Synthesis and Some Transformations of 2-Acetamido-5-amino-3,4,6-tri-*O*-benzyl-2,5-dideoxy-D-glucono-1,5-lactam

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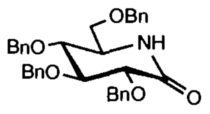
The lactam **21** was obtained in an overall yield of 72% from the hydroxy amide **16** by oxidation with the *Dess-Martin* periodinane, acid-catalysed isomerization of the oxidation products in toluene, whereupon **18**/**19** precipitated, and reductive dehydroxylation of **18**/**19** ($Et_3SiH/BF_3 \cdot OEt_2$; *Scheme 1*). The amide **16** was obtained by ammonolysis of the *N*-acetylglucosamine-derived lactone **15**. Depending on the oxidation method, **16** yielded the keto amide **17**, the hydroxy lactams **18**/**19**, and the pyrrolidinecarboxamide **20** in widely different proportions. The pyrrolidinecarboxamide **20** was not reduced under the conditions of the reductive dehydroxylation. Hydrogenolysis of the benzyl-protected lactam **21** gave the trihydroxy lactam **22**, while reduction with $NaBH_4/BF_3 \cdot OEt_2$ led to the 2-acetamidopiperidine derivative **24** (*Scheme 2*). Selective (*tert*-butoxy)carbonylation of the lactam **21** (→ **25**) followed by $NaBH_4$ reduction and acid-catalysed solvolysis in EtOH led to the α-ethoxycarbamates **28**/**29**. Similarly, (*tert*-butoxy)carbonylation of **1** (→ **31**) followed by reduction to **32**/**33** and glycosidation yielded the ethoxycarbamate **34**. Treatment of the GlcNAc-derived ethyl glycosides **28**/**29** with $Me_3SiCN/BF_3 \cdot OEt_2$ gave the equatorial amino nitrile **30**. Under similar conditions, the Glc-derived glycoside **34** led to the iminooxazolidinone **35**. In the presence of a larger proportion of Me_3SiCN at 5°, **34** was transformed into the axial, selectively monodebenzylated amino nitrile **36**.

Introduction. – We, and *Pandit* and coworkers have reported an advantageous synthesis of 2,3,4,6-tetra-*O*-benzyl-D-gluconolactam (**1**) [1–4] that has been optimized [5][6] to provide **1** in overall yields of 70–75% from 2,3,4,6-tetra-*O*-benzylglucose. The lactam **1** proved a versatile intermediate in the synthesis of β-glucosidase inhibitors such as deoxynojirimycin (**2**) [7–9], D-nojirilactam (**3**) [2][8], the D-gluconhydroximo-1,5-lactam **4** [5] and related *N*-arylcarbamates **5** [5], the indolizines **6**–**9** [10], the tetrahydroimidazopyridines **10** [6][11] and **11** [10], the triazole **12** [6], and the tetrazole **13** [12][13].



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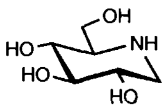

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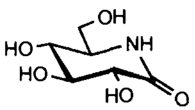

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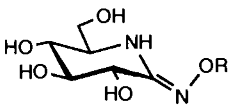

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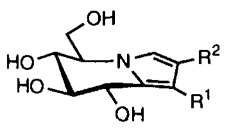
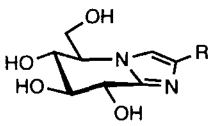
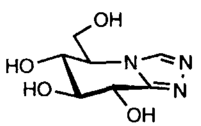
5 R = CONHAr



6 $R^1 = R^2 = CO_2Me$
7 $R^1 = H, R^2 = CO_2Me$
8 $R^1 = CO_2Me, R^2 = H$
9 $R^1 = R^2 = CH_2OH$



10 R = H
11 R = Ts



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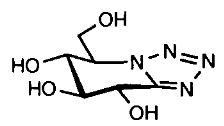

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In a similar way, the 2-acetamido-2-deoxylactam **21** should be a useful precursor of *N*-acetylglucosaminidase inhibitors. We report its synthesis from *N*-acetyl-3,4,6-tri-*O*-benzylglucosamine (**14**) and the results of studies aiming at the selective transformation of the lactam function.

Synthesis. – The hemiacetals **14** [14] (*Scheme 1*) were prepared from *N*-acetylglucosamine by allylation, benzylation, and deallylation in an overall yield of 24%[1]). Oxidation of **14** with the *Dess-Martin* periodinane [15][16] yielded 98% of pure lactone **15** on a scale of up to 4 g[2]). Oxidation of **14** according to *Swern* [18] yielded 85% of recrystallized **15** on a scale of up to 50 g. Ammonolysis of **15** led quantitatively to the hydroxy amide **16**. The products of the oxidation of **16** depended strongly upon the reagents and conditions. Oxidation with DMSO/pyridine · SO_3 [19] afforded the oxo amide **17** almost quantitatively and in a degree of purity exceeding 90%, as judged from the ^{1}H-NMR spectrum of the crude. *Jones* oxidation [20] of **16** gave a mixture of the D-*gluco*/L-*ido* hydroxy lactams **18**/**19** (4:1; *ca.* 60%), readily separated by chromatography. Oxidation by pyridinium chlorochromate (PCC) [21] led to a mixture of the hydroxy lactams **18**/**19** and the pyrrolidinecarboxamide **20**[3]) (**18**/**19**/**20** 35:15:50; 70%)[4]). Oxidation of **16** by the *Dess-Martin* periodinane led quantitatively to a mixture of the oxo-amide **17**, the hydroxy lactams **18**/**19**, and the pyrrolidinecarboxamide **20** (**17**/**18**/**19**/**20** 44:16:12:28)[5]). These results suggest that the cyclization is catalysed by traces of acid, similarly to what has been observed in the synthesis of **1**. Indeed, a solution of the oxo amide **17** in $CDCl_3$ was transformed within 36 h into a 33:15:52 mixture of **18**/**19**/**20**. Addition of 5% AcOH [5] to a solution of **17** in $CHCl_3$ had no influence on the ratio **18**/**19**, but sligthly disminished the proportion of **20**, **17** being transformed within 48 h at room temperature into a 40:20:40 mixture of **18**/**19**/**20**. This finding and the results of the oxidation of **16** with the *Jones* reagent suggest that **18** and **19** equilibrate rapidly, while **20** is only slowly transformed into **18**/**19**. A CH_2Cl_2/MeCN solution of the pyrrolidinecarboxamide **20** was indeed stable in the presence of $BF_3 \cdot OEt_2$ at −15°. At 5°, it was transformed, within 24 h, into a 69:21:10 mixture of **18**/**19**/**20**. Under the same conditions, equilibration between the isolated hydroxy lactams **18** and **19** began already at −15°. At 5°, each isomer led to a 75:25 mixture of **18**/**19**. Conceivably, the equilibration of **18** and **19** proceeds without ring opening, by elimination/addition of H_2O, while the equilibration between **18**/**19** and **20** requires ring opening, elimination of H_2O being disfavoured by the allylic strain [24][25] of the resulting cation.

The plan for the synthesis of the lactam **21** involved the reductive dehydroxylation of the hydroxy lactams **18**/**19** by Et_3SiH and $BF_3 \cdot OEt_2$ [26][27] under conditions favouring the equilibration of the oxidation products of **16**. We first treated the crude oxo amide **17** with $Et_3SiH/BF_3 \cdot OEt_2$ at 5°. This yielded 40% of **21**. Reductive dehydroxy-

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[1]) This synthesis proved more convenient for batch sizes exceeding 5 g than the method of *Harrison* and *Fletcher* [14] (perbenzylation, hydrolysis, acetylation, deacetylation); it was scaled up to 50 g of *N*-acetylglucosamine.

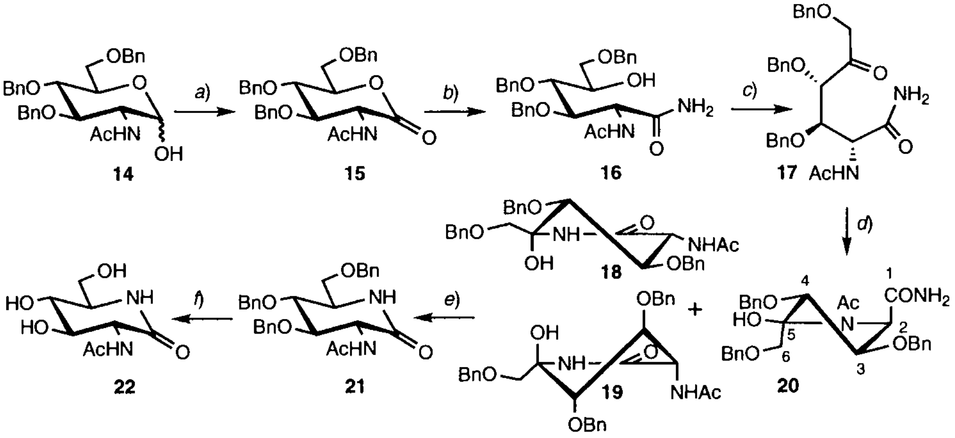
[2]) As the hemiacetals **14** are poorly soluble in CH_2Cl_2, the *Dess-Martin* oxidation had to be performed in (EtOH-free) $CHCl_3$. Oxidation of **14** with DMSO/Ac_2O [17] gave a mixture of **15** and the anomeric acetates of **14**.

[3]) Isolated after reductive dehydroxylation of the mixture **17**–**20**; see below.

[4]) The formation of such tautomers is well known, *e.g.* see [22][23].

[5]) According to TLC, the cyclization of **17** occurred during workup, while drying the organic phases ($MgSO_4$).

Scheme 1



a) *Dess-Martin* periodinane; 98% *or* $C_2O_2Cl_2$, DMSO, Et_3N; 85%. *b*) NH_3; > 99%. *c*) DMSO, pyridine · SO_3 *or Dess-Martin* periodinane. *d*) $BF_3 \cdot OEt_2$, CH_2Cl_2, *or* AcOH, toluene. *e*) $BF_3 \cdot OEt_2$, Et_3SiH, CH_2Cl_2, MeCN; 72% from **16**. *f*) H_2, 10% Pd/C, MeOH; 72%.

lation of the mixture **17**–**20** resulting from the oxidation of **16** by periodinane gave 55% of **21**. No products resulting from a reductive dehydroxylation of the pyrrolidinecarboxamide **20** were detected. This is in keeping with the destabilization of the acyliminium intermediate derived from **20** that was already postulated to rationalize the slow transformation of **20** into **18**/**19**. Up to 15% of the pyrrolidinecarboxamide **20** were isolated by chromatography of the crude reduction products. Thus, the slow transformation of **20** into the hydroxy lactams **18**/**19** led to an unsatisfactory yield of **21**. To obtain a high yield of **21**, we had to increase the proportion of the hydroxy lactams before reduction, but treatment of the oxidation products first with $BF_3 \cdot OEt_2$ (12–24 h, 5°) and then with Et_3SiH failed to improve this yield. As the hydroxy lactams **18**/**19** proved much less soluble in toluene than the pyrrolidine **20**, the oxo amide **17** was cyclized in toluene in the presence of AcOH. The solution of **17** in toluene/AcOH changed to a suspension of increasing density, and the crude consisted of a 83:17 mixture of the hydroxy lactams **18**/**19** that were reductively dehydroxylated. This procedure gave the lactam **21** in an overall yield of 72% from **16** on a 1.1-g scale. Hydrogenolysis of **21** yielded the trihydroxy lactam **22**[6]).

Activation of the cyclic carbonyl group of the lactam **21** failed, using either *Lawesson*'s reagent [30][7]), or $(Et_3O)BF_4$ under the conditions described by *Hoos et al.* [5] for the activation of the lactam **1**. Large amounts of starting material were reisolated. Prolonged heating of **21** with *Lawesson*'s reagent in toluene (48 h, 90°) led to partial epimerization, and the *manno*-configurated **23** was isolated in 33% yield (*Scheme 2*).

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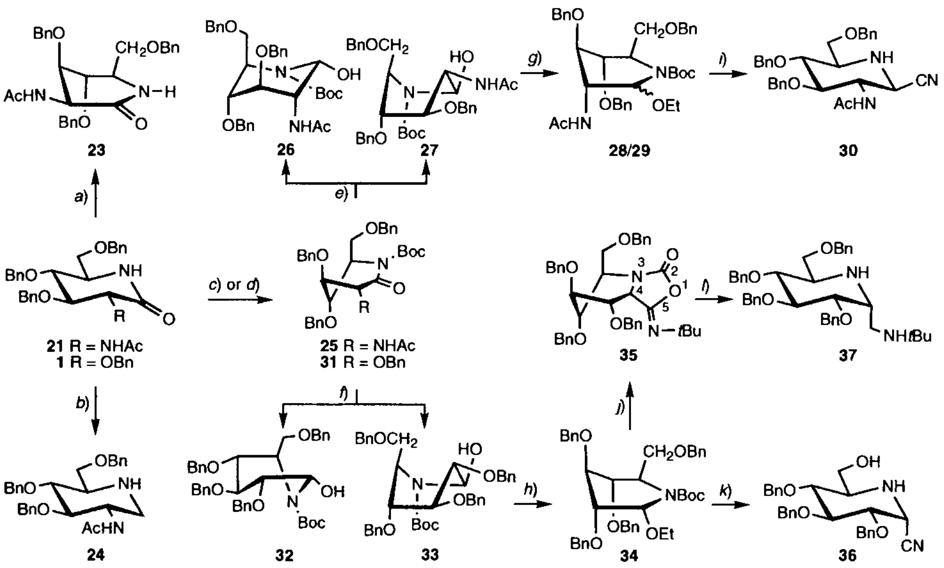
[6]) The lactam **22** has been prepared by oxidation of 2-acetamido-2-deoxynojirimycin [28]; however, details of the synthesis have so far not been published. It is a good inhibitor of a bovine-kidney *N*-acetylglucosaminidase [28]. The competitive inhibition of additional *N*-acetylglucosaminidases by **22** has been reported by *Horsch et al.* [29]; again, no details for the preparation of **22** were published.

[7]) This result was not changed by varying the thionating agent or the solvent.

Scheme 2



a) **21**, *Lawesson*'s reagent, toluene; 33%. *b)* **21**, $BF_3 \cdot OEt_2$, $NaBH_4$, THF; 70%. *c)* **21**, Boc_2O, DMAP, MeCN; 95%. *d)* **1**, Boc_2O, DMAP, MeCN; 88%. *e)* **25**, $NaBH_4$, EtOH, pH 6; 91%. *f)* **31**, $NaBH_4$, EtOH, pH 6; 75%. *g)* EtOH, TsOH · H_2O; 77% (**28**/**29** 2:1). *h)* **33**, EtOH, TsOH · H_2O; 91%. *i)* 13 equiv. of Me_3SiCN, 13 equiv. of $BF_3 \cdot OEt_2$; 55%. *j)* 18 equiv. of Me_3SiCN, 18 equiv. of $BF_3 \cdot OEt_2$; 77%. *k)* 53 equiv. of Me_3SiCN, 5 equiv. of $BF_3 \cdot OEt_2$; 30%. *l)* $LiAlH_4$, THF; 53%.

Treatment of the *gluco*-lactam **21** with piperidine in $CDCl_3$ led to a 78:22 mixture of **23**/**21**. Isolation of the isomers by FC yielded 40% of **23** and 11 % of **21**, both partially deuteriated at C(2). Similar treatment of **23** led to a 89:11 mixture of **23**/**21**. Reduction of the lactam **21** with $NaBH_4$ and $BF_3 \cdot OEt_2$ [31–35] proceeded regioselectively and yielded 70% of the protected 2-acetamido-2-deoxynojirimycin **24**.

The carbonyl group at C(5) of the oxo-amide **17** gives rise to an IR absorption at 1733 cm^{-1} and to a *s* at 207.45 ppm in the ^{13}C-NMR spectrum. The disappearance of the *d* corresponding to *H*NAc and the two *s* corresponding to CONH_2 (4.87 and 7.71 ppm) in the ^1H-NMR spectrum of **20** allow to distinguish the pyrrolidinecarboxamide **20** from the hydroxylactams **18**/**19** characterized by a *d* (**18**: 6.50–6.97 ppm, depending on the concentration of **18**, $J = 7.8$ Hz; **19**: 6.06 ppm, $J = 8.4$ Hz) corresponding to *H*NAc and a *s* (**18**: 6.87 ppm; **19**: 6.74 ppm) corresponding to *H*N–C(5). The (5*R*)-configuration of **20** is postulated on the following grounds: the carboxamido and the (benzyloxy)methyl substituents are expected to be pseudo-axial to avoid the interaction with the acetamido group; the value of 5.9 Hz for $J(3,4)$ is in keeping with an approximate $^4T_3$ conformation where H–C(4) is *cis* to BnO–C(3) and HO–C(5); this is confirmed by the chemical shift of H–C(4) (4.51 ppm as compared to 3.82 ppm for **18** and 3.89 ppm for **19**) and by a NOE observed for H–C(3) (*dd* at 4.17 ppm) upon irradiation at the signal of H–C(6) (3.29 ppm). The absence of rotamers of **20** is in accordance with an H-bond between a pseudo-equatorial HO–C(5) and the AcN group. While the coupling constants of the hydroxylactam **18** evidence a $^4H_3$ conformation, those of the diastereoisomer **19** suggest a $^3H_4$ conformation 8) probably stabilized by an intramolecular H-bond between *H*NAc and Bn*O*–C(4) (D-*gluco*: $J(2,3) = 8.4$ and $J(3,4) = 9.6$ Hz; L-*ido* $J(2,3) = 4.4$ and $J(3,4) = 5.5$ Hz). H–C(2) of **19** is located in the plane of the carbamoyl group and notably

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8) In contrast to the $^4H_3$ conformation adopted by the analogous hydroxy lactam derived from 2,3,4,6-tetra-*O*-benzylglucose [2].

deshielded (**18**: 3.99 ppm; **19**: 4.78 ppm). The configuration of the hydroxy lactams **18**/**19** was assigned on the basis of NOEs observed upon irradiation at the frequence of HO–C(5). For **18**, irradiation at 5.59 ppm (HO–C(5)) led to a NOE for the H–C(3) *t* at 4.03 ppm ((D_6)DMSO), and for **19**, irradiation at 6.05 ppm (HO–C(5)) led to a NOE for the H–C(4) *d* at 3.78 ppm ((D_6)DMSO). In accordance with the configuration of **18**/**19**, H–C(3) of **18** is deshielded by the *cis*-oriented HO–C(5) (**18**: 4.24 ppm; **19**: 3.97 ppm). The D-*gluco* configuration of the benzylated lactam **21** was assigned on the basis of the X-ray structure analysis of the trihydroxy lactam **22**[9]. It possesses a ${}^4H_3$ conformation in the solid state, similar to nojirilactam (**2**) [36]. The coplanar arrangement of C(5), N(1), C(1), and C(2) of crystalline **22** is expressed by the small value of the C(5)–N(1)–C(1)–C(2) torsion angle (0.5°). Surprisingly, the N–H bond of the acetamido group is *cis* to C(2)–H. Acetamides crystallizing exclusively as (*Z*)-*syn* conformers such as **22** are rare [37]. To the best of our knowledge, the only known example is an *arabino*-1,4-lactone-derived acetamide [38]. In solution, the acetamides **18**–**21** are mixtures of the (*Z*)-*anti* and (*Z*)-*syn* conformers, as indicated by the moderate values ($\approx$ 8.0 Hz) of the coupling constant between H–C(2) and N*H*Ac. As shown by the vicinal *J*(H,H), the lactam **21** adopts the ${}^4C_1$ conformation in solution.

The carbonyl groups of the *manno*-lactam **23** give rise to a C=O absorption at 1665 cm^{-1} and to two ^{13}C *s* (169.07 and 170.55 ppm). *J*(2,3) = 3.4 Hz, *J*(3,4) = 2.4 Hz, *J*(4,5) = 3.7 Hz are characteristic of a ${}^3S$ conformation[10]. The regioselectivity of the reduction of the lactam **21** to the piperidine derivative **24** is evidenced by the typical ^{1}H-NMR signals of the acetamido group of **24** (NH: *d*, 5.00 ppm, *J* = 6.5 Hz; Me: *s*, 1.73 ppm) and two new *dd* at 2.27 and 3.32 ppm corresponding to $CH_2(1)$ (J_{gem} = 12.9 Hz). The *ddd* at 2.74 ppm corresponding to H–C(5) is shifted to higher fields as compared to the H–C(5) signal of the lactam **21** ($\Delta\delta$ = 0.9 ppm). The *J*(H,H) values for **24** (*J*(1ax,2) = 10.1, *J*(1eq,2) = 5.4, *J*(2,3) = 9.6, *J*(3,4) = 8.3, and *J*(4,5) = 8.0 Hz) are in agreement with a ${}^4C_1$ conformation.

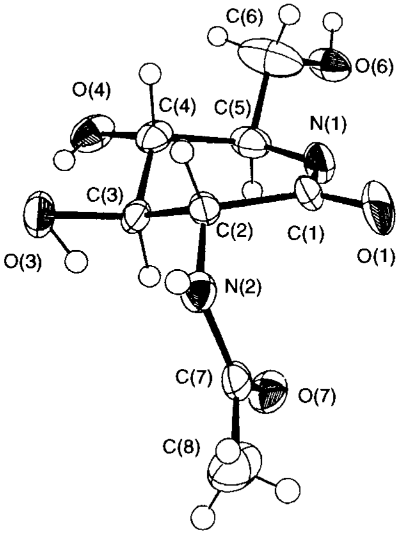

Figure. *X-Ray analysis of the trihydroxy lactam* **22**

Treatment of the lactam **21** with Boc_2O [39–41] (*Scheme 2*) led to the *N*-acylcarbamate **25** (95%). Reduction of **25** with $NaBH_4$ in EtOH at pH 6 [42] gave regioselectively the anomeric hydroxy carbamates **26**/**27** (54:46) that were separated by FC (91%). Reduction at lower pH led to a mixture of the hydroxy carbamates **26**/**27** and the

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[9] Crystallographic data have been deposited at the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-101230. Copies of the data can be obtained, free of charge, on application to the *CCDC*, 12 Union Road, Cambridge CB2 1EW, UK (fax: +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk.

[10] Also adopted by the related tetrazole [23].

ethoxy carbamates **28/29**. The ethoxy carbamates **28/29** (2:1) were obtained in 77% yield by glycosylation (EtOH/TsOH · H_2O) of the hydroxy carbamates **26/27**. Treatment of the 2:1 mixture **28/29** with excess Me_3SiCN and $BF_3 \cdot OEt_2$ gave diastereoselectively the equatorial amino nitrile **30** in a yield of 55%[11]). The stereoselectivity reflects the neighbouring-group participation of the acetamido group [45].

The same sequence of transformations was applied to the tetrabenzylated gluconolactam **1**, leading *via* the *N*-Boc-protected lactam **31** [46] to a mixture of the hydroxy carbamates **32/33** (30:70; 75%), separated by FC. Glycosidation of the hydroxy carbamate **33** with EtOH/TsOH · H_2O yielded 91% of the α-ethoxy carbamate **34**[12]). Treatment of the ethoxypiperidine **34** with excess Me_3SiCN and $BF_3 \cdot OEt_2$ (18 equiv. each), at −78°, did not lead to a nitrile, but to the bicyclic imino carbamate **35** (77%). Presumably, the introduction of the cyano substituent at C(1) is followed by the $BF_3 \cdot OEt_2$-promoted cleavage of the $Me_3C{-}O$ bond, transfer of the *tert*-butyl cation to the nitrile group, and cyclization[13]). Treatment of **34** with smaller amounts of $BF_3 \cdot OEt_2$ (5 equiv.) in the presence of a large excess of Me_3SiCN (53 equiv.) at 5° yielded 30% of the selectively monodebenzylated axial amino nitrile **36**. Probably, the Boc-protected amino nitrile is in equilibrium with the acyliminium cation that is intramolecularly attacked by O−C(6) leading, by cleavage of the Bn group at O−C(6), to an intermediate *N,O*-acetal. Cleavage of this acetal with $BF_3 \cdot OEt_2$, before or after loss of the Boc group, and introduction of the cyanide with inversion of configuration lead to the tribenzylated axial amino nitrile **36**.

The regioselectivity of the (*tert*-butoxy)carbonylation of **21** is evidenced by the *d* for HN−C(2) ($J = 8.6$ Hz, 6.05 ppm) of **25**, the disappearance of the *s* corresponding to HN−C(5), and the strong deshielding of H−C(5) ($\Delta\delta \approx 1.1$ ppm). The H−C(2) signal is also affected, but to a lower extent ($\Delta\delta \approx 0.7$ ppm). The *N*-Boc-protected lactams **25** and **31** are a mixture of $^4H_3$ and $^5S_1$ conformers as evidenced by the small value of $J(3,5)$ (**25**: 1.2 Hz; **31**: *ca.* 1 Hz). The reduction of the acyl carbamate **25** to the hydroxy carbamates **26/27** is again reflected by the chemical-shift changes for H−C(2) and H−C(5) ($\Delta\delta$ (H−C(2)) ≈ -0.4 ppm, $\Delta\delta$ (H−C(5)) ≈ -0.2 ppm). The acetamido and oxycarbonylamino groups give rise to C=O absorptions at 1680–1690 cm^{-1}. To minimize the $A^{(1,3)}$ strain [24][25] between the (*tert*-butoxy)carbonyl and the $BnOCH_2{-}C(5)$, and/or the HO−C(1) groups [48], one expects the hydroxy carbamate **26** to adopt a conformation with a pseudo-axial $BnOCH_2{-}C(5)$. The J(H,H) values of **26** values ($J(1,2) = 3.4$, $J(2,3) = 4.8$, $J(3,4) = 4.3$, and $J(4,5) = 2.4$ Hz), however, are too large for a $^1C_4$ conformation and do not fit with a boat conformation; they are best rationalized by assuming a mixture of $^5C_2$ and $^2S_4$ conformers. The broadening of the ^1H-signals of **26** in $CDCl_3$ indicates a mixture of rotamers. The J(OH,1) value of **26** (5.9 Hz) does not fit with the value expected for HO−C(1) involved in a H-bond with the Boc group. However, a H-bond between HO−C(1) and the acetamido group, requiring a deviation of H−C(2)−N−H from coplanarity is in agreement with the moderate value of $J(\mathrm{N}H\mathrm{Ac},2)$ (6.8 Hz). The conformation of the hydroxy carbamate **32** is notably different from the one of **26**; as the only change consists of the replacement of the 2-acetamido group by a benzyloxy group, this is in keeping with the involvement of the acetamido group of **26** in a H-bond. The hydroxy carbamate **32** adopts a $B_{3,N}$ conformation ($J(1,2) \approx 2$, $J(2,3) = 6.2$, $J(3,4) = 9.2$, and $J(4,5) = 6.4$ Hz). The rotation about the N−CO_2(*t*-Bu) bond of **32** is hindered, giving rise to a broadening of signals in the ^1H- and ^{13}C-NMR spectra. The (1*S*)-configurated hydroxy carbamates **27** and **33** adopt a similar flattened $^{5,2}B$ conformation, as shown by the J(H,H) values (**27**: $J(1,2) = 3.0$, $J(2,3) = 7.7$, $J(3,4) = 0.8$, and $J(4,5) = 2.5$ Hz; **33**: $J(1,2) = 3.1$, $J(2,3) = 6.5$, $J(3,4) = 0$, and $J(4,5) = 1.2$ Hz). A small coupling constant (*ca.* 1 Hz) between H−C(3) and H−C(5) is in keeping with their diequatorial orientation. The large

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[11]) Piperidinose-derived acyliminium cations have been generated by *Suzuki* and *Hashimoto* [43] as key intermediates in the synthesis of oligosaccharide analogues. More recently, *Schmidt* and coworkers [44] have reported the synthesis of *C*-glycosides from anomeric fluorides derived from *N*-Z-protected nojirimycin.

[12]) The α-D-glycoside **34** was selectively obtained by glycosidation of a 3:7 mixture of **32/33**.

[13]) A similar participation of the Boc group has recently been reported by *Lhommet* and coworkers [47].

J(OH,1) values (**27**: 10.3 Hz; **33**: 11.2 Hz) are rationalized by postulating a H-bond between HO–C(1) and O–C(6). The ^{1}H-NMR spectrum of the ethoxy derivatives **28** and **29** are characterized by small coupling constants, but the signals overlap in several solvents and complicate the conformational analysis. The rotation about the N–CO$_2$(t-Bu) bond of the ethoxy carbamate **34** is hindered by the pseudo-equatorial BnOCH$_2$–C(5) group, giving rise to two signals each for H–C(1) and H–C(5). Similarly, in the ^{13}C-NMR spectrum of **34**, the C(1), C(5), C(6), and CO$_2$(t-Bu) signals appear each as two *s*. The conformation of **34** is assumed to be similar to the one of **28**/**29**, the larger J(H,H) values indicating the participation of the $^4C_1$ conformer ($J(2,3) = 6.6$ and $J(3,4) = 8.9$ Hz). The pseudo-axial position of the ethoxy group is evidenced by the small value of J(1,2) (2.2 Hz).

The ^{13}C-NMR spectra of the amino nitriles **30** and **36** show the characteristic *s* of the CN group at 118.15 and 117.78 ppm, respectively. The IR spectra show no CN absorption, similarly to other α-hetero-substituted nitriles [49–52]. The J(H,H) values for the amino nitrile **30** are characteristic of a $^5C_2$ conformation and an equatorial substituent at C(2) ($J(2,3) = 9.5$, $J(3,4) = 9.0$, $J(4,5) = 8.6$, and $J(5,6) = 8.7$ Hz). The J(H,H) values for **36** are in accordance with a $^5C_2$ conformation and the axial position of the nitrile group ($J(2,3) = 5.6$, $J(3,4) = 9.5$, $J(4,5) = 9.0$, and $J(5,6) = 9.7$ Hz). The debenzylation of the BnOCH$_2$ group causes a shift of the *t* corresponding to C(7) towards higher fields ($\Delta\delta = 7$ ppm). The MS of the imino-oxazolidinone **35** is in agreement with the proposed constitution. The ^{13}C-NMR spectrum shows five *d* between 50 and 75 ppm. Me$_3$C resonates at higher field than in the starting material ($\Delta\delta = 25$ ppm), evidencing the cleavage of a Me$_3$C–O and the formation of an Me$_3$C–N bond. To determine the configuration at C(4), **35** was reduced to the axial homonojirimycin derivative **37** which adopts the $^5C_2$ conformation. The value of J(2,3) (5.9 Hz) evidences the α-D-configuration of **37** and consequently the (4*S*)-configuration of **35**.

We thank *R. Husi* for the preparation of **14**, Dr. *B. Bernet* and *R. Hoos* for helpful discussions, Dr. *B. Schweizer* for the X-ray analysis, Ms. *B. Brandenberg* for the NOE measurements, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. Solvents were distilled before use. Normal workup implies distribution of the crude product between CH$_2$Cl$_2$ and sat. aq. NH$_4$Cl soln. and ice, unless indicated otherwise, drying of the org. layer (MgSO$_4$), filtration, and evaporation of the filtrate. TLC: *Merck* silica gel *60F-254* plates; detection by heating with 'mostain' (400 ml of 10% H$_2$SO$_4$ soln., 20 g of (NH$_4$)$_6$Mo$_7$O$_{24}$ · 6H$_2$O, 0.4 g of Ce(SO$_4$)$_2$). Flash chromatography (FC): silica gel *Merck 60* (0.04–0.063 mm). M.p.: uncorrected. Optical rotations: 1-dm cell. UV Spectra ($\lambda_{\max}$ in nm (log ε)): 1-cm quartz cell. IR Spectra: KBr or 3% CHCl$_3$ soln. ^{1}H-NMR (300 MHz, if not indicated otherwise) and ^{13}C-NMR (75 MHz, if not indicated otherwise): 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.

Preparation of **14** [14] *from* N-*Acetylglucosamine.* A soln. of *N*-acetylglucosamine (50 g, 0.226 mol) in allyl alcohol (520 ml) was treated with BF$_3$ · OEt$_2$ (4.6 ml, 0.037 mol), refluxed for 5 h, and evaporated. The residue was dried *i.v.*, dissolved in DMF (500 ml), treated with NaH (19.4 g, 0.808 mol), then within 30 min, dropwise at $T < 40°$, with a soln. of benzyl bromide (88 ml, 0.741 mol) in DMF (400 ml), and stirred for 2 h. The mixture was cooled to 5°, treated with MeOH (20 ml), and poured on H$_2$O/ice (500 ml). Extraction with AcOEt, followed by evaporation and drying *i.v.* gave a residue that was dissolved in DMSO (800 ml). The resulting soln. was warmed to 35°, treated with *t*-BuOK (25 g, 0.22 mol), heated at 60° for 30 min, and poured on ice. Extraction with AcOEt/Et$_2$O 4:1 (3 × 300 ml), followed by evaporation and drying *i.v.* gave a residue that was dissolved in THF/H$_2$O 4:1 (600 ml). The resulting soln. was treated with I$_2$ (85 g, 0.335 mol), stirred for 30 min, treated with Na$_2$SO$_3$, and extracted with AcOEt (3 × 350 ml). The combined org. phases were washed with aq. Na$_2$SO$_3$ soln. and then with H$_2$O, dried (MgSO$_4$), and evaporated. Recrystallization of the residue in boiling MeOH (1 l) gave **14** (19.8 g, 17.8%). Evaporation of the mother liquor and recrystallization in MeOH (500 ml) gave additional **14** (7.3 g, 6.5%). White crystals. M.p. 218°.

*2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucono-1,5-lactone* (**15**) [17]. *a*) At −70°, a soln. of freshly distilled oxalyl chloride (11 ml, 0.128 mol) in CH$_2$Cl$_2$ (350 ml) was treated dropwise within 1 h with a soln. of DMSO (20 ml) in CH$_2$Cl$_2$ (250 ml). The resulting soln. was stirred for 50 min and treated dropwise within 55 min with a soln. of **14** (27.1 g, 0.055 mol) in CH$_2$Cl$_2$/DMSO 25:4 (290 ml), stirred for 1 h at −70°, warmed to −40° within 1 h, cooled to −70°, and treated with Et$_3$N (40 ml; addition dropwise within 5 min). The mixture was stirred for 1 h at −70°, warmed to r.t., and washed with H$_2$O (3 × 300 ml). After drying (MgSO$_4$), filtration, and evaporation, the residue (brown oil) was treated under stirring with Et$_2$O (500 ml). Filtration of the resulting precipitate and drying *i.v.* gave **15** (22.9 g, 85%). White solid.

b) A soln. of **14** (4 g, 8.13 mmol) in CH_2Cl_2 (800 ml) was treated with *Dess-Martin* periodinane (5 g, 16.8 mmol), stirred for 30 min, treated again with *Dess-Martin* periodinane (1 g, 3.4 mmol), stirred for 20 min, treated with sat. aq. $NaHCO_3/Na_2S_2O_3$ soln., and stirred for 1 h. The aq. phase was extracted three times with CH_2Cl_2. Drying of the combined org. phases ($MgSO_4$) and evaporation gave **15** (3.9 g, 98%). M.p. 142° ($CHCl_3/Et_2O$) ([17]: 141–142° (MeOH)). R_f (AcOEt): 0.52. IR ($CHCl_3$): 3460*m*, 3090*w*, 3067*m*, 3043*w*, 3007*m*, 2927*m*, 2870*w*, 1750*s*, 1718*w*, 1684*s*, 1675*s*, 1653*m*, 1636*w*, 1624*w*, 1616*w*, 1603*w*, 1576*w*, 1570*w*, 1559*w*, 1540*m*, 1506*s*, 1497*s*, 1473*m*, 1456*s*, 1436*w*, 1419*w*, 1364*m*, 1286*w*, 1253*w*, 1139*m*, 1091*s*, 1028*m*, 914*w*. ^{1}H-NMR ($CDCl_3$): 1.86 (*s*, Ac); 3.72–3.82 (*m*, 2 H–C(6)); 3.95–4.05 (*m*, H–C(3), H–C(4), H–C(5)); 4.45–4.52 (*m*, PhC*H*), H–C(2)); 4.58–4.68 (*m*, 3 PhC*H*); 4.80 (*d*, *J* = 11.8, PhC*H*); 4.82 (*d*, *J* = 11.2, PhC*H*); 6.46 (*d*, *J* = 5.8, NH); 7.22–7.32 (*m*, 15 arom. H). ^{13}C-NMR ($CDCl_3$): 22.63 (*q*, Me); 55.55 (*d*, C(2)); 67.82 (*t*, C(6)); 73.62 (*t*, PhCH_2); 74.64 (*t*, 2 PhCH_2); 76.08, 78.54, 79.67 (3*d*, C(3), C(4), C(5)); 127.91–128.51 (several *d*); 137.57 (*s*); 137.63 (*s*); 137.98 (*s*); 168.88, 170.55 (2*s*, 2 C=O). FAB-MS: 49 (23), 490 (55, $[M + 1]^+$), 382 (13), 244 (28), 181 (46), 91 (100). Anal. calc. for $C_{29}H_{31}NO_6$ (489.57): C 71.15, H 6.38, N 2.86; found: C 70.92, H 6.47, N 2.84.

*2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-gluconamide* (**16**). A soln. of **15** (22.9 g, 0.047 mol) in CH_2Cl_2 (400 ml) was added dropwise within 25 min to condensed ammonia (100 ml) at –78°. The cooling bath was removed, the reaction flask fitted with a cold-finger cooling trap, and the soln. kept at reflux for 30 min. After removal of the cooling trap, evaporation of NH_3 and CH_2Cl_2 gave **16** (24.2 g, > 99%) as a foam. R_f (acetone/CH_2Cl_2 1:1) 0.27. IR ($CHCl_3$): 3488*m*, 3406*m*, 3099*w*, 3067*w*, 3043*w*, 3007*s*, 2927*m*, 2869*m*, 1692*s*, 1671*s*, 1588*m*, 1497*s*, 1454*m*, 1398*m*, 1368*m*, 1262*m*, 1088*s*, 1028*s*, 914*w*. ^{1}H-NMR ($CDCl_3$): 1.95 (*s*, Ac); 2.86–2.88 (br. *s*, OH); 3.57–3.70 (*m*, 2 H–C(6), H–C(4)); 3.93–4.00 (*m*, H–C(5)); 4.40 (*dd*, *J* = 2.8, 5.7, H–C(3)); 4.43–4.62 (*m*, 4 PhC*H*); 4.65–4.80 (*m*, 2 PhC*H*, H–C(2)); 5.74 (br. *s*, NH); 6.55 (br. *s*, NH); 6.82 (*d*, *J* = 7.1, N*H*Ac); 7.20–7.32 (*m*, 15 arom. H). ^{1}H-NMR (CD_3COCD_3): 1.97 (*s*, Ac); 3.67 (*dd*, *J* = 5.5, 9.7, H–C(6)); 3.76 (*dd*, *J* = 3.8, 9.7, H′–(6)); 3.79 (*t*, *J* = 6.5, H–C(4)); 3.93–4.03 (*m*, H–C(5)); 4.21–4.29 (br. *s*, exchange with CD_3OD, OH); 4.51 (*dd*, *J* = 2.5, 6.4, H–C(3)); 4.54 (*d*, *J* = 12.4, PhC*H*); 4.59 (*d*, *J* = 12.1, PhC*H*); 4.65–4.74 (*m*, 3 PhC*H*); 4.77 (*d*, *J* = 10.9, PhC*H*); 4.85 (*dd*, *J* = 2.5, 8.5, H–C(2)); 6.70 (br. *s*, exchange slowly with CD_3OD, NH); 7.05 (br. *s*, exchange slowly with CD_3OD, NH); 7.43–7.23 (*m*, 15 arom. H); 7.48 (*d*, *J* = 8.4, N*H*Ac). ^{13}C-NMR ($CDCl_3$): 23.23 (*q*, Me); 52.90 (*d*, C(2)); 70.55 (*d*, C(5)); 70.94 (*t*, C(6)); 73.59 (*t*, PhCH_2); 74.25 (*t*, PhCH_2); 74.54 (*t*, PhCH_2); 78.51, 78.84 (2*d*, C(3), C(4)); 127.82–128.65 (several *d*); 137.43 (*s*); 137.67 (*s*); 137.84 (*s*); 170.82, 172.69 (2*s*, 2 C=O). FAB-MS: 530 (8), 529 (18, $[M + Na]^+$), 508 (27, $[M + 2]^+$), 507 (58, $[M + 1]^+$), 181 (52), 162 (37), 91 (100).

*2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*D-xylo-*hex-5-ulosonamide* (**17**). A soln. of pyridine · SO_3 (12.5 mg, 0.079 mmol) in DMSO (1 ml) was kept at r.t. for 15 min and then added dropwise at 20° to a soln. of **16** (47 mg, 0.09 mmol) in DMSO/Et_3N 25:21 (62 ml). The mixture was stirred at < 25° for 1.5 h and then poured into toluene/H_2O. The aq. phase was extracted five times with toluene. Drying and evaporation of the combined org. phases gave **17** (> 90% pure according to ^{1}H-NMR). R_f (acetone/CH_2Cl_2 1:1) 0.40. IR ($CHCl_3$): 3486*m*, 3387*m*, 3090*w*, 3067*w*, 3043*w*, 3001*s*, 2927*w*, 2871*w*, 1733*m*, 1692*s*, 1674*s*, 1616*w*, 1588*w*, 1497*s*, 1455*m*, 1435*m*, 1402*m*, 1310*m*, 1253*m*, 1054*s*, 1014*s*, 948*m*. ^{1}H-NMR ($CDCl_3$): 1.88 (*s*, Ac); 3.94 (*d*, *J* = 18.1, H–C(6)); 4.02 (*d*, *J* = 18.1, H′–C(6)); 4.07 (*d*, *J* = 3.9, H–C(4)); 4.26–4.33 (*m*, 3 PhC*H*); 4.38 (*t*, *J* = 3.8, irrad. at 4.07 → *d*, *J* ≈ 3.8, H–C(3)); 4.42 (*d*, *J* = 11.1, PhC*H*); 4.47–4.57 (*m*, 2 PhC*H*, H–C(2)); 5.82 (br. *s*, NH); 6.58 (br. *s*, NH); 6.74 (*d*, *J* = 6.9, N*H*Ac); 7.02–7.30 (*m*, 15 arom. H). ^{1}H-NMR (CD_3COCD_3): 1.93 (*s*, Ac); 4.33 (*d*, *J* = 5.2, H–C(4)); 4.34 (*d*, *J* = 18.0, H–C(6)); 4.40 (*d*, *J* = 18.0, H′–C(6)); 4.52 (*s*, PhCH_2); 4.58 (*dd*, *J* = 5.2, 3.4, H–C(3)); 4.61 (*s*, PhCH_2); 4.62 (*d*, *J* = 10.9, PhC*H*); 4.71 (*d*, *J* = 10.8, PhC*H*); 4.75 (*dd*, *J* = 3.4, 8.5, H–C(2)); 5.59 (*d*, *J* = 8.5, N*H*Ac); 6.70 (br. *s*, NH); 7.05 (br. *s*, NH); 7.10–7.50 (*m*, 15 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 23.20 (*q*, Me); 52.24 (*d*, C(2)); 73.60 (*t*, C(6)); 74.21 (*t*, PhCH_2); 74.36 (*t*, PhCH_2); 74.46 (*t*, PhCH_2); 77.62, 82.25 (2*d*, C(3), C(4)); 128.19–129.56 (several *d*); 136.77 (*s*); 137.01 (*s*); 138.20 (*s*); 171.10, 172.43 (2*s*, 2 C=O); 207.45 (*s*, C(5)).

Oxidation of **16**. a) *With* Dess-Martin *Periodinane*. A soln. of **16** (1.1 g, 2.17 mmol) in CH_2Cl_2 (50 ml) was treated with *Dess-Martin* periodinane (1.2 g, 4 mmol), stirred for 30 min, treated again with *Dess-Martin* periodinane (0.5 g, 1.7 mmol), stirred for 50 min, treated with sat. aq. $NaHCO_3/Na_2S_2O_3$ soln., and stirred for 1 h. The aq. phase was extracted with CH_2Cl_2 (3 × 200 ml). Drying ($MgSO_4$) of the combined org. phases and evaporation gave **17**/**18**/**19**/**20** 44:16:12:28 (1.15 g, quant.; ^{1}H-NMR, assignment based on Ac signals). A soln. of this residue in toluene (50 ml) was treated with AcOH (0.5 ml). The resulting soln. (which showed increasing precipitation after a few h) was stirred at r.t. for 3 d and treated with sat. aq. $NaHCO_3$ soln. (20 ml). The aq. phase was extracted with CH_2Cl_2 (3 × 250 ml). Drying of the combined org. phases ($MgSO_4$) and evaporation gave **18**/**19** 87:13 (1.05 g, 96%).

b) *With* Jones *reagent.* At 0°, a soln. of **16** (164.7 mg, 0.33 mmol) in acetone (20 ml) was treated with a soln. of CrO_3 (56 mg, 0.56 mmol) in H_2O/conc. H_2SO_4 83:17 (0.33 ml), stirred for 1 h at 0° and for 4 h at r.t., and treated with ice/sat. aq. Na_2CO_3 soln. Normal workup and FC (toluene/acetone 2:1) gave **18** (72.4 mg, 44%) and **19** (16.5 mg, 10%).

*2-Acetamido-5-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*D-glucono-*1,5-lactam* (**18**). Crystallization of **18** (72.4 mg) from MeOH/hexane/Et_2O 5:20:7 (3.2 ml) gave 22.4 mg of white crystals. M.p. 164° (MeOH/hexane/Et_2O). R_f (acetone/CH_2Cl_2 1:1) 0.27. IR ($CHCl_3$): 3457*w*, 3379*m*, 3090*w*, 3067*w*, 3043*w*, 3008*m*, 2927*m*, 2857*w*, 1685*s*, 1602*m*, 1512*m*, 1498*m*, 1454*s*, 1369*m*, 1301*m*, 1238*w*, 1100*s*, 1028*w*, 1000*w*. ^1H-NMR ($CDCl_3$): 1.81 (*s*, Ac); 3.42 (*d*, $J = 9.8$, 2 H–C(6)); 3.82 (*d*, $J = 9.6$, H–C(4)); 3.99 (*t*, $J \approx 8.0$, H–C(2)); 4.24 (*dd*, $J = 8.4, 9.6$, H–C(3)); 4.44 (*d*, $J = 11.8$, PhC*H*); 4.54 (*d*, $J = 11.8$, PhC*H*); 4.63 (*d*, $J = 12.1$, PhC*H*); 4.66 (*d*, $J = 11.5$, PhC*H*); 4.80 (*s*, exchange with D_2O, OH); 4.82 (*d*, $J = 11.6$, PhC*H*); 4.91 (*d*, $J = 11.2$, PhC*H*); 6.87 (br. *s*, exchange with D_2O, HN–C(5)); 6.97 (*d*, $J = 7.8$, exchange with D_2O, N*H*Ac); 7.15–7.36 (*m*, 15 arom. H). ^1H-NMR ((D_6)DMSO): 1.81 (*s*, Ac); 3.26–3.36 (covered by H_2O signal, H–C(6)); 3.56 (*d*, $J = 9.3$, H'–C(6)); 3.78 (*d*, $J = 10.0$, H–C(4)); 4.03 (*t*, $J = 9.8$, H–C(3)); 4.19 (*t*, $J = 9.2$, H–C(2)); 4.39 (*d*, $J = 12.1$, PhC*H*); 4.51 (*d*, $J = 10.9$, PhC*H*); 4.54 (*d*, $J = 11.8$, PhC*H*); 4.59 (*d*, $J = 11.5$, PhC*H*); 4.66 (*d*, $J = 11.5$, PhC*H*); 4.77 (*d*, $J = 11.2$, PhC*H*); 5.59 (*s*, OH); 7.18–7.30 (*m*, 15 arom. H); 8.24 (*s*, HN–C(5)); 8.34 (*d*, $J = 8.7$, N*H*Ac). ^{13}C-NMR ($CDCl_3$): 22.68 (*q*, Me); 56.51 (*d*, C(2)); 71.95 (*t*, C(6)); 73.65 (*t*, PhCH_2); 74.77 (*t*, PhCH_2); 75.26 (*t*, PhCH_2); 78.07, 78.61 (2*d*, C(3), C(4)); 82.20 (*s*, C(5)); 128.01–129.06 (several *d*); 137.24 (*s*); 137.51 (*s*); 138.14 (*s*); 169.83, 171.44 (2*s*, 2 C=O). FAB-MS: 506 (4), 505 (12, $[M + 1]^+$), 489 (4), 488 (23), 487 (55, $[M - OH]^+$).

*2-Acetamido-5-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*L*-idono-1,5-lactam* (**19**). Crystallization of **19** (16.5 mg) from $CHCl_3$/MeOH/hexane/Et_2O 4:6:40:15 (6.5 ml; induced by the slow evaporation of 1 ml of solvent) gave 2.4 mg of white crystals. M.p. 142° ($CHCl_3$/MeOH/hexane/Et_2O). R_f (acetone/CH_2Cl_2 1:1) 0.21. IR ($CHCl_3$): 3439*w*, 3377*w*, 3042*w*, 3008*w*, 2927*s*, 2854*m*, 1679*s*, 1602*m*, 1497*m*, 1456*m*, 1370*w*, 1098*w*, 1002*w*. ^1H-NMR ($CDCl_3$): 1.84 (*s*, Ac); 3.62 (*d*, $J = 9.4$, H–C(6)); 3.70 (*d*, $J = 9.4$, H'–C(6)); 3.89 (*d*, $J = 5.5$, H–C(4)); 3.97 (*dd*, $J = 4.4, 5.4$, H–C(3)); 4.54 (*d*, $J = 11.2$, PhC*H*); 4.58 (*d*, $J = 12.5$, PhC*H*); 4.62 (*d*, $J = 10.6$, PhC*H*); 4.64 (*d*, $J = 11.8$, PhC*H*); 4.71 (*d*, $J = 11.8$, PhC*H*); 4.78 (*dd*, $J = 4.4, 8.2$, irrad. at 6.06 → *d*, $J \approx 3.7$, H–C(2)); 4.80 (*d*, $J = 11.8$, PhC*H*); 4.82–4.89 (br. *s*, exchange with D_2O, OH); 6.06 (*d*, $J = 8.4$, N*H*Ac); 6.74 (*s*, HN–C(5)); 7.17–7.40 (*m*, 15 arom. H). ^1H-NMR ((D_6)DMSO): 1.82 (*s*, Ac); 3.42 (*d*, $J = 9.3$, H–C(6)); 3.59 (*d*, $J = 9.3$, H'–C(6)); 3.78 (*d*, $J = 5.6$, H–C(4)); 3.84 (*dd*, $J = 5.6, 9.3$, H–C(3)); 4.47–4.55 (*m*, 3 PhC*H*); 4.58–4.73 (*m*, 2 PhC*H*, H–C(2)); 4.84 (*d*, $J = 12.1$, PhC*H*); 6.05 (*s*, OH); 7.18–7.20 (*m*, 15 arom. H); 7.72 (*s*, HN–C(5)); 8.09 (*d*, $J = 9.4$, N*H*Ac). ^{13}C-NMR ($CDCl_3$): 23.00 (*q*, Me); 52.21 (*d*, C(2)); 72.64 (*t*, C(6)); 73.06 (*t*, PhCH_2); 73.94 (*t*, PhCH_2); 73.99 (*t*, PhCH_2); 77.22, 77.30 (2*d*, C(3), C(4)); 84.41 (*s*, C(5)); 128.14–129.06 (several *d*); 136.99 (2*s*); 137.42 (*s*); 168.21, 170.13 (2*s*, 2 C=O). FAB-MS: 506 (5), 505 (10, $[M + 1]^+$), 487 (40, $[M - OH]^+$).

Equilibration of **18**, **19**, *and* **20**. *a*) At –40°, a soln. of **18** (5 mg, 0.009 mmol) in CH_2Cl_2/MeCN 1:1 (3 ml) was treated with 0.8M $BF_3 \cdot OEt_2$ in MeCN (0.025 ml), kept for 23 h at 5° then for 26 h at –15°. The mixture was treated with ice/sat. aq. Na_2CO_3 soln. Normal workup gave **18**/**19** 76:24 (5 mg, 100%).

b) As *a* with **19** (7.5 mg, 0.015 mmol), kept for 23 h at 5° and for 26 h at –15° → **18**/**19** 73.5:26.5 (7 mg, 93%).

c) As *a* with **20** (6.5 mg, 0.013 mmol) in CH_2Cl_2/MeCN 1:1 (4 ml), kept for 8 h at 5° and for 12 h at –15° → **18**/**19**/**20** 10:69:21 (7.5 mg, > 99%).

*2-Acetamido-5-amino-3,4,6-tri-*O*-benzyl-2,5-dideoxy-*D*-glucono-1,5-lactam* (**21**). *a*) From **18**/**19** 87:13. At –50°, a soln. of **18**/**19** 87:13 (1.05 g, 2.02 mmol) obtained from **16** by oxidation with *Dess-Martin* periodinane in CH_2Cl_2/MeCN 1:1 (40 ml) was treated dropwise within 20 min with a soln. of $BF_3 \cdot OEt_2$ (1.3 ml, 10.3 mmol) and Et_3SiH (1 ml, 6.3 mmol) in CH_2Cl_2/MeCN 1:1 (30 ml). The soln. was warmed to –5° within 30 min, then cooled to –40° and poured into ice/sat. aq. Na_2CO_3 soln. (25 ml). Normal workup and recrystallization of the residue (1 g) from Et_2O/CH_2Cl_2 5:1 (30 ml) gave **21** (692 mg, 68%). The mother liquors gave, after evaporation, filtration through silica gel (AcOEt), and recrystallization (Et_2O/CH_2Cl_2), a second crop (37 mg, 4%) of crystals. Total yield: 72% from 1.1 g of **16**.

b) From **18**. At –15°, a soln. of **18** (5.5 mg, 0.011 mmol) in CH_2Cl_2 (2 ml) was treated dropwise within 5 min with a soln. of $BF_3 \cdot OEt_2$ (0.05 ml, 0.40 mmol) and Et_3SiH (0.05 ml, 0.31 mmol) in MeCN (2 ml). The soln. was stirred for 30 min at –5° and treated with sat. aq. Na_2CO_3 soln. Normal workup gave **21** (5.1 mg, 96%).

c) From the crude product obtained from **16** by oxidation with *Dess-Martin* periodinane, without intermediary equilibration. The crude residue obtained by oxidation of **16** (60 mg, 0.12 mmol) with *Dess-Martin* periodinane was dried *i.v.*, dissolved in CH_2Cl_2 (5 ml) and treated dropwise at –40° with a soln. of Et_3SiH (0.1 ml, 0.63 mmol) and $BF_3 \cdot OEt_2$ (0.1 ml, 0.8 mmol) in MeCN (6 ml). The soln. was warmed to 0° within 1 h, stirred at 0° for 4.5 h, then cooled to –20°, and treated with sat. aq. Na_2CO_3 soln. Normal workup and crystallization from Et_2O/hexane (8 ml) gave **21** (18.3 mg, 32%) as white crystals. Evaporation of the filtrate and crystallization from Et_2O/hexane 5:3 gave a second crop of **21** (2.9 mg, 5%). Evaporation of the filtrate and FC (AcOEt) gave **20** (6.5 mg, 11%) and **21** (7.8 mg, 13.5%).

Data of **21**: M.p. 150°. R_f (acetone/CH_2Cl_2 1:1) 0.15. IR ($CHCl_3$): 3460*m*, 3391*m*, 3068*w*, 3006*m*, 2866*m*, 1675*s*, 1602*m*, 1510*m*, 1498*m*, 1454*m*, 1366*m*, 1316*m*, 1269*m*, 1100*s*, 1028*m*, 1003*w*, 914*w*. ^1H-NMR ($CDCl_3$): 1.90 (*s*, Ac); 3.31 (*t*, $J \approx 8.6$, irrad. at 3.65 → change, H−C(6)); 3.59 (*dd*, $J = 2.8$, 9.0, irrad. at 3.31 → change, H′−C(6)); 3.60 (*t*, $J \approx 8.4$, irrad. at 4.01 → change, H−C(4)); 3.62–3.72 (*m*, irrad. at 3.31 → change, H−C(5)); 4.01 (*t*, $J = 8.6$, irrad. at 3.65 → change, H−C(3)); 4.12 (*t*, $J = 8.4$, irrad. at 4.01 → change, irrad. at 5.81 → *d*, $J \approx 8.0$, H−C(2)); 4.46 (*s*, PhC*H*$_2$); 4.57 (*d*, $J \approx 11.2$, PhC*H*); 4.68 (*d*, $J = 11.5$, PhC*H*); 4.83 (*d*, $J = 11.5$, PhC*H*); 4.85 (*d*, $J = 11.3$, PhC*H*); 5.81 (*d*, $J = 7.8$, N*H*Ac); 6.00 (*s*, HN−C(5)); 7.15–7.50 (*m*, 15 arom. H). ^1H-NMR (C_6D_6): 1.73 (*s*, Ac); 3.16 (*dd*, $J = 6.7$, 9.5, H−C(6)); 3.36 (*dd*, $J = 2.8$, 9.3, H′−C(6)); 3.54 (*t*, $J = 8.3$, H−C(4)); 3.57–3.67 (*m*, H−C(5)); 4.10 (*d*, $J = 12.1$, PhC*H*); 4.17 (*t*, $J \approx 7.6$, H−C(3)); 4.17 (*d*, $J = 12.7$, PhC*H*); 4.23 (*t*, $J = 8.1$, H−C(2)); 4.39 (*d*, $J = 11.6$, PhC*H*); 4.70 (*s*, PhC*H*$_2$); 4.73 (*d*, $J = 11.5$, PhC*H*); 6.51 (*s*, HN−C(5)); 6.57 (*d*, $J = 7.2$, N*H*Ac); 7.00–7.32 (*m*, 15 arom. H). ^1H-NMR (CD_3COCD_3): 1.89 (*s*, Ac); 3.53–3.63 (*m*, H−C(5), H−C(6)); 3.71–3.76 (*m*, H′−C(6)); 3.83 (*t*, $J = 8.3$, irrad. at 3.57 → *d*, $J \approx 8.7$, H−C(4)); 4.03 (*t*, $J = 9.0$, H−C(3)); 4.25 (*t*, $J = 8.9$, irrad. at 7.47 → *d*, $J \approx 9.3$, H−C(2)); 4.51 (*d*, $J = 12.1$, PhC*H*); 4.54 (*d*, $J = 12.1$, PhC*H*); 4.63 (*d*, $J = 11.3$, PhC*H*); 4.77 (*d*, $J = 11.5$, PhC*H*); 4.80 (*d*, $J = 11.4$, PhC*H*); 4.87 (*d*, $J = 11.2$, PhC*H*); 6.66 (*s*, HN−C(5)); 7.25–7.40 (*m*, 15 arom. H); 7.47 (*d*, $J = 7.8$, N*H*Ac). ^{13}C-NMR ($CDCl_3$): 22.79 (*q*, Me): 54.00, 54.61 (2*d*, C(2), C(5)); 69.98 (*t*, C(6)); 73.05 (*t*, PhCH$_2$); 74.31 (*t*, PhCH$_2$); 74.38 (*t*, PhCH$_2$); 77.09, 79.45 (2*d*, C(3), C(4)); 127.56–128.25 (several *d*); 136.97 (*s*); 137.11 (*s*); 137.64 (*s*); 168.25, 170.23 (2*s*, 2 C=O). FAB-MS: 490 (26), 489 (60, $[M + 1]^+$), 201 (12), 181 (11), 154 (14).

*Data of (5*R*)-2-Acetamido-3,4,6-tri-O-benzyl-2-deoxy-*D-xylo*-hex-5-ulo-5,2-furanosonamide* (**20**): R_f (acetone/CH_2Cl_2 1:1) 0.47. IR ($CHCl_3$): 3472*m*, 3325*m*, 3182*w*, 3088*w*, 3067*w*, 3043*w*, 3002*s*, 2926*m*, 2873*w*, 1731*w*, 1690*s*, 1604*m*, 1496*m*, 1455*m*, 1434*m*, 1388*m*, 1339*m*, 1310*m*, 1253*m*, 1144*m*, 1094*s*, 1054*s*, 1030*s*, 948*m*. ^1H-NMR ($CDCl_3$): 2.05 (*s*, Ac); 3.29 (*d*, $J = 9.1$, H−C(6)); 4.06 (*d*, $J = 10.5$, PhC*H*); 4.07 (*s*, exchange with CD_3OD, OH); 4.17 (*dd*, $J = 3.0$, 5.7, H−C(3)); 4.32 (*d*, $J = 10.3$, irrad. at 4.06 → *s*, PhC*H*); 4.38 (*d*, $J = 9.0$, irrad. at 3.29 → *s*, H′−C(6)); 4.506 (*d*, $J = 5.9$, H−C(4)); 4.51 (*d*, $J = 3.1$, H−C(2)); 4.58 (*d*, $J = 11.2$, PhC*H*); 4.69 (*d*, $J = 11.8$, PhC*H*); 4.87 (br. *s*, slow exchange with CD_3OD, NH); 4.88 (*d*, $J = 11.8$, PhC*H*); 4.99 (*d*, $J = 11.2$, PhC*H*); 7.05–7.11 (*m*, 2 arom. H); 7.12–7.20 (*m*, 1 arom. H); 7.30–7.40 (*m*, 12 arom. H); 7.71 (br. *s*, slow exchange with CD_3OD, NH). ^{13}C-NMR ($CDCl_3$): 23.15 (*q*, Me); 62.28 (*d*, C(2)); 69.03 (*t*, C(6)); 73.47 (*t*, 3 PhCH$_2$); 78.30, 79.71 (2*d*, C(3), C(4)); 87.03 (*s*, C(5)); 127.59–129.33 (several *d*); 136.34 (*s*); 137.37 (*s*); 137.54 (*s*); 171.05, 173.02 (2*s*, 2 C=O). FAB-MS: 527 (3, $[M + Na]^+$), 505 (4, $[M + 1]^+$), 445 (15), 355 (3), 273 (2), 91 (100).

*2-Acetamido-5-amino-2,5-dideoxy-*D*-glucono-1,5-lactam* (**22**). A suspension of 10% Pd/C (98 mg) in MeOH (4 ml) was hydrogenated at 6 bar for 2 h, treated with **21** (100 mg, 0.20 mmol), hydrogenated at 6 bar for 60 h, and filtered through *Celite*. Evaporation of the filtrate and recrystallization from MeOH/H_2O/acetone gave **22** (32 mg, 72%). White crystals suitable for X-ray analysis. M.p. 219°. R_f (AcOEt/MeOH 1:1) 0.15. ^1H-NMR (D_2O): 2.03 (*s*, Ac); 3.31–3.36 (*m*, H−C(5)); 3.71 (*dd*, $J = 5.0$, 12.1, irrad. at 3.34 → *d*, $J \approx 12.8$, H−C(6)); 3.71 (*t*, $J = 9.7$, irrad. at 3.34 → *d*, $J \approx 10.6$, irrad. at 3.87 → change, H−C(4)); 3.79 (*dd*, $J = 2.7$, 12.0, irrad. at 3.34 → *d*, $J \approx 11.2$, H′−C(6)); 3.87 (*t*, $J = 10.0$, H−C(3)); 4.10 (*d*, $J = 10.3$, irrad. at 3.87 → change, H−C(2)). ^{13}C-NMR (D_2O): 24.59 (*q*, Me); 57.59, 59.18 (2*d*, C(2), C(5)); 62.88 (*t*, C(6)); 70.75, 73.74 (2*d*, C(3), C(4)); 173.75, 177.26 (2*s*, 2 C=O). FAB-MS: 460 (20, $[2M + Na]^+$), 443 (12), 307 (100), 220 (11), 219 (30, $[M + 1]^+$), 218 (8), 217 (12), 216 (13), 201 (20).

X-Ray Analysis of **22**. Monoclinic *P*21 (No. 4); $a = 8.174$, $b = 7.063$, $c = 8.634$ Å; $\beta = 106.76°$; $V = 477.29$ Å^3; $D_{calc} = 1.518$ Mg/m^3; $Z = 2$. The reflexions were measured on an *Enraf-Nonius-CAD4* diffractometer (graphite monochromator, MoK_α, λ 0.71073) at 293 K. $R = 0.0429$, $R_w = 0.1199$. The structure was solved with the direct-methods routine of SHELX-86, and the refinement was performed with SHELXL-92 [53][54].

*2-Acetamido-5-amino-3,4,6-tri-O-benzyl-2,5-dideoxy-*D*-mannono-1,5-lactam* (**23**). *a*) A soln. of **21** (10 mg, 0.02 mmol) in toluene (2 ml) was treated with *Lawesson*'s reagent (5 mg, 0.013 mmol) and heated for 48 h at 90°. Normal workup and FC (CH_2Cl_2/acetone 2:1) gave **23** (3.3 mg, 33%).

b) In a NMR tube, a soln. of **21** (10 mg, 0.02 mmol) in $CDCl_3$ (0.6 ml) was treated with piperidine (0.007 ml, 0.07 mmol), leading after 5 d at 50° to **21**/**23** 22:78. Evaporation and FC (CH_2Cl_2/acetone 2:1) gave **23** (4 mg, 40%) and **21** (1.1 mg, 11%).

c) Similarly as for *b*, **23** (4 mg, 0.008 mmol; obtained in *b*)) gave, after 7 d at 55°, **21**/**23** 11:89. **23**: R_f (CH_2Cl_2/acetone 1:1) 0.38. IR ($CHCl_3$): 3398*m*, 3090*w*, 3067*w*, 3007*m*, 2962*w*, 2924*w*, 1665*s*, 1628*m*, 1511*m*, 1498*w*, 1454*w*, 1403*w*, 1364*w*, 1262*m*, 1094*s*, 1074*s*, 1028*m*. ^1H-NMR ($CDCl_3$): 2.00 (*s*, Ac); 3.42–3.43

(*m*, H–C(4), 2 H–C(6)); 3.69 (*ddd*, *J* = 1.4, 4.3, 8.4, H–C(5)); 4.36 (*d*, *J* = 12.0, PhC*H*); 4.37 (*dd*, *J* = 2.3, 3.1, H–C(3)); 4.39–4.54 (*m*, 4 PhC*H*); 4.61 (*d*, *J* = 11.8, PhC*H*); 4.77 (*dd*, *J* = 2.5, 5.9, H–C(2)); 6.00 (*s*, HN–C(5)), 6.46 (*d*, *J* = 5.9, N*H*Ac); 7.21–7.40 (*m*, 15 arom. H). ^{1}H-NMR (CD_3OCD_3): 1.98 (*s*, Ac); 3.55–3.78 (*m*, H–C(5), 2 H–C(6)); 3.91 (*dd*, *J* = 2.4, 3.7, irrad. at 4.25 → *d*, *J* = 4.0, H–C(4)); 4.25 (*t*, *J* = 2.8, H–C(3)); 4.52 (*s*, PhCH_2); 4.54 (*d*, *J* = 11.0, PhC*H*); 4.55 (*d*, *J* = 11.8, PhC*H*); 4.61 (*d*, *J* = 11.8, PhC*H*); 4.69 (*d*, *J* = 11.8, PhC*H*); 4.80 (*dd*, *J* = 3.4, 6.9, irrad. at 4.25 → *d*, *J* ≈ 7.2, H–C(2)); 6.73 (*s*, HN–C(5)); 7.12 (*d*, *J* = 7.0, N*H*Ac); 7.30–7.41 (*m*, 15 arom. H). ^{13}C-NMR ($CDCl_3$): 23.37 (*q*, Me); 51.88 (*d*, C(5)); 55.57 (*d*, C(2)); 70.71 (*t*, C(6)); 71.75 (*t*, PhCH_2); 73.29 (*t*, PhCH_2); 73.55 (*t*, PhCH_2); 74.68, 76.39 (2*d*, C(3), C(4)); 128.19–129.04 (several *d*); 137.42 (*s*); 137.63 (*s*); 138.77 (*s*); 169.07, 170.55 (2*s*, 2 C=O). FAB-MS: 977 (5, $[2\,M + 1]^+$), 490 (38), 489 (100, $[M + 1]^+$), 447 (7), 381 (4), 91 (72).

*2-Acetamido-3,4,6-tri-*O*-benzyl-1,2,5-trideoxy-1,5-imino-*D*-glucitol* (**24**). A soln. of $BF_3 \cdot OEt_2$ (0.05 ml, 0.40 mmol) in THF (3 ml) was treated with **21** (19.2 mg, 0.039 mmol), heated for 9 min at 50°, cooled to 4°, and treated with $NaBH_4$ (100 mg, 2.6 mmol). The mixture was stirred for 20 min at 4° and then treated with ice/CH_2Cl_2. The residue obtained after normal workup was dissolved in MeOH (2 ml) and treated (using a *Pasteur* pipette) with six drops of conc. HCl soln. and the resulting soln. evaporated. After repetition of this operation, the residue was dissolved in CH_2Cl_2 and treated with ice/H_2O, then with 7% aq. KOH soln. (3 ml → pH 10). The aq. phase was extracted with CH_2Cl_2 and the combined org. phase dried ($MgSO_4$), and evaporated. Recrystallization of the residue from AcOEt/hexane at r.t. gave **24** (13 mg, 70%). R_f (AcOEt/MeOH 10:2) 0.17. IR ($CHCl_3$): 3420*w*, 3090*w*, 3067*w*, 3007*m*, 2927*m*, 2857*m*, 1667*s*, 1515*m*, 1497*m*, 1454*m*, 1358*w*, 1313*w*, 1261*m*, 1100*s*, 1028*m*, 910*w*. ^{1}H-NMR ($CDCl_3$): 1.73 (*s*, Ac); 1.77 (br. *s*, exchange with CD_3OD, HN–C(5)); 2.27 (*dd*, *J* = 10.1, 12.9, irrad. at 3.76 → change, H_{ax}–C(1)); 2.74 (*ddd*, *J* = 3.0, 4.9, 8.0, H–C(5)); 3.32 (*dd*, *J* = 5.4, 12.9, irrad. at 2.27 → *d*, *J* ≈ 4.7, irrad. at 3.76 → change, H_{eq}–C(1)); 3.34 (*dd*, *J* = 8.3, 9.6, irrad. at 3.76 → change, H–C(3)); 3.52 (*t*, *J* ≈ 8.7, H–C(4)); 3.62 (*dd*, *J* = 3.0, 9.0, H–C(6)); 3.68 (*dd*, *J* = 5.0, 9.1, H′–C(6)); 3.75–3.77 (*m*, irrad. at 2.27 → change, irrad. at 5.00 → change, H–C(2)); 4.47 (*d*, *J* = 11.7, PhC*H*); 4.50 (*d*, *J* = 11.8, PhC*H*); 4.55 (*d*, *J* = 11.2, PhC*H*); 4.64 (*d*, *J* = 12.0, PhC*H*); 4.83 (*d*, *J* = 11.0, PhC*H*); 4.87 (*d*, *J* = 12.1, PhC*H*); 5.00 (*d*, *J* = 6.5, irrad. at 3.76 → *s*, exchange with CD_3OD, N*H*Ac); 7.25–7.42 (*m*, 15 arom. H). ^{13}C-NMR ($CDCl_3$): 23.07 (*q*, Me); 47.63 (*t*, C(1)); 51.90 (*d*, C(5)); 59.37 (*d*, C(2)); 69.08 (*t*, C(6)); 73.38 (*t*, PhCH_2); 74.06 (*t*, PhCH_2); 77.48 (*t*, PhCH_2); 80.18, 82.54 (2*d*, C(3), C(4)); 127.87–128.70 (several *d*); 137.85 (*s*); 137.99 (*s*); 138.37 (*s*); 170.41 (*s*, C=O). FAB-MS: 476 (8), 475 (15, $[M + 1]^+$), 91 (86).

*2-Acetamido-3,4,6-tri-*O*-benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-2,5-dideoxy-*D*-glucono-1,5-lactam* (**25**). A soln. of **21** (290 mg, 0.59 mmol) and DMAP (17.0 mg, 0.14 mmol) in MeCN (10 ml) was treated with Boc_2O (50 mg, 0.23 mmol), stirred for 40 min, treated again with Boc_2O (100 mg, 0.46 mmol), and stirred for 30 min. Normal workup gave **25** (332 mg, 95%). R_f (AcOEt/hexane 1:1) 0.28. IR ($CHCl_3$): 3434*m*, 3090*w*, 3067*w*, 3008*m*, 2986*m*, 2963*m*, 2931*m*, 2869*m*, 1775*s*, 1731*s*, 1681*s*, 1602*m*, 1511*m*, 1498*m*, 1474*m*, 1455*m*, 1394*m*, 1370*s*, 1287*s*, 1261*s*, 1152*s*, 1098*s*, 1028*s*, 909*w*, 844*w*. ^{1}H-NMR ($CDCl_3$): 1.49 (*s*, Me_3C); 2.01 (*s*, Ac); 3.63 (*ddd*, *J* = 1.2, 3.8, 8.2, irrad. at 4.05 → *dd*, *J* ≈ 0.8, 7.9, irrad. at 4.96 → *dd*, *J* ≈ 0.8, 3.9, H–C(3)); 3.64 (*dd*, *J* = 5.6, 9.5, H–C(6)); 3.77 (*dd*, *J* = 7.2, 9.6, H′–C(6)); 4.05 (*dd*, *J* = 2.5, 3.9, H–C(4)); 4.49–4.65 (*m*, 6 PhC*H*); 4.77–4.80 (*m*, irrad. at 4.05 → *t*, *J* ≈ 5.7, 6.1, H–C(5)); 4.96 (*t*, *J* = 8.4, irrad. at 6.05 → *d*, *J* ≈ 8.3, H–C(2)); 6.05 (*d*, *J* = 8.6, irrad. at 4.96 → *s*, N*H*Ac); 7.24–7.36 (*m*, 15 arom. H). ^{13}C-NMR ($CDCl_3$): 23.28 (*q*, Me); 27.92 (*q*, Me_3C); 54.58 (*d*, C(5)); 57.58 (*d*, C(2)); 69.27 (*t*, C(6)); 71.39 (*t*, PhCH_2); 72.56 (*t*, PhCH_2); 73.25 (*t*, PhCH_2); 75.94, 81.45 (2*d*, C(3), C(4)); 83.91 (*s*, Me_3*C*); 127.72–128.54 (several *d*); 137.38 (*s*); 137.65 (br. *s*, 2 C); 152.06 (*s*, NCO_2); 168.47, 170.26 (2*s*, 2 C=O). FAB-MS: 1177 (8, $[2\,M + 1]^+$), 589 (5, $[M + 1]^+$), 588 (1), 491 (10), 490 (44), 489 (100), 273 (13), 154 (14).

*2-Acetamido-3,4,6-tri-*O*-benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-2,5-dideoxy-α- and -β-*D*-glucopyranose* (**26** and **27**). At −10°, a soln. of **25** (240 mg, 0.41 mmol) in EtOH (12 ml) was treated with $NaBH_4$ (130 mg, 3.43 mmol). The pH of the suspension was adjusted to 6–6.5 by addition of 1N HCl. The addition of $NaBH_4$ (90 mg, 2.38 mmol) and the pH regulation was repeted every 50 min till completion of the reaction. The soln. was treated with ice/sat. aq. NH_4Cl soln. The aq. phase was neutralized with 1N HCl. Normal workup and FC (AcOEt/hexane 1:2 → 1:0) of the residue (**26**/**27** 7:6) gave **26** (41.5 mg, 17%), **26**/**27** 80:20 (53.4 mg, 22%), **26**/**27** 70:30 (40.8 mg, 17%), **26**/**27** 20:80 (39.6 mg, 16%), and **27** (43.2 mg, 18%).

Data of **26**: R_f (AcOEt/hexane 1:1) 0.22. $[\alpha]_D^{25} = -1.7$ (c = 0.32, $CHCl_3$). IR ($CHCl_3$): 3502*w*, 3403*m*, 3008*m*, 2884*m*, 2961*m*, 2930*m*, 2873*m*, 1690*s*, 1518*m*, 1455*m*, 1374*s*, 1318*m*, 1166*m*, 1074*s*, 1046*s*, 941*w*, 909*w*, 892*w*. ^{1}H-NMR (CD_3COCD_3): 1.44 (br. *s*, Me_3C); 1.78 (*s*, Ac); 3.62 (*dd*, *J* = 4.7, 9.4, irrad. at 4.04 → *m*, irrad. at 4.55 → *m*, H–C(6)); 3.77 (*t*, *J* = 4.8, irrad. at 4.34 → *d*, *J* ≈ 4.2, H–C(3)); 4.04 (*t*, *J* = 9.5, irrad. at 4.55 → *d*, *J* ≈ 8.9, H′–C(6)); 4.14 (*dd*, *J* = 2.4, 4.3, irrad. at 3.77 → *d*, *J* ≈ 1.9, irrad. at 4.55 → *d*, *J* ≈ 4.0, H–C(4)); 4.29–4.39 (br. *s*, irrad. at 3.77 → br. *d*, *J* ≈ 6.8, H–C(2)); 4.55–4.60 (*m*, PhC*H*, H–C(5)); 4.61–4.74

(*m*, 5 PhC*H*); 4.75 (*d*, *J* = 5.9, irrad. at 5.57 → *s*, OH); 5.57 (*dd*, *J* = 3.4, 5.3, irrad. at 4.34 → *d*, *J* ≈ 5.4, irrad. at 4.75 → *d*, *J* ≈ 3.1, H–C(1)); 6.96 (br. *d*, *J* = 6.8, irrad. at 4.34 → *s*, NH); 7.25–7.40 (*m*, 15 arom. H). ^{13}C-NMR (CDCl$_3$): 23.23 (*q*, Me); 28.33 (*q*, *Me*$_3$C); 48.48 (*d*, C(2)); 51.44 (*d*, C(5)); 70.06 (*t*, C(6)); 71.52 (*t*, PhCH$_2$); 72.57 (*t*, PhCH$_2$); 72.97 (*t*, PhCH$_2$); 71.52, 74.95 (2*d*, C(2), C(3)); 77.63 (*d*, C(1)); 80.68 (*s*, Me$_3$*C*); 128.22–129.24 (several *d*); 139.18 (*s*); 139.31 (*s*); 139.66 (*s*); 155.40, 169.22 (*s*, 2 C=O). ESI-MS: 1204 (22, [2 *M* + Na]$^+$), 906 (36), 629 (10), 613 (100, [*M* + Na]$^+$), 466 (95), 365 (60).

Data of **27**: *R*$_f$ (AcOEt/hexane 1:1) 0.17. $[\alpha]_D^{25}$ = 7.3 (*c* = 0.75 CHCl$_3$). IR (CHCl$_3$): 3500*w*, 3408*m*, 3067*w*, 3008*m*, 2930*m*, 2868*w*, 1684*s*, 1603*w*, 1515*m*, 1455*m*, 1370*s*, 1316*m*, 1262*m*, 1165*m*, 1073*s*, 1023*m*. ^{1}H-NMR (CDCl$_3$): 1.58 (br. *s*, Me$_3$C); 1.96 (*s*, Ac); 3.50 (*dd*, *J* = 0.8, 7.7, irrad. at 4.30 → br. *s*, H–C(3)); 3.62 (*dd*, *J* = 4.7, 8.8, irrad. at 4.45 → *d*, *J* ≈ 8.5, H–C(6)); 3.68 (*t*, *J* = 8.8, 10.1, irrad. at 4.45 → *d*, *J* ≈ 8.6, H′–C(6)); 4.00 (*d*, *J* = 10.3, irrad. at 5.16 → *s*, exchange with CD$_3$OD, OH); 4.19 (*dd*, *J* = 0.9, 2.5, irrad. at 4.45 → *d*, *J* = 0.8, irrad. at 3.50 → *d*, *J* ≈ 2.3, H–C(4)); 4.26 (*d*, *J* = 12.5, PhC*H*); 4.30 (*ddd*, *J* = 3.0, 8.0, 9.4, irrad. at 3.50 → *dd*, *J* ≈ 2.8, 9.3, irrad. at 5.16 → *dd*, *J* ≈ 7.9, 9.7, irrad. at 5.74 or addn. of CD$_3$OD → *dd*, *J* ≈ 3.0, 7.7, H–C(2)); 4.40–4.55 (*m*, 4 PhC*H*), H–C(5)); 4.65 (*d*, *J* = 11.7, PhC*H*); 5.16 (*dd*, *J* = 3.0, 10.3, addn. of CD$_3$OD → *d*, *J* ≈ 2.9, H–C(1)); 5.74 (*d*, *J* = 9.6, slow exchange with CD$_3$OD (> 12 h), irrad. at 4.30 → br. *s*, N*H*Ac); 7.20–7.38 (*m*, 15 arom. H). ^{13}C-NMR (CDCl$_3$): 23.45 (*q*, Me); 28.31 (*q*, *Me*$_3$C); 52.98 (2*d*); 68.72 (*t*, C(6)); 70.90 (*t*, PhCH$_2$); 71.54 (*t*, PhCH$_2$); 73.05 (*t*, PhCH$_2$); 74.55, 76.48, 78.81 (3*d*, C(1), C(3), C(4)); 81.35 (*s*, Me$_3$*C*); 127.54–128.71 (several *d*); 136.49 (*s*); 137.57 (*s*); 138.24 (*s*); 154.44 (*s*, NCO$_2$); 169.39 (*s*, C=O). ESI-MS: 1204 (15, [2 *M* + Na]$^+$), 906 (24), 629 (15), 613 (100, [*M* + Na]$^+$), 465 (60), 365 (40).

*Ethyl 2-Acetamido-3,4,6-tri-*O*-benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-2,5-dideoxy-α- and -β-*D*-glucopyranoside* (**28** and **29**). A soln. of **26**/**27** 7:6 (28 mg, 0.047 mmol) in EtOH (1 ml) was treated with TsOH · H$_2$O (10 mg, 0.05 mmol), stirred for 15 min, and treated with sat. aq. NaHCO$_3$ soln. Normal workup and FC (AcOEt/hexane 1:2) gave **28**/**29** 2:1 (22.6 mg, 77%). *R*$_f$ (AcOEt/hexane 1:1) 0.37. IR (CHCl$_3$): 3400*m*, 3008*m*, 2979*m*, 2871*m*, 1689*s*, 1518*m*, 1454*m*, 1374*s*, 1320*m*, 1169*m*, 1074*s*. ^{1}H-NMR (CDCl$_3$; 2:1 diastereoisomer mixture): selected data: 1.14 (*t*, *J* = 7.0, Me); 1.46 (*s*, Me$_3$C); 1.74 (*s*, Ac); 3.38–3.48 (*m*, irrad. at 1.14 → *d*, *J* = 9.3, 0.67 H), 3.52–3.56 (*m*, irrad. at 1.14 → *d*, *J* = 9.0, 1.34 H, OCH$_2$); 3.60–3.73 (*m*, irrad. at 4.05 → change, irrad. at 4.12 → change, irrad. at 4.96 → change, 1.67 H, PhC*H*; 0.67 H, H–C(3), 0.67 H, H–C(6)); 4.05 (br. *s*, 0.33 H, H–C(4)); 3.97 (br. *s*, 0.67 H, H–C(4)); 4.12 (br. *t*, *J* ≈ 9.5, irrad. at 3.60 → change, irrad. at 4.96 → *d*, *J* = 9.0, 0.67 H, H–C(6)); 4.35–4.49 (*m*, PhC*H*); 4.54 (br. *d*, *J* = 7.5, irrad. at 5.33 → change, irrad. at 6.80 → *s*, 0.67 H, H–C(2)); 4.63–4.77 (*m*, irrad. at 3.65 → change, irrad. at 5.42 → change, irrad. at 6.55 → change, 1.33 H, PhC*H*, 0.33 H, H–C(2)); 4.82 (*d*, *J* = 11.2, 0.33 H, PhC*H*); 4.96 (br. *t*, *J* = 5.9, irrad. at 3.65 → br. *d*, *J* ≈ 6.9, irrad. at 4.05 → change, irrad. at 4.12 → change, 0.67 H, H–C(5)); 5.33 (br. *s*, 0.67 H), 5.42 (br. *s*, 0.33 H, H–C(1)); 6.55 (*d*, *J* = 8.7, irrad. at 4.70 → *s*, 0.33 H), 6.80 (*d*, *J* = 8.7, 0.67 H, NH); 7.28–7.41 (*m*, 15 arom. H). ^{1}H-NMR (C$_6$D$_6$; 2:1 diastereoisomer mixture): selected data: 1.10 (*t*, *J* = 7.0, Me); 1.41 (*s*, Me$_3$C); 1.56 (*s*, 1 H), 1.57 (*s*, 2 H, Ac); 3.40–3.53 (*m*, irrad. at 1.10 → *J* ≈ 8.7, 0.67 H, OCH$_2$); 3.57–3.77 (*m*, irrad. at 1.10 → change, irrad. at 5.14 → change, 1.34 H, OCH$_2$, 0.33 H, H–C(3)); 3.87–4.00 (*m*, irrad. at 5.37 → change, 0.67 H, H–C(6)); 4.00–4.13 (*m*); 4.13 (br. *s*, 0.67 H, H–C(4)); 4.17–4.50 (*m*); 4.54 (*d*, *J* = 11.5, 0.67 H), 4.59 (*d*, *J* = 11.5, 0.67 H, PhC*H*); 4.72 (*d*, *J* = 11.5, 0.33 H, PhC*H*); 4.88–4.98 (*m*, 0.33 H, H–C(5), 0.67 H, H–C(2)); 5.14 (br. *d*, *J* = 8.7, 0.33 H, H–C(2)); 5.32–5.42 (*m*, irrad. at 3.93 → br. *d*, *J* ≈ 7.5, 0.67 H, H–C(5)); 5.71 (br. *s*, 0.67 H), 5.99 (br. *s*, 0.33 H, H–C(1)); 6.49 (*d*, *J* = 7.8, irrad. at 5.14 → *s*, 0.33 H, exchange slowly with CD$_3$OD), 6.75 (*d*, *J* = 8.7, irrad. at 4.94 → *s*, 0.67 H, exchange slowly with CD$_3$OD, NH); 7.00–7.40 (*m*, 15 arom. H). ^{13}C-NMR (CDCl$_3$; 2:1 diastereoisomer mixture): signals of major diastereoisomer: 14.97 (*q*, Me); 23.40 (*q*, *Me*CO); 28.41 (*q*, *Me*$_3$C); 46.76 (*d*); 50.32 (*d*); 63.28 (*t*); 69.83 (*t*); 71.12 (*t*); 71.37 (*t*); 72.89 (*t*); 73.63 (*d*); 74.55 (*d*); 80.80 (*s*); 83.03 (*d*); 127.00–129.00 (several *d*); 137.86 (*s*); 138.33 (*s*); 138.94 (*s*); 156.64 (*s*, NCO$_2$); 169.39 (*s*, C=O); signals of minor diastereoisomer: 15.18 (*q*, Me); 23.40 (*q*, *Me*CO); 28.41 (*q*, *Me*$_3$C); 46.16 (*d*); 52.63 (*d*); 63.92 (*t*); 70.30 (*t*); 71.12 (*t*); 71.59 (*t*); 73.10 (*t*); 74.27 (*d*); 74.55 (*d*); 80.80 (*s*); 82.58 (*d*); 127.00–129.00 (several *d*); 137.86 (*s*); 138.40 (*s*); 138.76 (*s*); 156.04 (*s*, NCO$_2$); 169.39 (*s*, C=O). ESI-MS: 948 (15), 657 (10), 641 (100, [*M* + Na]$^+$), 465 (60), 365 (40).

*3-Acetamido-4,5,7-tri-*O*-benzyl-2,3,6-trideoxy-2,6-imino-*D*-glycero-*D*-*gulo*-heptononitrile* (**30**). At 5°, a soln. of **28**/**29** 2:1 (9 mg, 0.015 mmol) in CH$_2$Cl$_2$ (1 ml) was treated dropwise with Me$_3$SiCN (0.025 ml, 0.20 mmol) and BF$_3$ · OEt$_2$, (0.025 ml, 0.20 mmol), stirred for 1 h at r.t., and poured into ice/sat. aq. NH$_4$Cl soln. Normal workup and FC (AcOEt/hexane 1:2 → 2:1) gave **30** (4 mg, 55%). *R*$_f$ (AcOEt/hexane 1:1) 0.05. IR (CHCl$_3$): 3451*w*, 3340*w*, 3067*w*, 3008*m*, 2928*m*, 2869*m*, 1676*s*, 1497*w*, 1454*m*, 1369*m*, 1263*m*, 1098*s*. ^{1}H-NMR (CDCl$_3$): 1.86 (*s*, Ac); 2.25–2.33 (*m*, irrad. at 2.87 → change, NH); 2.82–2.91 (*m*, irrad. at 2.29 → *dt*, *J* = 4.5, 9.0, irrad. at 3.41 → change, irrad. at 3.62 → *d*, *J* ≈ 9.0, addn. of CD$_3$OD → *dt*, *J* ≈ 5.3, 9.0, H–C(6)); 3.41 (*t*, *J* = 8.7, irrad. at 2.87 → *d*, *J* ≈ 8.1, H–C(5)); 3.57–3.67 (*m*, irrad. at 2.87 → change, irrad. at 3.95 → change, H–C(3), 2 H–C(7)); 3.95 (*dd, J* = 8.6, 9.0, irrad. at 3.41 → *d, J* ≈ 9.3, irrad. at 3.62 → change, H–C(4)); 4.17 (*dd, J* = 7.0, 9.5, irrad. at 2.29 → *d, J* ≈ 9.7, irrad. at 3.62 → change, addn. of CD_3OD → *d, J* = 10.0, H–C(2)); 4.48 (*s*, $PhCH_2$); 4.51 (*d, J* = 12.3, PhC*H*); 4.64 (*d, J* = 11.5, PhC*H*); 4.78 (*d, J* = 10.9, PhC*H*); 4.83 (*d, J* = 11.5, PhC*H*); 5.71 (*d, J* = 8.0, irrad. at 3.62 → change, exchange with CD_3OD, N*H*Ac); 7.40–7.17 (*m*, 15 arom. H). ^{13}C-NMR ($CDCl_3$): 23.47 (*q*, Me); 48.18 (*d*, C(2)); 55.66, 58.42 (2*d*, C(3), C(6)); 69.06 (*t*, C(7)); 73.51 (*t*, $PhCH_2$); 74.79 (*t*, $PhCH_2$); 74.94 (*t*, $PhCH_2$); 79.75 (*d*), 80.38 (*d*, C(4), C(5)); 118.15 (*s*, CN); 127.80–129.00 (several *d*); 137.58 (*s*); 137.73 (*s*); 138.03 (*s*); 170.66 (*s*, C=O). FAB-MS: 999 (2, [2 *M* + 1]$^+$), 501 (39), 500 (100, [*M* + 1]$^+$), 499 (6), 460 (26), 371 (10), 365 (22).

*2,3,4,6-Tetra-*O*-benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-5-deoxy-*D*-glucono-1,5-lactam* (**31**). A soln. of **1** [2][4] (232 mg, 0.43 mmol) and DMAP (16 mg, 0.13 mmol) in MeCN (7 ml) was treated with Boc_2O (200 mg, 0.92 mmol) and stirred for 5.5 h. Normal workup and FC (Et_2O/hexane 2.5) gave **31** (242 mg, 88%). R_f (Et_2O/hexane 2:1) 0.62. IR ($CHCl_3$): 3090*w*, 3067*m*, 3008*m*, 2979*m*, 2933*m*, 2869*m*, 1776*s*, 1732*s*, 1604*m*, 1497*s*, 1454*s*, 1394*m*, 1370*s*, 1291*s*, 1252*s*, 1151*s*, 1098*s*, 1074*s*, 1028*m*. ^{1}H-NMR ($CDCl_3$): 1.53 (*s*, Me_3C); 3.49 (*dd, J* = 4.7, 9.7, irrad. at 4.64 → *d, J* ≈ 9.0, H–C(6)); 3.62 (*dd, J* = 6.2, 9.7, irrad. at 4.64 → *d, J* ≈ 9.0, H′–C(6)); 3.86 (*ddd, J* = 0.9, 4.4, 8.4, irrad. at 4.21 → *d, J* ≈ 4.0, irrad. at 4.64 → *dd, J* ≈ 4.4, 8.4, H–C(3)); 3.92 (*dd, J* = 2.7, 4.5, irrad. at 4.64 → *d, J* ≈ 4.4, H–C(4)); 4.21 (*d, J* = 8.4, H–C(2)); 4.40 (*d, J* = 11.8, PhC*H*); 4.46 (*d, J* = 11.8, PhC*H*); 4.55 (*d, J* = 10.9, PhC*H*); 4.57 (*s*, $PhCH_2$); 4.60 (*d, J* = 11.5, PhC*H*); 4.60–4.68 (*m*, H–C(5)); 4.73 (*d, J* = 12.5, PhC*H*); 5.07 (*d, J* = 11.2, PhC*H*); 7.24–7.32 (*m*, 20 arom. H). ^{13}C-NMR ($CDCl_3$): 28.06 (*q*, *Me*$_3$C); 57.91 (*d*, C(5)); 69.73 (*t*, C(6)); 71.85 (*t*, $PhCH_2$); 73.39 (*t*, $PhCH_2$); 73.71 (*t*, $PhCH_2$); 74.24 (*t*, $PhCH_2$); 76.33, 79.81, 81.96 (3*d*, C(2), C(3), C(4)); 83.84 (*s*, Me$_3$*C*); 127.94–128.72 (several *d*); 137.79 (*s*, 2 C); 138.18 (*s*); 138.24 (*s*); 152.35 (*s*, NCO_2); 170.02 (*s*, C(1)). FAB-MS: 1298 (10, [2 *M* + Na]$^+$), 660 (12), 638 (6, [*M* + 1]$^+$), 637 (12), 561 (13), 560 (38), 539 (62), 538 (100), 536 (8, [*M* – Boc]$^+$).

*2,3,4,6-Tetra-*O*-benzyl-5-{[(*tert*-(butoxy)carbonyl]amino}-5-deoxy-α- and -β-*D*-glucopyranose* (**32** and **33**). At 5°, a soln. of **31** (242 mg, 0.38 mmol) in EtOH (10 ml) was treated with $NaBH_4$ (220 mg, 5.8 mmol) and the pH of the suspension adjusted to 6 by addition of aq. 1N HCl. The soln. was stirred for 13 h, treated with ice/sat. aq. NH_4Cl soln., and neutralized with 1N HCl. Normal workup and FC (Et_2O/hexane 1:3 → 1:2) of the residue (**32**/**33** 30:70) gave **32** (43 mg, 18%) and **33** (139.5 mg, 57.5%).

Data of **32**: R_f (Et_2O/hexane 2:1) 0.22. IR ($CHCl_3$): 3401*m*, 3067*w*, 3008*m*, 2981*m*, 2932*m*, 2871*m*, 1694*s*, 1497*w*, 1454*m*, 1394*s*, 1368*s*, 1329*s*, 1258*w*, 1163*m*, 1072*s*. ^{1}H-NMR ($CDCl_3$): 1.45 (*s*, Me_3C); 3.42 (br. *d, J* = 9.7, irrad. at 3.63 → change, irrad. at 4.14 → *d, J* ≈ 8.7, H–C(6)); 3.59–3.67 (*m*, irrad. at 3.71 → change, irrad. at 4.02 → change, irrad. at 4.14 → change, H–C(3), H′–C(6)); 3.71 (br. *d, J* = 6.2, irrad. at 3.63 → change, irrad. at 5.67 → change, H–C(2)); 4.02 (*dd, J* = 6.4, 9.2, irrad. at 3.63 → change, irrad. at 4.14 → *d, J* ≈ 8.7, H–C(4)); 4.10–4.18 (*m*, H–C(5), exchange with CD_3OD, OH); 4.37–4.59 (*m*, 4 PhC*H*); 4.62 (*d, J* = 11.5, PhC*H*); 4.73–4.84 (*m*, 3 PhC*H*); 5.47–5.77 (*m*, H–C(1)); 7.26–7.36 (*m*, 20 arom. H). ^{1}H-NMR (CD_3COCD_3): 1.44 (*s*, Me_3C); 3.56 (*t, J* = 8.1, irrad. at 3.99 → *d, J* ≈ 8.1, H–C(3)); 3.60 (*dd, J* = 4.1, 9.6, irrad. at 4.28 → *d, J* ≈ 9.3, H–C(6)); 3.71 (*dd, J* = 3.7, 8.1, irrad. at 5.62 → *d, J* ≈ 7.8, H–C(2)); 3.73 (*dd, J* = 6.5, 9.3, irrad. at 4.28 → *d, J* ≈ 9.7, H′–C(6)); 3.99 (*dd, J* = 5.0, 8.4, irrad. at 4.28 → *d, J* ≈ 8.1, H–C(4)); 4.23–4.33 (*m*, H–C(5)); 4.55 (*d, J* = 11.8, PhC*H*); 4.60 (*d, J* = 12.1, PhC*H*); 4.64 (*d, J* = 11.8, PhC*H*); 4.71 (*d, J* = 11.5, PhC*H*); 4.75 (*d, J* = 12.5, PhC*H*); 4.79 (*d*, = 11.5, PhC*H*); 4.80 (*d, J* = 11.8, PhC*H*); 4.82 (*d, J* = 11.5, PhC*H*); 4.86–4.90 (br. *s*, exchange with CD_3OD, OH); 5.58–5.65 (br. *s*, H–C(1)); 7.20–7.55 (*m*, 20 arom. H). ^{13}C-NMR ($CDCl_3$): 28.36 (*q*, *Me*$_3$C); 57.45 (br. *d*, C(5)); 67.74 (*t*, C(6)); 72.61 (*t*, $PhCH_2$); 73.58 (*t*, $PhCH_2$); 74.21 (*t*, $PhCH_2$); 74.49 (*t*, $PhCH_2$); 81.28 (*s*, Me$_3$*C*); 75.86 (*d*); 79.00 (br. *d*); 82.92 (*d*); 84.83 (br. *d*); 127.50–129.50 (several *d*); 137.19 (*s*); 138.26 (*s*); 138.49 (*s*); 138.86 (*s*); 154.29 (*s*, C=O). ^{13}C-NMR (CD_3COCD_3): 28.48 (*q*, *Me*$_3$C); 57.53 (br. *d*, C(5)); 70.72 (*t*, C(6)); 73.43 (br. *t*, $PhCH_2$); 73.53 (br. *t*, $PhCH_2$); 73.79 (*t*, $PhCH_2$); 74.75 (*t*, $PhCH_2$); 79.02 (*d*); 80.36 (br. *d*); 81.14 (*s*, Me$_3$*C*); 83.47 (*d*); 84.42 (*d*); 128.38–129.50 (several *d*); 139.39 (*s*); 139.91 (*s*); 139.98 (*s*); 140.25 (*s*); 155.30 (*s*, C=O). FAB-MS: 623 (2), 622 (5, [*M* – OH]$^+$), 524 (9), 523 (39), 522 (100, [*M* – Boc – OH + 1]$^+$), 432 (14), 415 (7), 414 (22), 253 (33).

Data of **33**: R_f (Et_2O/hexane 2:1) 0.17. IR ($CHCl_3$): 3431*m*, 3067*w*, 3008*m*, 2981*m*, 2932*m*, 2871*m*, 1694*s*, 1497*w*, 1454*m*, 1393*s*, 1369*s*, 1332*s*, 1258*w*, 1163*m*, 1072*s*. ^{1}H-NMR ($CDCl_3$): 1.54 (*s*, Me_3C); 3.52 (*dd, J* = 9.0, 10.3, irrad. at 4.45 → *d, J* ≈ 9.0, H–C(6)); 3.60 (*dd, J* = 4.4, 8.7, irrad. at 4.45 → *d, J* ≈ 9.0, H′–C(6)); 3.70 (*dd, J* = 3.1, 6.5, irrad. at 4.01 → *d, J* ≈ 3.1, irrad. at 5.56 → *d, J* ≈ 6.5, H–C(2)); 4.01 (*dd, J* ≈ 1.0, 6.9, irrad. at 4.45 → *d, J* = 6.9, irrad. at 3.70 → change, H–C(3)); 4.20 (*d, J* = 11.2, irrad. at 5.56 → *s*, exchange with CD_3OD, OH); 4.22 (*d, J* = 1.2, irrad. at 4.45 → *s*, H–C(4)); 4.43–4.51 (*m*, H–C(5)); 4.48 (*s*, $PhCH_2$); 4.53 (*s*, $PhCH_2$); 4.57 (*d, J* = 11.8, PhC*H*); 4.65 (*d, J* = 11.8, PhC*H*); 4.71 (*d, J* = 11.8, PhC*H*); 4.83 (*d, J* = 11.8, PhC*H*); 5.56 (*dd, J* = 3.1, 11.2, irrad. at 4.20 → *d, J* = 3.1, addn. of CD_3OD → br. *d, J* ≈ 2.8, H–C(1)); 7.29–7.40 (*m*, 20 arom. H). ^{13}C-NMR ($CDCl_3$): 28.48 (*q*, *Me*$_3$C); 53.60 (*d*, C(5)); 69.02 (*t*, C(6)); 71.75 (*t*, $PhCH_2$); 71.96

(*t*, PhCH$_2$); 72.01 (*t*, PhCH$_2$); 73.13 (*t*, PhCH$_2$); 74.41 (*d*), 74.81 (*d*), 80.51 (*d*), 80.99 (*d*, C(1), C(2), C(3), C(4)); 81.33 (*s*, Me$_3$C); 127.94–128.72 (several *d*); 136.82 (*s*); 138.08 (*s*); 138.34 (*s*); 138.54 (*s*); 155.07 (*s*, C=O). FAB-MS: 622 (10, [*M* – OH]$^+$), 524 (10), 523 (44), 522 (100, [*M* – Boc – OH + 1]$^+$), 414 (23), 253 (13).

*Ethyl 2,3,4,6-Tetra-*O*-benzyl-5-{[(*tert*-butoxy)carbonyl]amino}-5-deoxy-α-*D*-glucopyranoside* (**34**). A soln. of **33** (76 mg, 0.12 mmol) in EtOH (2 ml) was treated with TsOH · H$_2$O (10 mg, 0.05 mmol), stirred for 20 min, and treated with sat. aq. NaHCO$_3$ soln. Normal workup gave **34** (72 mg, 91%). R_f (Et$_2$O/hexane 1:2) 0.45. IR (CHCl$_3$): 3090*w*, 3067*m*, 2980*m*, 2932*m*, 2904*m*, 2870*m*, 1690*s*, 1497*w*, 1454*m*, 1393*w*, 1368*s*, 1262*w*, 1163*m*, 1072*s*. ^{1}H-NMR (CD$_3$COCD$_3$, (*Z*)/(*E*) 1:1): 1.11 (*t*, *J* = 7.0, Me); 1.46 (*s*, Me$_3$C); 3.42–3.52 (*m*, OC*H*Me); 3.56 (*dd*, *J* = 6.7, 8.9, irrad. at 3.75 → *d*, *J* ≈ 9.0, irrad. at 4.00 → br. *d*, *J* ≈ 4.0, H–C(3)); 3.63–3.72 (*m*, irrad. at 4.22 → change, H–C(6), OC*H*Me); 3.75 (*dd*, *J* = 2.2, 6.5, irrad. at 5.53 → *d*, *J* ≈ 6.5, H–C(2)); 3.72–3.83 (*m*, irrad. at 4.22 → change, H′–C(6)); 3.93–4.07 (*m*, irrad. at 4.22 → br. *d*, *J* ≈ 6.5, H–C(4)); 4.07–4.20 (br. *s*, irrad. at 3.68 → change, irrad. at 5.78 → change, 0.5 H), 4.21–4.33 (br. *s*, irrad. at 3.68 → change, irrad. at 5.78 → change, 0.5 H, H–C(5)); 4.53 (*d*, *J* = 11.8, PhC*H*); 4.58 (*d*, *J* = 11.8, PhC*H*); 4.63–4.82 (*m*, 6 PhC*H*); 5.40–5.50 (br. *s*, 0.5 H), 5.57–5.66 (br. *s*, 0.5 H, H–C(1)); 7.28–7.41 (*m*, 20 arom. H). ^{13}C-NMR (CD$_3$COCD$_3$, (*Z*)/(*E*) 1:1): 15.39 (*q*, Me); 28.51 (*q*, *Me*$_3$C); 56.85, 57.63 (br. *d*, C(5)); 63.73 (*t*, CH$_2$Me); 70.85, 71.53 (*t*, C(6)); 72.83, 72.93 (2*t*, PhCH$_2$); 73.69 (*t*, PhCH$_2$); 74.18 (br. *t*, PhCH$_2$); 74.42 (*t*, PhCH$_2$); 81.02 (*s*, Me$_3$C); 78.39, 83.92, 84.19 (3*d*, C(2), C(3), C(4)); 85.45, 86.18 (2*d*, C(1)); 128.38–129.50 (several *d*); 139.68 (*s*); 139.86 (*s*); 140.17 (*s*); 140.25 (*s*); 155.70, 156.50 (2*s*, C=O). FAB-MS: 668 (5, [*M* + 1]$^+$), 667 (3), 622 (19), 567 (4), 566 (10), 524 (12), 523 (48), 522 (100), 476 (18), 460 (10), 414 (22), 400 (23).

*(4S)-5[(*tert*-Butyl)imino]-2,3,4,5-tetrahydro-(5-amino-2,3,4,6-tetra-*O*-benzyl-1,5-dideoxy-*D*-glucopyranoso)-*[N^5,*1*-C]*-1,3-oxazol-2-one* (**35**). At −78°, a soln. of **34** (9 mg, 0.013 mmol) in CH$_2$Cl$_2$ (1 ml) was treated dropwise with Me$_3$SiCN (0.03 ml, 0.24 mmol) and BF$_3$ · OEt$_2$ (0.03 ml, 0.24 mmol), warmed to r.t. within 3 h, then poured into ice/sat. aq. NH$_4$Cl soln. Normal workup and FC (Et$_2$O/hexane 1:2) gave **35** (6.7 mg, 77%). R_f (Et$_2$O/hexane 1:2) 0.1. IR (CHCl$_3$): 3090*w*, 3067*m*, 2970*m*, 2930*m*, 2869*m*, 1800*s*, 1727*s*, 1675*w*, 1497*w*, 1454*s*, 1393*w*, 1366*s*, 1262*s*, 1094*s*. ^{1}H-NMR (CDCl$_3$, 200 MHz): 1.32 (*s*, Me$_3$C); 3.61–3.71 (*m*, 2 H–C(6′)); 3.70 (*t*, *J* ≈ 3.3, irrad. at 3.88 → *d*, *J* ≈ 4.2, H–C(3′)); 3.75 (*t*, *J* = 3.1, irrad. at 4.37 → *d*, *J* ≈ 2.9, H–C(4′)); 3.88 (*t*, *J* = 2.5, irrad. at 4.32 → *d*, *J* ≈ 2.1, H–C(2′)); 4.24 (*d*, *J* = 12.0, PhC*H*); 4.32 (*d*, *J* = 12.0, PhC*H*); 4.32 (*d*, *J* = 2.5, irrad. at 3.88 → *s*, H–C(4)); 4.33–4.44 (*m*, H–C(5′)); 4.44 (*d*, *J* = 12.0, PhC*H*); 4.48 (*d*, *J* = 11.0, PhC*H*); 4.55 (*d*, *J* = 12.5, PhC*H*); 4.58 (*s*, PhC*H*$_2$); 4.60 (*d*, *J* = 12.0, PhC*H*); 7.06–7.23 (*m*, 2 arom. H); 7.26–7.32 (*m*, 18 arom. H). ^{13}C-NMR (CDCl$_3$): 30.07 (*q*, *Me*$_3$C); 52.39 (*d*, C(4)); 55.25 (*s*, Me$_3$C); 56.41 (*d*, C(5′)); 67.45 (*t*, C(6′)); 72.26 (*d*); 72.31 (*t*, PhCH$_2$); 72.37 (*t*, PhCH$_2$); 73.10 (*t*, PhCH$_2$); 73.24 (*t*, PhCH$_2$); 74.04 (*d*); 74.88 (*d*); 127.74–129.00 (several *d*); 137.41 (*s*); 137.76 (*s*); 138.09 (*s*); 138.21 (*s*); 146.76 (*s*, C=N); 154.42 (*s*, C=O). FAB-MS: 1299 (5), 1298 (6), 816 (16), 815 (21), 651 (13), 650 (48), 649 (100, [*M* + 1]$^+$), 648 (8), 624 (23), 623 (49), 622 (3), 593 (10), 549 (15), 523 (32), 522 (74, [*M* – CO$_2$CN(*t*-Bu) + 1]$^+$), 520 (12).

*3,4,5-Tri-*O*-benzyl-2,6-dideoxy-2,6-imino-*D*-glycero-*D*-*ido*-heptononitrile* (**36**). At 5°, a soln. of **34** (10 mg, 0.015 mmol) in CH$_2$Cl$_2$ (2 ml) was treated dropwise with Me$_3$SiCN (0.1 ml, 0.8 mmol) and BF$_3$ · OEt$_2$ (0.01 ml, 0.08 mmol), stirred for 1 h at r.t., and poured into ice/sat. aq. NH$_4$Cl soln. Normal workup and FC (Et$_2$O/hexane 1:1 → 2:1) gave **36** (2 mg, 30%). R_f (Et$_2$O/hexane 2:1) 0.1. IR (CHCl$_3$): 3356*w*, 3067*m*, 3008*m*, 2928*m*, 2872*m*, 1497*m*, 1454*s*, 1363*s*, 1131*m*, 1070*s*. ^{1}H-NMR (CDCl$_3$): 1.44 (br. *s*, exchange with CD$_3$OD, OH); 1.97–2.10 (*m*, exchange with CD$_3$OD, NH); 3.05 (*dddd*, *J* = 2.8, 5.9, 6.5, 9.3, irrad. at 3.82 → br. *dd*, *J* ≈ 5.6, 9.0, addn. of CD$_3$OD → 3.01, *ddd*, *J* = 2.9, 6.4, 9.6, H–C(6)); 3.30 (*dd*, *J* = 9.0, 9.7, irrad. at 3.05 → *d*, *J* ≈ 8.1, H–C(5)); 3.55 (*dd*, *J* = 5.6, 10.9, irrad. at 3.05 → *d*, *J* ≈ 10.1, addn. of CD$_3$OD → 3.46, *dd*, *J* = 6.4, 11.0, H–C(7)); 3.59 (*dd*, *J* = 5.5, 9.5, H–C(3)); 3.82 (*dd*, *J* = 2.8, 10.9, irrad. at 3.05 → *d*, *J* ≈ 10.9, addn. of CD$_3$OD → 3.83, *dd*, *J* = 2.7, 10.8, H′–(7)); 3.85 (*t*, *J* = 9.2, H–C(4)); 4.10 (*d*, *J* = 5.6, H–C(2)); 4.61 (*d*, *J* = 11.9, PhC*H*); 4.68 (*d*, *J* = 11.8, PhC*H*); 4.79 (*d*, *J* = 12.1, PhC*H*); 4.85 (*d*, *J* = 10.9, PhC*H*); 4.90 (*d*, *J* = 11.2, PhC*H*); 4.99 (*d*, *J* = 11.2, PhC*H*); 7.27–7.37 (*m*, 15 arom. H). ^{13}C-NMR (CDCl$_3$): 49.85 (*d*, C(2)); 57.57 (*d*, C(6)); 62.86 (*t*, C(7)); 73.55 (*t*, PhCH$_2$); 75.30 (*t*, PhCH$_2$); 76.19 (*t*, PhCH$_2$); 78.43, 78.58, 84.31 (3*d*, C(3), C(4), C(5)); 117.78 (*s*, CN); 127.80–129.10 (several *d*); 137.68 (*s*); 138.28 (*s*); 138.62 (*s*). FAB-MS: 460 (1), 459 (4, [*M* + 1]$^+$), 432 (2), 342 (1), 324 (2), 306 (3), 261 (1), 253 (1), 234 (1), 218 (1), 200 (8), 199 (3), 188 (1), 187 (8), 186 (57), 185 (8), 108 (64), 107 (12), 92 (14), 91 (100).

*3,4,5,7-Tetra-*O*-benzyl-1-[(*tert*-butyl)amino]-1,2,6-trideoxy-2,6-imino-*D-glycero-L-ido-*heptitol* (**37**). A soln. of **35** (10 mg, 0.012 mmol) in THF (2 ml) was treated with LiAlH$_4$ (10 mg, 0.26 mmol), stirred for 1 h at r.t., and poured into ice/sat. aq. NH$_4$Cl soln. Normal workup and FC (AcOEt/MeOH 1:0 → 9:1) gave a residue which was dissolved in C$_6$D$_6$ (0.6 ml), treated with TsOH · H$_2$O (5 mg, 0.026 mmol), heated at reflux for 2 min, and poured into sat. aq. NaHCO$_3$ soln. Normal workup gave **37** (5 mg, 53%). R_f (AcOEt) 0.1. IR (CHCl$_3$): 3356*w*, 3067*m*, 3008*m*, 2928*m*, 2872*m*, 1497*m*, 1454*s*, 1363*s*, 1131*m*, 1070*s*. ^{1}H-NMR (C$_6$D$_6$): 1.02 (*s*, Me$_3$C); 1.20–1.30

(*m*, exchange with CD$_3$OD, 2 NH); 2.78 (*t*, $J = 11.2$, irrad at 3.76 → *d*, $J \approx 10.3$, H−C(1)); 2.87–2.95 (*m*, H−C(6)); 3.01 (*dd*, $J = 3.4$, 11.2, irrad. at 2.78 → *d*, $J \approx 3.4$, irrad. at 3.76 → *d*, $J \approx 11.2$, H′−C(1)); 3.71–3.81 (*m*, H−C(2)); 3.50 (*t*, $J = 9.3$, irrad. at 2.91 → *d*, $J \approx 8.7$, H−C(5)); 3.58 (*dd*, $J = 2.5$, 9.0, irrad. at 2.91 → *d*, $J \approx 8.4$, H−C(7)); 3.62 (*dd*, $J = 5.9$, 9.3, irrad. at 3.76 → *d*, $J \approx 9.0$, irrad. at 3.82 → *d*, $J \approx 5.0$, H−C(3)); 3.64 (*dd*, $J = 4.7$, 9.3, irrad. at 2.91 → *d*, $J \approx 7.8$, H′−C(7)); 3.82 (*t*, $J = 9.2$, H−C(4)); 4.20 (*d*, $J = 11.8$, PhC*H*); 4.30 (*d*, $J = 11.8$, PhC*H*); 4.54 (*d*, $J = 11.2$, PhC*H*); 4.57 (*d*, $J = 11.2$, PhC*H*); 4.68 (*d*, $J = 11.5$, PhC*H*); 4.86 (*d*, $J = 11.2$, PhC*H*); 4.97 (*d*, $J = 11.2$, PhC*H*); 5.07 (*d*, $J = 11.2$, PhC*H*); 7.00–7.50 (*m*, 20 arom. H).

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