Towards the Synthesis of 1-Deoxy-1-nitropiperidinoses

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In the course of the first of several attempts to elaborate methods for the synthesis of 1-nitropiperidinoses, lincosamine was transformed into lactam **6** *via* hemiacetal **1**, lactone **2**, amide **3**, oxo amide **4**, and its cyclic tautomer **5**. Treatment of the *N*-Boc-protected lactam oxime **9**, obtained from lactam **6**, with brominating agents failed to provide the bromonitroso carbamate **10**. The *N*-Boc-protected lactam **13** derived from **6** was reduced to hemiacetal **14**, but the corresponding *N*-Boc-aminooxime did not tautomerise to the *C(1)*-hydroxylamine, and nitrone **17**, a potential precursor of the nitropiperidine **12**, was not formed. Oxidation of the anomeric azide **20** with HOF·MeCN failed to provide the expected nitropiperidine **21**. The phosphinimines **22** derived from **20** did not react with O_3. In the next approach to 1-nitropiperidinoses, we treated the *N*-Boc-protected hemiacetal **25**, obtained from the known gluconolactam **23** with *N*-benzylhydroxylamine. The resulting nitrone **26** exits in equilibrium with the anomeric *N*-benzyl-glycosylhydroxylamine that was oxidized to the anomeric nitrone **28**. Ozonolysis of **28** led to the hemiacetal **25**, resulting from the desired, highly reactive protected nitropiperidinose **29**, that was evidenced by an IR band at 1561 cm^{-1}. Similarly to the synthesis of nitrone **26**, reaction of the *N*-tosyl-protected hemiacetal **31** with *N*-benzylhydroxylamine and oxidation provided the anomeric *N*-benzylhydroxylamines **33** *via* the *p*-toluenesulfonamido nitrone **32**. Their oxidation with MnO_2 led to the anomeric nitrone **34**. Ozonolysis of **34** as evidenced by ^{1}H-NMR and ReactIR spectroscopy led to the highly reactive nitropiperidinose **35**. Like **29**, **35** was transformed during workup, and only the hemiacetal **31** was isolated. The similarly prepared lincosamine-derived nitrone **17** was subjected to ReactIR-monitored ozonolysis that evidenced the formation of the protected nitropiperidinose **12**, but only led to the isolation of **14**. The facile transformation of the nitropiperidinoses to hemiacetals is rationalised by heterolysis of the anomeric C,N bond, recombination of the ion pair, and denitrosation of the resulting anomeric nitrite by a nucleophile. Attempts to convert the 1-deoxy-1-nitropiperidinose **35** to uloses **43** by base-catalysed *Michael* additions or *Henry* reactions were unsuccessful.

Introduction. – 1-Deoxy-1-nitropiperidinoses, carbohydrates where the ring O-atom of a nitropyranose is replaced by an NH or NR group, are not known. These nitropiperidinoses should be deprotonated under mild conditions, without β-elimination, resulting in an inversion of polarity. This should allow elongating the C-chain at the anomeric centre by a *Michael* addition, or reaction with an aldehyde, similarly as it is known for 1-deoxy-1-nitropyranoses [1–4]. It appeared necessary to protect the ring N-atom of nitropiperidinoses by a strong π- and σ-acceptor substituent to prevent the intrinsically facile heterolysis of the anomeric C,N bond, generating a nitrite anion and an immonium cation. An even more readily occurring solvolysis of a chain-elongated, *N*-protected nitropiperidine should allow introduction of a second substituent at the anomeric centre, *viz.,* a hetero-nucleophile, or a C-nucleophile derived from a weakly basic carbanion, as in a *Kornblum* reaction [5]. Thus, 1-deoxy-1-*C*-nitropiperidinoses

possess a high potential for the synthesis of a variety of piperidinoses modified at C(1) and C(2), the introduction of substituents at the ring N-atom adding a further dimension of diversity.

Naturally occurring [6] and synthetic piperidinose derivatives, and other saccharide mimics possessing a ring N-atom, such as pyrrolidines, indolizidines, pyrrolizidines, and nortropanes, with nojirimycin and deoxynojirimycin as prototypes, were thoroughly studied as glycosidase inhibitors [7], and their chemistry has been reviewed periodically [6][8]. A range of biological properties of piperidinoses and other N-containing sugars are known, beyond their activity as glycosidase inhibitors [9].

For these reasons, we considered it worthwhile to explore the synthesis and transformations of 1-deoxy-1-nitropiperidinoses, in spite of the obvious obstacle of the facile solvolysis of the anomeric C,N bond. We had a particular interest in exploring their application to the synthesis of novel lincomycin analogues [10][11]. In spite of the need for new antibiotics, pyranosyl moieties of carbohydrate-derived antibiotics have not, to the best of our knowledge, been replaced by piperidinosyl analogues. Chain-elongated, piperidine-derived analogues of lincomycin appeared attractive. Molecular modelling[1]) of the crystal structure of the 50S ribosomal subunit of the eubacterium *Deinococcus radiodurans* [12] in complex with clindamycin revealed a cavity around C(1) that allows introducing two substituents at the anomeric centre besides replacing C(5)–O by a C(5)–NH or NR group (R = alkyl, acyl, sulfonyl).

We planned to prepare such lincomycin analogues *via* an intermediate nitropiperidinose, to be synthesized by analogy to the known methods for the preparation of nitropyranoses [1][2]. The first route should proceed *via* an *N*-Boc-protected lincosamine-derived 1,5-lactam. We considered that the transformation of such a lactam into the corresponding hydroximolactam [13], followed by treatment with Br_2, oxidation of the intermediate bromo-nitroso carbamate to the bromo-nitro carbamate, and debromination should lead to the desired *N*-Boc-protected nitropiperidines. According to the alternative route [3], we planned to reduce the *N*-Boc-protected lactam to an *N*-protected piperidinose and transform it into an *N*-(acylamino)-alkylnitrone. Ozonolysis of this nitrone should lead to an *N*-Boc-protected nitropiperidinose.

Synthesis. – Following the first of the above mentioned methods for the synthesis of nitropyranoses, we prepared the required lincosamine-derived lactam **6** (*Scheme 1*) from the known protected *galacto*-octopyranose **1** [11] according to a method developed by our group [13][14] and by others [15][16]. Oxidation of **1** with *Dess–Martin*'s periodinane led to the lactone **2**. Ammonolysis of crude **2** gave amide **3** that was oxidized with *Dess–Martin*'s periodinane to the oxo amide **4**. *In situ* acid-catalysed tautomerisation to **5** and reduction with $NaCNBH_3$ led to the desired lactam **6**. It was purified by column chromatography, and obtained as a colourless oil in 60% overall yield on a 30-g scale.

To prepare the required lactam-oxime intermediate **9** (*Scheme 2*; *cf.* [13][17]), we treated lactam **6** with *Lawesson*'s reagent. The expected thiolactam **7** was isolated in a yield of 75%. *N*-Boc Protection of **7**, followed by treatment of the resulting

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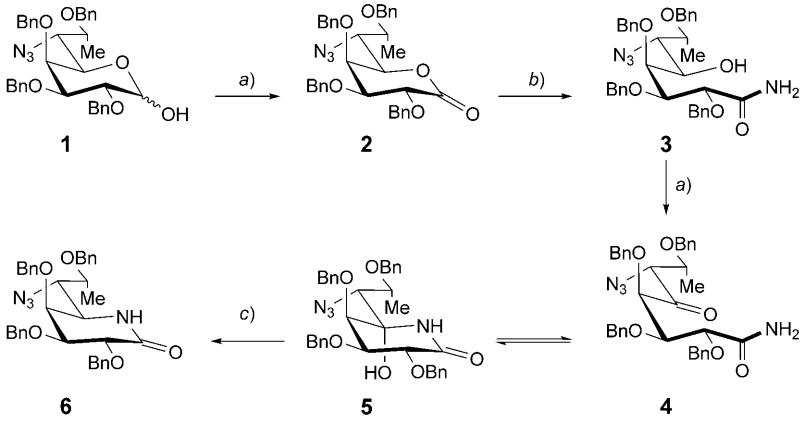
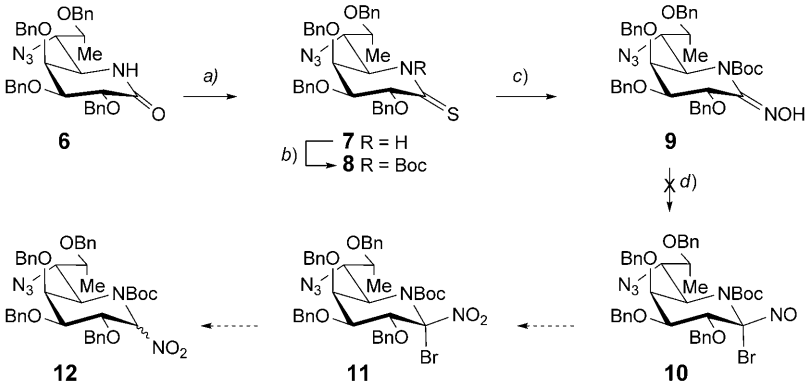
[1]) Molecular modelling was performed using the Moloc program. We thank *Paul Gerber*, *Gerber Molecular Design*, for access to the programme.

Scheme 1



a) *Dess–Martin*'s periodinane, CH_2Cl_2. *b*) NH_3, CH_2Cl_2, $-40°$ to $25°$. *c*) HCO_2H, $NaBH_3CN$, MeCN, $70°$; 58% from **1**.

Scheme 2



a) *Lawesson*'s reagent, toluene, $60°$; 75%. *b*) Boc_2O, 4-(Dimethylamino)pyridine (DMAP), CH_2Cl_2. *c*) $NH_2OH \cdot HCl$, $NaHCO_3$, MeOH; 90% from **7**. *d*) Conditions tried: 1. Br_2, NaOH, $0°$; 2. Br_2, Py, $-78°$ to $25°$; 3. *N*-bromoacetamide, ZnO, H_2O, CH_2Cl_2, $25°$; 4. *N*-bromosuccinimide, $NaHCO_3$, CH_2Cl_2, H_2O, $25°$; 5. oxone, KBr, *Alox*, $CHCl_3$, $45°$ to reflux.

N-Boc-thiolactam **8**[2]) with $NH_2OH \cdot HCl$ yielded 90% of the lactam oxime **9** (*Scheme 2*).

The coupling constants for the pyranose ring of lactone **2**, lactam **6**, thiolactam **7**, and lactam oxime **9** in $CDCl_3$ solution, compiled in *Table 1* (*Exper. Part*), evidence for all these compounds a preferred $^4C_1$ conformation. The equatorial orientation of the

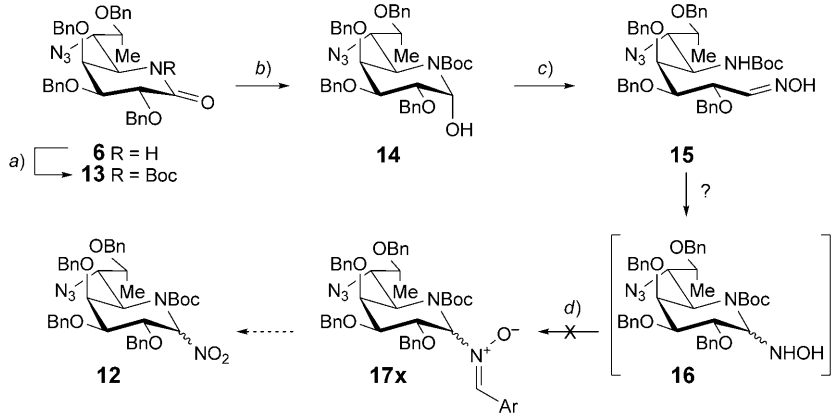
[2]) Attempts to isolate thiolactam **8** resulted in decomposition; it was used directly for the synthesis of **9**.

side chain of the *N*-Boc-protected lactam oxime **9** is surprising in view of the allylic strain [18]. It is tempting to rationalise the ring conformation of **9** by postulating a (*Z*)-configuration and an intramolecular H-bond to the *N*-alkoxy carbonyl group. There is, however, no evidence for this H-bond, and the related *N*-Boc-protected piperidines **18** and **19** (see below *Scheme 4*) that cannot form such a H-bond (and possess an axial C(1)OAc group) also adopt a $^4C_1$ conformation.

We had expected bromination of **9** to yield the bromo-nitroso intermediate **10** that we intended to oxidize to the bromo-nitro carbamate **11** and then debrominate to the desired nitropiperidine **12**. Unfortunately, all attempts to transform **9** into the bromo-nitroso carbamate **10** (*Scheme 2*) failed to provide the desired product. Although **9** was consumed, TLC revealed a complex mixture of products that could not be separated. No blue or blue-green colour characteristic of nitroso compounds was ever observed, and the IR spectrum of the reaction mixture did not show any nitroso band at 1560 cm^{-1}.

In a second approach, we first aimed at transforming the *N*-Boc-protected lactam **13** to one of the nitrones **17x** (*Scheme 3*). *N*-Boc protection of lactam **6** yielded 80% of the desired **13** that was reduced with *Super-Hydride*® to the *N*,*O*-hemiacetal **14**. Treating **14** with $NH_2OH \cdot HCl$ led to a 7:3 (*E*/*Z*)-mixture of the *N*-Boc-protected amino oximes **15**[3]) (85% from **13**).

Scheme 3



a) Boc_2O (Boc = (*tert*-butoxy)carbonyl), DMAP, $ClCH_2CH_2Cl$, 70°; 80%. *b*) *Super-Hydride*® (1.0M $LiEt_3BH$ in THF), THF. *c*) $NH_2OH \cdot HCl$, $NaHCO_3$, EtOH; 85% from **13**.

The ^{1}H-NMR spectrum of the *N*-Boc-protected lactam **13** in $CDCl_3$ shows a *W* coupling of 1.5 Hz between H–C(3) and H–C(5). Together with the other relevant coupling constants (*Table 1* in *Exper. Part*), this suggests a conformational equilibrium with contributions of E_4, $^3H_4$, and $^2S_4$. The configuration of **14** is evidenced by the *J*(1,2) value of 3.6 Hz and the downfield shift of H–C(5); the ring conformation is close to $^4C_1$.

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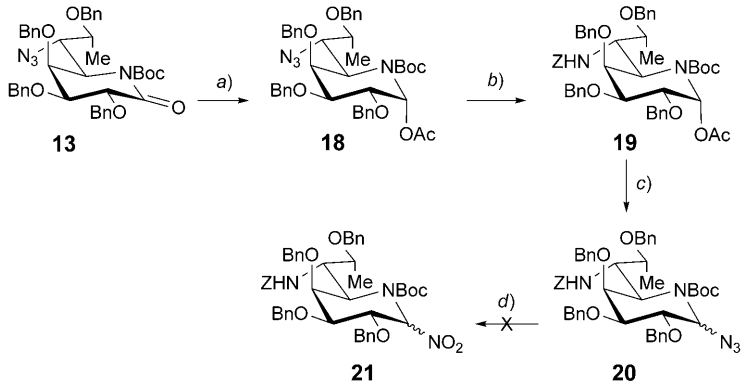
[3]) The ^{1}H-NMR spectrum of **15** in (D_6)DMSO at 100° shows the H–C(1) signal of the (*E*)-oxime at δ 7.44 ppm (*d*, *J* = 7.5 Hz, 0.7 H), while H–C(1) of the (*Z*)-oxime resonates at 6.95 ppm (*d*, *J* = 6.5 Hz, 0.3 H). The ^{1}H-NMR spectrum did not show any signal of the cyclic tautomer **16**.

The oximes **15** did not react with benzaldehyde, 4-chlorobenzaldehyde, or the more highly electrophilic 4-nitrobenzaldehyde under neutral, acidic, or basic conditions to form a desired nitrone **17x**. It appeared that the *N*-Boc protecting group significantly reduced the nucleophilicity of the N-atom, preventing tautomerisation to the cyclic hydroxylamine **16** and condensation with the aldehydes.

In view of this result, we modified our approach. Recently, *Carmeli* and *Rozen* have described the oxidation of alkyl azides to NO_2 derivatives by a HOF·MeCN complex [19]. To apply this method to lincosamine, we had to replace the N_3 group at C(6) by a NHCbz group, and to synthesise glycosyl azide **20** as precursor of the desired nitro derivative (*Scheme 4*). Azide **20** was prepared from lactam **13** that was reduced to the *N*,*O*-hemiacetal, and acetylated to yield 90% of **18** (*Scheme 4*). This azido acetate was reduced with propane-1,3-dithiol in a pyridine/Et_3N/H_2O mixture [20], and the resulting amine was *N*-(benzyloxy)carbonylated to **19** (75%). Treatment of **19** with TMS-N_3 and $BF_3 \cdot OEt_2$ [21] yielded 83% of the glycosyl azides **20**. The ^{1}H-NMR spectra of **18** and **19** in (D_6)DMSO evidence a very similar $^4C_1$ conformation. The α-D-configuration of **18** and **19** was deduced from $J(1,2) = 4.2$ Hz, while the spectrum of **20** in (D_6)DMSO, recorded at 100°, evidenced a mixture of rotamers that precluded the determination of the anomeric configuration.

Scheme 4

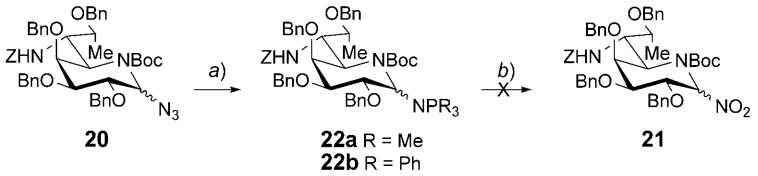


a) 1. *Super-Hydride*®, THF, 0°; 2. Ac_2O, DMAP, Et_3N, CH_2Cl_2; 90%. *b*) 1. Propane-1,3-dithiol, Et_3N, Py, H_2O; 2. CbzCl (Cbz = (benzyloxy)carbonyl), Et_3N, CH_2Cl_2; 75%. *c*) Me_3SiN_3 (TMS-N_3), $BF_3 \cdot OEt_2$, CH_2Cl_2; 83%. *d*) HOF·MeCN, $CHCl_3$.

Numerous attempts to oxidise azide **20** with HOF·MeCN failed to provide the desired nitro derivative **21**. Analysis of the reaction mixture by IR spectroscopy did not show the characteristic bands of a NO_2 group at 1560 and at 1360 cm^{-1}.

Our next approach to the desired 1-nitropiperidinose was based upon the ozonolysis of phosphimines, according to a method reported by *Corey et al.* [22]. Me_3P or Ph_3P transformed the azide **20** to the methyl and phenyl phosphimines **22a** and **22b**, respectively. Solutions of the phosphimines in MeOH or CH_2Cl_2 were treated with O_3, and the reaction was followed by IR spectroscopy, monitoring the disappearance of the N_3 band at 2102 cm^{-1}. However, under these reaction conditions the phosphimines **22** did not react with O_3 (*Scheme 5*).

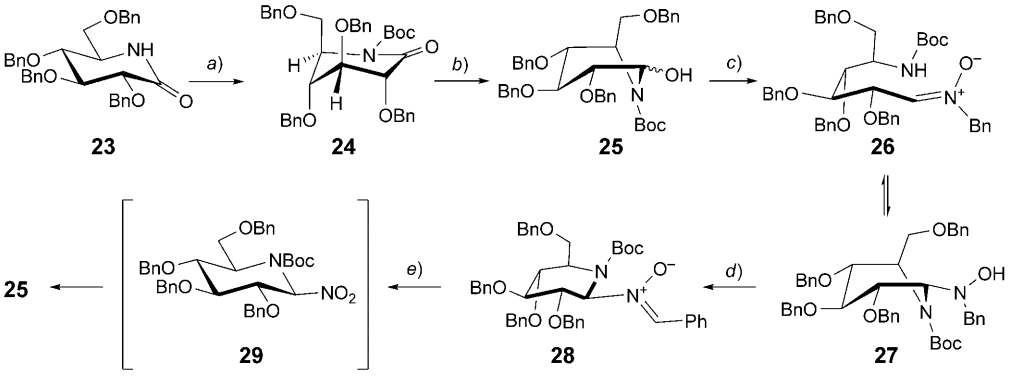
Scheme 5



a) R_3P (R = Me, Ph), THF. *b*) O_3, CH_2Cl_2 or MeOH, $-78°$.

To avoid a conceivable influence of the *galacto*-configuration upon our attempts of obtaining 1-nitropiperidinoses (*cf.* [23]), it appeared commendable to explore further methods using the known 2,3,4,6-tetra-*O*-benzyl-gluconolactam **23** [14] (*Scheme 6*). We aimed at treating the known *N*,*O*-hemiacetal **25** [24], obtained by reduction of the *N*-protected gluconolactam **24**, with BnNHOH · HCl to obtain an open-chain nitrone **26**. This nitrone is significantly more highly electrophilic than oxime **15**, and should thus equilibrate with its cyclic tautomer, the *N*-Bn-hydroxylamine **27** (*Scheme 6*) that we hoped to oxidise to the cyclic nitrone **28** and further to the desired nitropiperidinose **29**.

Scheme 6



a) Boc_2O, DMAP, MeCN; 88% [24]. *b*) $NaBH_4$, 1N HCl to pH 6, EtOH; 75% [24]. *c*) BnNHOH, Py, 60°; 80%. *d*) MnO_2, $ClCH_2CH_2Cl$, reflux; 90%. *e*) O_3, CH_2Cl_2, $-78°$.

The protected *N*,*O*-hemiacetal **25** was prepared from the *O*-benzylated gluconolactam **23** by *N*-Boc protection (88%), followed by reduction with $NaBH_4$ at pH 6 in 75% yield [24] (*Scheme 6*). Reaction of **25** with BnNHOH in dry pyridine yielded 75% of a 1:1 mixture of the open-chain nitrone **26** and its cyclic tautomer, hydroxylamine **27** [25–27][4]). Treatment of the mixture **26**/**27** with MnO_2 oxidised **27** to the cyclic nitrone **28** that was isolated in a yield of 90%, evidencing the shift of the equilibrium **26** ⇌ **27** towards the *N*-benzyl hydroxylamine **27**. Not surprisingly, oxidation of **27** involves the benzylic CH_2 group, as reported for similar compounds [28]. The β-D-configuration of

[4]) Sharp ^{1}H-NMR signals were observed in (D_6)DMSO at 100°. Under these conditions, only signals for **27** were observed.

the anomeric centre and the (*Z*)-configuration of the nitrone were established by X-ray crystal structure analysis; the conformation will be discussed below. As expected, the broad peaks in the ^{1}H-NMR spectra of the carbamate **28** (in $CDCl_3$) at ambient temperature reveal the presence of rotamers. Sharp ^{1}H-NMR signals of **28** were observed only at 100° in (D_6)DMSO. Although the ^{1}H-NMR spectra of the reaction mixture resulting from ozonolysis at −78° did not show sharp peaks, we refrained from recording the spectra at a higher temperature, considering the presumed facile solvolysis of the expected 1-nitropiperidinoses. The only isolated products obtained by ozonolysis of **28** at −78° are indeed the known *N*,*O*-hemiacetals **25** [24] suggesting that the 1-nitropiperidinose **29** was formed, but rapidly solvolysed upon warming to ambient temperature and/or during workup.

The conformation of the anomers of **25** – the $B_{3,N}$ conformation of the α-D anomer is shown in *Scheme 6* – was determined before [24].

Crystals of the *N*-Boc-protected nitrone **28** were obtained by slow evaporation of a solution in MeOH/H_2O, and their structure was established by X-ray analysis[5]) (*Fig.*), revealing the β-D- and (*Z*)-configuration, and the ^2S_N conformation that lifts the oxyimino and the substituent at C(5) out of the plane of the *N*-Boc group and is also preferred in $CDCl_3$ solution.

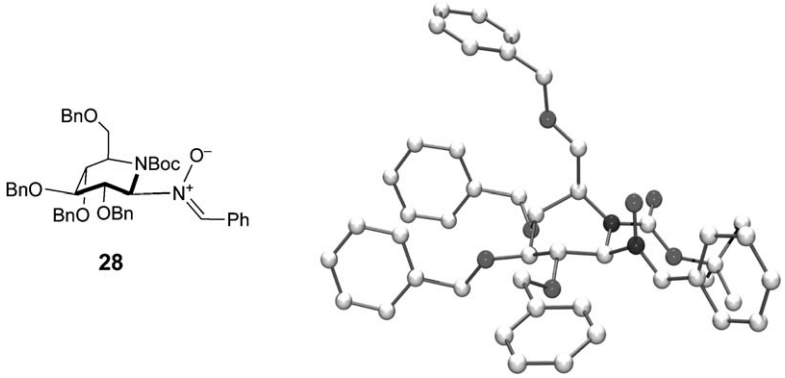


Figure. *Ball-and-stick representation of the crystal structure of the nitrone* **28**

As it proved difficult to *in situ* analyse the product of ozonolysis by ^{1}H-NMR spectroscopy, we monitored the ozonolysis of nitrone **28** by ReactIR at −78°. The IR spectrum of the *N*-Boc-protected nitrone **28** is characterised by a band at 1717 cm^{-1}, typical of a carbamoyl group, while the N=CH nitrone band (at *ca.* 1600 cm^{-1}) was weak, so that the reaction could not be monitored by following the disappearance of this band. Formation of the *N*-Boc-protected (presumably β-D-configured) 1-nitropiperidinose **29** is, however, supported by the appearance of a band at 1568 cm^{-1}, characteristic of a NO_2 group, and of a C=O band at 1701 cm^{-1} assigned to PhCHO.

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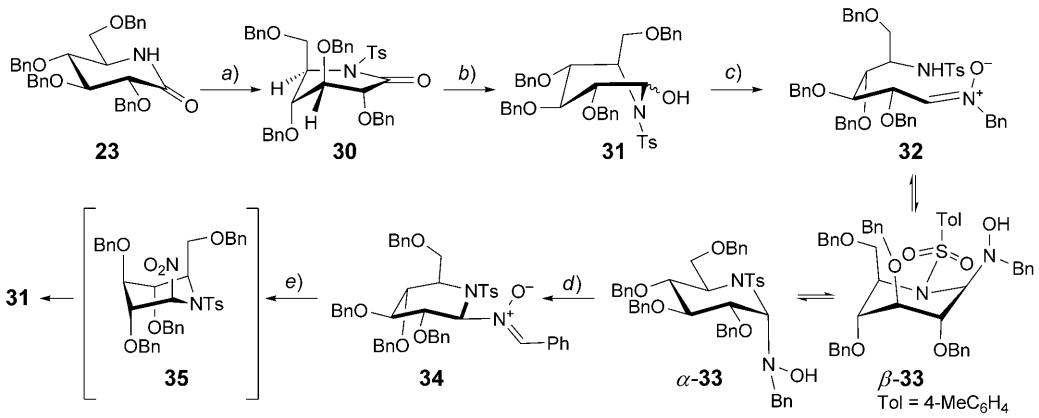
[5]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-699259. Copies of the data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif (or from the *CCDC*, 12 Union Road, Cambridge CB21EZ (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

The difficulty of analysing the product of ozonolysis by ^{1}H-NMR spectroscopy (on account of the rotamers) and the facile solvolysis of the *bona fide* **29** showed that the Boc group is not an appropriate *N*-protecting group. It was, therefore, substituted by the Ts group, although it has been evidenced that a *N*-sulfonyl group is rather a weaker electron acceptor than a *N*-carbonyl group [29]. The Ts group has, however, the advantage of not giving rise to discernible rotamers.

The *O*-benzylated gluconolactam **23** was *N*-tosylated by treatment with BuLi and TsCl [21] to yield 77% of the *N*-Ts lactam **30** (*Scheme 7*). Similarly as described for the Boc-protected gluconolactam **24** (*Scheme 6*), **30** was reduced with DIBAL-H to the *N*,*O*-hemiacetals **31** (85%). The reaction of **31** with BnNHOH in dry pyridine (*cf.* [25][26][28]) provided, after filtration through silica gel, mostly a *ca.* 3:1 β-D/α-D-mixture of the anomeric hydroxylamines α-**33**/β-**33** and small amounts of the open-chain nitrone **32** that correlated with a very polar spot on the TLC. The interpretation of the ^{1}H-NMR spectrum of the mixture **32**/**33** is based on J(1,2) of 2.0 Hz for the major (β-D), and of 7.2 Hz for the minor (α-D) isomer, evidencing a flattening of the chair for β-**33**. One large (8.0 Hz) and one small (2.0 Hz) J(5,6) value of β-**33** is in agreement with a pseudoaxial CH_2OBn group, shifted to higher fields by the toluyl group. The minor α-**33** is characterized by two similar J(5,6) values, denoting an equatorial CH_2OBn group. Both H–C(1) are equatorial, and thus shifted to lower field.

Scheme 7



a) BuLi, TsCl, DMAP, THF, $-78°$ to $0°$; 77%. *b*) Diisobutylaluminum hydride (DIBAL-H), toluene, $0°$; 85%. *c*) BnNHOH, Py, $100°$. *d*) MnO_2, $ClCH_2CH_2Cl$, reflux; 78% from **30**. *e*) O_3, CH_2Cl_2, $-78°$.

By comparison to the *N*-Boc-protected analogues **26**/**27**, the nitrone $\rightleftharpoons$ hydroxylamine equilibrium, **32** $\rightleftharpoons$ **33**, is displaced in favour of **33**, in agreement with the weaker electron-acceptor properties of the Ts group (*cf.* [29]) and, conceivably, less-destabilizing steric interactions. Oxidation of the mixture **32**/**33** with MnO_2 [28] led to the cyclic nitrone **34** in a yield of 78%.

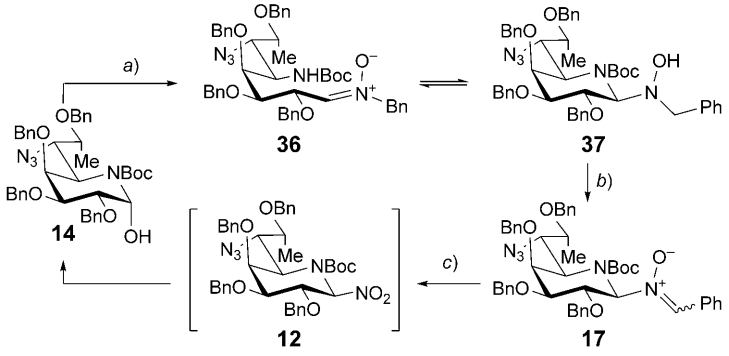
Similarly as in the *N*-Boc-protected series, the pyranose ring of the *N*-Ts lactam **30** exists as mixture of equilibrating $^3H_4$ and ^2S_N conformers, as evidenced by the coupling constants (*Table 2* in *Exper. Part*) and particularly by the *W* coupling (J =

1.5 Hz) between H–C(3) and H–C(5). The preferred conformation of the *N*-Ts nitrone **34** is ^2S_N, avoiding the allylic strain resulting from destabilizing interactions of the *N*-Ts group with an equatorial side chain at C(5) and the equatorial nitronyl substituent. The pyranose ring of α-D-**31** in $CDCl_3$ adopts a $B_{3,N}$ conformation, as depicted in *Scheme 7*, while β-D-**31** most likely adopts a conformational equilibrium between $^1C_4$ and $B_{3,N}$. The large J(1,OH) value of 11.8 Hz suggests an intramolecular H-bond with the pseudoaxial C(3)OBn group of the $^1C_4$ and the C(6)OBn group of the $B_{3,N}$ conformer.

Ozonolysis of the *N*-Ts nitrone **34** at $-78°$ in CH_2Cl_2 led to the *N*,*O*-hemiacetals **31**, similarly as observed for the *N*-Boc-protected analogue **28**, again suggesting that a 1-nitropiperidinose (**35**) was formed *in situ*, but solvolysed upon increasing the temperature. Ozonolysis of **34** in CD_2Cl_2 at $-78°$ was thus monitored by ^{1}H-NMR spectroscopy, starting at $-78°$ and slowly raising the temperature to $-10°$. The β-D-nitrone **34** was characterized by a chemical shift for H–C(1) of 5.45 ppm (J(1,2) = 7.9 Hz), while the H–C(1) signal of the ozonolysis product at $-10°$ was shifted downfield by 0.6 ppm (δ 6.05 ppm, J(1,2) = 3.6 Hz), and evidenced that a single product was formed. This chemical shift is in agreement with those observed for nitropyranoses [1][3]. J(1,2) of 3.6 Hz for the 1-nitropiperidinose **35** evidences either that the conformation of the piperidinose ring changed from ^2S_N towards $^1C_4$, or that the expected 1-nitropiperidinose isomerised to the α-D-anomer. No signal of the hydrolysis product **31** of **35** was observed up to $-10°$, indicating that the 1-nitropiperidinose **35** is stable up to that temperature. Solvolysis appears to occur upon warming to ambient temperature. The ozonolysis of the *N*-tosyl nitrone **34** was also followed by ReactIR. A comparison of the IR spectra of the nitrone and of the ozonolysis mixture revealed new bands of both the NO_2 group (1569 cm^{-1}) and the C=O group of PhCHO (1701 cm^{-1}).

The method developed for the synthesis of 1-nitropiperidinoses from gluconolactam **23** was then tested on the *N*-Boc-protected *N*,*O*-hemiacetal **14** derived from lincomycin (*Scheme 8*). The hemiacetal **14** reacted with BnNHOH in BuOH to give exclusively nitrone **36** as a single isomer in 90% yield. Attempted oxidation of **36** with

Scheme 8



a) BnNHOH, BuOH, 80°; 90%. *b*) LiI, PbO_2, Py, toluene, 60°; 63%. *c*) O_3, CH_2Cl_2, $-78°$.

MnO_2 in refluxing $ClCH_2CH_2Cl$ did not lead to the desired cyclic nitrone **17**, and starting material was recovered. We had to conclude that, under these reaction conditions, nitrone **36** did not cyclise to the cyclic hydroxylamine **37**. To favour the cyclisation, we explored activating **36** with a *Lewis* acid [30]. Treatment of **36** with MnO_2 and LiI in toluene and pyridine led indeed to the cyclic nitrone **17** in a yield of 30–35%. We assume that the Li^+ cation coordinates with the O^- of nitrone **36**, enhancing its electrophilic properties, and favouring cyclisation to the hydroxylamine **37** that is oxidised to nitrone **17**. As it is conceivable that LiI is oxidized to I_2 that might act as the oxidant, we treated nitrone **36** with I_2 in toluene and pyridine at 60°, but did not observe the desired nitrone **17**.

We screened *Lewis* acids, oxidising agents, and bases to optimise the oxidation of **36** to the nitrone **17**. The best result was obtained with 5 equiv. of PbO_2 and 2 equiv. of LiI in toluene/pyridine 2:1 at 60°, yielding 63% of a 1:2 mixture of two diastereoisomeric nitrones **17**.

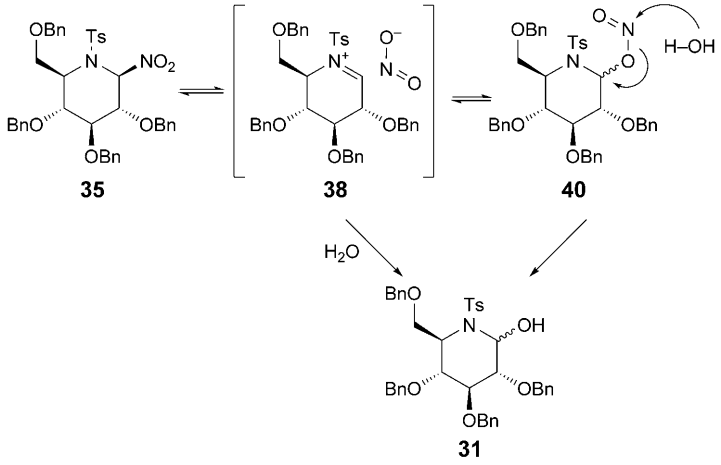
The mixture of rotamers due to the *N*-Boc group and the overlapping ^{1}H-NMR signals allowed only a tentative determination of the configuration and conformation of the two diastereoisomers of **17**. The ^{1}H-NMR spectrum of the mixture in (D_6)DMSO solution at 100° is characterised by two *singlet*s at 7.81 and at 7.73 ppm and two H–C(1) *doublet*s at 6.01 and 5.81 ppm ($J(1,2) = 5.1$ and 5.7 Hz), respectively. The coupling constants of the piperidinose ring of **17** are best interpreted in terms of a $B_{3,N}$ conformation, avoiding the allylic strain resulting from the interaction of the *N*-Boc group with an equatorial side chain at C(5) and the equatorial nitronyl substituents. The similarity of the coupling constants and the chemical shift for H–C(1) evidence the formation of (*E*/*Z*)-isomers rather than of two anomers.

Ozonolysis of nitrone **17** gave the *N*,*O*-hemiacetal **14** at ambient temperature, the only product to be isolated. It is assumed that the desired 1-deoxy-1-nitropiperidinose **12** was generated *in situ* and transformed to the *N*,*O*-hemiacetal **14** upon workup. As observed for the ozonolysis product of the *N*-Boc-protected gluconolactam derivative **28**, it was not possible to analyze the ozonolysis product of **17** by ^{1}H-NMR spectroscopy, and the ozonolysis of **17** was monitored by ReactIR. Two prominent new bands appeared, one characteristic of the NO_2 group (1561 cm^{-1}) and one of the C=O group of PhCHO (1701 cm^{-1}).

The mechanism for the solvolysis of the 1-nitropiperidinose has to account for the formation of the hemiacetals in the absence of H_2O. Heterolysis of the 1-nitropiperidinose **35** is assumed to generate the ion pair **38** that may evolve, by internal return, to the nitrite **40** that would be hydrolysed, during workup or chromatography, and lead to the *N*,*O*-hemiacetal **31** (*Scheme 9*). The nitrite **40** is expected to show a strong IR band at 1650 cm^{-1}. In agreement with ReactIR and ^{1}H-NMR spectroscopy following the progress of ozonolysis, no such band appeared during ozonolysis of the nitrones **17**, **28**, or **34** at −78°, meaning that the heterolysis/recombination occurs only at a higher temperature.

As the 1-nitropiperidinoses could not be isolated, we screened *Michael* additions and *Henry* reactions of the crude mixture of the *bona fide* *N*-tosylated 1-nitropiperidinose **35** obtained by ozonolysis of nitrone **34** at −78°. The mixture was treated with acrylonitrile, methyl acrylate, or 4-nitrobenzaldehyde, and a base (Et_4NOH, DBU, NaH, *t*-BuSNa, NaOMe, *t*-BuOK, Bu_4NF, or KF), slowly raising the temperature from

Scheme 9



$-78°$ to ambient temperature, speculating that deprotonation of **34** would occur before solvolysis. Addition of the resulting nitronate anion to the electrophile was expected to give a tertiary nitropiperidinose, and further, by an even more facile solvolysis, the corresponding ulose. However, none of the conditions led to the desired products, and the hemiacetal **31** was isolated in every case, suggesting that deprotonation was at least incomplete. Conceivably, the allylic strain of a nitronate anion raises the pK_{HA} value of these nitropiperidines, as the nitronate anions might have to be pyramidalised, as it was evidenced for nitrofuranose-derived anions [31], meaning that sensibly stronger bases are required. In our opinion, a combination of strongly electron-accepting substituents of the hydroxy group, and of the ring N-atom will stabilize such nitropiperidinose sufficiently to allow their isolation and selective transformation.

We thank Dr. *B. Bernet* for carefully checking and commenting the analytical data, Dr. *P. Seiler* for determining the crystal structure, and the *Swiss National Science Foundation* and *Syngenta AG*, Basel, for their generous support.

Experimental Part

General. See [10].

6-Azido-2,3,4,7-tetra-O-*benzyl-6,8-dideoxy*-D-erythro-D-galacto-*octono-1,5-lactone* (**2**). A soln. of the crude hemiacetal **1** (28 g, 46 mmol) in CH_2Cl_2 (1 l) was treated at 25° with a soln. of *Dess–Martin* periodinane (30 g, 70 mmol) in CH_2Cl_2 (100 ml), stirred for 6 h, and diluted with a 1:1 mixture of a sat. $NaHCO_3$ soln. and a sat. $Na_2S_2O_3$ soln. (500 ml). The layers were separated, and the aq. layer was extracted twice with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated to afford **2** (27 g, quant.), which was used for the next step without further purification. Colourless oil. R_f (hexane/AcOEt 4:1) 0.48. $[\alpha]_D^{25} = +88.1$ ($c = 1.51$, $CHCl_3$). IR (ATR): 3062*w*, 3031*w*, 2924*w*, 2888*w*, 2104*s*, 1740*m*, 1497*w*, 1464*w*, 1453*w*, 1407*w*, 1380*w*, 1360*m*, 1350*m*, 1291*w*, 1277*w*, 1234*w*, 1207*w*, 1184*s*, 1137*s*, 1092*s*, 1076*s*, 1054*s*, 1043*s*, 1025*s*, 999*m*, 984*m*, 955*m*, 940*m*, 899*w*, 874*m*, 827*w*, 809*w*, 789*w*, 743*s*, 732*s*, 694*s*, 662*m*, 611*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 1*; additionally, 7.45–7.25 (*m*, 20 arom. H); 5.18 (*d*, $J = 11.1$), 5.05 (*d*, $J = 10.8$), 4.81 (*d*, $J = 10.8$),

4.80 (*d*, *J* = 12.0), 4.74 (*d*, *J* = 12.0), 4.69 (*d*, *J* = 12.0), 4.60 (*d*, *J* = 12.0), 4.53 (*d*, *J* = 12.0) (4 PhC*H*$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 1*; additionally, 138.04, 137.46, 137.23, 137.20 (4*s*); 128.46–127.25 (several *d*); 75.22, 74.91, 73.00, 71.02 (4*t*, 4 PhC*H*$_2$). HR-ESI-MS: 646.2337 (65, $[M+K]^+$, $C_{36}H_{37}KN_3O_6^+$; calc. 646.7932), 630.2577 (100, $[M+Na]^+$, $C_{36}H_{37}N_3NaO_6^+$; calc. 630.2575). Anal. calc. for $C_{36}H_{37}N_3O_6$ (607.70): C 71.15, H 6.14, N 6.91; found: C 70.88, H 6.18, N 7.01.

Table 1. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz]*, and ^{13}C-NMR Chemical Shifts* [ppm] *of the Lactones and Lactames* **2**, **6**, **7**, **9**, *and* **13**, *of the N,O-Hemiacetal* **14** *in $CDCl_3$, and of the Glycosyl Acetates* **18** *and* **19** *in (D_6)DMSO*

	2	**6**	**7**	**9**	**13**[a])	**14**	**18**	**19**[b])
H–C(1)	–	–	–	–	–	4.80	6.75	6.81
H–C(2)	4.49	4.38	4.49	4.55	4.30	3.94	3.92	3.89
H–C(3)	3.87	3.82	3.78	3.83	3.96	3.70	3.97	3.73
H–C(4)	4.23	4.27	4.27	4.24	3.95	4.26	4.32	4.19
H–C(5)	3.79	3.16	3.21	3.12	4.30	3.25	3.1	3.43
H–C(6)	4.17	3.73–3.71	3.66–3.58	3.89	4.38	4.77	4.93	5.25
H–C(7)	4.10	3.73	3.66–3.58	3.77	3.61	4.08	3.98	3.82
H_3C(8)	1.22	1.32	1.39	1.32	1.32	11.23	1.10	1.01
J(1,2)	–	–	–	–	–	3.6	4.2	4.2
J(2,3)	9.3	9.9	9.3	8.4	5.1	9.3	9.9	9.3
J(3,4)	2.4	1.5	1.2	2.1	4.5	3.3	3.0	3.3
J(4,5)	1.5	2.4	2.1	3.0	3.6	2.1	0	0
J(5,6)	10.2	9.3	8.7	9.6	7.8	10.8	10.8	10.5
J(6,7)	2.7	5.7	[a])	4.8	6.9	2.1	2.1	3.3
J(7,Me)	6.3	5.7	5.4	6.0	5.7	6.3	6.3	6.3
C(1)	169.24	171.50	203.17	151.43	169.39	80.83	79.97	
C(2)	76.93	76.98	80.89	76.16	79.51	77.19	75.18	
C(3)	80.21	81.04	81.48	81.61	80.26	78.03	76.61	
C(4)	72.26	73.81	73.94	73.59	70.51	74.76	74.95	
C(5)	76.87	55.84	60.82	55.59	56.37	53.97	54.73	
C(6)	61.75	64.47	64.50	64.41	64.85	63.61	63.26	
C(7)	74.91	76.48	76.57	74.42	71.95	75.18	75.07	
C(8)	13.57	15.96	15.13	15.53	16.18	13.54	13.54	

[a]) *J*(3,5) = 1.5 Hz. [b]) The majority of the ^{13}C-signals were broad and not assigned.

6-Azido-2,3,4,7-tetra-O-*benzyl-6,8-dideoxy*-D-erythro-D-galacto-*octonamide* (**3**). NH_3 was condensed at −40° into a soln. of **2** (27 g, 41 mmol) in CH_2Cl_2 (200 ml), and the mixture was stirred for 4 h. Evaporation gave **3** (25 g, quant.), which was used for the next step without further purification. Pale yellow powder. R_f (hexane/AcOEt 3:2) 0.43. $[\alpha]_D^{25} = -11.7$ (*c* = 1.03, $CHCl_3$). IR (ATR): 3445*w*, 3356*w*, 3188*w*, 3065*w*, 3031*w*, 2984*w*, 2942*w*, 2890*w*, 2101*m*, 1680*s*, 1587*w*, 1497*w*, 1454*w*, 1395*w*, 1380*m*, 1348*w*, 1327*w*, 1305*w*, 1274*m*, 1261*m*, 1217*w*, 1085*s*, 1072*s*, 1025*m*, 936*w*, 906*w*, 880*w*, 748*s*, 694*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): 7.41–7.26 (*m*, 20 arom. H); 6.67 (br. *s*, NH); 5.84 (br. *s*, NH); 4.66 (*d*, *J* = 11.4), 4.63 (*s*), 4.53 (*d*, *J* = 12.0), 4.53 (*d*, *J* = 11.7), 4.47 (*d*, *J* = 11.4), 4.44 (*d*, *J* = 11.7), 4.43 (*d*, *J* = 12.0) (4 PhC*H*$_2$); 4.16–4.11 (*m*, H–C(2), H–C(3)); 4.02 (*qd*, *J* = 6.3, 2.4, H–C(7)); 3.96 (br. *d*, *J* = 6.0, H–C(4)); 3.69 (*dd*, *J* = 10.2, 3.0, H–C(6)); 3.61 (br. *dd*, *J* = 10.2, 7.8, H–C(5)); 2.75 (*d*, *J* = 7.8, OH); 1.18 (*d*, *J* = 6.3, Me). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): 174.49 (*s*, C=O); 138.33, 137.58, 137.32, 136.42 (4*s*); 128.66–127.29 (several *d*); 79.84 (*d*, C(3)); 79.60 (*d*, C(2)); 77.08 (*d*, C(4)); 75.76 (*d*, C(7)); 75.42, 73.75, 73.29, 70.57 (4*t*, 4 PhC*H*$_2$); 69.67 (*d*, C(5)); 64.45 (*d*, C(6)); 13.49 (*q*, Me). HR-ESI-MS: 663.2562 (38,

$[M+K]^+$, $C_{36}H_{40}KN_3O_6^+$; calc. 663.2579), 647.2835 (100, $[M+Na]^+$, $C_{36}H_{40}N_3NaO_6^+$; calc. 647.2840), 625.3008 (20, $[M+H]^+$, $C_{36}H_{41}N_4O_6^+$; calc. 625.3021).

6-Azido-2,3,4,7-tetra-O-*benzyl-6,8-dideoxy*-D-glycero-D-galacto-*oct-5-ulosonamide* (**4**). A soln. of **3** (25 g, 40 mmol) in CH_2Cl_2 (600 ml) was treated at 25° with a soln. of *Dess–Martin* periodinane (30 g, 70 mmol) in CH_2Cl_2 (200 ml), stirred for 6 h, and treated with a 1:1 mixture of a sat. $NaHCO_3$ soln. and a sat. $Na_2S_2O_3$ soln. (200 ml). The layers were separated, and the aq. layer was extracted twice with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated to afford **4** (23 g, quant.), which was used for the next step without further purification. Colourless oil. R_f (hexane/AcOEt 1:1) 0.47. $[\alpha]_D^{25} = +54.3$ ($c = 0.99$, $CHCl_3$). IR (ATR): 3473*w*, 3327*w*, 3063*w*, 3031*w*, 2975*w*, 2927*w*, 2872*w*, 2103*m*, 1726*m*, 1684*m*, 1584*w*, 1496*w*, 1454*w*, 1395*w*, 1379*w*, 1337*w*, 1268*w*, 1211*w*, 1107*m*, 1086*m*, 1068*s*, 1026*m*, 911*w*, 822*w*, 735*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): 7.41–7.10 (*m*, 20 arom. H); 6.61 (br. *d*, *J* = 3.3, NH); 5.75 (br. *d*, *J* = 3.3, NH); 4.53 (*d*, *J* = 11.4), 4.51 (*d*, *J* = 11.7, 2 H) (3 PhC*H*); 4.50 (*d*, *J* = 7.2, H–C(2)); 4.48 (*d*, *J* = 10.2), 4.40 (*d*, *J* = 11.1), 4.37 (*d*, *J* = 11.4), 4.34 (*d*, *J* = 11.4) (4 PhC*H*); 4.24 (*d*, *J* = 6.6, H–C(6)); 4.17 (*dd*, *J* = 7.2, 2.7, H–C(3)); 4.13 (*d*, *J* = 3.0, H–C(4)); 3.98 (*quint.*, *J* = 6.3, H–C(7)); 3.93 (*d*, *J* = 11.4, PhC*H*); 1.25 (*d*, *J* = 6.0, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 206.78 (*s*, C(5)); 173.22 (*s*, C(1)); 137.37, 137.03, 136.83, 136.37 (4*s*); 128.55–127.64 (several *d*); 81.65 (*d*, C(3)); 81.12 (*d*, C(2)); 79.57 (*d*, C(4)); 75.77 (*d*, C(7)); 75.23, 74.10, 72.07, 70.83 (4*t*, 4 Ph*C*H_2); 67.82 (*d*, C(6)); 16.57 (*q*, Me). HR-MALDI-MS: 661.2391 (38, $[M+K]^+$, $C_{36}H_{38}KN_4O_6^+$; calc. 661.2423), 645.2679 (100, $[M+Na]^+$, $C_{36}H_{38}N_4NaO_6^+$; calc. 645.2684), 623.2854 (20, $[M+H]^+$, $C_{36}H_{39}N_4O_6^+$; calc. 623.2876).

5-Amino-6-azido-2,3,4,7-tetra-O-*benzyl-5,6,8-trideoxy*-D-erythro-D-galacto-*octono-1,5-lactam* (**6**). A soln. of **4** (23 g, 36 mmol) in MeCN (670 ml) and 98% HCOOH (250 ml) was treated with $NaCNBH_3$ (14 g, 22.3 mmol), heated to 70° for 4 h, cooled to 25°, and poured into AcOEt/sat. aq. $NaHCO_3$ soln. The layers were separated, and the aq. layer was extracted twice with AcOEt. The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 1:1) gave **6** (13 g, 58% from **1**). Yellow oil. R_f (hexane/AcOEt 3:1) 0.19. $[\alpha]_D^{25} = +106.2$ ($c = 1.27$, $CHCl_3$). IR (ATR): 3212*w*, 3064*w*, 3030*w*, 2936*w*, 2869*w*, 2107*s*, 1672*s*, 1496*w*, 1453*m*, 1381*w*, 1345*w*, 1289*m*, 1208*w*, 1100*s*, 1046*m*, 1026*m*, 908*w*, 819*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 1*; additionally, 7.47–7.26 (*m*, 20 arom. H); 6.80 (br. *s*, NH); 5.24 (*d*, *J* = 11.4), 5.19 (*d*, *J* = 10.8), 4.86 (*d*, *J* = 11.1), 4.84 (*d*, *J* = 12.0), 4.77 (*d*, *J* = 12.0), 4.65 (*d*, *J* = 11.7), 4.63 (*d*, *J* = 10.8), 4.48 (*d*, *J* = 11.7) (4 PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 1*; additionally, 138.02, 137.92, 137.77, 136.93 (4*s*); 128.55–127.40 (several *d*); 75.42, 74.27, 73.14, 70.80 (4*t*, 4 Ph*C*H_2). HR-MALDI-MS: 645.2478 (38, $[M+K]^+$, $C_{36}H_{38}KN_4O_5^+$; calc. 645.2474), 629.2740 (60, $[M+Na]^+$, $C_{36}H_{38}N_4NaO_5^+$; calc. 629.2734), 607.2920 (100, $[M+H]^+$, $C_{36}H_{39}N_4O_5^+$; calc. 607.2915). Anal. calc. for $C_{36}H_{38}N_4O_5$ (606.72): C 71.27, H 6.31, N 9.23; found: C 71.02, H 6.43, N 9.04.

5-Amino-6-azido-2,3,4,7-tetra-O-*benzyl-5,6,8-trideoxy*-D-erythro-D-galacto-*octono-1,5-thiolactam* (**7**). A soln. of **6** (660 mg, 1.09 mmol) in toluene (20 ml) was treated with *Lawesson*'s reagent (400 mg, 0.98 mmol), heated to 60° for 2 h, and evaporated. FC (hexane/AcOEt 98:2 → 4:1) gave **7** (520 mg, 75%). Yellow oil. R_f (hexane/AcOEt 4:1) 0.46. $[\alpha]_D^{25} = +122.4$ ($c = 0.46$, $CHCl_3$). IR (ATR): 3297*w*, 3063*w*, 3030*w*, 2870*w*, 2108*s*, 1595*w*, 1496*m*, 1453*m*, 1380*w*, 1356*w*, 1288*m*, 1263*w*, 1209*w*, 1177*w*, 1091*m*, 1059*m*, 1025*m*, 907*m*, 730*s*, 694*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 1*; additionally, 9.04 (br. *s*, NH); 7.53–7.49 (*m*, 2 arom. H); 7.40–7.21 (*m*, 18 arom. H); 5.45 (*d*, *J* = 10.8), 5.20 (*d*, *J* = 10.8), 4.89 (*d*, *J* = 10.8), 4.81 (*d*, *J* = 12.3), 4.74 (*d*, *J* = 11.7), 4.71 (*d*, *J* = 11.7), 4.63 (*d*, *J* = 10.8), 4.47 (*d*, *J* = 11.7) (4 PhCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 138.23, 138.10, 137.96, 136.51 (4*s*); 129.10–127.78 (several *d*); 76.57, 74.07, 73.41, 71.08 (4*t*, 4 Ph*C*H_2). HR-MALDI-MS: 645.2506 (10, $[M+Na]^+$, $C_{36}H_{38}N_4NaO_4^+$; calc. 645.2506), 623.2687 (100, $[M+H]^+$, $C_{36}H_{39}N_4O_4^+$; calc. 623.2687). Anal. calc. for $C_{36}H_{38}N_4O_4S$ (622.79): C 69.43, H 6.25, N 8.69; found: C 69.26, H 6.25, N 8.69.

(Z)-6-Azido-2,3,4,7-tetra-O-*benzyl-5*-C-*{[(*tert*-butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-D-galacto-*octonhydroximo-1,5-lactam* (**9**). A soln. of **7** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 ml) was treated with DMAP (2 mg, 0.16 mmol) and Boc_2O (70 mg, 0.32 mmol), stirred for 1 h, diluted with MeOH (5 ml), treated with $NH_2OH \cdot HCl$ (56 mg, 0.80 mmol) and $NaHCO_3$ (68 mg, 0.80 mmol), heated to 60°,

stirred for 1 h, and evaporated. A soln. of the residue in AcOEt was washed with H_2O and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 1:1) gave **9** (103 mg, 90%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.59. $[\alpha]_D^{25} = +38.2$ ($c = 0.84$, $CHCl_3$). IR (ATR): 3365*w*, 3063*w*, 3030*w*, 2869*w*, 2106*s*, 1710*m*, 1644*m*, 1496*w*, 1453*m*, 1381*w*, 1358*w*, 1288*m*, 1207*w*, 1069*m*, 1026*m*, 953*w*, 911*w*, 732*s*, 694*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 1*; additionally, 7.42–7.25 (*m*, 20 arom. H); 7.07 (br. *s*, OH); 5.09 (*d*, $J = 11.1$), 4.94 (*d*, $J = 11.4$), 4.79 (*d*, $J = 11.7$), 4.73 (*d*, $J = 11.4$), 4.71 (*d*, $J = 11.4$), 4.66 (*d*, $J = 11.4$), 4.62 (*d*, $J = 12.0$), 4.50 (*d*, $J = 12.0$) (4 PhCH_2); 1.49 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 158.90 (*s*, C=O); 138.06, 137.92, 137.85, 137.40 (4*s*); 128.37–127.54 (several *d*); 81.84 (*s*, Me_3C); 73.98 (2 C), 72.79, 70.77 (3*t*, 4 PhCH$_2$); 28.18 (*q*, Me_3C). HR-MALDI-MS: 644.2860 (5, $[M - \text{Boc} + \text{H} + \text{Na}]^+$, $C_{36}H_{39}N_5NaO_5^+$; calc. 644.2843), 622.3035 (100, $[M - \text{Boc} + 2\,\text{H}]^+$, $C_{36}H_{40}N_5O_5^+$; calc. 622.3024).

6-Azido-2,3,4,7-tetra-O-*benzyl-5*-C-*{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-D-galacto-*octono-1,5-lactam* (**13**). A soln. of **6** (100 mg, 0.16 mmol) and DMAP (20 mg, 0.16 mmol) in $ClCH_2CH_2Cl$ was heated to 70°, treated with Boc_2O (70 mg, 0.32 mmol), stirred for 6 h, and evaporated. FC (hexane/AcOEt 98:2 → 4:1) gave **13** (90 mg, 80%). Colourless oil. R_f (hexane/AcOEt 4:1) 0.53. $[\alpha]_D^{25} = +59.1$ ($c = 1.08$, $CHCl_3$). IR (ATR): 3030*w*, 2977*w*, 2930*w*, 2870*w*, 2114*m*, 1709*s*, 1693*m*, 1654*w*, 1496*w*, 1453*w*, 1367*m*, 1308*w*, 1278*w*, 1251*m*, 1207*w*, 1150*m*, 1122*m*, 1074*s*, 1027*m*, 965*w*, 934*w*, 909*w*, 857*w*, 790*w*, 773*w*, 732*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 1*; additionally, 7.41–7.25 (*m*, 20 arom. H); 4.80 (*d*, $J = 11.7$), 4.77 (*d*, $J = 11.4$), 4.74 (*d*, $J = 11.1$), 4.71 (*d*, $J = 11.4$), 4.70 (*d*, $J = 11.7$), 4.52 (*d*, $J = 10.8$), 4.25 (*d*, $J = 10.8$), 4.22 (*d*, $J = 11.4$) (4 PhCH_2); 1.50 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 1*; additionally, 152.44 (*s*, C=O of Boc); 137.90, 137.66, 137.51, 137.27 (4*s*); 128.35–127.61 (several *d*); 81.14 (*s*, Me_3C); 75.33, 74.78, 74.10, 73.42 (4*t*, 4 PhCH$_2$); 28.11 (*q*, Me_3C). HR-MALDI-MS: 729.3246 (30, $[M + \text{Na}]^+$, $C_{41}H_{46}N_4NaO_7^+$; calc. 729.3259), 629.2734 (41, $[M - \text{Boc} + \text{H} + \text{Na}]^+$, $C_{36}H_{38}N_4NaO_5^+$; calc. 629.2734), 607.2913 (100, $[M - \text{Boc} + 2\,\text{H}]^+$, $C_{36}H_{39}N_4O_5^+$; calc. 607.2915). Anal. calc. for $C_{41}H_{46}N_4O_7$ (706.84): C 69.67, H 6.56, N 7.93; found: C 69.51, H 6.65, N 7.86.

6-Azido-2,3,4,7-tetra-O-*benzyl-5*-C-*{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-*α*-D-galacto-*octopyranose* (**14**). At 0°, a soln. of **13** (870 mg, 1.23 mmol) in THF (10 ml) was treated dropwise with a 1M *Super-Hydride*® soln. (6.2 ml, 6.2 mmol), stirred for 1 h, and treated with a sat. aq. $NaHCO_3$ soln. THF was evaporated, and the aq. layer was extracted twice with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated to afford **14** (880 mg, quant.), which was used for the next step without further purification. Colourless oil. R_f (hexane/AcOEt 4:1) 0.35. $[\alpha]_D^{25} = +48.2$ ($c = 1.05$, $CHCl_3$). IR (ATR): 3212*w*, 3064*w*, 3031*w*, 2980*w*, 2931*w*, 2871*w*, 2110*m*, 1734*m*, 1714*m*, 1496*w*, 1454*w*, 1393*w*, 1368*w*, 1285*m*, 1256*m*, 1208*w*, 1147*s*, 1094*s*, 1051*m*, 1026*m*, 911*w*, 848*w*, 733*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$, 60°; assignments based on selective homodecoupling experiments): 7.46–7.25 (*m*, 20 arom. H); 4.80 (br. *s*, H–C(1), after addition of D_2O: *d*, $J = 3.3$); 4.77 (br. *d*, $J = 10.8$, H–C(6)); 4.91 (*d*, $J = 11.7$), 4.81 (*d*, $J = 11.7$), 4.79 (*d*, $J = 11.4$), 4.78 (*d*, $J = 11.4$) (2 PhCH_2); 4.74, 4.66 (2*s*, 2 PhCH_2); 4.26 (br. *d*, $J = 2.1$, H–C(4)); 4.08 (*qd*, $J = 6.3, 2.1$, H–C(7)); 3.94 (*dd*, $J = 9.3, 3.6$, H–C(2)); 3.70 (*dd*, $J = 9.0, 3.3$, H–C(3)); 3.25 (br. *d*, $J = 10.8$, H–C(5)); 3.02 (br. *s*, exchange with D_2O, OH); 1.36 (*s*, *t*-Bu); 1.23 (*d*, $J = 6.3$, Me). ^{13}C-NMR (75 MHz, $CDCl_3$, 60°): 154.24 (*s*, C=O); 138.85, 138.62, 138.38, 138.08 (4*s*); 128.30–127.15 (several *d*); 80.95 (*s*, Me_3C); 80.83 (*d*, C(1)); 78.03 (*d*, C(3)); 77.19 (*d*, C(2)); 75.80 (*d*, C(7)); 74.76 (*d*, C(4)); 74.22, 73.45, 72.89, 70.52 (4*t*, 4 PhCH_2); 63.31 (*d*, C(6)); 53.97 (*d*, C(5)); 28.21 (*q*, Me_3C); 13.54 (*q*, Me). HR-MALDI-MS: 747.3167 (30, $[M + \text{K}]^+$, $C_{41}H_{48}KN_4O_7^+$; calc. 747.3155), 731.3421 (100, $[M + \text{Na}]^+$, $C_{41}H_{48}N_4NaO_7^+$; calc. 731.3415), 607.2877 (80, $[M - \text{Boc} + \text{H}]^+$, $C_{36}H_{39}N_4O_5^+$; calc. 607.2920), 591.2970 (55, $[M - \text{Boc} - \text{OH} + 2\,\text{H}]^+$, $C_{36}H_{39}N_4O_4^+$; calc. 591.2966). Anal. calc. for $C_{41}H_{48}N_4O_7$ (708.85): C 69.47, H 6.83, N 7.90; found: C 69.51, H 6.85, N 7.83.

(E/Z)-6-Azido-2,3,4,7-tetra-O-*benzyl-5*-C-*{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-D-galacto-*octose Oxime* (**15**). A soln. of crude **14** (880 mg, 1.23 mmol) in abs. EtOH (50 ml) was added to a soln. of $NH_2OH \cdot HCl$ (2.78 g, 0.041 mmol) and $NaHCO_3$ (1.39 g, 0.02 mmol) in abs. EtOH (150 ml). The mixture was heated to 80° for 24 h, cooled to 25°, and evaporated. A soln. of the residue in AcOEt was washed with H_2O and brine, dried (Na_2SO_4), and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **15** (760 mg, 85% from **13**). Colourless oil. R_f (hexane/AcOEt 2:1) 0.53. $[\alpha]_D^{25} = +7.2$ ($c = 1.1$, $CHCl_3$). IR (ATR): 3428*w* (br.), 3064*w*, 3031*w*, 2978*w*, 2872*w*, 2104*m*, 1712*m*, 1688*w*, 1495*m*, 1454*m*, 1391*w*, 1366*w*,

1307*w*, 1254*w*, 1162*m*, 1069*s*, 1027*m*, 939*w*, 912*w*, 733*s*, 695*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°, (*E*/*Z*) 7:3; assignments based on selective homodecoupling experiments): 11.09 (*s*, OH (*Z*)); 10.81 (*s*, OH (*E*)); 7.44 (*d*, *J* = 7.5, H–C(1) (*E*)); 7.37–7.25 (*m*, 20 arom. H); 6.95 (*d*, *J* = 6.0, H–C(1) (*Z*)); 5.97 (br. *s*, N*H*Boc); 5.05 (*dd*, *J* = 6.0, 2.7, H–C(2) (*Z*)); 4.73–4.39 (*m*, 4 PhCH_2); 4.32 (*dd*, *J* = 7.5, 4.2, H–C(2) (*E*)); 4.02 (*t*, *J* = 7.2, 1 H); 3.87–3.68 (*m*, 4 H); 1.35 (*s*, *t*-Bu (*Z*)); 1.33 (*s*, *t*-Bu (*E*)); 1.20 (*d*, *J* = 6.0, Me). ^{13}C-NMR (75 MHz, (D_6)DMSO, 100°; (*E*/*Z*) 7:3): 154.92 (*s*, C=O); 149.74 (*d*, C(1) (*E*)); 147.72 (*d*, C(1) (*Z*)); 138.35–137.87 (several *s*); 127.95–127.02 (several *d*); 80.39 (*d*, 1 C (*E*)); 78.55 (*d*, 1 C (*Z*)); 77.10 (*d*, 1 C (*E*)); 76.71 (*d*, 1 C (*Z*)); 75.22 (*d*, 1 C (*E*)); 73.84 (*t*, Ph*C*H$_2$ (*E*)); 73.62 (*t*, Ph*C*H$_2$ (*Z*)); 73.53 (*t*, Ph*C*H$_2$ (*Z*)); 73.19 (*t*, Ph*C*H$_2$ (*E*)); 71.84 (*d*, 1 C (*E*)); 70.85 (*t*, Ph*C*H$_2$ (*Z*)); 70.22 (*t*, Ph*C*H$_2$ (*E*)); 69.83 (*t*, Ph*C*H$_2$); 64.99 (*d*, C(6)); 50.44 (*d*, C(5)); 28.07 (*q*, *Me*$_3$C); 13.92 (*q*, Me); *s* of Me$_3$*C* hidden by the noise. HR-MALDI-MS: 762.3274 (6, $[M+K]^+$, $C_{41}H_{49}KN_5O_7^+$; calc. 762.3264), 746.3533 (17, $[M+Na]^+$, $C_{41}H_{49}N_5NaO_7^+$; calc. 746.3524), 724.3709 (100, $[M+H]^+$, $C_{41}H_{50}N_5O_7^+$; calc. 724.3405). Anal. calc. for $C_{41}H_{49}N_5O_7$ (723.87): C 68.03, H 6.82, N 9.67; found: C 67.79, H 6.85, N 9.42.

1-O-*Acetyl-6-azido-2,3,4,7-tetra*-O-*benzyl-5-{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-α-D-galacto-*octopyranose* (**18**). At 0°, a soln. of **13** (460 mg, 0.66 mmol) in THF (50 ml) was treated dropwise with a 1M *Super-Hydride*® soln. (2.6 ml, 2.6 mmol), stirred for 1 h, and treated with a sat. aq. $NaHCO_3$ soln. After evaporation of THF, the aq. layer was extracted twice with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated to afford crude **14**. A soln. of crude **14** in CH_2Cl_2 (20 ml) was treated with Et_3N (2 ml), DMAP (40 mg, 0.30 mmol), and Ac_2O (1 ml), stirred for 12 h, and evaporated. A soln. of the residue in AcOEt was washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **18** (470 mg, 90% from **13**). R_f (hexane/AcOEt 4:1) 0.40. $[\alpha]_D^{25} = +30.0$ ($c = 1.17$, $CHCl_3$). IR (ATR): 3031*w*, 2978*w*, 2932*w*, 2870*w*, 2107*m*, 1754*m*, 1734*m*, 1715*m*, 1496*w*, 1454*w*, 1368*w*, 1340*w*, 1286*m*, 1254*m*, 1225*w*, 1154*s*, 1118*m*, 1093*m*, 1053*s*, 1026*s*, 938*w*, 862*w*, 817*w*, 735*s*, 696*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°; assignments based on selective homodecoupling experiments): see *Table 1*, additionally: 7.40–7.23 (*m*, 20 arom. H); 4.86 (*d*, *J* = 11.7), 4.80 (*d*, *J* = 12.0), 4.72 (*d*, *J* = 11.7, 2 H), 4.64 (*d*, *J* = 11.7), 4.58 (*d*, *J* = 11.7), 4.56 (*d*, *J* = 10.5), 4.53 (*d*, *J* = 11.7) (4 PhCH_2); 2.06 (*s*, AcO); 1.31 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$, 60°): see *Table 1*, additionally, 168.23 (*s*, OC=O); 152.98 (*s*, NC=O); 138.52, 138.42, 137.92, 138.08 (4*s*); 127.88–127.03 (several *d*); 81.10 (*s*, Me$_3$*C*); 73.64, 72.33, 71.95, 69.87 (4*t*, 4 Ph*C*H$_2$); 27.71 (*q*, *Me*$_3$C); 20.32 (*q*, *Me*C=O). HR-MALDI-MS: 789.3310 (27, $C_{43}H_{50}KN_4O_8^+$, $[M+K]^+$; calc. 789.3260), 773.3527 (71, $[M+Na]^+$, $C_{43}H_{50}N_4NaO_7^+$; calc. 773.3521), 591.2960 (100, $[M - Boc - OAc + 2\,H]^+$, $C_{36}H_{39}N_4O_4^+$; calc. 591.2966). Anal. calc. for $C_{43}H_{50}N_4O_8$ (750.89): C 68.78, H 6.71, N 7.46; found: C 69.84, H 6.68, N 7.31.

1-O-*Acetyl-2,3,4,7-tetra*-O-*benzyl-6-{[(benzyloxy)carbonyl]amino}-5-{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-α-D-galacto-*octopyranose* (**19**). A 1M soln. of **18** (770 mg, 1.03 mmol) in pyridine/H_2O 5:1 (12 ml) was treated with propane-1,3-dithiol (2.1 ml, 20.7 mmol) and Et_3N (2 ml), stirred for 6 h, and evaporated. At 0°, a soln. of the residue in CH_2Cl_2 (20 ml) was treated with Et_3N (1 ml, 7.21 mmol) and CbzCl (740 µl, 5.15 mmol), warmed to 25°, stirred for 4 h, and diluted with sat. aq. $NaHCO_3$ soln. The layers were separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 85:5 → 4:1) gave **19** (677 mg, 75%). R_f (hexane/AcOEt 4:1) 0.20. $[\alpha]_D^{25} = +44.7$ ($c = 1$, $CHCl_3$). IR (ATR): 3335*w*, 3032*w*, 2977*w*, 1720*s*, 1498*m*, 1454*m*, 1369*m*, 1307*m*, 1228*s*, 1159*m*, 1092*s*, 1032*m*, 953*w*, 902*w*, 856*w*, 738*s*, 698*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°): see *Table 1*, additionally: 7.40–7.16 (*m*, 25 arom. H); 6.8 (br. *s*, NH); 5.15 (br. *d*, *J* = 12.6), 5.03 (*d*, *J* = 12.6) (PhCH_2); 4.64 (*s*, PhCH_2); 4.61–4.52 (*m*, 5 PhC*H*); 4.45 (*d*, *J* = 12.0, PhC*H*); 3.89 (*dd*, *J* = 9.3, 4.2, H–C(2)); 3.82 (*qd*, *J* = 6.3, 3.6, H–C(7)); 3.73 (*dd*, *J* = 9.3, 3.3, H–C(3)); 2.03 (*s*, AcO); 1.27 (*s*, *t*-Bu). ^{13}C-NMR (300 MHz, (D_6)DMSO, 100°): 168.21 (*s*, OC=O); 155.93, 153.11 (2*s*, 2 NC=O); 139.22, 138.71, 138.49, 137.95, 137.25 (5*s*); 129.00–126.00 (several *d*); 80.57 (*s*, Me$_3$*C*); 80.00–51.00 (broad signals); 27.83, 27.70 (2*q*, 2 *Me*$_3$C); 21.00–20.00 (broad signals, Me). HR-MALDI-MS: 897.3760 (14, $[M+K]^+$, $C_{51}H_{58}KN_2O_{10}^+$; calc. 897.3723), 881.3983 (22, $[M+Na]^+$, $C_{51}H_{58}N_2NaO_{10}^+$; calc. 881.3984), 699.3413 (100, $[M - Boc - OAc + 2\,H]^+$, $C_{44}H_{47}N_2O_6^+$; calc. 699.3434).

2,3,4,7-Tetra-O-*benzyl-6-{[(benzyloxy)carbonyl]amino}-5-{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy*-D-erythro-α-D-galacto-*octopyranosyl Azide* (**20**). A soln. of **19** (670 mg, 0.78 mmol) and TMS-N_3 (1.04 ml, 7.8 mmol) in CH_2Cl_2 (20 ml) was treated with 4-Å mol. sieves, stirred for 30 min at 25°, cooled to −50°, treated with $BF_3 \cdot OEt_2$ (106 µl, 0.86 mmol), stirred for 15 min, diluted with sat. aq. $NaHCO_3$ soln.,

and filtered over *Celite*. The layers were separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. layers were dried ($MgSO_4$) and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **20** (550 mg, 83%). R_f (hexane/AcOEt 4:1) 0.30. $[\alpha]_D^{25} = +16.8$ ($c = 1$; $CHCl_3$). IR (ATR): 3064*w*, 3031*w*, 2976*w*, 2931*w*, 2865*w*, 2101*m*, 1719*m*, 1700*m*, 1586*w*, 1497*w*, 1453*w*, 1367*m*, 1326*m*, 1304*m*, 1223*m*, 1159*m*, 1092*s*, 1065*s*, 1053*s*, 1026*m*, 908*m*, 856*w*, 729*s*, 695*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°): broad signals. HR-MALDI-MS: 880.3664 (14, $[M+K]^+$, $C_{49}H_{55}KN_5O_8^+$; calc. 880.3682), 864.3959 (34, $[M+Na]^+$, $C_{49}H_{55}N_5NaO_8^+$; calc. 864.3943), 699.3404 (100, $[M - Boc - N_3 + 2H]^+$, $C_{44}H_{47}N_2O_6^+$; calc. 699.3434).

2,3,4,6-Tetra-O-*benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-1,5-deoxy-d-glucopyranose N-Benzylimine N-Oxide* (**26**) *and 2,3,4,6-Tetra*-O-*benzyl-1*-N-*benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-5-deoxy-1*-N-*hydroxy-β*-D-*glucopyranosylamine* (**27**). A soln. of BnNHOH · HCl (490 mg, 3.06 mmol) in MeOH was treated with $NaHCO_3$ (120 mg, 1.41 mmol), stirred for 15 min, and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O and brine. The org. layer was dried ($MgSO_4$) and evaporated to afford BnNHOH. A soln. of **25** [14] (390 mg, 0.61 mmol) in dry pyridine (5 ml) was treated with BnNHOH and 4-Å mol. sieves, heated for 12 h at 80°, filtered, and evaporated. TLC showed two spots in a ratio of *ca.* 1:1. FC (hexane/AcOEt 98:2 → 0:100) provided two fractions that revealed the same two spots on TLC (*ca.* 1:1) corresponding to **26**/**27** (340 mg, 75%). Colourless oil. **26**: R_f (hexane/AcOEt 4:1) 0.59. **27**: R_f (AcOEt) 0.50. **26**/**27**: $[\alpha]_D^{25} = +13.25$ ($c = 1.18$, $CHCl_3$). IR (ATR): 3251*w*, 3030*w*, 2869*w*, 1692*m*, 1604*w*, 1496*w*, 1453*w*, 1391*w*, 1365*w*, 1340*w*, 1257*w*, 1208*w*, 1164*m*, 1090*m*, 1056*s*, 1025*s*, 1006*s*, 862*w*, 818*w*, 735*s*, 696*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°; assignments based on selective homodecoupling experiments): see *Table 2*; additionally, 7.77 (br. *s*, 1 arom. H); 7.38–7.21 (*m*, 24 arom. H); 4.76 (*d*, $J = 12.9$), 4.76 (*d*, $J = 10.8$), 4.64 (*d*, $J = 11.7$), 4.61 (*d*, $J = 11.1$), 4.46 (*d*, $J = 12.3$), 4.40 (*d*, $J = 12.0$), 4.08 (*d*, $J = 13.8$), 3.70 (*d*, $J = 14.1$) (4 PhCH_2); 3.02 (*s*, OH, HDO); 1.41 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, (D_6)DMSO, 100°): see *Table 2*; additionally, 154.76 (*s*, C=O); 138.70, 138.59, 138.44 (2 C), 138.06 (4*s*); 128.52–126.21 (several *d*); 79.95 (*s*, Me_3C); 73.27, 73.01, 72.17, 71.15, 59.25 (5*t*, 5 PhCH_2); 27.96 (*q*, Me_3C). HR-MALDI-MS: 783.3411 (38, $[M+K]^+$, $C_{46}H_{52}KN_2O_7^+$; calc. 783.3412), 767.3652 (77, $[M+Na]^+$, $C_{46}H_{52}N_2NaO_7^+$; calc. 767.3667, 544.2460 (13, $[M - Boc - BnNHOH + H + Na]^+$, $C_{34}H_{35}NNaO_4^+$; calc. 544.2458), 522.2629 (55, $[M - Boc - BnNOH + 2H]^+$, $C_{34}H_{36}NO_4^+$; calc. 522.2639). Anal. calc. for $C_{46}H_{52}N_2O_7$ (744.93): C 74.17, H 7.04, N 3.76; found: C 73.90, H 7.17, N 3.83.

2,3,4,6-Tetra-O-*benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-5-deoxy-1*-N-(*phenylmethylidene)-β*-D-*glucopyranosylamine* N-*Oxide* (**28**). A soln. of **26**/**27** (130 mg, 0.17 mmol) and MnO_2 (73 mg, 0.85 mmol) in $ClCH_2CH_2Cl$ (5 ml) was kept at reflux for 48 h, cooled to r.t., filtered over *Celite*, and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **28** (120 mg, 90%). Colourless crystals. M.p. 68–70°. R_f (hexane/AcOEt 4:1) 0.44. $[\alpha]_D^{25} = -60.6$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3062*w*, 3030*w*, 2975*w*, 2931*w*, 2868*w*, 1705*m*, 1578*w*, 1564*w*, 1496*w*, 1454*m*, 1391*w*, 1366*m*, 1331*m*, 1255*w*, 1213*w*, 1156*m*, 1133*m*, 1067*s*, 1027*s*, 924*w*, 881*w*, 852*w*, 806*w*, 773*w*, 733*s*, 693*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°; assignments based on selective homodecoupling experiments): see *Table 2*; additionally, 8.29–8.22 (*m*, 2 arom. H); 7.91 (br. *s*, CH=N); 7.44–7.08 (*m*, 23 arom. H); 4.75 (*s*, PhCH_2); 4.73 (*d*, $J = 11.8$), 4.67 (*d*, $J = 11.7$) (2 PhC*H*); 4.62 (*s*, PhCH_2); 4.56 (*d*, $J = 11.7$), 4.41 (*d*, $J = 11.1$) (2 PhC*H*); 1.36 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, (D_6)DMSO, 100°): see *Table 2*; additionally, 153.66 (*s*, C=O); 138.30, 138.15, 137.93, 137.53 (4*s*); 134.45 (*d*, CH=N); 130.44 (*s*); 129.77–127.17 (several *d*); 81.20 (*s*, Me_3C); 74.46, 72.87, 72.32, 71.34 (4*t*, 4 PhCH_2); 27.84 (*q*, Me_3C). HR-MALDI-MS: 781.3248 (38, $[M+K]^+$, $C_{46}H_{50}KN_2O_7^+$; calc. 781.3250), 765.3506 (77, $[M+H+Na]^+$, $C_{46}H_{50}N_2NaO_7^+$; calc. 765.3510), 544.2460 (13, $[M - Boc - PhCHNO + H + Na]^+$, $C_{34}H_{35}NNaO_4^+$; calc. 544.2458), 522.2629 (55, $[M - Boc - PhCHNO + H]^+$, $C_{34}H_{36}NO_4^+$; calc. 522.2639). Anal. calc. for $C_{46}H_{50}N_2O_7$ (742.91): C 74.37, H 6.78, N 3.77; found: C 74.18, H 6.87, N 3.66.

Crystal-Structure Analysis of **28**. Crystals of **28** were obtained by slow evaporation of a soln. of **28** in MeOH/H_2O (dimensions of the analyzed crystal: cube 0.15 × 0.13 × 0.10 mm). $C_{46}H_{50}N_2O_7$, M_r 742.88, orthorhombic $P2_12_12_1$; $a = 9.1192(11)$, $b = 12.2196(12)$, $c = 36.9155(16)$, $V = 4113.6(7)$ Å^3, $D_x = 1.200$ Mg/m^3, $Z = 4$. The reflections were measured on a *Bruker Nonius-Kappa CCD* diffractometer (graphite monochromator, MoK_α radiation, $\lambda = 0.71070$) at 220 K. All the calculations were performed using maXus (*Bruker Nonius*, Delft, *MacScience*, Japan). The structure was solved by direct methods and refined by full-matrix least-squares analysis (SHELXL-97) including an isotropic extinction correction. All non-H-atoms were refined anisotropically (H-atoms isotropic, whereby H-positions are based on

Table 2. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz], *and ^{13}C-NMR Chemical Shifts* [ppm] *of the* N-*Bocylated and* N-*Tosylated 5-Amino-5-deoxyglucopyranose Derivatives* **27** *and* **28** *in (D_6)DMSO at 100°, of* **30** *and* **31** *in $CDCl_3$, and of* **34** *and* **35** *in CD_2Cl_2*

	27	**28**	**30**	α-D-**31**[a])	β-D-**31**[a])	**34**	**35**[c])
H–C(1)	5.08	5.53	–	5.37	5.70	5.43	6.04
H–C(2)	4.25–4.18	4.31	4.31	3.62	3.74	4.30	4.51
H–C(3)	3.58	3.77	3.72	3.19	3.81	3.40	3.54
H–C(4)	3.96	3.95	4.01	3.86	4.07	3.82	3.88
H–C(5)	4.25–4.18	3.91–3.82	4.82	4.03–3.99	3.97–3.91	4.36–4.29	4.07
H_a–C(6)	3.78	3.91–3.82	3.83	3.69	3.97–3.91	3.86	3.82
H_b–C(6)	3.78	3.91–3.82	3.78	3.53	3.69–3.65	3.66	3.70
J(1,OH)	–	–	–	6.2	11.8	–	–
J(1,2)	[b])	8.4	–	3.5	3.0	7.9	3.6
J(2,3)	6.6	9.9	7.5	8.1	6.8	10.8	6.3
J(3,4)	9.3	5.1	2.7	8.2	5.6	6.0	5.3
J(3,5)	–	–	1.5	–	–	–	–
J(4,5)	7.2	[b])	2.7	4.8	2.3	1.1	1.2
J(5,6_a)	5.7	[b])	10.8	5.9	[b])	10.1	4.0
J(5,6_b)	5.7	[b])	6.6	3.1	[b])	4.8	8.8
J(6_a,6_b)	5.7	[b])	10.8	9.7	[b])	10.1	9.3
C(1)	83.17	84.71	168.83			85.95	
C(2)	78.42	80.42	79.69			75.71	
C(3)	80.57	81.82	81.73			82.04	
C(4)	77.44	76.05	75.90			81.64	
C(5)	59.25	55.76	60.14			57.99	
C(6)	71.00	70.29	70.06			71.91	

[a]) The majority of the ^{13}C-signals were not assigned. [b]) Not determined.

stereochemical considerations). $R = 0.0398$, $R_w = 0.0872$ for 500 parameters and 3189 reflections, $\theta < 24.10°$.

2,3,4,6-Tetra-O-*benzyl-5-deoxy-5-[(4-methylphenylsulfonyl)amino]*-D-*glucono-1,5-lactam* (**30**). A soln. of **23** [14] (1 g, 1.86 mmol) in THF (20 ml) was cooled to −78°, treated with a 1.6M BuLi in hexane (1.5 ml, 1.86 mmol), stirred for 15 min, treated with DMAP (227 mg, 1.86 mmol) and TsCl (710 mg, 3.72 mmol), allowed to warm to 25°, stirred for 1 h, diluted with sat. NH_4Cl soln., and extracted with CH_2Cl_2 (3×). The combined org. layers were washed with H_2O and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95:5 → 4:1) gave **30** (1.0 g, 77%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.63. $[\alpha]_D^{25} = +1.3$ ($c = 1.58$, $CHCl_3$). IR (ATR): 3063*w*, 3031*w*, 2923*w*, 2866*w*, 1721*m*, 1596*w*, 1495*w*, 1453*m*, 1397*w*, 1352*m*, 1307*w*, 1292*w*, 1264*w*, 1187*m*, 1168*s*, 1072*s*, 1026*m*, 909*w*, 888*w*, 811*w*, 732*s*, 695*s*, 674*m*, 655*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): see *Table 2*; additionally, 7.86 (br. *d*, *J* = 8.1, 2 arom. H); 7.32–7.25 (*m*, 16 arom. H); 7.21 (br. *dd*, *J* = 5.7, 2.4, 2 arom. H); 7.12 (br. *dd*, *J* = 7.2, 3.9, 2 arom. H); 7.06 (br. *d*, *J* = 8.1, 2 arom. H); 4.98 (*d*, *J* = 11.4, PhC*H*); 4.61 (*d*, *J* = 11.7), 4.53 (*d*, *J* = 11.4) (2 PhC*H*); 4.51 (*s*, PhCH_2); 4.47 (*d*, *J* = 11.4, PhC*H*); 4.39 (*s*, PhCH_2); 2.36 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 2*; additionally, 144.50, 137.45, 137.37, 137.26, 136.86, 135.41 (6*s*); 129.03–127.68 (several *d*); 74.06, 73.50, 72.95, 71.29 (4*t*, 4 PhCH_2); 21.74 (*q*, Me). HR-MALDI-MS: 730.2221 (38, $[M+K]^+$, $C_{41}H_{41}KNO_7S^+$; calc. 730.2235), 714.2486 (100, $[M+Na]^+$, $C_{41}H_{41}NNaO_7S^+$; calc. 714.2496). Anal. calc. for $C_{41}H_{41}NO_7S$ (691.84): C 71.18, H 5.97, N 2.02; found: C 70.90, H 6.16, N 1.99.

2,3,4,6-Tetra-O-*benzyl-5-deoxy-5-[(4-methylphenylsulfonyl)amino]*-α/β-D-*glucopyranose* (**31**). A soln. of DIBAL-H (4.2 ml, 4.16 mmol) in toluene (20 ml) was cooled to 0°, treated dropwise with a

soln. of **30** (720 mg, 1.04 mmol) in toluene (5 ml), stirred for 30 min, treated with ice cubes, and stirred for 30 min at 25°. After filtration over *Celite*, evaporation and FC (hexane/AcOEt 95:5 → 3:1) gave **31** (616 mg, 85%). Colourless oil. R_f (hexane/AcOEt 3:1) 0.54. $[\alpha]_D^{25} = +27.6$ ($c = 1.05$, $CHCl_3$). IR (ATR): 3422*w*, 3063*w*, 3030*w*, 2923*w*, 2869*w*, 1598*w*, 1496*w*, 1453*m*, 1397*w*, 1347*m*, 1307*w*, 1208*w*, 1161*s*, 1088*s*, 1070*s*, 1027*s*, 983*m*, 965*m*, 915*w*, 814*w*, 734*s*, 696*s*, 665*s*. ^{1}H-NMR (400 MHz, $CDCl_3$; assignments based on a DQF-COSY spectrum; α/β 7:3): 7.92 (*d*, $J = 8.3$, 2 arom. H (β)); 7.74 (*d*, $J = 8.3$, 2 arom. H (α)); 7.38–7.13 (*m*, 20 arom. H); 7.10 (*d*, $J = 8.6$, 2 arom. H (α)); 6.78 (*d*, $J = 8.1$, 2 arom. H (β)); 5.70 (*dd*, $J = 11.8$, 2.9, H–C(1) (β)); 5.37 (*dd*, $J = 6.2$, 3.5, H–C(1) (α)); 4.80 (*d*, $J = 11.5$, PhC*H* (β)); 4.68 (*d*, $J = 11.4$, PhC*H* (α)); 4.61 (2*d*, $J = 10.9$ and 11.6, 2 PhC*H* (α)); 4.55 (*d*, $J = 11.4$, 2 PhC*H* (α)); 4.49 (*s*, PhCH_2 (β)); 4.46–4.40 (*m*, PhC*H* (α), 3 PhC*H* (β)); 4.41 (*d*, $J = 11.5$, PhC*H* (α)); 4.35 (*d*, $J = 11.6$, PhC*H* (α)); 4.09 (*d*, $J = 5.7$, HO (α)); 4.07 (*dd*, $J = 5.6$, 2.3, H–C(4) (β)); 4.03–3.99 (*m*, PhC*H* (β), H–C(5) (α), HO (β)); 3.97–3.91 (*m*, PhC*H* (β), H–C(5) (β), H_a–C(6) (β)); 3.86 (*dd*, $J = 8.4$, 4.8, H–C(4) (α)); 3.81 (br. *d*, $J \approx 5.9$, H–C(3) (β)); 3.74 (*dd*, $J = 6.8$, 3.0, H–C(2) (β)); 3.69 (*dd*, $J = 9.7$, 5.9, H_a–C(6) (α)); 3.69–3.65 (*m*, H_b–C(6) (β)); 3.62 (*dd*, $J = 8.1$, 3.1, H–C(2) (α)); 3.53 (*dd*, $J = 9.7$, 3.1, H_b–C(6) (α)); 3.19 (*t*, $J = 8.2$, H–C(3) (α)); 2.35 (*s*, Me (β)); 2.33 (*s*, Me (α)). ^{13}C-NMR (100 MHz, $CDCl_3$; assignments based on a HSQC spectrum; α/β 7:3): 143.55–135.92 (several *s*); 129.48–127.49 (several *d*); 83.26 (*d*, C(2) (α)); 81.61 (*d*, C(1) (α)); 81.23 (*d*, C(2) (β)); 80.99 (*d*, C(3) (α)); 79.70 (*d*, C(3) (β)); 76.59 (*d*, C(1) (β)); 76.49 (*d*, C(4) (α)); 74.64 (*d*, C(4) (β)); 74.41 (*t*, PhCH_2 (α)); 73.54 (*t*, PhCH_2 (α)); 73.29 (*t*, PhCH_2 (β)); 73.14 (*t*, PhCH_2 (α)); 72.88 (*t*, PhCH_2 (α)); 72.20 (*t*, PhCH_2 (β)); 71.82 (*t*, PhCH_2 (β)); 71.35 (*t*, PhCH_2 (β)); 70.42 (*t*, *C*(6) (β)); 69.71 (*t*, *C*(6) (α)); 58.64 (*d*, C(5) (α)); 55.08 (*d*, C(5) (β)); 21.58 (*q*, Me (β)); 21.52 (*q*, Me (α)). HR-MALDI-MS: 732.2383 (38, $[M+K]^+$, $C_{41}H_{43}KNO_7S^+$; calc. 732.2392), 716.2664 (100, $[M+Na]^+$, $C_{41}H_{43}NNaO_7S^+$; calc. 716.2652). Anal. calc. for $C_{41}H_{43}NO_7S$ (693.86): C 70.97, H 6.25, N 2.02; found: C 70.88, H 6.45, N 1.96.

2,3,4,6-Tetra-O-*benzyl-1,5-dideoxy-5-[(4-methylphenylsulfonyl)amino]*-D-*glucopyranose* N-*Benzylimine* N-*Oxide* (**32**) *and 2,3,4,6-Tetra*-O-*benzyl-1*-N-*benzyl-5-deoxy-1*-N-*hydroxy-5-[(4-methylphenylsulfonyl)amino]*-α-D- and -β-D-*glucopyranosylamine* (**33**). A soln. of BnNHOH · HCl (230 mg, 1.44 mmol) in MeOH (5 ml) was treated with $NaHCO_3$ (120 mg, 1.44 mmol), stirred for 15 min, and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O and brine. The org. layer was dried ($MgSO_4$) and evaporated to afford BnNHOH. A mixture of the crude BnNHOH, **31** (200 mg, 0.28 mmol), and 4-Å mol. sieves in dry pyridine (5 ml) was heated for 12 h at 100° and evaporated. FC (hexane/AcOEt 98:2 → 1:1) afforded **32**/**33**. ^{1}H-NMR (300 MHz, $CDCl_3$; α-**33**/β-**33** *ca.* 3:1, traces of **32**): 7.76 (*d*, $J = 8.2$, 2 arom. H); 7.62 (*d*, $J = 8.2$, 2 arom. H); 7.40–7.05 (*m*, 26 arom. H, 1 H of α-**33**); 6.92 (*d*, $J = 7.4$, 1 arom. H of β-**33**); 5.60 (*d*, $J = 7.1$, H–C(1) of α-**33**); 5.26 (*d*, $J = 2.2$, H–C(1) of β-**33**); 5.19 (*dd*, $J = 6.1$, 7.4, H–C(2) of β-**33**); 4.82 (*d*, $J = 11.8$, PhC*H* of α-**33**); 4.70 (*d*, $J = 12.1$ and 11.6, 2 PhC*H* of α-**33**); 4.32 (*d*, $J = 11.3$, PhC*H* of α-**33**); 4.30 (*d*, $J = 11.6$, PhC*H* of α-**33**); 4.23 (*dt*, $J = 4.7$, 2.9, 1 H of α-**33**); 4.14 (*dd*, $J = 9.9$, 3.6, 1 H of α-**33**); 4.65–3.94 (*m*, 10 H and 4 H of α-**33**); 3.60 (*dd*, $J = 4.7$, 9.6, H_a–C(6) of β-**33**); 3.46 (*dq*, $J = 8.8$, 2.2, H_a–C(6) of α-**33**); 3.16 (*dd*, $J = 6.9$, 9.6, H_b–C(6) of β-**33**); 2.77 (*dd*, $J = 7.9$, 10.2, H_b–C(6) of α-**33**); 2.37 (*s*, Me of α-**33**); 2.31 (*s*, Me of β-**33**).

2,3,4,6-Tetra-O-*benzyl-5-deoxy-5-[(4-methylphenylsulfonyl)amino]-1*-N-*(phenylmethylidene)-β-*D-*glucopyranosylamine* N-*Oxide* (**34**). A soln. of **32**/**33** in $ClCH_2CH_2Cl$ (5 ml) was treated with MnO_2 (625 mg, 7.20 mmol), kept at reflux for 48 h, and filtered over *Celite*. Evaporation and FC (hexane/AcOEt 95:5 → 4:1) gave **34** (120 mg, 78% from **30**). Colourless oil. R_f (hexane/AcOEt 4:1) 0.38. $[\alpha]_D^{25} = -45.4$ ($c = 1.0$, $CHCl_3$). IR (ATR): 3062*w*, 3030*w*, 2869*w*, 1735*m*, 1597*w*, 1578*w*, 1563*w*, 1495*w*, 1453*m*, 1350*m*, 1305*w*, 1241*w*, 1207*w*, 1187*m*, 1165*s*, 1142*w*, 1086*s*, 1069*s*, 1027*m*, 982*w*, 904*w*, 836*w*, 811*w*, 734*s*, 693*s*, 665*m*. ^{1}H-NMR (300 MHz, CD_2Cl_2; assignments based on selective homodecoupling experiments): see *Table 2*; additionally, 8.19–8.14 (*m*, 2 arom. H); 7.64 (*s*, HC=N); 7.65–7.41 (*m*, 2 arom. H); 7.47–7.41 (*m*, 3 arom. H); 7.35–6.97 (*m*, 22 arom. H); 4.70 (*d*, $J = 10.6$), 4.67 (*d*, $J = 11.3$), 4.62 (*d*, $J = 11.8$), 4.61 (*d*, $J = 11.3$) (4 PhC*H*); 4.53 (*s*, PhCH_2); 4.42 (*d*, $J = 11.7$), 4.37 (*d*, $J = 10.8$) (2 PhC*H*); 2.28 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 2*; additionally, 143.98 (*d*, CH=N); 138.06, 137.98, 137.87, 137.23, 136.13, 135.83 (6*s*); 130.75–127.39 (several *d*); 75.99, 74.38, 73.14, 70.72 (4*t*, 4 PhCH_2); 21.74 (*q*, Me). HR-MALDI-MS: 835.2850 (38, $[M+K]^+$, $C_{48}H_{48}KN_2O_7S^+$; calc. 835.2814); 819.3059 (100, $[M+Na]^+$, $C_{48}H_{48}N_2NaO_7S^+$; calc. 819.3074). Anal. calc. for $C_{48}H_{48}N_2O_7S$ (796.98): C 72.34, H 6.07, N 3.51; found: C 72.05, H 6.14, N 3.42.

2,3,4,6-Tetra-O-*benzyl-1,5-dideoxy-5-[(4-methylphenylsulfonyl)amino]-1-nitro-α*-D-*glucopyranose* (**35**). A soln. of **34** (100 mg, 0.14 mmol) in CD_2Cl_2 (5 ml) was cooled to $-78°$. O_3 was bubbled through the soln. until disappearance of **34**. The soln. was purged with N_2, and a ^{1}H-NMR spectrum of the reaction mixture was recorded. ^{1}H-NMR (300 MHz, CD_2Cl_2, $-10°$ assignments based on selective homodecoupling experiments): see *Table 2*; additionally, 7.72 (*d*, *J* = 8.3, 1 arom. H); 7.36–6.99 (*m*, 23 arom. H); 4.67 (*s*, PhCH_2); 4.49 (*d*, *J* = 11.8), 4.41 (*d*, *J* = 12.1) (2 PhC*H*); 4.39 (*s*, PhCH_2); 4.28 (*d*, *J* = 11.6), 4.21 (*d*, *J* = 11.6) (2 PhC*H*); 2.27 (*s*, Me). TLC showed two spots, one of PhCHO, and one of **31**, identified by ^{1}H-NMR after evaporation of the solvent.

6-Azido-2,3,4,7-tetra-O-*benzyl-5-{[(*tert-*butoxy)carbonyl]amino}-1-5,6,8-trideoxy*-D-erythro-D-galacto-*octose* N-*Benzylimine* N-*Oxide* (**36**). A soln. of BnNHOH · HCl (225 mg, 1.41 mmol) in MeOH (5 ml) was treated with $NaHCO_3$ (120 mg, 1.41 mmol), stirred for 15 min, and evaporated. A soln. of the residue in CH_2Cl_2 was washed with H_2O and brine. The org. layer was dried ($MgSO_4$) and evaporated. A mixture of the residue (BnNHOH), **14** (200 mg, 0.282 mmol), and 4-Å mol. sieves in BuOH (10 ml) was heated to 80° for 12 h, cooled to 25°, filtered over *Celite*, and evaporated. A soln. of the residue in AcOEt was washed with 0.1N HCl and brine, dried ($MgSO_4$), and evaporated. FC (hexane/AcOEt 95 : 5 → 1 : 1) gave **36** (208 mg, 90%). Colourless oil. R_f (hexane/AcOEt 4 : 1) 0.19. $[\alpha]_D^{25} = +6.7$ (*c* = 1.02, $CHCl_3$). IR (ATR): 3434*w*, 3064*w*, 3031*w*, 2978*w*, 2927*w*, 2869*w*, 2103*m*, 1711*m*, 1584*w*, 1495*m*, 1454*m*, 1391*w*, 1381*w*, 1366*w*, 1306*w*, 1247*w*, 1220*w*, 1162*m*, 1070*s*, 1048*m*, 1027*m*, 940*w*, 909*w*, 859*w*, 733*s*, 695*s*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on selective homodecoupling experiments): 7.39–7.20 (*m*, 20 arom. H, NH); 6.60 (*d*, *J* = 6.6, H–C(1)); 5.09 (*dd*, *J* = 6.9, 2.4, H–C(2)); 4.98 (*d*, *J* = 10.2), 4.59 (*d*, *J* = 11.4), 4.57 (*d*, *J* = 11.1), 4.52 (*d*, *J* = 11.1), 4.51 (*d*, *J* = 12.0), 4.43 (*d*, *J* = 12.0, 2 H), 4.41 (*d*, *J* = 10.2), 4.37 (*d*, *J* = 12.0) (9 PhC*H*); 4.23 (br. *d*, *J* ≈ 9.0, H–C(4)); 4.09 (*d*, *J* = 11.1, PhC*H*); 3.77 (br. *t*, *J* = 10.2, H–C(5)); 3.73 (*dd*, *J* = 8.4, 2.4, H–C(3)); 3.71 (*qd*, *J* = 6.3, 2.4, H–C(7)); 3.55 (*dd*, *J* = 10.5, 2.1, H–C(6)); 1.37 (*s*, *t*-Bu); 1.31 (*d*, *J* = 6.0, Me). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): 155.00 (*s*, C=O); 138.16 (2*d*, HC=N, 1 arom. C); 137.88 (2 C), 137.59, 132.13 (3*s*, 4 arom. C); 129.35–127.25 (several *d*); 79.68 (*s*, Me_3C); 78.13 (*d*, C(3)); 76.45 (*d*, C(4)); 75.77 (*d*, C(7)); 74.87, 74.40 (2*t*, 2 Ph*C*H_2); 73.69 (*d*, C(2)); 72.14, 70.35, 69.85 (3*t*, 3 Ph*C*H_2); 65.44 (*d*, C(6)); 50.26 (*d*, C(5)); 28.30 (*q*, *Me*$_3$C); 14.10 (*q*, Me). HR-MALDI-MS: 852.3735 (69, $[M+K]^+$, $C_{48}H_{55}KN_5O_7^+$; calc. 852.3733), 836.3989 (100, $[M+Na]^+$, $C_{48}H_{55}N_5NaO_7^+$; calc. 836.3994), 814.4170 (41, $[M+H]^+$, $C_{48}H_{56}N_5O_7^+$; calc. 814.4174), 606.3075 (51, $[M - Boc - BnNOH + H + OH]^+$, $C_{36}H_{38}N_4O_5^+$; calc. 606.2842), 591.2963 (21, $[M - Boc - BnNOH + H]^+$, $C_{36}H_{38}N_4O_4^+$; calc. 591.2971). Anal. calc. for $C_{48}H_{55}N_5O_7$ (813.99): C 70.83, H 6.81, N 8.60; found: C 70.56, H 6.90, N 8.35.

*(*E*/*Z*)-6-Azido-2,3,4,7-tetra*-O-*benzyl-5-{[(*tert-*butoxy)carbonyl]amino}-5,6,8-trideoxy-1*-N-(*phenylmethylidene)*-D-erythro-*β*-D-galacto-*octopyranosylamine* N-*Oxide* (**17**). A soln. of **36** (110 mg, 0.13 mmol), LiI (36 mg, 0.27 mmol), and PbO_2 (325 mg, 1.35 mmol) in toluene/pyridine 2 : 1 (6 ml) was heated to 60° for 4 h, cooled to r.t., filtered over *Celite*, and evaporated. FC (Al_2O_3 Akt. 1, hexane/AcOEt 98 : 2 → 4 : 1) gave **17** (79 mg, 63%). Slightly pink oil. R_f (hexane/AcOEt 3 : 1) 0.17. $[\alpha]_D^{25} = -2.5$ (*c* = 1.2, $CHCl_3$). IR (ATR): 3031*w*, 2978*w*, 2932*w*, 2865*w*, 2107*m*, 1710*m*, 1578*w*, 1563*w*, 1496*w*, 1454*m*, 1368*m*, 1326*m*, 1244*m*, 1150*w*, 1091*s*, 1047*m*, 1026*m*, 922*w*, 875*w*, 849*w*, 805*w*, 776*w*, 732*s*, 693*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO, 100°; (*E*)/(*Z*) 3 : 2; assignments based on selective homodecoupling experiments): 7.39–7.20 (*m*, 2 arom. H); 7.84 (*s*, HC=N (*E*)); 7.73 (*s*, HC=N (*Z*)); 7.45–7.18 (*m*, 23 arom. H); 6.01 (*d*, *J* = 5.7, H–C(1) (*Z*)); 5.81 (*d*, *J* = 5.1, H–C(1) (*E*)); 4.92–4.26 (*m*, 11.4 H); 4.10 (br. *t*, *J* = 7.5, 1 H (*E*)); 3.96–3.86 (*m*, 1.4 H); 3.83 (*dd*, *J* = 8.1, 1.8, 1 H (*E*)); 1.38 (*s*, *t*-Bu (*E*)); 1.34 (*s*, *t*-Bu (*Z*)); 1.23 (*d*, *J* = 6.0, Me (*E*)); 1.15 (*d*, *J* = 6.3, Me (*Z*)). ^{13}C-NMR (75 MHz, $CDCl_3$, 60°; (*E*)/(*Z*) 3 : 2); 154.94 (*s*, C=O); 138.87–137.87 (several *s*); 131.91 (*s*); 130.32 (*s*); 130.23 (*d*, HC=N (*Z*)); 129.93 (*d*, HC=N (*E*)); 128.63–127.04 (several *d*); 86.46 (*d*, 1 C); 83.00 (*s*, Me_3C); 81.46 (*d*, C (*E*)); 80.37 (*d*, C (*Z*)); 77.87 (*d*, C (*E*)); 76.44 (*d*, C (*Z*)); 76.20 (*d*, C (*Z*)); 75.59 (*d*, C (*E*)); 75.08 (*d*, C (*Z*)); 74.32 (*t*, PhCH_2 (*E*)); 73.99 (*d*, C (*E*)); 73.84 (*t*, PhCH_2 (*Z*)); 73.68 (*t*, PhCH_2 (*Z*)); 73.43 (*t*, PhCH_2 (*E*), PhCH_2); 70.51 (*t*, PhCH_2 (*Z*)); 70.35 (*t*, PhCH_2 (*E*)); 65.25 (*d*, C(6)); 55.72 (*d*, C(5) (*Z*)); 55.59 (*d*, C(5) (*E*)); 28.21 (*q*, *Me*$_3$C (*E*)); 28.12 (*q*, *Me*$_3$C (*Z*)); 15.57 (*q*, Me). HR-ESI-MS: 850.3611 (2, $[M+K]^+$, $C_{48}H_{53}KN_5O_7^+$; calc. 850.3577); 834.3838 (100, $[M+Na]^+$, $C_{48}H_{53}N_5NaO_7^+$; calc. 834.3837). Anal. calc. for $C_{48}H_{53}N_5O_7$ (811.98): C 71.00, H 6.58, N 8.63; found: C 71.00, H 6.64, N 8.46.

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