Partially Hydroxylated 2,5-Disubstituted Bis-Tetrahydrofurans from Carbohydrates

Rainer Bruns,[a] Jürgen Kopf,[b] and Peter Köll*[a]

Dedicated to Prof. Dr. Günther Wulff on occasion of his 65th birthday

Abstract: The diverse bioactivities of annonaceous acetogenins have recently attracted increasing interest. Many of these natural products contain one or more 2,5-disubstituted tetrahydrofuran rings as a core unit; these are important for the bioactivity, since it is believed that these anchor the compounds to the surface of the membrane. Therefore, the synthesis of functionalized bis-tetrahydrofurans is an important task and we have developed a synthetic pathway to all four diastereomeric, partially hydroxylated bis-tetrahydrofurans, that is, 3,6:7,10-dianhydro-2,8,9-trideoxy-L-*erythro*-D-*ido*-undecitol (**1**), 3,6:7,10-dianhydro-2,8,9-trideoxy-D-*threo*-D-*ido*-undecitol (**2**), 3,6:7,10-dianhydro-2,8,9-trideoxy-L-*threo*-D-*ido*-undecitol (**3**), and 3,6:7,10-dianhydro-2,8,9-trideoxy-D-*erythro*-D-*ido*-undecitol (**4**) starting from D-glucose. The reaction of the aldose with Meldrum's acid led to the C-glycosidic 3,6-anhydro-1,4-lactone **6**, which was converted to the aldehyde building block 2,5-anhydro-3,4,7-tri-*O*-benzyl-6-deoxy-*aldehydo*-D-*ido*-heptose (**11**). Chain elongation of **11** with the Grignard reagent derived from 1-bromo-3-butene gave the diastereomers 3,6-anhydro-1,4,5-tri-*O*-benzyl-2,8,9,10,11-pentadeoxy-L-*glycero*-D-*ido*-undec-10-enitol (**12**) and 3,6-anhydro-1,4,5-tri-*O*-benzyl-2,8,9,10,11-pentadeoxy-D-*glycero*-D-*ido*-undec-10-enitol (**13**). The relative *threo* configuration of the major product **12** was confirmed by X-ray structure analysis. Epoxidation and subsequent cyclization afforded the *cis* and *trans* diastereomers **19** and **20**, respectively, in a 1:1 ratio. Subsequent cleavage of the protecting groups and separation of the isomers furnished the target compounds in good overall yields.

Keywords: annonaceous acetogenins · carbohydrates · cyclizations · natural products · synthetic methods · tetrahydrofurans

Introduction

The acetogenins found in Annonaceae, a relatively new and rapidly expanding class of natural compounds, have been attracting worldwide attention because of their potent biological activity profile.[1] The past few years have witnessed an explosion of activity in the isolation, structure elucidation, biological evaluation, and synthesis.[1–3] These compounds, derived from polyketides as biogenetic precursors, show interesting cytotoxic, antitumor, antimicrobial, antimalarial, antifeedant, pesticidal, and immunosuppressive effects.[1] Their structures are characterized by a long hydrocarbon skeleton terminated at one end by a butenolide moiety. The center unit contains one to three tetrahydrofuran rings, which are often flanked by hydroxyl groups. It is believed that the primary mode of action of these compounds is the inhibition of the mitochondrial NADH-ubiquinone oxidoreductase in complex I, which is a membrane bound and essential enzyme for ATP production, the depletion of which is likely to induce apoptosis.[4] Furthermore, it has been shown that these compounds also inhibit a ubiquinone-linked NADH oxidase found in the plasma membrane of specific tumor cell-lines, including some which show multidrug-resistance.[5] Acetogenins are generally lipophilic and are expected to be closely associated with the lipid membranes in which their enzyme targets reside. Recently, McLaughlin's group investigated the conformation of different acetogenins within liposomal membranes constructed from dimyristoylphosphatidylcholine by NMR spectroscopy.[6] They concluded that the tetrahydrofuran moiety anchored the compounds to the hydrophobic surface of the membrane and so enhance the bioactivity by restricting the location and the conformation of the acetogenins. Hydrogen bonding—either intramolecular between the flanking hydroxyl groups and the THF oxygen atoms or intermolecular to the backbone of the phospholipid—seems to play an important role in the restriction of the conformation.[6] Furthermore, the binding affinities of these compounds

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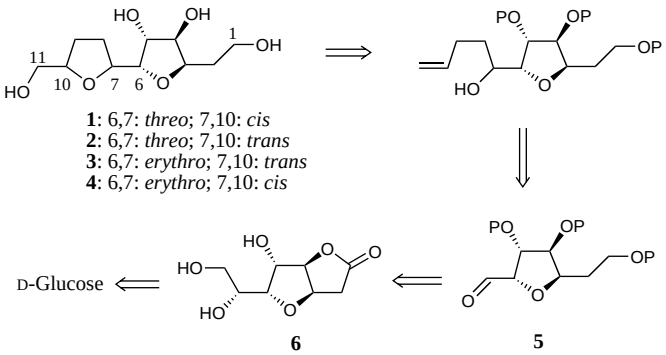
  0947-6539/00/0608-1337 $ 17.50+.50/0

towards mono- and divalent cations have been investigated in relation to their biological activity.[7]

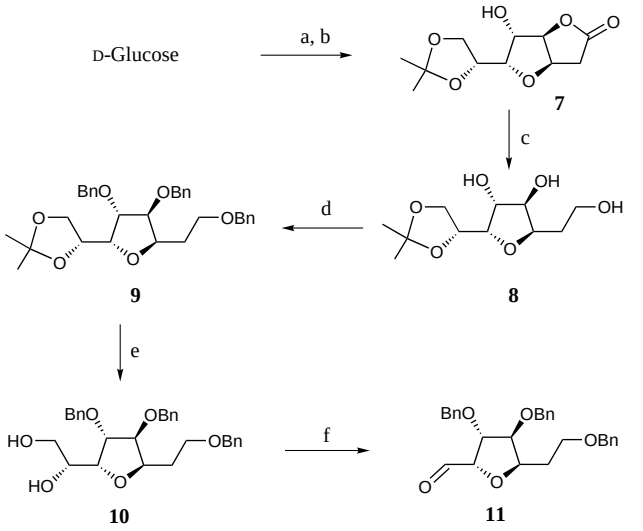
Therefore, the synthesis of 2,5-linked bis-tetrahydrofurans with additional substituents that would be able to develop supplementary hydrogen bonds is of interest. We now report a synthetic pathway to partially hydroxylated bis-tetrahydrofurans starting from D-glucose. To date, only a few reports have dealt with the synthesis of adjacent tetrahydrofurans derived from carbohydrates.[8] Our retrosynthetic analysis based on the use of an aldose is outlined in Scheme 1. Thus, the target compounds **1** to **4** may be constructed from the aldehyde **5** by chain elongation and subsequent cyclization. The key fragment **5** should be available from **6**, which in turn is easily prepared by the reaction of D-glucose with Meldrum's acid.[9, 10]



Scheme 1. Retrosynthetic strategy for the target compounds **1** to **4** starting from D-glucose.

Results and Discussion

Recently, we comprehensively studied the reaction of all diastereomeric aldopentoses and aldohexoses with Meldrum's acid which provides a facile route to C-glycosidic 1,4-lactones.[10] These compounds are almost ideal starting materials for our purposes. Thus, conversion of D-glucose with Meldrum's acid and subsequent protection of the vicinal diol as a ketal gave **7**,[11] as depicted in Scheme 2. Reduction of the lactone moiety with $LiAlH_4$ gave **8**. Protection of the hydroxyl functions as benzyl ethers produced **9**, and subsequent cleavage of the ketal moiety with acetic acid released the diol **10**. The reaction sequence was completed by periodate cleavage to afford the desired aldehyde **11**.



Scheme 2. Synthesis of the building block **11**. Reagents and conditions: a) Meldrum's acid, *t*$BuNH_2$, DMF, 40 °C, 5 d; b) acetone, H_2SO_4, RT, 16 h, 50 %; c) $LiAlH_4$, THF, 0 °C, 30 min, reflux, 5 h, RT 16 h, 96 %; d) BnBr, NaH, DMF, 0 °C – RT, 16 h, 83 %; e) THF/HOAc/H_2O, 60 °C, 93 %; f) $NaIO_4$, MeOH/H_2O, 0 °C, 30 min, 91 %.

The next step was the chain elongation of the building block **11**. Reaction of **11** with the Grignard reagent from 1-bromo-3-butene in a THF/Et_2O solvent mixture gave the diastereomeric products **12** and **13** in a 3:1 ratio as oily compounds (Scheme 3). In order to confirm the relative stereochemistry, we planned to perform an X-ray structure analysis. However, acetylation of the oily compounds to **14** and **15** did not provide crystalline materials. Since the crystallization of benzyl-protected compounds is often difficult, **12** was catalytically hydrogenated to **16**; this was once again an oily compound. Even the peracetylated product **17** could not be crystallized.

Abstract in German: *Aufgrund des vielfältigen physiologischen Wirkungsspektrums wird den Acetogeninen aus Annonaceae zur Zeit starke Aufmerksamkeit gewidmet. Zahlreiche dieser Naturstoffe enthalten als zentrales Element einen oder mehrere 2,5-disubstituierte Tetrahydrofuranringe, die für die biologische Aktivität von großer Bedeutung sind, da sie für eine Verankerung der Substanzen in der Zellmembran sorgen. Aus diesem Grunde ist die Synthese von funktionalisierten Bistetrahydrofuranen eine bedeutende Aufgabe, um Bausteine für die Synthese von nicht natürlichen Acetogeninen aus Annonaceen zu liefern. Wir beschreiben hier einen Syntheseweg ausgehend von D-Glucose zu den vier möglichen isomeren partiell hydroxylierten Bis-tetrahydrofuranen 3,6:7,10-Dianhydro-2,8,9-tridesoxy-L-erythro-D-ido-undecitol (**1**), 3,6:7,10-Dianhydro-2,8,9-tridesoxy-D-threo-D-ido-undecitol (**2**), 3,6:7,10-Dianhydro-2,8,9-tridesoxy-L-threo-D-ido-undecitol (**3**) und 3,6:7,10-Dianhydro-2,8,9-trideoxy-D-erythro-D-ido-undecitol (**4**). Die Reaktion der D-Glucose mit Meldrumsäure lieferte das C-glycosidische 3,6-Anhydro-1,4-lacton **6**, das in die aldehydische Schlüsselverbindung 2,5-Anhydro-3,4,7-tri-O-benzyl-6-desoxy-aldehydo-D-ido-heptose (**11**) übergeführt wurde. Die Umsetzung von **11** mit dem aus 1-Brom-3-buten abgeleiteten Grignardreagenz ergab die Diastereomere 3,6-Anhydro-1,4,5-tri-O-benzyl-2,8,9,10,11-pentadesoxy-L-glycero-D-ido-undec-10-enitol (**12**) und 3,6-Anhydro-1,4,5-tri-O-benzyl-2,8,9,10,11-pentadesoxy-D-glycero-D-ido-undec-10-enitol (**13**). Die relative threo-Konfiguration des Hauptproduktes **12** wurde durch Röntgenstrukturanalyse zweifelsfrei aufgeklärt. Epoxidierung der Doppelbindung und anschließende Cyclisierung führte zu den cis-, trans-Diastereomeren **19** und **20** in einem Verhältnis von 1:1. Abspaltung der Schutzgruppen und Trennung der Diastereomere lieferte die Zielstrukturen in guten Gesamtausbeuten.*

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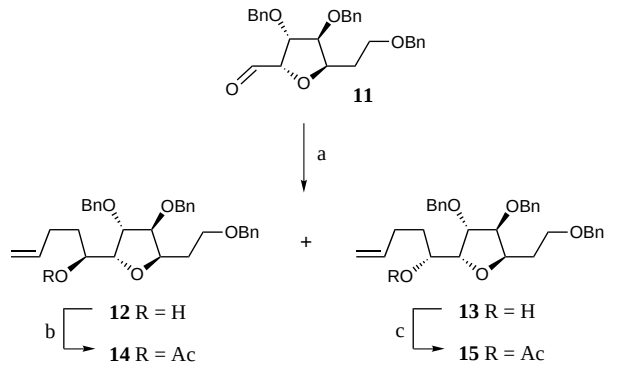
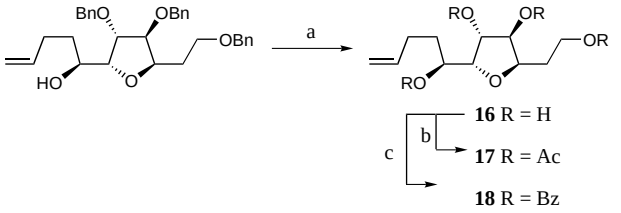


Scheme 3. Chain elongation of **11**; synthesis of **12** and **13**. Reagents and conditions: a) 1-bromo-3-butene, Mg, Et_2O; then **11**, THF, 0 °C, 2 h, RT, 16 h, 77 %, diastereomeric ratio 3:1; b) Ac_2O, pyridine, toluene, RT, 16 h, 76 %; c) Ac_2O, pyridine, toluene, RT, 16 h, 60 %.

Suitable material for X-ray crystallography was finally obtained by converting **16** to the benzoyl derivative **18** (Scheme 4). The ORTEP drawing of **18**,[12] shown in Figure 1, confirmed the relative *threo* configuration of the major diastereomer **12**. Crystallographic data for compound **18** is given in Table 1.

From the numerous available methodologies for the synthesis of THF rings,[13] we examined the ring closure by



Scheme 4. Determination of the stereochemistry; synthesis of **18**. Reagents and conditions: a) H_2, Pd/C (10 %), MeOH, RT, 16 h, 93 %; b) Ac_2O, pyridine, toluene, RT, 16 h, 87 %; c) BzCl, pyridine, toluene, RT, 2 h, 91 %.

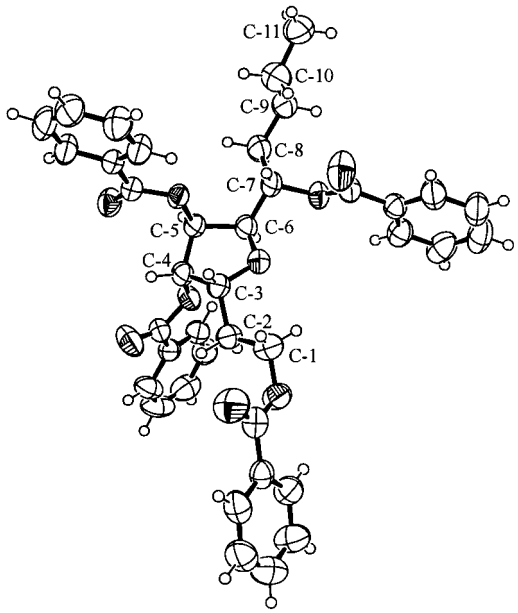
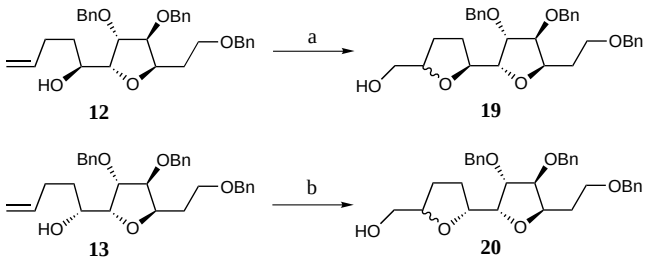


Figure 1. ORTEP drawing of **18**.

Table 1. Crystallographic data for **18**.

formula	$C_{39}H_{38}O_9$
M_w [g mol^{-1}]	650.69
crystal size [mm]	0.30 × 0.25 × 0.10
m.p. [°C]	109
crystal system	monoclinic
space group	$P2_1$
a [pm]	946.8(1)
b [pm]	1582.4(2)
c [pm]	1154.9(2)
β [°]	90.3(1)
V [pm^3]	1730.3(4) × 10^6
Z	2
$F(000)$	688
ρ_{calcd} [g cm^{-3}]	1.249
μ [cm^{-1}]	0.724
λ ($Cu_{K\alpha}$) [pm]	154.178
2θ range [°]	3.84 – 76.41
reflections measured	4037
independent reflections	3774
reflections with $[I > 2\sigma(I)]$	2359
parameters	473
R_1 (all data)	0.0988
R_1 $[I > 2\sigma(I)]$	0.0373
wR_2 (all data)	0.1072
wR_2 $[I > 2\sigma(I)]$	0.0852
flack parameter	0.0(2)
goodness of fit	1.045
diffractometer	Enraf-Nonius CAD4
temerature	room temperature

epoxidation of the double bond and subsequent intramolecular cyclization. According to Baldwin's rules,[14] the formation of the five-membered ring by five-*exo*-tet ring closure is favored over six-*endo*-tet ring closure, which would lead to the corresponding tetrahydropyran system. In order to build the second ring, **12** and **13** were treated with a slight excess of *meta*-chloroperoxybenzoic acid and catalytic amounts of racemic camphorsulfonic acid as shown in Scheme 5. Both

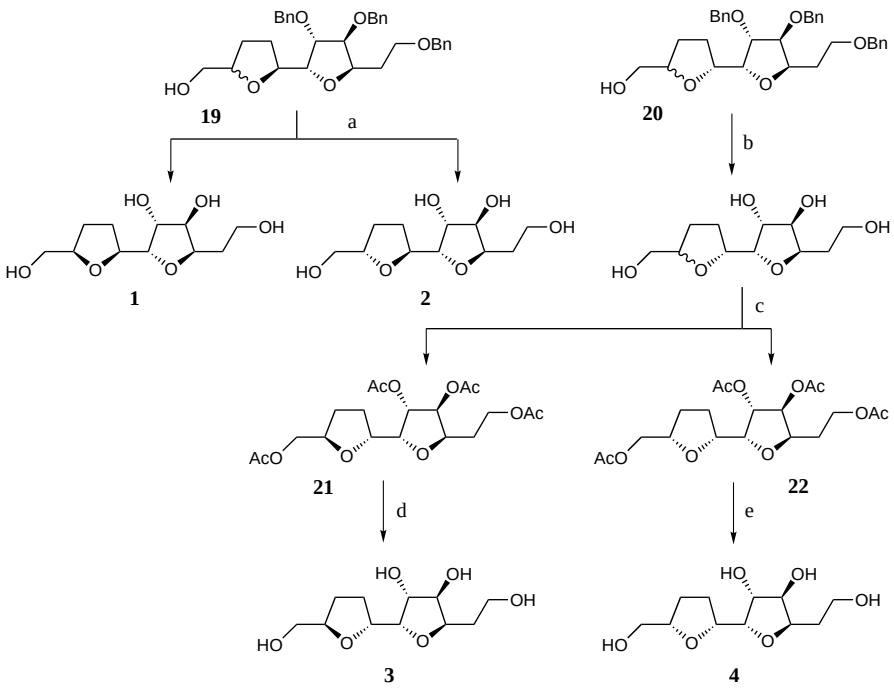


Scheme 5. Cyclization by epoxidation. Reagents and conditions: a) mCPBA, CSA, CH_2Cl_2, 0 °C, 2 h, RT, 16 h, 80 %, diastereomeric ratio 1:1; b) mCPBA, CSA, CH_2Cl_2, 0 °C, 2 h, RT, 16 h, 85 %, diastereomeric ratio 1:1.

reactions proceeded well; however, no stereochemical induction was observed during the epoxidation reaction. Thus both *cis* and *trans* stereoisomers of **19** and **20** were obtained in a 1:1 ratio. Since our synthetic plan was aimed at the formation of all four possible stereoisomers, we made no further efforts to achieve higher selectivities. Unfortunately, the isomers could not be separated either by column or HPLC chromatography on a preparative scale.

Catalytic hydrogenation of the diasteromeric mixtures **19** and **20** gave the unprotected target compounds (Scheme 6).

Whereas the oily target substances **1** and **2** could be separated by column chromatography, attempted separation of the *cis* and *trans* diastereomers of the *erythro*-configured products **3** and **4** was unsuccessful. However, this was finally achieved by an acetylation/deacetylation sequence. Thus, acetylation of the diasteromeric mixture gave the corresponding acetates **21** and **22** in good yields, which were easily separated by column chromatography. Subsequent treatment of the acetates with sodium methoxide gave the target compounds **3** and **4**, respectively, in good yields as syrups (Scheme 6).



Scheme 6. Cleavage of the protecting groups and separation of the target compounds. Reagents and conditions: a) H_2, Pd/C (10%), MeOH, RT, 16 h, **1**: 40%, **2**: 40%; b) H_2, Pd/C (10%), MeOH, RT, 16 h, 78%; c) Ac_2O, pyridine, toluene, RT, 16 h, **21**: 37%, **22**: 40%; d) NaOMe, MeOH, RT, 2 h, 90%; e) NaOMe, MeOH, RT, 2 h, 95%.

The determination of the *cis* and *trans* configuration of the tetrahydrofuran rings in the target compounds was deduced from the NOE effects between the methine protons H-7 and H-10 by means of 2D-NOESY NMR experiments at two different field strengths (7.04 and 11.74 T). In the case of **1**, we obtained a strong NOE effect, whereas in the case of **2** no effect was measurable. Therefore, **1** was assigned the *cis* configuration and **2** the *trans* configuration. Owing to serious signal crowding, we were unable to analyze the NOE spectra of **3** and **4** by this method. However, we obtained a strong NOE effect between H-7 and H-10 in the acetylated derivative **22**. Thus the configuration of the tetrahydrofuran ring in **22**, and consequently in **4**, is assigned as *cis*. Hence, the other isomer **21**, and consequently **3**, must be the *trans*-configured diastereomer.

Due to the waxy nature of the acetogenins and the resulting lack of crystallographic data, several empirical methods have been developed for the assignment of the relative stereochemistry of the tetrahydrofuran units. In order to classify **1** to **4** in this context, selected NMR data of the target compounds are summarized in Table 2.

According to Cassday's model,[15] the methine protons in *trans*-configured tetrahydrofurans should be more deshielded than in the *cis* isomers. Indeed, such a deshielding was observed for H-10 in the case of **2** and **3** relative to the corresponding signal for H-10 in **1** and **4**, respectively. With respect to **1**, H-7 in **2** was also consistent with this model, whereas no shift was observed in the case of **3**. Fujimoto's group solved the relative configuration of the tetrahydrofuran ring by analyzing the ^{13}C methine shifts.[16] In the case of a *cis* configuration the signals should be slightly deshielded.[16] In agreement with this proposal we observed that the resonance frequencies of C-7 and C-10 in **1** and **4** are shifted downfield relative to those in **2** and **3**, respectively, as shown in Table 2. Thus, the configurations assigned through NOE spectroscopy to the tetrahydrofuran rings provide further proof for these empirical methods.

Conclusion

In conclusion, we have developed a synthetic pathway to partially hydroxylated bis-tetrahydrofurans starting from inexpensive D-glucose. The key steps were a) the synthesis of the C-glycoside by reaction of the hexose with Meldrum's acid, b) the chain elongation of the aldehyde **11** with the Grignard reagent derived from 1-bromo-3-butene, and c) the cyclization after epoxidation. The target compounds **1**–**4** should be useful building blocks for the synthesis of hydroxy-

Table 2. Selected NMR data of target compounds **1** to **4**.[a,b]

	H-7	H-8′	H-8	H-9′	H-9	H-10	C-7	C-10
1	4.08–4.12	1.63–1.78[c]	2.04–2.10	1.63–1.78[c]	1.90–1.98	3.99–4.01	80.8	81.7
2	4.16–4.20	1.63–1.73[c]	2.10–2.16	1.63–1.73[c]	1.97–2.02	4.04–4.09	80.3	81.3
3	4.09–4.14	1.78–1.88[d]	2.09–2.15	1.65–1.72	1.97–2.04	4.01–4.08	77.8	81.2
4	4.09–4.13	1.86–1.98[c]	1.98–2.05	1.66–1.74	1.86–1.98[c]	3.92–3.97	78.7	81.3

[a] Chemical shifts are given in the δ scale in ppm. [b] The assignment was achieved by means of $^1H-^1H$ and $^1H-^{13}C$ correlated spectroscopy. [c] The signals partly overlapped. [d] Partly obscured by H-2′ and H-2.

0947-6539/00/0608-1340 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 8

lated derivatives of annonaceous acetogenins for the determination of structure–activity relationships of these natural compounds. Furthermore, variation of the stereochemistry of the hydroxylated ring should be easily achieved by applying the well-established reaction of Meldrum's acid with other aldoses.

Experimental Section

General methods: All solvents were purified and dried, if necessary, by standard procedures. NMR spectroscopic data were recorded on a Bruker Avance 500 or Avance 300 spectrometer. Chemical shifts are given in the δ scale in ppm relative to residual nondeuterated solvent signals as internal standard. Optical rotations were determined with a Perkin Elmer 343 polarimeter. Column chromatography was performed on silica gel 60 from Merck. Mass spectra were taken on a Finnigan MAT 212 with data system MSS or on a Finnigan MAT 95 with data system DEC-Station 5000 by using chemical ionization with *iso*-butane as reactant gas. Melting points were determined with a hot-stage microscope SM-Lux from Leitz and are not corrected. Microanalyses were carried out on a Fison Instruments EA 1108. The numbering of all compounds was carried out according to standard carbohydrate nomenclature.[17]

3,6-Anhydro-2-deoxy-7,8-*O*-isopropylidene-D-*glycero*-D-*ido*-octono-1,4-lactone (7): *tert*-Butylamine (12.25 mL, 0.12 mol) was added to a stirred suspension of Meldrum's acid (30.3 g, 0.21 mol) and anhydrous D-glucose (20.0 g, 0.11 mol) in DMF (150 mL). The reaction mixture was stirred at 40 °C for 5 days and evaporated to dryness under reduced pressure. Dry acetone (700 mL) and concentrated sulfuric acid (2 mL) were added to the residue. The reaction mixture was stirred for 16 h at RT. The solution was neutralized with a saturated aqueous solution of Na_2CO_3, and the organic solvent was removed under reduced pressure. The remaining solution was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by crystallization (CH_2Cl_2/petroleum ether) yielded compound **7** (13.5 g, 0.056 mol, 50 %). $R_f = 0.66$ (EtOAc); m.p. 127–128 °C; $[\alpha]_D^{21} = +38.1$ ($c = 1.1$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 4.96$ (dd, $^3J(2,3) = 5.7$ Hz, $^3J(3,4) = 4.5$ Hz, 1H; H-3), 4.87 (dd, $^3J(3,4) = 4.5$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 4.54 (dd, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 2.5$ Hz, 1H; H-5), 4.28 (ddd, $^3J(6,7) = 7.7$ Hz, $^3J(7,8') = 5.0$ Hz, $^3J(7,8) = 5.7$ Hz, 1H; H-7), 4.12 (dd, $^2J(8,8') = 8.9$ Hz, $^3J(7,8) = 5.7$ Hz, 1H; H-8), 3.94 (dd, $^2J(8,8') = 8.9$ Hz, $^3J(7,8') = 5.0$ Hz, 1H; H-8′), 3.93 (dd, $^3J(5,6) = 2.5$ Hz, $^3J(6,7) = 7.7$ Hz, 1H; H-6), 2.72 (dd, $^2J(2,2') = 18.5$ Hz, $^3J(2,3) = 5.7$ Hz, 1H; H-2), 2.63 (dd, $^2J(2,2') = 18.5$ Hz, $^3J(2',3) = 0$ Hz, 1H; H-2′), 1.40 (s, 3H; $C(CH_3)_2$), 1.33 (s, 3H; $C(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta =$ 175.3 (C-1), 109.7 ($C(CH_3)_2$), 87.6 (C-4), 81.8 (C-6), 77.4 (C-3), 74.3 (C-5), 73.3 (C-7), 67.4 (C-8), 31.1 (C-2), 25.1, 26.7 ($C(CH_3)_2$); MS (CI): *m*/*z* (%): 245 (100) $[M+H]^+$, 187 (21) $[M\text{H} - \text{acetone}]^+$; elemental analysis calcd (%) for $C_{11}H_{16}O_6$: C 54.08, H 6.61; found C 53.73, H 6.85.

3,6-Anhydro-7-deoxy-1,2-*O*-isopropylidene-D-*glycero*-L-*gulo*-octitol (8): A solution of **7** (6.0 g, 24.6 mmol) in dry THF (30 mL) was added dropwise over a period of 30 min to a suspension of $LiAlH_4$ (1.2 g, 30.8 mmol) in dry THF (100 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was heated under reflux for 5 h and then stirred for further 16 h at RT. The solution was cooled to 0 °C and water (1.2 mL), aqueous KOH (1.2 mL, 15 %), and more water (3.6 mL) was carefully added. The mixture was diluted with EtOAc (50 mL) and refluxed for 1 h. After cooling to RT the mixture was filtered through Celite and washed with a THF/EtOAc solvent mixture (30 mL, 1:1). The residue was suspended in a THF/EtOAc solvent mixture (60 mL, 1:1), refluxed for 15 min, and again filtered. This procedure was repeated three times. The combined filtrates were concentrated under reduced pressure. Column chromatography (EtOAc) gave compound **8** (5.85 g, 23.6 mmol, 96 %) as a syrup. $R_f = 0.22$ (EtOAc); $[\alpha]_D^{21} = -2.1$ ($c = 4.0$ in EtOAc); ^{1}H NMR (500.1 MHz, D_2O, 25 °C): $\delta =$ 4.37–4.41 (m, 1H; H-2), 4.28 (dd, $^3J(3,4) = 3.2$ Hz, $^3J(4,5) = 1.2$ Hz, 1H; H-4), 4.23 (dd, $^3J(2,3) = 7.0$ Hz, $^3J(3,4) = 3.2$ Hz, 1H; H-3), 4.20–4.22 (m, 1H; H-6), 4.16 (dd, $^2J(1',1) = 8.3$ Hz, $^3J(1,2) = 6.4$ Hz, 1H; H-1), 4.11 (dd, $^3J(4,5) = 1.2$ Hz, $^3J(5,6) = 3.1$ Hz, 1H; H-5), 3.97 (dd, $^2J(1',1) = 8.3$ Hz, $^3J(1',2) = 6.4$ Hz, 1H; H-1′), 3.65–3.75 (m, 2H; H-8′, H-8), 1.82–1.92 (m, 2H; H-7′, H-7), 1.39 (s, 3H; $C(CH_3)_2$), 1.45 (s, 3H; $C(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 109.5$ ($C(CH_3)_2$), 80.4 (C-3), 79.1 (C-6), 77.2 (C-5), 76.3 (C-4), 74.0 (C-2), 66.1 (C-1), 59.1 (C-8), 31.0 (C-7), 25.7, 24.3 ($C(CH_3)_2$); MS (CI): *m*/*z* (%): 249 (100) $[M+H]^+$, 191 (95) $[M+\text{H} - \text{acetone}]^+$, 173 (30) $[M+\text{H} - \text{acetone} - H_2O]^+$; elemental analysis calcd (%) for $C_{11}H_{20}O_6$: C 53.22, H 8.12; found C 52.84, H 8.10.

3,6-Anhydro-4,5,8-tri-*O*-benzyl-7-deoxy-1,2-*O*-isopropylidene-D-*glycero*-L-*gulo*-octitol (9): Sodium hydride (3.6 g, 90.6 mmol, 60 % suspension in oil) was added slowly to a solution of **8** (5.0 g, 20.1 mmol) in dry DMF (75 mL) at 0 °C and the mixture stirred for 45 min. Benzyl bromide (11.0 mL, 90.6 mmol) was then added dropwise at 0 °C. The reaction mixture was stirred for 16 h and allowed to warm up to RT. After addition of MeOH (20 mL), the solution was stirred for 30 min and partitioned between saturated aqueous NH_4Cl solution (130 mL) and CH_2Cl_2 (230 mL). The aqueous phase was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with saturated aqueous NaCl solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by column chromatography (EtOAc/petroleum ether 40/60 1:5) gave **9** as a syrup (8.70 g, 16.8 mmol, 83 %). $R_f = 0.45$ (EtOAc/petroleum ether 40/60); $[\alpha]_D^{21} = -12.8$ ($c = 4.4$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.23-7.36$ (m, 15H; Ph), 4.58 (d, $^2J =$ 12.1 Hz, 1H; CH_2Ph), 4.55 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.50 (d, $^2J =$ 12.1 Hz, 1H; CH_2Ph), 4.49 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.46 (d, $^2J =$ 12.1 Hz, 1H; CH_2Ph), 4.37 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.30–4.34 (m, 1H; H-2), 4.24 (ddd, $^3J(5,6) = 3.8$ Hz, $^3J(6,7') = 5.7$ Hz, $^3J(6,7) = 7.6$ Hz, 1H; H-6), 4.12 (dd, $^3J(2,3) = 7.0$ Hz, $^3J(3,4) = 3.8$ Hz, 1H; H-3), 4.08 (dd, $^2J(1',1) = 8.3$ Hz, $^3J(1,2) = 5.7$ Hz, 1H; H-1), 4.02 (d, $^3J(3,4) = 3.8$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 3.94 (dd, $^2J(1',1) = 8.3$ Hz, $^3J(1',2) = 6.4$ Hz, 1H; H-1′), 3.79 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 3.8$ Hz, 1H; H-5), 3.54 (dd, $^2J(8',8) =$ 0 Hz, $^3J(7',8) = 5.7$ Hz, $^3J(7,8) = 7.0$ Hz, 2H; H-8′, H-8), 1.88–2.04 (m, 2H; H-7′, H-7), 1.37 (s, 3H; $C(CH_3)_2$), 1.41 (s, 3H; $C(CH_3)_2$); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 138.6$, 138.1, 137.9, 128.7, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5 (Ph), 108.7 ($C(CH_3)_2$), 82.2 (C-4), 81.3 (C-5), 80.7 (C-3), 78.2 (C-6), 73.6 (C-2), 73.0, 72.4, 71.9 (CH_2Ph), 67.7 (C-8), 67.3 (C-1), 29.4 (C-7), 26.7, 25.7 ($C(CH_3)_2$; MS (CI): *m*/*z* (%): 519 (100) $[M+H]^+$, 461 (15) $[M+\text{H} - \text{acetone}]^+$; elemental analysis calcd (%) for $C_{32}H_{38}O_6$: C 74.11, H 7.38; found C 73.84, H 7.50.

3,6-Anhydro-4,5,8-tri-*O*-benzyl-7-deoxy-D-*glycero*-L-*gulo*-octitol (10): Compound **9** (8.7 g, 16.8 mmol) was dissolved in a mixture of THF/water/acetic acid (126 mL, 1:1:6) and stirred at 60 °C until thin-layer chromatography (TLC) showed complete consumption of the starting material. The solvent was removed under reduced pressure. The residue was co-evaporated two times in vacuo with water to remove any remaining acetic acid. The crude product was crystallized from CH_2Cl_2/*n*-hexane to give **10** (7.47 g, 15.6 mmol, 93 %). $R_f = 0.26$ (EtOAc/petroleum ether 40/60 1:1); m.p. 55 °C; $[\alpha]_D^{21} = -16.6$ ($c = 0.8$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.25-7.38$ (m, 15H; Ph), 4.59 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.54 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.51 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.47 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.45 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.42 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.29 (ddd, $^3J(5,6) = 3.2$ Hz, $^3J(6,7') = 5.6$ Hz, $^3J(6,7) = 7.8$ Hz, 1H; H-6), 4.15 (d, $^3J(3,4) = 3.8$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 4.07 (dd, $^3J(2,3) = 8.3$ Hz, $^3J(3,4) = 3.8$ Hz, 1H; H-3), 3.95–3.99 (m, 1H; H-2), 3.85 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 3.2$ Hz, 1H; H-5), 3.81 (dd, $^2J(1',1) = 11.5$ Hz, $^3J(1,2) = 3.8$ Hz, 1H; H-1), 3.68 (dd, $^2J(1',1) = 11.5$ Hz, $^3J(1',2) = 5.7$ Hz, 1H; H-1′), 3.56 (dd, $^2J(8',8) = 0$ Hz, $^3J(7',8) = 5.7$ Hz, $^3J(7,8) = 7.0$ Hz, 2H; H-8′, H-8), 1.92–2.09 (m, 2H; H-7′, H-7); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 138.5$, 137.8, 137.6, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6 (Ph), 82.1 (C-4), 81.7 (C-5), 79.7 (C-3), 78.1 (C-6), 73.0, 72.3, 72.1 (CH_2Ph), 69.8 (C-2), 67.6 (C-8), 64.9 (C-1), 29.3 (C-7); MS (CI): *m*/*z* (%): 479 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{29}H_{34}O_6$: C 72.78, H 7.16; found C 72.71, H 7.21.

2,5-Anhydro-3,4,7-tri-*O*-benzyl-6-deoxy-*aldehydo*-D-*ido*-heptose (11): A solution of $NaIO_4$ (1.05 g, 4.9 mmol) in MeOH/water (20 mL, 1:3) was added dropwise to a cooled solution of **10** (1.17 g, 2.45 mmol) in MeOH (20 mL) at such a rate that the reaction temperature did not exceed 5 °C. After stirring for further 30 min at 0 °C, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried (Na_2SO_4). Evaporation of the solvent gave the crude product **11** (990 mg, 2.22 mmol, 91 %), which was immediately subjected to Grignard addition without further purification. An analytically

pure sample was obtained by column chromatography (EtOAc/petroleum ether 40/60 2:3). $R_f = 0.74$ (EtOAc/petroleum ether 60/60 2:3); $[\alpha]_D^{21} = -20.8$ ($c = 1.7$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 9.66$ (d, $^3J(1,2) = 2.6$ Hz, 1H; H-1), 7.21–7.36 (m, 15H; Ph), 4.53 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.51 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.49 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.48–4.51 (m, 1H; H-5), 4.47 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.46 (dd, $^3J(1,2) = 2.6$ Hz, $^3J(2,3) = 5.1$ Hz, 1H; H-2), 4.42 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.37 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.32 (d, $^3J(2,3) = 5.1$ Hz, $^3J(3,4) = 0$ Hz, 1H; H-3), 3.85 (d, $^3J(3,4) = 0$ Hz, $^3J(4,5) = 3.2$ Hz, 1H; H-4), 3.58–3.65 (m, 2H; H-7′, H-7), 1.99–2.13 (m, 2H; H-6′, H-6); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 202.0$ (C-1), 138.4, 137.5, 137.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5 (Ph), 84.3 (C-2), 83.9 (C-3), 81.6 (C-4), 80.0 (C-5), 73.1, 72.5, 72.1 (CH_2Ph), 67.4 (C-7), 29.1 (C-6); MS (CI): m/z (%): 447 (100) $[M+H]^+$; HRMS: calcd for $C_{28}H_{31}O_5$ $[M+H]^+$ 447.2171; found 447.2171.

3,6-Anhydro-1,4,5-tri-*O*-benzyl-2,8,9,10,11-pentadeoxy-L-*glycero*-D-*ido*-undec-10-enitol (12) and 3,6-anhydro-1,4,5-tri-*O*-benzyl-2,8,9,10,11-pentadeoxy-D-*glycero*-D-*ido*-undec-10-enitol (13): A Grignard solution in anhydrous Et_2O (10 mL) was prepared from magnesium (760 mg, 31.3 mmol) and 3-bromobut-1-ene (4.65 g, 34.5 mmol). The solution was cooled to 0 °C and **11** (2.55 g, 5.7 mmol) in dry THF (15 mL) was added dropwise over 30 min. The reaction mixture was stirred for 2 h at 0 °C and then for an additional 16 h at RT. After addition of a saturated aqueous solution of NH_4Cl (30 mL), the mixture was extracted with *tert*-butyl methyl ether. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography (EtOAc/petroleum ether 40/60 1:3) gave the major diastereomer **12** (1.65 g, 3.28 mmol, 57%) and the minor diastereomer **13** (0.58 g, 1.15 mmol, 20%) as oils. The diastereomeric ratio was 3:1, as determined by ^{1}H NMR spectroscopy of the crude reaction product.

Compound 12: $R_f = 0.39$ (EtOAc/petroleum ether 40/60 1:3); $[\alpha]_D^{21} = -32.6$ ($c = 1.3$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.25-7.37$ (m, 15H; Ph), 5.77–5.85 (m, 1H; H-10), 5.03 (ddd, ^2J(11*trans*,11*cis*) = 1.9 Hz, ^3J(10,11*cis*) = 17.2 Hz, $^4J = 3.8$ Hz, 1H; H-11*cis*), 4.95 (dd, ^2J(11*trans*,11-*cis*) = 1.9 Hz, ^3J(10,11*trans*) = 10.2 Hz, 1H; H-11*trans*), 4.54 (d, ^2J = 12.1 Hz, 1H; CH_2Ph), 4.53 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.52 (d, ^2J = 12.1 Hz, 1H; CH_2Ph), 4.48 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.47 (d, ^2J = 12.1 Hz, 1H; CH_2Ph), 4.36 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.32 (ddd, $^3J(2',3) = 5.7$ Hz, $^3J(2,3) = 7.6$ Hz, $^3J(3,4) = 3.8$ Hz, 1H; H-3), 3.98 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 4.5$ Hz, 1H; H-5), 3.93 (dd, $^3J(5,6) = 4.5$ Hz, $^3J(6,7) = 5.7$ Hz, 1H; H-6), 3.87–3.91 (m, 2H; H-4, H-7), 3.59 (dd, $^2J(1',1) = 0$ Hz, $^3J(1,2') = 5.7$ Hz, $^3J(1,2) = 7.0$ Hz, 2H; H-1, H-1′), 2.11–2.18 (m, 1H; H-8′), 2.24–2.31 (m, 1H; H-8), 1.95–2.08 (m, 2H; H-2′, H-2), 1.44–1.51 (m, 1H; H-9′), 1.56–1.64 (m, 1H; H-9); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 138.6$ (C-10), 138.5, 137.9, 137.2, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 126.9 (Ph), 114.6 (C-11), 82.9 (C-5), 82.1 (C-4), 81.7 (C-6), 77.9 (C-3), 73.0, 72.2, 72.1 (CH_2Ph), 69.9 (C-7), 67.7 (C-1), 32.4 (C-2), 29.9 (C-8), 29.3 (C-9); MS (CI): m/z (%): 503 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{32}H_{38}O_5$: C 76.47, H 7.62; found C 76.59, H 7.26.

Compound 13: $R_f = 0.48$ (EtOAc/petroleum ether 40/60 1:3); $[\alpha]_D^{21} = -13.7$ ($c = 3.7$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.26-7.38$ (m, 15H; Ph), 5.81–5.89 (m, 1H; H-10), 5.04 (ddd, ^2J(11*trans*,11*cis*) = 1.9 Hz, ^3J(10,11*cis*) = 17.2 Hz, $^4J = 3.8$ Hz, 1H; H-11*cis*), 4.96 (dd, ^2J(11*trans*,11*cis*) = 1.9 Hz, ^3J(10,11*trans*) = 10.2 Hz, 1H; H-11*trans*), 4.58 (d, $^2J = 11.5$ Hz, 1H; CH_2Ph), 4.55 (d, $^2J = 11.5$ Hz, 1H; CH_2Ph), 4.52 (d, $^2J = 11.5$ Hz, 1H; CH_2Ph), 4.47 (d, $^2J = 11.5$ Hz, 1H; CH_2Ph), 4.48 (d, ^2J = 11.5 Hz, 1H; CH_2Ph), 4.38 (d, $^2J = 11.5$ Hz, 1H; CH_2Ph), 4.28 (ddd, $^3J(2',3) = 5.7$ Hz, $^3J(2,3) = 7.6$ Hz, $^3J(3,4) = 3.8$ Hz, 1H; H-3), 4.14 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 4.5$ Hz, 1H; H-5), 3.92 (dd, $^3J(5,6) = 4.5$ Hz, $^3J(6,7) = 7.6$ Hz, 1H; H-6), 3.89 (d, $^3J(3,4) = 3.8$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 3.83–3.87 (m, 1H; H-7), 3.58 (dd, $^2J(1',1) = 0$ Hz, $^3J(1,2') = 5.7$ Hz, $^3J(1,2) = 7.0$ Hz, 2H; H-1, H-1′), 2.10–2.18 (m, 1H; H-8′), 2.27–2.34 (m, 1H; H-8), 1.95–2.08 (m, 2H; H-2′, H-2), 1.47–1.53 (m, 1H; H-9′), 1.74–1.81 (m, 1H; H-9); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 138.8$ (C-10), 138.6, 137.8, 137.2, 128.7, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5 (Ph), 114.5 (C-11), 82.6 (C-5), 81.7 (C-4), 77.8 (C-6), 77.3 (C-3), 73.0, 72.2, 72.1 (CH_2Ph), 69.8 (C-7), 67.7 (C-1), 33.6 (C-2), 29.8 (C-8), 29.3 (C-9); MS (CI): m/z (%): 503 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{32}H_{38}O_5$: C 76.47, H 7.62; found C 76.09, H 7.61.

7-*O*-Acetyl-3,6-anhydro-1,4,5-tri-*O*-benzyl-2,8,9,10,11-pentadeoxy-L-*glycero*-D-*ido*-undec-10-enitol (14): Compound **12** (425 mg, 0.85 mmol) was dissolved in a mixture of dry pyridine (2.5 mL) and dry toluene (2.5 mL). Acetic anhydride (1 mL) was added and the reaction mixture stirred at RT for 16 h. The solvent was removed under reduced pressure, and toluene was repeatedly added and removed in vacuo. Column chromatography (EtOAc/petroleum ether 40/60 1:4) gave **14** (350 mg, 0.64 mmol, 76%) as an oil. $R_f = 0.45$ (EtOAc/petroleum ether 40/60 1:4); $[\alpha]_D^{21} = -16.6$ ($c = 2.1$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.25-7.35$ (m, 15H; Ph), 5.69–5.77 (m, 1H; H-10), 5.23–5.27 (m, 1H; H-7), 4.96 (dd, ^2J(11*trans*,11*cis*) = 1.9 Hz, ^3J(10,11*cis*) = 17.2 Hz, 1H; H-11*cis*), 4.92 (dd, ^2J(11*trans*,11*cis*) = 1.9 Hz, ^3J(10,11*trans*) = 10.2 Hz, 1H; H-11*trans*), 4.53 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.51 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.49 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.47 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.46 (d, ^2J = 12.1 Hz, 1H; CH_2Ph), 4.32 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.26 (ddd, $^3J(2',3) = 5.7$ Hz, $^3J(2,3) = 7.6$ Hz, $^3J(3,4) = 3.2$ Hz, 1H; H-3), 4.05 (dd, $^3J(5,6) = 5.1$ Hz, $^3J(6,7) = 7.6$ Hz, 1H; H-6), 3.92 (dd, $^3J(4,5) = 1.3$ Hz, $^3J(5,6) = 5.1$ Hz, 1H; H-5), 3.87 (dd, $^3J(3,4) = 3.2$ Hz, $^3J(4,5) = 1.3$ Hz, 1H; H-4), 3.53–3.59 (m, 2H; H-1′, H-1), 1.98 (s, 3H; COCH_3), 1.92–2.11 (m, 4H; H-2′, H-2, H-8′, H-8), 1.50–1.55 (m, 2H; H-9′, H-9); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 170.6$ (*C*OCH$_3$), 138.6, 137.9 (Ph), 137.8 (C-10), 137.3, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4 (Ph), 114.7 (C-11), 81.9 (C-5), 81.8 (C-4), 80.2 (C-6), 77.4 (C-3), 73.0, 72.1 (CH_2Ph), 72.0 (C-7), 71.9 (CH_2Ph), 67.8 (C-1), 30.3 (C-2), 29.5 (C-8), 29.3 (C-9), 21.2 (CO*C*H$_3$); MS (CI): m/z (%): 545 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{34}H_{40}O_6$: C 74.97, H 7.40; found C 74.62, H 7.75.

7-*O*-Acetyl-3,6-anhydro-1,4,5-tri-*O*-benzyl-2,8,9,10,11-pentadeoxy-D-*glycero*-D-*ido*-undec-10-enitol (15): Compound **13** (140 mg, 0.28 mmol) was dissolved in a mixture of dry pyridine (1 mL) and dry toluene (1 mL). Acetic anhydride (0.4 mL) was added, and the reaction mixture stirred at RT for 16 h. The solvent was removed under reduced pressure. The residue was co-evaporated twice in vacuo with toluene. Column chromatography (EtOAc/petroleum ether 40/60 1:4) gave **15** (90 mg, 0.17 mmol, 60%) as an oil. $R_f = 0.59$ (EtOAc/petroleum ether 40/60 1:4); $[\alpha]_D^{21} = -13.3$ ($c = 1.2$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.25-7.37$ (m, 15H; Ph), 5.75–5.83 (m, 1H; H-10), 5.16–5.20 (m, 1H; H-7), 4.99 (ddd, ^2J(11*trans*,11*cis*) = 1.3 Hz, ^3J(10,11*cis*) = 17.2 Hz, $^4J = 3.1$ Hz, 1H; H-11*cis*), 4.93 (dd, ^2J(11*trans*,11*cis*) = 1.3 Hz, ^3J(10,11*trans*) = 10.2 Hz, 1H; H-11*trans*), 4.52 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.49 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.46 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.44 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.41 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.38 (d, $^2J = 12.1$ Hz, 1H; CH_2Ph), 4.24 (ddd, $^3J(2',3) = 5.1$ Hz, $^3J(2,3) = 8.3$ Hz, $^3J(3,4) = 3.2$ Hz, 1H; H-3), 4.13 (dd, $^3J(5,6) = 4.5$ Hz, $^3J(6,7) = 7.3$ Hz, 1H; H-6), 3.96 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 4.5$ Hz, 1H; H-5), 3.78 (d, $^3J(3,4) = 3.2$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 3.55 (dd, $^2J(1',1) = 0$ Hz, $^3J(1,2') = 5.7$ Hz, $^3J(1,2) = 7.0$ Hz, 2H; H-1, H-1′), 1.74–2.13 (m, 6H; H-2′, H-2, H-8′, H-8, H-9′, H-9), 1.95 (s, 3H; COCH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 170.0$ (*C*OCH$_3$), 138.5 (Ph), 138.4 (C-10), 137.8, 137.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 125.0 (Ph), 114.4 (C-11), 81.6 (C-5), 81.4 (C-4), 80.3 (C-6), 78.0 (C-3), 73.0, 72.3, 72.0 (CH_2Ph), 71.5 (C-7), 67.6 (C-1), 30.6 (C-2), 29.4 (C-8), 29.3 (C-9), 21.1 (CO*C*H$_3$); MS (CI): m/z (%): 545 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{34}H_{40}O_6$: C 74.97, H 7.40; found C 74.63, H 7.26.

3,6-Anhydro-2,8,9,10,11-pentadeoxy-L-*glycero*-D-*ido*-undecitol (16): Compound **12** (300 mg, 0.60 mmol) was dissolved in MeOH (6 mL) and Pd/C (30 mg, 10%) added. The suspension was stirred for 16 h at RT under a hydrogen atmosphere. Filtration and concentration gave **16** (130 mg, 93%) as a syrup. $R_f = 0.10$ (EtOAc); $[\alpha]_D^{21} = -16.7$ ($c = 0.06$ in acetone); ^{1}H NMR (500.1 MHz, [D$_6$]DMSO, 25 °C): $\delta = 4.02-4.06$ (m, 1H; H-3), 3.84 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 3.2$ Hz, 1H; H-5), 3.75 (d, $^3J(3,4) = 2.6$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 3.62 (dd, $^3J(5,6) = 3.2$ Hz, $^3J(6,7) = 7.0$ Hz, 1H; H-6), 3.54–3.57 (m, 1H; H-7), 3.42–3.49 (m, 2H; H-1′, H-1), 1.60–1.69 (m, 2H; H-2′, H-2), 1.38–1.42 (m, 2H; H-8′, H-8), 1.23–1.29 (m, 4H; H-9′, H-9, H-10′, H-10), 0.83–0.86 (m, 3H; H-11); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO, 25 °C): $\delta = 82.4$ (C-6), 77.1 (C-5, C-7), 77.0 (C-4), 69.6 (C-3), 58.4 (C-1), 32.6 (C-2), 32.4 (C-8), 27.3 (C-9), 22.24 (C-10), 14.02 (C-11); MS (CI): m/z (%): 235 (100) $[M+H]^+$, 217 (30) $[M+H-H_2O]^+$, 199 (55) $[M+H-2xH_2O]^+$; HRMS: calcd for $C_{11}H_{23}O_5$ $[M+H]^+$ 235.1545; found 235.1510.

1,4,5,7-Tetra-*O*-acetyl-3,6-anhydro-2,8,9,10,11-pentadeoxy-L-*glycero*-D-*ido*-undecitol (17): Compound **16** (120 mg, 0.51 mmol) was dissolved in a mixture of dry pyridine (0.5 mL) and dry toluene (0.5 mL). Acetic

0947-6539/00/0608-1342 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 8

anhydride (0.2 mL) was added and the reaction mixture stirred at RT for 16 h. The solvent was removed under reduced pressure and toluene was repeatedly added and removed under reduced pressure. Column chromatography (EtOAc/petroleum ether 40/60 1:3) gave **17** (180 mg, 0.64 mmol, 87%) as an oil. $R_f = 0.31$ (EtOAc/petroleum ether 40/60 1:3); $[\alpha]_D^{21} = +15.4$ ($c = 1.1$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 5.28$ (dd, $^3J(4,5) = 2.5$ Hz, $^3J(5,6) = 5.7$ Hz, 1H; H-5), 5.23 (dd, 1H; $^3J(3,4) = 4.5$ Hz, $^3J(4,5) = 2.5$ Hz, H-4), 5.01 (ddd, $^3J(6,7) = 5.7$ Hz, $^3J(7,8') = 4.5$ Hz, $^3J(7,8) = 8.3$ Hz, 1H; H-7), 4.29 (ddd, $^3J(2',3) = 5.2$ Hz, $^3J(2,3) = 7.6$ Hz, $^3J(3,4) = 4.5$ Hz, 1H; H-3), 4.14–4.20 (m, 2H; H-1, H-6), 4.05–4.10 (m, 1H; H-1′), 2.08 (s, 3H; $COCH_3$), 2.06 (s, 3H; $COCH_3$), 2.05 (s, 3H; $COCH_3$), 2.01 (s, 3H; $COCH_3$), 1.75–1.79 (m, 2H; H-2′, H-2), 1.42–1.52 (m, 2H; H-8′, H-8), 1.21–1.30 (m, 4H; H-9′, H-9, H-10′, H-10), 0.83–0.85 (m, 3H; H-11); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 170.9$, 170.4, 169.7, 169.5 ($COCH_3$), 78.7 (C-6), 77.4 (C-4), 76.5 (C-5), 75.8 (C-3), 71.5 (C-7), 65.4 (C-1), 30.7 (C-2), 28.4 (C-8), 27.5 (C-9), 22.4 (C-10), 21.2, 20.9, 20.7, 20.6 ($COCH_3$), 13.82 (C-11); MS (CI): *m*/*z* (%): 403 (30) $[M+H]^+$, 343 (100) $[M+H-HOAc]^+$; HRMS: calcd for $C_{19}H_{31}O_9$ $[M+H]^+$ 403.1968; found 403.1968.

3,6-Anhydro-1,4,5,7-tetra-*O*-benzoyl-2,8,9,10,11-pentadeoxy-L-*glycero*-D-*ido*-undecitol (18): Benzoyl chloride (0.19 mL, 1.66 mmol) was added to a solution of **16** (75 mg, 0.32 mmol) in a mixture of dry pyridine (1 mL) and dry toluene (1 mL). The reaction mixture was stirred for 2 h at RT. After addition of a saturated aqueous solution of NH_4Cl (5 mL), the mixture was stirred for 15 min and then the solution extracted with CH_2Cl_2. The combined organic layers were washed with saturated aqueous NaCl solution and dried (Na_2SO_4). Removal of the solvent and addition of toluene to the residue followed by concentration gave the crude product, which was purified by column chromatography (EtOAc/petroleum ether 40/60 1:5). Crystallization from acetone/*n*-hexane gave **18** (190 mg, 0.29 mmol, 91%). $R_f = 0.37$ (EtOAc/petroleum ether 40/60 1:5); m.p. 109 °C; $[\alpha]_D^{21} = +50.0$ ($c = 0.7$ in acetone); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): $\delta = 7.35-8.10$ (m, 20H; Ph), 5.81 (dd, $^3J(4,5) = 4.1$ Hz, $^3J(5,6) = 5.5$ Hz, 1H; H-5), 5.67 (dd, $^3J(3,4) = 4.1$ Hz, $^3J(4,5) = 4.1$ Hz, 1H; H-4), 5.53 (ddd, $^3J(6,7) = 6.2$ Hz, $^3J(7,8') = 6.4$ Hz, $^3J(7,8) = 8.3$ Hz, 1H; H-7), 4.75 (ddd, $^3J(2',3) = 8.6$ Hz, $^3J(2,3) = 4.8$ Hz, $^3J(3,4) = 4.1$ Hz, 1H; H-3), 4.60 (dd, $^3J(5,6) = 5.5$ Hz, $^3J(6,7) = 6.2$ Hz, 1H; H-6), 4.37–4.42 (m, 2H; H-1′, H-1), 2.04–2.16 (m, 2H; H-2′, H-2), 1.62–1.77 (m, 2H; H-8′, H-8), 1.15–1.35 (m, 2H; H-9′, H-9, H-10′, H-10), 0.74–0.77 (m, 3H; H-11); ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 166.4$, 166.0, 165.2, 165.1 (COC_6H_5), 133.6, 132.9, 132.8, 130.4, 130.2, 129.9, 129.8, 129.6, 129.6, 129.1, 128.9, 128.5, 128.4, 128.3, 128.2 (Ph), 79.6 (C-6) , 78.3 (C-4) , 77.2 (C-5) , 76.7 (C-3) , 72.5 (C-7), 62.0 (C-1), 31.0 (C-2) , 28.9 (C-8), 27.3 (C-9), 22.4 (C-10), 13.8 (C-11); MS (CI): *m*/*z* (%): 651 (75) $[M+H]^+$, 529 (100) $[MH-HO_2CC_6H_5]^+$; elemental analysis calcd (%) for $C_{39}H_{38}O_9$: C 71.99, H 5.89; found C 71.61, H 5.86.

3,6:7,10-Dianhydro-1,4,5-tri-*O*-benzyl-2,8,9-trideoxy-L-*erythro*-D-*ido*-undecitol (*cis*-19) and 3,6:7,10-dianhydro-1,4,5-tri-*O*-benzyl-2,8,9-trideoxy-D-*threo*-D-*ido*-undecitol (*trans*-19): 3-Chloroperoxybenzoic acid (590 mg, 2.39 mmol, 70%) and (±)-camphorsulfonic acid (90 mg) were added to a solution of **12** (1.0 g, 1.99 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and for further 16 h at RT. The mixture was diluted with *tert*-butyl methyl ether (100 mL) and washed with an aqueous solution of $Na_2S_2O_3$ (2 × 30 mL, 10%), a saturated aqueous solution of $NaHCO_3$ (2 × 30 mL) and a saturated aqueous solution of NaCl (2 × 30 mL). Drying (Na_2SO_4) and removal of the solvent under reduced pressure gave the crude mixture of diastereomeric products ***trans*-19** and ***cis*-19** (830 mg, 1.60 mmol, 80%) as an oil. The diastereomeric ratio was 1:1, as determined by ^{1}H NMR spectroscopy of the crude product. Separation of the diastereomers by column chromatography failed.

3,6:7,10-Dianhydro-2,8,9-trideoxy-L-*erythro*-D-*ido*-undecitol (1) and 3,6:7,10-dianhydro-2,8,9-trideoxy-D-*threo*-D-*ido*-undecitol (2): The diastereomeric mixture **19** (540 mg, 1.04 mmol) was dissolved in MeOH (11 mL) and Pd/C (50 mg, 10%) added. The suspension was stirred for 16 h under a hydrogen atmosphere. Filtration, concentration under reduced pressure, and column chromatography ($CHCl_3$/MeOH 5:1) gave **1** (100 mg, 0.42 mmol, 40%) and **2** (100 mg, 0.42 mmol, 40%) as oils.

Compound 1: $R_f = 0.24$ ($CHCl_3$/MEOH 5:1); $[\alpha]_D^{21} = +3.6$ ($c = 2.0$ in methanol); ^{1}H NMR (500.1 MHz, [D$_4$]MeOH, 25 °C): $\delta = 4.27$ (ddd, $^3J(2',3) = 6.0$ Hz, $^3J(2,3) = 7.8$ Hz, $^3J(3,4) = 3.2$ Hz, 1H; H-3), 4.08–4.12 (m, 1H; H-7), 4.05 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 3.4$ Hz, 1H; H-5), 3.99–4.01 (m, 1H; H-10), 3.93 (d, $^3J(3,4) = 3.2$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 3.92 (dd, $^3J(5,6) = 3.4$ Hz, $^3J(6,7) = 7.3$ Hz, 1H; H-6), 3.67–3.72 (m, 2H; H-1′, H-1), 3.54 (dd, $^2J(11',11) = 11.6$ Hz, $^3J(10,11) = 4.4$ Hz, 1H; H-11), 3.49 (dd, $^2J(11',11) = 11.6$ Hz, $^3J(10,11') = 5.6$ Hz, 1H; H-11′), 2.04–2.10 (m, 1H; H-8), 1.90–1.98 (m, 1H; H-9), 1.80–1.91 (m, 2H; H-2′, H-2), 1.63–1.78 (m, 2H; H-8′, H-9′); ^{13}C NMR (125.8 MHz, [D$_4$]MeOH , 25 °C): $\delta = 84.3$ (C-6), 81.7 (C-10), 80.8 (C-7), 79.8 (C-3), 79.1 (C-4), 78.9 (C-5), 65.8 (C-11), 60.4 (C-1), 33.0 (C-2), 28.8 (C-8), 28.3 (C-9); MS (CI): *m*/*z* (%): 249 (100) $[M+H]^+$; HRMS: calcd for $C_{11}H_{21}O_6$ $[M+H]^+$ 249.1338; found 249.1334.

Compound 2: $R_f = 0.22$ ($CHCl_3$/MeOH 5:1); $[\alpha]_D^{21} = +0.85$ ($c = 1.1$ in methanol); ^{1}H NMR (500.1 MHz, [D$_4$]MeOH, 25 °C): $\delta = 4.27$ (ddd, $^3J(2',3) = 6.0$ Hz, $^3J(2,3) = 7.7$ Hz, $^3J(3,4) = 3.3$ Hz, 1H; H-3), 4.16–4.20 (m, 1H; H-7), 4.04–4.09 (m, 1H; H-10), 4.04 (dd, $^3J(4,5) = 1.0$ Hz, $^3J(5,6) = 3.7$ Hz, 1H; H-5), 3.95 (dd, $^3J(3,4) = 3.3$ Hz, $^3J(4,5) = 1.0$ Hz, 1H; H-4), 3.65–3.73 (m, 2H; H-1′, H-1), 3.62 (dd, $^3J(5,6) = 3.7$ Hz, $^3J(6,7) = 7.2$ Hz, 1H; H-6), 3.54 (dd, $^2J(11',11) = 11.6$ Hz, $^3J(10,11) = 4.3$ Hz, 1H; H-11), 3.50 (dd, $^2J(11',11) = 11.6$ Hz, $^3J(10,11') = 5.8$ Hz, 1H; H-11′), 2.10–2.16 (m, 1H; H-8), 1.97–2.02 (m, 1H; H-9), 1.78–1.90 (m, 2H; H-2′, H-2), 1.63–1.73 (m, 2H; H-8′, H-9′); ^{13}C NMR (125.8 MHz, [D$_4$]MeOH , 25 °C): $\delta = 84.7$ (C-6), 81.3 (C-10), 80.3 (C-7), 79.8 (C-3), 79.1 (C-4), 78.9 (C-5), 65.4 (C-11), 60.4 (C-1), 33.1 (C-2), 29.4 (C-8), 28.7 (C-9); MS (CI): *m*/*z* (%): 249 (100) $[M+H]^+$; CIMS: calcd for $C_{11}H_{21}O_6$ $[M+H]^+$ 249.1338; found 249.1336.

3,6:7,10-Dianhydro-1,4,5-tri-*O*-benzyl-2,8,9-trideoxy-L-*threo*-D-*ido*-undecitol (*trans*-20)[18] and 3,6:7,10-dianhydro-1,4,5-tri-*O*-benzyl-2,8,9-trideoxy-D-*erythro*-D-*ido*-undecitol (*cis*-20): 3-Chloroperoxybenzoic acid (542 mg, 2.20 mmol, 70%) and (±)-camphorsulfonic acid (80 mg) were added to a solution of **13** (920 mg, 1.83 mmol) in CH_2Cl_2 (18 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and for further 16 h at RT. The mixture was diluted with *tert*-butyl methyl ether (90 mL) and washed twice with an aqueous solution of $Na_2S_2O_3$ (2 × 27 mL, 10%), a saturated aqueous solution of $NaHCO_3$ (2 × 27 mL) and brine(2 × 27 mL). Drying (Na_2SO_4) and removal of the solvent under reduced pressure gave the crude mixture of diastereomeric products ***trans*-20** and ***cis*-20** (810 mg, 1.56 mmol, 85%) as an oil. The diastereomeric ratio (1:1) was determined by ^{1}H NMR spectroscopy of the crude product. Separation of the diastereomers by column chromatography did not succeed.

1,4,5,11-Tetra-*O*-acetyl-3,6:7,10-dianhydro-2,8,9-trideoxy-L-*threo*-D-*ido*-undecitol (21)[19] and 1,4,5,11-tetra-*O*-acetyl-3,6:7,10-dianhydro-2,8,9-trideoxy-D-*erythro*-D-*ido*-undecitol (22): The diastereomeric mixture **20** (1.07 g, 2.06 mmol) was dissolved in MeOH (20 mL) and Pd/C (100 mg, 10%) added. The suspension was stirred for 16 h under a hydrogen atmosphere. Filtration and concentration under reduced pressure gave the *cis* and *trans* diastereomers **3** and **4** (400 mg, 1.61 mmol, 78%). The separation of the mixture could not achieved by column chromatography. The diastereomeric mixture was dissolved in a mixture of dry pyridine (8 mL) and dry toluene (8 mL). Acetic anhydride (3.2 mL) was added and the reaction mixture stirred for 16 h at RT. The solvent was removed and the residue co-evaporated two times with toluene. Column chromatography (EtOAc/petroleum ether 40/60 2:1) gave the products **21** (250 mg, 0.60 mmol, 37%) and **22** (270 mg, 0.65 mmol, 40%) as syrups.

Compound 21: $R_f = 0.61$ (EtOAc/petroleum ether 40/60 2:1); $[\alpha]_D^{21} = +9.1$ ($c = 2.2$ in acetone); ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): $\delta = 5.57$ (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 3.8$ Hz, 1H; H-5), 5.29 (d, $^3J(3,4) = 3.7$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 4.13–4.18 (m, 2H; H-1, H-3), 4.03–4.10 (m, 2H; H-1′, H-7), 3.98 (dd, $^3J(5,6) = 3.8$ Hz, $^3J(6,7) = 8.1$ Hz, 1H; H-6), 3.89–3.94 (m, 2H; H-10, H-11), 3.69–3.74 (m, 1H; H-11′), 1.79–1.85 (m, 1H; H-8), 1.69–1.73 (m, 2H; H-2′, H-2), 1.68, 1.63 (s, 3H; $COCH_3$), 1.60–1.66 (m, 1H; H-8′), 1.58, 1.49 ($COCH_3$), 1.46–1.51 (m, 1H; H-9), 1.11–1.17 (m, 1H; H-9′); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 170.0$, 168.8, 168.6 ($COCH_3$), 81.6 (C-6), 77.4 (C-4), 77.3 (C-3), 77.1 (C-10), 76.4 (C-7), 76.3 (C-5), 66.1 (C-11), 61.6 (C-1), 29.7 (C-2), 28.9 (C-8), 27.9 (C-9), 20.5, 20.4, 20.3, 20.0 ($COCH_3$); MS (CI): *m*/*z* (%): 417 (100) $[M+H]^+$, 357 (90) $[M+H-HOAc]^+$; HRMS: calcd for $C_{19}H_{29}O_{10}$ $[M+H]^+$ 417.1761; found 417.1761.

Compound 22: $R_f = 0.50$ (EtOAc/petroleum ether 40/60 2:1); $[\alpha]_D^{21} = +6.0$ ($c = 1.9$ in acetone); ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): $\delta = 5.61$ (dd, $^3J(4,5) = 1.0$ Hz, $^3J(5,6) = 2.0$ Hz, 1H; H-5), 5.37 (dd, $^3J(3,4) = 3.3$ Hz, $^3J(4,5) = 1.0$ Hz, 1H; H-4), 4.12–4.17 (m, 1H; H-1′), 4.20–4.25 (m, 2H; H-1, H-3), 4.07–4.10 (m, 2H; H-6, H-7), 3.99 (dd, $^2J(11',11) = 11.0$ Hz, $^3J(10,11) = 6.0$ Hz, 1H; H-11), 3.88 (dd, $^2J(11',11) = 11.0$ Hz, $^3J(10,11') =$

3.8 Hz, 1H; H-11′), 3.84 – 3.89 (m, 1H; H-10), 1.72 – 1.85 (m, 4H; H-2′, H-2, H-8′, H-8), 1.69, 1.65, 1.64. 1.56 (s, 3H; $COCH_3$), 1.41 – 1.48 (m, 1H; H-9), 1.28 – 1.35 (m, 1H; H-9′); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 170.1$, 170.0, 168.9, 168.5 ($COCH_3$), 81.7 (C-6), 77.4 (C-3, C-4), 77.3 (C-10), 77.1 (C-7), 76.5 (C-5), 66.3 (C-11), 61.7 (C-1), 29.1 (C-2), 29.0 (C-8), 27.5 (C-9), 20.5, 20.4, 20.3, 20.0 ($COCO_3$); MS (CI): *m*/*z* (%): 417 (100) $[M+H]^+$; CIMS: calcd for $C_{19}H_{29}O_{10}$ $[M+H]^+$ 417.1761; found 417.1758.

3,6:7,10-Dianhydro-2,8,9-trideoxy-L-*threo*-D-*ido*-undecitol (3)[20]: A solution of NaOMe (1.5 mL, 1.0 N) was added dropwise to a solution of **21** (150 mg, 0.36 mmol) in dry MeOH (15 mL) at RT. The reaction mixture was stirred until TLC indicated complete consumption of the starting material. The mixture was then neutralized by the addition of small portions of acidic cationic ion exchange resin (IR 120, H^+). Filtration, concentration in vacuo, and column chromatography (EtOAc/MeOH 8:1) gave the compound **3** (80 mg, 0.32 mmol, 90%) as an oil. $R_f = 0.27$ (EtOAc/MeOH 8:1); $[\alpha]_D^{21} = -7.41$ ($c = 1.6$ in methanol); ^{1}H NMR (500.1 MHz, [D$_4$]MeOH, 25 °C): $\delta = 4.19$ (ddd, $^3J(2',3) = 6.0$ Hz, $^3J(2,3) = 7.7$ Hz, $^3J(3,4) = 3.2$ Hz, 1H; H-3), 4.14 (d, $^3J(4,5) = 0$ Hz, $^3J(5,6) = 3.3$ Hz, 1H; H-5), 4.09 – 4.14 (m, 1H; H-7), 4.01 – 4.08 (m, 1H; H-10), 3.96 (d, $^3J(3,4) = 3.2$ Hz, $^3J(4,5) = 0$ Hz, 1H; H-4), 3.88 (dd, $^3J(5,6) = 3.3$ Hz, $^3J(6,7) = 8.2$ Hz, 1H; H-6), 3.62 – 3.72 (m, 2H; H-1′, H-1), 3.52 (dd, $^2J(11',11) = 11.5$ Hz, $^3J(10,11) = 3.8$ Hz, 1H; H-11), 3.45 (dd, $^2J(11',11) = 11.5$ Hz, $^3J(10,11') = 6.0$ Hz, 1H; H-11′), 2.09 – 2.15 (m, 1H; H-8), 1.97 – 2.04 (m, 1H; H-9), 1.78 – 1.88 (m, 3H; H-2′, H-2, H-8′), 1.65 – 1.72 (m, 1H; H-9′); ^{13}C NMR (125.8 MHz, [D$_4$]MeOH , 25 °C): $\delta = 83.6$ (C-6), 81.2 (C-10), 79.7 (C-3), 78.7 (C-4), 78.4 (C-5), 77.8 (C-7), 65.4 (C-11), 60.4 (C-1), 32.9 (C-2), 30.8 (C-8), 28.5 (C-9); MS (CI): *m*/*z* (%): 249 (100) $[M+H]^+$; CIMS: calcd for $C_{11}H_{21}O_6$ $[M+H]^+$ 249.1338; found 249.1336.

3,6:7,10-Dianhydro-2,8,9-trideoxy-D-*erythro*-D-*ido*-undecitol (4): A solution of NaOMe (0.5 mL, 1.0 N) was added dropwise to a solution of **22** (50 mg, 0.12 mmol) in dry MeOH (5 mL) at RT. The reaction mixture was stirred until TLC indicated the complete consumption of the starting material. The mixture was neutralized by the addition of small portions of acidic cationic ion exchange resin (IR 120, H^+). Filtration, concentration in vacuo, and column chromatography (EtOAc/MeOH 8:1) gave the compound **4** (27 mg, 0.11 mmol, 95%) as an oil. $R_f = 0.27$ (EtOAc/MeOH 8:1); $[\alpha]_D^{21} = +1.1$ ($c = 1.6$ in methanol); ^{1}H NMR (500.1 MHz, [D$_4$]MeOH, 25 °C): $\delta = 4.19$ (ddd, $^3J(2',3) = 6.3$ Hz, $^3J(2,3) = 7.5$ Hz, $^3J(3,4) = 3.2$ Hz, 1H; H-3), 4.14 (dd, $^3J(4,5) = 0.9$ Hz, $^3J(5,6) = 3.5$ Hz, 1H; H-5), 4.09 – 4.13 (m, 1H; H-7), 3.96 (dd, $^3J(3,4) = 3.2$ Hz, $^3J(4,5) = 0.9$ Hz, 1H; H-4), 3.92 – 3.97 (m, 1H; H-10), 3.92 (dd, $^3J(5,6) = 3.5$ Hz, $^3J(6,7) = 7.4$ Hz, 1H; H-6), 3.56 (dd, $^2J(11',11) = 11.5$ Hz, $^3J(10,11) = 4.1$ Hz, 1H; H-11), 3.62 – 3.71 (m, 2H; H-1′, H-1), 3.47 (dd, $^2J(11',11) = 11.5$ Hz, $^3J(10,11') = 6.0$ Hz, 1H; H-11′), 1.98 – 2.05 (m, 1H; H-8), 1.86 – 1.98 (m, 2H; H-8′, H-9), 1.77 – 1.86 (m, 2H; H-2′, H-2), 1.66 – 1.74 (m, 1H; H-9′); ^{13}C NMR (125.8 MHz, [D$_4$]MeOH , 25 °C): $\delta = 83.4$ (C-6), 81.3 (C-10), 79.7 (C-3), 78.8 (C-4), 78.7 (C-7), 78.3 (C-5), 66.0 (C-11), 60.3 (C-1), 32.9 (C-2), 29.6 (C-8), 28.3 (C-9); MS (CI): *m*/*z* (%): 249 (100) $[M+H]^+$; CIMS: calcd for $C_{11}H_{21}O_6$ $[M+H]^+$ 249.1338; found 249.1342.

Acknowledgement

We thank Mrs. M. Ehmen, Mr. D. Neemeyer, and Mr. K.-H. Plate who performed the analytical work, and Dr. A. Lützen who assisted with the NOESY experiments. Financial support from the Fonds der Chemischen Industrie and by the Heinz-Neumüller-Foundation is appreciated.

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[19] Systematic[17] name: 1,7,8,11-tetra-*O*-acetyl-2:5;6:9-dianhydro-3,4,10-trideoxy-D-*threo*-D-*galacto*-undecitol.
[20] Systematic[17] name: 2,5:6,9-dianhydro-3,4,10-trideoxy-D-*threo*-D-*galacto*-undecitol.

Received: September 10, 1999 [F2026]