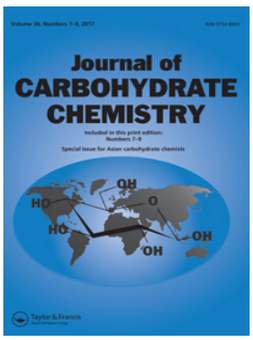

Journal of Carbohydrate Chemistry

ISSN: 0732-8303 (Print) 1532-2327 (Online) Journal homepage: http://www.tandfonline.com/loi/lcar20

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To cite this article: Joachim Thiem & Bernhard Schöttmer (2017) Formation of aureolic acid oligodeoxy mono-, di-, and trisaccharides employing the dibromomethyl methyl ether reaction, Journal of Carbohydrate Chemistry, 36:7, 279-293, DOI: 10.1080/07328303.2017.1397682

To link to this article: https://doi.org/10.1080/07328303.2017.1397682

JOURNAL OF CARBOHYDRATE CHEMISTRY
2017, VOL. 36, NO. 7, 279–293
https://doi.org/10.1080/07328303.2017.1397682

Formation of aureolic acid oligodeoxy mono-, di-, and trisaccharides employing the dibromomethyl methyl ether reaction

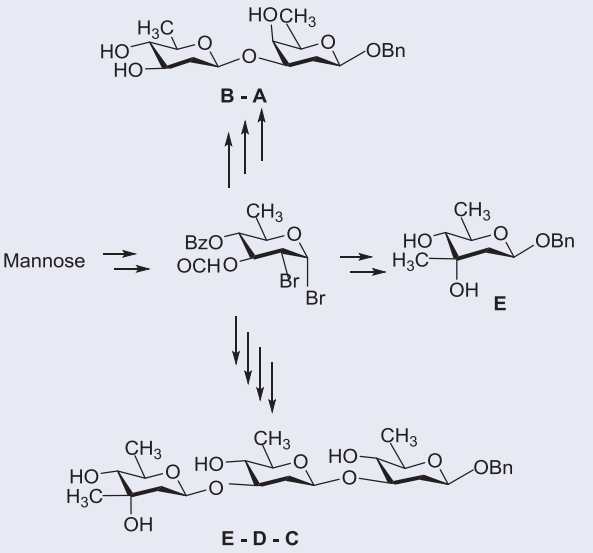
Joachim Thiem and Bernhard Schöttmer

University of Hamburg, Faculty of Science, Department of Chemistry, Martin-Luther-King-Platz 6, Hamburg, Germany

ABSTRACT

2,3-Isopropylidene D-rhamnopyranoside **2** obtained from mannose was treated with dibromomethyl methyl ether to give 2,6-dideoxy-2-bromo-glucopyranosyl bromide **5**. Correspondingly, the D-*talo* precursor **3** led to the epimeric galacto-pyranosyl bromide **4**. Both glycopyranosyl bromides were glycosylated selectively to give exclusively β,1-3-linked glycopyranosides by silver triflate catalysis. The 3-*exo*-methylene component was epoxidized with *m*CPBA to give after reductive oxirane opening the 3-*C*-methyl-β-D-*ribo*-hexopyranoside structure **17**. A corresponding build up led to the trisaccharide structure **21**. Formation of the *exo*-methylene derivative **25**, its epoxidation to **26** and reductive opening gave stereoselectively the all-β-linked methyl-branched trisaccharide **27**, representing the mithramycin E-D-C- trisaccharide.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 23 August 2017
Accepted 23 October 2017

KEYWORDS
Aureolic acids; Oligodeoxyoligosaccharides; Mithramycin; Dibromomethyl methyl ether method; β-Glycosylation for 2-Deoxysaccharides

CONTACT Prof. Dr. Joachim Thiem thiem@chemie.uni-hamburg.de University of Hamburg, Faculty of Science, Department of Chemistry, Martin- Luther-King-Platz 6, D-20146 Hamburg, Germany.

Introduction

Syntheses of oligosaccharides or glycoconjugates by glycosylation of normal saccharides has achieved a status generally accepted as solved, although often individual problems may require modified approaches, often rather particular solutions.[1] For instance, stereospecific glycosylations of 2-deoxy sugars were extensively studied and resulted in many unusual and modified approaches. One of the particularly effective methods in formation of 2-deoxy-α-glycosides is the *N*-iodosuccinimide (NIS) method.[2,3] More recently some interesting alternative procedures were suggested.[4,5] For formation of 2-deoxy-β-glycosides the dibromomethyl methyl ether (DBE) pathway showed to be an ideally suited access.[2,3] Recently also some other approaches were proposed.[6–8] Among the plethora of glycosylated natural products[9] the ubiquitous deoxy saccharides represent dominant structural components,[10] thus, effective preparative accesses are of utmost importance.

Anthracycline antitumor antibiotics are well studied in the past decades.[11,12] The most important members of the aureolic acid group are the cytostatics chromomycin A_3, olivomycin A, and the extremely effective yet rather toxic mithramycin (Figure 1), whose constitution could be finally secured.[13,14] Attached to the tetrahydroanthraquinone nucleus at the phenolic 6-OH is the B-A disaccharide having D-*arabino* and D-*lyxo* configuration. At the 2-OH position the E-D-C trisaccharide moiety with D-*ribo* and twice D-*arabino* configuration is found. The saccharides are linked throughout via anomeric β-configurations. Since all sugars display 2, 6-dideoxy structures it was of special attraction to employ the DBE method[15] for the formation of these mithramycin oligodeoxyoligosaccharides.

Results and discussion

Synthesis of the mithramycin B-A disaccharide unit

As a follow-up to previous synthetic approaches for the B-A entity of mithramycin,[13] the present approach was to employ the DBE method throughout.[16] Isopropylidenation of methyl α-D-rhamnopyranoside[17] led to compound **1**, which was further benzoylated to give crystalline **2**.[18] Derivative **1** was oxidized by pyridinium dichromate in dichloromethane at room temperature to give the corresponding 4-ulose (L-configuration[19]). By reduction with $LiAlH_4$ the *talo* compound was obtained,[19] the benzoylation of which resulted in the formation of crystalline compound **3**. Treatment of **3** with zinc bromide and dibromomethyl methyl ether in anhydrous dichloromethane at room temperature gave the 2-bromo-galactopyranosyl bromide **4** in a good yield. By glycosylation with benzyl alcohol in the presence of silver carbonate the crystalline glycoside **6** was obtained in a moderate yield. This in turn could be deformylated with acid methanol to give in a good yield compound **7**, which was used as the acceptor structure in the glycosylation to follow.

As donor molecule for the glycosylation reaction, compound **5** was obtained by DBE reaction of **2**.[18] In a solvent mixture of toluene and nitromethane (4:1) the

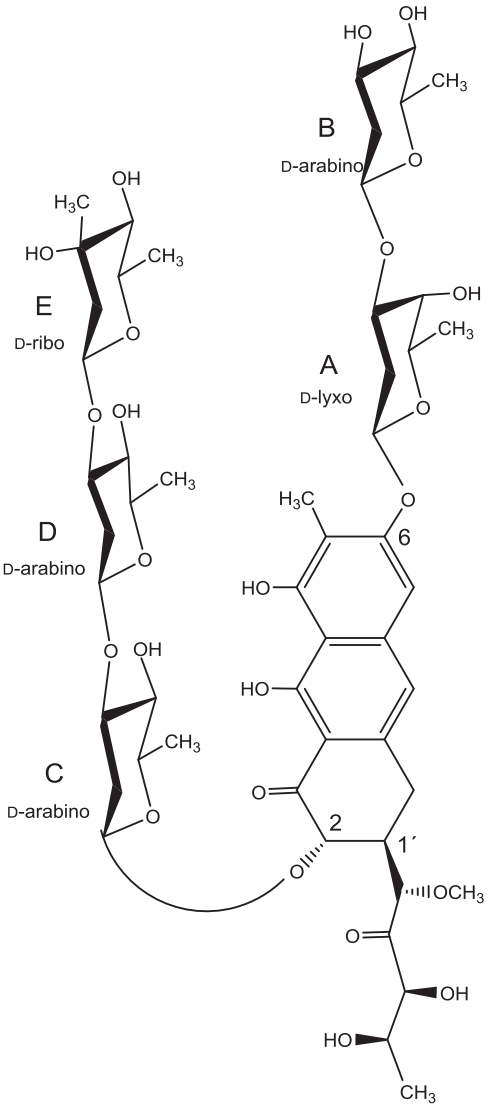
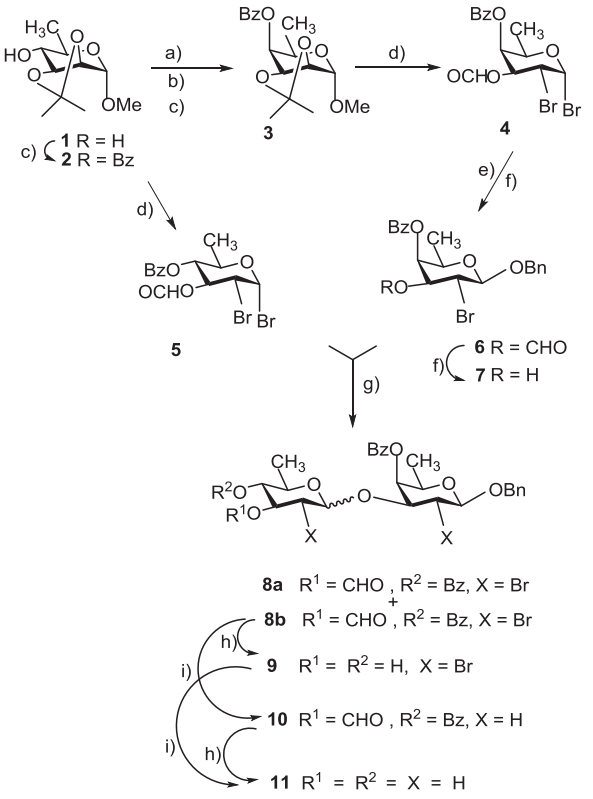


Figure 1. Mithramycin.

components were treated with silver triflate at −78°C to give the α-1,3- (**8*α***) and the β-1,3-interglycosidically linked derivative **8*β*** in about a 60% yield and a ratio of α:β = 1:3, which were separated by HPLC. Zemplén deacylation cleaved both the formate and the benzoate functionalities in the non-reducing terminal ring, but for unknown reasons the benzoate in the reducing moiety remained intact, resulting in compound **9**. Following radical reduction of **8*β*** with tri-*n*-butyl stannic hydride, the tetradeoxy component **10** was obtained in a good yield. As above its Zemplén treatment led to the final derivative **11**, which alternatively could be obtained by radical reduction of compound **9**. Both methods gave yields close to 80% (Scheme 1).



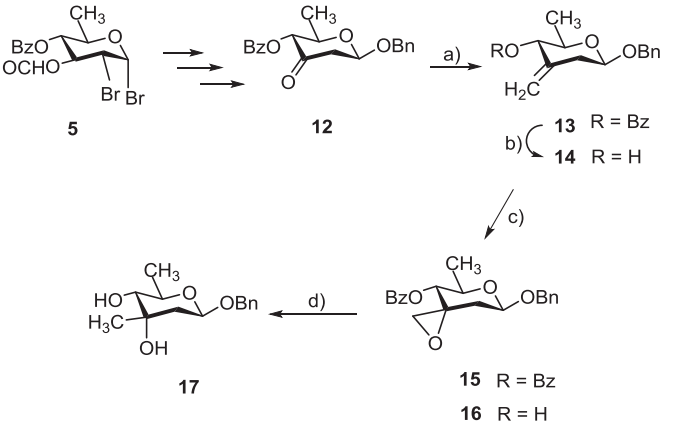
Reaction conditions: a) PDC, CH_2Cl_2 ; b) $LiAlH_4$, dioxane; c) BzCl, pyridine ; d) Br_2CHOMe, $ZnBr_2$, CH_2Cl_2, 0 °C; e) BnOH, Ag_2CO_3, 20 °C; f) MeOH, HCl, 20 °C; g) AgOTf, toluene/nitromethane 4:1, -78°C; h) NaOMe/MeOH; i) Bu_3SnH,toluene, 60°C,1h.

Scheme 1. Synthesis of the mithramycin B-A unit.

Synthesis of the mithramycin E unit

Starting with derivative **5** a four step preparation led to the crystalline 3-ulose **12,**[20] which on treatment with methyl lithium gave a mixture of benzyl β-D-olivomycoside and benzyl β-D-mycaroside in a ratio of *arabino*:*ribo* = 2:1, apparently due to the missing of a directing axial anomeric functionality.[20] Therefore, an alternative approach was devised to obtain the *ribo* component exclusively. Treatment of **12** by Wittig reaction using methyltriphenyl phosphonium bromide and *n*-butyl lithium[21] gave the *exo*-methylene derivative **13** cleanly, which was debenzoylated by Zemplén method to give compound **14**.

In structure **14** the *exo*-methylene group together with the (*S*)-configured hydroxy group at C-4 represented an ideal allylic alcohol system for employment of Sharpless asymmetric epoxidation.[22] Considering the well-established and often successfully reported requirements for a stereoselective Sharpless epoxidation,[22–25]



Reaction conditions: a) Ph_3PBr/n-BuLi ; b) NaOMe/MeOH; c) *m*-Cl-C_6H_4-CO_3H; d) $LiAlH_4$, THF.

Scheme 2. Synthesis of the mithramycin E unit.

the oxidizing system for compound **14** using *tert*-butyl hydroperoxide and tetra isopropyl ortho-titanate should contain (*R,R*)-diethyl-(+)-tartrate as directing catalyst to give a (*Re*)-attack resulting in the desired (*3R*) – epoxide. Surprisingly, under manifold varied conditions there was no evidence for the formation of any epoxide. Even taking the "wrong" (*S,S*)-diethyl-(-)-tartrate no transformation could be observed. Perhaps in this particular case limits for the utilization of the Sharpless method became apparent.It could be discussed, whether the arrangement of internal chirality in the sugar component may account for this result.

In this situation an application of the well-established *m*-chloroperbenzoic acid for normal epoxidation (Prilezhaev reaction) was considered and applied to benzoate **13**. Gratifyingly, by reaction in dichloromethane at room temperature the desired (*3R*)-configured spiro-epoxide **15** was obtained in an 83% yield with high stereoselectivity. Evidently, the preferential attack to the *exo*-methylene sugar component occurred from "underneath" and perhaps also influenced by the internal chirality at carbons 1, 4, and 5, resulting in an unexpected high stereoselectivity for the achiral reagent. A corresponding epoxidation of compound **14** under the above conditions likewise resulted in a good yield (84%) and extraordinary high stereoselectivity to give the desired (*3R*)-epoxide **16**. Finally, reductive opening of the epoxide with lithium aluminum hydride in tetrahydrofuran resulted in the β-glycoside **17** of mycarose[14,20] in a 75% yield (Scheme 2).

Synthesis of the mithramycin E-D-C trisaccharide unit

Based on previous studies,[20] the construction of the E-D-C-trisaccharide unit was approached. First, the D-C-discacharide unit **19** having two β-1,3-linked *gluco* moieties was synthesized under silver triflate catalysis at −78°C employing compound **5**[18] and the benzyl glycoside **18**.[26] The formate functionality was cleaved with

hydrochloric acid in methanol to give the crystalline compound **20**.[21] Another glycosylation with glycosyl bromide **5** under the above conditions led to the all-β-1,3-linked trisaccharide **21** in a 70% yield. The α:β-ratio was determined to be about 1:10.[20] The formate residue at the non-reducing terminus could be cleaved as above to give the crystalline component **22**. Under radical conditions employing tri-*n*-butyl stannic hydride all three bromo functions could be removed to give compound **23**, and this in turn was cleanly oxidized using pyridinium dichromate in anhydrous dichloromethane to give the crystalline 3″-ulose **24** in a 78% yield.[20]

In contrast to the successful employment of the Wittig reaction[27] *en route* formation of the E monosaccharide unit, olefination in this trisaccharide case had to be altered, since the basic reaction conditions led to considerable elimination events with cleavage of the saccharide units. Also modification of the Wittig reaction (Schlosser variation[28]), trimethylsulfonium iodide/sodium hydride (Corey)[29] or the CH_2I_2-Zn-$TiCl_4$ reagent system (Takai) [30] likewise led to eliminations or low yields. Finally, even Peterson olefination[31] of compound **24** with freshly prepared trimethylsilyl magnesium chloride in anhydrous tetrahydrofuran could also result in some elimination, however, the *exo*-methylene trisaccharide component **25** could be obtained in a moderate yield of 22% after chromatographic purification.

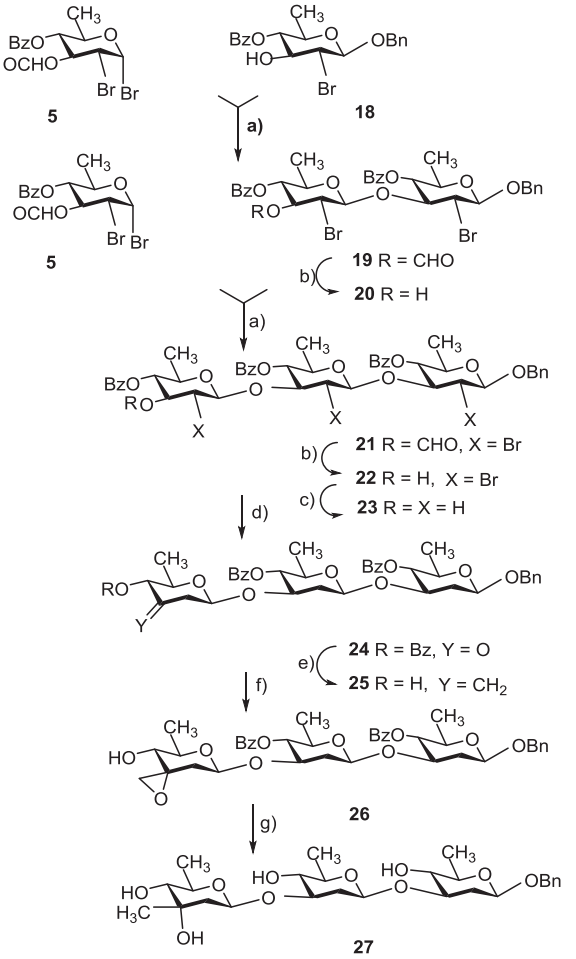
Further epoxidation of **25** could be nicely performed stereoselectively again employing simply *m*-chloroperbenzoic acid as discussed above in the monosaccharide case to give epoxy trisaccharide **26** in a 65% yield. As the final step, reductive opening of the epoxide with $LiAlH_4$ in THF resulted in the formation of target E-D-C-trisaccharide unit of mithramycin with all β-1,3-interglycosidically linked 2,6-dideoxy saccharide moieties and the correct D-*ribo* structure at the non-reducing terminus **27** in a 68% yield (Scheme 3).

Conclusion

Initially, the D-*arabino*-β,1-3-D-*lyxo* (B-A) disaccharide structure of mithramycin was prepared selectively by the DBE reaction. The *C*-3-methyl-branched D-*ribo* component (E) was obtained by use of a Prilezhaev epoxidation. Finally, the E-D-C trisaccharide of mithramycin comprising the 3″-metyl-branched D-*ribo* as well as two subsequent D-*arabino* components, all β-1,3-interglycosidically linked, was synthesized. Thus, the demanding formation of β-2,6-dideoxy oligosaccharides in aureolic acid could be solved employing the DBE method throughout.

Experimental

General Methods. All reactions were monitored by thin layer chromatography on silica gel foils GF_{254} (Merck). Detection was by UV or spraying with 10% ethanolic sulfuric acid and subsequent heating. Column chromatography was done on silica gel 60 (40–63 μm, Merck) by flash mode with the solvent mixture recorded.



Reaction conditions: a) AgOTf, toluene and nitromethane 4:1, -78 °C; b) MeOH, HCl, 20 °C; c) Bu_3SnH, toluene, 60 °C, 1h; d) $(C_5H_6N)_2Cr_2O_7$, HOAc, CH_2Cl_2; e) $(H_3C)_3SiCH_2MgCl$; f) m-Cl-C_6H_4-CO_3H; g) $LiAlH_4$, THF.

Scheme 3. Synthesis of the mithramycin E-D-C unit.

^{1}H NMR (300 MHz) was done on Bruker WM-300 and signal assignment was by ^{1}H,^{1}H-COSY experiments. Mass spectra were recorded by the CI method on Varian MAT 44S. Melting points are uncorrected and were taken with on Reichert heating microscope. Optical rotations were measured with Perkin-Elmer polarimeters 241 using sodium D line (589 nm), cuvette length 10 cm, and temperature 20°C.

Methyl 4-O-benzoyl-6-deoxy-2,3-O-isopropylidene-α-D-talopyranoside (3).

Reaction of methyl 6-deoxy-2,3-O-isopropylidene-α-D-talopyranoside[19] (3.34 g, 15.3 mmol) dissolved in anhydrous pyridine (20 mL) was treated with benzoylchloride (8.0 mL, 0.07 mmol) at 0°C. After 24h at room temperature dichloromethane (150 mL) was added, and the mixture was washed four times with diluted sulfuric

acid (1N) and water (two times), then dried over $MgSO_4$ and purified on silica gel with toluene/ethyl acetate 3:1. Crystallization was from methanol to give **3** as colorless crystals. Yield 3.2 g (65%), mp 132°C, $[\alpha]_D^{20} = +63.8$ ($c = 1.0$, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.46–7.15$ (m, 5H, Aryl-H), 4.99 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1), 4.09 (dd, 1H, $J_{1,2}$ 1.2, $J_{2,3}$ 6.5 Hz, H-2), 4.44 (dd, 1H, $J_{2,3}$ 6.5, $J_{3,4}$ 5.4 Hz H-3), 5.30 (dd, 1H, $J_{3,4}$ 5.4, $J_{4,5}$ 2.0 Hz, H-4), 4.06 (dq, 1H, $J_{4,5}$ 2.0, $J_{5,6}$ 6.6 Hz H-5), 1.25 (d, 3H, $J_{5,6}$ 6.6 Hz, 6-CH_3), 3.45 (s, 3H, OCH_3), 1.19 and 1.28 (each s, each 3H, isoprop-CH_3). Calcd. for $C_{17}H_{22}O_6$ (322.4): C, 63.34; H, 8.88. Found: C, 63.44; H, 6.87.

4-*O*-Benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-α-D-galactopyranosyl bromide (4). A solution of compound **3** (1.18 g, 3.66 mmol) in anhydrous dichloromethane (25 mL) was treated at 0°C with dibromomethyl methyl ether (1.25 mL, 7.6 mmol) and zinc bromide (187 mg, 0.83 mmol). Overnight the mixture was stirred at room temperature. Then the reddish solution was cooled to 0°C diluted with cold dichloromethane (20 mL) and washed with cold hydrochloric acid (4N), dried over $MgSO_4$ and quickly purified over silica gel by elution with cold dichloromethane (100 mL). After evaporation **4** was obtained as colorless syrup; yield 1.08 g (70%), $[\alpha]_D^{20} = +297.6$ ($c = 0.13$, CH_2Cl_2). The labile compound can be kept as solution in anhydrous dichloromethane at −20°C for some time. ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.43–8.06$ (m, 5H, Aryl-H), 8.03 (d, 1H, $J_{3,OCHO}$ 0.9 Hz, OCHO), 6.59 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.52 (dd, 1H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.9 Hz, H-2), 5.65 (ddd, 1H, $J_{2,3}$ 10.9, $J_{3,4}$ 3.5, $J_{3,OCHO}$ 0.9 Hz H-3), 5.30 (dd, 1H, $J_{3,4}$ 3.5, $J_{4,5}$ 1.4 Hz, H-4), 4.06 (dq, 1H, $J_{4,5}$ 1.4, $J_{5,6}$ 6.6 Hz H-5), 1.26 (d, 3H, $J_{5,6}$ 6.6 Hz, 6-CH_3).Calcd. for $C_{14}H_{14}Br_2O_5$ (422.1): C, 39.84; H, 3.34. Found: C, 38.54; H, 3.41.

Benzyl 4-*O*-benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-β-D-galacto-pyranoside (6). A solution of compound **4** (95 mg, 0.22 mmol) in a mixture of anhydrous ether and dichloromethane (4 mL, 1:1) was treated at 0°C with benzyl alcohol (0.1 mL, 0.96 mmol) and silver carbonate (220 mg, 11.3 mmol). Under exclusion of light stirring was continued at room temperature overnight. After filtration via Celite/active charcoal the mixture was evaporated and the remainder purified by column chromatography on silica (dichloromethane/*n*-hexane 5:1). The syrup was crystallized from ether/*n*-hexane to give **6** as colorless crystals. Yield 48 mg (48%), mp 119°C, $[\alpha]_D^{20} = +51.0$ ($c = 0.9$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.25–8.10$ (m, 10H, Aryl-H), 8.01 (d, 1H, $J_{3,OCHO}$ 0.9 Hz, OCHO), 4.67 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.12 (dd, 1H, $J_{1,2}$ 8.5, $J_{2,3}$ 11.0 Hz, H-2), 4.29 (ddd, 1H, $J_{2,3}$ 11.0, $J_{3,4}$ 3.3, $J_{3,OCHO}$ 0.9 Hz H-3), 5.48 (dd, 1H, $J_{3,4}$ 3.3, $J_{4,5}$ 1.0 Hz, H-4), 4.70 and 4.97 (AB, 2H, $J_{AB} = 11.8$ Hz, CH_2-C_6H_5), 3.82 (dq, 1H, $J_{4,5}$ 1.0, $J_{5,6}$ 6.5 Hz H-5), 1.31 (d, 3H, $J_{5,6}$ 6.5 Hz, 6-CH_3). Calcd. for $C_{21}H_{21}BrO_6$ (449.3): C, 56.14; H, 4.71. Found: C, 56.02; H, 4.73.

Benzyl 4-*O*-benzoyl-2-bromo-2,6-dideoxy-β-D-galactopyranoside (7). A solution of compound **6** (480 mg, 1.10 mmol) in methanol (60 mL) was treated with 2 drops of concentrated HCl and kept overnight at room temperature. After addition of sodium hydrogen carbonate and evaporation the residue was dissolved in dichloromethane (50 mL), successively washed with aqueous sodium hydrogen carbonate and water, dried over $MgSO_4$, filtered and evaporated to give **7** as

colorless syrup. Yield 371 mg (80%), $[\alpha]_D^{20} = +36.4$ ($c = 0.7$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): δ=7.21-8.14 (m, 10H, Aryl-H), 4.60 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.07 (dd, 1H, $J_{1,2}$ 8.4, $J_{2,3}$ 10.6 Hz, H-2), 3.97 (ddd, 1H, $J_{2,3}$ 10.6, $J_{3,4}$ 3.5, $J_{3,3\text{-OH}}$ 3.8 Hz H-3), 5.40 (dd, 1H, $J_{3,4}$ 3.5, $J_{4,5}$ 1.1 Hz, H-4), 4.71 and 4.98 (AB, 2H, J_{AB} = 12.0 Hz, CH_2-C_6H_5), 3.85 (dq, 1H, $J_{4,5}$ 1.1, $J_{5,6}$ 6.4 Hz H-5), 2.55 (d, 1H, $J_{3,3\text{-OH}}$ 3.8 Hz, OH-3), 1.29 (d, 3H, $J_{5,6}$ 6.4 Hz, 6-CH_3). Calcd. for $C_{20}H_{21}BrO_5$ (421.3): C, 57.01; H, 5.02. Found: C, 57.10; H, 5.09.

Benzyl 4-*O*-benzoyl-3-*O*-(4-O-benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-*α*-D-glucopyranosyl)-2-bromo-2,6-dideoxy-*β*-D-galactopyranoside (8*α*) and Benzyl 4-*O*-benzoyl-3-*O*-(4-O-benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-*β*-D-gluco-pyranosyl)-2-bromo-2,6-dideoxy-*β*-D-galactopyranoside (8*β*). A solution of compound **7** (57 mg, 0.14 mmol) and compound **5**[18] (70 mg, 0.17 mmol) in a mixture of anhydrous nitromethane and toluene(5 mL, 1:4) was stirred with activated molecular sieves (4 A, Merck) under nitrogen for 1 h. The mixture was cooled to −78°C and silver triflate (57 mg, 0.21 mmol) added. Following stirring for 30 h under nitrogen and exclusion of light the mixture was gradually warmed to room temperature. After filtration purification by HPLC (dichloro-methane/*n*-hexane/ethyl acetate 10:12:1) the mixture of **8α:8β** (1:3) was obtained. Yield 58 mg (56%).

Compound **8α**: yield 12 mg (14%), colorless syrup $[\alpha]_D^{20} = +42.6$ ($c = 0.45$, CH_2Cl_2). ^{1}H-NMR (300 MHz,C_6D_6): $\delta = 7.06–8.14$ (m, 15H, Aryl-H), 8.06 (d, 1H, $J_{3,OCHO}$ 0.7 Hz, OCHO), 6.10 (dt, 1H, $J_{2',3}$ 11.2, $J_{3',4'}$ 9.0, $J_{3',OCHO}$ 0.7 Hz H-3′), 5.36 (dd, 1H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 5.29 (d, 1H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.23 (t, 1H, $J_{3',4'}$ 9.0, $J_{4',5'}$ 10.0 Hz, H-4′), 4.88 (dq, 1H, $J_{4',5'}$ 10.0, $J_{5',6'}$ 6.4 Hz H-5′), 4.58 and 4.82 (AB, 2H, J_{AB} = 12.2 Hz, CH_2-C_6H_5), 4.48 (dd, 1H, $J_{1,2}$ 8.6, $J_{2,3}$ 10.8 Hz, H-2), 4.38 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 3.84 (dd, 1H, $J_{2,3}$ 10.8, $J_{3,4}$ 3.4 Hz H-3), 3.57 (dd, 1H, $J_{1',2'}$ 3.5, $J_{2',3'}$ 11.2 Hz, H-2′), 2.82 (dq, 1H, $J_{4,5}$ 0.8, $J_{5,6}$ 6.2 Hz H-5), 1.29 (d, 3H, $J_{5,6}$ 6.4 Hz, 6′-CH_3), 1.04 (d, 3H, $J_{5,6}$ 6.2 Hz, 6-CH_3).

Compound **8β**: yield 44 mg (42%), colorless syrup, $[\alpha]_D^{20} = +38.5$ ($c = 0.85$, CH_2Cl_2). ^{1}H-NMR (300 MHz,C_6D_6): δ = 7.02–8.14 (m, 15H, Aryl-H), 8.08 (d, 1H, $J_{3,OCHO}$ 0.8 Hz, OCHO), 5.59 (ddd, 1H, $J_{2',3}$ 10.8, $J_{3',4'}$ 10.4, $J_{3',OCHO}$ 0.8 Hz H-3′), 5.47 (dd, 1H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 4.92 (dd, 1H, $J_{3',4'}$ 10.4, $J_{4',5'}$ 9.8 Hz, H-4′), 4.69 (d, 1H, $J_{1',2'}$ 8.6 Hz, H-1′), 4.65 and 4.90 (AB, 2H, J_{AB} = 12.2 Hz, CH_2-C_6H_5), 4.57 (dd, 1H, $J_{1,2}$ 8.6, $J_{2,3}$ 10.4 Hz, H-2), 4.49 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 3.75 (dd, 1H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 3.52 (dd, 1H, $J_{1',2'}$ 8.6, $J_{2',3'}$ 10.8 Hz, H-2′), 3.19 (dq, 1H, $J_{4',5'}$ 9.8, $J_{5',6'}$ 6.2 Hz, H-5′), 3.10 (dq, 1H, $J_{4,5}$ 0.8, $J_{5,6}$ 6.4 Hz, H-5), 1.18 (d, 3H, $J_{5,6}$ 6.2 Hz, 6′-CH_3), 1.13 (d, 3H, $J_{5,6}$ 6.4 Hz, 6-CH_3). Calcd. for $C_{34}H_{34}Br_2O_{10}$ (762.4): C, 53.56; H, 4.49. Found for **8α**: C, 53.65; H, 4.44; found for **8β**: C, 53.68; H, 4.42.

Benzyl 4-*O*-benzoyl-3-*O*-(2-bromo-2,6-dideoxy-*β*-D-glucopyranosyl)-2-bromo-2,6-dideoxy-*β*-D-galactopyranoside (9). A solution of compound **8β** (36 mg, 0.054 mmol) in anhydrous methanol (5 mL) was treated with a catalytic amount of sodium methylate for 6 h at room temperature. After neutralization with

Amberlite IR 120 H^+ the residue was filtered, dissolved in ethyl acetate (10 mL) filtered and evaporated to give **9** as colorless syrup. Yield 23 mg (78%), $[\alpha]_D^{20} = +48.7$ ($c = 1.4$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.23$–8.04 (m, 10H, Aryl-H), 5.42 (dd, 1H, $J_{3,4}$ 3.5, $J_{4,5}$ 0.8 Hz, H-4), 3.15 (dd, 1H, $J_{3',4'}$ 8.2, $J_{4',5'}$ 9.2 Hz, H-4′), 4.78 (d, 1H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.70 and 4.96 (AB, 2H, $J_{AB} = 11.8$ Hz, CH_2-C_6H_5), 4.22 (dd, 1H, $J_{1,2}$ 8.5, $J_{2,3}$ 10.9 Hz, H-2), 4.59 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 3.96 (dd, 1H, $J_{2,3}$ 10.9, $J_{3,4}$ 3.5 Hz H-3), 3.54 (m, 2H, H-2′, −3′), 3.37 (dq, 1H, $J_{4',5'}$ 9.2, $J_{5',6'}$ 6.2 Hz H-5′), 3.80 (dq, 1H, $J_{4,5}$ 0.8, $J_{5,6}$ 6.6 Hz H-5), 1.68 and 2.74 (bs, 2H, OH),1.28 (d, 3H, $J_{5,6}$ 6.2 Hz, 6′-CH_3), 1.26 (d, 3H, $J_{5,6}$ 6.6 Hz, 6-CH_3). Calcd. for $C_{26}H_{30}Br_2O_8$ (630.3): C, 49.54; H, 4.80. Found: C, 49.46; H, 4.72.

Benzyl 4-*O*-benzoyl-3-*O*-(4-O-benzoyl-2,6-dideoxy-3-O-formyl-*β*-D-arabino-hexopyranosyl)-2,6-dideoxy-*β*-D-lyxo-hexopyranoside (10). A solution of compound **8*β*** (136 mg, 0.18 mmol) in anhydrous toluene (23 mL) was treated under nitrogen with tri-*n*-butyl stannic hydride (290 μL, 1.0 mmol) and a catalytic amount of α,α'-azo-bis-isobutyronitrile and stirred for 3 h at 50°C. After evaporation of the solvent the residue was purified by chromatography (toluene/ethyl acetate 12:1) to give **10** as colorless syrup. Yield 92 mg (85%), $[\alpha]_D^{20} = -4.3$ ($c = 1.1$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): δ=7.16–8.21 (m, 15H, Aryl-H), 8.07 (d, 1H, $J_{3,OCHO}$ 0.8 Hz, OCHO), 5.39 (bd, 1H, $J_{3,4}$ 3.0, $J_{4,5}$ 1.2 Hz, H-4), 5.19 (dddd, 1H, $J_{2a',3'}$ 9.8, $J_{2e',3'}$ 5.4, $J_{3',4'}$ 9.4, $J_{3',OCHO}$ 0.8 Hz, H-3′), 4.97 (t, 1H, $J_{3',4'}$ 9.4, $J_{4',5'}$ 9.6 Hz, H-4′), 4.71 (dd, 1H, $J_{1',2a'}$ 9.6, $J_{1',2e'}$ 2.2 Hz, H-1′), 4.65 and 4.95 (AB, 2H, $J_{AB} = 12.2$ Hz, CH_2-C_6H_5), 4.59 (dd, 1H, $J_{1,2a}$ 9.4, $J_{1,2e}$ 2.4 Hz, H-1), 4.03 (ddd, 1H, $J_{2a,3}$ 8.2, $J_{2e,3}$ 4.8, $J_{3,4}$ 3.0 Hz, H-3), 3.69 (dq, 1H, $J_{4,5}$ 1.2, $J_{5,6}$ 6.4 Hz, H-5), 3.55 (dq, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 6.2 Hz, H-5′), 2.22 (ddd, 1H, $J_{1',2e'}$ 2.2, $J_{2a',2e'}$ 10.6, $J_{2a',3'}$ 5.4 Hz, H-2e′), 2.08 (mc, 1H, $J_{1,2e}$ 2.4, $J_{2a,2e}$ 10.5, $J_{2e,3}$ 4.8 Hz, H-2e), 2.07 (mc, 1H, $J_{1,2a}$ 9.4, $J_{2a,2e}$ 10.5, $J_{2a,3}$ 8.2 Hz, H-2a), 1.69 (ddd, 1H, $J_{1',2a'}$ 9.6, $J_{2a',2e'}$ 10.6, $J_{2a',3'}$ 9.8 Hz, H-2a′), 1.27 (d, 3H, $J_{5,6}$ 6.4 Hz, 6-CH_3), 1.22 (d, 3H, $J_{5,6}$ 6.2 Hz, 6′-CH_3). Calcd. for $C_{34}H_{36}O_{10}$ (604.7): C, 67.54; H, 6.00. Found: C, 67.62; H, 6.06.

Benzyl 4-*O*-benzoyl-3-*O*-(2,6-dideoxy-3-O-formyl-*β*-D-arabino-hexopyrano-syl)- 2,6-dideoxy-*β*-D-lyxo-hexopyranoside (11). a) A solution of compound **10** (45 mg, 0.07 mmol) in anhydrous methanol (7 mL) was treated with a catalytic amount of sodium methylate for 2 h at room temperature. After neutralization with Amberlite IR 120 H^+ the residue was filtered, dissolved in ethyl acetate (10 mL) filtered and evaporated to give **78** as colorless syrup. Yield 26 mg (78%).

b) A solution of compound **9** (70 mg, 0.11 mmol) in anhydrous toluene (20 mL) was treated under nitrogen with tri-*n*-butyl stannic hydride (175 μL, 0.6 mmol) and a catalytic amount of α,α'-azo-bis-isobutyronitrile and stirred for 1 h at 60°C. After evaporation of the solvent the residue was purified by chromatography (toluene/ethyl acetate 12:1) to give **11** as colorless syrup. Yield 39 mg (75%), $[\alpha]_D^{20} = -7.4$ ($c = 1.3$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.16$–8.21 (m, 10H, Aryl-H), 5.35 (bd, 1H, $J_{3,4}$ 3.0, $J_{4,5}$ 0.7 Hz, H-4), 4.97 (t, 1H, $J_{3',4'}$ 8.0, $J_{4',5'}$ 9.0 Hz, H-4′), 4.63 and 4.94 (AB, 2H, $J_{AB} = 12.2$ Hz, CH_2-C_6H_5), 4.56 (dd, 1H, $J_{1',2a'}$ 9.2, $J_{1',2e'}$ 2.0 Hz, H-1′), 4.55 (dd, 1H, $J_{1,2a}$ 9.2, $J_{1,2e}$ 1.8 Hz, H-1), 4.01 (ddd,

1H, $J_{2a,3}$ 8.2, $J_{2e,3}$ 4.8, $J_{3,4}$ 3.0 Hz, H-3), 3.68 (dq, 1H, $J_{4,5}$ 0.7, $J_{5,6}$ 6.4 Hz H-5), 3.46 (mc, 1H, $J_{3',4'}$ 8.0 Hz, H-3′), 3.19 (dq, 1H, $J_{4',5'}$ 9.0, $J_{5',6'}$ 6.2 Hz H-5′), 2.10 (ddd, 1H, $J_{1,2e}$ 1.8, $J_{2a,2e}$ 11.6, $J_{2e,3}$ 4.8 Hz, H-2e), 2.02 (mc, 1H, $J_{1,2a}$ 9.2, $J_{2a,2e}$ 11.6, $J_{2a,3}$ 8.2 Hz, H-2a), 2.01 (mc, 1H, $J_{1',2e'}$ 2.0 Hz, H-2e′), 1.60 (mc, 1H, $J_{1',2a'}$ 9.2 Hz, H-2a′), 1.31 (d, 3H, $J_{5,6}$ 6.4 Hz, 6-CH_3), 1.33 (d, 3H, $J_{5,6}$ 6.2 Hz, 6′-CH_3). Calcd. for $C_{26}H_{32}O_8$ (472.5): C, 66.09; H, 6.83. Found: C, 65.98; H, 6.78.

Benzyl 4-*O*-benzoyl-3-*C*-methylen-2,3,6-trideoxy-β-D-erythro-hexopyranoside (13). A solution of methyl triphenyl phosphonium bromide (436 mg, 1.2 mmol) in anhydrous THF (20 mL) was treated under nitrogen with *n*-butyl lithium in *n*-hexane (436 μL, 1.0 mmol) at 0°C to give a yellow suspension. Under vigorous stirring compound **12**[18] (173 mg, 0.51 mmol) was added and stirred another 30 min at room temperature. Diethyl ether (7 mL) was added, filtered and the remainder evaporated. Purification was by column chromato-graphy (toluene/ethyl acetate 20:1) to give **13** as colorless syrup. Yield 110 mg (64%), $[\alpha]_D{}^{20} = -70.6$ ($c = 1.0$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.32$–8.12 (m, 10H, Aryl-H), 4.62 (dd, 1H, $J_{1,2a}$ 9.2, $J_{1,2e}$ 2.6 Hz, H-1), 4.92 and 5.28 (mc, 2H, $CH_2 = C$), 4.92 (mc, 1H, $J_{4,5}$ 9.1 Hz, H-4), 4.64 and 4.95 (AB, 2H, $J_{AB} = 11.9$ Hz, CH_2-C_6H_5), 3.60 (dq, 1H, $J_{4,5}$ 9.1, $J_{5,6}$ 6.2 Hz H-5), 2.70 (dd, 1H, $J_{1,2e}$ 2.6, $J_{2a,2e}$ 13.3 Hz, H-2e), 2.55 (dd, 1H, $J_{1,2a}$ 9.2, $J_{2a,2e}$ 13.3 Hz, H-2a), 1.37 (d, 3H, $J_{5,6}$ 6.2 Hz, 6-CH_3). Calcd. for $C_{21}H_{22}O_4$ (338.4): C, 74.54; H, 6.55. Found: C, 74.16; H, 6.47.

Benzyl 3-*C*-methylen-2,3,6-trideoxy-β-D-erythro-hexopyranoside (14). A solution of compound **13** (107 mg, 0.32 mmol) in anhydrous methanol (10 mL) was treated with a catalytic amount of sodium methylate for 24 h at room temperature. After neutralization with Amberlite IR 120 H^+ the residue was filtered, dissolved in ethyl acetate (20 mL) filtered and evaporated to give **14** as colorless syrup. Yield 51 mg (66%), $[\alpha]_D{}^{20} = -11.8$ ($c = 0.9$, CH_2Cl_2). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.21$–7.62 (m, 5H, Aryl-H), 4.90 and 5.05 (bs, 2H, $CH_2 = C$), 4.57 and 4.88 (AB, 2H, $J_{AB} = 11.8$ Hz, CH_2-C_6H_5), 4.48 (dd, 1H, $J_{1,2a}$ 9.0, $J_{1,2e}$ 2.4 Hz, H-1), 3.71 (mc, 1H, $J_{4,5}$ 8.8 Hz, H-4), 3.20 (dq, 1H, $J_{4,5}$ 8.8, $J_{5,6}$ 6.1 Hz H-5), 2.60 (dd, 1H, $J_{1,2e}$ 2.4, $J_{2a,2e}$ 13.2 Hz, H-2e), 2.38 (dd, 1H, $J_{1,2a}$ 9.0, $J_{2a,2e}$ 13.2 Hz, H-2a), 1.40 (d, 3H, $J_{5,6}$ 6.1 Hz, 6-CH_3). Calcd. for $C_{14}H_{18}O_3$ (234.3): C, 71.77; H, 7.74. Found: C, 71.69; H, 7.66.

Benzyl 3,3′-anhydro-4-*O*-benzoyl-2,6-dideoxy-3-*C*-hydroxymethyl-β-D-ribo-hexopyranoside (15). A solution of compound **13** (250 mg, 0.74 mmol) in 1,2-dichloroethane (20 mL) was stirred with *m*-chloroperbenzoic acid (312 mg, 1.8 mmol) for 24 h at room temperature. The solution was washed with aqueous sodium hydroxide (0.1 N) and trice with water, dried over $MgSO_4$, filtered, and evaporated. Purification by chromatography (toluene/ethyl acetate 4:1) gave **15** as colorless syrup. Yield 215 mg (83%), $[\alpha]_D{}^{20} = -33.7$ ($c = 0.7$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.17$–8.05 (m, 10H, Aryl-H), 5.15 (d, 1H, $J_{4,5}$ 9.3 Hz, H-4), 4.96 (dd, 1H, $J_{1,2a}$ 9.4, $J_{1,2e}$ 2.4 Hz, H-1), 4.62 and 4.93 (AB, 2H, $J_{AB} = 11.8$ Hz, CH_2-C_6H_5), 4.00 (dq, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 6.2 Hz H-5), 2.61 and 2.72 (AB, 2H, $J_{AB} = 4.2$ Hz, H_2C-epoxide), 2.32 (dd, 1H, $J_{1,2e}$ 2.4, $J_{2a,2e}$ 13.7 Hz, H-2e), 1.73 (dd, 1H, $J_{1,2a}$ 9.4, $J_{2a,2e}$ 13.7 Hz, H-2a), 1.32 (d, 3H, $J_{5,6}$ 6.2 Hz, 6-CH_3). Calcd. for $C_{21}H_{22}O_5$ (354.4): C, 71.17; H, 6.26. Found: C, 71.28; H, 6.31.

Benzyl 3,3′-anhydro-2,6-dideoxy-3-*C*-hydroxymethyl-*β*-D-ribo-hexopyrano-side (16). A solution of compound **14** (70 mg, 0.30 mmol) in 1,2-dichloroethane (10 mL) was stirred with *m*-chloroperbenzoic acid (139 mg, 0.80 mmol) for 24 h at room temperature. The solution was washed with aqueous sodium hydroxide (0.1 N) and trice with water, dried over $MgSO_4$, filtered, and evaporated. Purification by chromatography (toluene/ethyl acetate 4:1) gave **16** as colorless syrup. Yield 60 mg (84%), $[\alpha]_D^{20} = -15.8$ ($c = 0.6$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.17$–8.05 (m, 5H, Aryl-H), 4.79 (dd, 1H, $J_{1,2a}$ 9.8, $J_{1,2e}$ 2.2 Hz, H-1), 4.59 and 4.90 (AB, 2H, $J_{AB} = 11.8$ Hz, CH_2-C_6H_5), 3.46 (m, 2H, H-4, −5), 2.59 and 3.06 (AB, 2H, $J_{AB} = 4.4$ Hz, H_2C-epoxide), 2.28 (dd, 1H, $J_{1,2e}$ 2.2, $J_{2a,2e}$ 14.1 Hz, H-2e),1.68 (dd, 1H, $J_{1,2a}$ 9.8, $J_{2a,2e}$ 14.1 Hz, H-2a), 1.34 (d, 3H, $J_{5,6}$ 6.0 Hz, 6-CH_3). Calcd. for $C_{14}H_{18}O_4$ (250.3): C, 67.18; H, 7.25. Found: C, 67.22; H, 7.23.

Benzyl 2,6-dideoxy-3-*C*-methyl-*β*-D-ribo-hexopyranoside (17). A solution of compound **16** (20 mg, 0.08 mmol) in anhydrous THF (3 mL) was stirred with lithium aluminium hydride (5 mg, 0.13 mmol) for 24 h at room temperature. After cautious addition of methanol the residue was filtered, taken up in ethyl acetate (10 mL), washed with water, dried over $MgSO_4$ and evaporated to give **17** as colorless syrup. Yield 15 mg (75%), $[\alpha]_D^{20} = -40.9$ ($c = 0.7$, CH_2Cl_2), lit.[17] $[\alpha]_D^{20} = -44.1$ ($c = 0.42$, CH_2Cl_2). The ^{1}H-NMR (300 MHz, $CDCl_3$) data corresponded throughout.

Benzyl 4-*O*-benzoyl-3-*O*-[4-*O*-benzoyl-3-*O*-(3-*C*-methylen-2,3,6-trideoxy-*β*-D-erythro-hexopyranosyl)-2,6-dideoxy-*β*-D-arabino-hexopyranosyl]-2,6-dideoxy-*β*-D-arabino-hexopyranoside (25). Under nitrogen cover to magnesium chips (15 mg, 0.6 mmol) in anhydrous THF (5 mL) was added trimethylsilyl methyl chloride (71 mg, 0.6 mmol) and the reaction started by addition of some drops of 1,2-dibromo-ethane. After reflux for 1h and cooling to room temperature a solution of compound **24** [20] (50 mg, 0.06 mmol) in warm anhydrous toluene (2 mL) and stirred for another hour at 20°C. Following addition of aqueous ammonium sulfate solution (20 mL), extraction with dichloromethane (3 times, each 10 mL) and drying over $MgSO_4$, evaporation gave the raw material, which was purified by column chromatography (toluene/ethyl acetate 4:1) to give compound **25** as colorless syrup. Yield 10 mg (22%), $[\alpha]_D^{20} = -53.7$ ($c = 0.8$, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): $\delta = 7.26$–8.14 (m, 15H, Aryl-H), 4.91 (t, 1H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.6 Hz, H-4′), 4.79 and 4.93 (bd, 2H, $CH_2 = C$), 4.62 and 4.94 (AB, 2H, $J_{AB} = 12.0$ Hz, CH_2-C_6H_5), 4.66 (dd, 1H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.3 Hz, H-4), 4.58 (dd, 1H, $J_{1',2a'}$ 9.8, $J_{1',2e'}$ 2.1 Hz, H-1′), 4.56 (dd, 1H, $J_{1,2a}$ 9.7, $J_{1,2e}$ 2.0 Hz, H-1), 4.32 (dd, 1H, $J_{1'',2a''}$ 9.2, $J_{1'',2e''}$ 2.6 Hz, H-1″), 4.06 (ddd, 1H, $J_{2a',3'}$ 11.9, $J_{2e',3'}$ 5.3, $J_{3',4'}$ 9.5 Hz, H-3′), 3.99 (ddd, 1H, $J_{2a,3}$ 12.0, $J_{2e,3}$ 5.2, $J_{3,4}$ 9.2 Hz, H-3), 3.56 (dq, 1H, $J_{4',5'}$ 9.6, $J_{5',6'}$ 6.2 Hz, H-5′), 3.45 (dd, 1H, $J_{4'',5''}$ 9.0, $J_{4'',4''\text{-OH}}$ 7.0 Hz, H-4″), 3.38 (dq, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 6.2 Hz, H-5), 2.96 (dq, 1H, $J_{4'',5''}$ 9.0, $J_{5'',6''}$ 6.2 Hz, H-5″), 2.34 (dd, 1H, $J_{1'',2e''}$ 2.6, $J_{2a'',2e''}$ 13.6 Hz, H-2e″), 2.32 (ddd, 1H, $J_{1',2e'}$ 2.1, $J_{2a',2e'}$ 12.2, $J_{2e',3'}$ 5.3 Hz, H-2e′), 2.13 (ddd, 1H, $J_{1,2e}$ 2.0, $J_{2a,2e}$ 13.4, $J_{2e,3}$ 5.2 Hz, H-2e), 2.11 (dd, 1H, $J_{1'',2a''}$ 9.2, $J_{2a',2e'}$ 12.2, $J_{2a'',3''}$ 13.6 Hz, H-2a″), 1.82 (ddd, 1H, $J_{1',2a'}$ 9.8, $J_{2a',2e'}$ 12.2, $J_{2a',3'}$ 11.9 Hz, H-2a′), 1.58 (mc, 1H, $J_{1,2a}$ 9.7, $J_{2a,2e}$ 13.4,

$J_{2a,3}$ 12.0 Hz, H-2a), 1.46 (d,1H, $J_{4'',4''\text{-OH}}$ 7.0 Hz, 4″-OH), 1.31 (d, 3H, $J_{5',6'}$ 6.2 Hz, 6′-CH_3), 1.06 (d, 3H, $J_{5'',6''}$ 6.2 Hz, 6″-CH_3), 1.02 (d, 3H, $J_{5,6}$ 6.2 Hz, 6-CH_3). Calcd. for $C_{40}H_{46}O_{11}$ (702.8): CI with ammonia found $(M+NH_4)^+$ 721.

Benzyl 4-*O*-benzoyl-3-*O*-[4-*O*-benzoyl-3-*O*-(3,3′-anhydro-2,6-dideoxy-3-*C*-hydroxymethyl-*β*-D-ribo-hexopyranosyl)-2,6-dideoxy-*β*-D-arabino-hexopyranosyl]-2,6-dideoxy-*β*-D-arabino-hexopyranoside (26). A solution of compound **25** (8 mg, 0.01 mmol) in 1,2-dichloroethane (3 mL) was stirred with *m*-chloroperbenzoic acid (3.5 mg, 0.02 mmol) for 2 h at room temperature. The solution was washed with aqueous sodium hydroxide (0.1 N) and trice with water, dried over $MgSO_4$, filtered, and evaporated. Purification by chromato-graphy (toluene/ethyl acetate 4:1) gave **26** as colorless syrup. Yield 5 mg (65%), $[\alpha]_D^{20} = -66.9$ (c = 0.6, CH_2Cl_2). ^{1}H-NMR (300 MHz,$CDCl_3$): δ = 7.32–8.14 (m, 15H, Aryl-H), 4.91 (dd, 1H, $J_{3,4}$ 9.4, $J_{4,5}$ 9.3 Hz, H-4), 4.65 (t, 1H, $J_{3',4'}$ 9.0, $J_{4',5'}$ 9.3 Hz, H-4′), 4.64 (dd, 1H, $J_{1'',2a''}$ 10.0, $J_{1'',2e''}$ 2.0 Hz, H-1″), 4.61 and 4.92 (AB, 2H, J_{AB} = 12.0 Hz, CH_2-C_6H_5), 4.58 (dd, 1H, $J_{1,2a}$ 9.2, $J_{1,2e}$ 2.0 Hz, H-1), 4.57 (dd, 1H, $J_{1',2a'}$ 9.7, $J_{1',2e'}$ 1.8 Hz, H-1′), 4.04 (ddd, 1H, $J_{2a,3}$ 12.0, $J_{2e,3}$ 5.1, $J_{3,4}$ 9.4 Hz, H-3), 3.93 (ddd, 1H, $J_{2a',3'}$ 11.8, $J_{2e',3'}$ 5.3, $J_{3',4'}$ 9.0 Hz, H-3′), 3.56 (dq, 1H, $J_{4,5}$ 9.5, $J_{5,6}$ 6.4 Hz H-5), 3.39 (dq, 1H, $J_{4',5'}$ 9.3, $J_{5',6'}$ 6.2 Hz, H-5′), 3.16 (mc, 2H, H-4″,-5″), 2.47 and 2.91 (AB, 2H, J_{AB} = 4.5 Hz, CH_2-epoxide), 2.32 (ddd, 1H, $J_{1,2e}$ 2.0, $J_{2a,2e}$ 12.2, $J_{2e,3}$ 5.1 Hz, H-2e), 2.13 (ddd, 1H, $J_{1',2e'}$ 1.8, $J_{2a',2e'}$ 12.4, $J_{2e',3'}$ 5.3 Hz, H-2e′), 1.96 (dd, 1H, $J_{1'',2e''}$ 2.0, $J_{2a'',2e''}$ 14.0 Hz, H-2e″), 1.81 (ddd, 1H, $J_{1,2a}$ 9.2, $J_{2a,2e}$ 12.2, $J_{2a,3}$ 12.0 Hz, H-2a), 1.54 (ddd, 1H, $J_{1',2a'}$ 9.7, $J_{2a',2e'}$ 12.4, $J_{2a',3'}$ 11.8 Hz, H-2a′), 1.43 (dd, 1H, $J_{1'',2a''}$ 10.0, $J_{2a',2e'}$ 14.0, $J_{2a'',3''}$ 11.8 Hz, H-2a″), 1.31 (d, 3H, $J_{5,6}$ 6.4 Hz, 6-CH_3), 1.05 (d, 3H, $J_{5'',6''}$ 5.9 Hz, 6″-CH_3), 1.01 (d, 3H, $J_{5',6'}$ 6.2 Hz, 6′-CH_3). Calcd. for $C_{40}H_{46}O_{12}$ (718.8): CI with ammonia found $(M+NH_4)^+$ 737.

Benzyl 3-*O*-[3-*O*-(2,6-dideoxy-3-*C*-methyl-*β*-D-ribo-hexopyranosyl)-2,6-dideoxy-*β*-D-arabino-hexopyranosyl]-2,6-dideoxy-*β*-D-arabino-hexopyranoside (27). A solution of compound **26** (5 mg, 7 μmol) in anhydrous THF (2 mL) was stirred with lithium aluminium hydride (2 mg, 0.05 mmol) for 24 h at room temperature. After cautious addition of methanol the residue was filtered, taken up in ethyl acetate (5 mL), washed with water, dried over $MgSO_4$ and evaporated to give **27** as colorless syrup. Yield 2.4 mg (68%), $[\alpha]_D^{20} = -58.3$ (c = 0.15, CH_2Cl_2), ^{1}H-NMR [300 MHz,$(CD_3)_2CO$]: δ=7.18-8.04 (m, 5H, Aryl-H), 4.83 (dd, 1H, $J_{1'',2a''}$ 9.4, $J_{1'',2e''}$ 2.2 Hz, H-1″), 4.67 (dd, 1H, $J_{1',2a'}$ 9.6, $J_{1',2e'}$ 2.0 Hz, H-1′), 4.59 (dd, 1H, $J_{1,2a}$ 9.8, $J_{1,2e}$ 2.0 Hz, H-1), 4.55 and 4.82 (AB, 2H, J_{AB} = 12.0 Hz, CH_2-C_6H_5), 3.97 (d, 1H, $J_{4'',4''\text{-OH}}$ 7.8 Hz, 4″-OH), 3.69 (dq, 1H, $J_{4'',5''}$ 9.4, $J_{5'',6''}$ 6.4 Hz, H-5″), 3.59 (ddd, 1H, $J_{2a',3'}$ 10.8, $J_{2e',3'}$ 5.0, $J_{3',4'}$ 9.0 Hz, H-3′), 3.57 (ddd, 1H, $J_{2a,3}$ 9.8, $J_{2e,3}$ 4.8, $J_{3,4}$ 9.2 Hz, H-3), 3.31 (dq, 1H, $J_{4',5'}$ 9.8, $J_{5',6'}$ 6.2 Hz, H-5′), 3.22 (dq, 1H, $J_{4,5}$ 9.3, $J_{5,6}$ 6.0 Hz, H-5), 2.99 (dd, 1H, $J_{4'',5''}$ 9.4, $J_{4'',4''\text{-OH}}$ 7.8 Hz, H-4″), 2.93 (t, 1H, $J_{3',4'}$ 9.0, $J_{4',5'}$ 9.8 Hz, H-4′), 2.92 (1, 1H, $J_{3,4}$ 9.2, $J_{4,5}$ 9.3 Hz, H-4), 2.47 and 2.91 (AB, 2H, J_{AB} = 4.5 Hz, CH_2-epoxide), 2.17 (mc, 2H, H-2e, −2e′), 1.92 (dd, 1H, $J_{1'',2e''}$ 2.2, $J_{2a'',2e''}$ 13.4 Hz, H-2e″), 1.52 (mc, 3H, H-2a, −2a′, −2a″), 1.28 (d, 3H, $J_{5,6}$ 6.0 Hz, 6-CH_3), 1.26 (d, 3H, $J_{5',6'}$ 6.2 Hz, 6′-CH_3), 1.22 (d, 3H, $J_{5'',6''}$ 6.4 Hz, 6″-CH_3), 1.21 (s,

3H, 3″-CH_3). Calcd. for $C_{26}H_{40}O_{10}$ (512.6): CI with ammonia found $(M+NH_4)^+$ 531.

Acknowledgements

Partial support of these studies by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

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