Synthesis of an L-Fucose-Derived Cyclic Nitrone and its Conversion to α-L-Fucosidase Inhibitors[1])

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The L-*fuco*-nitrone **1** has been synthesized from allyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**4**) in 11 steps and an overall yield of 18%. The key step is the intramolecular alkylation of an intermediary 1,1-bis(hydroxylamine) derived from the tosyloxy oximes (*E*/*Z*)-**2**. The nitrone **1** has been transformed into the diamine **30**, the indolizidines **39** and **40**, the indolizidinones **34** and **35**, and the imidazole **44**, all inhibiting bovine epididymis α-L-fucosidase with IC_{50} values between 105 nM and 240 μM.

Introduction. – In spite of the importance of nitrones in organic synthesis [1–4], only a few carbohydrate-derived cyclic nitrones are known. Such nitrones have been prepared as intermediates in the synthesis of pyrrolizidines [5][6], indolizidines [7], pyrrolidinose *C*-disaccharides [8], and nucleoside analogues [9][10]; they have also been used to establish the configuration of esperamicins [11]. Their restricted use is surprising in view of the versatile character of nitrones and of their potential for the preparation of carbohydrate-derived heterocycles. Presumably, the restricted application is related to the difficulties of preparing such cyclic nitrones in a regioselective manner [7][12].

We have developed a regioselective synthesis of the protected L-fucose-derived nitrone **1** in view of the synthesis of α-L-fucosidase inhibitors. Although there are many inhibitors of α-L-fucosidases with micromolar or better inhibition constants [13–28], relatively little is known about the details of their mechanism of action.

White et al. have shown that human liver α-L-fucosidase is a retaining glycosidase [29]. Most likely, two carboxylic groups are involved in catalysis [30] of which one is protonated at the pH optimum and the other deprotonated, similar to what is known for other glycosidases [31]. There is evidence for a protein-bound intermediate [32]. Among the α-L-fucosidases from human liver, rat liver, dog lysosomes, *Caenorhabditis elegans*, and *Dictyostelium discoideum*, there is a high amino-acid-sequence homology, characterizing them as members of family 29[2]) according to *Henrissat*'s classification of glycosidases [33–35]. A crystal structure of an α-L-fucosidase has yet to be reported.

We planned to prepare **1** by an intramolecular nucleophilic substitution of a sulfonyloxy oxime (*Scheme 1*). This transformation is precedented by the synthesis of a

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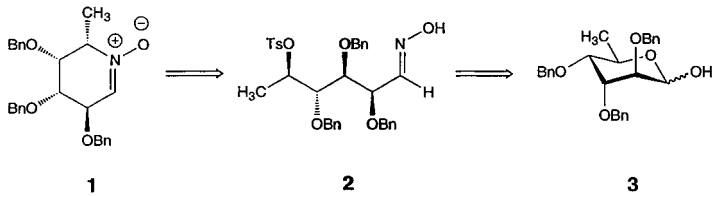
[1]) Part of this work is taken from the Diploma Thesis of *A.P.*, which was presented at the 'Royal Society of Chemistry, Carbohydrate Group Spring Meeting', Birmingham, 30.3.–1.4.1998.

[2]) Compare with recent information on the internet at the address http://www.expasy.ch/cgi-bin/lists?glycosid.txt

steroidal five-membered nitrone [36] and of a carbohydrate-derived dihydropyrrole-*N*-oxide [9]. We planned to convert **1** to three representative heterocycles, piperidines, indolizidines, and fused imidazoles, each incorporating a major structural motif typical for glycosidase inhibitors. The oxime **2**, required for the synthesis of **1**, should be readily accessible from the 6-deoxyaltropyranose **3**, and ultimately from D-glucose.

Scheme 1



1 **2** **3**

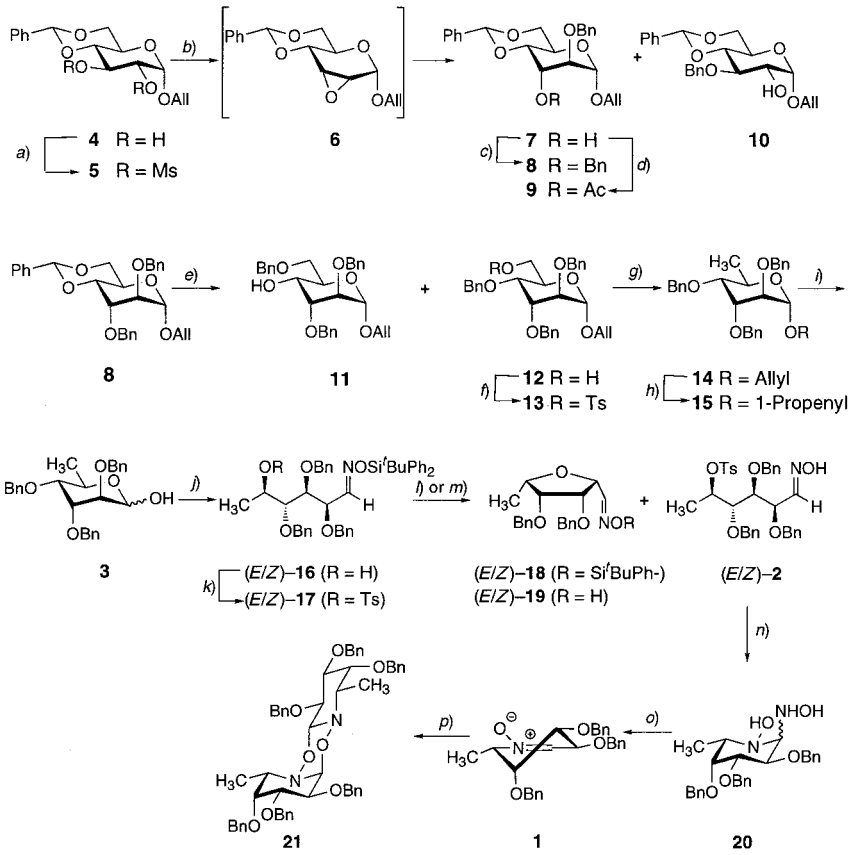
Synthesis of the Nitrone 1. – To prepare the 6-deoxyaltropyranose **3**, we intended to use the established procedure for the synthesis of altrosides from glucose [37], replacing the intermediary methyl by allyl glycosides (*Scheme 2*).

The crystalline dimesylate **5** was obtained in 80% yield from allyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**4**) [38] and treated with excess NaOBn for 15 h at 95°. This gave the monobenzylated altroside **7** (82%), obviating the isolation of the epoxide **6**. Minor amounts of **10** were formed by a well-precedented diequatorial epoxide opening [37]. Yields were comparable to those reported for the two-step procedure [37]. Benzylation of **7** afforded 94% of the dibenzyl ether **8**. Reductive opening of the 1,3-dioxane ring of **8** led mostly ($AlCl_3$/$LiAlH_4$) or exclusively ($AlCl_3$/$LiAlH_4$/BuLi) to the undesired 6-*O*-benzylated **11** in yields of up to 80%. This regioselectivity is in agreement with the dominating formation of 6-*O*-benzyl ethers upon treatment of other altropyranosides with $^{i}Bu_2AlH$ [39]. The regioselectivity of the reductive acetal opening is rationalised by the preferred formation of the benzylic C(6)-oxycarbenium cation *via* a complex of the *Lewis* acid with *O*C(4) and the *cis*-oriented *O*C(3) rather than with *O*C(6). Treating **8** with the non-chelating Me_3SiCl in the presence of $LiAlH_4$ at 23° led indeed to a mixture of **11** and the 4-*O*-benzyl ether **12** (**12**/**11** 2:1); replacing Me_3SiCl by Me_3SiBr and conducting the reaction in boiling Et_2O improved the **12**/**11** ratio to 7:1. Column chromatography yielded 75% of the desired primary alcohol **12**.

Tosylation of **12** to **13**, followed by deoxygenation with $LiAlH_4$, yielded the 6-deoxyaltropyranoside **14**. The synthesis of **14** from **8** was also carried out without purification of the intermediates, resulting in an overall yield of 65%.

The allyl glycoside **14** was isomerized to the enol ether **15** using {Ir(cod)(PPh_2-Me)$_2$}PF_6 (cod = cycloocta-1,5-diene) [40]. This procedure worked well on a scale of up to 2 g of **14**, but failed on a larger scale, possibly due to sulfur-containing impurities in the starting material. Only starting material was isolated. The isomerization of **14** to **15** with KO^{t}Bu in DMSO at 100° [41], however, proceeded well on a scale of up to 20 g, and yielded almost exclusively the propenyl ether (*Z*)-**15**. It was hydrolyzed with HgO/$HgCl_2$ in aqueous acetone, resulting in overall yields of 82–85% of **3** from **14**.

Scheme 2



a) MsCl (2 equiv.), pyridine; 80%. *b*) NaOBn (12 equiv.), BnOH; 82% of **7**. *c*) BnBr (1.5 equiv.), NaH (1.1 equiv.), BnBr, Bu_4NI; 94%. *d*) Ac_2O, cat. 4-(dimethylamino)pyridine (DMAP), pyridine; 75%. *e*) TMSBr (5 equiv.), $LiAlH_4$ (2 equiv.), Et_2O; 75% of **12**, 11% of **11**. *f*) TsCl (2 equiv.), pyridine; 93%. *g*) $LiAlH_4$ (2 equiv.), Et_2O; 92%. *h*) KO^{t}Bu (4 equiv.), DMSO 100° (→(*Z*)-**15**). *i*) $HgCl_2$/HgO acetone/H_2O; 83%. *j*) $NH_2OSiPh_2{}^t$Bu, cat. pyridinium *p*-toluenesulfonate (PPTA); 83% of (*E*)-**16**; 13% of (*Z*)-**16**. *k*) TsCl (1.2 equiv.), pyridine; 80% of (*E*)-**17**; 13% of (*Z*)-**17**. *l*) Neat at room temperature, 4 d; 75% of (*E*/*Z*)-**17** and 16% of (*E*/*Z*)-**18**. *m*) $Et_3N \cdot 3\,HF$, THF. *n*) $NH_2OH \cdot HCl$ (8 equiv.), Et_3N (8 equiv.). *o*) Column chromatography (silica gel); 60–66% of **1** and 20–24% (*E*/*Z*)-**19**. *p*) $FeCl_3$, H_2O, CH_2Cl_2; 44%.

Treatment of **3** with *O*-[(*tert*-butyl)diphenylsilyl]hydroxylamine[3]) led to the diastereoisomeric silyl ethers (*E*)-**16**/(*Z*)-**16** which were separated by chromatography, yielding 83% of (*E*)-**16** and 13% of (*Z*)-**16**.

Tosylation of the hydroxy oxime (*E*)-**16** with 1.2 equiv. of TsCl yielded 80% of the expected (*E*)-**17**, besides 13% of (*Z*)-**17**. Similarly, tosylation of (*Z*)-**16** led to a mixture, chromatography affording 69% of (*E*)-**17** and 21% of (*Z*)-**17**/(*E*)-**17** 4:1. Isomerization of oximes by reversible addition of chloride to the C=N bond is known [43].

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[3]) Freshly prepared according to [42]. Under otherwise identical conditions, the commercially available $NH_2OSi{}^t BuMe_2$ led to desilylated oximes.

Tosylation of (*E*)-**16** with 2 equiv. of TsCl led to a mixture of (*E*/*Z*)-**17** (64%) and the tetrahydrofurans (*E*/*Z*)-**18** (30%). The tetrahydrofurans **18** were also formed when the oxime sulfonates (*E*/*Z*)-**17** were kept at room temperature for a few days. Neighbouring group participation of BnO groups is well-known and has been used for the synthesis of *C*-furanosides [44].

Desilylation of the oxime silyl ethers (*E*)-**17** or (*Z*)-**17** proceeded with retention of configuration and led to a mixture of the tosyloxy oxime **2** and the tetrahydrofuran **19** as pure (*E*)- or (*Z*) diastereoisomers. $Et_3N \cdot 3\,HF$ (0°, THF) was most satisfactory among the reagents tested (Bu_4NF, HF · pyridine, KF, [18]-crown-6, AcOH or $Et_3N \cdot 3\,HF$), yielding 80% of (*E*)-**2** and 13% of (*E*)-**19** from (*E*)-**17**.

The crude desilylation product (*E*)-**2** was treated with excess $NH_2OH \cdot HCl$ and Et_3N in THF followed by aqueous workup. This led to the *bona fide* bis(hydroxylamines) **20**[4]) that were converted to the nitrone **1** (60–66% from **17**) by chromtography on silica gel[5]). The major by-product was the tetrahydrofuran (*E*)-**19** (20–24% from **17**). Similarly, treatment of (*Z*)-**2** with NH_2OH gave the nitrone **1** in about the same yields. Hydroxylamine is required for the transformation of **2**; heating of (*E*)- and (*Z*)-**2** in THF alone led to recovered starting material, besides small amounts of (*E*/*Z*)-**19**. Hydroxylamine did not, however, lead to a transformation of the silylated oximes (*E*/*Z*)-**17**; heating **17** in THF in the presence of $NH_2OH \cdot HCl$ and Et_3N again resulted in recovered starting material. These observations are in agreement with a nucleophilic addition of NH_2OH to the C=N bond of the oximes, followed by intramolecular nucleophilic substitution of the TsO group by a C(1) hydroxylamino group. In keeping with this mechanism, treatment of (*E*)-**2** with *N*-methylhydroxylamine in THF under reflux also led to the nitrone **1** (36%).

At room temperature, the nitrone **1** is slowly transformed into a complex mixture of polar and apolar products that were not investigated. At −78°, however, **1** proved stable for several weeks. Treatment with acid ($FeCl_3$ in aq. CH_2Cl_2; or AcOH in AcOEt) transformed **1** into the unsymmetric dimer **21**. Acid-catalyzed dimerization of nitrones in aprotic solvents is well precedented [46][47].

This synthesis of **1** required eleven steps from **5** and proceeded in an overall yield of *ca.* 18% on a scale of 10 to 30 g for the conversion of **5** to (*E*/*Z*)-**16**. Considering the limited stability of the tosylates (*E*/*Z*)-**17** and of the nitrone **1**, the last three steps were only performed on a 1-g scale.

A sample of **7** was acetylated. $J(2,3) = 3.2$ Hz, and $J(3,4) = 2.1$ Hz (δ(H–C(3)) at 5.31 ppm) of the resulting acetate **9** confirm the *altro*-configuration. The H–C(3) *t* of **10** appears at 3.85 ppm with a large coupling constant ($J \approx 9.3$ Hz), evidencing the *gluco*-configuration. H–C(2) gives rise to a complex signal at 3.73 ppm, which changes upon the addition of D_2O. The OH group of **12** gives rise to a *t* ($J \approx 5.6$ Hz) at 1.95 ppm and an IR band at 3512 cm^{-1} and that of **11** to a *d* ($J = 8.7$ Hz) at 2.50 ppm. H–C(4) of **11** resonates as a *dt* ($J =$ 3.1, 8.7 Hz) at 3.79 ppm. Tosylation of **12** to **13** resulted in a downfield shift of the H–C(6) signals, resonating at 4.30 ppm. The Me group of **14** resonates as a *d* ($J = 6.5$) at 1.29 ppm, and as a *q* at 17.84 ppm. The hemiacetal **3** (in $CDCl_3$) is a β-D/α-D 3 : 2 mixture. The ^{1}H-NMR signals of the minor component were assigned to the α-D-anomer on the basis of a comparison with the spectrum of **14**, the chemical shift of H–C(5) being revealing (4.28 ppm for **14**, 4.24 ppm for α-D-**3** and 4.01 ppm for β-D-**3**). H–C(1) of both anomers of **3** resonate at *ca.*

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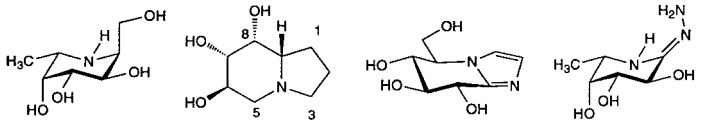
4) A ^{1}H-NMR spectrum ($CDCl_3$) of the crude product showed no sign of **1**, but broad signals at 5.2–5.4 and 5.6–5.7 ppm.

5) For a similar conversion of geminal bis(hydroxylamines) to nitrones, see [45].

5.0 ppm. The OH group gives rise to a large *d* at 4.98 ppm ($J = 11.4$) for α-D- and at 3.44 ppm ($J = 12.2$) for β-D-**3**, in keeping with the expected stronger intramolecular C(1)OH–OH(3) H-bond of α-D-**3**. By comparison, HO–C(3) of **7** resonates at 3.01 ppm with $J = 7.6$ Hz. (*E*)-**16** is characterized by a H–C(1) *d* ($J = 8.1$ Hz) at 7.81 ppm, while H–C(1) of (*Z*)-**16**, hidden by the Ar*H* signals (7.18–7.42 ppm), resonantes at higher field [48][49]. The C(1) *d* of (*Z*)-**16** (157.64 ppm) is shifted downfield relative to the corresponding signal of (*E*)-**16** (154.81 ppm). The structure of the tosylated oximes (*E*/*Z*)-**17** is evidenced by a Me *s* at 2.36 ppm for the (*E*)- and at 2.41 ppm for the (*Z*)-oxime. C(1) resonates as a *d* at 154.96 ppm for (*E*)-**17** and at 158.47 ppm for (*Z*)-**17**. The nitrone **1** is characterized by λ_{max} 247 nm (ε 7940 M^{-1} cm^{-1}) and a strong IR band at 1588 cm^{-1}. C(1) resonates as a *d* at 133.68 ppm and H–C(1) as a *dd* at 7.05 ppm ($J = 1.9$, 2.5 Hz), the smaller coupling corresponding to a long range interaction with H–C(5). The coupling constants (see below, *Table 2*) evidence a $^3H_4$-conformation. The dimer **21** has a FAB-MS peak at *m*/*z* 863. The C_1 symmetry was evidenced by the signals for H–C(1) at 5.85 ppm ($J = 3.3$ Hz) and for H–C(1′) at 4.42 ppm ($J = 8.3$ Hz).

Synthesis of α-L-Fucosidase Inhibitors. – The versatile character of cyclic carbohydrate-derived nitrones as advanced intermediates for the synthesis of glycosidase inhibitors was illustrated by a nucleophilic addition, a cycloaddition to an acrylate, and a transformation into a thiolactam. Thus, **1** was converted to the piperidine **30**, the indolizidines **39** and **40**, and the thiolactam **41** that was further transformed into the imidazole **44**.

A range of piperidines are known α-L-fucosidase-inhibitors [50]. Deoxyfuconojirimycin and the hydroxymethylene analogue **22** are among the strongest inhibitors of bovine epididymis α-L-fucosidase [14][15]. We prepared the piperidine methanamine bis(hydrochloride) **30** to further investigate the influence of the substituent at the anomeric center.



22 **23** **24** **25**

Similarly to piperidines, many indolizidines inhibit α-glycosidases efficiently [50]. We converted nitrone **1** to the indolizidine **39** and **40**. Although there are indolizidines possessing a OH group at the five-membered ring in the same position as **39** and **40**, they have not been tested as glycosidase inhibitors [7][51][52]. To the best of our knowledge, **23** is the only indolizidine that has so far been tested against α-L-fucosidases [14].

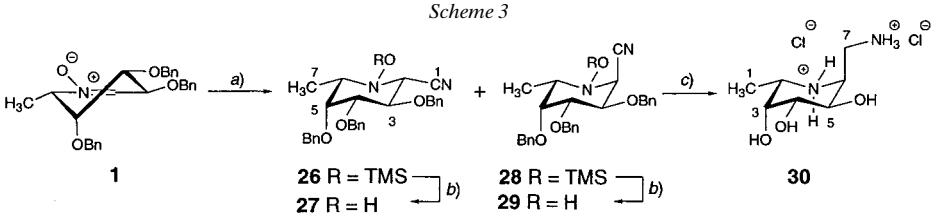
Tetrahydroimidazopyridines, such as **24**, are potent inhibitors of β-glycosidases [53][54][55]. To the best of our knowledge, only one imidazole has been shown to inhibit an α-glycosidase, *viz*. **24**, that inhibits brewers yeast α-glucosidase ($K_i = 59$ μM) [53]. The inhibitory power of compounds with an sp^2-hybridized anomeric center against α-glycosidases has been related to their basicity; while neutral lactone-type inhibitors are selective for β-glycosidases, their basic analogues are less selective [56][57]. This rule appears to be valid also for α-L-fucosidases. The L-fucono-1,5-lactone and -lactam are weak inhibitors of bovine epididymis α-L-fucosidase ($K_i = 8.5$ and 340 μM, resp.) [58], whereas the corresponding amidrazone **25** strongly inhibits recombinant human lysosomal α-L-fucosidase ($K_i = 820$ nM) [17].

The $AlMe_2Cl$-promoted addition of trimethylsilyl cyanide (TMSCN) [59] to **1** gave the diastereoisomeric *N*-[(silyloxy)amino] nitriles **26**/**28** and the desilylated **27** and **29**

(*Scheme 3*). Addition of TMSCN followed by desilylation (TsOH, MeOH) led predominantly to the axial nitrile **29** (86%), besides 5% of the equatorial **27**.

The reduction and hydrogenolysis of **29** with H_2 over Pd/C in MeOH/HCl yielded 75% of the bis(hydrochloride) **30**. Exploratory reductions of **29** with H_2 over Pd/C in MeOH/AcOH or in MeOH/HCO_2H led to mixtures, due to incomplete cleavage of the BnO groups. The bis(hydrochloride) **30** was not stable to storage at 23°, rapidly turning yellow. Addition of 0.01N HCl in Et_2O to a methanolic solution of the crude reduction product precipitated **30** as a slightly yellow solid that contained only traces of impurities (^{1}H-NMR spectroscopy) and proved stable at 4°.

Scheme 3



a) TMSCN (2 equiv.), cat. $AlMe_2Cl$, CH_2Cl_2. *b*) 3% TsOH · H_2O, MeOH; 86% of **29**, 5% of **27**. *c*) 10% Pd/C, H_2, HCl, MeOH; 75% of **30**.

For the synthesis of the indolizidines **39** and **40** (*Scheme 4*), we treated **1** with methyl acrylate, following a known method [7]. As expected, the 1,3-dipolar cycloaddition proceeded regioselectively [60][61] and led to a 3:2 mixture of the diasteroisomeric isoxazolidines **31** (55%) and **32** (34%) by exclusively axial C,C bond formation. As often observed [4], the major product **31** derives from an *exo*-addition.

Reductive cleavage of the N–O bond (Zn/AcOH) converted the isoxazolidine carboxylates **31** and **32** into the corresponding hydroxy lactams **33** and **34**, respectively (78%). The major diastereoisomer **33** was converted into the minor **34** by a *Mitsunobu* reaction with PhCOOH followed by transesterification in MeOH, confirming that **33**/**34** and **31**/**32** differ only by the configuration at C(2). The lactam **34** was debenzylated by $Pd(OH)_2$/C-catalyzed hydrogenolysis in MeOH, yielding 84% of **36**, while debenzylation of the isomeric **33** to **35** (87%) only proceeded in MeOH/AcOH.

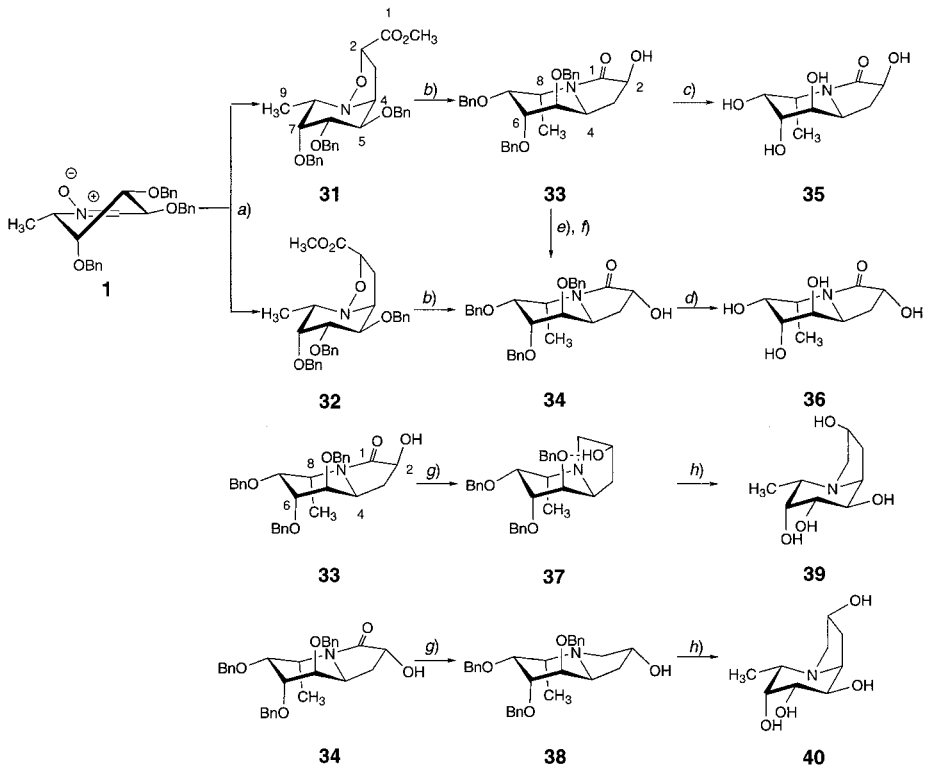
The lactams **33** and **34** were reduced with BH_3 in THF to the indolizidines **37** (74%) and **38** (85%), respectively. Hydrogenolytic debenzylation in MeOH/HCl afforded the indolizidines **39** and **40** as their hydrochlorides. Purification by ion-exchange chromatography gave the free amines **39** and **40** in 78 and 75% yield, respectively.

Tetrahydroimidazopyridines of the type **24** [62][53] have been most efficiently prepared by condensation of thiolactams with aminoacetaldehyde dimethyl acetal followed by acid-promoted cyclization. Thiolactams are available from nitrones by fragmentation of their cycloadducts[6]) to thiocarbonyl compounds, 1,1′-carbonothioyl-bis[1*H*-imidazole] and 1,1′-carbonothioylbis[1*H*-1,2,4-triazole] being particularly well suited for this purpose [64].

Treatment of the nitrone **1** with 1,1′-carbonothioylbis[1*H*-1,2,4-triazole] in pyridine/toluene 1:1 at ambient temperature yielded 84% of the thiolactam **41**, while the less

[6]) For the isolation of cycloadducts that cannot undergo the fragmentation, see [63].

Scheme 4



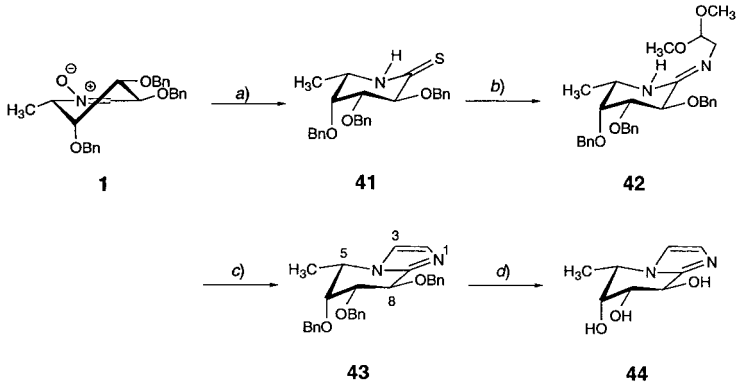
a) Methyl acrylate (10 equiv.), toluene; 55% of **31**, 34% of **32**. *b*) Zn (8 equiv.), AcOH; 78%. *c*) 10% $Pd(OH)_2$/C, H_2, MeOH, AcOH; 84%. *d*) 10% $Pd(OH)_2$/C, H_2, MeOH; 87%. *e*) Ph_3P (1.5 equiv.), diethyl diazenedicarboxylate (DEAD) (1.5 equiv.), PhCOOH (1.5 equiv.). *f*) 1% soln. NaOMe in MeOH; 71% (two steps). *g*) $BF_3 \cdot THF$ (2.7 equiv.), THF; 74% (**33** → **37**), 85% (**34** → **38**). *h*) 10% $Pd(OH)_2$, MeOH, 1M HCl in Et_2O; 78% (**37** → **39**), 75% (**38** → **40**).

reactive 1,1′-carbonothioylbis[1*H*-imidazole] led to only low yields of **41** (*Scheme 5*). It was not possible to detect any intermediates by TLC, suggesting that fragmentation of the cycloadducts is faster than their formation.

The thiolactam **41** reacted with aminoacetaldehyde dimethyl acetal in the presence of $Hg(OAc)_2$ to the amidine **42** which was cyclized by exposure to $TsOH \cdot H_2O$ in toluene/H_2O. The imidazole **43** was isolated in a yield of 75% and debenzylated to yield 76% of **44**.

The structure of **29** is evidenced by FAB-MS signals at *m*/*z* 459 ($[M+H]^+$) and at *m*/*z* 432 ($[M+H-CN]^+$) and by a CN *s* at 115.48 ppm. The axial orientation of the CN group is evidenced by $J = 5.0$ Hz of the H–C(2) *d* at 4.36 ppm. HO–N exchanges with D_2O and resonates as a *s* at 5.30 ppm. The equatorial isomer **27** is characterized by $J = 10.0$ Hz for the *d* at 3.50 ppm of the H–C(2), a *s* at 5.73 ppm for HO–N and a *s* at 117.78 ppm for the CN group. The bis(hydrochloride) **30** is characterized by a C(7) *t* at 38.83 ppm and by two *H*–C(7) *dd* at 3.40 ($J = 4.4$, 14.0 Hz) and 3.71 ppm ($J = 8.4$, 14.0 Hz). The ^{1}H-NMR spectrum ((D$_6$)DMSO) shows 3*s* for NH^+ at 9.56 (1 H), 9.23 (1 H), and 8.35 ppm (3 H). The ^{1}H-NMR spectrum of **31** exhibits broad signals. The MeOCO group is evidenced by ^{13}C-NMR signals at 51.99 (*q*) and 171.35 ppm (*s*), and by an IR band

Scheme 5



a) 1,1′-Carbonothioyl[1*H*-1,2,4-triazole] (1.2 equiv.), pyridine/toluene 1:1; 84%. *b*) Aminoacetaldehyde dimethyl acetal (5 equiv.), $Hg(OAc)_2$ (1.5 equiv.), THF. *c*) $TsOH \cdot H_2O$ (0.5 equiv.), toluene, H_2O, 75% (2 steps). *d*) 10% $Pd(OH)_2$/C, AcOEt, MeOH, H_2O, 76%.

at 1742 cm^{-1}. The spectra of **32** are better resolved, particularly at higher temperature. H_a–C(3) of **32** ((D_5)PhCl, 75°) resonates at 2.30 (*ddd*, $J = 6.2$, 8.7, 12.8 Hz), H_b–C(3) at 2.52 ppm (*td*, $J \approx 8.7$, 12.5 Hz), and H–C(2) at 4.31 ppm (*t*, $J \approx 8.7$ Hz).

The lactams **33** and **34**, and hence the isoxazolidines **31** and **32**, differ only by the configuration at C(2), as shown by the conversion of **33** to **34**. The 4,5-*cis*-configuration is deduced from $J(4,5) \approx 5.5$ Hz for **31**, **32**, **39**, and **40** and $J(4,5) \approx 2$ Hz for **33**–**37**, excluding a 4,5-*trans*-diaxial arrangement (*Table 1*). As evidenced by the coupling constants, **31**, **32**, **39**, and **40** adopt a $^4C_7$ conformation of the piperidine ring and **33**–**38** a flattened $^7C_4$ conformation. Force-field calculations (macromodel MM3) of the lactams **35** and **36** confirm a flattened $^7C_4$ conformation[7]). The configuration at C(2) was deduced by comparing the coupling constants of the lactams **35** and **36** to those corresponding to the calculated conformers (*Table 1*) and to those of related hydroxy lactams [65][66][67]. Similarly, the coupling constants of the indolizidine **39**, correspond to those of a related indolizidin-2-ol [7]. The assignment is in keeping with the $\Delta[M]_D$ values for **33**/**34** in $CHCl_3$ (– 256°) and **35**/**36** in MeOH (– 95°) relative to those of the enantiomeric 3-hydroxypyrrolidin-2-ones in $CHCl_3$ ($[M]_D(S) - [M]_D(R) = -228°$) [68][69].

The thiolactam **41** is characterized by a C(1) *s* at 202.34 ppm and a broad NH signal at 7.81 ppm. J(H,H) of **41** evidence a $^3H_4$ conformation (*Table 2*). The protected imidazole **43** is a flattened $^7H_6$ conformation and the unprotected **44** a $^7H_6$ one (*cf.* [53]). An IR band at 3608 cm^{-1} for **38** (free OH group), absent for **37**, hints at an intramolecular H-bond, further evidenced by a downfield shift of the OH signal (**37**: 2.60 ppm, **38**: 1.98 ppm), and only compatible with a *cis*-annulation of **37**. MM3* Calculations suggest a *cis*-annulation for **37** and a *trans*-annulation for **38**.

Inhibition of Bovine Epididymis α-L-Fucosidase. – The piperidine **30**, the indolizidines **39** and **40**, the indolizidinones **35** and **36**, and the imidazole **44** were tested as inhibitors of bovine epididymis α-L-fucosidase (*Table 3*).

The diamine **30** ($IC_{50} = 105$ nM) is about as strong an inhibitor as the deoxy-L-fuconojirimycin ($IC_{50} = 90$ nM [14], $K_i = 6.2$ nM [15] against bovine epididymis α-L-fucosidase), evidencing that the primary amino group does not contribute to the binding of the enzyme.

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7) Calculations showed an energy difference of 3.7 kcal/mol between the $^7C_4$ and the next stable $^NS_2$ conformers of **36**. The same analysis of **35** resulted in an energy difference of 2.6 kcal/mol in favour of the $^7C_4$ conformation.

Table 1. *Coupling Constants* J [Hz] *of the Protected Lactams* **33** *and* **34**, *of the Deprotected Lactams* **35** *and* **36**, *and of the Indolizidines* **37**–**40**, *and Calculated Coupling Constants for* **35** *and* **36** (carbohydrate numbering)

	33	**34**	**35**	**36**	calc. **35**	calc. **36**	**37**	**38**	**39**	**40**
J(1a,2)	–	–	–	–	–	–	–	4.7	6.2	4.7
J(1b,2)	–	–	–	–	–	–	–	6.2	~0	6.5
J(2,3a)	5.3	7.7	7.5	7.5	7.3	7.8	~0	7.8	4.7	7.2
J(2,3b)	8.7	9.0	8.7	8.7	9.4	8.6	6.2	1.9	7.4	~0
J(3a,4)	5.0	9.3	7.5	9.3	6.1	8.8	6.8	8.1	12.4	12.1
J(3b,4)	7.8	1.3	7.2	1.9	10.9	1.7	8.7	6.9	5.9	6.5
J(4,5)	2.8	2.2	2.2	1.9	2.2	2.2	2.2	[a])	5.6	5.3
J(5,6)	3.4	3.7	3.7	3.7	3.6	3.5	3.1	2.7	7.5	8.1
J(6,7)	2.8	2.8	3.1	3.4	3.1	3.4	3.1	3.1	[a])	3.1
J(7,8)	6.5	6.5	6.9	6.5	6.1	5.9	5.9	5.3	1.9	2.7

[a]) Not determined.

Table 2. *Coupling Constants* J [Hz] *of the Nitrone* **1**, *the Thiolactam* **41**, *and the Imidazoles* **43** *and* **44** (carbohydrate numbering)

	1	**41**	**43**	**44**
J(2,3)	6.8	8.4	5.6	9.0
J(3,4)	1.9	2.2	1.9	2.2
J(4,5)	3.7	2.5	4.7	2.2

Table 3. IC_{50} *Values of the Inhibitors against* Bovine Epididymis α-L-*Fucosidase*

	30	**39**	**40**	**35**	**36**	**44**
IC_{50}	105 nM	580 nM	5 μM	240 μM	100 μM	150 μM

The indolizidine **39** ($IC_{50} = 580$ nM) is about as strong an inhibitor as the related **23** ($K_i = 240$ nM) [14], whereas **40** is 10 times weaker ($IC_{50} = 5$ μM). Overlay of the three indolizidines shows that C(3) of **23** corresponds to the Me group of **39** and **40**. Thus, **39** and **40** are the equivalent of two rotamers of 1-(2-hydroxyethyl)-*N*-methyldeoxyfuconojirimycin and **23** is the equivalent of *N*-ethyldeoxyfuconojirimycin. This comparison shows that substitution at C(1) has a minor effect on the inhibition by *N*-alkyldeoxyfuconojirimycin, but that the exact orientation of the hydroxyethyl group is relevant.

The imidazole **44** ($IC_{50} = 150$ μM, $pK_{HA} = 5.6$) is a weak inhibitor of bovine epididymis α-L-fucosidase. The corresponding amidrazone **25** is a stronger inhibitor ($K_i = 820$ nM against recombinant human lysosomal α-L-fucosidase) [17]. The difference may be attributed to the expected higher pK_{HA} value of the amidrazone[8]), *i.e.*, to a complete protonation of the amidrazone and the ensuing in a charge/charge interaction with the catalytical nucleophile, but only a partial protonation of the imidazole that apparently cannot form a H-bond with the catalytic acid [70]. In keeping with the importance of a basic center, the indolizidinones **35** ($IC_{50} = 240$ μM) and **36** ($IC_{50} = 100$ μM) are only weak inhibitors of bovine epididymis α-L-fucosidase.

[8]) $pK_{HA} = 8.5$ for the corresponding glucose-derived analogue [57].

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Experimental Part

General. α-L-Fucosidase was purchased from *Böhringer Mannheim* as a suspension. Solvents were distilled before use. Normal workup implies distribution of the crude product between the org. layer and the indicated aq. layer, drying of the org. layer (Na_2SO_4), filtration, and evaporation of the filtrate. TLC: *Merck* silica gel *60* F_{254} plates; if not otherwise indicated, detection by treating the plates with an anisaldehyde soln. (10 ml of anisaldehyde, 10 ml of conc. H_2SO_4 soln., 2 ml of AcOH, 180 ml of EtOH) followed by heating. Flash chromatography (FC): silica gel (*Fluka* or *Merck 60*; 0.040–0.063 mm). HPLC: *Spherisorb*® SiO_2 (5 mm) column (20 × 250 mm); detection at 254 nm; t_R in min. M.p.: uncorrected. NMR Spectra: chemical shifts δ in ppm and coupling constants J in Hz. FAB- and CI-MS: 3-nitrobenzyl alcohol and NH_3 as matrix, resp., unless indicated otherwise.

Allyl 4,6-O-*Benzylidene-2,3-bis*-O-*(methanesulfonyl)*-α-D-*glucopyranoside* (**5**). A soln. of **4** [71] (18 g, 63.3 mmol) in pyridine (110 ml) was cooled to 0°, treated dropwise with MsCl (12.1 ml, 155 mmol), and stirred at 21° for 6 h (→ yellowish soln. and formation of a white precipitate). After addition of H_2O (200 ml) and extraction of the aq. layer with CH_2Cl_2, the org. layer was worked up in the usual way (sat. aq. NH_4Cl soln., H_2O). Residual pyridine was removed by co-evaporation with toluene. The resulting yellow powder was recrystallized in CH_2Cl_2/Et_2O 1:1 to give **5** (22.3 g, 80%). Colourless powder. M.p. 132°. R_f (AcOEt/hexane 1:1) 0.58. $[\alpha]_D^{25} = 67.9$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 2980*m*, 2940*m*, 2873*m*, 1731*w*, 1457*m*, 1415*m*, 1368*s*, 1178*s*, 1098*s*, 1049*s*, 1018*s*, 974*s*, 962*s*, 934*m*, 841*s*, 590*w*, 529*m*, 509*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.98 (*s*, MsO); 3.17 (*s*, MsO); 3.74 (*t*, $J \approx 9.3$, H–C(4)); 3.78 (*t*, $J \approx 10.0$, H–C(6)); 4.06 (*dt*, $J \approx 5.0$, 10.0, H–C(5)); 4.13 (*tdd*, $J \approx$ 1.3, 6.2, 12.8, 1 H, CH_2=CHCH_2); 4.26 (*tdd*, $J \approx 0.9$, 5.6, 12.7, 1 H, CH_2=CHCH_2); 4.33 (*dd*, $J = 5.0$, 10.0, H–C(6)); 4.64 (*dd*, $J = 3.7$, 9.3, H–C(2)); 5.11 (*t*, $J \approx 9.3$, H–C(3)); 5.18 (*d*, $J = 3.7$, H–C(1)); 5.28 (*qd*, $J \approx 0.9$, 10.3, 1 olef. H); 5.37 (*qd*, $J \approx 0.9$, 16.5, 1 olef. H); 5.56 (*s*, PhC*H*); 5.93 (*dddd*, $J \approx 5.6$, 6.2, 10.3, 16.5, 1 olef. H); 7.26–7.47 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 38.94 (*q*, MsO); 39.05 (*q*, MsO); 62.61 (*d*, C(5)); 68.81 (*t*, C(6)); 69.69 (*t*, CH_2=CH*C*H$_2$); 75.99 (*d*, C(3)); 77.40 (*d*, C(2)); 79.30 (*d*, C(4)); 97.07 (*d*, C(1)); 102.26 (*d*, Ph*C*H); 119.10 (*t*, 1 olef. C); 126.30 (*d*, 2 arom. C); 128.74 (*d*, 2 arom. C); 129.83 (*d*, 1 arom. C); 133.00 (*d*, 1 olef. C); 136.56 (*s*, 1 arom. C). FAB-MS: 465 (100, $[M+1]^+$), 205 (14), 154 (23), 149 (19), 137 (31), 136 (27), 127 (12), 109 (14), 107 (21), 105 (27). Anal. calc. for $C_{18}H_{24}O_{10}S_2$ (464.51): C 46.54, H 5.21, O 34.44, S 13.81; found: C 46.38, H 5.21, O 34.42, S 13.80.

Allyl 2-O-*Benzyl-4,6*-O-*benzylidene*-α-D-*altropyranoside* (**7**). A soln. of Na (9.6 g, 420 mmol) in $PhCH_2OH$ (320 ml) was treated portionwise with **5** (12 g, 25.9 mmol) and stirred for 30 min at 21° and then for 15 h at 90°. The brown soln. was cooled to 21°, diluted with AcOEt (500 ml), and worked up in the usual way (sat. aq. NH_4Cl soln., H_2O). The residual $PhCH_2OH$ was removed by distillation at 100°/0.5 Torr. FC (hexane/AcOEt 1:0 → 4:1) gave **7** (8.4 g, 82%) and **10** (0.85 g, 8%; m.p. = 134–135° and $[\alpha]_D^{25} = 79.1$ ($c = 1.2$, $CHCl_3$)) in accordance with those reported in [72], both as colourless solids. Recrystallization of **7** in AcOEt/hexane 1:2 gave a colourless powder.

Data of **7**: M.p. 140°. R_f (toluene/CH_2Cl_2/Et_2O 4:1:1) 0.55. $[\alpha]_D^{25} = 32.0$ ($c = 0.75$, $CHCl_3$). IR ($CHCl_3$): 3521*m*, 3068*m*, 3008*m*, 2936*m*, 2872*m*, 1955*w*, 1880*w*, 1813*w*, 1723*w*, 1647*w*, 1604*w*, 1497*w*, 1468*w*, 1455*m*, 1382*m*, 1313*m*, 1282*m*, 1248*m*, 1165*m*, 1135*s*, 1098*s*, 1029*s*, 939*m*, 917*m*, 887*w*, 858*m*, 828*w*, 640*w*, 618*w*, 599*w*, 556*w*, 521*w*, 512*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.01 (*d*, $J = 7.6$, addition of D_2O → exchange, OH); 3.76 (*dd*, $J = 1.3$, 3.4, H–C(2)); 3.86 (*t*, $J \approx 10.0$, H–C(6)); 4.01 (*dd*, $J = 10.0$, 2.8, H–C(4)); 4.03 (*tdd*, $J \approx 1.3$, 6.2, 13.1, 1 H, CH_2=CHCH_2); 4.18–4.29 (*m*, 1 H of CH_2=CHCH_2, H–C(3), H–C(5)); 4.34 (*dd*, $J = 5.0$, 10.0, H–C(6)); 4.63 (*d*, $J = 12.1$, PhC*H*); 4.68 (*d*, $J = 11.8$, PhC*H*); 4.91 (br. *s*, H–C(1)); 5.23 (*qd*, $J \approx 1.3$, 10.3, 1 olef. H); 5.28 (*qd*, $J \approx 1.3$, 16.3, 1 olef. H); 5.66 (*s*, PhC*H*); 5.88 (*dddd*, $J = 5.3$, 6.2, 10.3, 16.5, 1 olef. H); 7.09–7.41 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 58.66 (*d*, C(5)); 67.30 (*d*, C(3)); 68.77 (*t*, C(6)); 69.31 (*t*, CH_2=CH*C*H$_2$); 72.78 (*t*, Ph*C*H$_2$); 76.93, 76.96 (2*d*, C(2), C(4)); 98.13 (*d*, C(1)); 102.47 (*d*, Ph*C*H); 118.55 (*t*, 1 olef. C); 126.54–129.38 (several *d*, 10 arom. C); 133.39 (*d*, 1 olef. C); 137.56 (*s*, 1 arom. C); 137.64 (*s*, 1 arom. C). FAB-MS: 399 (34, $[M+1]^+$), 341 (100, $[M-OAll]^+$), 339 (23), 281 (37), 249 (26), 235 (23), 221 (36), 207 (34), 181 (35), 175 (23), 149 (32), 136 (25), 133 (37), 131 (32), 107 (38), 105 (48). Anal. calc. for $C_{23}H_{26}O_6$ (398.45): C 69.33, H 6.58, O 24.09; found: C 69.14, H 6.47, O 23.80.

Data of Allyl 3-O-*benzyl-4,6*-O-*benzylidene*-α-D-*glucopyranoside* (**10**): R_f (toluene/CH_2Cl_2/Et_2O 4:1:1) 0.31. IR ($CHCl_3$): 3569*m*, 3068*m*, 3008*m*, 2935*m*, 2870*m*, 1954*w*, 1880*w*, 1813*w*, 1648*w*, 1497*m*, 1454*m*, 1371*s*,

1345*m*, 1312*m*, 1171*m*, 1129*s*, 1074*s*, 1041*s*, 1005*s*, 934*m*, 656*m*, 577*w*, 524*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.31 (*d*, *J* = 8.0, addition of D_2O → exchange, OH); 3.64 (*t*, *J* ≈ 9.4, H–C(4)); 3.73 (*m*, addition of D_2O → change, H–C(2)); 3.74 (*t*, *J* ≈ 10.3, H–C(6)); 3.85 (*t*, *J* ≈ 9.3, H–C(3)); 3.88 (*dt*, *J* ≈ 4.8, 9.8, H–C(5)); 4.06 (*tdd*, *J* ≈ 1.3, 6.3, 12.8, 1 H, CH_2=CHCH_2); 4.23 (*tdd*, *J* ≈ 1.5, 5.4, 12.8, 1 H, CH_2=CHCH_2); 4.28 (*dd*, *J* = 4.9, 10.2, H–C(6)); 4.80 (*d*, *J* = 11.6, PhC*H*); 4.96 (*d*, *J* = 11.6, PhC*H*); 4.96 (*d*, *J* = 3.9, H–C(1)); 5.23 (*qd*, *J* ≈ 1.2, 10.4, 1 olef. H); 5.32 (*qd*, *J* ≈ 1.5, 17.2, 1 olef. H); 5.56 (*s*, PhC*H*); 5.94 (*dddd*, *J* = 5.4, 6.4, 10.4, 17.1, 1 olef. H); 7.24–7.50 (*m*, 10 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 62.40 (*d*, C(5)); 68.37, 68.56 (2*t*, C(6), CH_2=CHCH_2); 72.05 (*d*); 74.46 (*t*, PhCH_2); 78.65 (*d*); 81.57 (*d*), 97.64 (*d*, C(1)); 100.91 (*d*, PhC*H*); 117.95 (*t*, 1 olef. C); 125.70–128.65 (several *d*, 10 arom. C); 133.09 (*d*, 1 olef. C); 137.42 (*s*, 1 arom. C); 139.01 (*s*, 1 arom. C).

*Allyl 3-*O*-Acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-altropyranoside* (**9**). A soln. of **7** (120 mg, 0.30 mmol) in pyridine/Ac_2O 1:1 (1 ml) was treated with 4-(dimethylamino)pyridine (3 mg) and stirred for 12 h at 21°, diluted with CH_2Cl_2, and worked up in the usual way (sat. aq. NH_4Cl soln.). The remaining pyridine was removed by evaporation with toluene. FC (hexane/AcOEt 1:0 → 2:1) gave **9** (25 mg, 75%). Colourless oil. R_f (hexane/AcOEt 2:1) 0.62. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.10 (*s*, Ac); 3.80 (*t*, *J* ≈ 11.8, 1 H–C(6)); 3.84 (*d*, *J* = 3.1, H–C(2)); 3.92 (*tdd*, *J* ≈ 1.3, 5.6, 13.4, 1 H, (CH_2=CHCH_2); 4.12 (*dd*, *J* = 2.1, 9.0, H–C(4)); 4.21 (*tdd*, *J* ≈ 1.6, 4.7, 13.4, 1 H, CH_2=CHCH_2); 4.18–4.38 (*m*, H–C(5), 1 H–C(6)); 4.66 (*d*, *J* = 11.8, PhC*H*); 4.77 (*d*, *J* = 11.8, PhC*H*); 4.77 (*s*, H–C(1)); 5.22 (*qd*, *J* ≈ 1.2, 10.6, 1 olef. H); 5.27 (*qd*, *J* ≈ 1.6, 17.4, 1 olef. H); 5.31 (*dd*, *J* = 1.6, 3.2, H–C(3)); 5.61 (*s*, PhC*H*); 5.88 (*dddd*, *J* = 4.7, 5.6, 10.3, 17.4, 1 olef. H); 7.26–7.50 (*m*, 10 arom. H).

*Allyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-*D*-altropyranoside* (**8**). A soln. of **7** (15.6 g, 39.2 mmol) in anh. THF (120 ml) was treated slowly at 23° with NaH (1.1 g, 45.8 mmol). The suspension was heated to 60°, treated dropwise with BnBr (5.5 ml, 46.3 mmol), followed by Bu_4NI (0.8 g, 2.1 mmol), and stirred at 60° for 12 h. After dilution with CH_2Cl_2, the orange soln. was worked up in the usual way (brine). FC (hexane/AcOEt 1:0 → 4:1) gave **8** (18.0 g, 94%). Colourless oil. R_f (hexane/AcOEt 4:1) 0.41. $[\alpha]_D^{25} = 35.5$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3068*m*, 3008*m*, 2934*m*, 2869*m*, 1953*w*, 1878*w*, 1814*w*, 1731*m*, 1644*w*, 1603*w*, 1469*m*, 1455*m*, 1382*m*, 1311*m*, 1269*m*, 1248*m*, 1167*m*, 1140*s*, 1100*s*, 1029*s*, 916*m*, 859*w*, 644*w*, 606*w*, 548*w*, 520*w*, 504*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.75 (*dd*, *J* = 0.6, 2.8, H–C(2)); 3.81 (*t*, *J* ≈ 10.3, 1 H–C(6)); 4.00 (*t*, *J* ≈ 2.8, H–C(3)); 4.06 (*dd*, *J* = 2.8, 10.0, H–C(4)); 4.00–4.10 (*m*, 1 H, CH_2=CHCH_2); 4.27 (*tdd*, *J* ≈ 1.6, 4.7, 13.4, 1 H, CH_2=CHCH_2); 4.34 (*dd*, *J* = 5.3, 10.3, 1 H–C(6)); 4.47 (*dt*, *J* = 5.3, 10.3, H–C(5)); 4.55 (*s*, PhCH_2); 4.71 (*d*, *J* = 12.5, PhC*H*); 4.83 (*d*, *J* = 12.5, PhC*H*); 4.86 (*d*, *J* = 0.6, H–C(1)); 5.20 (*qd*, *J* ≈ 1.6, 10.6, 1 olef. H); 5.32 (*qd*, *J* ≈ 1.6, 17.4, 1 olef. H); 5.60 (*s*, PhC*H*); 5.93 (*dddd*, *J* = 4.7, 5.9, 10.6, 17.4, 1 olef. H); 7.26–7.57 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 58.81 (*d*, C(5)); 68.28 (*t*, C(6)); 69.57 (*t*, CH_2=*C*HCH_2); 72.67 (*t*, PhCH_2); 72.88 (*t*, PhCH_2); 73.03 (*d*, C(3)); 76.59, 77.57 (2*d*, C(2), C(4)); 98.05 (*d*, C(1)); 102.47 (*d*, PhC*H*); 117.34 (*t*, 1 olef. C); 126.58–129.28 (several *d*, 15 arom. C); 134.28 (*d*, 1 olef. C); 137.69 (*s*, 1 arom. C); 138.13 (*s*, 1 arom. C); 139.05 (*s*, 1 arom. C). FAB-MS: 489 (36, $[M+1]^+$), 327(17), 325 (15), 281 (24), 221 (46), 207 (61), 193 (23), 191 (22), 181 (21), 154 (26), 147 (100), 136 (74), 133 (58), 107 (47). Anal. calc. for $C_{30}H_{32}O_6$ (488.58): C 73.75, H 6.60, O 19.65; found: C 73.47, H 6.82, O 19.43.

Reductive Acetal Cleavage of **8**. A soln. of $LiAlH_4$ (5.14 g, 135 mmol) in anh. Et_2O (50 ml) was treated dropwise with Me_3SiBr (43.7 ml, 338 mmol) at 0°. The suspension was stirred for 30 min at 23°, heated to reflux and then treated dropwise during 20 min with a soln. of **8** (32.0 g, 67 mmol) in anh. Et_2O (50 ml). The mixture was refluxed for another 30 min, until TLC (hexane/AcOEt 2:1) indicated the complete conversion of the reactant. The suspension was cooled to 0°. AcOEt was added dropwise followed by H_2O, until the residual $LiAlH_4$ was destroyed. The mixture was worked up in the usual way (1N HCl, sat. aq. $NaHCO_3$ soln., H_2O). Removing the solvent *in vacuo* gave a colourless oil (32.5 g). Thereof, 1 g (3.1 %) was separated by FC (hexane/AcOEt 1:0 → 1:1) to give **12** (0.75 g, 75%) and **11** (0.11 g, 11%).

*Allyl 2,3,4-Tri-*O*-benzyl-α-*D*-altropyranoside* (**12**): Colourless oil. R_f (hexane/AcOEt 2:1) 0.38. $[\alpha]_D^{25} = 66.3$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3512*m* (br.), 3070*m*, 3008*s*, 2932*s*, 2894*m*, 2860*s*, 1956*w*, 1886*w*, 1816*w*, 1731*w*, 1603*w*, 1590*w*, 1497*m*, 1472*m*, 1454*s*, 1428*m*, 1393*m*, 1363*m*, 1306*m*, 1267*w*, 1248*w*, 1115*s*, 1068*s*, 1028*m*, 924*s*, 824*m*, 613*m*, 556*w*, 536*w*, 504*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.95 (*t*, *J* ≈ 5.6, addition of D_2O → exchange, OH); 3.75 (*dd*, *J* = 0.9, 3.1, H–C(2)); 3.77–3.86 (*m*, H–C(3), H–C(4), 2 H–C(6)); 3.99 (*tdd*, *J* ≈ 1.3, 5.9, 13.4, 1 H, CH_2=CHCH_2); 4.19–4.21 (*m*, H–C(5)); 4.22 (*tdd*, *J* ≈ 1.6, 6.2, 13.4, 1 H, CH_2=CHCH_2); 4.42 (*d*, *J* = 12.1, PhC*H*); 4.45 (*d*, *J* = 11.5, PhC*H*); 4.52 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 11.8, PhC*H*); 4.54 (*d*, *J* = 12.1, PhC*H*); 4.65 (*d*, *J* = 12.1, PhC*H*); 4.83 (*s*, H–C(1)); 5.15 (*qd*, *J* ≈ 1.6, 10.6, 1 olef. H); 5.32 (*qd*, *J* ≈ 1.6, 17.4, 1 H, CH_2=CHCH$_2$); 5.89 (*dddd*, *J* = 5.9, 6.2, 10.6, 17.5, 1 H, CH_2=CHCH_2); 7.26–7.57 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 62.90 (*t*, C(6)); 67.85 (*d*, C(5)); 68.21 (*t*, CH_2=C*H*CH$_2$); 71.56 (*t*, PhCH_2); 72.03 (*t*, PhCH_2); 72.69 (*t*, PhCH_2); 72.82 (*d*, C(4)); 73.02 (*d*, C(3)); 75.36 (*d*, C(2)); 98.33 (*d*, C(1)); 117.02 (*t*, 1 olef. C); 127.81–128.75 (several *d*, 15 arom. C); 134.43 (*d*, 1 olef. C); 138.02 (*s*, 1 arom. C); 138.40 (*s*, 1 arom. C); 138.65

(*s*, 1 arom. C). FAB-MS: 461 (10), 355 (29), 341 (34), 327 (35), 325 (28), 281 (78), 267 (35), 221 (99), 207 (100), 193 (31), 181 (53), 154 (55), 147 (95), 137 (47). Anal. calc. for $C_{30}H_{34}O_6$ (490.60): C 73.45, H 6.99; found: C 73.19, H 7.15.

Allyl 2,3,6-Tri-O-*benzyl*-α-D-*altropyranoside* (**11**): Colourless oil. R_f (hexane/AcOEt 2:1) 0.50. IR ($CHCl_3$): 3552*w*, 3068*w*, 3008*m*, 2962*m*, 2908*m*, 2868*m*, 1952*w*, 1698*w*, 1602*w*, 1496*m*, 1454*s*, 1397*m*, 1351*m*, 1262*s*, 1098*s*, 1050*s*, 1017*s*, 931*m*, 865*m*, 818*s*, 652*w*, 629*w*, 601*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.50 (*d*, $J = 8.7$, OH); 3.69 (*dd*, $J = 5.6$, 10.6, 1 H–C(6)); 3.76–3.80 (*m*, H–C(2), H–C(3) 1 H–C(6)); 3.79 (*dt*, $J \approx 3.1$, 8.7, H–C(4)); 3.98 (*tdd*, $J \approx 1.6$, 5.9, 13.1, 1 olef. H); 4.06 (*ddd*, $J = 3.2$, 5.6, 8.7, H–C(5)); 4.27 (*tdd*, $J \approx 1.3$, 5.0, 13.1, 1 H, CH_2=CHCH_2); 4.43 (*d*, $J = 11.5$, PhC*H*); 4.56 (*d*, $J = 12.1$, PhC*H*); 4.60 (*s*, PhCH_2); 4.66 (*d*, $J = 11.8$, PhC*H*); 4.69 (*d*, $J = 11.2$, PhC*H*); 4.90 (*s*, H–C(1)); 5.15 (*qd*, $J \approx 1.3$, 10.4, 1 olef. H); 5.27 (*qd*, $J \approx 1.6$, 16.5, 1 olef. H); 5.92 (*dddd*, $J = 5.0$, 5.6, 10.6, 16.5, 1 olef. H); 7.25–7.36 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 65.44 (*d*, C(4)); 69.49 (*d*, C(5)); 68.26 (*t*, CH_2=CHCH_2); 70.43 (*t*, C(6)); 72.24 (*t*, PhCH_2); 72.82 (*t*, PhCH_2); 73.52 (*t*, PhCH_2); 74.58 (*d*); 76.19 (*d*); 98.19 (*d*, C(1)); 117.07 (*t*, 1 olef. C); 127.70–128.67 (several *d*, 15 arom. C); 134.49 (*d*, 1 olef. C); 137.90 (*s*, 1 arom. C); 138.45 (*s*, 1 arom. C); 138.65 (*s*, 1 arom. C). FAB-MS: 400 (7), 355 (28), 327 (39), 281 (36), 267 (36), 136 (51), 91 (100, Bn^+).

Allyl 2,3,4-Tri-O-*benzyl-6*-O-*[(4-methylphenyl)sulfonyl]*-α-D-*altropyranoside* (**13**). A soln. of crude **12** (31.5 g) in pyridine (56 ml) was treated with TsCl (25.3 g, 133 mmol) at 0° and stirred at 22° for 4 h when TLC (hexane/AcOEt 2:1) indicated complete conversion of the reactant. The mixture was poured on H_2O and extracted with CH_2Cl_2. The org. layer was worked up in the usual way (sat. aq. $NaHCO_3$ soln., H_2O). Evaporation left a yellow oil which was filtered through silica gel (hexane/AcOEt 2:1). After evaporation, recrystallization in Et_2O/pentane 2:3 gave **13** (31 g, 75% from **8**). Colourless powder. M.p. 69–70°. R_f (hexane/AcOEt 2:1) 0.56. $[\alpha]_D^{25} = 61.2$ ($c = 0.73$, $CHCl_3$). IR ($CHCl_3$): 3089*w*, 3067*m*, 3008*m*, 2927*m*, 2872*m*, 1953*w*, 1809*w*, 1730*w*, 1644*w*, 1600*m*, 1496*m*, 1454*s*, 1365*s*, 1308*m*, 1266*s*, 1177*s*, 1143*s*, 1098*s*, 1045*s*, 1029*s*, 976*s*, 843*m*, 658*m*, 606*m*, 572*m*, 555*s*, 524*m*, 512*w*, 504*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.41 (*s*, Me); 3.73 (*dd*, $J = 1.2$, 3.1, H–C(3)); 3.75–3.80 (*m*, H–C(5)); 3.80 (*dd*, $J = 3.1$, 9.1, H–C(4)); 3.92 (*tdd*, $J \approx 1.6$, 5.9, 13.4, 1 H, CH_2=CHCH_2); 4.17 (*tdd*, $J \approx 1.6$, 5.0, 13.4, 1 H, CH_2=CHCH_2); 4.28 (*d*, $J = 1.3$, H–C(2)); 4.30–4.36 (*m*, 2 H–C(6)); 4.35 (*d*, $J = 11.5$, PhC*H*); 4.43 (*d*, $J = 12.5$, PhC*H*); 4.44 (*d*, $J = 11.5$, PhC*H*); 4.48 (*d*, $J = 12.1$, PhC*H*); 4.55 (*d*, $J = 12.1$, PhC*H*); 4.61 (*d*, $J = 12.1$, PhC*H*); 4.78 (*s*, H–C(1)); 5.15 (*qd*, $J \approx 1.6$, 10.6, 1 olef. H); 5.27 (*qd*, $J \approx 1.6$, 17.1, 1 olef. H); 5.87 (*dddd*, $J = 4.7$, 5.9, 10.6, 17.1, 1 olef. H); 7.01–7.41 (*m*, 17 arom. H); 7.82 (*td*, $J \approx 1.8$, 8.4, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.68 (*q*, Me); 65.91 (*d*, C(5)); 68.14 (*t*, CH_2=CHCH_2); 69.97 (*t*, C(6)); 71.28 (*t*, PhCH_2); 71.94 (*t*, PhCH_2); 72.25, 72.38 (2*d*, C(3), C(4)); 72.62 (*t*, PhCH_2); 74.93 (*d*, C(2)); 97.93 (*d*, C(1)); 117.06 (*t*, 1 olef. C); 128.03–129.54 (several *d*, 17 arom. C); 129.97 (*d*, 2 arom. C); 133.37 (*d*, 1 olef. C); 134.29 (*s*, 1 arom. C); 138.01 (*s*, 1 arom. C); 138.08 (*s*, 1 arom. C); 138.47 (*s*, 1 arom. C); 144.86 (*s*, 1 arom. C). FAB-MS: 667 (30, $[M + Na]^+$), 645 (18, $[M + 1]^+$), 643 (92), 587 (25), 527 (20), 496 (28), 495 (88), 405 (24), 271 (29), 253 (56), 181 (45), 90 (100). Anal. calc. for $C_{37}H_{40}O_8S$ (644.78): C 68.92, H 6.25, O 19.85; found: C 68.78, H 6.22, O 19.80.

Allyl 2,3,4-Tri-O-*benzyl-6-deoxy*-α-D-*altropyranoside* (**14**). A soln. of **13** (23 g, 35.7 mmol) in anh. Et_2O (55 ml) was treated with $LiAlH_4$ (2.7 g, 71.1 mmol) in small portions at 22°. The resulting suspension was heated for 2 h to reflux, cooled to 0°, and treated dropwise with AcOEt followed by H_2O. Usual workup (1N HCl, sat. aq. $NaHCO_3$ soln., H_2O) and FC (hexane/Et_2O 1:0 → 3:1) gave **14** (15.6 g, 92%). Colourless oil. R_f (hexane/AcOEt 2:1) 0.77. $[\alpha]_D^{25} = -19.1$ ($c = 0.79$, $CHCl_3$). IR ($CHCl_3$): 3088*w*, 3066*w*, 3007*m*, 2929*m*, 2871*m*, 1952*w*, 1875*w*, 1814*w*, 1727*w*, 1692*w*, 1659*w*, 1643*w*, 1603*m*, 1548*w*, 1496*m*, 1454*s*, 1369*m*, 1266*m*, 1146*s*, 1091*s*, 1028*s*, 992*s*, 911*m*, 840*w*, 606*m*, 542*w*, 535*w*, 526*m*, 514*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.29 (*d*, $J = 6.5$, 3 H–C(6)); 3.52 (*dd*, $J = 2.5$, 8.7, H–C(4)); 3.78–3.82 (*m*, H–C(2), H–C(3)); 4.04 (*tdd*, $J \approx 1.3$, 5.9, 13.1, 1 H, CH_2=CHCH_2); 4.28 (*qd*, $J = 6.5$, 8.7, H–C(5)); 4.20–4.40 (*m*, 1 H, CH_2=CHCH_2); 4.48 (*d*, $J = 11.8$, PhC*H*); 4.49 (*d*, $J = 12.1$, PhC*H*); 4.55 (*d*, $J = 11.8$, 2 PhC*H*); 4.60 (*d*, $J = 11.8$, PhC*H*); 4.68 (*d*, $J = 12.1$, PhC*H*); 4.80 (*s*, H–C(1)); 5.18 (*qd*, $J \approx 1.6$, 10.6, 1 olef. H); 5.33 (*qd*, $J \approx 1.6$, 17.1, 1 olef. H); 5.94 (*dddd*, $J = 5.0$, 5.9, 10.6, 16.8, 1 olef. H); 7.20–7.40 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.84 (*q*, C(6)); 64.49 (*d*, C(5)); 68.47 (*t*, CH_2=CHCH_2); 71.60 (*t*, PhCH_2); 72.00 (*t*, PhCH_2); 72.88 (*t*, PhCH_2); 73.06, 75.78 (2*d*, C(3), C(4)); 77.77 (*d*, C(2)); 98.07 (*d*, C(1)); 116.87 (*t*, 1 olef. C); 126.56–129.38 (several *d*, 15 arom. C); 134.63 (*d*, 1 olefin. C); 138.27 (*s*, 1 arom. C); 138.65 (*s*, 1 arom. C); 138.77 (*s*, 1 arom. C). FAB-MS: 417 (5, $[M - OAll]^+$, 5), 281 (10), 253 (24), 181 (100), 154 (36), 147 (44), 136 (55), 107 (46), 105 (36). Anal. calc. for $C_{30}H_{32}O_5$ (474.60): C 75.92, H 7.22, O 16.86; found: C 75.78, H 7.19, O 17.09.

2,3,4-Tri-O-*benzyl-6-deoxy*-D-*altropyranose* (**3**). *a*) A soln. of **14** (25 g, 52.7 mmol) in anh. DMSO (115 ml) was treated with KO^{t}Bu (25.7 g, 229 mmol) at 21° and stirred at 100° for 1.5 h until complete isomerization of **14** to (*Z*)-**15** (evidenced by ^{1}H-NMR). The brown soln. was cooled to 25° and treated with a sat. aq. NH_4Cl soln.

The aq. layer was extracted with CH_2Cl_2, and the combined organic layers were worked up in the usual way (brine). The resulting brown oil was dissolved in acetone/H_2O 10:1 (340 ml), treated with yellow HgO (11.8 g, 52.7 mmol) and a soln. of $HgCl_2$ (13 g, 47.8 mmol) in acetone/H_2O 10:1 (120 ml), and stirred for 15 min at 21°. After evaporation *in vacuo* to a volume of 70 ml, addition of CH_2Cl_2 and usual workup (sat. aq. KI soln., H_2O), the resulting brown oil was filtered through silica gel (50 g, hexane/AcOEt 1:1). Evaporation and crystallization from hexane/AcOEt 1:1 gave **3** (19.0 g, 83%). Colourless crystals.

b) A soln. of **14** (2.6 g, 5.6 mmol) in anh. THF (13 ml) was treated with $\{Ir(cod)[PMePh_2]_2\}PF_6$ (cod = cycloocta-1,5-diene; 50 mg, 60 μmol), and the resulting red suspension was stirred at 21° under H_2, until the colour changed to yellow. H_2 was replaced by Ar and stirring was continued for 2.5 h until the isomerization of **14** to (*E*/*Z*)-**15** was complete (^{1}H-NMR control). After evaporation, the residue was dissolved in acetone/H_2O 10:1 (35 ml), treated with yellow HgO (1.22 g, 5.6 mmol) and a soln. of $HgCl_2$ (0.97 g, 4.5 mmol) in acetone/H_2O 10:1 (11 ml), and stirred for 15 min at 21°. After concentration to a volume of *ca.* 10 ml, addition of CH_2Cl_2, usual workup (sat. aq. KI soln., H_2O), and crystallization from hexane/AcOEt 1:1 gave **3** (2 g, 85%). Colourless crystals. R_f (hexane/AcOEt 2:1) 0.48. M.p. 105°. IR ($CHCl_3$): 3571*m*, 3068*m*, 3008*m*, 2934*m*, 2870*m*, 1956*w*, 1602*w*, 1497*w*, 1454*s*, 1371*s*, 1345*m*, 1312*m*, 1266*m*, 1172*m*, 1130*s*, 1074*s*, 1041*s*, 1003*s*, 933*m*, 653*m*, 575*m*, 526*m*, 513*w*, 503*w*. ^{1}H-NMR (500 MHz, $CDCl_3$, α-D/β-D 2:3): 1.29 (*d*, *J* = 6.2, 1.8 H), 1.34 (*d*, *J* = 6.2, 1.2 H, 3 H–C(6)); 3.36 (*dd*, *J* = 2.8, 9.5, 0.6 H), 3.51 (*dd*, *J* = 2.7, 9.4, 0.4 H, H–C(4)); 3.44 (*d*, *J* = 12.2, addition of $D_2O \rightarrow$ exchange, 0.6 H), 5.04 (*d*, *J* = 11.4, addition of $D_2O \rightarrow$ exchange, 0.4 H, OH); 3.49 (*dd*, *J* = 1.7, 3.7, 0.6 H); 3.61 (*dd*, *J* = 1.2, 3.8, 0.4 H, H–C(2)); 3.88 (*t*, *J* ≈ 3.3, 0.6 H), 3.88–3.89 (*ddd*, *J* ≈ 1.5, 2.5, 3.5, H–C(3)); 4.01 (*qd*, *J* = 6.2, 9.5, 0.6 H), 4.24 (*qd*, *J* ≈ 6.2, 9.7, 0.4 H, H–C(5)); 4.40 (*d*, *J* = 12.2, 0.4 H, 4.40 (*s*, 1.2 H), 4.44 (*d*, *J* = 12.0, 0.6 H), 4.45 (*d*, *J* = 12.2, 0.4 H), 4.46 (*d*, *J* = 11.6, 0.6 H), 4.47 (*d*, *J* = 12.2, 0.6 H), 4.49 (*d*, *J* = 11.6, 0.4 H), 4.53 (*d*, *J* = 11.8, 0.4 H), 4.54 (*d*, *J* = 12.3, 0.4 H), 4.63 (*d*, *J* = 12.2, 0.6 H), 4.71 (*d*, *J* = 11.8, 0.4 H, 6 PhC*H*); 4.98 (br. *td*, *J* ≈ 1.5, 11.7, addition of $D_2O \rightarrow$ br. *s*, 0.4 H), 5.03 (*dd*, *J* = 1.7, 12.2, addition of $D_2O \rightarrow$ br. *s*, 0.6 H, H–C(1)); 7.19–7.36 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$, α-D/β-D 2:3): signals of α-D-**3**: 17.74 (*q*, C(6)); 68.34 (*d*, C(5)); 71.74 (*t*, PhCH_2); 71.81 (*d*, C(4)); 73.49 (*t*, PhCH_2); 74.47 (*t*, PhCH_2); 77.41 (*d*); 77.52 (*d*); 92.53 (*d*, C(1)); 128.19–128.99 (several *d*, 15 arom. C); signals of β-D-**3**: 17.74 (*q*, C(6)); 62.63 (*d*, C(5)); 71.55 (*d*, C(4)); 71.65 (*t*, PhCH_2); 72.72 (*t*, PhCH_2); 73.04 (*t*, PhCH_2); 77.33 (*d*); 77.55 (*d*); 91.20 (*d*, C(1)); 128.19–128.99 (several *d*, 15 arom. C); 135.22 (*s*, 1 arom. C); 135.69 (*s*, 1 arom. C); 135.85 (*s*, 1 arom. C). FAB-MS: 435 (3, $[M+1]^+$), 433 (49), 417 (49, $[M-OH]^+$), 325 (22), 253 (20), 181 (78), 91 (100).

*(Z)-Prop-1-enyl 2,3,4-Tri-*O*-benzyl-6-deoxy-*α*-*D*-altropyranose* (**15**). In an additional exper., FC (hexane/Et_2O 1:0 → 3:1) of the crude product obtained by the conversion of **14** (90 mg, 0.19 mmol) with KO^{t}Bu (100 mg, 0.89 mmol) in DMSO (0.5 ml) as described above gave (*Z*)-**15** (82 mg, 91%). Colourless oil. R_f (hexane/AcOEt 2:1) 0.77. IR ($CHCl_3$): 3089*w*, 3066*m*, 3008*m*, 2924*m*, 2870*m*, 1952*w*, 1877*w*, 1812*w*, 1731*m*, 1672*m*, 1605*w*, 1496*w*, 1454*s*, 1374*s*, 1318*m*, 1248*m*, 1154*m*, 1091*s*, 1028*s*, 911*m*, 868*w*, 818*m*, 609*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.27 (*d*, *J* = 6.5, 3 H–C(6)); 1.59 (*dd*, *J* = 1.9, 6.8, Me); 3.49 (*dd*, *J* = 3.1, 8.4, H–C(4)); 3.81 (*t*, *J* ≈ 3.1, H–C(3)); 3.85 (*dd*, *J* = 1.6, 3.1, H–C(2)); 4.27 (*qd*, *J* = 6.5, 8.4, H–C(5)); 4.47 (*d*, *J* = 11.8, PhC*H*); 4.48 (*d*, *J* = 12.1, PhC*H*); 4.54 (*d*, *J* = 12.5, PhC*H*); 4.56 (*d*, *J* = 12.5, PhC*H*); 4.58 (*d*, *J* = 12.1, PhC*H*); 4.68 (*d*, *J* = 12.1, PhC*H*); 4.94–5.04 (*m*, 1 vinyl. H); 4.97 (br. *s*, H–C(1)); 6.13 (*qd*, *J* = 1.9, 6.1, 1 olef. H); 7.23–7.39 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 9.36 (*q*, Me); 17.78 (*q*, C(6)); 64.68 (*d*, C(5)); 71.60 (*t*, PhCH_2); 71.93 (*t*, PhCH_2); 72.85 (*t*, PhCH_2); 72.57 (*d*, C(4)); 74.56, 77.43 (2*d*, C(2), C(3)); 98.54 (*d*, C(1)); 103.72 (*t*, 1 olef. C); 127.84–128.75 (9*d*, 15 arom. C); 138.02 (*s*, 1 arom. C); 138.47 (*s*, 1 arom. C); 138.58 (*s*, 1 arom. C); 142.35 (*d*, 1 olef. C).

*(E)- and (Z)-2,3,4-Tri-*O*-benzyl-6-deoxy-*D*-altrose* O-*[(*tert*-Butyl)diphenylsilyl]oxime* ((*E*)-**16** and (*Z*)-**16**, resp.). A soln. of **3** (7.2 g, 16.6 mmol) in CH_2Cl_2 (26 ml) was treated with pyridinium *p*-toluenesulfonate (170 mg, 0.68 mmol), *O*-[(*tert*-butyl)diphenylsilyl]hydroxylamine (9.14 g, 33.6 mmol), and molecular sieves 3 Å (50 mg, powder (*Union Carbide*)). The resulting suspension was stirred at 22° under Ar for 3 d until complete conversion (TLC (toluene/Et_2O 9:1) control). Addition of CH_2Cl_2, usual workup (sat. aq. $NaHCO_3$ soln., H_2O), and FC (hexane/Et_2O 1:0 → 1:1) gave (*E*)-**16** (9.4 mg, 83%) and (*Z*)-**16** (1.5 g, 13%), both as colourless oils.

*Data of (*E*)-***16***: R_f (toluene/Et_2O 9:1) 0.40. IR ($CHCl_3$): 3592*w*, 3068*m*, 3008*s*, 2929*s*, 2872*m*, 1954*w*, 1876*w*, 1814*w*, 1711*m*, 1658*w*, 1602*m*, 1548*w*, 1496*m*, 1454*s*, 1428*m*, 1364*s*, 1266*s*, 1248*m*, 1097*s*, 1040*s*, 1028*s*, 990*s*, 932*s*, 844*w*, 610*m*, 544*w*, 533*m*, 523*m*, 512*m*, 504*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.21 (*s*, ^{t}Bu); 1.21 (*d*, *J* = 6.2, 3 H–C(6)); 2.65 (*d*, *J* = 4.4, addition of $D_2O \rightarrow$ exchange, OH); 3.46 (*dd*, *J* = 5.0, 6.5, H–C(4)); 3.84 (*t*, *J* ≈ 5.0, H–C(3)); 4.11 (*m*, addition of $D_2O \rightarrow$ change, H–C(5)); 4.25 (*dd*, *J* = 5.0, 8.1, H–C(2)); 4.36 (*d*, *J* = 11.8, PhC*H*); 4.52 (*d*, *J* = 11.2, PhC*H*); 4.58 (*d*, *J* = 11.2, PhC*H*); 4.63 (*d*, *J* = 11.8, PhC*H*); 4.69 (*d*, *J* = 11.5, PhC*H*); 4.77 (*d*, *J* = 11.5, PhC*H*); 7.16–7.43 (*m*, 21 arom. H); 7.68–7.73 (*m*, 4 arom. H); 7.81 (*d*, *J* = 8.1, H–C(1)).

^{13}C-NMR (75 MHz, $CDCl_3$): 19.37 (*s*, Me_3C); 19.48 (*q*, C(6)); 27.16 (*q*, Me_3C); 68.34 (*d*, C(5)); 71.22 (*t*, PhCH_2); 73.77 (*t*, PhCH_2); 74.37 (*t*, PhCH_2); 77.62 (*d*, C(2)); 81.62 (*d*); 83.56 (*d*); 127.87–128.72 (several *d*, 19 arom. C); 130.04 (*d*, 2 arom. C); 133.59 (*s*, 1 arom. C); 133.73 (*s*, 1 arom. C); 135.90 (*d*, 4 arom. C); 137.50 (*s*, 1 arom. C); 138.05 (*s*, 1 arom. C); 138.52 (*s*, 1 arom. C); 154.81 (*d*, C(1)). FAB-MS: 688 (100, $[M+1]^+$), 580 (9), 199 (14), 181 (9), 137 (9), 136 (7), 105 (6). Anal. calc. for $C_{30}H_{32}NO_5$ (687.95): C 75.07, H 7.18, N 2.04; found: C 75.19, H 7.23, N 2.03.

*Data of (*Z*)-***16***: R_f* (toluene/Et_2O 9:1) 0.28. IR ($CHCl_3$): 3498*m*, 3070*m*, 3008*s*, 2961*m*, 2933*s*, 2860*s*, 1955*w*, 1886*w*, 1815*w*, 1590*w*, 1548*w*, 1497*m*, 1472*m*, 1454*s*, 1428*m*, 1392*m*, 1363*m*, 1336*m*, 1306*m*, 1263*m*, 1115*s*, 1070*s*, 1028*s*, 911*s*, 823*m*, 650*w*, 613*m*, 533*w*, 503*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, ^{t}Bu); 1.24 (*d*, *J* = 6.2, 3 H–C(6)); 2.51 (*d*, *J* = 4.4, addition of D_2O → exchange, OH); 3.71 (*dd*, *J* = 5.0, 6.8, H–C(4)); 4.06 (*dd*, *J* = 3.1, 6.9, H–C(3)); 4.09–4.15 (*m*, addition of D_2O → change, H–C(5)); 4.47 (*d*, *J* = 11.5, PhC*H*); 4.49 (*d*, *J* = 11.5, PhC*H*); 4.56 (*d*, *J* = 11.5, PhC*H*); 4.60 (*d*, *J* = 12.1, PhC*H*); 4.65 (*d*, *J* = 12.2, PhC*H*); 4.66 (*d*, *J* = 11.8, PhC*H*); 5.35 (*dd*, *J* = 3.1, 6.2, H–C(2)); 7.18–7.42 (*m*, 21 arom. H, H–C(1)); 7.69–7.76 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 18.48 (*s*, Me_3C); 19.42 (*q*, C(6)); 27.17 (*q*, Me_3C); 68.67 (*d*, C(5)); 72.53 (*t*, PhCH_2); 72.59 (*d*, C(2)); 73.87 (*t*, PhCH_2); 74.76 (*t*, PhCH_2); 81.02 (*d*); 82.61 (*d*); 127.71–128.77 (several *d*, 19 arom. C); 130.17 (*d*, 2 arom. C); 133.29 (*s*, 1 arom. C); 133.31 (*s*, 1 arom. C); 135.87 (*d*, 4 arom. C); 137.45 (*s*, 1 arom. C); 137.81 (*s*, 1 arom. C); 138.76 (*s*, 1 arom. C); 157.64 (*d*, C(1)). FAB-MS: 688 (73, $[M+1]^+$), 417 (15), 325 (18), 271 (13), 253 (48), 181 (50), 91 (100).

*(*E*)- and (*Z*)-2,3,4-Tri-*O*-benzyl-6-deoxy-5-*O*-[(4-methylphenyl)sulfonyl]-*D*-altrose* O-[(tert-Butyl)diphenylsilyl]oxime ((*E*)-**17** and (*Z*)-**17**). *a*)* At 0° a soln. of (*E*)-**16** (1.77 g, 2.6 ml) in pyridine (1.8 ml) was treated with TsCl (590 mg, 3.1 mmol) and stirred at 22° for 48 h (→ precipitation of a white solid). After completion of the conversion (TLC (toluene/Et_2O 9:1) control), H_2O was added to the mixture. The aq. layer was extracted with CH_2Cl_2, and the combined org. layers were worked up in the usual way (brine). FC (hexane/Et_2O 1:0 → 1:1) gave (*E*)-**17** (1.73 g, 80%) and (*Z*)-**17** (0.28 g, 13%), both as colourless oils.

b) The same procedure was applied to (*Z*)-**16** (1.40 g, 2.03 mmol) with TsCl (450 mg, 2.33 mmol) in pyridine (1.6 ml) to yield (*E*)-**17** (1.17 g, 69%) and (*Z*)-**17**/(*E*)-**17** 4:1 (0.35 g, 21%).

*Data of (*E*)-***17***: R_f* (toluene/Et_2O 9:1) 0.70. IR ($CHCl_3$): 3090*w*, 3069*m*, 3008*m*, 2933*m*, 2860*m*, 1956*w*, 1888*w*, 1816*w*, 1730*m*, 1602*m*, 1591*w*, 1497*m*, 1472*m*, 1455*m*, 1428*s*, 1393*w*, 1363*w*, 1337*w*, 1306*w*, 1265*m*, 1115*s*, 1070*s*, 1028*m*, 1010*m*, 930*s*, 866*w*, 823*m*, 640*w*, 616*m*, 558*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.21 (*s*, ^{t}Bu); 1.27 (*d*, *J* = 6.5, irrad. at 5.02 → *s*, 3 H–C(6)); 2.36 (*s*, Me); 3.45 (*dd*, *J* = 4.4, 8.4, H–C(3)); 3.85 (*dd*, *J* = 1.9, 8.4, irrad. at 5.02 → *d*, *J* = 8.4, irrad. at 3.45 → *d*, *J* = 1.9, H–C(4)); 4.20 (*dd*, *J* = 5.0, 8.0, irrad. at 3.45 → *d*, *J* = 8.1, H–C(2)); 4.21 (*d*, *J* = 12.0, PhC*H*); 4.23 (*d*, *J* = 11.8, PhC*H*); 4.49 (*d*, *J* = 11.6, 2 PhC*H*); 4.64 (*d*, *J* = 11.8, PhC*H*); 4.68 (*d*, *J* = 11.2, PhC*H*); 5.02 (*dq*, *J* = 1.7, 6.3, H–C(5)); 7.14–7.48 (*m*, 23 arom. H); 7.69–7.80 (*m*, 6 arom. H, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.10 (*q*, C(6)); 19.48 (*s*, Me_3C); 21.76 (*q*, Me); 27.30 (*q*, Me_3C); 71.14 (*t*, PhCH_2); 73.64 (*t*, PhCH_2); 74.24 (*t*, PhCH_2); 77.84 (*d*, C(2)); 79.91 (*d*, C(5)); 80.17 (*d*); 81.09 (*d*); 127.76–128.82 (several *d*, 21 arom. C); 130.17 (*d*, 2 arom. C); 130.24 (*d*, 1 arom. C); 130.27 (*d*, 1 arom. C); 133.59 (*s*, 1 arom. C); 133.76 (*s*, 1 arom. C); 134.48 (*s*, 1 arom. C); 136.04 (*d*, 4 arom. C); 137.91 (*s*, 1 arom. C); 138.02 (*s*, 1 arom. C); 138.26 (*s*, 1 arom. C); 144.91 (*s*, 1 arom. C); 154.96 (*d*, C(1)). FAB-MS: 688 (100, $[M+1]^+$), 580 (9), 199 (14), 181 (9), 137 (9), 136 (7), 105 (5).

*Data of (*Z*)-***17***: R_f* (toluene/Et_2O 9:1) 0.64. IR ($CHCl_3$): 3070*w*, 3008*m*, 2932*m*, 2860*m*, 1957*w*, 1889*w*, 1731*s*, 1599*w*, 1497*m*, 1472*m*, 1455*m*, 1428*m*, 1374*m*, 1361*m*, 1248*s*, 1176*s*, 1156*m*, 1114*s*, 1069*s*, 1046*m*, 1029*m*, 1008*m*, 917*m*, 869*w*, 818*s*, 634*w*, 607*m*, 568*m*, 556*m*, 504*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*, ^{t}Bu); 1.10–1.17 (*m*, 3 H–C(6)); 2.41 (*s*, Me); 3.87 (*dd*, *J* = 1.9, 9.3, H–C(3)); 4.11 (*dd*, *J* = 0.9, 9.3, H–C(4)); 4.31 (*d*, *J* = 11.5, PhC*H*); 4.35 (*d*, *J* = 12.1, PhC*H*); 4.39 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 11.8, PhC*H*); 4.58 (*d*, *J* = 11.5, PhC*H*); 4.82 (*d*, *J* = 11.5, PhC*H*); 5.01 (*dq*, *J* = 0.9, 6.2, H–C(5)); 4.20 (*dd*, *J* = 1.9, 5.3, H–C(2)); 7.14–7.48 (*m*, 23 arom. H, H–C(1)); 7.69–7.80 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.32 (*q*, C(6)); 19.35 (*s*, Me_3C); 21.70 (*q*, Me); 27.09 (*q*, Me_3C); 72.72 (*t*, PhCH_2); 72.84 (*d*, C(2)); 74.03 (*t*, PhCH_2); 74.76 (*t*, PhCH_2); 78.64 (*d*, C(5)); 79.18 (*d*); 81.35 (*d*); 127.58–128.73 (several *d*, 21 arom. C); 130.06 (*d*, 2 arom. C); 130.19 (*d*, 1 arom. C); 130.22 (*d*, 1 arom. C); 133.18 (*s*, 1 arom. C); 133.25 (*s*, 1 arom. C); 134.49 (*s*, 1 arom. C); 135.81 (*d*, 4 arom. C); 137.58 (*s*, 2 arom. C); 138.55 (*s*, 1 arom. C); 144.76 (*s*, 1 arom. C); 158.47 (*d*, C(1)).

*Decomposition of (*E*)-***17***.* (*E*)-**17** (50 mg, 73 μmol) was allowed to stand for 4 d at 23°. FC of the resulting yellow oil gave (*E*)-**17** (37 mg, 75%) and (*E*)-(**18**) (7 mg, 16%), both as colourless oils.

*Data of (*E*)-2,5-Anhydro-3,4-di-*O*-benzyl-6-deoxy-*L*-galactose* O-[(tert-Butyl)diphenylsilyl]oxime ((*E*)-**18**): R_f* (toluene/Et_2O 9:1) 0.71. IR ($CHCl_3$): 3089*w*, 3071*m*, 3007*s*, 2960*s*, 2933*s*, 2892*m*, 2860*m*, 1957*w*, 1887*w*, 1819*w*, 1743*w*, 1599*m*, 1590*m*, 1497*m*, 1472*s*, 1454*s*, 1428*s*, 1392*m*, 1362*m*, 1308*w*, 1263*m*, 1176*s*, 1115*s*, 1068*s*, 1028*s*, 932*s*, 823*s*, 610*w*, 556*w*, 507*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*s*, ^{t}Bu); 1.33 (*d*, *J* = 6.5, 3 H–C(6)); 3.88

(*t*, $J \approx 4.0$, H–C(4)); 4.08 (*dq*, $J = 4.0, 6.2$, H–C(5)); 4.22 (*dd*, $J = 4.1, 7.5$, H–C(3)); 4.45 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 12.5$, PhC*H*); 4.61 (*dd*, $J = 7.2, 8.4$, H–C(2)); 4.65 (*d*, $J = 11.8$, PhC*H*); 4.92 (*d*, $J = 12.1$, PhC*H*); 7.20–7.43 (*m*, 16 arom. H); 7.62–7.75 (*m*, 4 arom. H); 7.87 (*d*, $J = 8.4$, H–C(1)). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.94 (*q*, C(6)); 19.42 (*s*, Me_3C); 27.18 (*q*, *Me*$_3$C); 72.42 (*t*, Ph*C*H$_2$); 73.63 (*t*, Ph*C*H$_2$); 76.07 (*d*); 76.59 (*d*); 79.00 (*d*); 81.67 (*d*); 127.62–129.88 (several *d*, 14 arom. C); 130.11 (*d*, 2 arom. C); 133.89 (*s*, 1 arom. C); 134.02 (*s*, 1 arom. C); 135.87 (*d*, 4 arom. C); 138.60 (*s*, 1 arom. C); 138.92 (*s*, 1 arom. C); 156.23 (*d*, C(1)). FAB-MS: 1159 (1, $[2M+1]^+$), 580 (100, $[M+1]^+$), 578 (9), 522 (10), 199 (10), 154 (12), 91 (47).

1,5-Anhydro-2,3,4-tri-O-*benzyl-1,6-dideoxy-1-imino*-L-*galactitol* N-*Oxide* (**1**) *and* (E)*-2,5-Anhydro-3,4-di*-O-*benzyl-6-deoxy*-L-*galactose Oxime* ((*E*)-**19**). A soln. of (*E*)-**17**/(*Z*)-**17** 6:1 (1.86 g, 2.21 mmol) in anh. THF (75 ml) was treated at 0° dropwise with $Et_3N \cdot 3$ HF (4.4 ml), stirred for 2.5 h at 0°, diluted with Et_2O, and worked up in the usual way (H_2O). The crude intermediate was dissolved in anh. THF (19 ml), treated with $NH_2OH \cdot HCl$ (1.23 g, 17.7 mmol) and Et_3N (2.5 ml, 17.7 mmol), and heated to 60° for 36 h. Cooling to 25°, dilution with Et_2O, workup in the usual way (H_2O) and FC (hexane/AcOEt 3:1 → 0:1) gave (*E*)-**19** (150 mg, 20%) and **1** (590 mg, 62%), both as colourless oils.

Data of **1**: R_f (AcOEt/hexane 3:1) 0.11. UV (MeOH): 247 (3.90). IR ($CHCl_3$): 3090*w*, 3068*w*, 3007*s*, 2941*m*, 2871*m*, 1952*w*, 1811*w*, 1716*w*, 1588*s*, 1497*m*, 1455*s*, 1352*m*, 1311*w*, 1248*w*, 1147*m*, 1069*s*, 1028*s*, 912*w*, 823*w*, 603*w*, 531*w*, 507*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.55 (*d*, $J = 6.5$, 3 H–C(6)); 3.87 (*dd*, $J = 1.9, 6.9$, irrad. at 4.51 → *d*, $J = 1.9$, H–C(3)); 3.90–4.02 (*m*, irrad. at 1.55 → *dd*, $J = 1.9, 3.7$, irrad. at 7.05 → change, H–C(5)); 4.00 (*dd*, $J = 2.2, 3.7$, H–C(4)); 4.51 (*ddd*, $J = 1.9, 3.1, 6.8$, irrad. at 7.05 → *dd*, $J = 1.9, 6.8$, H–C(2)); 4.64 (*d*, $J = 11.5$, PhC*H*); 4.65 (*d*, $J = 11.5$, PhC*H*); 4.67 (*d*, $J = 11.5$, PhC*H*); 4.69 (*d*, $J = 11.5$, PhC*H*); 4.76 (*s*, PhC*H*$_2$); 7.05 (*dd*, $J = 1.9, 2.5$, H–C(1)); 7.24–7.37 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.54 (*q*, C(6)); 66.90 (*d*, C(5)); 70.00 (*t*, Ph*C*H$_2$); 72.63 (*t*, Ph*C*H$_2$); 73.14 (*d*, C(2)); 75.05 (*t*, Ph*C*H$_2$); 75.24 (*d*); 78.56 (*d*); 127.87–128.86 (several *d*, 15 arom. C); 133.68 (*d*, C(1)); 137.60 (*s*, 1 arom. C); 137.94 (*s*, 1 arom. C); 138.05 (*s*, 1 arom. C). FAB-MS: 863 (49, $[2M+1]^+$), 432 (100, $[M+1]^+$), 391 (11).

Data of (E)-**19**: R_f (toluene/Et_2O 8:2) 0.16. IR ($CHCl_3$): 3538*m*, 3089*w*, 3067*w*, 3008*s*, 2977*w*, 2930*m*, 2872*m*, 1952*w*, 1879*w*, 1813*w*, 1711*w*, 1587*w*, 1496*m*, 1454*s*, 1417*m*, 1365*m*, 1318*m*, 1248*m*, 1165*m*, 1086*s*, 1028*s*, 1009*s*, 910*m*, 871*w*, 822*w*, 603*m*, 554*w*, 503*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.33 (*d*, $J = 6.5$, 3 H–C(6)); 3.90 (*t*, $J \approx 4.1$, H–C(4)); 4.10 (*dq*, $J = 4.1, 6.5$, H–C(5)); 4.3 (*dd*, $J = 4.1, 7.2$, H–C(3)); 4.56 (*d*, $J = 12.1$, PhC*H*); 4.60–4.67 (*m*, H–C(2)); 4.63 (*d*, $J = 12.1$, PhC*H*); 4.64 (*d*, $J = 12.1$, PhC*H*); 4.83 (*d*, $J = 12.1$, PhC*H*); 7.20–7.38 (*m*, 10 arom. H); 7.71 (*d*, $J = 8.4$, H–C(1)).

Desilylation of (E)-**17**/(*Z*)-**17**. In an additional exper., FC of the crude after desilylation of (*E*)-**17**/(*Z*)-**17** 6:1 (53 mg, 63 μmol), which was carried out as described above (75 μl $Et_3N \cdot 3$ HF, 1.5 ml THF), gave (*E*)-**2** (26 mg, 69%), (*Z*)-**2** (4 mg, 11%), and (*E*)-**19** (3 mg, 16%), all as colourless oils.

Data of (E)-**2**: R_f (toluene/Et_2O 8:2) 0.35. IR ($CHCl_3$): 3581*m*, 3333*w*, 3090*w*, 3067*w*, 3008*m*, 2928*m*, 2872*m*, 1732*w*, 1599*w*, 1497*s*, 1455*m*, 1399*w*, 1358*s*, 1307*m*, 1292*m*, 1262*w*, 1177*s*, 1095*s*, 1071*s*, 1028*m*, 917*s*, 872*m*, 818*m*, 556*m*, 534*w*, 525*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*d*, $J = 6.5$, 3 H–C(6)); 2.40 (*s*, Me); 3.64 (*dd*, $J = 4.4, 8.4$, H–C(3)); 3.94 (*dd*, $J = 1.6, 8.4$, H–C(4)); 4.23 (*dd*, $J = 4.4, 7.8$, H–C(2)); 4.27 (*d*, $J = 11.2$, PhC*H*); 4.32 (*d*, $J = 11.5$, PhC*H*); 4.50 (*d*, $J = 11.2$, PhC*H*); 4.59 (*d*, $J = 11.8$, PhC*H*); 4.96 (*d*, $J = 11.2$, 2 PhC*H*); 5.00 (*dq*, $J = 1.6, 6.5$, H–C(5)); 7.21–7.35 (*m*, 17 arom. H, OH); 7.43 (*d*, $J = 7.8$, H–C(1)); 7.72 (*td*, $J \approx 1.9, 8.7$, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.72 (*q*, C(6)); 21.51 (*q*, Me); 72.18 (*t*, Ph*C*H$_2$); 73.41 (*t*, Ph*C*H$_2$); 74.01 (*t*, Ph*C*H$_2$); 77.44 (*d*); 79.35 (*d*); 79.95 (*d*); 80.81 (*d*); 127.60–128.48 (several *d*, 17 arom. C); 129.82 (*d*, 2 arom. C); 134.14 (*s*, 1 arom. C); 137.56 (*s*, 2 arom. C); 137.94 (*s*, 1 arom. C); 144.61 (*s*, 1 arom. C); 153.08 (*d*, C(1)). FAB-MS: 604 (27, $[M+1]^+$), 601 (30), 587 (33), 543 (34), 522 (27), 432 (64), 342 (46), 327 (32), 207 (29), 181 (42), 154 (58), 136 (88), 107 (42).

Data of (Z)-**2**: R_f (toluene/Et_2O 8:2) 0.38. IR ($CHCl_3$): 3581*m*, 3325*m*, 3090*m*, 3067*m*, 3008*m*, 2930*m*, 2872*m*, 1952*w*, 1734*w*, 1599*m*, 1497*m*, 1454*s*, 1397*m*, 1359*s*, 1308*m*, 1261*m*, 1177*s*, 1153*m*, 1095*s*, 1070*s*, 1028*s*, 917*m*, 874*m*, 818*m*, 598*w*, 556*m*, 521*w*, 505*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*d*, $J = 6.5$, 3 H–C(6)); 2.39 (*s*, Me); 3.69 (*dd*, $J = 2.8, 8.7$, H–C(3)); 4.01 (*dd*, $J = 1.3, 8.6$, H–C(4)); 4.25 (*d*, $J = 11.5$, PhC*H*); 4.32 (*d*, $J = 11.5$, PhC*H*); 4.45 (*d*, $J = 11.5$, PhC*H*); 4.57 (*d*, $J = 11.5$, PhC*H*); 4.66 (*d*, $J = 11.2$, PhC*H*); 4.72 (*d*, $J = 11.2$, PhC*H*); 4.98 (*dq*, $J = 1.6, 6.5$, H–C(5)); 5.01 (*dd*, $J = 2.8, 5.9$, H–C(2)); 6.96 (*d*, $J = 5.9$, H–C(1)); 7.19–7.35 (*m*, 17 arom. H); 7.73 (*td*, $J \approx 1.9, 8.7$, 2 arom. H); 7.99 (br. *s*, addition of D_2O → exchange, OH). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.55 (*q*, C(6)); 21.68 (*q*, Me); 72.20 (*d*, C(2)); 72.34 (*t*, Ph*C*H$_2$); 73.74 (*t*, Ph*C*H$_2$); 74.05 (*t*, Ph*C*H$_2$); 78.48 (*d*); 79.44 (*d*); 81.33 (*d*); 127.79–128.67 (several *d*, 17 arom. C); 130.00 (*d*, 2 arom. C); 134.22 (*s*, 1 arom. C); 137.64 (*s*, 2 arom. C); 138.41 (*s*, 1 arom. C); 144.53 (*s*, 1 arom. C); 153.08 (*d*, C(1)). FAB-MS: 604 (27, $[M+1]^+$), 432 (41), 327 (60), 281 (100), 221 (60), 206 (80), 91 (100).

2,3,4-Tri-O-*benzyl-5,6-dideoxy-5-(hydroxyamino)*-α-L-*galactopyranose 2′,3′,4′*-Tri-O-*benzyl-5′,6′-dideoxy-5′-(hydroxyamino)*-β-L-*galactopyranose 1*,N′:*1′*,N-*Dianhydride* (=*(1*R,*2*S,*3*S,*4*R,*4a*S,*7*R,*8*S,*9*S,*10*R,*10a*R)*-2,3,4,8,9,10-Hexakis(benzyloxy)octahydro-1,7-dimethyl-1*H,*7*H-*dipyrido[1,2*-b:*1′,2′*-e*][1,4,2,5]dioxadiazine*; **21**). A soln. of **1** (80 mg, 0.19 mmol) in CH_2Cl_2 (1 ml) was treated with an aq. $FeCl_3$ soln. (1.9 ml, 0.2 mM) and stirred at 21° for 2 d. Addition of CH_2Cl_2, usual workup (H_2O), and FC (hexane/AcOEt 1:0 → 1:1) gave **21** (35 mg, 44%). Colourless solid. M.p. 178–179 (dec.) R_f (pentane/AcOEt 5:1) 0.70. IR ($CHCl_3$): 3089*w*, 3067*w*, 3007*s*, 2938*m*, 2875*m*, 1952*w*, 1877*w*, 1812*w*, 1604*w*, 1497*m*, 1454*s*, 1356*m*, 1284*w*, 1265*m*, 1153*s*, 1118*s*, 1048*s*, 1028*s*, 965*m*, 911*m*, 856*w*, 818*w*, 631*w*, 600*w*, 536*w*, 526*w*, 516*w*, 508*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.18 (*d*, *J* = 6.2, 3 H–C(6′)); 1.20 (*d*, *J* = 6.3, 3 H–C(6)); 2.69 (*dq*, *J* = 2.0, 6.2, H–C(5′)); 3.49 (*dd*, *J* = 3.0, 9.8, H–C(3′)); 3.67–3.70 (*m*, H–C(3), H–C(5), H–C(4′)); 3.72 (br. *s*, H–C(4)); 3.96 (*dd*, *J* = 8.3, 9.8, H–C(2′)); 4.21 (*dd*, *J* = 3.3, 10.0, H–C(2)); 4.42 (*d*, *J* = 8.3, H–C(1′)); 4.60 (*d*, *J* = 11.4, PhC*H*); 4.66 (*d*, *J* = 11.6, PhC*H*); 4.67 (*d*, *J* = 11.8, PhC*H*); 4.69 (*d*, *J* = 11.6, PhC*H*); 4.70 (*d*, *J* = 10.8, PhC*H*); 4.74 (*d*, *J* = 11.9, PhC*H*); 4.76 (*d*, *J* = 11.3, PhC*H*); 4.82 (*d*, *J* = 11.7, PhC*H*); 4.83 (*d*, *J* = 11.8, PhC*H*); 4.88 (*d*, *J* = 10.8, PhC*H*); 4.94 (*d*, *J* = 11.3, PhC*H*); 4.96 (*d*, *J* = 11.3, PhC*H*); 5.85 (*d*, *J* = 3.3, H–C(1)); 7.27–7.35 (*m*, 30 arom. H). FAB-MS: 863 (20, $[M+1]^+$), 518 (25), 459 (29), 432 (92), 401 (27), 342 (34), 281 (60), 267 (30), 221 (50), 207 (66), 147 (100), 136 (58).

Treatment of **1** *with Me$_3$SiCN*. A soln. of **1** (110 mg, 0.26 mmol) in anh. CH_2Cl_2 (2.1 ml) was treated dropwise with freshly distilled Me_3SiCN (0.05 ml, 0.39 mmol) and a 1M soln. of Me_2AlCl in hexane (0.26 ml, 0.26 mmol) at 0° under Ar and stirred for 1.5 h. Addition of CH_2Cl_2 and usual workup (sat. aq. $NaHCO_3$ soln., H_2O) gave a crude mixture, which was treated with a 3% soln. of $TsOH \cdot H_2O$ in MeOH (3 ml) and stirred at 23° for 20 min. After addition of a sat. aq. soln. of $NaHCO_3$, evaporation of the org. solvent, and extraction of the aq., layer with CH_2Cl_2, usual workup (sat. aq. $NaHCO_3$ soln., H_2O) and FC (hexane/AcOEt 1:0 → 1:1) gave **29** (101 mg, 86%) and **27** (6 mg, 5%).

2,6-Anhydro-3,4,5-tri-O-*benzyl-2,7-dideoxy-2-(hydroxyamino)*-L-*glycero*-D-gluco-*heptononitrile* (**29**). Colourless solid. M.p. 144–145°. R_f (AcOEt/hexane 1:1) 0.26. $[\alpha]_D^{25} = -6.1$ (*c* = 0.91, $CHCl_3$). IR ($CHCl_3$): 3561*m*, 3355*m*, 3090*m*, 3067*m*, 3007*m*, 2941*m*, 2873*m*, 1952*w*, 1876*w*, 1812*w*, 1605*w*, 1497*m*, 1454*s*, 1368*m*, 1347*m*, 1315*m*, 1292*m*, 1262*s*, 1145*s*, 1112*s*, 1055*s*, 1028*s*, 1012*s*, 911*m*, 818*m*, 607*m*, 536*w*, 504*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.17 (*d*, *J* = 6.5, 3 H–C(7)); 3.00–3.11 (*m*, H–C(6)); 3.71 (*t*, *J* ≈ 2.9, H–C(5)); 4.25 (*dd*, *J* = 2.8, 9.6, H–C(4)); 4.15 (*dd*, *J* = 5.0, 10.0, H–C(3)); 4.36 (*d*, *J* = 5.0, H–C(2)); 4.60 (*d*, *J* = 11.2, PhC*H*); 4.62 (*d*, *J* = 11.5, PhC*H*); 4.75 (*d*, *J* = 11.5, PhC*H*); 4.82 (*d*, *J* = 11.8, PhC*H*); 4.86 (*d*, *J* = 11.2, PhC*H*); 4.94 (*d*, *J* = 11.5, PhC*H*); 5.30 (*s*, addition of D_2O → exchange, OH); 7.24–7.40 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.15 (*q*, C(7)); 60.28, 62.01 (2*d*, C(2), C(6)); 73.81 (*t*, Ph*C*H$_2$); 74.00 (*t*, Ph*C*H$_2$); 74.13 (*d*, C(4)); 75.89 (*t*, Ph*C*H$_2$); 77.10 (*d*); 81.44 (*d*); 115.48 (*s*, C(1)); 127.89–128.91 (several *d*, 15 arom. C); 137.79 (*s*, 1 arom. C); 138.16 (*s*, 1 arom. C); 138.52 (*s*, 1 arom. C). FAB-MS: 459 (21, $[M+1]^+$), 432 (21 $[M-CN]^+$), 355 (20), 342 (45), 327 (44), 281 (100), 267 (44), 221 (54), 207 (50), 147 (50).

2,6-Anhydro-3,4,5-tri-O-*benzyl-2,7-dideoxy-2-(hydroxyamino)*-L-glycero-D-manno-*heptononitrile* (**27**). Colourless oil. R_f (hexane/AcOEt 1:1) 0.28. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.20 (*d*, *J* = 5.9, 3 H–C(7)); 2.50–2.55 (*m*, H–C(6)); 3.43 (*dd*, *J* = 2.8, 10.0, H–C(4)); 3.50 (*d*, *J* = 10.0, H–C(2)); 3.72 (br. *s*, H–C(5)); 4.29 (*t*, *J* ≈ 10.0, H–C(3)); 4.67 (*d*, *J* = 11.5, PhC*H*); 4.74 (*d*, *J* = 11.5, PhC*H*); 4.79 (*d*, *J* = 11.8, PhC*H*); 4.92 (*d*, *J* = 12.0, PhC*H*); 4.97 (*d*, *J* = 12.0, PhC*H*); 4.99 (*d*, *J* = 11.5, PhC*H*); 5.73 (*s*, addition of D_2O → exchange, OH); 7.26–7.43 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.60 (*q*, C(7)); 63.45, 63.60 (2*d*, C(2), C(6)); 73.52 (*t*, Ph*C*H$_2$); 75.64 (*t*, Ph*C*H$_2$); 76.23 (*t*, Ph*C*H$_2$)); 76.39 (*d*); 77.35 (*d*); 83.71 (*d*); 117.78 (*s*, C(1)); 127.83–128.91 (several *d*, 15 arom. C); 137.51, 138.08 (2*s*, 3 arom. C).

Isolation of Me$_3$Si Adduct **28**. In an additional experiment FC of the crude after Me_3SiCN addition at **1** (110 mg, 0.26 mmol), which was carried out as described above (0.05 ml of Me_3SiCN, 0.26 ml of 1M Me_2AlCl in hexane, 2.1 ml of CH_2Cl_2), gave **26**/**28** *ca.* 1:15 (35 mg, 26%) and **27**/**29** *ca.* 1:15 (4 mg, 11%).

2,6-Anhydro-3,4,5-tri-O-*benzyl-2,7-dideoxy-2-{[(trimethylsilyl)oxy]amino}*-L-glycero-D-gluco-*heptononitrile* (**28**). Colourless oil. R_f (hexane/AcOEt 1:1) 0.62. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.08 (*s*, Me_3Si); 1.13 (*d*, *J* = 6.2, 3 H–C(7)); 2.98–3.02 (*m*, H–C(6)); 3.69 (*dd*, *J* = 1.9, 2.1, H–C(5)); 3.77–3.83 (*m*, H–C(4)); 4.09–4.15 (*m*, H–C(2)); 4.29 (*t*, *J* ≈ 10.0, H–C(3)); 4.59 (*d*, *J* = 11.5, PhC*H*); 4.65 (*d*, *J* = 12.1, PhC*H*); 4.77 (*d*, *J* = 11.8, PhC*H*); 4.87 (*d*, *J* = 11.5, PhC*H*); 4.94 (*d*, *J* = 11.5, PhC*H*); 4.98 (*d*, *J* = 11.5, PhC*H*); 7.26–7.43 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −0.37 (*q*, Me_3Si); 15.96 (*q*, C(7)); 61.52, 63.02 (2*d*, C(2), C(6)); 73.92 (*t*, Ph*C*H$_2$); 73.96 (*t*, Ph*C*H$_2$); 74.68 (*d*, C(4)); 75.67 (*t*, Ph*C*H$_2$); 77.74 (*d*); 81.31 (*d*); 115.79 (*s*, C(1)); 127.73–128.86 (*d*, 15 arom. C); 138.02 (*s*, 1 arom. C); 138.76 (*s*, 1 arom. C); 139.05 (*s*, 1 arom. C).

2,7-Diamino-2,6-anhydro-1,2,7-trideoxy-L-glycero-D-galacto-*heptitol Bis(hydrochloride)* (**30**). A soln. of **29** (54 mg, 0.13 mmol) in MeOH (10 ml) was treated with 1N HCl in Et_2O (0.5 ml) and 10% Pd/C (54 mg), and hydrogenated at 6 bar for 2 d. The mixture was filtered through *Celite* and evaporated (→ slightly yellow

colour). The residue was dissolved in MeOH and treated with 0.01N HCl in Et_2O leading to precipitation of **30** (18 mg, 75%). Slightly yellow solid. R_f (CH_2Cl_2/MeOH/20% aq. NH_3 soln. 5:4:1, developed with ninhydrin) 0.23. $[\alpha]_D^{25} = -3.40$ ($c = 1.0$, MeOH). IR (KBr): 3389*m* (br.), 2928*m*, 1627*w*, 1457*m*, 1160*w*, 1076*s*, 1049*m*, 960*w*, 877*w*, 575*m*. ^{1}H-NMR (300 MHz, D_2O): 1.37 (*d*, $J = 6.5$, 3 H–C(1)); 3.40 (*dd*, $J = 4.4$, 14.0, 1 H–C(7)); 3.60 (*dq*, $J = 1.6$, 6.5, H–C(2)); 3.71 (*dd*, $J = 8.4$, 14.0, 1 H–C(7)); 3.87 (*dd*, $J = 3.1$, 9.7, irrad. at 4.24 → *d*, $J = 3.1$, H–C(4)); 4.00–4.06 (*m*, irrad. at 4.24 → change, H–C(3), H–C(6)); 4.24 (*dd*, $J = 5.6$, 9.7, H–C(5)). ^{13}C-NMR (75 MHz, D_2O): 16.42 (*q*, C(1)); 38.83 (*t*, C(7)); 54.23, 54.91 (2*d*, C(2), C(6)); 68.65 (*d*, C(4)); 71.62 (*d*); 72.06 (*d*). ESI-MS (CH_3OH): 177 (100, $[M - HCl_2]^+$), 160 (81), 130 (18), 100 (32), 57 (45), 56 (31), 44 (89).

Cycloaddition of **1** *and Methyl Acrylate.* A soln. of **1** (255 mg, 0.6 mmol) in anh. toluene (2.6 ml) was treated with methyl acrylate (0.51 ml, 6 mmol) and stirred for 15 h at 22°. Evaporation and FC (hexane/AcOEt 2:1 → 1:1) gave **31** (168 mg, 55%) and **32** (115 mg, 34%).

*Methyl 2,*N*:4,8-Dianhydro-5,6,7-tri-*O*-benzyl-3,4,9-trideoxy-4-(hydroxyamino)-*L*-*threo*-*D*-ido-nononate* (**31**): Colourless oil. R_f (hexane/Et_2O 1:1). 0.11. $[\alpha]_D^{25} = 20.2$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3008*s*, 2929*s*, 2856*m*, 1742*s*, 1602*m*, 1497*m*, 1454*s*, 1438*m*, 1352*s*, 1261*m*, 1152*s*, 1116*s*, 1058*s*, 1028*s*, 912*w*, 649*w*, 603*w*, 514*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.35 (*d*, $J = 6.2$, 3 H–C(9)); 2.19–2.26 (*m*, 2 H–C(3)); 2.40–2.48 (*m*, H–C(8)); 3.32 (*s*, MeO); 3.41–3.44 (*m*, H–C(6), H–C(7)); 4.13 (*td*, $J \approx 6.5$, 11.5, H–C(4)); 4.28 (*d*, $J = 11.8$, PhC*H*); 4.43 (*d*, $J = 11.5$, PhC*H*); 4.45–4.53 (*m*, H–C(2), H–C(5)); 4.54 (*d*, $J = 11.8$, PhC*H*); 4.62 (*d*, $J = 12.1$, PhC*H*); 4.69 (*d*, $J = 12.2$, PhC*H*); 4.94 (*d*, $J = 11.2$, PhC*H*); 7.24–7.39 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.82 (*q*, C(9)); 32.85 (*t*, C(3)); 51.99 (*q*, MeO); 56.37, 62.34 (2*d*, C(4), C(8)); 72.63 (*t*, Ph*C*H$_2$); 73.07 (*t*, 2 Ph*C*H$_2$); 74.34, 75.36, 76.79 (3*d*, C(5), C(6), C(7)); 79.14 (br. *d*, C(2)); 127.07–128.03 (several *d*, 15 arom. C); 137.86 (*s*, 1 arom. C); 137.99 (*s*, 1 arom. C); 138.08 (*s*, 1 arom. C); 171.35 (*s*, C(1)). FAB-MS: 518 (100, $[M+1]^+$), 502 (11), 458 (9), 426 (13), 410 (8), 91 (39). Anal. calc. for $C_{31}H_{35}NO_6$ (517.62): C 71.93, H 6.82, N 2.71 found: C 71.67, H 6.99, N 2.49.

*Methyl 2,*N*:4,8-Dianhydro-5,6,7-tri-*O*-benzyl-3,4,9-trideoxy-4-(hydroxyamino)-*L*-*threo*-*D*-gulo-nononate* (**32**): Colourless oil. M.p. 119–120°. R_f (hexane/Et_2O 1:1) 0.16. $[\alpha]_D^{25} = 27.1$ ($c = 1.00$, $CHCl_3$). IR ($CHCl_3$): 3067*w*, 3008*s*, 2929*s*, 2856*m*, 1741*s*, 1602*m*, 1497*m*, 1454*s*, 1438*m*, 1352*s*, 1261*m*, 1152*s*, 1116*s*, 1058*s*, 1028*s*, 912*w*, 649*w*, 603*w*, 514*w*. ^{1}H-NMR (300 MHz, C_5D_5Cl, 75°): 1.54 (*d*, $J = 5.9$, 3 H–C(9)); 2.30 (*ddd*, $J = 6.2$, 8.7, 12.8, 1 H–C(3)); 2.52 (*td*, $J \approx 8.7$, 12.5, 1 H–C(3)); 3.15 (*dq*, $J = 1.7$, 5.9, H–C(8)); 3.36 (*s*, MeO); 3.50–3.57 (*m*, H–C(7)); 3.56 (*dd*, $J = 2.8$, 9.7, H–C(6)); 3.81 (*td*, $J = 5.9$, 8.2, H–C(4)); 4.31 (*t*, $J \approx 8.7$, H–C(2)); 4.44 (*dd*, $J = 5.9$, 9.7, H–C(5)); 4.50 (*d*, $J = 11.5$, PhC*H*); 4.51 (*d*, $J = 11.8$, PhC*H*); 4.53 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 12.1$, PhC*H*); 4.57 (*d*, $J = 12.5$, PhC*H*); 4.87 (*d*, $J = 11.2$, PhC*H*); 7.06–7.38 (*m*, 15 arom. H). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.23 (*d*, $J = 6.2$, 3 H–C(9)); 2.44 (*td*, $J = 9.0$, 12.8, 1 H–C(3)); 2.60 (*ddd*, $J = 6.8$, 8.4, 13.1, 1 H–C(3)); 2.86–3.00 (*m*, H–C(8)); 3.68 (*dd*, $J = 2.8$, 9.7, H–C(6)); 3.68–3.76 (*m*, H–C(7)); 3.73 (*s*, MeO); 3.80–3.90 (*m*, H–C(4)); 4.51 (*t*, $J \approx 9.0$, H–C(2)); 4.42–4.52 (*m*, H–C(5)); 4.65 (*d*, $J = 11.5$, PhC*H*); 4.70 (*d*, $J = 11.5$, PhC*H*); 4.73 (*d*, $J = 11.8$, PhC*H*); 4.74 (*d*, $J = 11.2$, PhC*H*); 4.82 (*d*, $J = 11.8$, PhC*H*); 4.92 (*d*, $J = 11.5$, PhC*H*); 7.24–7.39 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.29 (br. *q*, C(9)); 33.64 (*t*, C(3)); 52.45 (*q*, MeO); 57.48, 64.31 (2*d*, C(4), C(8)); 73.16 (*t*, Ph*C*H$_2$); 73.78 (*t*, Ph*C*H$_2$); 75.04 (*t*, Ph*C*H$_2$); 75.77, 77.30, 77.59 (3*d*, C(5), C(6), C(7)); 80.30 (br. *d*, C(2)); 127.66–128.77 (several *d*, 15 arom. C); 138.65 (*s*, 2 arom. C); 138.78 (*s*, 1 arom. C); 173.88 (*s*, C(1)). FAB-MS: 1035 (1, $[2M+1]^+$), 518 (100, $[M+1]^+$), 502 (3), 458 (7), 426 (13), 410 (9), 91 (33).

*4-Amino-4,8-anhydro-5,6,7-tri-*O*-benzyl-3,4,9-trideoxy-*L*-threo-*D*-ido-nonono-1,4-lactam* (**33**). A soln. of **31** (115 mg, 0.22 mmol) in AcOH (1.2 ml) was treated with Zn (110 mg, 1.68 mmol) at 21° and stirred at 60° for 4 h until complete conversion (TLC (hexane/AcOEt 1:2) control). Filtration, dilution with Et_2O, usual work-up (sat. aq. $NaHCO_3$ soln., H_2O), and FC (hexane/AcOEt 1:0 → 1:2) gave **33** (84 mg, 78%). Colourless oil. R_f (hexane/AcOEt 1:2, developed with mostain) 0.11. $[\alpha]_D^{25} = -58.9$ ($c = 0.98$, $CHCl_3$). IR ($CHCl_3$): 3470*m*, 3090*m*, 3067*m*, 3007*m*, 2961*m*, 2872*m*, 1952*w*, 1685*s*, 1497*m*, 1455*s*, 1439*m*, 1366*m*, 1287*s*, 1262*s*, 1169*m*, 1104*s*, 1028*s*, 910*w*, 865*w*, 818*m*, 640*w*, 602*w*, 575*w*, 540*w*, 530*w*, 516*w*, 504*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.39 (*d*, $J = 7.2$, 3 H–C(9)); 1.86 (*td*, $J \approx 5.0$, 13.4, 1 H–C(3)); 2.32 (*td*, $J \approx 8.1$, 13.4, 1 H–C(3)); 3.04 (*d*, $J = 7.5$, addition of D_2O → exchange, OH); 3.45 (*dd*, $J = 2.8$, 3.4, H–C(5)); 3.76 (*dd*, $J = 2.8$, 6.5, H–C(7)); 3.95 (*t*, $J \approx 3.1$, H–C(6)); 4.07 (*ddd*, $J = 2.8$, 5.0, 7.8, H–C(4)); 4.21 (*ddd*, $J = 5.3$, 7.5, 8.7, addition of D_2O → *dd*, $J = 5.0$, 8.4, H–C(2)); 4.36 (*d*, $J = 11.5$, PhC*H*); 4.40 (*d*, $J = 12.8$, PhC*H*); 4.44 (*d*, $J = 12.8$, PhC*H*); 4.58 (*d*, $J = 11.8$, PhC*H*); 4.64 (*quint.*, $J \approx 6.8$, H–C(8)); 4.68 (*d*, $J = 12.1$, PhC*H*); 4.86 (*d*, $J = 12.1$, PhC*H*); 7.12–7.16 (*m*, 2 arom. H); 7.26–7.41 (*m*, 13 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.88 (*q*, C(9)); 28.62 (*t*, C(3)); 45.64, 49.44 (2*d*, C(4), C(8)); 70.49 (*d*); 71.40 (*t*, Ph*C*H$_2$); 72.79 (*t*, Ph*C*H$_2$); 73.61 (*d*); 73.90 (*t*, Ph*C*H$_2$); 74.79 (*d*); 75.78 (*d*); 127.73–128.96 (several *d*, 15 arom. C); 136.84 (*s*, 1 arom. C); 138.41 (*s*, 1 arom. C); 138.65

(*s*, 1 arom. C); 173.56 (*s*, C(1)). FAB-MS: 975 (12, $[2M+1]^+$), 488 (100, $[M+1]^+$), 181 (7), 133 (12), 91 (96). Anal. calc. for $C_{30}H_{33}NO_5 \cdot 1.125\ H_2O$ (507.87): C 70.95, H 6.94, N 2.76; found: C 70.85, H 6.69, N 2.66.

4-Amino-4,8-anhydro-5,6,7-tri-O-*benzyl-3,4,9-trideoxy*-L-threo-D-gulo-*nonono-1,4-lactam* (**34**). The procedure for the conversion of **31** to **33** was applied to **32** (69 mg, 0.13 mmol) in AcOH (0.7 ml) with Zn (70 mg, 1.1 mmol) to give **34** (51 mg, 78%). Colourless oil. R_f (hexane/AcOEt 1:2, developed with mostain) 0.11. $[\alpha]_D^{25} = -15.6$ ($c = 0.94$, $CHCl_3$). IR ($CHCl_3$): 3571*m*, 3369*m*, 3090*w*, 3067*m*, 3008*m*, 2961*m*, 2872*m*, 1952*w*, 1812*w*, 1681*s*, 1496*m*, 1455*s*, 1439*m*, 1367*m*, 1354*m*, 1289*s*, 1262*s*, 1100*s*, 1027*s*, 908*m*, 886*m*, 818*m*, 605*m*, 560*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.43 (*d*, $J = 7.2$, 3 H–C(9)); 1.94 (*ddd*, $J = 7.7, 9.3, 13.4$, H–C(3)); 2.15 (*ddd*, $J =$ 1.3, 9.0, 13.4, H–C(3)); 2.94 (*s*, OH); 3.46 (*dd*, $J = 2.2, 3.7$, H–C(5)); 3.67 (*dd*, $J = 2.8, 6.5$, H–C(7)); 3.90 (*t*, $J \approx 3.1$, H–C(6)); 4.13 (*td*, $J \approx 1.8, 9.3$, H–C(4)); 4.31 (*d*, $J = 11.5$, PhC*H*); 4.39–4.45 (*m*, H–C(2)); 4.43 (*d*, $J = 11.8$, PhC*H*); 4.45 (*d*, $J = 11.8$, PhC*H*); 4.50 (*d*, $J = 12.1$, PhC*H*); 4.59 (*quint.*, $J \approx 6.9$, H–C(8)); 4.67 (*d*, $J = 11.8$, PhC*H*); 4.86 (*d*, $J = 11.8$, PhC*H*); 7.10–7.14 (*m*, 2 arom. H); 7.22–7.40 (*m*, 13 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.47 (*q*, C(9)); 29.23 (*t*, C(3)); 45.64, 49.46 (2*d*, C(4), C(8)); 70.35 (*d*); 71.43 (*t*, Ph*C*H$_2$); 72.50 (*t*, Ph*C*H$_2$); 73.94 (*t*, Ph*C*H$_2$); 74.02 (*d*); 74.96 (*d*); 77.33 (*d*); 127.66–128.85 (several *d*, 15 arom. C); 133.61 (*s*, 1 arom. C); 138.49 (*s*, 1 arom. C); 138.75 (*s*, 1 arom. C); 174.61 (*s*, C(1)). FAB-MS: 975 (2, $[2M+1]^+$), 488 (100, $[M+1]^+$), 133 (18), 91 (23). Anal. calc. for $C_{30}H_{33}NO_5 \cdot 0.5H_2O$ (496.61): C 72.56, H 6.90, N 2.82; found: C 72.63, H 6.92, N 2.75.

4-Amino-4,8-anhydro-2-O-*benzoyl-5,6,7-tri*-O-*benzyl-3,4,9-trideoxy*-L-threo-D-gulo-*nonono-1,4-lactam and Its Conversion to* **34**. A soln. of **33** (18 mg, 37 µmol) in anh. Et_2O (0.15 ml) was treated with diethyl diazenedicarboxylate (DEAD; 8.5 µl, 55.5 µmol), benzoic acid (7 mg, 55.5 µmol), and Ph_3P (15 mg, 55.5 µmol) and stirred for 18 h at 22°. The mixture was filtered, diluted with Et_2O and worked up as usual (H_2O). Preparative TLC (hexane/AcOEt 1:2) gave the title compound (18 mg, 83%). Colourless oil. R_f (hexane/AcOEt 1:2, developed with mostain) 0.46. IR ($CHCl_3$): 3089*w*, 3067*w*, 3008*m*, 2942*w*, 2872*w*, 1694*s*, 1603*w*, 1586*w*, 1469*w*, 1453*m*, 1353*m*, 1353*m*, 1316*m*, 1296*m*, 1274*s*, 1116*s*, 1072*s*, 1027*m*, 904*w*, 868*w*, 818*w*, 603*w*, 572*w*, 524*w*, 513*w*, 502*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.48 (*d*, $J = 7.2$, 3 H–C(9)); 2.00 (*ddd*, $J = 7.7, 9.0, 13.4$, 1 H–C(3)); 2.45 (*ddd*, $J = 1.6, 9.0, 13.4$, 1 H–C(3)); 3.49 (*dd*, $J = 1.9, 3.4$, H–C(5)); 3.73 (*dd*, $J = 2.8, 6.2$, H–C(7)); 3.91 (*t*, $J \approx 3.1$, H–C(6)); 4.20 (*td*, $J \approx 1.9, 9.3$, H–C(4)); 4.38 (*d*, $J = 11.8$, PhC*H*); 4.45 (*d*, $J = 11.5$, PhC*H*); 4.49 (*d*, $J = 12.5$, PhC*H*); 4.57 (*d*, $J = 12.1$, PhC*H*); 4.68 (*d*, $J = 11.8$, PhC*H*); 4.70 (*quint.*, $J \approx 6.9$, H–C(8)); 4.87 (*d*, $J = 11.8$, PhC*H*); 5.61 (*dd*, $J = 7.5, 9.0$, H–C(2)); 7.19–7.22 (*dd*, $J = 1.6, 6.9$, 2 arom. H); 7.26–7.40 (*m*, 15 arom. H); 7.56 (*tt*, $J \approx 1.3, 7.2$, 1 arom. H); 8.08 (*dd*, $J = 1.6, 6.9$, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.48 (*q*, C(9)); 28.92 (*t*, C(3)); 45.48, 49.11 (2*d*, C(4), C(8)); 70.98 (*d*); 71.90 (*t*, Ph*C*H$_2$); 72.05 (*t*, Ph*C*H$_2$)); 73.42 (*t*, Ph*C*H$_2$)); 73.45 (*d*); 74.28 (*d*); 76.64 (*d*); 127.66–128.85 (several *d*, 20 arom. C); 132.78 (*s*, 1 arom. C); 137.34 (*s*, 1 arom. C); 138.06 (*s*, 1 arom. C); 138.24 (*s*, 1 arom. C); 169.42 (*s*, 1 C=O); 173.41 (*s*, C(1)). FAB-MS: 592 ($[M+1]^+$, 100), 281 (5), 207 (5), 147 (13), 136 (7), 104 (31).

A soln. of the 2-*O*-benzoyl derivative (see above) (10 mg, 17 µmol) in a 1% soln. of NaOMe in MeOH (1 ml) was stirred for 2 h at 22°. After addition of sat. aq. NH_4Cl soln. and extraction with Et_2O, the combined org. layers were worked up in the usual way (brine). Prep. TLC (hexane/AcOEt 1:3) gave **34** (7 mg, 85%). Colourless oil.

4-Amino-4,8-anhydro-3,4,9-trideoxy-L-threo-D-ido-*nonono-1,4-lactam* (**35**). A suspension of **33** (32 mg, 65.7 µmol) and 20% $Pd(OH)_2$/C on charcoal (16 mg) in AcOH/MeOH 1:1 (1 ml) was hydrogenated at 6 bar for 2 d. Filtration through *Celite*, evaporation, FC (AcOEt/MeOH/H_2O 20:5:2), and lyophilization yielded **35** (12 mg, 84%). Colourless amorphous solid. R_f (AcOEt/MeOH/H_2O 13:5:2, developed with mostain) 0.63. $[\alpha]_D^{25} = -31.2$ ($c = 0.7$, MeOH). IR (KBr): 3371*m* (br.), 3009*m*, 2975*m*, 2932*s*, 1668*s*, 1455*s*, 1442*m*, 1384*w*, 1366*w*, 1355*w*, 1320*w*, 1301*m*, 1276*m*, 1112*m*, 1093*m*, 1066*m*, 1042*m*, 1030*s*, 994*w*, 958*w*, 886*w*, 868*w*, 827*w*, 771*w*, 742*w*, 682*s*, 668*w*, 527*w*, 544*w*, 440*w*, 414*w*. ^{1}H-NMR (300 MHz, CD_3OD): 1.26 (*d*, $J = 7.2$, 3 H–C(9)); 1.87 (*td*, $J \approx 7.5$, 13.1, 1 H–C(3)); 2.36 (*ddd*, $J = 7.2$, 8.7, 13.1, 1 H–C(3)); 3.69 (*dd*, $J = 2.5$, 3.7, H–C(5)); 3.90 (*dd*, $J = 3.1$, 6.9, H–C(7)); 3.86 (*t*, $J \approx 3.1$, irrad. at $3.69 \rightarrow d$, $J = 3.1$, H–C(6)); 3.97 (*dt*, $J \approx 2.2$, 7.2, irrad. at $3.69 \rightarrow t$, $J \approx 7.5$, H–C(4)); 4.22 (*quint.* $J \approx 7.2$, irrad. at $1.26 \rightarrow d$, $J = 6.9$, H–C(8)); 4.26 (*dd*, $J = 7.5$, 8.4, H–C(2)). ^{13}C-NMR (75 MHz, CD_3OD): 13.11 (*q*, C(9)); 29.50 (*t*, C(3)); 49.65, 49.82 (2*d*, C(4), C(8)); 66.16 (*d*); 70.72 (*d*); 71.80 (*d*); 74.43 (*d*, C(2)); 176.26 (*s*, C(1)). CI-MS (MeOH): 218 (2, $[M+1]^+$), 217 (1), 145 (2), 127 (1), 110 (1), 100 (1), 100 (2), 45 (18), 43 (38), 33 (24), 32 (47), 31 (100), 29 (45), 28 (24).

4-Amino-4,8-anhydro-3,4,9-trideoxy-L-threo-D-gulo-*nonono-1,4-lactam* (**36**). A suspension of **34** (18 mg, 37 µmol) and 20% $Pd(OH)_2$/C (9 mg) in MeOH (1 ml) was hydrogenated at 6 bar for 24 h at 22°. Filtration through *Celite*, evaporation, FC (AcOEt/MeOH/H_2O 20:5:2), and lyophilization yielded **36** (7 mg, 87%). Colourless amorphous solid. R_f (AcOEt/MeOH/H_2O 13:5:2). $[\alpha]_D^{25} = 14.0$ ($c = 0.5$, MeOH). 0.57. IR (KBr): 3389*s*, 2926*m*, 1669*m*, 1573*m*, 1441*s*, 1297*m*, 1277*m*, 1245*w*, 1199*w*, 1129*w*, 1076*m*, 1045*m*, 989*w*, 908*w*, 872*w*,

661*w*, 618*w*. ^{1}H-NMR (300 MHz, CD_3OD): 1.30 (*d*, *J* = 7.2, 3 H–C(9)); 1.87 (*ddd*, *J* = 7.2, 9.3, 13.4, 1 H–C(3)); 2.36 (*ddd*, *J* = 1.9, 8.7, 13.4, 1 H–C(3)); 3.70 (*dd*, *J* = 1.9, 3.7, H–C(5)); 3.72 (*dd*, *J* = 3.4, 6.5, H–C(7)); 3.86 (*t*, *J* ≈ 3.4, H–C(6)); 4.09 (*td*, *J* ≈ 1.9, 9.3, H–C(4)); 4.22 (*quint.*, *J* ≈ 6.9, H–C(8)); 4.40 (*dd*, *J* = 7.5, 8.7, H–C(2)). ^{13}C-NMR (75 MHz, CD_3OD): 12.95 (*q*, C(9)); 30.94 (*t*, C(3)); 49.65, 50.62 (2*d*, C(4), C(8)); 66.28 (*d*); 71.69 (*d*); 72.84 (*d*); 74.50 (*d*, C(2)); 176.49 (*s*, C(1)). CI-MS (MeOH): 218 (100, $[M+1]^+$), 217 (15), 200 (14), 145 (50), 127 (19), 100 (26), 44 (23), 33 (27), 32 (47), 29 (36), 28 (31). CI-MS: 218 (100, $[M+1]$), 199 (14), 145 (50), 128 (13), 127 (19), 110 (11), 100 (26), 72 (12), 70 (13), 44 (23), 31 (92).

1-Amino-1,4:4,8-dianhydro-5,6,7-tri-O-*benzyl-1,3,9-trideoxy*-L-threo-D-ido-*nonitol* (**37**). A soln. of **33** (157 mg, 0.32 mmol) in H_2O-free THF (1.0 ml) was treated with a 1M soln. of BH_3 in THF (0.87 ml, 2.7 equiv.) at 0°. The resulting soln. was heated during 3 h to 60°. After cooling to 23°, MeOH (1 ml) was added, followed by 1N HCl in Et_2O (0.17 ml). The resulting mixture was evaporated *in vacuo* at 23°, the residue treated again with MeOH (1 ml) and 1N HCl in Et_2O (0.17 ml) and evaporated. After addition of Et_2O, the residue was worked up in the usual way (sat aq. $NaHCO_3$ soln., brine). FC (AcOEt) gave **37** (113 mg, 74%). Colourless oil. R_f (AcOEt) 0.10. $[\alpha]_D^{25} = -22.1$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3458*w*, 3089*w*, 3066*m*, 3007*s*, 2940*s*, 2870*s*, 2975*m*, 1951*w*, 1876*w*, 1811*w*, 1723*w*, 1605*w*, 1586*w*, 1496*m*, 1454*s*, 1402*m*, 1370*m*, 1310*m*, 1248*m*, 1159*s*, 1096*s*, 1066*s*, 1028*s*, 996*m*, 912*m*, 818*w*, 598*m*, 523*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.19 (*d*, *J* = 6.5, 3 H–C(9)); 1.67 (br. *dd*, *J* = 6.9, 13.7, irrad. at 3.16 → br. *d*, *J* = 13.7, 1 H–C(3)); 2.06 (*ddd*, *J* = 6.2, 8.7, 13.7, irrad. at 3.16 → *dd*, *J* = 6.5, 13.7, 1 H–C(3)); 2.60 (br. *s*, OH); 2.73–2.81 (*m*, 2 H–C(1)); 3.16 (*ddd*, *J* = 1.9, 6.8, 8.7, irrad. at 3.43 → change, H–C(4)); 3.43 (*dd*, *J* = 2.2, 3.1, irrad. at 3.16 → *d*, *J* = 3.1, H–C(5)); 3.55 (*quint.*, *J* ≈ 6.5, irrad. at 1.19 → *d*, *J* = 5.7, H–C(8)); 3.87 (*t*, *J* ≈ 3.1, irrad. at 3.43 → *d*, *J* = 3.1, H–C(6)); 3.94 (*dd*, *J* = 3.1, 5.9, H–C(7)); 4.10–4.20 (br. *s*, irrad. at 2.78 → *d*, *J* = 5.6, H–C(2)); 4.42 (*d*, *J* = 11.8, PhC*H*); 4.49 (*d*, *J* = 12.1, 2 PhC*H*); 4.54 (*d*, *J* = 12.1, PhC*H*); 4.63 (*d*, *J* = 12.1, PhC*H*); 4.79 (*d*, *J* = 12.1, PhC*H*); 7.22–7.37 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 6.67 (*q*, C(9)); 35.24 (*t*, C(3)); 51.32 (*d*); 52.41 (*d*, C(4), C(8)); 58.65 (*t*, C(1)); 70.25 (*d*); 71.04 (*t*, Ph*C*H$_2$); 72.85 (*t*, Ph*C*H$_2$); 73.43 (*t*, Ph*C*H$_2$); 75.31 (*d*); 75.75 (*d*); 76.22 (*d*); 127.47–128.56 (several *d*, 15 arom. C); 137.97 (*s*, 1 arom. C); 138.93 (*s*, 1 arom. C); 139.05 (*s*, 1 arom. C). FAB-MS: 474 (100, $[M+1]^+$), 382 (29), 327 (11), 325 (13), 281 (13), 207 (13), 147 (17), 134 (13), 91 (35).

1-Amino-1,4:4,8-dianhydro-5,6,7-tri-O-*benzyl-1,3,9-trideoxy*-L-threo-D-gulo-*nonitol* (**38**). The procedure for the conversion of **33** to **37** was applied to **34** (82 mg, 0.17 mmol) in H_2O-free THF (0.6 ml) with a 1M soln. of BH_3 in THF (0.45 ml, 0.45 mmol) to give **38** (73 mg, 85%). Colourless oil. R_f (AcOEt) 0.10. $[\alpha]_D^{25} = -3.6$ (*c* = 1.1, $CHCl_3$). IR ($CHCl_3$): 3608*w*, 3441*w*, 3088*w*, 3066*m*, 3008*s*, 2962*s*, 2866*m*, 1951*w*, 1875*w*, 1811*w*, 1722*w*, 1605*w*, 1496*m*, 1454*s*, 1398*m*, 1361*m*, 1311*m*, 1261*s*, 1159*s*, 1098*s*, 1028*s*, 915*m*, 865*m*, 818*s*, 598*m*, 509*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.23 (*d*, *J* = 6.8, irrad. at 3.45 → *s*, 3 H–C(9)); 1.46 (*ddd*, *J* = 1.9, 6.9, 13.1, irrad. at 4.50 → *dd*, *J* = 6.9, 13.1, irrad. at 3.30 → *dd*, *J* = 1.9, 13.0, H–C(3)); 1.98 (br. *s*, OH); 2.14 (*ddd*, *J* = 7.8, 8.1, 13.0, irrad. at 4.50 → *dd*, *J* = 8.1, 13.1, irrad. at 3.30 → *dd*, *J* = 7.8, 13.0, H–C(3)); 2.59 (*dd*, *J* = 4.7, 9.6, irrad. at 4.50 → *d*, *J* = 9.3, irrad. at 3.30 → *d*, *J* = 5.3, 1 H–C(1)); 3.30 (*dd*, *J* = 6.2, 9.6, irrad. at 4.50 → *d*, *J* = 9.6, irrad. at 2.59 → *d*, *J* = 5.9, 1 H–C(1)); 3.27–3-32 (*m*, irrad. at 3.45 → change, H–C(4)); 3.34–3.49 (*m*, irrad. at 1.23 → change, irrad. at 3.87 → change, irrad. at 3.30 → change, H–C(5), H–C(8)); 3.77 (*t*, *J* ≈ 3.1, irrad. at 3.45 → *d*, *J* = 3.1, irrad. at 3.87 → *d*, *J* = 2.7, H–C(6)); 3.87 (*dd*, *J* = 3.1, 5.3, irrad. at 3.45 → *d*, *J* = 2.9, H–C(7)); 4.39 (*d*, *J* = 12.1, PhC*H*); 4.43 (*d*, *J* = 11.8, PhC*H*); 4.44–4-53 (*m*, irrad. at 2.59 → change, irrad. at 3.30 → change, H–C(2)); 4.50 (*d*, *J* = 11.7, PhC*H*); 4.52 (*d*, *J* = 11.6, PhC*H*); 4.62 (*d*, *J* = 12.1, PhC*H*); 4.74 (*d*, *J* = 12.2, PhC*H*); 7.21–7.38 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.85 (*q*, C(9)); 35.13 (*t*, C(3)); 51.55 (*d*), 52.33 (*d*, C(4), C(8)); 58.54 (*t*, C(1)); 70.06 (*d*); 71.00 (*t*, Ph*C*H$_2$); 72.89 (*t*, Ph*C*H$_2$); 73.17 (*t*, Ph*C*H$_2$); 75.04 (*d*); 75.45 (*d*); 76.35 (*d*); 127.39–129.53 (several *d*, 15 arom. C); 137.97 (*s*, 1 arom. C); 138.79 (*s*, 1 arom. C); 138.97 (*s*, 1 arom. C). FAB-MS: 474 (100, $[M+1]^+$), 382 (40), 366 (14), 281 (6), 221 (6), 207 (6), 147 (8), 91 (62).

1-Amino-1,4:4,8-dianhydro-1,3,9-trideoxy-L-threo-D-ido-*nonitol* (**39**). A suspension of **37** (54 mg, 0.11 mmol) and 10% Pd/C (54 mg) in MeOH (1.5 ml) was hydrogenated at 6 bar for 24 h at 22°. Filtration through *Celite* and evaporation yielded crude **39** · HCl. Purification by ion-exchange chromatography (*Amberlite CG-120*, NH_4^+ form, eluted with $H_2O \rightarrow 0.1$M aq. NH_3) and lyophilization yielded **39** (18 mg, 78%). Colourless hygroscopic amorphous solid. R_f (AcOEt/MeOH/2M aq. NH_3 6 : 3 : 1): 0.15. $[\alpha]_D^{25} = -23.0$ (*c* = 0.1, MeOH). IR (KBr): 3450*s*, 3342*s*, 2944*s*, 2870*m*, 1636*w*, 1462*m*, 1428*s*, 1407*m*, 1386*m*, 1333*m*, 1303*m*, 1281*m*, 1259*m*, 1224*w*, 1191*w*, 1147*s*, 1100*s*, 1083*s*, 1008*s*, 973*m*, 932*s*, 882*w*, 852*w*, 836*w*, 748*w*, 712*w*, 645*w*, 516*m*. ^{1}H-NMR (300 MHz, D_2O): 1.14 (*d*, *J* = 6.5, 3 H–C(9)); 1.72 (*dt*, *J* ≈ 4.7, 13.1, H–C(3)); 2.31 (*td*, *J* ≈ 7.4, 13.6, H–C(3)); 2.91 (*dd*, *J* ≈ 6.2, 13.3, 1 H–C(1)); 3.01 (br. *d*, *J* ≈ 13.1, 1 H–C(1)); 3.12 (*dq*, *J* = 1.9, 6.8, H–C(8)); 3.22 (*td*, *J* ≈ 5.9, 12.4, H–C(4)); 3.84–3.88 (*m*, H–C(6), H–C(7)); 4.07 (*dd*, *J* = 5.6, 7.5, H–C(5)); 4.45–4.66 (*m*, H–C(2)). ^{13}C-NMR (75 MHz, D_2O): 15.60 (*q*, C(9)); 35.86 (*t*, C(3)); 56.29, 63.44 (*d*, C(4), C(8)); 60.93 (*t*, C(1)); 70.72

(*d*); 73.58 (*d*); 73.77 (*d*); 74.60 (*d*). CI-MS: 204 (77, $[M+1]^+$), 188 (100, $[M-Me]^+$), 186 (56), 132 (26), 131 (46), 130 (27), 112 (20), 94 (22), 86 (96), 68 (26). HR-FAB-MS: 204.1238 ($[M+1]^+$; calc. 204.1236).

1-Amino-1,4:4,8-dianhydro-1,3,9-trideoxy-L-threo-D-gulo-*nonitol* (**40**). The procedure for the conversion of **37** to **39** was applied to **37** (38 mg, 0.08 mmol) in MeOH (0.8 ml) with 10% Pd/C (38 mg). Purification by ion-exchange chromatography (*Amberlite CG-120*, NH_4^+ form, eluted with $H_2O \rightarrow 0.1$M aq. NH_3) and lyophilization yielded **40** (12 mg, 75%). Colourless hygroscopic amorphous solid. R_f (AcOEt/MeOH/2M aq. NH_3 7:2:1): 0.17. $[\alpha]_D^{25} = -25.2$ ($c = 0.4$, MeOH). IR (KBr): 3458*w*, 3089*w*, 3066*m*, 3007*s*, 2940*s*, 2870*s*, 2795*m*, 1951*w*, 1876*w*, 1811*w*, 1723*w*, 1605*w*, 1586*w*, 1496*m*, 1454*s*, 1402*m*, 1370*m*, 1310*m*, 1248*m*, 1159*s*, 1096*s*, 1066*s*, 1028*s*, 996*m*, 912*m*, 818*w*, 598*m*, 523*w*. ^{1}H-NMR (300 MHz, D_2O): 1.18 (*d*, $J = 6.5$, 3 H–C(9)); 1.83 (br. *dd*, $J \approx 6.5$, 14.0, 1 H–C(3)); 2.16 (*ddd*, $J = 7.2$, 12.1, 14.0, 1 H–C(3)); 2.85 (*dd*, $J = 4.7$, 12.7, 1 H–C(1)); 3.00 (*dq*, $J = 2.5$, 6.5, H–C(8)); 3.51 (*dd*, $J = 6.5$, 12.7, 1 H–C(1)); 3.70 (*td*, $J \approx 5.9$, 12.1, H–C(4)); 3.77 (*dd*, $J = 3.1$, 8.1, H–C(6)); 3.84 (*t*, $J \approx 2.7$, H–C(7)); 4.09 (*dd*, $J = 5.3$, 8.1, H–C(5)); 4.54 (br. *q*, $J \approx 6.0$, H–C(2)). ^{13}C-NMR (75 MHz, D_2O): 15.18 (*q*, C(9)); 35.45 (*t*, C(3)); 58.02, 62.80 (*d*, C(4), C(8)); 61.69 (*t*, C(1)); 69.96 (*d*); 70.86 (*d*); 73.00 (*d*); 73.35 (*d*). CI-MS: 204 (89, $[M+1]^+$), 188 (100, $[M-Me]^+$), 186 (58), 147 (24), 132 (24), 86 (80), 68 (21), 31 (75). Anal. calc. for $C_9H_{17}NO_4 \cdot 0.6H_2O$ (214.05): C 50.50, H 8.57, N 6.54; found: C 50.29, H 8.41, N 6.41.

5-Amino-2,3,4-tri-O-*benzyl-5,6-dideoxy*-L-*galactonothio-1,5-lactam* (**41**). A soln. of **1** (150 mg, 0.35 mmol) in toluene/pyridine 1:1 (3 ml) was treated with 1,1′-carbonothioyl[1*H*-1,2,4-triazole] (73 mg, 0.41 mmol) and stirred for 13 h at 23°. Addition of CH_2Cl_2, usual workup (sat. NH_4Cl soln., H_2O), and FC (hexane/AcOEt $1:0 \rightarrow 1:1$) gave **41** (130 mg, 84%). Colourless oil. R_f (hexane/AcOEt 1:1, developed with mostain) 0.68. IR ($CHCl_3$): 3360*m*, 3066*m*, 3008*m*, 2962*s*, 2857*m*, 1715*m*, 1674*m*, 1574*w*, 1513*m*, 1498*m*, 1454*m*, 1415*m*, 1356*m*, 1308*m*, 1262*s*, 1098*s*, 1014*s*, 910*m*, 864*m*, 599*w*, 580*w*, 572*w*, 544*w*, 529*w*, 514*m*, 503*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.27 (*d*, $J = 6.5$, 3 H–C(6)); 3.57 (*dq*, $J = 2.5$, 6.5, H–C(5)); 3.81 (*dd*, $J = 2.2$, 8.4, H–C(3)); 3.82–3.92 (*m*, H–C(4)); 4.47 (*d*, $J = 8.4$, H–C(2)); 4.64 (*d*, $J = 11.5$, PhC*H*); 4.65 (*d*, $J = 12.1$, PhC*H*); 4.76 (*d*, $J = 11.8$, PhC*H*); 4.85 (*d*, $J = 10.3$, PhC*H*); 4.92 (*d*, $J = 11.5$, PhC*H*); 5.40 (*d*, $J = 10.6$, PhC*H*); 7.26–7.48 (*m*, 15 arom. H); 7.81 (br. *s*, NH). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.04 (*q*, C(6)); 54.14 (*d*, C(5)); 74.10 (*t*, Ph*C*H$_2$); 75.00 (*t*, Ph*C*H$_2$); 76.23 (*d*, C(2)); 76.82 (*t*, Ph*C*H$_2$); 80.39 (*d*); 81.43 (*d*); 127.83–128.96 (several *d*, 15 arom. C); 138.24 (*s*, 1 arom. C); 138.42 (*s*, 1 arom. C); 138.45 (*s*, 1 arom. C); 202.34 (*s*, C(1)). FAB-MS: 448 (100, $[M+1]^+$), 446 (21), 147 (15), 136 (11), 91 (64), 73 (32).

*(5*S*,6*R*,7*R*,8*R*)-6,7,8-Tris(benzyloxy)-5,6,7,8-tetrahydro-5-methylimidazo[1,2-*a*]pyridine* (**43**). A soln. of **41** (68 mg, 0.15 mmol) in anh. THF (8.5 ml) was treated with $Hg(OAc)_2$ (73 mg, 0.23 mmol) and then dropwise with aminoacetaldehyde dimethyl acetal (80 µl, 0.75 mmol) at 0°. The soln., which slowly turned black, was stirred for 3.5 h at 0°. After dilution with CH_2Cl_2, usual workup (sat. NH_4Cl soln., H_2O), filtration through *Celite*, and evaporation gave a residue which was dissolved in toluene (4.4 ml) and H_2O (0.4 ml), treated with $TsOH \cdot H_2O$ (77 mg, 0.40 mmol) and stirred at 70° for 19.5 h. Dilution with CH_2Cl_2, work-up in the usual way (H_2O), evaporation, and FC (alumina, act. grade I, hexane/AcOEt $1:0 \rightarrow 1:2$) gave **43** (52 mg, 75%). Colourless oil. R_f (hexane/AcOEt 1:1, developed with mostain) 0.22. $[\alpha]_D^{25} = -29.0$ ($c = 1.1$, $CHCl_3$). IR ($CHCl_3$): 3090*w*, 3067*w*, 3008*s*, 2929*m*, 2859*m*, 1953*w*, 1810*w*, 1671*m*, 1602*m*, 1520*w*, 1496*s*, 1485*s*, 1454*s*, 1380*m*, 1355*s*, 1296*s*, 1262*s*, 1090*s*, 1071*s*, 1028*s*, 910*w*, 820*w*, 601*w*, 530*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.56 (*d*, $J = 6.8$, Me); 4.08 (*dd*, $J = 1.9$, 5.6, H–C(7)); 4.16 (*dd*, $J = 1.9$, 4.7, H–C(6)); 3.86 (*dq*, $J = 4.7$, 6.9, H–C(5)); 4.64 (*d*, $J = 11.5$, PhC*H*); 4.70 (*d*, $J = 12.1$, PhC*H*); 4.76 (*d*, $J = 12.1$, PhC*H*); 4.79 (*d*, $J = 11.8$, PhC*H*); 4.82 (*d*, $J = 11.8$, PhC*H*); 4.88 (*d*, $J = 5.6$, H–C(8)); 5.10 (*d*, $J = 11.8$, PhC*H*); 6.88 (*d*, $J = 1.2$), 7.11 (*d*, $J = 0.9$, H–C(2), H–C(3)); 7.25–7.38 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.86 (*q*, Me); 52.91 (*d*, C(5)); 72.69 (*t*, Ph*C*H$_2$); 73.06 (*d*); 73.11 (*t*, 2 Ph*C*H$_2$); 75.26 (*d*); 79.65 (*d*); 117.29 (*d*, C(3)); 129.77 (*d*, C(2)); 127.74–128.93 (9*d*, 15 arom. C); 138.23 (*s*, 1 arom. C); 138.45 (*s*, 1 arom. C); 138.71 (*s*, 1 arom. C); 143.73 (*s*, C(8a)). FAB-MS: 455 (100, $[M+1]^+$), 347 (10), 901 (11). Anal. calc. for $C_{29}H_{30}N_2O_3$ (454.57): C 76.63, H 6.65, N 6.16; found: C 76.51, H 6.78, N 6.00.

*(5*S*,6*R*,7*R*,8*R*)-5,6,7,8-Tetrahydro-5-methylimidazo[1,2-*a*]pyridine-6,7,8-triol* (**44**). A soln. of **43** (65 mg, 0.14 mmol) in AcOEt/MeOH/H_2O 5:17:3 (4 ml) was treated with AcOH (1.7 ml) and 10% $Pd(OH)_2$/C (65 mg) and hydrogenated at 6 bar for 18 h at 22°. Filtration through *Celite*, evaporation, FC (MeCN/H_2O $1:0 \rightarrow 7:3$), and lyophilization gave **44** (20 mg, 76%). Colourless amorphous solid. R_f (MeCN/H_2O 7:3, developed with mostain) 0.25. $[\alpha]_D^{25} = -14.3$ ($c = 0.5$, MeOH). IR (KBr): 3417*m* (br.), 2926*s*, 1622*m*, 1455*s*, 1261*m*, 1098*s*, 937*w*, 751*m*, 545*m*. ^{1}H-NMR (300 MHz, D_2O): 1.53 (*d*, $J = 6.5$, Me); 3.96 (*dd*, $J = 2.2$, 9.0, H–C(7)); 4.19 (*t*, $J \approx 2.2$, H–C(6)); 4.35 (*dq*, $J = 2.2$, 6.5, H–C(5)); 4.82 (*d*, $J = 9.0$, H–C(8)); 7.20, 7.24 (2*s*, H–C(2), H–C(3)). ^{13}C-NMR (75 MHz, D_2O): 15.36 (*q*, Me); 53.58 (*d*, C(5)); 66.62 (*d*, C(8)); 72.40 (*d*); 73.77 (*d*); 118.05 (*d*, C(3)); 127.76 (*d*, C(2)); 145.93 (*s*, C(8a)). CI-MS (MeOH): 185 (100, $[M+1]^+$), 158 (69), 151 (67), 149 (62), 135

(52), 132 (58), 97 (49), 69 (53), 44 (52). Anal. calc. for $C_8H_{12}N_2O_3 \cdot 0.5H_2O$ (193.20): C 49.73, H 6.78, N 14.49; found: C 50.01, H 7.01, N 13.23.

Inhibition of α-L-Fucosidase from Bovine Epidydimis. Determination of the IC_{50} was performed at 25° using 400 µl of a trisodium citrate buffer (pH 5.5), which contained the following assay components: 4-nitrophenyl α-L-fucopyranoside (0.75 mM) as substrate, and the inhibitor in different concentrations which bracket the IC_{50} value. Measurements were started by addition of 200 µl of an aq. soln. of α-L-fucosidase (5 µg/ml). The reaction was stopped after 10 min by addition of 400 µl of glycine buffer (pH 10) and the absorption was measured at 400 nm.

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