219. Deoxy-nitrosugars

6th Communication[1])

Stereoelectronic Control in the Reductive Denitration of Tertiary Nitro Ethers. A Synthesis of '*C*-Glycosides'

by **Franz Baumberger** and **Andrea Vasella***

Organisch-Chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

(20.VII.83)

Summary

The separate, radical denitration with Bu_3SnH of the pyranose derivatives **3**, **4**, **9**, and **10** gave in good yields exclusively the '*C*-glycosides' **5** and **11**, respectively *(Scheme 1)*. Similar reduction of the cyclohexyl derivatives **15**, **16**, **19** and **20** gave 4:1 mixtures of **17**, **18**, **21** and **22**, respectively, always with predominant formation of an axial C,H-bond. In the furanose series a divergent behaviour was observed for the D-mannose-derived nitro ethers **25** and **27** and the D-ribose-derived nitro ethers **30** and **31**, respectively, in that the former two gave isomerically homogeneous reduction products (**26** and **28**, respectively; *Scheme 3*) and the latter a 1:1 mixture of the diastereoisomers **32** and **33** *(Scheme 4)*. The stereochemical results were explained on the basis of the stereoelectronic effect of the ring O-atom, the preferred conformation of the intermediate, pyramidal alkoxyalkyl radicals and steric effects in the trioxabicyclo[3.3.0]octane ring system.

1. Introduction. – Tertiary nitroalkanes are reductively denitrated by treatment with the sodium salt of methanethiol [2], with ethylene glycol and KOH [3], with *N*-benzyl-1,4-dihydronicotinamide [4] or with tributyltin hydride (Bu_3SnH) [5] [6]. As far as it is known, these reactions follow a radical-chain mechanism and proceed *via* planar radical intermediates. As expected, the few stereochemically relevant reductions so far studied occur without stereospecificity [2] and with a variable diastereoselectivity [7] which is difficult to predict[2]).

In the case of conformationally biased α-nitro ethers, however, the analogous reductive denitrations are expected to occur with a high degree of diastereoselectivity.

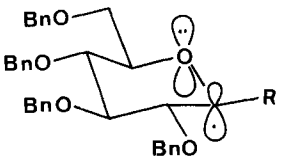
---

[1]) 5th Communication: [1].

[2]) The steric course of the similar reduction of thionoesters [7–16] and tertiary benzoates [17] by Bu_3SnH has been explained by steric and polar factors.

It is known that the intermediates, *viz.* alkoxyalkyl radicals, are pyramidal [17–20] and that the non-bonded C-orbital prefers an orientation which allows conjugative delocalization[3]) with the π-type orbital on the O-atom [22], *i.e.* a (pseudo)axial orientation in 1-oxacycloalk-2-yl radicals [23] [24]. This is substantiated by a stereoelectronic preference for the radical abstraction of (pseudo)axial α- and β-H-atoms in conformationally biased cyclic ethers [21] [23] [25–29][4]). The same stereoelectronic effect should also control the reverse reactions and this has been shown for the H-transfer to 1,3-dioxanyl radicals [27].

We wished to check, if the radical denitration with Bu_3SnH of carbohydrate nitro ethers such as **3** and **4** *(Scheme 1)* will indeed diastereoselectively lead (*via* a common intermediate **1**) to the corresponding anhydroalditol such as **5** with two equatorial side chains. Further insight into the stereoselectivity of this reaction was expected from the reduction of conformationally biased nitrocyclohexanes *(Scheme 2)* and from conformationally more flexible furanose derivatives (*Scheme 3* and *4*). Since such tertiary carbohydrate nitro ethers are easily available [31] from 1-deoxy-1-nitroaldoses [32] [33] *via Michael* additions or *via* the *Henry* reaction, the reductive denitration would open a way to '*C*-glycosides' (= anhydroalditols) which have attracted much recent interest (see *e.g.* [34–48] and ref. cited therein).



1

Results. – Base-catalyzed reaction of the D-gluco-deoxynitroaldose **2** [32] [33] with excess paraformaldehyde followed by acetylation gave the nitro ethers **3** and **4** in a yield of 56% and with a ratio of 85:15 (^{1}H-NMR)[5]). The isomers were separated by prep. HPLC. Their IR spectra showed NO_2-bands at 1552 cm^{-1} (major compound) and 1566 cm^{-1} (minor compound); the assignment of the anomeric configuration was based on the observation that the IR absorption of an axial NO_2-group of secondary nitro ethers is shifted to lower wave numbers [33]. Separate treatment of **3** or **4** with Bu_3SnH in the presence of α,α'-azoisobutyronitrile (reflux in benzene) gave the 2,6-anhydroalditol **5** in yields of 95 and 87%, respectively, and traces of minor compounds that were not isolated. The configuration of **5** was proven by its transformation into the alcohol **6**[6]) and further into the *meso*-pentabenzyl ether **7**. The *meso* nature of **7** was evident from its ^{1}H- and ^{13}C-NMR spectra. The similar reaction sequence starting with the D-*manno*-deoxynitroaldose **8** [32] [33], gave the tertiary nitro ethers **9** (65%) and **10** (12%). Again, separate treatment of **9** and **10**

---

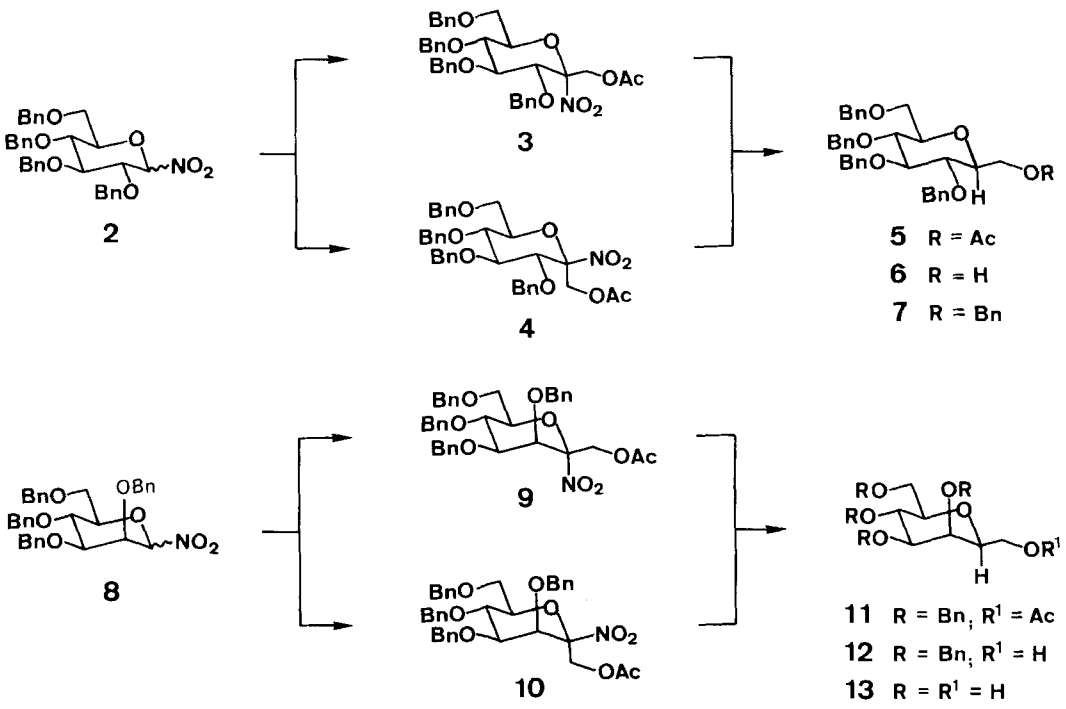
3) See [21] and ref. cited therein.

4) A similar stereoelectronic control in the cleavage of a C,O-bond is described in [30].

5) Partial solvolytic displacement of the NO_2-group occurred during the reaction, see [31].

6) The ^{1}H-NMR spectra and the specific rotation were different from those of the anomeric alcohol obtained by *Sinaÿ et al.* [37]. We thank Professor *Sinaÿ* for the relevant spectra.

Scheme 1



with Bu_3SnH, as above, gave the protected 2,6-anhydro-D-*glycero*-D-*galacto*-heptitol **11** as the only observed isomer. Deprotection of **11** (deacetylation to **12** followed by hydrogenolysis) gave the known [49], free anhydroheptitol **13**.

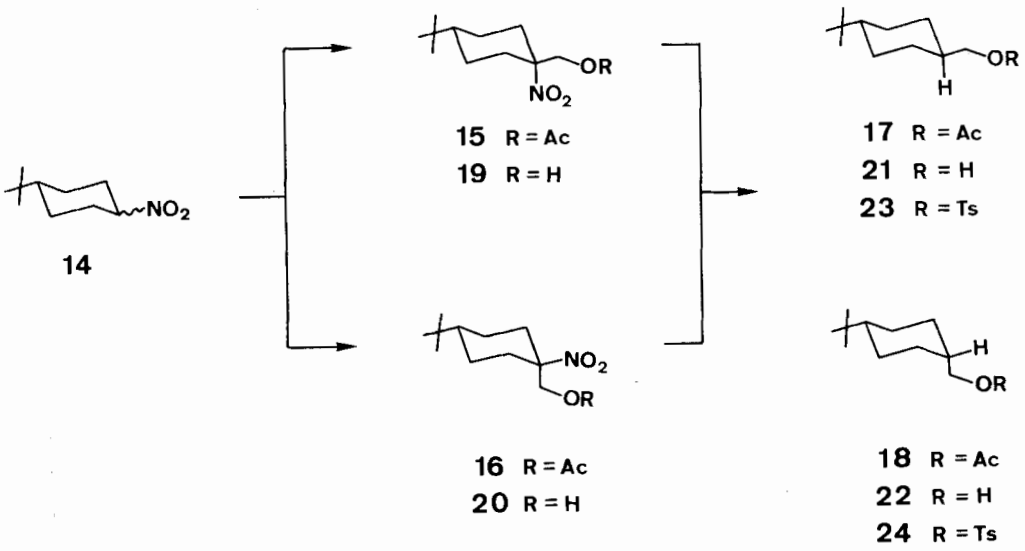
To evaluate the influence of the ring-O-atom on the diastereoselectivity of the reduction, we treated the tertiary nitro compounds **15**, **16**, **19** and **20** with Bu_3SnH under the same conditions as above. The crystalline nitro alcohols **19** and **20** were obtained (>95%, 7:3) from 1-(*tert*-butyl)-4-nitrocyclohexane (**14**) [50] [51] and acetylated to give **15** and **16**. Their configuration was inferred from the ^{1}H-NMR spectra. The signals of the equatorial H–C(2 and 6) were very similar to those found for the corresponding H-atoms of **14** and were interpreted according to *Huitric & Trager* [50].

Separate reduction of the acetates **15** and **16** gave a mixture of the denitrated acetates **17** and **18** in a high yield and with a ratio of 83:17, as determined by ^{1}H-NMR spectroscopy[7]) and GC. Similarly, the separate reduction of the alcohols **19** and **20** gave a 4:1 mixture (^{1}H-NMR) of **21** and **22** [53] in over 95%. The acetates **17** and **18** and the alcohols **21** and **22** could not be separated, but pure samples of the *trans*- and *cis*-tosylates **23** and **24** [54] were obtained by HPLC.

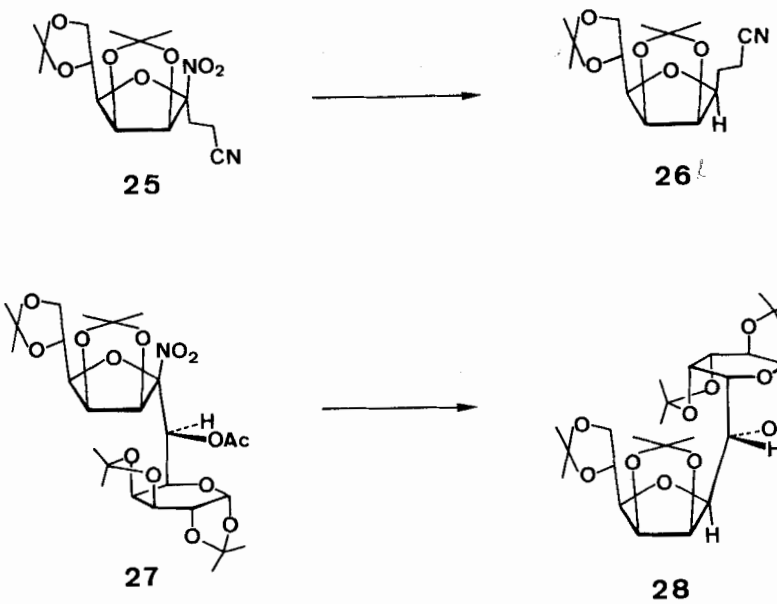
---

[7]) Based on the integrals for the acetoxymethyl group. Both diastereomers had been prepared and characterized [52].

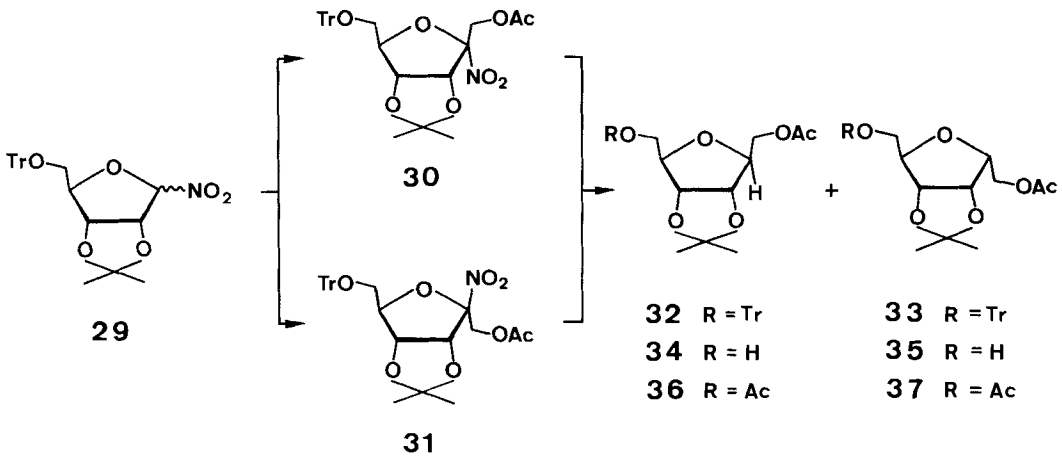
Scheme 2



Scheme 3



Scheme 4



The behaviour of five-membered, tertiary nitro ethers was checked for trioxabicyclo[3.3.0]octane derivatives of the D-*manno*[8])- and D-*ribo*-series (*Scheme 3* and *4*). Compound **25** [31] upon reduction with Bu_3SnH, gave the 4,7-anhydroaldonitrile **26** as the main product (58%)[9]). The configuration at C(4) of **26** was deduced from its ^{1}H-NMR spectrum ($J(4,5) = 3.8$ Hz [55]). Similar reduction of the dodecosulose **27** [31] gave (89%) the anhydro compound **28** as a single, crystalline isomer. Here again, the value of 3.7 Hz for $J(7,8)$ is consistent with a 7,8-*cis*-configuration (signal assignment by ^{1}H-shift-correlated 2-D NMR spectroscopy). Separate reduction of the psicofuranose derivatives **30** and **31** (from **29**, see [31]), however, gave a 47:53 mixture[10]) of the *allo*- and *altro*-anhydroalditols **32** and **33** in a combined yield of 90 and 87%, respectively *(Scheme 4)*. Their configuration was determined by transformation of **32** into the *meso*-diacetate **36** and of **33** into the known [56] diacetate **37**. This was achieved by detritylation ($FeCl_3$ [57], 78%) of the mixture of **32/33**, separation of the alcohols **34** and **35**, and then, on one hand, back-tritylation to pure **32** and **33** and, on the other hand, acetylation to **36** and **37**.

Discussion. – The reductive denitration of the conformationally biased, tertiary nitro ethers of the pyranose series leads to '*C*-glycosides' in good yields and – according to expectation – with a diastereoselective formation of an axial C,H-bond. In the furanose series, the explanation of the diastereoselectivity requires an evaluation of both steric and stereoelectronic factors. Since the tertiary nitro ethers are obtained from carbohydrate derivatives with inverse polarity at the anomeric center [31], this access to '*C*-glycosides' complements earlier methods.

---

[8]) Configurational prefix refers to the furanose ring only.

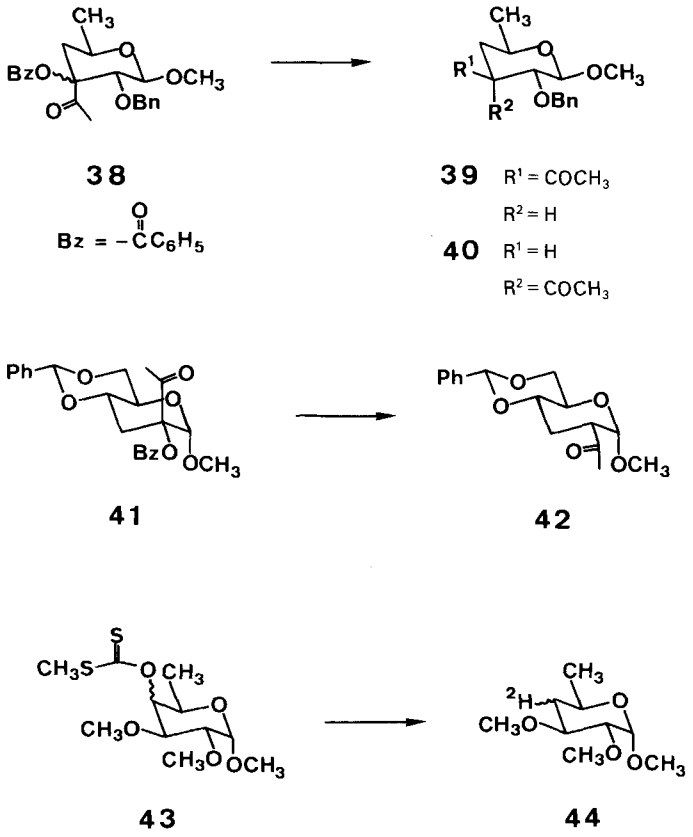
[9]) The IR spectra of three by-products were not consistent with the structure of diastereoisomers.

[10]) The ratio was determined by HPLC. The same ratio of products was obtained from a reduction of **30** with Bu_2SnH_2.

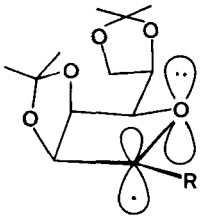
The assumption of a common intermediate - an alkoxyalkyl radical such as **1** - is in agreement with the formation of the same product(s) from either anomeric starting material. The high tendency for the axial C,H-bond formation in cyclohexanes makes it difficult to evaluate the extent of the stereoelectronic effect of the ring-O-atom. The stabilizing conjugative interaction in tetrahydropyran-2-yl radicals seems to be rather weak (from the degree of pyramidalization at C(1) as deduced from the hyperfine coupling constants, see [21]) and a similar reactivity of the cyclohexyl- and tetrahydropyran-2-yl radicals has been proposed [21]. The influence of the axial configuration of the vicinal alkoxy substituent in **9** and **10** is not required for the diastereoselectivity.

2-Alkoxyalkyl radicals prefer a coplanar arrangement of the non-bonded, singly occupied orbital and the C,O-bond [58]. This effect can influence the steric course of radical reductions as inferred from the following examples[11]). Reduction of either epimer of **38** (Bu_3SnH) gave a 4:1 mixture of **39** and **40** [17] (*Scheme 5;* the coplanar arrangement mentioned cannot be attained without ring distortion;

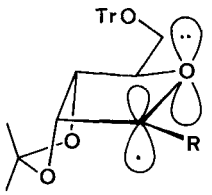
Scheme 5



[11]) For a discussion of the stabilizing effect of β-alkoxy groups on C-radicals see [59].



45



46

the steric behaviour is very similar to the cyclohexyl case). Reduction of **41** gave **42** exclusively [17] (additional influence of the axial C(1),O-bond). Reduction of either epimer of **43** resulted in a 1:1 mixture of the epimeric, monodeuteriated reduction products **44** [14] (coplanar arrangement of the non-bonded C-orbital and the C(5),O-bond and preference for an attack *anti* to the C,O-bond against the tendency for axial C,O-bond formation).

The relatively high proportion of *endo*-attack by Bu_3SnH on the intermediate D-*ribo*-radical is surprising, particularly when compared to the results in the D-*manno*-series. This can be explained as the result of a steric effect, favouring *exo*-attack and a stereoelectronic effect, favouring *endo*-attack in the D-ribo and *exo*-attack in the D-*manno*-series. The stereoelectronic effect depends on the conformation of the furanose-ring in the intermediate radical[12]). This conformation is dominated by the preferred pseudoequatorial orientation of the *endo*-dioxolanyl side chain in the D-*manno*-radical **45** and the *exo*-trityloxymethyl side chain in the D-*ribo*-radicals **46** (*cf.* [55]). The different conformation of the furanosyl ring in **45** and **46** entails pyramidalization of the non-bonded C-atom in the *endo*-direction in the D-*ribo*-series and in the *exo*-direction in the D-*manno* case. This means that the stereoelectronic effect is at least as strong as the steric bias for *exo*-attack on a trioxabicyclo[3.3.0]octane system assuming the extreme case of conformational homogeneity around the radical center.

We thank the *Swiss National Science Foundation* and *Sandoz AG*, Basle, for generous support and Prof. Dr. *H. Fischer* and Dr. *H. Paul* for helpful discussions.

Experimental Part

General Remarks. See [61]. Benzene was extracted with conc. H_2SO_4, washed with H_2O and distilled from Na. DMF was distilled from CaH_2, anh. MeOH from Mg. Paraformaldehyde and α,α'-azaisobutyronitrile (AIBN) were obtained from *Fluka*. Bu_3SnH was prepared according to a procedure of *Kuivila* [62]. Acetylations were carried out at 0° in pyridine/Ac_2O 2:1. Excess of pyridine and Ac_2O were removed at 40°/0.5 Torr. TLC: Substances were detected by spraying the plates with 0.025 M I_2 in 10% aq. H_2SO_4 or with a 10% solution of phosphomolybdic acid in EtOH, in each case followed by heating at about 200°. GLC was performed on a *Hewlett-Packard 5880* apparatus using a *SP 2100* column, anal. HPLC on a *Kontron* apparatus (LC pump *410*) with a UV detector, prep. HPLC on a *Du Pont 8800;* detection by differential refractometer.

---

[12]) Assuming both kinetic control and a low activation energy for H-transfer from Bu_3SnH (2.95 to 3.97 kcal/mol for alkyl radicals [60]).

General Procedure for the Reductive Denitration. A 3-necked flask equipped with a condenser, a dropping funnel and a gas inlet tube was dried at 120° and then cooled under Ar. Freshly distilled Bu_3SnH (5 mmol) and AIBN (0.2–0.4 mmol) in benzene (5 ml) were added dropwise within 1–2 h to a degassed, boiling solution of the nitro compound (1 mmol) in benzene (15 ml). When TLC indicated the disappearance of the nitro compound, the cooled mixture was concentrated and the residue was purified by chromatography on SiO_2.

1-O-Acetyl-3,4,5,7-tetra-O-benzyl-2-deoxy-2-nitro-D-gluco-heptulopyranoses (3 and 4). To a stirred solution of 1.5 g (2.6 mmol) of 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-nitro-D-glucopyranose (**2**) [32] in 50 ml anh. MeOH were added 790 mg (26 mmol) of paraformaldehyde and 72 mg (0.5 mmol) of K_2CO_3. The mixture was stirred for 3 h at r.t., poured into 150 ml Et_2O and extracted with H_2O. The crude product was purified by flash chromatography [63] (60 g SiO_2, Et_2O/hexane 1:2) yielding 870 mg (56%) of a material, 500 mg (0.83 mmol) of which were acetylated affording after flash chromatography (25 g SiO_2, Et_2O/hexane), 530 mg (quant.) of **3/4**. R_f 0.45 (hexane/AcOEt 2:1). The anomers were separated by prep. HPLC (*Zorbax-Sil,* Et_2O/hexane 4:1, $k'=2.1$ for **3**, $k'=2.5$ for **4**).

Data of **3**. $[\alpha]_D^{25}+55°$ ($c=1.6$, $CHCl_3$). IR: 3085*w*, 3065*w*, 3030 sh, 3005*m*, 2910*w*, 2870*m*, 1751*s*, 1567*s*, 1552*s*, 1495*m*, 1452*s*, 1382 sh, 1365*s*, 1220*s*, 1120 sh, 1091*s*, 1072*s*, 1028*s*, 693*m*. ^{1}H-NMR: 7.45–7.10 (*m*, 20 arom. H); 4.85–4.35 (*m*, 11 H); 4.30–3.70 (*m*, 5 H); 1.93 (*s*, CH_3). ^{13}C-NMR: 169.45 (*s*); 138.04 (*s*); 137.67 (*s*); 137.41 (*s*); 136.54 (*s*); 128.43 (*d*); 128.33 (*d*); 128.21 (*d*); 128.05 (*d*); 127.93 (*d*); 127.82 (*d*); 127.74 (*d*); 127.63 (*d*); 127.47 (*d*); 110.62 (*s*); 79.51 (*d*); 76.54 (*d*); 76.12 (*d*); 75.90 (*d*); 75.23 (*t*); 74.32 (*t*); 73.95 (*t*); 73.23 (*t*); 68.09 (*t*); 63.83 (*t*); 20.56 (*q*). MS (70 eV): 552 (<0.2), 503 (<0.1), 444 (<0.1), 429 (<0.1), 413 (<0.1), 397 (<0.1), 353 (<0.1), 307 (<0.2), 271 (<0.3), 259 (<0.5), 253 (2), 181 (6), 91 (100), 43 (5).

$C_{37}H_{39}NO_9$ (641.73) Calc. C 69.25 H 6.13 N 2.19% Found C 69.13 H 6.40 N 2.19%

Data of **4**. $[\alpha]_D^{25}+2.4°$ ($c=1.6$, $CHCl_3$). IR: 3090*w*, 3065*w*, 3030 sh, 3005*m*, 2955*m*, 2925*m*, 2870*m*, 1748*s*, 1566*s*, 1558 sh, 1495*w*, 1452*s*, 1381*m*, 1365*s*, 1280 sh, 1220*s*, 1158m, 1073*s*, 1028*s*, 693*m*. ^{1}H-NMR: 7.50–7.05 (*m*, 20 arom. H); 5.10–4.40 (*m*, 10 H); 4.35–3.60 (*m*, 6 H); 1.98 (*s*, CH_3). ^{13}C-NMR: 169.83 (*s*); 138.02 (*s*); 137.59 (*s*); 137.34 (*s*); 136.45 (*s*); 128.47 (*d*); 128.38 (*d*); 128.30 (*d*); 128.23 (*d*); 128.13 (*d*); 127.83 (*d*); 127.76 (*d*); 127.70 (*d*); 127.48 (*d*); 109.84 (*s*); 81.18 (*d*); 79.17 (*d*); 76.72 (*d*); 76.17 (*d*); 74.80 (*t*); 73.98 (*t*); 73.80 (*t*); 73.40 (*t*); 68.68 (*t*); 62.24 (*t*); 20.59 (*q*). MS: indistinguishable from that of **3**.

$C_{37}H_{39}NO_9$ (641.73) Calc. C 69.25 H 6.13 N 2.19% Found C 69.45 H 6.27 N 2.04%

1-O-Acetyl-2,6-anhydro-3,4,5,7-tetra-O-benzyl-D-glycero-D-gulo-heptitol (**5**). A) *From* **3**. Denitration of 285 mg (0.44 mmol) of **3** gave, after chromatography (30 g SiO_2, AcOEt/hexane 1:4) 250 mg (95%) of **5**, $[\alpha]_D^{25}=-4.4°$ ($c=1.3$, $CHCl_3$). IR: 3090*w*, 3065*w*, 3030 sh, 3005*m*, 2910 sh, 2870*m*, 1740*s*, 1497*m*, 1455*m*, 1385 sh, 1365*m*, 1310*w*, 1220*s*, 1150*m*, 1095*s*, 1065*s*, 1030*s*, 695*m*. ^{1}H-NMR: 7.45–7.07 (*m*, 20 arom. H); 5.00–4.05 (*m*, 10 H); 3.90–3.30 (*m*, 7 H); 2.00 (*s*, CH_3). ^{13}C-NMR: 170.53 (*s*); 138.35 (*s*); 138.10 (*s*); 137.92 (*s*); 137.62 (*s*); 128.36 (*d*); 128.31 (*d*); 128.27 (*d*); 128.20 (*d*); 127.93 (*d*); 127.77 (*d*); 127.62 (*d*); 127.51 (*d*); 127.44 (*d*); 87.10 (*d*); 79.14 (*d*); 78.28 (*t*); 78.03 (*d*); 77.00 (*t*); 75.50 (*d*); 75.01 (*d*); 74.97 (*t*); 73,40 (*t*); 68.85 (*t*); 63.47 (*t*); 20.91 (*q*). MS (70 eV): 505 (2), 399 (1), 291 (1), 181 (8), 91 (100), 43 (5).

$C_{37}H_{40}O_7$ (596.76) Calc. C 74.47 H 6.76% Found C 74.41 H 6.64%

B) *From* **4**. Denitration of 55 mg (0.086 mmol) of **4** gave 45 mg (87%) of **5**. IR and ^{1}H-NMR spectra indistinguishable from those in *A*.

2,6-Anhydro-1,3,4,5,7-penta-O-benzyl-D-glycero-D-gulo-heptitol (**7**). A solution of 130 mg (0.22 mmol) of **5** was kept at r.t. in 7.5 ml of 2% NaOMe in MeOH for 30 min (TLC, AcOEt/hexane 1:2). The solvent was evaporated and the residue was purified by flash chromatography (15 g SiO_2, Et_2O) giving crude **6** (quant.) as a colourless oil, which was crystallized from AcOEt/hexane. Colourless needles, m.p. 93.0–93.5°, $[\alpha]_D^{25}=+8.6°$ ($c=1.1$, $CHCl_3$). IR: 3595*w*, 3460 br., 3090*w*, 3070*w*, 3035 sh, 3005*m*, 2920 sh, 2870*m*, 1496*m*, 1454*s*, 1398*w*, 1362*m*, 1306*w*, 1220 br., 1146*s*, 1098*s*, 1064 sh, 1028*s*, 1000*m*, 694*m*. ^{1}H-NMR: 7.45–7.05 (*m*, 20 arom. H); 4.97–4.43 (*m*, 4 CH_2–Ph); 4.00–3.20 (*m*, 9 H); 2.15 (br., OH).

A mixture of 120 mg (0.22 mmol) of **6**, 120 mg (2.2 mmol) of KOH, 250 µl (2.2 mmol) of benzyl chloride and 3 ml dioxane was kept at 50° for 15 min and then diluted with 5 ml of Et_2O. The KOH

was filtered off and the filtrate was concentrated. Flash chromatography (25 g SiO_2, hexane/Et_2O 3:1) afforded 123 mg (86%) of **7** as colourless crystals, m.p. 55.0–55.5°. IR: 3090*w*, 3065*m*, 3030 sh, 3005*s*, 2910 sh, 2870*s*, 1496*m*, 1454*s*, 1362*m*, 1310*w*, 1154*m*, 1092*s*, 1060*s*, 1030*s*, 694*m*. ^{1}H-NMR: 7.45–7.05 (*m*, 25 arom. H); 4.90–4.45 (*m*, 5 C*H*$_2$Ph); 3.87–3.30 (*m*, 9 H). ^{13}C-NMR: 138.45 (*s*); 138.07 (*s*); 137.96 (*s*); 128.14 (*d*); 128.10 (*d*); 127.69 (*d*); 127.56 (*d*); 127.43 (*d*); 127.31 (*d*); 87.07 (*d*); 79.00 (*d*); 78.26 (*d*); 75.36 (*t*); 74.82 (*t*); 73.31 (*t*); 69.04 (*t*). MS (70 eV): 553 (3), 339 (2), 249 (2), 181 (17), 91 (100).

$C_{42}H_{44}O_6$ (644.82) Calc. C 78.23 H 6.88% Found C 77.96 H 6.67%

*1-O-Acetyl-3,4,5,7-tetra-O-benzyl-2-deoxy-2-nitro-*D-manno*-heptuolopyranoses (***9** *and* **10**). A solution of 285 mg (0.5 mmol) of 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-nitro-D-*manno*-pyranose (**8**) [32] in 5 ml of DMF, 150 mg (5 mmol) of paraformaldehyde and 28 mg (0.2 mmol) K_2CO_3 was kept at r.t. until disappearance of **8** (20 min) as indicated by TLC (hexane/AcOEt 2:1) and then poured into 25 ml of Et_2O. Normal workup gave a residue, which was dried *i.v.* and acetylated (0°, 30 min). TLC (hexane/Et_2O 3:1) showed 4 spots, the major ones (= fastest and slowest moving ones) corresponded to **9** and **10**. The residue obtained after evaporation of the solvent was separated by flash chromatography (40 g SiO_2, Et_2O/hexane 1:4), giving 205 mg (65%) of **9** (α-D), 42 mg (12%) of **10** (β-D) and 56 mg of two nonidentified by-products. All compounds were slightly yellow oils.

Data of **9**. $[\alpha]_D^{25} = +54.5°$ ($c = 1.4$, $CHCl_3$). IR: 3090*w*, 3060*w*, 3030 sh, 3005*m*, 2925*m*, 2870*m*, 1752*s*, 1560 sh, 1554*s*, 1495*s*, 1454*m*, 1365*m*, 1220*s*, 1104*s*, 1072*s*, 1028*m*, 694*m*. ^{1}H-NMR: 7.43–7.03 (*m*, 20 arom. H); 5.10–4.02 (*m*, 12 H); 3.95–3.70 (*m*, 3 H); 3.60 (*dd*, $J = 9.0$ and 2.5, H–C(4)); 1.97 (*s*, CH_3). ^{13}C-NMR: 169.17 (*s*); 138.07 (*s*); 137.77 (*s*); 137.45 (*s*); 137.20 (*s*); 128.41 (*d*); 128.36 (*d*); 128.20 (*d*); 128.17 (*d*); 127.93 (*d*); 127.84 (*d*); 127.77 (*d*); 127.70 (*d*); 127.60 (*d*); 127.39 (*d*); 111.95 (*s*); 79.91 (*d*); 77.88 (*d*); 75.54 (*t*); 74.95 (*t*); 74.43 (*d*); 73.34 (*t*); 73.06 (*t*); 72.83 (*d*); 68.28 (*t*); 64.51 (*t*); 20.49 (*q*). MS (70 eV): 505 (0.3), 503 (0.5), 413 (0.5), 373 (2), 304 (3), 253 (3), 181 (21), 91 (100), 43 (20).

$C_{37}H_{39}NO_9$ (641.73) Calc. C 69.25 H 6.13 N 2.19% Found C 68.99 H 5.94 N 2.13%

Data of **10**. $[\alpha]_D^{25} = -38.8°$ ($c = 1.7$, $CHCl_3$). IR: 3085*w*, 3060*w*, 3030 sh, 3005*m*, 2955*m*, 2925*m*, 2870*m*, 1754*s*, 1577*s*, 1558 sh, 1453*m*, 1367*m*, 1215*s*, 1097*s*, 1052*s*, 1028*s*. ^{1}H-NMR: 7.45–7.05 (*m*, 20 arom. H); 4.95–3.60 (*m*, 16 H); 2.00 (*s*, CH_3). ^{13}C-NMR: 169.53 (*s*); 138.30 (*s*); 137.79 (*s*); 137.36 (*s*); 137.11 (*s*); 128.50 (*d*); 128.24 (*d*); 128.15 (*d*); 128.10 (*d*); 128.01 (*d*); 127.83 (*d*); 127.78 (*d*); 127.65 (*d*); 127.53 (*d*); 127.44 (*d*); 127.29 (*d*); 126.99 (*d*); 109.46 (*s*); 80.83 (*d*); 77.89 (*d*); 76.25 (*d*); 75.91 (*t*); 74.80 (*t*); 74.11 (*d*); 73.56 (*t*); 73.20 (*t*); 68.56 (*t*); 60.97 (*t*); 20.39 (*q*). MS (70 eV): 594 (< 1), 552 (< 1), 443 (< 1), the other peaks corresponded to those of **9**.

$C_{37}H_{39}NO_9$ (641.73) Calc. C 69.25 H 6.13 N 2.19% Found C 69.54 H 6.36 N 2.16%

*1-O-Acetyl-2,6-anhydro-3,4,5,7-tetra-O-benzyl-*D-glycero-D-galacto-*heptitol* (**11**). A) *From* **9**. Denitration of 51 mg (0.08 mmol) of **9** was terminated after 2½ h (TLC, hexane/AcOEt 3:1). Evaporation of the solvent and flash chromatography of the residue (15 g SiO_2, hexane/Et_2O 2:1) gave 40 mg (84%) of **11**, $[\alpha]_D^{25} = +5.7°$ ($c = 1.3$, $CHCl_3$). IR: 3090*w*, 3065*w*, 3030 sh, 3005*m*, 2870*m*, 1740*s*, 1495*w*, 1453*s*, 1377*s*, 1225*s*, 1135 sh, 1110*s*, 1050*s*, 1028*s*, 694*m*. ^{1}H-NMR: 7.50–7.05 (*m*, 20 arom. H); 5.15–4.40 (*m*, 8 H); 4.40–3.32 (*m*, 9 H); 1.97 (*s*, CH_3). ^{13}C-NMR: 170.44 (*s*); 138.31 (*s*); 138.14 (*s*); 128.36 (*d*); 128.19 (*d*); 128.07 (*d*); 127.95 (*d*); 127.78 (*d*); 127.56 (*d*); 127.44 (*d*); 84.83 (*d*); 79.88 (*d*); 75.74 (*d*); 75.22 (*d,t*); 74.18 (*t*); 73.42 (*d,t*); 72.63 (*t*); 69.45 (*t*); 63.59 (*t*); 20.91 (*q*). MS (70 eV): 505 (2), 446 (< 0.2), 413 (< 0.2), 291 (< 0.5), 201 (1), 181 (7), 105 (3), 91 (100), 57 (22), 43 (15).

$C_{37}H_{40}O_7$ (596.73) Calc. C 74.47 H 6.76% Found C 74.63 H 7.01%

B) *From* **10**. In an analogous way, denitration of 60 mg (0.09 mmol) of **10** gave after flash chromatography (25 g SiO_2, hexane/Et_2O 2:1) 27 mg (49%) **11**. The ^{1}H-NMR and IR spectra of this product were identical with those in *A*.

*2,6-Anhydro-*D-glycero-D-galacto-*heptitol* (**13**) [49]. A solution of 480 mg (0.8 mmol) of **11** in 40 ml of a 2% solution of NaOMe in MeOH was kept for 1 h at r.t. Usual workup (Et_2O, H_2O) gave 428 mg (96%) of **12**. Slightly yellow oil, $[\alpha]_D^{25} = +15.1°$ ($c = 1.5$, $CHCl_3$). IR: 3590*w*, 3480 br., 3085*w*, 3065*w*, 3030 sh, 3002*m*, 2865*m*, 1495*m*, 1454*m*, 1362*m*, 1086*s*, 1047*s*, 1028*s*, 909*s*, 690*m*. ^{1}H-NMR: 7.48–7.05 (*m*, 20 arom. H); 5.07–4.40 (*m*, 4 C*H*$_2$Ph); 4.07–3.25 (*m*, 9 H); 1.95 (br., OH).

A solution of 120 mg (0.22 mmol) of **12** in 2.2 ml of AcOH was hydrogenated for 2.5 h in the presence of 60 mg of 10% Pd/C. After disappearance of the starting material (TLC, EtOH/H_2O 7:3), the precipitate was filtered off *(Celite)* and washed with EtOH. The filtrate was concentrated and the residue was purified by chromatography (10 g SiO_2, EtOH/H_2O 9:1) and then by distribution between H_2O and AcOEt. Lyophilisation of the aq. solution yielded 36 mg (85%) of **13** as a colourless solid, which was crystallized from EtOH, m.p. 129–130° ([49]: 142–144°), $[\alpha]_D^{25} = -33.4°$ ($c = 1.5$, H_2O) ([49]: $[\alpha]_D = -33.6°$).

$C_7H_{14}O_6$ (194.19) Calc. C 43.30 H 7.27% Found C 43.55 H 7.35%

trans- *and* cis-*4-(*tert-*Butyl)-1-nitrocyclohexylmethyl acetates* (**15** *and* **16**, *respectively*). A stirred solution of 110 mg (0.59 mmol) of 1-(*tert*-butyl)-4-nitrocyclohexane (**14**) [51], 178 mg (5.9 mmol) of paraformaldehyde and 16 mg (0.12 mmol) of K_2CO_3 in 3.5 ml of anh. MeOH was kept at r.t. until **14** had disappeared (¾ h; TLC, hexane/AcOEt 7:3). The mixture was diluted with 10 ml of Et_2O. Usual workup gave a colourless solid (**19** and **20**). Acetylation of this solid gave, after flash chromatography (20 g SiO_2, hexane/AcOEt 20:1), 104 mg (68%) of **15** and 46 mg (30%) of **16**.

Data of **15**. M.p. 84–86° (from hexane). IR: 3020*w*, 2960*s*, 2910 sh, 2870*m*, 2845*w*, 1746*s*, 1736 sh, 1545*s*, 1476*w*, 1458*m*, 1450*m*, 1428*m*, 1375*m*, 1365*s*, 1350*w*, 1336*w*, 1324*w*, 1220*s*, 1152*s*, 1142*m*, 838*w*. ^{1}H-NMR: 4.29 (*s*, CH_2OAc); 2.72 (*d*, $J = 12$, H_{eq}–C(2), H_{eq}–C(6)); 2.11 (*s*, CH_3); 1.95–1.00 (*m*, 7 H); 0.90 (*s*, 3 CH_3). ^{13}C-NMR: 169.78 (*s*); 89.11 (*s*); 69.75 (*t*); 46.82 (*d*); 32.31 (*s*); 31.58 (*t*); 27.30 (*q*); 22.55 (*t*); 20.46 (*q*). MS (70 eV): 211 (< 1), 201 (4), 154 (6), 135 (6), 111 (7), 95 (21), 94 (25), 93 (41), 81 (10), 79 (16), 57 (100).

$C_{13}H_{23}NO_4$ (257.33) Calc. C 60.68 H 9.01 N 5.44% Found C 60.91 H 9.06 N 5.29%

Data of **16**. Colourless oil, b.p. 125°/0.01 Torr. IR: 3020*w*, 2965*s*, 2910 sh, 2875*m*, 1748*s*, 1736 sh, 1545*s*, 1480 sh, 1462*m*, 1448m, 1388*m*, 1374*s*, 1368*s*, 1339*w*, 1272 sh, 1220*s*, 1050*s*. ^{1}H-NMR: 4.53 (*s*, CH_2OAc); 2.47–1.50 (*m*, 6 H); 2.03 (*s*, CH_3); 1.43–0.97 (*m*, 3 H); 0.87 (*s*, 3 CH_3). ^{13}C-NMR: 169.71 (*s*); 89.06 (*s*); 63.23 (*t*); 46.67 (*d*); 32.07 (*s*); 31.63 (*t*); 27.29 (*q*); 23.67 (*t*); 20.36 (*q*). MS: indistinguishable from that of **15**.

$C_{13}H_{23}NO_4$ (257.33) Calc. C 60.68 H 9.01 N 5.44% Found C 60.68 H 8.79 N 5.19%

The corresponding alcohols **19** and **20** were obtained by flash chromatography (SiO_2, hexane/AcOEt 10:1) of the crude addition product.

trans-*4-(*tert-*Butyl)-1-nitrocyclohexylmethanol* (**19**). M.p. 125–126°. IR: 3620*m*, 2965*s*, 2875*m*, 1538*s*, 1462*m*, 1447*m*, 1433*m*, 1370*m*, 1100*w*, 1060*m*, 840*w*. ^{1}H-NMR: 3.75 (*s*, CH_2O); 2.68 (*d*, $J = 12$, H_{eq}–C(2), H_{eq}–C(6)); 2.20 (br., OH); 1.90–0.93 (*m*, 7 H); 0.87 (*s*, 3 CH_3).

cis-*4-*tert-*Butyl-1-nitrocyclohexylmethanol* (**20**). M.p. 97.0–97.5°. IR: 3600*m*, 2970*s*, 2880*m*, 1538*s*, 1465*m*, 1400*w*, 1372*m*, 1344*w*, 1066*s*, 983*w*, 930*w*, 867*w*. ^{1}H-NMR: 4.00 (*d*, $J = 6$, CH_2O); 2.53–0.98 (*m*, 10 H); 0.88 (*s*, 3 CH_3).

trans- *and* cis-*4-(*tert-*Butyl)cyclohexylmethyl acetates (***17*** *and* ***18***, *respectively).* A) *From* **15**. Acetate **15** (100 mg, 0.39 mmol) was treated with Bu_3SnH as described above. After 7 h, TLC (hexane/AcOEt 10:1) indicated the disappearence of **15**. The mixture was concentrated and the residue was purified by flash chromatography (25 g SiO_2, hexane/AcOEt 40:1) yielding 78 mg (95%) of **17/18** (83:17, by ^{1}H-NMR and GLC (140°)), colourless oil, b.p. (mixture) 125–130°/15 Torr. IR: 2940*s*, 2920 sh, 2880*m*, 1727*s*, 1468*w*, 1450*w*, 1392*w*, 1365*m*, 1248*s*, 1220*s*, 1034*m*, 1025 sh. ^{1}H-NMR: 4.05 (*d*, $J = 7.5$, 0.17 CH_2OAc); 3.84 (*d*, $J = 6.0$, 0.83 CH_2OAc); 2.03 (*s*, CH_3); 1.96–0.90 (*m*, 10 H); 0.86 (*s*, 3 CH_3) ([52]: 4.03 (CH_2OAc of **18**) and 3.81 (CH_2OAc of **17**)). ^{13}C-NMR. **17**: 170.93 (*s*); 69.64 (*t*); 48.03 (*d*); 37.24 (*d*); 32.41 (*s*); 30.12 (*t*); 27.55 (*q*); 26.66 (*t*); 20.91 (*q*). **18**: 164.05, 65.42, 48.30, 32.51, 31.69, 27.71, 27.47, 22.04, 20.99, ([52]: 64.81 (C(1) of **18**); 69.54 (C(1) of **17**). MS (70 eV): 157 (2), 156 (2), 152 (9), 137 (8), 97 (42), 96 (32), 95 (40), 94 (11), 81 (56), 79 (15), 68 (12), 67 (34), 61 (14), 57 (100), 56 (46), 54 (11), 43 (73).

$C_{13}H_{24}O_2$ (212.34) Calc. C 73.54 H 11.39% Found C 73.26 H 11.67%

B) *From* **16**. An analogous denitration of 190 mg (0.74 mmol) of **16** gave 143 mg (91%) of **17/18** with the same ratio of the *trans*- to *cis*-isomer.

The mixture **17/18** was deacetylated by 2% NaOMe in MeOH giving **21/22**. A mixture of **21** and **22** (81:19 by ^{1}H-NMR) was also obtained by denitration of **19** or **20**. B.p. (mixture) 120°/15 Torr. IR (CCl_4): 3640*m*, 3350 br., 2940*s*, 2860*s*, 1478*m*, 1468*m*, 1449*m*, 1392*m*, 1364*s*, 1236*w*, 1082*w*, 1032*s*, 1021*m*, 1008*m*. ^{1}H-NMR (CCl_4): 3.48 (*d*, J=7.5, 0.19 CH_2O); 3.30 (*d*, J=6.0, 0.81 CH_2O); 2.89 (*s*, OH); 2.00–0.55 (*m*, 10 H); 0.86 (*s*, 3 CH_3); ([53]: 3.47 (*d*, J=7, CH_2O of **22**); 3.29 (*d*, J=5, CH_2O of **21**)).

The mixture **21/22** was transformed into the toluenesulfonates **23/24** [54], which were separated by analytical HPLC (*Zorbax-NH$_2$*, hexane/THF 97:3) into **23**, m.p. 95–96° ([54]: 95.5–96.0°) and **24**, m.p. 82–83° ([54]: 83–84°).

*4,7-Anhydro-2,3-dideoxy-5,6:8,9-di-*O*-isopropylidene-*D*-glycero-*D*-galacto-nononitrile* (**26**). To the degassed solution of 200 mg (0.58 mmol) of **25** [31] and 20 mg (0.12 mmol) of AIBN in 7.6 ml of benzene was added slowly (1½ h) a solution of 770 µl (2.90 mmol) of Bu_3SnH in 2.4 ml of benzene. The mixture was kept under reflux until **25** had disappeared (6 h, TLC, hexane/AcOEt 1:1)[13]. The solvent was evaporated. Flash chromatography (25 g SiO_2, hexane/Et_2O 2:1) of the residue separated only the excess of Bu_3SnH from the mixture. Prep. HPLC (*Zorbax-Sil*, hexane/Et_2O 2:1) of the sirupy crude product afforded 100 mg (58%) of **26** as the main product. The IR spectra of 3 by-products (small amounts) were not compatible with the structure of the epimer of **26**.

Data of **26**. B.p. 135–140°/10^{-4} Torr, $[\alpha]_D^{25} = -21°$ (c=1.5, $CHCl_3$). IR: 2995*s*, 2940*s*, 2870*m*, 2250*m*, 1455*m*, 1384*s*, 1374*s*, 1230*s*, 1163*s*, 1111*s*, 1070*s*, 1053 sh, 998*m*, 982*m*, 866*m*, 842*s*. ^{1}H-NMR (200 MHz): 4.82 (*dd*, J=6.1 and 3.5, H–C(6)); 4.68 (*dd*, J=6.1 and 3.8, H–C(5)); 4.48–4.33 (*m*, H–C(8)); 4.17–3.98 (*ddd*, *AB*-part of an *ABX*-system, $H_2C(9)$); 3.72–3.60 (*m*, H–C(4)); 3.56 (*dd*, J=7.3 and 3.5, H–C(7)); 2.60–2.45 (*m*, $H_2C(2)$); 2.22–1.88 (*m*, $H_2C(3)$); 1.45 (*s*, CH_3); 1.44 (*s*, CH_3); 1.37 (*s*, CH_3); 1.33 (*s*, CH_3). ^{13}C-NMR: 118.98 (*s*); 112.10 (*s*); 108.53 (*s*); 81.23 (*d*); 80.68 (*d*); 80.47 (*d*); 79.20 (*d*); 72.67 (*d*); 66.36 (*t*); 26.57 (*q*); 25.39 (*q*); 25.01 (*q*); 24.35 (*q*); 24.22 (*t*); 13.86 (*t*). MS (70 eV): 282 (22), 239 (1), 224 (4), 164 (7), 123 (11), 101 (47), 95 (16), 59 (19), 43 (100).

$C_{15}H_{23}NO_5$ (297.36) Calc. C 60.59 H 7.80 N 4.71% Found C 60.35 H 7.68 N 4.69%

*6-Acetoxy-7,10-anhydro-1,2:3,4:8,9:11,12-tetra-*O*-isopropylidene-α-*D*-erythro-*L*-manno-*D*-galacto-dodeco-1,5-pyranose* (**28**). A solution of 230 µl (0.87 mmol) of Bu_3SnH in 0.5 ml of benzene was added dropwise to a solution of 100 mg (0.17 mmol) of **27** [31] and 12 mg (0.07 mmol) of AIBN in 3.4 ml of benzene. The mixture was kept under reflux for 10 h until **27** had disappeared (TLC, $CHCl_3$/AcOEt 9:1). After evaporation of the solvent, the residue was purified by flash chromatography (15 g SiO_2, hexane/Et_2O 6:4) yielding 85 mg (89%) of **28** as a colourless foam, m.p. 174–175° (dec.), $[\alpha]_D^{25} = -45°$ (c=1.2, $CHCl_3$). IR: 2990*s*, 2935*m*, 1745*s*, 1452*w*, 1382*s*, 1370*s*, 1225*s*, 1166*s*, 1095*s*, 1070*s*, 1045 sh, 1005*s*. ^{1}H-NMR (200 MHz): 5.71 (*dd*, J=9.3 and 4.9, H–C(6)); 5.49 (*d*, J=5.1, H–C(1)); 4.89 (*dd*, J=6.4 and 3.7, H–C(8)); 4.70 (*dd*, J=6.4 and 3.8, H–C(9)); 4.61 (*dd*, J=8.0 and 2.5, H–C(3)); 4.40–4.16 (*m*, H–C(2), H–C(4), H–C(5), H–C(11)); 4.11–3.95 (*ddd*, *AB*-part of an *ABX*-system, $H_2C(12)$); 3.77 (*dd*, J=4.9 and 3.7, H–C(7)); 3.44 (*dd*, J=6.7 and 3.8, H–C(10)); 2.03 (*s*, CH_3); 1.57 (*s*, CH_3); 1.44 (*s*, CH_3), 1.40 (*s*, 2 CH_3); 1.35 (*s*, CH_3); 1.32 (*s*, CH_3); 1.30 (*s*, CH_3); 1.25 (*s*, CH_3). ^{13}C-NMR: 169.21 (*s*); 112.37 (*s*); 109.54 (*s*); 108.86 (*s*); 96.43 (*d*); 81.30 (*d*); 80.32 (*d*); 80.15 (*d*); 79.72 (*d*); 73.29 (*d*); 70.56 (*d*); 70.06 (*d*); 66.66 (*t*); 66.58 (*d*); 26.60 (*q*); 25.91 (*q*); 25.75 (*q*); 25.55 (*q*); 25.47 (*q*); 24.91 (*q*); 24.56 (*q*); 24.23 (*q*); 20.83 (*q*). MS (70 eV): 544 (<1), 529 (29), 486 (1), 471 (2), 443 (2), 293 (5), 251 (5), 235 (5), 193 (8), 151 (6), 141 (6), 129 (6), 113 (18), 101 (60), 100 (38), 85 (17), 71 (17), 59 (28), 43 (100).

$C_{26}H_{40}O_{12}$ (544.60) Calc. C 57.34 H 7.40% Found C 57.43 H 7.14%

*1-*O*-Acetyl-2,5-anhydro-3,4-*O*-isopropylidene-6-*O*-trityl-*D*-allitol* (**32**) *and* *-*D*-altritol* (**33**). A) *From* **30**. Denitration of 800 mg (1.5 mmol) of **30** [31] afforded after 6 h (TLC, toluene/AcOEt 15:1) and purification by flash chromatography (80 g SiO_2, hexane/Et_2O 4:1) 656 mg (90%) of **32/33** as a colourless oil, slowly crystallizing from a concentrated Et_2O solution, m.p. 92–100°. Anal. HPLC (*Zorbax-ODS*, MeOH/H_2O/acetonitrile 1:34:65, 50°, k'=3.8 and 4.1) indicated a ratio of 46:54. ^{1}H-NMR: 7.65–7.10 (*m*, 15 arom. H); 4.95–4.05 (*m*, $H_2C(1)$, H–C(2), H–C(3), H–C(4), H–C(5)); 3.50–3.05 (*m*, $H_2C(6)$); 2.12 (*s*, 1.6 CH_3); 1.95 (*s*, 1.4 CH_3); 1.55, 1.49 (2 *s*, CH_3); 1.35, 1.32 (2 *s*, CH_3).

---

[13]) Detection: spraying with a vanillin reagent (1 g vanillin, 400 ml MeOH and 100 ml 50% aq. H_2SO_4), followed by heating to about 200°.

B) *From* **31**. Denitration of 40 mg (0.075 mmol) of **31** [31] afforded after 8 h and flash chromatography (15 g SiO_2, hexane/Et_2O 4:1) 32 mg (87%) of **32/33** in a ratio of 48:52 (^{1}H-NMR).

*1-O-Acetyl-2,5-anhydro-3,4-O-isopropylidene-*D*-allitol* (**34**) *and -*D*-altritol* (**35**). According to [57] a solution of 290 mg (0.59 mmol) of a mixture of **32/33** in 70 ml of 1% MeOH in CH_2Cl_2 was treated with 12 mg of anh. $FeCl_3$. After 2 h at r.t. 0.5 g of $Na_2CO_3 \cdot 10\ H_2O$ was added, the mixture filtered and the solvent evaporated. Flash chromatography (45 g SiO_2, hexane/AcOEt 6:4) of the residue gave 48 mg (34%) of **34** and 65 mg (44%) of **35** as colourless oils.

Data of **34**. $[\alpha]_D^{25} = -6.2°$ ($c = 1.0$, $CHCl_3$). IR: 3605*w*, 3030 sh, 2990*m*, 2935*m*, 2880 sh, 1742*s*, 1453*w*, 1383*s*, 1372*s*, 1220*s*, 1157*m*, 1116*m*, 1078*s*, 1041*s*, 862*m*. ^{1}H-NMR: 4.70 (*dd*, $J = 7$ and 4, H–C(1)); 4.52 (*dd*, $J = 7$ and 3, H–C(1)); 4.35–4.00 (*m*, 4 H); 3.80 (*dd*, $J = 12$ and 3, H–C(6)); 3.60 (*dd*, $J = 12$ and 4, H–C(6)); 2.43 (br., OH); 2.10 (*s*, CH_3); 1.54 (*s*, CH_3); 1.34 (*s*, CH_3).

$C_{11}H_{18}O_6$ (246.26) Calc. C 53.65 H 7.37% Found C 53.60 H 7.26%

Data of **35**. $[\alpha]_D^{25} = +10.8°$ ($c = 1.1$, $CHCl_3$). IR: 3630*w*, 3030 sh, 2998*m*, 2942*m*, 2880 sh, 1740*s*, 1456*w*, 1386*s*, 1375*s*, 1230*s*, 1165*m*, 1122*s*, 1078*s*, 1040*s*, 875*m*. ^{1}H-NMR: 4.90–4.00 (*m*, 6 H); 3.67 (*t*, $J = 4.5$, $H_2C(6)$); 2.22 (br., OH); 2.10 (*s*, CH_3); 1.48 (*s*, CH_3); 1.33 (*s*, CH_3).

$C_{11}H_{18}O_6$ (246.26) Calc. C 53.65 H 7.37% Found C 53.84 H 7.44%

*1,6-Di-O-acetyl-2,5-anhydro-3,4-O-isopropylidene-*D*-allitol* (**36**). Acetylation of 48 mg (0.20 mmol) of **34** gave after chromatography (10 g SiO_2, hexane/Et_2O 2:1) 42 mg (75%) of **36**, b.p. 100°/10^{-4} Torr. IR: 3025 sh, 2985*w*, 2925*w*, 2895 sh, 1742*s*, 1450*w*, 1381*m*, 1370*m*, 1220*s*, 1155*m*, 1080*s*, 1040*s*, 862*m*. ^{1}H-NMR: 4.55 (br. *s*, H–C(3) and H–C(4)); 4.45–3.95 (*m*, $H_2C(1)$, H–C(2), H–C(5) and $H_2C(6)$); 2.10 (*s*, 2 CH_3); 1.55 (*s*, CH_3); 1.35 (*s*, CH_3). ^{13}C-NMR: 170.34 (*s*); 114.43 (*s*); 82.27 (*d*); 81.90 (*d*); 64.25 (*t*); 27.37 (*q*); 25.48 (*q*); 20.77 (*q*). MS (70 eV): 273 (24), 153 (25), 111 (12), 69 (15), 68 (15), 59 (11), 43 (100).

$C_{13}H_{20}O_7$ (288.30) Calc. C 54.16 H 6.99% Found C 53.89 H 7.16%

*1,6-Di-O-Acetyl-2,5-anhydro-3,4-O-isopropylidene-*D*-altritol* (**37**) [56]. Acetylation of 65 mg (0.26 mmol) of **35** gave after chromatography (15 g SiO_2, hexane/Et_2O 2:1) 72 mg (96%) **37**, b.p. 115–120°/10^{-4} Torr. $[\alpha]_D^{20} = +1.6°$ ($c = 1.2$, $CHCl_3$; [56]: +3° ($CHCl_3$)). ^{1}H-NMR: same as in [56].

REFERENCES

[1] *B. Aebischer, R. Hollenstein & A. Vasella,* Helv. Chim. Acta *66*, 1748 (1983).
[2] *N. Kornblum, S.C. Carlson & R.G. Smith,* J. Am. Chem. Soc. *101*, 647 (1979).
[3] *A.L. Krasuska, H. Piotrowska & T. Urbanski,* Tetrahedron Lett. *1979*, 1243.
[4] *N. Ono, R. Tamura & A. Kaji,* J. Am. Chem. Soc. *102*, 2581 (1980).
[5] *N. Ono, H. Miyake, R. Tamura & A. Kaji,* Tetrahedron Lett. *1981*, 1705.
[6] *D.D. Tanner, E.V. Blackburn & G.E. Diaz,* J. Am. Chem. Soc. *103*, 1557 (1981).
[7] *N. Ono, H. Miyake & A. Kaji,* J. Chem. Soc., Chem. Commun. *1982*, 33.
[8] *D.H.R. Barton & S.W. McCombie,* J. Chem. Soc., Perkin Trans. 1 *1975*, 1574.
[9] *D.H.R. Barton & R. Subramanian,* J. Chem. Soc., Chem. Commun. *1976*, 867.
[10] *D.H.R. Barton & R. Subramanian,* J. Chem. Soc., Perkin Trans. 1 *1977*, 1718.
[11] *C. Copeland & R.V. Stick,* Aust. J. Chem. *30*, 1269 (1977).
[12] *J.J. Patroni & R.V. Stick,* Aust. J. Chem. *31*, 445 (1978).
[13] *J.J. Patroni & R.V. Stick,* Aust. J. Chem. *32*, 411 (1979).
[14] *T.S. Fuller & R.V. Stick,* Aust. J. Chem. *33*, 2509 (1980).
[15] *D.H.R. Barton, W.B. Motherwell & A. Stange,* Synthesis *1981*, 743.
[16] *D.H.R. Barton, W. Hartwig, R.S.H. Motherwell, W.B. Motherwell & A. Stange,* Tetrahedron Lett. *1982*, 2019.
[17] *H. Redlich, H.-J. Neumann & H. Paulsen,* Chem. Ber. *110*, 2911 (1977).
[18] *A.J. Dobbs, B.C. Gilbert & R.O.C. Norman,* J. Chem. Soc. (A) *1971*, 124.

[19] *A. L. J. Beckwith & P. K. Tindal,* Aust. J. Chem. *24*, 2099 (1971).
[20] *L. Corvaja, G. Giacometti & M. Brustolon,* Z. Phys. Chem. N.F. *82*, 272 (1972).
[21] *V. Malatesta & J. C. Scaiano,* J. Org. Chem. *47*, 1455 (1982).
[22] *O. Eisenstein, N. T. Anh, Y. Jean, A. Devaquet, J. Cantacuzène & L. Salem,* Tetrahedron *30*, 1717 (1974).
[23] *V. Malatesta, R. D. McKelvey, B. W. Babcock & K. U. Ingold,* J. Org. Chem. *44*, 1872 (1979).
[24] *A. R. Gregory & V. Malatesta,* J. Org. Chem. *45*, 122 (1980).
[25] *K. Hayday & R. D. McKelvey,* J. Org. Chem. *41*, 2222 (1976).
[26] *V. Malatesta & K. U. Ingold,* J. Am. Chem. Soc. *103*, 609 (1981).
[27] *A. L. J. Beckwith & C. J. Easton,* J. Am. Chem. Soc. *103*, 615 (1981).
[28] *B. C. Gilbert, D. M. King & C. B. Thomas,* J. Chem. Soc., Perkin Trans. 2 *1983*, 675.
[29] *F. Tureček & V. Hanuš,* Tetrahedron *39*, 1499 (1983).
[30] *C. M. Rynard, C. Thankachan & T. T. Tidwell,* J. Am. Chem. Soc. *103*, 1196 (1979).
[31] *B. Aebischer, J. H. Bieri, R. Prewo & A. Vasella,* Helv. Chim. Acta *65*, 2251 (1982).
[32] *B. Aebischer & A. Vasella,* Helv. Chim. Acta *66*, 789 (1983).
[33] *B. Aebischer, A. Vasella & H. P. Weber,* Helv. Chim. Acta *65*, 621 (1982).
[34] *S. Hanessian & A. G. Pernet,* Adv. Carbohydr. Chem. Biochem. *33*, 111 (1976).
[35] *T. Sato & R. Noyori,* Bull. Chem. Soc. Jpn. *53*, 1195 (1980).
[36] *G. Rémy, L. Cottier & G. Descotes,* Can. J. Chem. *58*, 2660 (1980).
[37] *J. R. Pougny, M. A. M. Nassr & P. Sinaÿ,* J. Chem. Soc., Chem. Commun. *1981*, 375.
[38] *R. D. Dawe & B. Fraser-Reid,* J. Chem. Soc., Chem. Commun. *1981*, 1180.
[39] *L. A. Reed III, Y. Ito, S. Masamune & K. B. Sharpless,* J. Am. Chem. Soc. *104*, 6468 (1982).
[40] *R. Tschesche & W. Widera,* Justus Liebigs Ann. Chem. *1982*, 902.
[41] *T. L. Cupps, D. S. Wise & L. B. Townsend,* J. Org. Chem. *47*, 5115 (1982).
[42] *A. P. Kozikowski & K. L. Sorgi,* Tetrahedron Lett. *1982*, 2281.
[43] *F. Germain, Y. Chapleur & B. Castro,* Synthesis *1983*, 119.
[44] *A. P. Kozikowski, K. L. Sorgi, B. C. Wang & Z. Xu,* Tetrahedron Lett. *1983*, 1563.
[45] *S. Czernecki & V. Dechavanne,* Can. J. Chem. *61*, 533 (1983).
[46] *S. Yougai & T. Miwa,* J. Chem. Soc., Chem. Commun. *1983*, 68.
[47] *N. Katagiri, K. Takashima, T. Kato, S. Sato & C. Tamura,* J. Chem. Soc., Perkin Trans. 1 *1983*, 201.
[48] *R. R. Schmidt & M. Hoffmann,* Angew. Chem. *95*, 417 (1983).
[49] *J. C. Sowden, C. H. Bowers & K. O. Lloyd,* J. Org. Chem. *29*, 130 (1964).
[50] *A. C. Huitric & W. F. Trager,* J. Org. Chem. *27*, 1926 (1962).
[51] *E. J. Corey & M. Estreicher,* Tetrahedron Lett. *1980*, 117.
[52] *G. W. Buchanan, J. B. Stothers & S. Wu,* Can. J. Chem. *47*, 3113 (1969).
[53] *H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan & J. F. Simeone,* J. Am. Chem. Soc. *92*, 2800 (1970).
[54] *N. Mori,* Bull. Chem. Soc. Jpn. *34*, 1567 (1961).
[55] *H. Ohrui, G. H. Jones, H. G. Moffatt, M. L. Maddox, A. T. Christensen & S. K. Byram,* J. Am. Chem. Soc. *97*, 4602 (1975).
[56] *K. Bischofberger, St. J. Eitelman & A. Jordaan,* J. Chem. Soc., Perkin Trans. 1 *1977*, 745.
[57] *A. Vasella,* Helv. Chim. Acta *60*, 426 (1977).
[58] *B. C. Gilbert, M. Trenwith & A. J. Dobbs,* J. Chem. Soc., Perkin Trans. 2 *1974*, 1772.
[59] *D. H. R. Barton, W. Hartwig & W. B. Motherwell,* J. Chem. Soc., Chem. Commun. *1982*, 447.
[60] *C. Chatgilialoglu, K. U. Ingold & J. C. Scaiano,* J. Am. Chem. Soc. *103*, 7739 (1981).
[61] *B. Aebischer, H. Hanssen, A. Vasella & W. Schweizer,* J. Chem. Soc., Perkin Trans. 1 *1982*, 2139.
[62] *H. G. Kuivila,* Synthesis *1970*, 499.
[63] *W. C. Still, M. Kahn & A. Mitra,* J. Org. Chem. *43*, 2923 (1978).