, 67.3 (2*d*, *J* = 153, *J* = 155, C(3'), C(5')); 65.5 (*t*, *J* = 151, C(6)); 62.3 (*t*, *J* = 149, C(7')); 35.7 (*d*, *J* = 135, C(3)); 29.2 (*t*, *J* = 129, C(2)); 21.0–20.4 (6*q*, *J* = 130, MeCOO). CI-MS (NH₃): 592 (100, [*M* + 18]⁺), 515 (32), 435 (22), 243 (30), 102 (77). Anal. calc. for C₂₅H₃₄O₁₅ (574.53): C 52.26, H 5.96; found: C 52.29, H 5.92.

1,4,6-Tri-O-acetyl-2,3-dideoxy-3-C-[(1*R*)-1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-α-D-arabino-hexopyranose (10). A mixture of **9** (130 mg, 0.23 mmol), Ac₂O (4.7 ml), and CF₃COOH (1.1 ml) was stirred at 20° for 2 h, then poured onto ice (10 ml), and neutralized with sat. aq. soln. NaHCO₃ (pH 8). The mixture was extracted with AcOEt (3 × 15 ml), the combined org. extract washed with brine (30 ml), dried (MgSO₄), and evaporated, and the residue submitted to FC (silica gel, light petroleum ether/AcOEt 1 : 2): 102 mg of **10** (67%), 4 : 1 mixture of α- and β-D-anomers. White solid. M.p. 69–71°. [α]₅₈₉²⁵ = +32, [α]₅₄₆²⁵ = +37, [α]₄₃₅²⁵ = +65, [α]₄₀₅²⁵ = +78 (*c* = 0.21, CHCl₃). UV (MeCN): 195 (2200). IR (KBr): 1750, 1435, 1375, 1230, 1035, 910, 600. ¹H-NMR (400 MHz, CDCl₃): α-D-anomer: 6.16 (*br. d*, ³*J*(1,2_{ax}) = 1.6, H–C(1)); 5.19 (*dd*, ³*J*(4',5') = 9.3, ³*J*(3',4') = 9.3, H–C(4')); 5.04–4.94 (*m*, 4 H, H–C(1'), H–C(3'), H–C(4), H–C(5')); 4.21 (*dd*, ²*J* = 12.3, ³*J*(6',7'a) = 4.5, H_a–C(7)); 4.16 (*m*, CH₂(6)); 3.97 (*dd*, ²*J* = 12.3, ³*J*(6',7'b) = 2.4, H_b–C(7)); 3.92 (*ddd*, ³*J*(5',6') = 9.3, ³*J*(6',7'a) = 4.5, ³*J*(6',7'b) = 2.4, H–C(6')); 3.77–3.73 (*m*, 2 H, H–C(2'), H–C(5)); 2.68 (*m*, H–C(3)); 2.26 (*m*, H_{ax}–C(2)); 2.12–1.97 (H_{eq}–C(2), 8 MeCOO); β-D-anomer: 5.64 (*dd*, ³*J*(1,2_{ax}) = 9.6, ³*J*(1,2_{eq}) = 2.4, H–C(1)). ¹³C-NMR (100.6 MHz, CDCl₃): α-anomer: 170.7, 170.5, 170.3, 170.1, 170.1, 169.5, 169.3, 169.2 (8s, COO); 90.7 (*d*, *J* = 175, C(1)); 76.2 (2*d*, *J* = 140, C(2'), C(5)); 74.2 (*d*, *J* = 146, C(4)); 70.9 (*d*, *J* = 145, C(6')); 68.6, 67.4, 67.4, 66.6 (4*d*, *J* = 146–150, C(1'), C(3'), C(4), C(5')); 62.6 (*t*, *J* = 149, C(6)); 62.3 (*t*, *J* = 148, C(7)); 36.9 (*d*, *J* = 131, C(3)); 29.3 (*t*, *J* = 133, C(2)); 21.1–20.4 (8*q*, *J* = 130, MeCOO); β-D-anomer: 93.5 (*d*, *J* = 165, C(1)). CI-MS (NH₃): 694 (12, [*M* + 18]⁺), 634 (44), 617 (85), 557 (100), 496 (62), 321 (27), 81 (34). Anal. calc. for C₂₉H₄₀O₁₈ (676.62): C 51.48, H 5.96; found: C 51.23, H 6.03.

1,6-Anhydro-3-C-[(1*R*)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-1',4'-O-isopropylidene-β-D-arabino-hexopyranose (11). A mixture of **8** (50 mg, 0.07 mmol), 2,2-dimethoxypropane (2 ml), dry acetone (2 ml), and TsOH (16 mg) was stirred at 20° for 4.5 h. After the addition of AcOEt (10 ml) and H₂O (20 ml), the aq. phase was extracted with AcOEt (3 × 10 ml), the combined org. extract washed with sat. aq. NaHCO₃ soln. (20 ml) and brine (20 ml), dried (MgSO₄), and evaporated, and the residue submitted to FC (silica gel, light petroleum ether/AcOEt 7 : 3) 28 mg (54%) of **11**. Colorless oil.

[α]₅₈₉²⁵ = –26, [α]₅₄₆²⁵ = –30, [α]₄₃₅²⁵ = –48, [α]₄₀₅²⁵ = –55 (*c* = 0.19, CHCl₃). UV (MeCN): 206 (33200). IR (KBr): 2890, 1495, 1455, 1365, 1265, 1200, 1080, 1030, 895, 735, 700. ¹H-NMR (400 MHz, CDCl₃): 7.39–7.23 (*m*, 20 arom. H); 5.47 (*d*, ³*J*(1,2_{eq}) = 5.5, H–C(1)); 4.91–4.60 (*m*, 8 H, OCH₂Ph); 4.31 (*dd*, ³*J*(5,6*exo*) = 3.7, ³*J*(4,5) = 1.5, H–C(5)); 4.01 (*dd*, ³*J*(1',3) = 10.3, ³*J*(1',2') = 2.0, H–C(1')); 3.83 (*dd*, ³*J*(3',4') = 9.3, ³*J*(2',3') = 9.3, H–C(3')); 3.78 (*dd*, ²*J* = 11.3, ³*J*(6',7'a) = 1.9, H_a–C(7)); 3.74–3.68 (*m*, H–C(4'), H_{endo}–C(6), H_b–C(7)); 3.65 (*dd*, ³*J*(3,4) = 10.8, ³*J*(4,5) = 1.5, H–C(4)); 3.59 (*dd*, ³*J*(5',6') = 9.3, ³*J*(4',5') = 9.3, H–C(5')); 3.52 (*dd*, ²*J* = 6.8, ³*J*(5,6*exo*) = 3.7, H_{exo}–C(6)); 3.37 (*ddd*, ³*J*(5',6') = 9.3, ³*J*(6',7'b) = 4.6, ³*J*(6',7'a) = 1.9, H–C(6')); 3.23 (*dd*, ³*J*(2',3') = 9.3, ³*J*(1',2') = 2.0, H–C(2')); 2.09 (*dddd*, ³*J*(2_{ax},3) = 12.8, ³*J*(3,4) = 10.8, ³*J*(1',3) = 10.3, ³*J*(2_{eq},3) = 7.0, H–C(3)); 1.97 (*ddd*, ²*J* = 12.8, ³*J*(2_{eq},3) = 7.0, ³*J*(1,2_{eq}) = 5.5, H_{eq}–C(2)); 1.46 (*s*, Me_{ax}); 1.42 (*s*, Me_{eq}); 1.00 (*dd*, ²*J* = 12.8, ³*J*(2_{ax},3) = 12.8, H_{ax}–C(2)). ¹³C-NMR (100.6 MHz, CDCl₃): 138.6, 138.5, 138.3,

138.1 (4s, 4 arom. C); 128.5–127.4 (20d, arom. CH); 100.4 (s, Me₂C); 99.1 (d, $J = 173$, C(1)); 87.5 (d, $J = 140$, C(4')); 80.0 (d, $J = 140$, C(6')); 78.4 (d, $J = 144$, C(5')); 77.3 (d, C(2')); 76.7 (d, C(3')); 76.4 (d, C(4)); 75.5 (d, $J = 157$, C(5)); 75.5 (t, $J = 141$, OCH₂Ph); 75.0 (t, $J = 140$, OCH₂Ph); 74.8 (t, $J = 137$, OCH₂Ph); 73.4 (t, $J = 141$, OCH₂Ph); 71.2 (d, $J = 138$, C(1')); 68.9 (t, $J = 142$, C(7')); 68.7 (t, $J = 151$, C(6)); 30.6 (d, $J = 137$, C(3)); 30.3 (t, $J = 130$, C(2)); 30.1 (q, $J = 127$, Me); 20.1 (q, $J = 129$, Me). CI-MS (NH₃): 740 (2, [M + 18]⁺), 666 (1), 632 (2), 360 (1), 282 (1), 181 (2), 141 (1), 91 (100). Anal. calc. for C₄₄H₅₀O₉ (722.88): C 73.11, H 6.97; found: C 72.34, H 7.02.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-2-(phenylthio)-β-D-galactopyranose (12). To a soln. of **6** [8] (0.60 g, 0.88 mmol) and thiophenol (93 μl, 0.91 mmol) in CH₂Cl₂ (2.4 ml) cooled to 0° was added Et₃N (24 μl, 0.17 mmol). The mixture was stirred at 0° for 20 min MeOH (2.4 ml) and NaBH₄ (50 mg, 1.32 mmol) were added, and the mixture was stirred at 0° for 2 h. CH₂Cl₂ (10 ml), and 1M aq. HCl (2 ml) were added under stirring. After the addition of H₂O (10 ml), the aq. phase was extracted with CH₂Cl₂ (3 × 15 ml), the combined org. phase washed with sat. aq. NaHCO₃ soln. (20 ml) and brine (20 ml), dried (MgSO₄), and evaporated, and the residue submitted to FC (silica gel, light petroleum ether/AcOEt 7:3): 574 mg (82%) of **12**. Colorless oil. $[\alpha]_{589}^{25} = -1.7$, $[\alpha]_{546}^{25} = -2.4$, $[\alpha]_{435}^{25} = -6.6$, $[\alpha]_{405}^{25} = -9.5$ ($c = 0.84$, CHCl₃). UV (MeCN): 254 (7600), 214 (18900). IR (film): 3480, 3060, 3030, 2870, 1585, 1455, 1360, 1100, 1025, 915, 735, 700. ¹H-NMR (400 MHz, C₆D₆): 7.49–6.89 (m, 25 arom. H); 6.08 (s, H–C(1)); 5.11–4.89 (m, 6 H, H–C(1'), 5 OCH₂Ph); 4.55–4.52 (m, 2 H, H–C(4), OCH₂Ph); 4.44 (d, $^3J = 7.5$, H_{endo}–C(6)); 4.23 (dd, $^3J(4,5) = 7.2$, $^3J(5,6_{exo}) = 5.2$, H–C(5)); 4.21–4.13 (m, OCH₂Ph); 3.97 (dd, $^3J(3',4') = 9.3$, $^3J(2',3') = 9.3$, H–C(3')); 3.89 (d, $^3J(2,3) = 8.7$, H–C(2)); 3.74 (dd, $^3J(4',5') = 9.3$, $^3J(3',4') = 9.3$, H–C(4')); 3.48–3.42 (m, H–C(5'), H_{exo}–C(6), H_a–C(7)); 3.32–3.24 (m, H–C(6'), H_b–C(7)); 3.12 (d, $^3J(2',3') = 9.3$, H–C(2')); 1.99 (ddd, $^3J(2,3) = 8.7$, $^3J(6,6) = 5.1$, H–C(3)). ¹³C-NMR (100.6 MHz, C₆D₆): 139.3, 138.8, 138.7, 137.9, 135.4 (5s, 5 arom. C); 131.6–127.0 (25d, arom. CH); 105.0 (d, $J = 174$, C(1)); 87.3 (d, $J = 140$, C(4')); 81.0 (d, $J = 139$, C(2)); 78.8 (d, $J = 144$, C(5)); 78.6 (d, $J = 143$, C(3)); 77.8 (d, $J = 140$, C(6)); 75.7 (t, $J = 144$, OCH₂Ph); 75.5 (t, $J = 143$, OCH₂Ph); 75.0 (t, $J = 141$, OCH₂Ph); 73.9 (d, $J = 155$, C(5)); 73.5 (t, $J = 142$, OCH₂Ph); 69.9 (t, $J = 142$, C(7)); 68.9 (d, $J = 144$, C(1')); 67.5 (d, $J = 148$, C(4)); 62.5 (t, $J = 152$, C(6)); 51.0 (d, $J = 145$, C(2)); 42.3 (d, $J = 128$, C(3)). CI-MS (NH₃): 791 (2, M⁺), 682 (1), 593 (1), 253 (1), 91 (100). Anal. calc. for C₄₇H₅₀O₉S (790.97): C 71.37, H 6.37; found: C 71.39, H 6.26.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-β-D-lyxo-hexopyranose (13). As described for **8**, with **12** (690 mg, 0.87 mmol), THF (45 ml), and Raney-Ni (ca. 6 g) (4 h; TLC with light petroleum ether/AcOEt 1:1). FC (silica gel, light petroleum ether/AcOEt 3:2) gave 506 mg (85%) of **13**. White solid: M.p. 74°. $[\alpha]_{589}^{25} = -0.8$, $[\alpha]_{546}^{25} = -1.5$, $[\alpha]_{435}^{25} = -1.7$, $[\alpha]_{405}^{25} = -1.9$ ($c = 0.27$, CHCl₃). UV (MeCN): 209 (23700). IR (KBr): 3425, 2870, 1680, 1495, 1455, 1360, 1120, 1065, 865, 735, 695. ¹H-NMR (400 MHz, CDCl₃): 7.33–7.11 (m, 20 arom. H); 5.45 (dd, $^3J(1,2_{exo}) = 3.0$, $^3J(1,2_{endo}) = 1.3$, H–C(1)); 4.92–4.48 (m, 8 H, OCH₂Ph); 4.34 (m, H–C(4), H–C(5)); 4.21 (d, $^3J(1',3) = 8.6$, H–C(1')); 4.16 (d, $^2J = 7.9$, H_{endo}–C(6)); 3.72–3.67 (m, H–C(3'), H–C(4'), H_a–C(7)); 3.60 (dd, $^2J = 10.5$, $^3J(6',7b) = 5.0$, H_b–C(7)); 3.57–3.53 (m, H–C(5'), H_{exo}–C(6)); 3.47 (ddd, $^3J(5',6') = 9.7$, $^3J(6',7b) = 5.0$, $^3J(6',7a) = 1.9$, H–C(6')); 3.34 (d, $^3J(2',3') = 8.7$, H–C(2')); 2.21 (m, H–C(3)); 1.86 (ddd, $^2J = 14.8$, $^3J(2_{exo},3) = 7.2$, $^3J(1,2_{exo}) = 3.0$, H_{exo}–C(2)); 1.73 (ddd, $^2J = 14.8$, $^3J(2_{endo},3) = 5.3$, $^3J(1,2_{endo}) = 1.3$, H_{endo}–C(2)). ¹³C-NMR (100.6 MHz, CDCl₃): 138.5, 138.0, 137.9, 137.6 (4s, 4 arom. C); 128.5–127.7 (20d, arom. CH); 99.7 (d, $J = 171$, C(1)); 87.0 (d, $J = 142$, C(4')); 78.8 (d, $J = 140$, C(2)); 78.2 (d, $J = 144$, C(6)); 78.1 (d, $J = 143$, C(5)); 77.5 (d, $J = 144$, C(3)); 75.6 (t, $J = 142$, OCH₂Ph); 75.2 (t, $J = 141$, OCH₂Ph); 75.1 (t, $J = 142$, OCH₂Ph); 74.6 (d, $J = 157$, C(5)); 73.5 (t, $J = 143$, OCH₂Ph); 70.5 (d, $J = 151$, C(1')); 69.2 (t, $J = 141$, C(7)); 68.9 (d, $J = 148$, C(4)); 63.3 (t, $J = 152$, C(6)); 35.5 (d, $J = 128$, C(3)); 32.3 (t, $J = 127$, C(2)). CI-MS (NH₃): 701 (35, [M + 18]⁺), 683 (82), 338 (12), 181 (11), 91 (100). Anal. calc. for C₄₁H₄₆O₉ (682.81): C 72.11, H 6.79; found: C 71.96, H 6.79.

4-O-Acetyl-1,6-anhydro-2,3-dideoxy-3-C-[(1R)-1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-β-D-lyxo-hexopyranose (14). Metallic Na (450 mg, 19 mmol) was added to liquid NH₃ (25 ml; condensed at –78°). A soln. of **13** (506 mg, 0.74 mmol) in anh. THF (5 ml) was added dropwise under stirring. After stirring at –78° for 40 min, solid NH₄Cl (1 g) was added and the cooling bath removed. Once at 20°, the residue was taken up in MeOH and purified by FC (silica gel, CH₂Cl₂/MeOH 2:1). The obtained oil was mixed with Ac₂O (6.6 ml), pyridine (10 ml), and DMAP (0.5 mg) and stirred at 20° for 15 h. Evaporation gave a residue that was taken up in toluene (10 ml), and the solvent was evaporated again. The latter operation was repeated and the residue purified by FC (silica gel, light petroleum ether/AcOEt 1:2): 352 mg (83%, 2 steps) of **14**. White solid: M.p. 184–186°. $[\alpha]_{589}^{25} = +14$, $[\alpha]_{546}^{25} = +15$, $[\alpha]_{435}^{25} = +18$, $[\alpha]_{405}^{25} = +21$ ($c = 0.19$, CHCl₃). UV (MeCN): final absorbance at 193 (1300). IR (KBr): 3470, 2960, 1750, 1435, 1375, 1315, 1245, 1115, 1030, 910, 600. ¹H-NMR (400 MHz, CDCl₃): 5.57 (d, $^3J(1,2_{exo}) = 0.56$, H–C(1)); 5.24 (dd, $^3J(1',3) = 10.6$, $^3J(1',2') = 2.2$,

H–C(1'')); 5.16 (*dd*, $^3J(4',5')=9.5$, $^3J(3',4')=9.5$, H–C(4'')); 5.13 (*dd*, $^3J(4,5)=7.6$, $^3J(3,4)=5.4$, H–C(4)); 5.05 (*dd*, $^3J(5',6')=9.5$, $^3J(4',5')=9.5$, H–C(5'')); 4.92 (*dd*, $^3J(3',4')=9.5$, $^3J(2',3')=9.5$, H–C(3'')); 4.79 (*dd*, $^3J(4,5)=7.6$, $^3J(5,6\text{exo})=4.6$, H–C(5)); 4.25 (*dd*, $^2J=12.2$, $^3J(6',7'a)=6.5$, H_a–C(7'')); 4.08 (*dd*, $^2J=12.2$, $^3J(6',7'a)=2.4$, H_b–C(7'')); 3.84 (*d*, $^2J=7.7$, H_{endo}–C(6)); 3.61 (*ddd*, $^3J(5',6')=9.5$, $^3J(6',7'a)=6.5$, $^3J(6',7'b)=2.4$, H–C(6'')); 3.53 (*dd*, $^3J(2',3')=9.5$, $^3J(1',2')=2.2$, H–C(2'')); 3.43 (*dd*, $^2J=7.7$, $^3J(5,6\text{exo})=4.6$, H_{exo}–C(6)); 2.48 (*ddd*, $^3J(2\text{endo},3)=11.5$, $^3J(1',3)=10.6$, $^3J(2\text{exo},3)=6.5$, $^3J(3,4)=5.4$, H–C(3)); 2.08–1.98 (H_{exo}–C(2), 6 MeCOO); 1.52 (*dd*, $^2J=13.4$, $^3J(2\text{endo},3)=11.5$, H_{endo}–C(2)). ¹³C-NMR (100.6 MHz, CDCl₃): 170.8, 170.4, 170.3, 169.9, 169.6, 169.3 (8s, COO); 98.4 (*d*, $J=174$, C(1)); 76.5, 76.3 (2*d*, $J=151$, C(2'), C(6'')); 74.7 (*d*, $J=151$, C(4'')); 72.3 (*d*, $J=159$, C(5)); 68.5, 68.4 (2*d*, $J=154$, $J=154$, C(4), C(5'')); 67.9 (*d*, $J=149$, C(1'')); 67.3 (*d*, $J=152$, C(3'')); 62.8 (*t*, $J=151$, C(7'')); 62.5 (*t*, $J=149$, C(6)); 31.0 (*t*, $J=129$, C(2)); 30.6 (*d*, $J=134$, C(3)); 20.7–20.5 (6*q*, $J=129$, MeCOO). CI-MS (NH₃): 592 (100, [*M*+18]⁺), 515 (7), 338 (14). Anal. calc. for C₂₅H₃₄O₁₅ (574.53): C 52.26, H 5.96; found: C 52.15, H 5.97.

1,4,6-Tri-O-acetyl-3-C-[(1R)-1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-D-lyxo-hexopyranose (15a/15b). As described for **10**, with **14** (458 mg, 0.36 mmol), Ac₂O (16 ml), and CF₃COOH (4 ml) (for 24 h). Workup as described, with ice (50 ml), NaHCO₃ soln. AcOEt (3 × 100 ml), and brine (200 ml) followed by FC: 489 mg (90%) of **15**, 5:1 mixture of α- and β-D-anomer. White solid. M.p. 77–80°. [α]₃₈₉²⁵ = +37, [α]₃₄₆²⁵ = +43, [α]₄₃₅²⁵ = +75, [α]₄₀₅²⁵ = +90 (*c* = 0.19, CHCl₃). UV (MeCN): 223 (1560). IR (KBr): 1750, 1435, 1375, 1235, 1035, 920, 600. ¹H-NMR (400 MHz, CDCl₃): α-D-anomer: 6.24 (br. *d*, $^3J(1,8)$, H–C(1'')); 5.20–5.14 (*m*, H–C(4'), H–C(5'')); 5.03 (*dd*, $^3J(1',3)=10.2$, $^3J(1',2')=2.4$, H–C(1'')); 5.02 (br. *s*, H–C(4)); 4.95 (*dd*, $^3J(3',4')=9.4$, $^3J(2',3')=9.4$, H–C(3'')); 4.22 (*dd*, $^2J=12.6$, $^3J(6',7'a)=3.2$, H_a–C(7'')); 4.21 (*m*, H–C(5)); 4.17–4.11 (*m*, H_a–C(6), H_b–C(7'')); 3.88 (*dd*, $^2J=11.7$, $^3J(5,6b)=7.4$, H_b–C(6)); 3.57 (*dd*, $^3J(2',3')=9.4$, $^3J(1',2')=2.4$, H–C(2'')); 3.55 (*m*, H–C(6'')); 2.77 (*m*, H–C(3)); 2.12, 2.10, 2.06, 2.05, 2.04, 2.03, 1.99, 1.98 (H_{ax}–C(2), 8 MeCOO); 1.65 (*dd*, $^2J=13.5$, $^3J=3.3$, H_{eq}–C(2)); β-D-anomer: 5.78 (*dd*, $^3J(1,2\text{ax})=9.8$, $^3J(1,2\text{eq})=2.4$, H–C(1)). ¹³C-NMR (100.6 MHz, CDCl₃): α-D-anomer: 170.6, 170.5, 170.5, 170.3, 170.2, 169.6, 169.3, 169.3 (8s, COO); 91.2 (*d*, $J=176$, C(1)); 76.5, 75.7 (2*d*, $J=141$, C(2'), C(6'')); 74.7 (*d*, $J=148$, C(4'')); 70.5 (*d*, $J=144$, C(5)); 67.8 (*d*, $J=154$, C(5'')); 67.5, 64.1 (2*d*, $J=147$, $J=50$, C(1'), C(4)); 67.1 (*d*, $J=153$, C(3'')); 63.3 (*t*, $J=149$, C(6)); 61.6 (*t*, $J=149$, C(7'')); 33.3 (*d*, $J=128$, C(3)); 26.0 (*t*, $J=130$, C(2)); 21.0–20.5 (8*q*, $J=130$, MeCOO); β-D-anomer: 93.2 (*d*, $J=167$, C(1)). CI-MS (NH₃): 694 (17, [*M*+18]⁺), 617 (100), 557 (24), 496 (73), 436 (51), 169 (53), 84 (42). Anal. calc. for C₂₉H₄₀O₁₈ (676.62): C 51.48, H 5.96; found: C 51.54, H 5.96.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-2,3-dideoxy-1',4'-O-isopropylidene-2-(phenylthio)-β-D-galactopyranose (16). As described for **11**, with **12** (34 mg, 0.04 mmol), 2,2-dimethoxypropane (2 ml), acetone (2 ml), and TsOH (12 mg) (for 15 h). FC (silica gel, light petroleum ether/AcOEt 9:1) gave 32 mg (90%) of **16**. Colorless oil. [α]₃₈₉²⁵ = +8.1, [α]₃₄₆²⁵ = +4.9, [α]₄₃₅²⁵ = –1.6, [α]₄₀₅²⁵ = –4.9 (*c* = 0.06, CHCl₃). UV (MeCN): 253 (6000), 210 (19000). IR (KBr): 2900, 1455, 1360, 1225, 1070, 920, 740, 695. ¹H-NMR (400 MHz, CDCl₃): 7.35–7.22 (*m*, 25 arom. H); 5.45 (*s*, H–C(1)); 5.02–4.56 (*m*, 8 H, OCH₂Ph); 4.6 (*dd*, $^3J(4,5)=7.6$, $^3J(5,6\text{exo})=5.2$, H–C(5)); 4.50 (*dd*, $^3J(4,5)=7.6$, $^3J(3,4)=7.6$, H–C(4)); 4.33 (*d*, $^2J=7.6$, H_{endo}–C(6)); 4.14 (*dd*, $^3J(1',3)=10.4$, $^3J(1',2')=1.7$, H–C(1'')); 3.85 (*dd*, $^3J(3',4')=9.3$, $^3J(2',3')=9.3$, H–C(3'')); 3.83 (*dd*, $^2J=11.5$, $^3J(6'a,7')=3.2$, H_a–C(7'')); 3.75 (*m*, H–C(4'), H–C(5'')); 3.69 (*dd*, $^2J=11.5$, $^3J(6',7'b)=1.8$, H_b–C(7'')); 3.62 (*dd*, $^3J(2',3')=9.3$, $^3J(1',2')=1.7$, H–C(2'')); 3.56 (*dd*, $^2J=7.6$, $^3J(5,6\text{exo})=5.2$, H_{exo}–C(6)); 3.38 (*m*, H–C(6'')); 3.01 (*d*, $^3J(2,3)=5.7$, H–C(2)); 2.67 (*ddd*, $^3J(1',3)=10.4$, $^3J(3,4)=7.6$, $^3J(2,3)=5.7$, H–C(3)); 1.41 (*s*, Me_b); 1.34 (*s*, Me_a). ¹³C-NMR (100.6 MHz, CDCl₃): 138.7, 138.6, 138.6, 138.3, 134.4 (5*s*, 5 arom. C); 130.9–127.5 (25*d*, arom. CH); 103.1 (*d*, $J=180$, C(1)); 100.6 (*s*, Me₂C); 87.9 (*d*, $J=143$, C(4'')); 79.2 (*d*, $J=141$, C(6'')); 78.3 (*d*, $J=145$, C(5'')); 77.3, 77.2 (2*d*, $J=146$, $J=146$, C(2'), C(3'')); 75.4 (*t*, $J=141$, OCH₂Ph); 74.9 (*t*, $J=145$, OCH₂Ph); 74.6 (*t*, $J=145$, OCH₂Ph); 73.5 (*t*, $J=142$, OCH₂Ph); 71.9 (*d*, $J=157$, C(5)); 69.7 (*d*, $J=145$, C(1'')); 68.6 (*t*, $J=142$, C(7'')); 63.5 (*d*, $J=149$, C(4)); 62.9 (*t*, $J=152$, C(6)); 48.3 (*d*, $J=143$, C(2)); 34.8 (*d*, $J=135$, C(3)); 26.7, 24.9 (2*q*, $J=127$, Me₂C). CI-MS (NH₃): 849 (0.2, [*M*+18]⁺), 831 (0.3), 722 (0.5), 633 (1.4), 575 (0.3), 493 (1.2), 220 (5), 91 (100).

(1S,5R)-3-C-[(1R)-2,6-Anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-6,8-dioxabicyclo[3.2.1]oct-2-en-4-one (18). Within 40 min, 1*M* Et₃AlI in toluene (3.6 ml, 3.6 mmol) was added dropwise to a stirred soln. of **5** [22] (1.55 g, 2.6 mmol) and levoglucosenone (**17**; 0.50 g, 3.9 mmol) in anhyd. CH₂Cl₂ (9 ml) cooled to –78° under Ar. After stirring at –78° for 16 h, the cooling bath was removed and Et₂O (20 ml) and then 1*M* aq. HCl (20 ml) were added under vigorous stirring (red → yellowish). After the addition of H₂O (20 ml), the aq. phase was extracted with Et₂O (3 × 30 ml) and the combined org. phase washed with brine (30 ml), dried (MgSO₄), and evaporated. FC (silica gel, light petroleum ether/AcOEt 3:2) gave 479 mg (30%) of **18**, 282 mg (20%) of **5**, and 209 mg (40%) of **17**. White solid. M.p. 48–51°. [α]₃₈₉²⁵ = –90, [α]₃₄₆²⁵ = –112,

$[\alpha]_{435}^{25} = -361$, $[\alpha]_{405}^{25} = -825$ ($c = 0.28$, CHCl_3). UV (MeCN): 212 (18300). IR (KBr): 3400, 2865, 1700, 1455, 1360, 1095, 1070, 885, 735, 695. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.35–7.07 (m , 21 H, $\text{H-C}(4)$, arom. H); 5.32 (s , $\text{H-C}(1)$); 4.93–4.79 (m , 6 H, $\text{H-C}(5)$, OCH_2Ph); 4.76 (br. s , $\text{H-C}(1')$); 4.54–4.40 (m , 3 H, OCH_2Ph); 3.78 (dd , $^3J(3',4') = 9.2$, $^3J(2',3') = 9.2$, $\text{H-C}(3')$); 3.75 (dd , $^3J(4',5') = 9.2$, $^3J(3',4') = 9.2$, $\text{H-C}(4')$); 3.72 (dd , $^2J = 6.7$, $^3J(5,6_{\text{exo}}) = 4.4$, $\text{H}_{\text{exo}}-\text{C}(6)$); 3.64 (m , $\text{CH}_2(7')$); 3.58 (d , $^2J = 6.7$, $\text{H}_{\text{endo}}-\text{C}(6)$); 3.56 (dd , $^3J(5',6') = 9.2$, $^3J(4',5') = 9.2$, $\text{H-C}(5')$); 3.53 (dd , $^3J(2',3') = 9.2$, $^3J(1',2') = 1.3$, $\text{H-C}(2')$); 3.40 (ddd , $^3J(5',6') = 9.2$, $^3J(6',7a) = 4.3$, $^3J(6',7b) = 2.4$, $\text{H-C}(6')$). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 188.2 (s , $\text{C}(4)$); 143.3 (d , $J = 166$, $\text{C}(2)$); 138.4, 138.2, 138.0, 137.8, 137.1 ($5s$, $\text{C}(3)$, 4 arom. C); 128.3–127.6 ($20d$, arom. CH); 101.0 (d , $J = 179$, $\text{C}(1)$); 86.8 (d , $J = 139$, $\text{C}(4')$); 78.8, 78.1 ($2d$, $J = 143$, $J = 145$, $\text{C}(2')$, $\text{C}(5')$); 78.4 (d , $J = 144$, $\text{C}(6')$); 77.7 (d , $J = 146$, $\text{C}(3')$); 75.5, 74.9, 74.8, 73.2 (t , $J = 144$, 4 OCH_2Ph); 72.3 (d , $J = 160$, $\text{C}(1)$); 69.0 (t , $J = 143$, $\text{C}(7')$); 66.1 (t , $J = 153$, $\text{C}(7)$); 65.2 (d , $J = 146$, $\text{C}(1')$). CI-MS (NH_3): 696 (88, $[M + 18]^+$), 587 (8.7), 181 (6.4), 108 (34), 91 (100). Anal. calc. for $\text{C}_{41}\text{H}_{42}\text{O}_9$ (678.77): C 72.55, H 6.24; found: C 72.39, H 6.21.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-3,4-dideoxy-4-(phenylthio)- β -D-altropyranose (19). To a soln. of **18** (0.73 g, 1.08 mmol) and thiophenol (114 μl , 1.10 mmol) in CH_2Cl_2 (3 ml) cooled to 0° was added Et_3N (30 μl , 0.22 mmol). The mixture was stirred at 0° for 45 min, cooled to -78° , and THF (3 ml) and 1*M* diisobutylaluminium hydride (1.8 ml, 1.8 mmol) were added. The mixture was stirred 3 h more at -78° , then CH_2Cl_2 (10 ml) and 1*M* aq. HCl (2 ml) were added under stirring. After the addition of H_2O (10 ml), the aq. phase was extracted with CH_2Cl_2 (3×15 ml), the combined org. phase washed with sat. aq. NaHCO_3 soln. (20 ml) and brine (20 ml), dried (MgSO_4) and evaporated, and the residue submitted to FC (silica gel, light petroleum ether/AcOEt 7:3): 630 mg (74%) of **19**. White solid. M.p. $150-151^\circ$. $[\alpha]_{435}^{25} = -12$, $[\alpha]_{405}^{25} = -14$, $[\alpha]_{335}^{25} = -31$, $[\alpha]_{205}^{25} = -41$ ($c = 0.22$, CHCl_3). UV (MeCN): 252 (13200), 214 (26800). IR (KBr): 3470, 2900, 1455, 1365, 1070, 740, 695. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.37–7.16 (m , 25 arom. H); 5.09 (d , $^3J(1,2) = 2.1$, $\text{H-C}(1)$); 4.94–4.40 (m , 9 H, $\text{H-C}(5)$, OCH_2Ph); 4.67 (br. d , $^3J(1',\text{OH}) = 10.1$, $\text{H-C}(1')$); 4.35 (d , $^3J(2,\text{OH}) = 6.1$, $\text{OH-C}(2)$); 4.15 (d , $^2J = 7.9$, $\text{H}_{\text{endo}}-\text{C}(6)$); 3.74–3.67 (m , $\text{H-C}(4')$, $\text{H}_{\text{exo}}-\text{C}(6)$); 3.65–3.56 (m , $\text{H-C}(2)$, $\text{H-C}(3')$, $\text{H-C}(4)$, $\text{H-C}(6')$, $\text{H}_a-\text{C}(7')$); 3.47 (d , $^3J(2',3') = 9.5$, $\text{H-C}(2')$); 3.56 (dd , $^2J = 9.9$, $^3J(6',7b) = 8.3$, $\text{H}_b-\text{C}(7')$); 3.36 (dd , $^3J(5',6') = 9.3$, $^3J(4',5') = 9.3$, $\text{H-C}(5')$); 2.11 (d , $^3J(1',\text{OH}) = 10.1$, $\text{OH-C}(1')$); 1.69 (ddd , $^3J(3,4) = 11.6$, $^3J(2,3) = 8.6$, $^3J(1',3) = 1.8$, $\text{H-C}(3)$). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 138.3, 137.5, 137.4, 137.0, 134.3 ($5s$, 5 arom. C); 130.7–127.0 ($25d$, arom. CH); 102.6 (d , $J = 174$, $\text{C}(1)$); 87.0 (d , $J = 143$, $\text{C}(4')$); 79.9 (d , $J = 139$, $\text{C}(2')$); 78.6 (d , $J = 141$, $\text{C}(5')$); 78.2 ($2d$, $J = 138$, $J = 138$, $\text{C}(3')$, $\text{C}(6')$); 75.6 (t , $J = 143$, OCH_2Ph); 75.5 (t , $J = 143$, OCH_2Ph); 75.1 (t , $J = 144$, OCH_2Ph); 75.1 (d , $J = 158$, $\text{C}(5)$); 73.5 (t , $J = 143$, OCH_2Ph); 69.4 (t , $J = 142$, $\text{C}(7')$); 66.2 (d , $J = 143$, $\text{C}(2)$); 65.8 (d , $J = 144$, $\text{C}(1')$); 65.5 (t , $J = 147$, $\text{C}(6)$); 47.7 (d , $J = 145$, $\text{C}(4)$); 47.4 (d , $J = 128$, $\text{C}(3)$). CI-MS (NH_3): 808 (45, $[M + 17]^+$), 791 (36, M^+), 108 (23), 91 (100). Anal. calc. for $\text{C}_{47}\text{H}_{50}\text{O}_9\text{S}$ (790.97): C 71.37, H 6.37; found: C 70.75, H 6.48.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-3,4-dideoxy- β -D-arabino-hexopyranose (20). As described for **8**, with **19** (285 mg, 0.36 mmol), THF (14 ml), and Raney-Ni (ca. 6 g) (30 min); TLC with light petroleum ether/AcOEt 1:1: 179 mg (72%) of **20**. White solid. M.p. $150-151^\circ$. $[\alpha]_{435}^{25} = -12$, $[\alpha]_{405}^{25} = -17$, $[\alpha]_{335}^{25} = -29$, $[\alpha]_{205}^{25} = -33$, ($c = 0.19$, CHCl_3). UV (MeCN): 214 (25100). IR (KBr): 3495, 3410, 2890, 1450, 1360, 1105, 1065, 740, 695. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 7.33–7.15 (m , 20 arom. H); 5.26 (s , $\text{H-C}(1)$); 4.92–4.73 (m , 5 H, OCH_2Ph); 4.54–4.44 (m , 4 H, $\text{H-C}(5)$, OCH_2Ph); 3.76–3.66 (m , $\text{H-C}(1')$, $\text{H-C}(3')$, $\text{H-C}(4')$, $\text{CH}_2(6)$, $\text{H}_a-\text{C}(7')$); 3.58–3.54 (m , $\text{H-C}(2)$, $\text{H}_b-\text{C}(7')$, $\text{OH-C}(2)$); 3.47–3.44 (m , $\text{H-C}(5')$, $\text{H-C}(6')$); 3.25 (d , $^3J(2',3') = 8.3$, $\text{H-C}(2')$); 2.80 (d , $^3J(\text{OH},1') = 7.7$, $\text{OH-C}(1')$); 2.08 (m , $\text{H-C}(3)$); 1.62 (ddd , $^2J = 13.6$, $^3J(3,4_{\text{endo}}) = 11.5$, $^3J(4_{\text{endo}},5) = 3.1$, $\text{H}_{\text{endo}}-\text{C}(4)$); 1.49 (ddd , $^2J = 13.6$, $^3J(3,4_{\text{exo}}) = 6.0$, $^3J(4_{\text{exo}},5) = 1.4$, $\text{H}_{\text{exo}}-\text{C}(4)$). $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3): 138.4, 138.0, 137.7, 137.7 (4s, 4 arom. C); 128.5–127.6 ($20d$, arom. CH); 101.8 (d , $J = 174$, $\text{C}(1)$); 87.1 (d , $J = 142$, $\text{C}(4')$); 78.8, 78.3 ($2d$, $J = 141$, $J = 142$, $\text{C}(5')$, $\text{C}(6')$); 77.9 (d , $J = 140$, $\text{C}(2')$); 77.4 (d , $J = 140$, $\text{C}(3')$); 75.6 (t , $J = 145$, OCH_2Ph); 75.1 (t , $J = 147$, OCH_2Ph); 75.0 (t , $J = 147$, OCH_2Ph); 73.4 (t , $J = 142$, OCH_2Ph); 73.0 (d , $J = 144$, $\text{C}(1')$); 72.8 (d , $J = 150$, $\text{C}(5)$); 72.3 (d , $J = 143$, $\text{C}(2)$); 69.3 (t , $J = 142$, $\text{C}(7')$); 68.0 (t , $J = 150$, $\text{C}(6)$); 39.3 (d , $J = 130$, $\text{C}(3)$); 30.6 (t , $J = 128$, $\text{C}(4)$). CI-MS (NH_3): 700 (70, $[M + 18]^+$), 683 (53), 665 (39), 591 (7), 181 (15), 91 (100). Anal. calc. for $\text{C}_{41}\text{H}_{46}\text{O}_9$ (682.81): C 72.11, H 6.79; found: C 72.17, H 6.82.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-3,4-dideoxy- β -D-arabino-hexopyranose (21). As described for **9** (first reaction), with **20** (100 mg, 0.14 mmol), 10% $\text{Pd}(\text{OH})_2/\text{C}$ (100 mg), and MeOH (20 ml): 47 mg (quant.) of **21**. White solid. M.p. $76-80^\circ$. $[\alpha]_{435}^{25} = -58$, $[\alpha]_{405}^{25} = -66$, $[\alpha]_{335}^{25} = -110$, $[\alpha]_{205}^{25} = -131$ ($c = 0.19$, MeOH). UV (MeCN): 194 (7700). IR (KBr): 3405, 2925, 1650, 1090, 1010, 890, 495. $^1\text{H-NMR}$ (400 MHz, CD_3OD): 5.24 (d , $^3J(1,2) = 1.3$, $\text{H-C}(1)$); 4.56 (m , $\text{H-C}(5)$); 3.91–3.89 (m , $\text{H-C}(1')$, $\text{H}_{\text{endo}}-\text{C}(6)$); 3.86 (dd , $^2J = 12.1$, $^3J(6',7a) = 2.0$, $\text{H}_a-\text{C}(7')$); 3.74 (dd , $^2J = 9.8$, $^3J(5,6_{\text{exo}}) = 5.5$, $\text{H}_{\text{exo}}-\text{C}(6)$); 3.71

(*dd*, $^2J = 12.1$, $^3J(6',7'b) = 5.2$, $H_b-C(7')$); 3.61 (*dd*, $^3J(2,3) = 9.3$, $^3J(1,2) = 1.3$, $H-C(2)$); 3.52 (*dd*, $^3J(3',4') = 9.0$, $^3J(2',3') = 9.0$, $H-C(3')$); 3.39 (*dd*, $^3J(4',5') = 9.0$, $^3J(3',4') = 9.0$, $H-C(4')$); 3.34 (*dd*, $^3J(5',6') = 9.0$, $^3J(4',5') = 9.0$, $H-C(5')$); 3.24 (*ddd*, $^3J(5',6') = 9.0$, $^3J(6',7'b) = 5.2$, $^3J(6',7'a) = 2.0$, $H-C(6')$); 3.23 (*dd*, $^3J(2',3') = 9.0$, $^3J(1',2') = 0.8$, $H-C(2')$); 2.17 (*m*, $H-C(3)$); 1.70–1.67 (*m*, $CH_2(4)$). ^{13}C -NMR (100.6 MHz, CD_3OD): 103.2 (*d*, $J = 172$, $C(1)$); 81.4 (*d*, $J = 141$, $C(6')$); 79.8 (*d*, $J = 143$, $C(4')$); 79.6 (*d*, $J = 138$, $C(2')$); 74.4 (*d*, $J = 155$, $C(5)$); 73.5, 73.4 (*2d*, $J = 142$, $C(1')$, $C(2)$); 71.1 (*d*, $J = 144$, $C(5')$); 70.7 (*d*, $J = 144$, $C(3')$); 69.1 (*t*, $J = 149$, $C(6)$); 62.5 (*t*, $J = 142$, $C(7')$); 39.7 (*d*, $J = 128$, $C(3)$); 31.8 (*t*, $J = 128$, $C(4)$). CI-MS (NH_3): 340 (48, $[M + 18]^+$), 323 (39), 305 (78), 160 (34), 143 (100), 127 (98), 81 (58).

2-O-Acetyl-1,6-anhydro-3,4-dideoxy-3-C-[(1R)-1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-β-D-arabino-hexopyranose (22). As described for **9** (second reaction), with **21** (47 mg, 0.14 mmol), Ac_2O (0.6 ml), pyridine (2.4 ml), and DMAP (0.2 mg) (co-evaporation with toluene (5 ml) twice); 70 mg (83%) of **22**. White solid. M.p. 80–84°. $[\alpha]_{589}^{25} = -53$, $[\alpha]_{546}^{25} = -55$, $[\alpha]_{435}^{25} = -94$, $[\alpha]_{405}^{25} = -115$ ($c = 0.11$, $CHCl_3$). UV (MeCN): 191 (6400). IR (KBr): 2955, 1750, 1440, 1375, 1240, 1100, 1035, 980, 900. 1H -NMR (400 MHz, $CDCl_3$): 5.39 (*d*, $^3J(1,2) = 1.4$, $H-C(1)$); 5.17 (*dd*, $^3J(4',5') = 9.3$, $^3J(3',4') = 9.3$, $H-C(4')$); 5.05, 5.03 (*2dd*, $^3J(3',4') = 9.3$, $^3J(2',3') = 9.3$, $^3J(5',6') = 9.3$, $^3J(4',5') = 9.3$, $H-C(3')$, $H-C(5')$); 5.04 (*dd*, $^3J(1',3) = 8.0$, $^3J(1',2') = 2.4$, $H-C(1')$); 4.75 (*dd*, $^3J(2,3) = 10.2$, $^3J(1,2) = 1.4$, $H-C(2)$); 4.57 (*m*, $H-C(5)$); 4.17–4.11 (*m*, $CH_2(7')$); 3.85 (*br. d*, $^2J = 7.1$, $H_{endo}-C(6)$); 3.81 (*dd*, $^2J = 7.1$, $^3J(5,6_{exo}) = 4.3$, $H_{exo}-C(6)$); 3.62 (*ddd*, $^3J(5',6') = 9.3$, $^3J(6',7'a) = 6.3$, $^3J(6',7'b) = 2.8$, $H-C(6')$); 3.60 (*dd*, $^3J(2',3') = 9.3$, $^3J(1',2') = 2.4$, $H-C(2')$); 2.66 (*dddd*, $^3J(3,4_{exo}) = 12.2$, $^3J(2,3) = 10.2$, $^3J(1',3) = 8.0$, $^3J(3,4_{endo}) = 5.8$, $H-C(3)$); 2.10, 2.08, 2.07, 2.04, 1.99, 1.97 (6s, $H_{exo}-C(4)$, 6 $MeCOO$); 1.66 (*ddd*, $^2J = 13.6$, $^3J(3,4_{endo}) = 5.8$, $^3J(4_{endo},5) = 1.5$, $H_{endo}-C(4)$). ^{13}C -NMR (100.6 MHz, $CDCl_3$): 170.5, 170.3, 170.3, 170.1, 169.5, 169.5 (6s, COO); 99.2 (*d*, $J = 177$, $C(1)$); 76.5, 76.2 (*2d*, $J = 143$, $J = 147$, $C(2')$, $C(6')$); 74.3 (*d*, $J = 154$, $C(4')$); 73.6 (*d*, $J = 149$, $C(2)$); 72.7 (*d*, $J = 158$, $C(5)$); 69.3, 68.5, 67.1 (*3d*, $J = 145$, $J = 155$, $J = 155$, $C(1')$, $C(3')$, $C(5')$); 68.1 (*t*, $J = 150$, $C(6)$); 62.7 (*t*, $J = 149$, $C(7')$); 33.6 (*d*, $J = 132$, $C(3)$); 30.1 (*t*, $J = 130$, $C(4)$); 20.9–20.5 (6q, $J = 130$, $MeCOO$). CI-MS (NH_3): 592 (100, $[M + 18]^+$), 575 (6), 515 (5), 117 (5). Anal. calc. for $C_{25}H_{34}O_{15}$ (574.53): C 52.26, H 5.96; found: C 52.32, H 5.99.

1,2,6-Tri-O-acetyl-3,4-dideoxy-3-C-[(1R)-1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol-1-C-yl]-α-D-arabino-hexopyranose (23a/23β). To a soln. of **22** (50 mg, 0.09 mmol) in Ac_2O (3.7 ml), cooled to 0° with stirring under Ar, 125 μl of a dil. triethylsilyl trifluoromethanesulfonate soln. (50 μl of TESOTf in 2.5 ml Ac_2O) was added and the reaction followed by TLC (light petroleum ether/ $AcOEt$ 1:2) to completion (generally 5–10 min). A sat. aq. $NaHCO_3$ soln. (10 ml) was then added and, after stirring at 0° for 30 min, the aq. mixture was extracted with $AcOEt$ (3 × 15 ml), the combined org. extract washed with sat. aq. $NaHCO_3$ soln. (20 ml) and then with brine (20 ml), dried ($MgSO_4$), and evaporated. FC (silica gel, light petroleum ether/ $AcOEt$ 1:2) afforded 58 mg (98%) of **23**, 6:1 mixture of α- and β-D-anomers **23a/23β**. White solid. M.p. 64–67°. $[\alpha]_{589}^{25} = +33$, $[\alpha]_{546}^{25} = +37$, $[\alpha]_{435}^{25} = +64$, $[\alpha]_{405}^{25} = +81$ ($c = 0.16$, $CHCl_3$). UV (MeCN): final absorbance at 223 (1200). IR (KBr): 1745, 1440, 1370, 1230, 1035, 605. 1H -NMR (400 MHz, $CDCl_3$): **23a**: 6.00 (*br. s*, $H-C(1)$); 5.67 (*dd*, $^3J(1',3) = 10.5$, $^3J(1',2') = 2.3$, $H-C(1')$); 5.19 (*dd*, $^3J(4',5') = 9.3$, $^3J(3',4') = 9.3$, $H-C(4')$); 5.10 (*dd*, $^3J(5',6') = 9.3$, $^3J(4',5') = 9.3$, $H-C(5')$); 5.01 (*dd*, $^3J(3',4') = 9.3$, $^3J(2',3') = 9.3$, $H-C(3')$); 4.63 (*br. s*, $H-C(2)$); 4.22 (*dd*, $^2J = 12.3$, $^3J(6',7'a) = 5.6$, $H_b-C(7')$); 4.18–4.09 (*m*, $H-C(5)$, $H_a-C(6)$, $H_b-C(6)$, $H_b-C(7')$); 3.65 (*dd*, $^3J(2',3') = 9.3$, $^3J(1',2') = 2.3$, $H-C(2')$); 3.59 (*ddd*, $^3J(5',6') = 9.3$, $^3J(6',7'a) = 5.6$, $^3J(6',7'b) = 2.4$, $H-C(6')$); 2.40 (*m*, $H-C(3)$); 2.14, 2.13, 2.11, 2.11, 2.09, 2.04, 2.01, 2.00 (8s, 8 $MeCOO$); 1.95 (*ddd*, $^2J = 14.7$, $^3J(4_{ax},5) = 11.8$, $^3J(3,4_{ax}) = 5.9$, $H_{ax}-C(4)$); 1.56 (*br. d*, $^2J = 14.7$, $H_{eq}-C(4)$); **23β**: 6.09 (*d*, $^3J(1,2) = 2.5$, $H-C(1)$). ^{13}C -NMR (100.6 MHz, $CDCl_3$): **23a**: 170.8, 170.5, 170.4, 170.3, 169.4, 169.3, 169.3, 168.6 (8s, COO); 91.4 (*d*, $J = 177$, $C(1)$); 76.7 (*d*, $J = 140$, $C(6')$); 76.2 (*d*, $J = 138$, $C(2')$); 74.5 (*d*, $J = 146$, $C(4')$); 68.1 (*d*, $J = 154$, $C(5')$); 67.4 (*2d*, $J = 148$, $J = 148$, $C(1')$, $C(3')$); 66.1 (*t*, $J = 148$, $C(6)$); 65.7 (*d*, $J = 153$, $C(2)$); 65.3 (*d*, $J = 148$, $C(5)$); 62.3 (*t*, $J = 149$, $C(7')$); 35.8 (*d*, $J = 136$, $C(3)$); 23.5 (*t*, $J = 130$, $C(4)$); 21.0–20.5 (8q, $J = 130$, $MeCOO$); **23β**: 89.8 (*d*, $J = 170$, $C(1)$). CI-MS (NH_3): 694 (100, $[M + 18]^+$), 617 (82), 117 (3). Anal. calc. for $C_{29}H_{40}O_{18}$ (676.62): C 51.46, H 5.96; found: C 51.31, H 6.04.

1,6-Anhydro-3-C-[(1R)-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol-1-C-yl]-3,4-dideoxy-1',2-O-isopropylidene-β-D-arabino-hexopyranose (24). As described for **11**, with **20** (59 mg, 0.09 mmol), 2,2-dimethoxypropane (2.5 ml), acetone (2.5 ml), and $TsOH$ (20 mg) (for 3.5 h). Workup as described, with $AcOEt$ (10 ml), H_2O (10 ml), $AcOEt$ (3 × 10 ml), sat. aq. $NaHCO_3$ soln. (10 ml), and brine (10 ml), followed by FC: 15 mg (25%) of **24**. White solid. M.p. 159–161°. $[\alpha]_{589}^{25} = -13$, $[\alpha]_{546}^{25} = -18$, $[\alpha]_{435}^{25} = -28$, $[\alpha]_{405}^{25} = -31$ ($c = 0.16$, $CHCl_3$). UV (MeCN): 208 (34150). IR (KBr): 2875, 1455, 1360, 1100, 1025, 750, 700. 1H -NMR (400 MHz, $CDCl_3$): 7.37–7.19 (*m*, 20 arom. H); 5.31 (*s*, $H-C(1)$); 4.91–4.59 (*m*, 8 H, OCH_2Ph); 4.44 (*m*, $H-C(5)$); 4.03 (*dd*, $^3J(1',3) = 10.3$, $^3J(1',2') = 2.3$, $H-C(1')$); 3.84 (*dd*, $^3J(3',4') = 9.4$, $^3J(2',3') = 9.4$, $H-C(3')$); 3.73 (*dd*, $^3J(2,3) = 9.1$, $^3J(1,2) = 1.0$, $H-C(2)$); 3.72–3.65 (*m*, $H-C(4')$, $H_{endo}-C(6)$, $H_{exo}-C(6)$, $H_a-C(7')$),

H_b–C(7''))); 3.54 (*dd*, $^3J(5',6') = 9.4$, $^3J(4',5') = 9.4$, H–C(5'))); 3.35 (*ddd*, $^3J(5',6') = 9.4$, $^3J(6',7'a) = 5.6$, $^3J(6',7'b) = 2.0$, H–C(6'))); 3.21 (*dd*, $^3J(2',3') = 9.4$, $^3J(1',2') = 2.3$, H–C(2'))); 2.42 (*dddd*, $^3J(3,4_{ax}) = 12.3$, $^3J(1',3) = 10.2$, $^3J(2,3) = 9.1$, $^3J(3,4_{eq}) = 5.8$, H–C(3))); 1.47–1.44 (*m*, CH₂(4)); 1.46 (*s*, Me); 1.43 (*s*, Me). ¹³C-NMR (100.6 MHz, CDCl₃): 138.6, 138.3, 138.3, 138.0 (4s, 4 arom. C); 128.5–127.5 (20d, arom. CH); 101.1 (*d*, *J* = 172, C(1)); 100.3 (*s*, Me₂C); 87.6 (*d*, *J* = 147, C(4'))); 79.7 (*d*, *J* = 138, C(6'))); 78.6 (*d*, *J* = 141, C(5'))); 76.8 (*d*, C(2'))); 76.7 (*d*, C(3'))); 75.5 (*t*, *J* = 143, OC H₂Ph); 75.1 (*t*, *J* = 144, OCH₂Ph); 74.8 (*t*, *J* = 144, OCH₂Ph); 74.2 (2*d*, *J* = 152, *J* = 152, C(2), C(5)); 73.1 (*t*, *J* = 141, OCH₂Ph); 70.5 (*d*, *J* = 138, C(1'))); 69.1 (2*t*, *J* = 140, *J* = 140, C(6), C(7'))); 32.5 (*d*, *J* = 135, C(3)); 30.0, 20.3 (2*q*, *J* = 128, Me₂C); 28.3 (*t*, *J* = 131, C(4)). CI-MS (NH₃): 740 (76, [M + 18]⁺), 631 (8), 181 (21), 91 (100).

REFERENCES

- [1] T. W. Rademacher, R. B. Parekh, R. A. Dwek, *Annu. Rev. Biochem.* **1988**, 57, 785; H. Lis, N. Sharon, *Eur. J. Biochem.* **1993**, 218, 1; G. W. Hart, *Curr. Opin. Cell. Biol.* **1992**, 4, 1017; A. Varki, H. H. Freeze, in 'Subcellular Biochemistry', Eds. A. H. Maddy and J. R. Harris, Plenum Press, New York, 1994, p. 71; P. Sears. C.-H. Wong, *Angew. Chem., Int. Ed.* **1999**, 38, 2301.
- [2] C. R. Bertozzi, L. L. Kiessling, *Science (Washington, D.C.)* **2001**, 291, 2357; P. M. Rudd, T. Elliott, P. Cresswell, I. A. Wilson, R. A. Dwek, *Science (Washington, D.C.)* **2001**, 291, 2370; 'Glycosciences: Status and Perspectives', Eds. H.-J. Gabius and S. Gabius, Chapman & Hall, London, U.K., 1997; P. Sears. C.-H. Wong, *Proc. Natl. Acad. Sci. U.S.A.* **1996**, 93, 12086; L. L. Kiessling, N. L. Pohl, *Chem. Biol.* **1996**, 3, 71; J. Beuth, H. L. Ko, G. Pulverer, G. Uhlenbruck, H. Pichlmaier, *Glycoconjugate J.* **1995**, 12, 1; L. A. Lasky, *Annu. Rev. Biochem.* **1995**, 64, 113; T. Toyokuni, A. K. Singhal, *Chem. Soc. Rev.* **1995**, 24, 231; A. Varki, *Proc. Natl. Acad. Sci. U.S.A.* **1994**, 91, 7390; T. Feizi, *Curr. Opin. Struct. Biol.* **1993**, 3, 701; S. Hakomori, *Curr. Opin. Immun.* **1991**, 3, 646; S. A. Wharton, W. Weis, J. J. Skehel, D. C. Wiley, 'The Influenza Virus', Plenum, New York 1989.
- [3] J. Alper, *Science (Washington, D.C.)* **2001**, 291, 2339; M. Bols, *Acc. Chem. Res.* **1998**, 31, 1; J. J. Barchi Jr., *Curr. Pharm. Des.* **2000**, 6, 485; J. H. Musser, M. B. Anderson, P. Fugedi, *Pharm. News* **1996**, 3, 11; M. S. Mulligan, J. C. Paulson, S. DeFrees, Z. L. Zheng, J. B. Lowe, P. A. Ward, *Nature (London)* **1993**, 364, 149; G. Ragupathi, L. Howard, S. Cappello, R. R. Koganty, D. Qiu, B. M. Longenecker, M. A. Reddish, K. O. Lloyd, P. O. Livingston, *Cancer Immunol. Immunother.* **1999**, 48, 1; G. D. MacLean, B. M. Longenecker, *Can. J. Oncol.* **1994**, 4, 249; G. D. MacLean, M. Reddish, R. R. Koganty, T. Wong, S. Gandhi, M. Smolenski, J. Samuel, J. M. Nabholz, B. M. Longenecker, *Cancer Immunol. Immunother.* **1993**, 36, 215; F. M. Platt, G. R. Neises, G. Reinkensmeier, M. J. Townsend, V. H. Perry, R. L. Proia, B. Winchester, R. A. Dwek, T. D. Butters, *Science (Washington, D.C.)* **1997**, 276, 428.
- [4] D. E. Levy, C. Tang, in 'The Chemistry of C-Glycosides', Tetrahedron Organic Chemistry Series, Eds. J. E. Baldwin and P. D. Magnus, Pergamon-Elsevier Science, Oxford, 1995; M. H. D. Postma, in 'C-Glycoside Synthesis', CRC, Boca Raton, FL, 1995; P. Vogel, R. Ferritto, K. Kraehenbuehl, A. Baudat, in 'Carbohydrate Mimics, Concept and Methods', Ed. Y. Chapleur, Wiley-VCH, Weinheim, 1998, p. 19, and ref. cit. therein; Y. Du, R. J. Linhardt, I. R. Vlahov, *Tetrahedron* **1998**, 54, 9913.
- [5] G. F. Springer, *Science (Washington, D.C.)* **1984**, 224, 1198; H. J. Jennings, F. E. Ashton, A. Gamian, F. Michon, R. Roy, *Can. Prog. Biotechnol.* **1987**, 3, 149; J. Taylor-Papadimitriou, A. A. Epenetos, *Trends Biotechnol.* **1994**, 12, 227; G. D. MacLean, M. A. Reddish, M. B. Bowen-Yacyshyn, S. Poppema, B. M. Longenecker, *Cancer Invest.* **1994**, 12, 46; P. D. Rye, N. V. Bovin, E. V. Vlasova, R. A. Walker, *Glycobiology* **1995**, 5, 385; G. F. Springer, *Crit. Rev. Oncol.* **1995**, 6, 57; G. Ragupathi, *Cancer Immunol. Immunother.* **1996**, 43, 152; D. K. C. Cooper, R. Oriol, 'Glycobiology in Xenotransplantation Research', in 'Glycosciences', Ed. S. Gabius, Chapman & Hall, Weinheim, 1997, p. 531; Y. J. Kim, A. Varki, *Glycoconj. J.* **1997**, 14, 569; S. Hakomori, Y. Zhang, *Chem. Biol.* **1997**, 4, 97; E. C. Hallberg, V. Strokkan, T. D. H. Cairns, M. E. Breimer, B. E. Samuelsson, *Xenotransplantation* **1998**, 5, 246; S. Hakomori, *Acta Anat.* **1998**, 161, 79; S. D. Kuduk, J. B. Schwarz, X.-T. Chen, P. W. Glunz, D. Sames, G. Ragupathi, P. O. Livingston, S. J. Danishefsky, *J. Am. Chem. Soc.* **1998**, 120, 12474; T. F. Orntoft, E. M. Vestergaard, *Electrophoresis* **1999**, 20, 362; R. Lo-Man, S. Bay, S. Vichier-Guerre, E. Deriaud, D. Cantacuzene, C. Leclerc, *Cancer Res.* **1999**, 59, 1520; J. R. Allen, S. J. Danishefsky, *J. Am. Chem. Soc.* **1999**, 121, 10875; B. Kuberan, R. J. Linhardt, *Curr. Org. Chem.* **2000**, 4, 653; E. Bousquet, A. Spadaro, M. S. Pappalardo, R. Bernardini, R. Romeo, L. Panza, G. Ronsisvalle, *J. Carbohydr. Chem.* **2000**, 19, 527.
- [6] C. Pasquarello, R. Demange, P. Vogel, *Bioorg. Med. Chem. Lett.* **1999**, 9, 793; C. Pasquarello, S. Picasso, R. Demange, M. Malissard, E. G. Berger, P. Vogel, *J. Org. Chem.* **2000**, 65, 4251.

- [7] Y.-H. Zhu, R. Demange, P. Vogel, *Tetrahedron: Asymmetry* **2000**, *11*, 263.
- [8] S. Saadat, C. E. Ballou, *J. Biol. Chem.* **1983**, *258*, 1813; Z. Szurmai, J. Kerékgyártó, J. Harangi, A. Lipták, *Carbohydr. Res.* **1987**, *164*, 313.
- [9] P. Ossowski, Å. Pillotti, P. J. Garegg, B. Lindberg, *J. Biol. Chem.* **1984**, *259*, 11337; J. K. Sharp, P. Albersheim, P. Ossowski, Å. Pillotti, P. J. Garegg, B. Lindberg, *J. Biol. Chem.* **1984**, *259*, 11341; P. Fuegedi, W. Birberg, P. J. Garegg, Å. Pillotti, *Carbohydr. Res.* **1987**, *164*, 297.
- [10] E. Altman, J.-R. Brisson, M. B. Perry, *Can. J. Chem.* **1990**, *68*, 329.
- [11] Y. Wang, P. G. Goekjian, D. M. Ryckman, Y. Kishi, *J. Org. Chem.* **1988**, *53*, 4151; R. W. Armstrong, B. R. Teegarden, *J. Org. Chem.* **1992**, *57*, 915; Z. J. Witczak, R. Chhabra, J. Chojnacki, *Tetrahedron Lett.* **1997**, *38*, 2215; M. H. D. Postema, D. Calimente, *Tetrahedron Lett.* **1999**, *40*, 4755; M. Koketsu, B. Kuberan, R. J. Lindhardt, *Org. Lett.* **2000**, *2*, 3361; A. Dondoni, L. Knieto, M. Martinkova, J. Imrich, *Chem. – Eur. J.* **1997**, *3*, 424; O. Eyrish, W.-D. Fessner, *Angew. Chem., Int. Ed.* **1995**, *34*, 1639; S. D. Burke, G. Zhang, J. L. Buchanan, *Tetrahedron Lett.* **1995**, *36*, 7023.
- [12] H. Paulsen, V. Rutz, I. Brockhausen, *Liebigs Ann. Chem.* **1992**, *747*; S. Oscarson, U. Tedebark, *Carbohydr. Res.* **1995**, *278*, 271; J. Ø. Duus, N. Nifant'ev, A. S. Shashkov, E. A. Khatuntseva, K. Bock, *Carbohydr. Res.* **1996**, *288*, 25; U. Gambert, R. Gonzalez Lio, E. Farkas, J. Thiem, V. Verez Bencomo, A. Lipták, *Bioorg. Med. Chem.* **1997**, *5*, 1285.
- [13] U. Spohr, M. Bach, R. G. Spiro, *Can. J. Chem.* **1993**, *71*, 1919.
- [14] T. Feizi, *Biochem. Soc. Trans.* **1992**, *20*, 274.
- [15] M. Guisepina Monti, S. Ghiaioni, D. Barbieri, C. Francesci, G. Marverti, M. S. Moruzzi, *Biochem. Biophys. Res. Commun.* **1999**, *257*, 460.
- [16] A. Itoh, S. Ozawa, K. Oshima, H. Nozaki, *Tetrahedron Lett.* **1980**, *21*, 361; A. Itoh, S. Ozawa, K. Oshima, H. Nozaki, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 274.
- [17] D. A. Evans, K. T. Chapman, E. M. Carreira, *J. Am. Chem. Soc.* **1988**, *110*, 3560.
- [18] S. D. Rychnovsky, B. N. Rogers, T. I. Richardson, *Acc. Chem. Res.* **1998**, *31*, 9.
- [19] Y. Wang, P. G. Goekjian, D. M. Ryckman, W. H. Miller, S. A. Babirad, Y. Kishi, *J. Org. Chem.* **1992**, *57*, 482.
- [20] H. E. Zimmerman, M. D. Traxler, *J. Am. Chem. Soc.* **1957**, *79*, 1920.
- [21] C. Marquis, F. Cardona, I. Robina, G. Wurth, P. Vogel, *Heterocycles* **2002**, *56*, 181.
- [22] Y. Wang, S. A. Babirad, Y. Kishi, *J. Org. Chem.* **1992**, *57*, 468; T. Haneda, P. G. Goekjian, S. H. Kim, Y. Kishi, *J. Org. Chem.* **1992**, *57*, 490.
- [23] K. Kraehenbuehl, S. Picasso, P. Vogel, *Helv. Chim. Acta* **1998**, *81*, 1439; I. Navarro, P. Vogel, *Helv. Chim. Acta* **2002**, *85*, 152.

Received July 12, 2002