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Synthesis and NMR spectroscopy of nine stereoisomeric 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids

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Abstract

Derivatives of 5,7-diamino-3,5,7,9-tetradeoxynon-2-ulosonic acids are essential constituents of some bacterial polysaccharides and glycoproteins. In order to establish reliably the configuration of the natural sugars, nine stereoisomeric 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids were synthesized, including di-*N*-acetyl-legionaminic and -pseudaminic acids (the D-glycero-D-galacto and L-glycero-L-manno isomers, respectively) and their isomers at C-4, C-5, C-7, and C-8 having the L-glycero-D-galacto, D-glycero-D-talo, L-glycero-D-talo, D-glycero-L-altro, L-glycero-L-altro, D-glycero-L-manno, and L-glycero-L-gluco configurations. Synthesis was performed by condensation of 2,4-diacetamido-2,4,6-trideoxy-L-gulose, -D-mannose, -D-talose, and -L-allose with oxalacetic acid under basic conditions, the reaction of the last two precursors being accompanied by epimerisation at C-2. The ^{1}H and ^{13}C NMR data of the synthetic compounds are discussed. Acetylated methyl esters of the C-7 and C-8 isomeric nonulosonic acids were prepared and used for analysis of the side-chain conformation by NMR spectroscopy.

Keywords: 5,7-Diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids, synthesis; 2,4-Diacetamido-2,4,6-trideoxyhexoses; Legionaminic acid; Pseudaminic acid; Lipopolysaccharide components

1. Introduction

N-Acyl and *O*-acetyl derivatives of various 5,7-diamino-3,5,7,9-tetradeoxynon-2-ulosonic acids are known as components of glycopolymers of Gram-negative bacteria, including lipopolysaccharides,[1–3] a capsular polysaccharide,[4] and glycoproteins.[5,6] They play a role in immunospecificity, endow the cell surface with peculiar physicochemical properties, and are likely involved in bacterial virulence. Whereas the relative configuration within the conformationally rigid pyranose ring (C-4,5,6) of the higher sugars could be easily established using ^{1}H NMR and NOE spectroscopy, reliable determination of the configuration in the flexible side chain (C-7,8) required data from model compounds. To solve this problem, we synthesised, for the first time, nine stereoisomeric 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids. Synthesis of four of these sugars has been reported in preliminary communications.[7,8]

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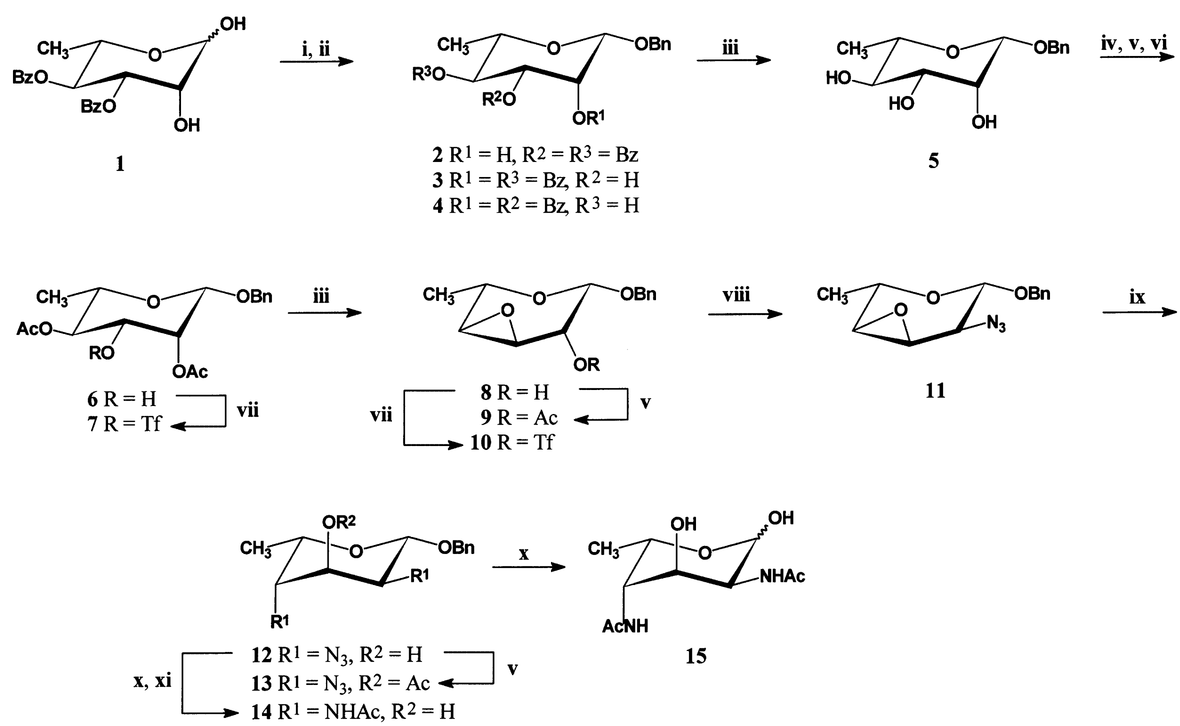
2. Results and discussion

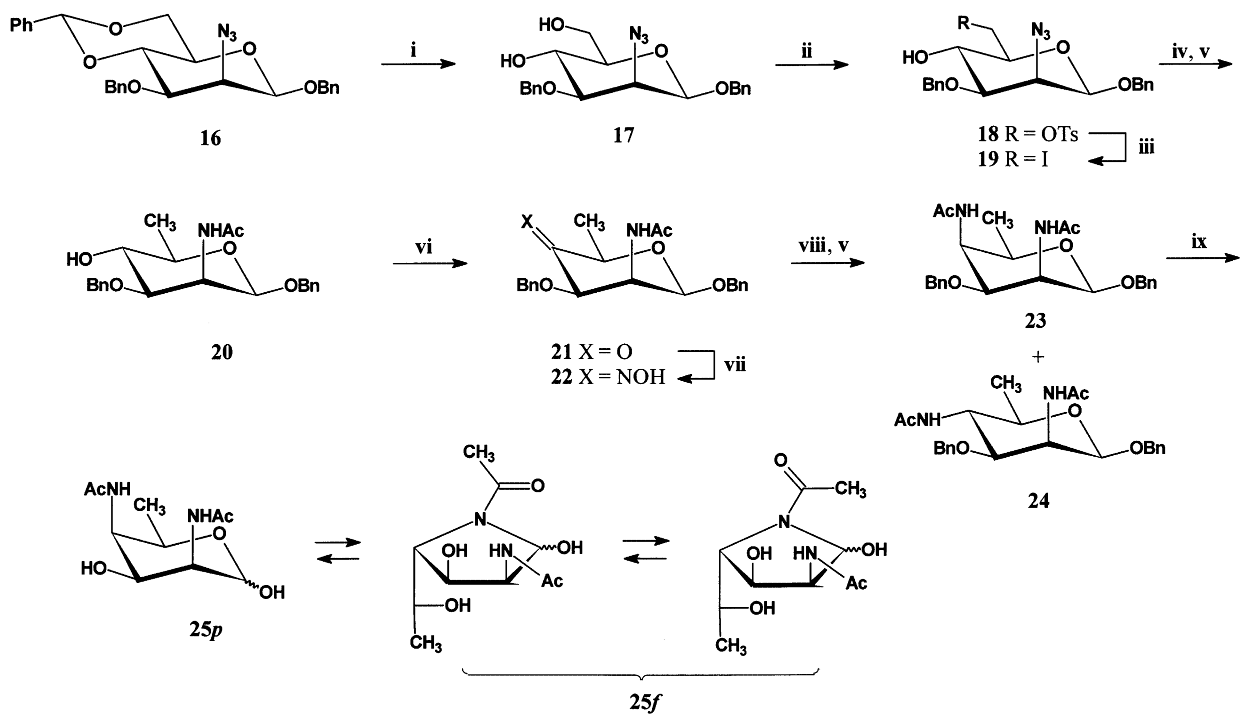
By analogy with the synthesis of *N*-acetylneuraminic acid,[9] di-*N*-acetyl derivatives of 5,7-diamino-3,5,7,9-tetradeoxynon-2-ulosonic acids could be obtained by condensation of 2,4-diacetamido-2,4,6-trideoxyhexoses with oxalacetic acid under basic conditions. Four chiral centers in the C_6 precursors, C-2,3,4,5, correspond to the centers C-5,6,7,8 in the target C_9 acids, and the fifth asymmetric center, C-4, is formed on condensation. 2,4-Diacetamido-2,4,6-trideoxy-L-gulose (**15**), -D-talose (**25**), -D-mannose (**32**), and -L-allose (**48**) were used as the C_6 precursors (See Schemes 1–4). They possess the same, L,L configuration at C-2 and C-3 (C-5 and C-6 in the expected C_9 acids), whereas the configurations at C-4 and C-5 vary, thus adopting all possible stereochemical combinations at C-7 and C-8 in the higher sugars (D,L; L,D; D,D; and L,L; respectively).

The 2,4-diacetamido-2,4,6-trideoxyhexoses **15**, **25**, **32**, and **48** were synthesized as follows. L-Rhamnose, the most readily available 6-deoxyhexose, served as the progenitor of **15**. Since introduction of an azido group (as a precursor of the acetamido function) is accompanied by inversion of the configuration, azidation at positions 2 and 4 would lead directly to the desirable configurations of C-2 and C-4. Hence, one additional inversion at C-3 has to be performed to achieve the target L-gulo configuration.

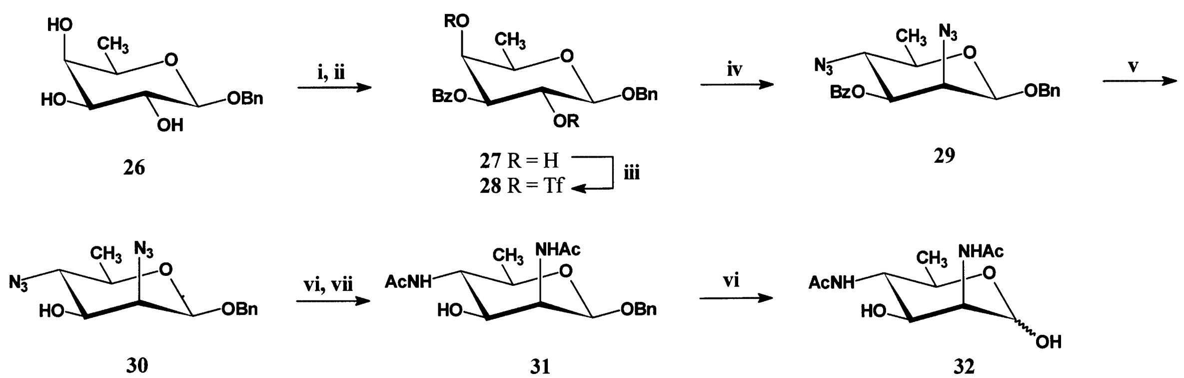
The prerequisite for successful S_N2 substitution of an axial sulfonate group at C-2 is that the substituent at C-1 is equatorial (see Ref. [10] and references cited therein). Therefore, benzyl β-L-rhamnopyranoside was thought to be the precursor of choice. This was prepared by Bu_2SnO-mediated benzylation of 1,2-diol **1**[11] (Scheme 1). As expected,[12] the reaction occurred in a regio- and stereoselective manner, though it was accompanied by migration of benzoyl protecting groups. As a result, a mixture of benzyl β-rhamnopyranoside dibenzoates **2-4** was obtained in total yield of 90–95% and **2**:**3**:**4** ratios of ∼4:3:1. These compounds were separated and their structures proved by ^{1}H NMR spectroscopy. Most importantly, the β-configuration of **2**–**4** was demonstrated by a relatively high-field posi-



Scheme 1. Reagents and conditions: **i**, Bu_2SnO, benzene, reflux; **ii**, BnBr, Bu_4NBr, benzene, reflux; **iii**, MeONa, MeOH; **iv**, trimethyl orthoacetate, PTSA, MeCN, rt; **v**, Ac_2O, pyridine, rt; **vi**, 80% aq AcOH, rt; **vii**, Tf_2O, pyridine, CH_2Cl_2, 0 °C; **viii**, NaN_3, DMF, rt; **ix**, NaN_3, NH_4Cl, aq EtOH, reflux; **x**, H_2, $Pd(OH)_2/C$, MeOH, 30°C; **xi**, Ac_2O, MeOH, rt.



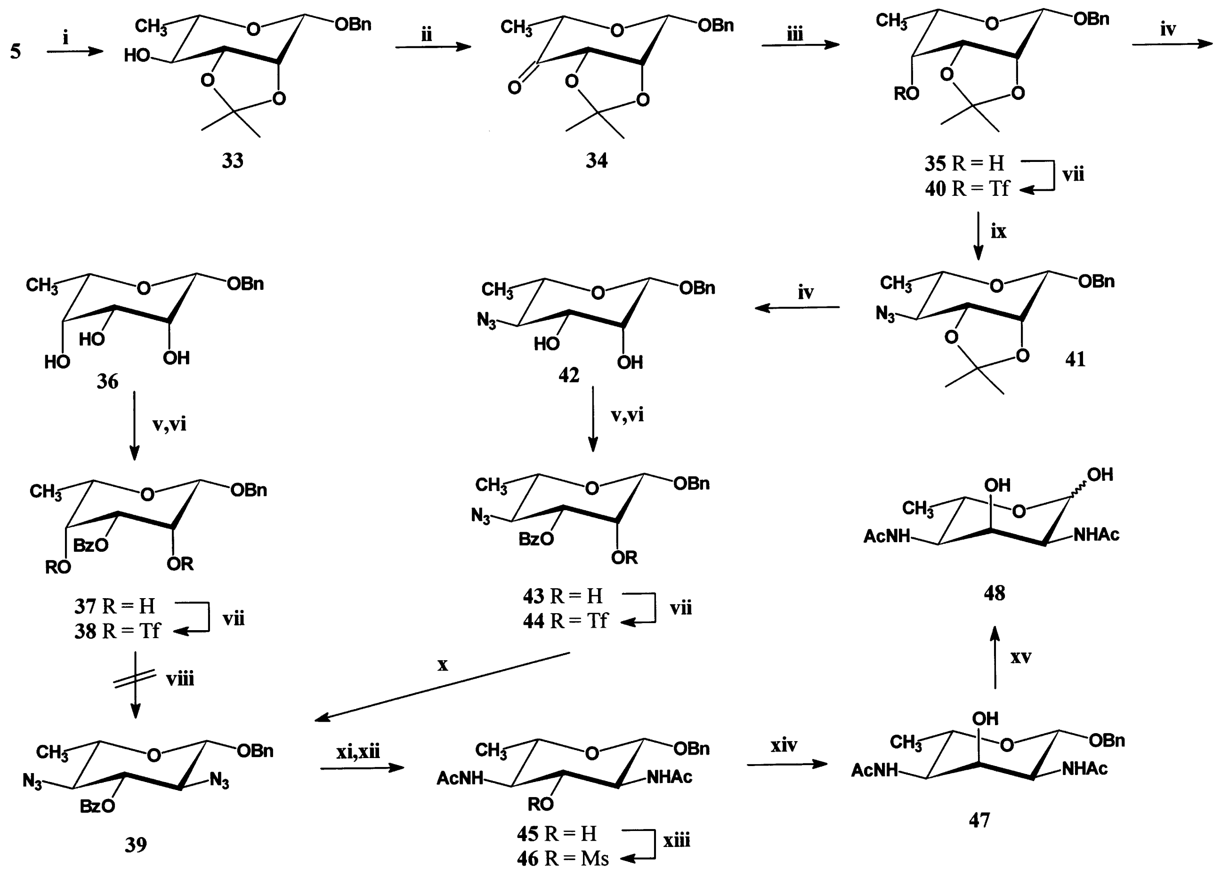
Scheme 2. Reagents and conditions: **i**, pyridinium perchlorate, aq MeCN, 80 °C; **ii**, TsCl, pyridine, 0°C → rt; **iii**, NaI, MeCN, 80 °C; **iv**, H_2, $Pd(OH)_2/C$, *i*-Pr_2NEt, MeOH, 30 °C; **v**, Ac_2O, MeOH, rt; **vi**, oxalyl chloride, DMSO, *i*-Pr_2NEt, CH_2Cl_2, − 60 °C; **vii**, $NH_2OH·HCl$, pyridine, CH_2Cl_2, rt; **viii**, $NaBH_4$, $NiCl_2·6H_2O$, MeOH, − 35 °C; **ix**, H_2, $Pd(OH)_2/C$, aq MeOH, rt.



Scheme 3. Reagents and conditions: **i**, Bu_2SnO, benzene, reflux; **ii**, BzCl, benzene, 0 °C → rt; **iii**, Tf_2O, pyridine, CH_2Cl_2, 0 °C; **iv**, Bu_4NN_3, toluene, 60 → 100 °C; **v**, MeONa, MeOH, rt; **vi**, H_2, $Pd(OH)_2/C$, MeOH, 30 °C; **vii**, Ac_2O, MeOH, rt.

tion at δ 3.5–3.8 of the signal for H-5 (in α-rhamnopyranosides H-5 would resonate at δ 4.1–4.3[13]). The positions of the benzoyl groups in **2**–**4** were inferred from the low-field chemical shifts of the signals for H-3,4, H-2,4, and H-2,3, respectively. Debenzoylation of the mixture of **2**–**4** with sodium methoxide in methanol yielded **5**.

Treatment of **5** with trimethyl orthoacetate in the presence of TsOH, followed by acetylation of OH-4 and hydrolytic opening of the orthoester ring in the 2,3-orthoester, yielded 2,4-diacetate **6**. Low-field positions of the signals for H-2 and H-4 in the ^1H NMR spectrum proved the location of the acetyl groups in **6**. Reaction of **6** with triflic anhydride in the presence of pyridine led to triflate **7**, which readily gave the 3,4-anhydro-L-altroside **8** on treatment with sodium methoxide in methanol. The structure of **8**, particularly the position of the epoxy group, was confirmed by NMR analysis of **8** and its acetate **9**. The transformation of **8** into **9** resulted in a downfield shift of the signal for H-2 (δ 4.02 →



Scheme 4. Reagents and conditions: **i**, 2,2-dimethoxypropane, PTSA, acetone, rt; **ii**, oxalyl chloride, DMSO, *i*-Pr_2NEt, CH_2Cl_2, − 60 °C; **iii**, $NaBH_4$, aq EtOH, rt; **iv**, 80% aq AcOH, 40 °C; **v**, Bu_2SnO, benzene, reflux; **vi**, BzCl, benzene, 0 °C → rt; **vii**, Tf_2O, pyridine, CH_2Cl_2, 0 °C; **viii**, Bu_4NN_3, toluene, 60 °C; **ix**, NaN_3, DMF, dibenzo-18-crown-6, rt; **x**, NaN_3, DMF, rt; **xi**, $LiAlH_4$, THF, 0 °C → rt; **xii**, Ac_2O, MeOH, rt; **xiii**, MsCl, pyridine, CH_2Cl_2, 0 °C → rt; **xiv**, AcONa, aq 2-methoxyethanol, reflux; **xv**, H_2, $Pd(OH)_2/C$, aq MeOH, 35 °C.

5.25), thus indicating the position of the hydroxy group in **8**. This finding excluded conversion of the 3,4-L-altro-epoxide into the 2,3-L-manno-isomer that might proceed under basic conditions.[14] Compound **8** had the necessary configuration of C-3, a free OH-2 group required for subsequent introduction of an azido group, and a 3,4-epoxy function suitable for introduction of the second azido group at position 4.

As anticipated, conversion of **8** into triflate **10** and subsequent reaction with sodium azide in DMF resulted in a high yield of azide **11**. A large $J_{1,2}$ coupling constant value of 7.6 Hz in the ^{1}H NMR spectrum of **11** showed that the azido group was pseudo-equatorial. Opening of the epoxide ring in **11** by treatment with sodium azide in the presence of ammonium chloride in boiling aqueous ethanol[15] furnished diazide **12**. Large $J_{1,2}$ and small $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ coupling constant values in the ^{1}H NMR spectra of **12** and the derived acetate **13** were in accordance with the β-L-gulo configuration. Chemical shifts for H-2 (δ 3.69), H-3 (δ 5.33), and H-4 (δ 3.48) in the spectrum of **13** demonstrated that the azido groups were at C-2 and C-4. Hydrogenolysis of **12** over $Pd(OH)_2/C$ reduced the azido groups, whereas the benzyl group remained intact (compare published data[16]). Following N-acetylation, hydrogenolysis of the diacetamido derivative **14** proceeded smoothly providing the target sugar **15** in high yield. According to ^{1}H NMR data, **15** exists in aqueous solution in the pyranose form as a mixture of α- and β-anomers in a ratio of ~ 1:5.

2-Azido-2-deoxy derivative **16**[17] was used as a starting compound for preparation of 2,4-diacetamido-2,4,6-trideoxy-D-talose (**25**). De-

Table 1
NMR data for 2,4-diacetamido-2,4,6-trideoxy-D-talose **25** (D_2O, 30 °C)

Form (content,%)	^{1}H NMR data (chemical shift, δ; coupling constant, Hz) H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6}$)	H-6	^{13}C NMR data (chemical shifts, δ) C-1	C-2	C-3	C-4	C-5	C-6
α-**25*p***	5.18	4.12	4.24	4.18	4.43	1.18	94.2	52.8	66.7	52.7	66.7	17.0
(18)	(2.0)	(4.6)	(4.2)	(2.8)	(6.6)							
β-**25*p***	4.97	4.36	4.12	4.12	3.91	1.18	94.6	53.4	69.6	52.0	71.7	17.1
(32)	(1.9)	(4.2)	—	(<1)	(6.4)							
α-**25*f*** major	5.38	4.51	4.29	4.09	4.04	1.24	86.9	60.9	71.6	70.6	69.0	20.5
(20)	(5.3)	(5.0)	(<1)	(6.2)	(6.3)							
α-**25*f*** minor	5.47	4.38	4.25	3.85	3.91	1.33	84.9	59.9	72.1	73.9	68.7	20.6
(14)	(6.3)	(4.8)	(<1)	(8.9)	(6.2)							
β-**25*f*** major	5.51	4.45	4.31	4.19	4.16	1.11	82.0	55.0	71.3	70.5	67.0	19.2
(13.5)	(5.6)	(4.9)	(<1)	(5.1)	(6.5)							
β-**25*f*** minor	5.58	4.38	4.25	3.98	3.77	1.25	80.0	53.4	72.8	71.9	67.9	20.0
(2.5)	(6.2)	(4.3)	(<1)	(7.9)	(6.1)							

oxygenation at C-6 and introduction of an amino function with inversion of the configuration at C-4 had to be carried out to obtain the desired structure. To this aim, the benzylidene group in **16** was removed by treatment with pyridinium perchlorate[18] in aqueous acetonitrile (Scheme 2). Selective tosylation of the resulting diol **17**, followed by substitution of the tosyloxy group in **18** with iodide, afforded the 6-iodo derivative, **19**. Simultaneous reduction of the azido group and deiodination without affecting the benzyl protective groups occurred on hydrogenation over $Pd(OH)_2/C$ in the presence of *N*,*N*-diisopropylethylamine. Following N-acetylation, the 2-acetamido-2,6-dideoxy derivative **20** was obtained in 84% yield. The use of $LiAlH_4$ in THF for reduction of **19** was less effective giving only 49% of **20**. A direct S_N2 substitution at C-4 in the manno series is known to be complicated;[19] therefore, the reaction sequence oxidation-oximation-reduction was applied to introduce the second amino group into **20**. Swern oxidation of **20** gave the ketone **21**, which was converted, without isolation, into the oxime **22**. Reduction of the latter with $NaBH_4$–$NiCl_2$ in methanol at −35 °C[20] and subsequent N-acetylation gave a mixture of talo and manno isomers **23** and **24** in a ratio of 8:1. The structures of **23** and **24** were proved by ^{1}H NMR spectroscopy. Large $J_{3,4}$ and $J_{4,5}$ coupling constant values (each of ~10 Hz) and a small $J_{2,3}$ value (4.2 Hz) showed **24** to have the manno configuration. No well-resolved spectrum could be obtained for **23** even at elevated temperatures that could be accounted for by a restricted internal rotation of spatially close axial acetamido groups at C-2 and C-4 and the 3-*O*-benzyl group. Nevertheless, based on the line width for H-3 and H-5, it was concluded that $J_{2,3}$ and $J_{3,4}$ coupling constant values did not exceed 4 Hz and $J_{4,5}$ was less than 2 Hz. These data were in good agreement with the expected talo configuration of **23**.[21] Hydrogenolysis of **23** over $Pd(OH)_2/C$ afforded the target hexose **25**.

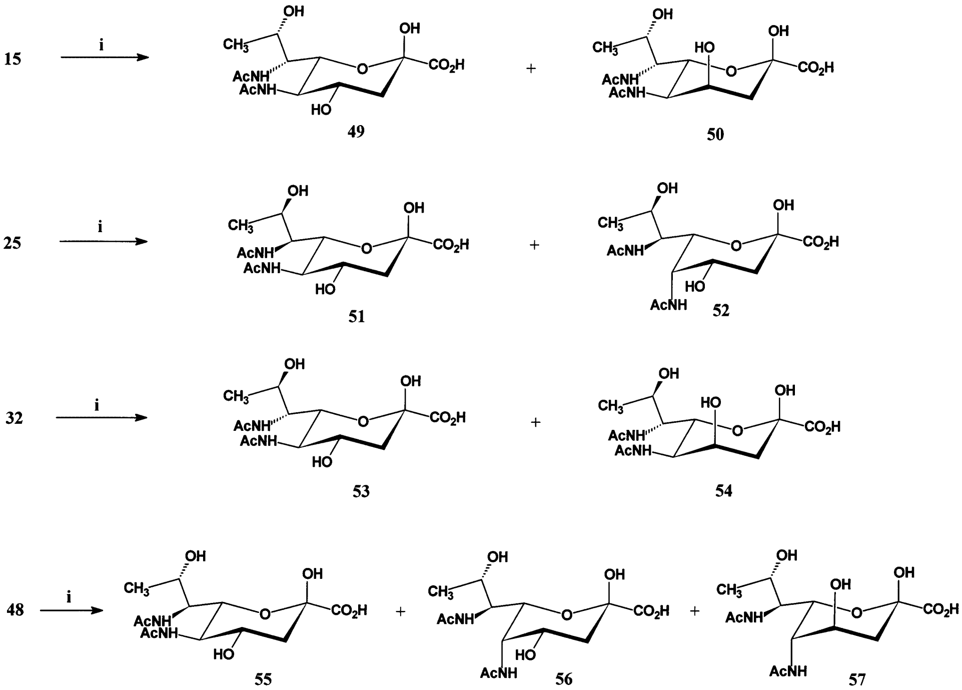
The behaviour of **25** in aqueous solution is noteworthy. The ^{1}H and ^{13}C NMR spectra of **25**, which were assigned using 2D COSY, TOCSY, and HSQC techniques (Table 1), contained six anomeric signals. Comparison with published data for talopyranose and its derivatives, including ^{13}C NMR chemical shifts and coupling constant values,[21,22] enabled identification of α- and β-pyranoses **α-25*p*** and **β-25*p***. The four other signals belonged to α- and β-furanoses **α-25*f*** and **β-25*f***, as followed from the coupling constant values (compare published data[23]) and characteristic changes in the ^{13}C NMR chemical shifts, especially those for C-1 and C-4, compared to the data of talofuranose[22] and **25*p*** (Table 1). Each of **α-25*f*** and **β-25*f*** existed as two stereoisomers (*E* and *Z*) at the 4-acetamido group,[24] which were not assigned, and designated as major and minor (Table 1). The

^{1}H NMR signals for the stereoisomers within each anomeric pair coalesced when the spectrum was run at 90 °C. Therefore, 2,4-diacetamido-2,4,6-trideoxy-D-talose (**25**) represents a rare example of a 4-acylamino-4-deoxyhexose that exists in aqueous solution to a significant extent in the furanose form. Most likely, the reason for this unusual behavior is destabilization of the pyranose form by unfavourable 1,3-diaxial interaction of the acetamido groups.

2,4-Diacetamido-2,4,6-trideoxy-D-mannose (**32**) was prepared from benzyl β-D-fucopyranoside (**26**)[25] using at the key step the known approach to β-mannosides based on simultaneous substitution with inversion at positions 2 and 4 in β-galactosides[26] (Scheme 3). Bu_2SnO-mediated selective benzoylation of **26** gave 3-benzoate **27**, as followed from a low-field position of the signal for H-3 in the ^{1}H NMR spectrum. Conversion of **27** into ditriflate **28** and its subsequent reaction with tetrabutylammonium azide in toluene resulted in diazide **29** in high yield. Large $J_{3,4}$ and $J_{4,5}$ coupling constant values (each of $\sim$10 Hz) and small $J_{1,2}$ and $J_{2,3}$ values (<1 and 2.5 Hz, respectively) in the ^{1}H NMR spectrum confirmed the manno configuration of **29**. Conventional debenzoylation of **29** afforded **30**. Further transformations of **30** were similar to those described above in synthesis of **15** and included reduction of the azido groups by hydrogenation, N-acetylation (**30** → **31**), and removal of the benzyl protecting group (**31** → **32**). According to NMR data, the hexose **32** exists in aqueous solution exclusively in the pyranose form (α,β ratio $\sim$1:1).

Benzyl β-L-rhamnopyranoside **5** was chosen as the starting compound for preparation of 2,4-diacetamido-2,4,6-trideoxy-L-allose (**48**). To provide the proper D configuration at C-4, which would lead to the necessary L configuration on azidation, the L-rhamnoside **5** was converted into L-taloside **35** (Scheme 4). Conventional isopropylidenation of **5** gave **33**, which was subjected to the known[27] oxidation–reduction procedure to afford, via ketone **34**, L-taloside **35** in nearly quantitative yield. In an attempt to apply the same approach that was successively used for the synthesis of the manno isomer **32**, the isopropylidene group was removed and the resulting triol **36** was selectively benzoylated via dibutylstannylene derivative to yield monobenzoate **37**. However, instead of the expected diazide **39**, reaction of 2,4-ditriflate **38** obtained from **37** with tetrabutylammonium azide gave a complex mixture of products that was not further investigated. Therefore, another approach based on a consecutive introduction of azido groups to positions 4 and 2 was exploited. Azidation of 4-triflate **40** with sodium azide in DMF in the presence of a crown ether[28] furnished azide **41** with the necessary configuration of C-4. To liberate HO-2 for introduction of the second azido group, **41** was subjected to deacetalation followed by Bu_2SnO-mediated selective 3-O-benzoylation of diol **42**. Monobenzoate **43** thus obtained was converted into triflate **44**, which was then converted to the target diazide **39** by reaction with sodium azide in DMF. Large values of all coupling constants in the ^{1}H NMR spectrum proved unambiguously the L-gluco configuration of **39**. $LiAlH_4$ reduction of azido groups in **39** with concomitant removal of the benzoyl group and subsequent N-acetylation resulted in the diacetamido derivative **45**. Mesylation of **45** afforded mesylate **46**. Inversion of the configuration at C-3 mediated by participation of a neighbouring acetamido group(s) was achieved by heating of **46** in aqueous 2-methoxyethanol in the presence of sodium acetate[16] to give the L-allo derivative **47** in high yield. The configuration of **47** was confirmed by large $J_{1,2}$ and $J_{4,5}$ coupling constant values (8.6 and 10.2 Hz) and small $J_{2,3}$ and $J_{3,4}$ values (2.8 and 2.3 Hz, respectively). Conventional removal of the anomeric benzyl group afforded hexose **48**, which occurred in the pyranose form (α,β ratio of 1:3.3, NMR data).

Condensation of compounds **15**, **25**, **32**, and **48** with oxalacetic acid was performed in the presence of sodium tetraborate at pH 10.5[9] (Scheme 5). Acidic reaction products were isolated by anion exchange chromatography, and then the individual isomers of 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids were separated by reversed-phase C_{18} HPLC.



Scheme 5. Reagents and conditions: **i**, oxalacetic acid, $Na_2B_4O_7$, pH 10.5, rt Only main isomers of acids **49**–**57** with an equatorial carboxyl group are shown.

Compounds **15** and **32** with the threo configuration of the fragment C-3–C-4 afforded pairs of epimers at C-4 having the L-glycero-D-galacto/D-talo (**49**/**50**) and D-glycero-D-galacto/D-talo (**53**/**54**) configurations, respectively, in a nearly 1:1 ratio. Compounds **25** and **48** with the erythro configuration of the fragment C-3–C-4 gave the equatorial HO-4 epimers having the D-glycero-L-altro (**51**) and L-glycero-L-altro (**55**) configuration, respectively, with no axial HO-4 epimers. The reason for this unexpected stereoselectivity is not clear. In addition to **51** and **55**, compounds **25** and **48** afforded, as minor products, isomeric nonulosonic acids with an axial AcNH-5 group having the D-glycero-L-manno (**52**), L-glycero-L-manno(**56**), and L-glycero-L-gluco (**57**) configuration. They evidently resulted from epimerisation at C-2 in the starting monosaccharides prior to condensation.

The structures of the synthesised acids were proved by ESIMS and NMR spectral data. Major peaks corresponding to either $[M+Na]^+$ (positive mode) or $[M-H]^-$ (negative mode) pseudomolecular ions were observed in the ESIMS spectra of **49**–**57**. The data of the ^{1}H and ^{13}C NMR spectra of both free acids and sodium salts are given in Tables 2 and 3. They demonstrated the pyranose form of all sugars, which existed in aqueous solution as mixtures of anomers with a high predominance of the anomer having an equatorial carboxyl group (β for **49**, **50**, **53**, and **54**, and α for **51**, **52**, **55**–**57**). The ratios of the free acids anomers are given in Table 2. The configuration within the pyranose ring followed from the $^3J_{H,H}$ coupling constant values determined from the ^{1}H NMR spectra. Large $J_{3a,4}$, $J_{4,5}$, and $J_{5,6}$ values for **49**, **51**, **53**, and **55** indicated equatorial substituents at C-4, C-5, and C-6. Large $J_{5,6}$ and small $J_{3a,4}$ and $J_{4,5}$ values for **50** and **54** showed that the OH-4 group is axial. In contrast, large $J_{3a,4}$ and small $J_{4,5}$ and $J_{5,6}$ values for **52** and **56** confirmed the axial orientation of the AcNH-5 group. Finally, small $J_{3a,4}$, $J_{4,5}$, and $J_{5,6}$ values for **57** demonstrated that both OH-4 and AcNH-5 are axial.

Four of the synthesised isomers occur in nature. These are the D-glycero-D-galacto and L-glycero-L-manno isomers called legionaminic[3,8] and pseudaminic[1] acid, respectively, as well as C-4 and C-8 epimers of legionaminic acid having the D-glycero-D-talo and L-glycero-D-galacto configuration (4- and

Table 2
[1]H NMR data for 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids (δ_H; $J_{H,H}$, Hz; D_2O, 30 °C)

Compound	α:β ratio	Form	H-3e ($J_{3,3}$)	H-3a ($J_{3a,4}$)	H-4 ($J_{3e,4}$)	H-5 ($J_{4,5}$)	H-6 ($J_{5,6}$)	H-7 ($J_{6,7}$)	H-8 ($J_{7,8}$)	H-9 ($J_{8,9}$)	CH_3CON
49α	1:19	H	2.69	1.71	3.82	3.67	3.85	3.93	4.00	1.20	1.98, 2.02
			(13.0)	(12.0)	(4.9)	(10.4)	(10.4)	(<2)	(6.4)	(6.3)	
49α		Na	2.62	1.61	3.83	3.63	3.82	3.90	3.98	1.17	
			(12.7)	(12.0)	(4.7)	(10.1)	(10.1)	(1.7)	(6.4)	(6.5)	
49β		H	2.32	1.86	3.95	3.73	4.16	3.95	3.91	1.18	1.96, 2.00
			(13.1)	(11.5)	(4.8)	(10.2)	(10.3)	(2.0)	(6.4)	(6.2)	
49β		Na	2.20	1.79	3.89	3.70	4.06	3.89	3.90	1.15	1.97, 2.01
			(13.0)	(11.5)	(4.8)	(10.2)	(10.3)	(1.3)	(6.3)	(5.8)	
50α	1:8	H	2.65	1.94	4.08	3.84	4.47	3.89	4.08	1.28	1.96, 2.04
			(14.4)	(2.7)	(3.6)	(2.7)	(10.5)			(6.3)	
50α		Na	2.40	2.03	3.97	3.84	4.26	3.87	3.95	1.18	1.96, 2.02
			(15.0)		(2.7)	(2.6)	(10.4)	(2.0)		(6.3)	
50β		H	2.18 [a]	2.13 [a]	4.11	3.89	4.48	3.95	3.96	1.21	1.97, 2.01
			(14.9)	(3.3)	(2.9)	(2.8)	(10.6)	(1.3)		(5.7)	
50β		Na	2.10 [a]	2.06 [a]	4.09	3.88	4.42	3.90	3.98	1.20	1.97, 2.01
			(14.8)	(3.1)	(2.9)	(2.6)	(10.6)	(1.9)	(6.5)	(6.3)	
51β	13.3:1	H	2.71	1.75	3.82	3.81	3.56	3.91	4.40	1.08	
51β		Na	2.70	1.68	3.75	3.79	3.42	3.93	4.41	1.05	
			(12.5)	(11.1)	(4.5)	(9.8)	(9.8)	(5.1)	(1.8)	(6.3)	
51α		H	2.34	1.93	3.99	3.86	3.90	3.92	4.42	1.08	2.06
			(13.2)	(11.6)	(4.8)	(9.4)	(10.1)	(2.8)	(<1)	(6.4)	
51α		Na	2.24	1.86	3.95	3.83	3.83	3.89	4.43	1.05	2.05
			(13.1)	(11.5)					(<1)	(6.5)	
51α (333 K)		Na	2.22	1.91	3.93	3.82	3.85	3.88	4.39	1.06	2.05
			(13.1)	(11.5)	(4.9)	(9.5)	(10.6)	(<1)	(<1)	(6.5)	
52β	12.5:1	H	2.50	1.64	4.10	4.22	4.14	3.86	4.25	1.10	
			(13.2)	(12.8)	(4.9)	(4.5)	(2.1)	(10.4)	(1.6)	(6.4)	
52α		H	2.03	1.82	4.25	4.29	4.27	3.82	4.12	1.09	
			(13.4)	(12.3)	(5.0)	(4.3)	(1.8)	(10.1)	(1.2)	(6.6)	
52α		Na	1.99	1.79	4.18	4.24	4.19	3.77	4.12	1.07	1.98, 1.99
			(13.2)	(12.3)	(4.8)	(4.0)	(1.0)	(10.2)	(<2)	(6.6)	
53α	1:18	H	2.73	1.71	3.82	3.68	3.93		3.94	1.16	1.97
			(12.9)	(11.9)	(4.7)		(10.3)				
53α		Na	2.75	1.61	3.66	3.67	3.77	3.82	3.93	1.16	1.95
			(12.9)	(11.8)	(3.9)						
53β		H	2.31	1.87	3.98	3.72	4.31	3.91	3.85	1.16	1.99, 2.00
			(13.1)	(11.7)	(4.8)	(10.3)	(10.5)	(1.9)	(8.9)	(6.2)	
53β		Na	2.19	1.82	3.94	3.70	4.23	3.85	3.85	1.15	1.99, 2.00
			(12.9)	(12.2)	(4.8)	(10.7)	(10.5)	(<2)			
54α	1:5.4	H	2.69	1.94	4.10	3.86	4.55	3.88	4.00	1.20	1.96, 2.00
			(14.4)	(3.5)	(3.0)	(2.9)	(10.8)	(2.3)	(8.6)	(6.4)	
54α		Na	2. 54	1.95	4.02	3.85	4.42	3.82	3.93	1.16	1.96
			(14.7)	(3.6)	(2.9)	(2.8)	(10.7)	(2.4)	(8.9)		
54β		H	2.19	2.14	4.13	3.90	4.63	3.92	3.92	1.18	1.98, 1.99
			(14.9)	(3.4)	(3.0)	(2.9)	(10.8)			(5.5)	
54β		Na	2.11	2.07	4.10	3.88	4.56	3.86	3.91	1.17	1.98, 1.99
			(14.8)	(3.2)	(2.7)	(2.9)	(10.8)	(<2)	(8.7)	(6.1)	
55β	8.3:1	H	2.70	1.72	3.79	3.85	3.57	4.13	4.07	1.21	
			(12.8)	(12.2)	(4.5)	(10.7)	(10.7)	(3.3)	(6.0)	(6.3)	
55β		Na	2.61	1.61	3.81	3.82	3.54	4.08	4.06	1.19	2.03, 2.05
			(12.9)	(11.2)	(4.3)		(10.1)	(3.4)		(6.3)	

Table 2 (*Continued*)

Compound	α:β ratio	Form	H-3e ($J_{3,3}$)	H-3a ($J_{3a,4}$)	H-4 ($J_{3e,4}$)	H-5 ($J_{4,5}$)	H-6 ($J_{5,6}$)	H-7 ($J_{6,7}$)	H-8 ($J_{7,8}$)	H-9 ($J_{8,9}$)	CH_3CON
55α		H	2.32	1.93	3.94	3.91	3.94	4.16	4.06	1.18	2.04, 2.08
			(13.3)	(12.5)	(4.4)	(10.2)	(10.2)	(2.8)	(5.8)	(6.4)	
55α		Na	2.21	1.89	3.89	3.88	3.84	4.13	4.08	1.16	2.02, 2.07
			(13.2)	(11.3)	(4.3)		(11.0)	(3.0)	(6.0)	(6.3)	
56β	7.5:1	H	2.48	1.62	4.08	4.29	3.96	4.15	4.18	1.12	
			(13.0)	(12.9)	(4.7)	(3.6)	(2.4)	(10.5)	(3.4)		
56β		Na	2.41	1.55	4.08	4.26	3.75	4.01	4.04	1.125	
			(13.1)	(12.2)	(4.9)	(3.7)	(<2)	(10.5)	(3.4)		
56α		H	2.01	1.80	4.20	4.27	4.08	4.17	4.10	1.10	1.90, 2.01
			(12.8)	(12.0)	(4.6)	(3.7)	(<2)	(10.7)	(3.3)	(6.5)	
56α		Na	1.92	1.78	4.16	4.24	4.02	4.13	4.11	1.11	1.97, 2.00
			(13.2)	(12.0)	(5.2)	(3.7)	(1.0)	(10.7)	(3.3)	(6.5)	
57β	4:1	H	2.48	1.92	4.00	3.85	4.36	4.15	4.24	1.21	1.95, 1.99
			(14.8)	(2.9)	(3.1)	(2.6)	(2.2)	(10.3)	(4.0)	(6.5)	
57β		Na	2.22	1.97	3.90	3.82	4.16	4.16	4.08	1.11	
57α		H	1.95	2.13	4.00	3.91	4.42	4.22	4.16	1.15	1.97, 1.98
			(15.2)		(3.7)	(3.3)	(2.1)	(10.5)	(3.5)	(6.6)	
		Na	1.85	2.09	3.97	3.88	4.42	4.17	4.17	1.14	1.97, 1.98
57α			(15.2)	(3.6)	(3.6)	(3.3)	(2.1)	(10.5)		(6.3)	

[a] Assignment could be interchanged.

8-epilegionaminic acid, respectively). Using the synthetic models **53**, **54**, and **49**, the configurations of legionaminic, 4- and 8-epilegionaminic acids were confirmed in some bacterial polysaccharides and revised in others.[8] The ^{1}H and ^{13}C NMR spectroscopy and specific optical rotation data of the compound **56** fitted reasonably well those of pseudaminic acid derivatives isolated from bacterial polysaccharides[4,29], thus confirming the L-glycero-L-manno configuration of the natural monosaccharide.

Comparison of the NMR data of various isomers (Tables 2 and 3, free acids) revealed several regularities, which can be useful for determination of the configuration of naturally occurring compounds of this class. Thus, the $J_{6,7}$ coupling constant is dependent on the configuration at C-5: it is small (1.3–3.3 Hz) when AcNH-5 is equatorial (**49–51**, **53–55**) and large (10.1–10.7 Hz) when it is axial (**52**, **56**, **57**), indicating the syn (gauche)- and trans-like relationship for H-6 and H-7, respectively. In the D-galacto and D-talo isomers, when C-8 had the D configuration (**53**, **54**), the C-6 and C-8 signals appeared upfield by 2.0–2.3 and 1.4–2.0 ppm, respectively, compared to the corresponding L epimers (**49**, **50**). In the L-manno isomers, a significant difference was observed for the C-9 signal, which appeared at 20.0 ppm in the D epimer (**52**) at C-8 but at 16.7 ppm in the L epimer (**56**).

The chemical shifts are influenced also by the anomeric configuration. In the sugars with an equatorial OH-4 (**49**, **51**–**53**, **55**, **56**), the difference between the ^{1}H NMR resonances for H-3_{ax} and H-3_{eq} was 0.86–1.02 ppm for the anomer with an axial carboxyl group but only 0.21–0.46 ppm for the other anomer, independently of whether AcNH-5 is axial or equatorial. When OH-4 was axial and AcNH-5 equatorial (**50**, **54**), a typical difference of 0.71–0.75 or 0.05 ppm was observed for the anomers with an axial or an equatorial carboxyl group, respectively. In the ^{13}C NMR spectra, the clearest dependence was shown by the C-3 and C-6 resonances. Compared to the other anomer, in the anomer with an axial carboxyl group they both appeared upfield by 0.8–1.3 and 1.6–2.9 ppm when OH-4 was equatorial (**49**, **51**–**53**, **55**, **56**) or by 2.3–2.6 and 3.8–4.7 ppm, respectively, when OH-4 was axial (**50**, **54**, **57**).

For conformational studies by NMR spectroscopy, the L-glycero-D-galacto (**49**), D-glycero-L-altro (**51**), D-glycero-D-galacto (**53**), and

Table 3
^{13}C NMR data of 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids (δ_C; D_2O, 30 °C)

	Form	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	*C*H$_3$CON	CH$_3$*C*ON
49α	H	173.1	97.3	41.2	68.9	53.7	75.2	54.4	69.4	19.8		
49α	Na	176.7	98.2	41.7	69.7	54.2	75.2	54.4	70.1	19.8		
49β	H	174.3	96.5	40.4	68.3	54.1	72.9	54.4	69.3	19.8	23.1, 23.4	175.1, 175.2
49β	Na	177.3	97.5	40.8	68.6	54.2	72.9	54.4	69.7	19.8	23.1, 23.4	175.1, 175.3
50α	H			40.0	66.6	50.1	72.6	54.9	69.7	19.9		
50α	Na	176.1	96.5	38.9	66.7	50.4	72.2	54.9		19.9		
50β	H	174.5[a]	96.1	37.7	66.9	50.0	68.5	54.9	69.2	19.9	23.0, 23.1	174.6[a], 175.2
50β	Na	177.3	97.1	37.8	67.4	50.1	68.7	54.7	69.7	19.9	23.0, 23.1	174.5, 175.2
51β	H	172.9	97.2	41.1	68.7	54.7	77.3	54.3	66.5	20.0		
51β	Na	175.6	97.4	41.7	69.5	55.4	76.0	54.9	66.5	20.2		
51α	H	173.7	96.1	39.9	67.6	54.7	75.7	53.9	66.6	20.2	23.1, 23.3	175.2, 175.8
51α	Na	177.1	97.2	40.4	68.1	54.9	75.9	53.5	66.5	20.3	23.1, 23.3	175.2, 175.8
52β	H	173.9	96.0	36.8	68.0	49.1	73.0	54.4	67.4	20.0		
52α	H	174.7	96.8	35.5	66.1	49.9	70.3	54.4	66.0	20.0	23.1, 23.2	175.0, 175
52α	Na	177.6	97.8	36.0	66.7	50.1	70.2	54.6	66.0	20.0	22.3, 22.3	174.2, 175.0
53α	H		97.2	41.4	69.2	53.4	73.2	54.4	68.0	20.4		
53α	Na	176.6	98.6	41.9	70.1	53.4	72.8	54.8	68.2	20.4		
53β	H	174.4[a]	96.6	40.3	68.4	53.9	70.9	54.4	67.5	20.4	23.0, 23.4	175.0[a], 175.2
53β	Na	177.6	97.6	40.8	68.8	54.0	70.7	54.5	67.7	20.4	23.0, 23.4	175.0, 175.1
54α	H			40.2	66.9	49.7	70.3	55.0	68.2	19.8		
54α	Na	177.0	96.7	39.5	67.1	50.1	69.9	55.0	67.8	19.8		
54β	H	174.7[a]	96.3	37.6	67.1	49.7	66.5	54.7	67.2	20.4	23.0, 23.1	174.7[a], 175.0
54β	Na	177.6	97.3	37.8	67.6	49.9	66.2	54.8	67.4	20.4	22.9, 23.1	174.5, 174.9
55β	H	173.0	97.0	41.2	69.1	54.9	76.0	55.8	67.8	19.7		
55β	Na	175.4	98.0	41.7	69.8	55.2	75.8	55.9	67.8	19.8		
55α	H	173.7	96.1	39.9	68.2	55.3	73.7	55.5	67.6	19.7	23.3, 23.4	175.0, 175.9
55α	Na	177.1	97.1	40.4	68.9	55.7	73.8	55.2	67.6	19.8	23.2, 23.5	174.9, 175.8
56β	H			35.0	67.3	49.9	72.1	53.8	68.2	16.7		
56β	Na			35.9	67.0	50.1	72.2	54.2	68.3	16.6		
56α	H	174.9	97.0	35.6	66.1	49.9	71.4	54.0	68.1	16.7	23.2, 23.3	175.0, 175.9
56α	Na	177.4	97.7	36.0	66.5	50.1	71.4	54.2	68.1	16.6	23.1, 23.3	175.0, 175.9
57β	H		93.5	35.7	67.4	48.5	71.8	54.4	68.6	17.0		
57β	Na			34.8	67.6	49.5	71.5	53.8	68.6	17.0		
57α	H	174.6	96.4	33.3	67.1	48.9	67.1	53.8	67.9	16.7	23.0, 23.2	175.1
57α	Na	174.9	97.3	33.5	67.6	49.0	67.0	54.1	68.1	16.7	23.0, 23.2	175.1

[a] Assignment could be interchanged.

L-glycero-L-altro (**55**) isomers were converted to methyl esters **58**–**61** and then acetylated to 2,4,8-tri-*O*-acetyl derivatives **62**–**65**, respectively. These compounds were more convenient to analyze than the free acids because of a wider range of ^{1}H NMR chemical shifts and easier observation of signals for NH protons.

The L- and D-glycero-D-galacto esters **58** and **60** afforded mixtures of α- and β-acetates, **62** and **64**, in a 1:1 ratio. The D-and L-glycero-L-altro esters **59** and **61,** which differed from **58** and **60** in the configuration of C-7, gave predominantly α-acetates (α:β ratios were 13:1 and 6:1 for **63** and **65**, respectively). The anomeric configurations in **62**–**65** were assigned based on the ^{1}H and ^{13}C NMR data (Table 4) by analogy with anomers of methyl *N*-acetylneuraminate pentaacetate.[30,31] The $^3J_{H,H}$ coupling constant values in the acetates **62**–**65** and the parent free acids were essentially the same, and, hence, O-acetylation did not significantly change the conformation of the molecules.

Table 4
^{1}H and ^{13}C NMR data of methyl (5,7-diacetamido-2,4,8-tri-*O*-acetyl-3,5,7,9-tetradeoxynon-2-ulopyranos)onates (δ_H; δ_C; $J_{H,H}$, Hz; $CDCl_3$, rt)

Configuration (compound)	H-3eq ($J_{3eq,3ax}$)	H-3ax ($J_{3ax,4}$)	H-4 ($J_{3eq,4}$)	H-5 ($J_{4,5}$)	H-6 ($J_{5,6}$)	H-7 ($J_{6,7}$)	H-8 ($J_{7,8}$)	H-9 ($J_{8,9}$)	NH-5 ($J_{NH,5}$)	NH-9 ($J_{NH,7}$)
α-D-glycero-D-galacto (α-**64**)	2.71 (13.5)	2.11	5.28 (5.1)	3.85 (10.0)	4.53 (10.7)	4.38 (1.4)	4.88 (~7)	1.23 (6.4)	5.73 (9.4)	5.83 (10.0)
β-D-glycero-D-galacto (β-**64**)	2.55 (13.3)	1.80 (11.0)	5.66 (5.1)	3.45 (10.6)	4.34 (10.5)	4.40 (~1)	4.86 (~7)	1.21 (6.5)	5.94 (8.4)	6.88 (10.0)
α-L-glycero-D-galacto (α-**62**)	2.72 (13.6)	2.07	5.44 (5.1)	3.59 (9.5)	4.61 (10.0)	4.23 (~1)	5.14 (7.2)	1.31 (6.4)	5.81 (9.3)	5.87 (9.9)
β-L-glycero-D-galacto (β-**62**)	2.61 (13.2)	1.77 (11.2)	5.82 (5.0)	3.21 (10.2)	4.53 (10.3)	4.29 (~1)	5.10 (7.0)	1.17 (6.4)	5.99 (7.6)	6.73 (9.7)
α-D-glycero-L-altro (α-**63**)	2.39 (13.2)	1.94 (12.7)	5.18 (5.0)	4.42 (10.3)	3.69 (10.9)	4.06 (~1)	5.81 (~1)	1.19 (6.4)	5.86 (9.0)	6.38 (9.2)
α-L-glycero-L-altro (α-**65**)	2.48 (13.3)	1.95	5.21 (4.9)	4.14 (10.4)	3.83 (11.0)	4.59 (2.5)	5.01 (5.0)	1.29 (6.4)	6.11 (9.4)	6.40 (9.7)
β-L-glycero-L-altro (β-**65**)	2.65 (13.4)	2.03	5.05 (4.8)	4.07 (10.5)	4.15 (9.7)	4.53 (~2)	4.89 (6.8)	1.19 (6.3)	6.25 (8.8)	6.77 (9.8)
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	
α-D-glycero-D-galacto (α-**64**)		96.5	36.2	68.3	50.6	72.5	50.6	69.5	16.8	
β-D-glycero-D-galacto (β-**64**)	166.7	96.8	36.8	67.1	51.7	70.6	50.6	69.8	16.8	
α-L-glycero-D-galacto (α-**62**)	167.9	96.5	36.2	67.5	51.5	73.4	52.5	70.5	17.1	
β-L-glycero-D-galacto (β-**62**)	167.2	96.6	36.6	66.3	52.6	72.0	51.8	70.2	17.5	
α-D-glycero-L-altro (α-**63**)	166.5	96.9	36.1	68.3	50.3	75.9	51.2	65.9	19.1	
α-L-glycero-L-altro (α-**65**)	166.7	97.3	36.7	68.7	50.7	73.9	50.0	68.8	16.2	
β-L-glycero-L-altro (β-**65**)			36.1	68.7	50.9	75.1	52.3	69.1	16.2	

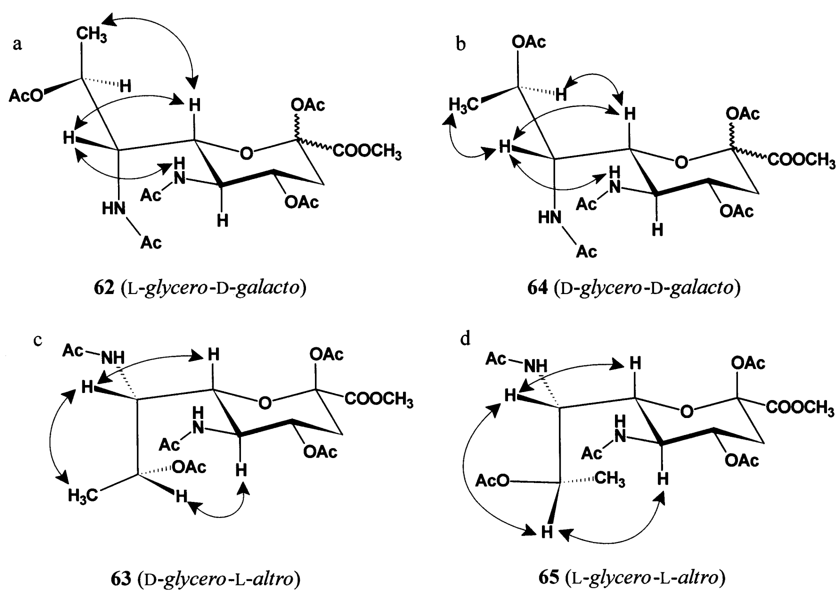


Fig. 1. NOE correlations and conformation of the side chain in methyl (5,7-diacetamido-2,4,8-tri-*O*-acetyl-3,5,7,9-tetradeoxynon-2-ulopyranos)onates (**62**-**65**). Only correlations designated in Table 5 as strong are shown.

Small $^{3}J_{H\text{-}6,H\text{-}7}$ coupling constant values (1–2.5 Hz) were observed for all O-acetylated compounds, thus indicating the gauche orientation of H-6 and H-7 (Fig. 1). Relatively large $^{3}J_{H\text{-}7,H\text{-}8}$ values of ~7 Hz for **62** (L-glycero-D-galacto) and **64** (D-glycero-D-galacto) showed the trans-like orientation of H-7 and H-8 in the predominant conformer. Almost

Table 5
NOE correlations for H-9, H-8, H-7 and NH-7 in methyl (5,7-diacetamido-2,4,8-tri-*O*-acetyl-3,5,7,9-tetradeoxynon-2-ulopyranos)onates (relative intensity in parentheses; s, strong; m, medium; w, weak)

Configuration (compound)	H-9	H-8	H-7	NH-7
D-glycero-D-galacto (**64**)	H-8 (s), H-7 (s), NH-7 (m)	H-7 (w), H-6 (s), NH-7 (m)	H-6 (s), NH-5 (s), NH-7 (m)	H-5 (m)
L-glycero-D-galacto (**62**)	H-8 (s), H-7 (m), H-6 (s)	H-7 (w), H-6 (m), NH-7 (m)	H-6 (s), NH-5 (s), NH-7 (m)	H-5 (m)
D-glycero-L-altro (**63**)	H-8 (s), H-7 (s), NH-7 (w)	H-7 (m), H-5 (s)	H-6 (s), NH-7 (m)	H-6 (w)
L-glycero-L-altro (**65**)	H-8 (s), H-7 (w), H-5 (w)	H-7 (s), H-5 (s), NH-5 (w)	H-6 (s), NH-5 (w)	H-9 (m), H-7 (m)

the same large value (5–7 Hz, depending on the anomeric configuration) was observed for **65** (L-glycero-L-altro), whereas in **63** (D-glycero-L-altro) it was significantly smaller (~ 1 Hz).

Correlations between H-7 and both H-6 and NH-5 in the L- and D-glycero-D-galacto isomers (**62** and **64**) that were revealed by a NOESY experiment defined the predominant rotamer around the C-6–C-7 bond (Table 5, Fig. 1(a) and (b)). This conformation was in agreement with a small $^3J_{H-6,H-7}$ value (1–1.4 Hz). The NOESY spectra of both **62** and **64** showed only a weak H-8,H-7 correlation that, together with a relatively large $^3J_{H-7,H-8}$ value (~ 7 Hz), indicated the trans-like orientation of H-7 and H-8. Strong H-9,H-7 and medium H-9,NH-7 correlations for **64** showed a spatial proximity of H-9 and H-7, and a strong H-8,H-6 correlation demonstrated that these protons are close to each other (Fig. 1(b)). In **62**, H-9 is more close to H-6 than to H-7 as followed from a stronger H-9,H-6 correlation compared to a H-9,H-7 correlation (Fig. 1(a)). Therefore, in **62** and **64**, predominant are the trans,trans and trans,cis side-chain (C-7–C-8–C-9) conformers, respectively.

An HMBC experiment optimized for a coupling constant of 8 Hz revealed a strong H-6,C-8 correlation for the D- and L-glycero-L-altro isomers (**63** and **65**), which corresponded to a $^3J_{H-6,C-8}$ coupling constant of > 5 Hz. This finding showed the trans-like orientation of H-6 and C-8 in the predominant rotamer around the C-6–C-7 bond,[32] which was confirmed by a strong H-7,H-6 correlation with no H-8,H-6 and H-9,H-6 correlations in the NOESY spectra of **63** and **65**. The most populated rotamers around the C-7–C-8 bond are characterized by strong H-9,H-7 and H-8,H-5 correlations for **63** and strong H-8,H-5 and weak H-9,H-5 correlations for **65** (Table 5, Fig. 1(c) and (d)). The presence of an intense H-7,H-8 correlation peak in the NOESY spectrum of **65** seems to be inconsistent with a relatively large $^3J_{H-7,H-8}$ value (5–7 Hz). This contradiction could be accounted for by a significant contribution of rotamers with a small H-7–C-7–C-8–H-8 dihedral angle. The predominant conformers of **63** and **64** have cis,trans and cis,cis side-chain orientation, respectively.

3. Experimental

NMR spectra were recorded on Bruker DRX-500 and Bruker AM-300 instruments. Spectra of hexose derivatives were measured for solutions in $CDCl_3$ unless otherwise stated, and ^1H NMR chemical shifts were referenced to a residual solvent signal. Spectra of 5,7-diacetamido-3,5,7,9-tetradeoxynon-2-ulosonic acids were measured for solutions in D_2O using acetone (δ_H 2.225, δ_C 31.45) as internal standard. Sodium salts were obtained by passing aqueous solutions of the acids through a short column of Amberlite IR-420 (Na^+ form). A mixing time of 300 or 900 ms was used in NOESY experiments with methyl (5,7-diacetamido-2,4,8-tri-*O*-acetyl-3,5,7,9-tetradeoxynon-2-ulopyranos)onates.

Melting points were determined with a Kofler apparatus and are uncorrected. Optical rotation values were measured on a JASCO DIP-360 polarimeter at 22 ± 2 °C. TLC was performed on Kieselgel 60 F_{254} plates (E. Merck), and visualization was accomplished using UV light or by charring with 10% H_2SO_4. Column chromatography was carried out on Silpearl silica gel (Chemapol) in a medium pressure mode. Preparative reversed-phase C_{18} HPLC was performed on a column (250 × 24 mm) of 7.5 μm Silasorb C_{18} (Czech Republic) in 0.05% aq CF_3CO_2H at 10 mL/min using a Knauer 98.00 refractometer for monitoring. ESIMS data were recorded with a Micromass Quattro system. All reactions involving air- or moisture-sensitive reagents were carried out in dry solvents under dry argon.

Benzyl 3,4-di-O-benzoyl-β-L-rhamnopyranoside (**2**), *benzyl 2,4-di-O-benzoyl-β-L-rhamnopyranoside* (**3**), *and benzyl 2,3-di-O-benzoyl-β-L-rhamnopyranoside* (**4**).—A mixture of **1** (7.8 g, 21 mmol) and Bu_2SnO (5.49 g, 22 mmol) in benzene (150 mL) was boiled with azeotropic removal of water for 2 h, whereupon a crystalline precipitate of the stannylene derivative formed. Tetrabutylammonium bromide (7.08 g, 22 mmol) and benzyl bromide (5 mL, 42 mmol) were added, and the mixture was boiled under reflux for 4 h. After cooling, the solution was washed thoroughly with water and concentrated. Column chromatography of the residue (95:5 toluene–EtOAc) gave a mixture of **2**–**4** (8.95 g, 92%) in ratios of ~4:3:1, which was used in the next step without separation.

A small portion of the above mixture was subjected to column chromatography (85:15 light petroleum–EtOAc) to give, in order of elution, pure compounds **2**, **3**, and **4**.

3,4-Dibenzoate **2**: mp 172–174 °C (EtOAc–hexane); $[\alpha]_D$ +129° (*c* 2). ^{1}H NMR: δ, 1.42 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 2.53 (br. s, 1 H, OH), 3.73 (dq, 1 H, H-5), 4.37 (dd, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 4.74, 4.99 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 4.75 (d, 1 H, $J_{1,2}$ 1.1 Hz, H-1), 5.28 (dd, 1 H, $J_{3,4}$ 10.8 Hz, H-3), 5.67 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 7.30–8.04 (m, 15 H, 3 Ph). Anal. Calcd for $C_{27}H_{26}O_7$: C, 70.12; H, 5.67. Found: C, 69.98; H, 5.59.

2,4-Dibenzoate **3**: mp 123–125 °C (EtOAc–hexane); $[\alpha]_D$ +91° (*c* 2). ^{1}H NMR: δ, 1.44 (d, 3 H, $J_{5,6}$ 6.1, H-6), 3.71 (dq, 1 H, H-5), 4.02 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.70, 4.93 (2 d, 2 H, J_{gem} 12.4 Hz, PhCH_2), 4.73 (s, 1 H, H-1), 5.23 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 5.72 (d, 1 H, $J_{2,3}$ 3.6 Hz, H-2), 7.28–8.21 (m, 15 H, 3 Ph). Anal. Calcd for $C_{27}H_{26}O_7$: C, 70.12; H, 5.67. Found: C, 70.13; H, 5.61.

2,3-Dibenzoate **4** had mp 135–137 °C (EtOAc–hexane), $[\alpha]_D$ +82° (*c* 1.7). ^{1}H NMR: δ, 1.54 (d, 3 H, $J_{5,6}$ 6.1, H-6), 2.43 (d, 1 H, $J_{4,OH}$ 4.6 Hz, OH), 3.52 (dq, 1 H, H-5), 3.92 (dt, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.71, 4.92 (2 d, 2 H, J_{gem} 12.3 Hz, PhCH_2), 4.78 (s, 1 H, H-1), 5.17 (dd, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 5.83 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 7.29—8.15 (m, 15 H, 3 Ph). Anal. Calcd for $C_{27}H_{26}O_7$: C, 70.12; H, 5.67. Found: C, 69.71; H, 5.65.

Benzyl β-L-rhamnopyranoside (**5**).—A solution of the above mixture of **2**–**4** (9.44 g, 20.4 mmol) in MeOH (50 mL) was treated with 2 M CH_3ONa (1 mL) for 5 h at 40 °C. The mixture was neutralized with Amberlite IR-120 (H^+), filtered, and the filtrate was concentrated. The residue was chromatographed (1:1 toluene–acetone) to yield **5** (4.40 g, 85%): mp 107–108 °C (EtOAc–hexane); $[\alpha]_D$ +103° (*c* 1.7). ^{1}H NMR ($CDCl_3$ + D_2O): δ, 1.33 (d, 3 H, $J_{5,6}$ 6.0 Hz, H-6), 3.16 (dq, 1 H, H-5), 3.34 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.42 (t, 1 H, $J_{4,5}$ 8.9 Hz, H-4), 3.89 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 4.36 (s, 1 H, H-1), 4.55, 4.84 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 7.23–7.34 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.43; H, 7.04.

Benzyl 2,4-di-O-acetyl-β-L-rhamnopyranoside (**6**).—*p*-Toluenesulfonic acid monohydrate (190 mg, 1 mmol) was added to a solution of **5** (8.86 g, 34.9 mmol) and trimethyl orthoacetate (13.2 mL, 105 mmol) in CH_3CN (100 mL), and the mixture was stirred for 30 min. Py (5 mL) was added, and the solvent was evaporated. The residue was dissolved in py (60 mL) and treated with Ac_2O (20 mL) overnight. The excess of Ac_2O was destroyed by adding water at 0 °C, the resulting mixture was diluted with $CHCl_3$, washed successively with water, M HCl, satd aq $NaHCO_3$, and water. The solvent was evaporated, and the residue was treated with 80%

aq AcOH (50 mL) for 15 min. The mixture was concentrated, and residual AcOH was coevaporated with toluene. Column chromatography of the residue (1:1 toluene–EtOAc) gave **6** (8.68g, 73.5%): mp 141–143 °C (EtOAc–hexane); $[\alpha]_D$ +64.5° (*c* 1.8). ^{1}H NMR: δ, 1.32 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 2.12, 2.21 (2 s, 6 H, 2 CH_3CO), 2.48 (d, 1 H, $J_{3,OH}$ 7.3 Hz, OH), 3.46 (dq, 1 H, H-5), 3.75 (ddd, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 4.57 (s, 1 H, H-1), 4.65, 4.90 (2 d, 2 H, J_{gem} 12.0 Hz, PhCH_2), 4.84 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.43 (d, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 7.29–7.38 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{22}O_7$: C, 60.34; H, 6.55. Found: C, 60.43; H, 6.63.

Benzyl 3,4-anhydro-6-deoxy-β-L-altropyranoside (**8**).—A solution of trifluoromethanesulfonic anhydride (Tf_2O) (8.4 mL, 50 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C to a solution of **6** (10.2 g, 30.2 mmol) and py (7.27 mL, 90 mmol) in CH_2Cl_2 (100 mL), and the mixture was stirred at the same temperature for 45 min. The solution was diluted with $CHCl_3$, washed successively with ice-cold water, M HCl, and water, and concentrated. The crude triflate **7** was dissolved in MeOH (70 mL) and treated with 2 M CH_3ONa (30 mL) for 30 min at rt. The solution was neutralised with AcOH, taken to dryness, and the residue was distributed between water and $CHCl_3$. The organic layer was separated, and the water layer was extracted twice with $CHCl_3$. The combined organic solution was concentrated, and the residue was subjected to column chromatography (3:2 toluene–EtOAc) to give **8** (5.66 g, 79%) as a syrup: $[\alpha]_D$ +87° (*c* 2.6). ^{1}H NMR: δ 1.47 (d, 3 H, $J_{5,6}$ 7.0 Hz, H-6), 2.63 (br, s, 1 H, OH), 3.04 (d, 1 H, H-4), 3.44 (dd, 1 H, $J_{3,4}$ 3.9 Hz, H-3), 4.02 (t, 1 H, $J_{2,3}$ 1.7 Hz, H-2), 4.07 (q, 1 H, H-5), 4.54 (d 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.58, 4.89 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 7.27–7.42 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.13; H, 6.95.

Conventional acetylation of **8** with Ac_2O in py afforded 2-acetate **9**. ^{1}H NMR: δ 1.50 (d, 3 H, $J_{5,6}$ 7.5 Hz, H-6), 2.17 (s, 3 H, CH_3CO), 3.07 (d, 1 H, H-4), 3.39 (dd, 1 H, $J_{3,4}$ 4.0 Hz, H-3), 4.10 (q, 1 H, H-5), 4.57, 4.86 (2 d, 2 H, J_{gem} 13.2 Hz, PhCH_2), 4.64 (d, 1 H, $J_{1,2}$ 2.1 Hz, H-1), 5.25 (t, 1 H, $J_{2,3}$ 1.8 Hz, H-2), 7.25–7.38 (m, 5 H, Ph).

Benzyl 3,4-anhydro-2-azido-2,6-dideoxy-β-L-allopyranoside (**11**).—Compound **8** (5.66 g, 24 mmol) was treated with Tf_2O (6.71 mL, 40 mmol) in the presence of py (5.82 mL, 72 mmol) in CH_2Cl_2 (75 mL) as described in the preparation of **7**. The crude triflate **10** obtained was dissolved in DMF (50 mL), sodium azide (7.8 g, 120 mmol) was added, and the mixture was stirred for 1 h at rt. The mixture was diluted with EtOAc, washed thoroughly with water, dried with $MgSO_4$ and concentrated. Column chromatography of the residue (85:15 light petroleum–EtOAc) gave **11** (5.22 g, 83%): mp 52–54 °C (hexane); $[\alpha]_D$ +78° (*c* 1.1). ^{1}H NMR: δ 1.44 (d, 3 H, $J_{5,6}$ 6.8 Hz, H-6), 3.17 (d, 1 H, H-4), 3.45 (dd, 1 H, $J_{3,4}$ 4.2 Hz, H-3), 3.69 (dd, 1 H, $J_{2,3}$ 2.2 Hz, H-2), 4.08 (q, 1 H, H-5), 4.58 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.62, 4.87 (2 d, 2 H, J_{gem} 11.4 Hz, PhCH_2), 7.29–7.41 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{15}N_3O_3$: C, 59.76; H, 5.79; N, 16.08. Found: C, 59.64; H, 5.80; N, 16.00.

Benzyl 2,4-diazido-2,4,6-trideoxy-β-L-gulopyranoside (**12**).—A solution of sodium azide (6.7 g, 103 mmol) and ammonium chloride (5.51 g, 103 mmol) in water (25 mL) was added to a solution of **11** (5.38 g, 20.6 mmol) in EtOH (100 mL). The mixture was boiled under reflux for 7 h, EtOH was distilled off, and the remaining aqueous solution was extracted three times with $CHCl_3$. The combined extract was concentrated, and the residue was subjected to column chromatography (92:8 toluene–EtOAc) to yield **12** (5.40 g, 86%) as a syrup: $[\alpha]_D$ +63° (*c* 2). ^{1}H NMR: δ 1.37 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6), 2.47 (s, 1 H, OH), 3.47 (dd, 1 H, $J_{4,5}$ 1.3 Hz, $J_{3,4}$ 3.4 Hz, H-4), 3.66 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 4.14 (m, 2 H, H-3,5), 4.67, 4.96 (2 d, 2 H, J_{gem} 11.8 Hz, PhCH_2), 4.77 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 7.30–7.41 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{16}N_6O_3$: C, 51.31; H, 5.30; N, 27.62. Found: C, 51.44; H, 5.35; N, 27.63.

Conventional acetylation of **12** with Ac_2O in py gave 3-acetate **13**. ^{1}H NMR: δ 1.38 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6), 2.05 (s, 3 H, CH_3CO), 3.48 (dd, 1 H, $J_{4,5}$ 1.7 Hz, H-4), 3.69 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 4.03 (dq, 1 H, H-5), 4.69, 4.96 (2 d, 2 H, J_{gem} 11.8 Hz, PhCH_2), 4.79 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 5.33 (t, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 7.30–7.42 (m, 5 H, Ph).

Benzyl 2,4-diacetamido-2,4,6-trideoxy-β-L-gulopyranoside (**14**).—20% $Pd(OH)_2/C$ (950 mg) was added to a solution of **12** (3.77 g, 12.4 mmol) in MeOH (60 mL), and the mixture was stirred vigorously in a hydrogen atmosphere for 2.5 h at 30–32 °C. The catalyst was filtered through Celite, washed with MeOH, and the combined filtrate and washings were concentrated to a volume of ~20 mL. Ac_2O (6 mL) was added, and the solution was kept for 1 h and evaporated. Residual Ac_2O was removed by coevaporation with toluene, and the residue was chromatographed (95:5 chloroform–MeOH) to give **14** (3.48 g, 84%) as an amorphous solid: $[\alpha]_D$ +46.5° (*c* 3). ^{1}H NMR ($CDCl_3 + D_2O$): δ 1.17 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6), 1.96, 2.02 (2 s, 6 H, CH_3CO), 3.87 (t, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 3.98 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.05 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 4.20 (dq, 1 H, H-5), 4.56, 4.86 (2 d, 2 H, J_{gem} 12.5 Hz, PhCH_2), 4.58 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 7.28–7.37 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{24}N_2O_5 \cdot 0.5 H_2O$: C, 59.11; H, 7.29; N, 8.11. Found: C, 59.28; H, 7.36; N, 8.45.

2,4-Diacetamido-2,4,6-trideoxy-L-gulopyranose (**15**).—A solution of **14** (4.45 g, 13.2 mmol) in MeOH (60 mL) was stirred with 20% $Pd(OH)_2/C$ (1 g) under hydrogen for 4 h at 32–34 °C, filtered through Celite, (Caution: Extreme fire hazard) and concentrated. Column chromatography of the residue (94:6 $CHCl_3$–MeOH) gave **15** (3.20g, 94%): mp 144–146 °C (MeOH–ether); $[\alpha]_D$ +6.3° → +78° (*c* 1.6, MeOH). ^{1}H NMR (D_2O): **15α**, δ 1.16 (d, 3 H[†], $J_{5,6}$ 6.6 Hz, H-6), 2.06, 2.07 (2 s, 6 H, 2 CH_3CO), 3.91 (t, 1 H, $J_{3,4}$ 3.8 Hz, H-3), 3.95 (dd, 1 H, $J_{4,5}$ 1.7 Hz, H-4), 4.11 (t, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 4.62 (dq, 1 H, H-5), 5.15 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1); **15β**, δ 1.18 (d, 3 H*, $J_{5,6}$ 6.5 Hz, H-6), 2.04, 2.08 (2 s, 6 H, 2 CH_3CO), 3.85 (dd, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 3.87 (dd, 1 H, $J_{4,5}$ 1.6 Hz, H-4), 3.94 (t, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 4.29 (dq, 1 H, H-5), 4.94 (d, 1 H, $J_{1,2}$ 8.9 Hz, H-1). The ratio **15α**:**15β** ≈ 1:5. Anal. Calcd for $C_{10}H_{18}N_2O_5 \cdot 0.25 H_2O$: C, 47.60; H, 7.39; N, 11.10. Found: C, 47.59; H, 7.50; N, 11.49.

[†] Integral intensities of signals for the compounds **15**, **32**, and **48** are given within anomeric series.

Benzyl 2-azido-3-O-benzyl-2-deoxy-β-D-mannopyranoside (**17**).—Pyridinium perchlorate (1.14 g, 6.34 mmol) was added to a solution of **16** (3.00 g, 6.34 mmol) in 90% aq CH_3CN (30 mL), and the mixture was heated at 80 °C for 4 h. Py (0.5 mL) was added, and the solvent was evaporated. The residue was distributed between water (50 mL) and $CHCl_3$ (50 mL), the organic layer was separated, and the water layer was extracted with $CHCl_3$ (3 × 50 mL). The combined extract was concentrated, and the residue was subjected to column chromatography (3:2 toluene–EtOAc) to give **17** (2.37 g, 97%) as a syrup: $[\alpha]_D$ −106° (*c* 1, $CHCl_3$). ^{1}H NMR: δ 3.26 (ddd, 1 H, H-5), 3.46 (dd, 1 H, $J_{3,4}$ 9.2 Hz, H-3), 3.82 (dd, 1 H, $J_{5,6a}$ 4.9 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.87 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.92 (dd, 1 H, $J_{5,6b}$ 3.7 Hz, H-6b), 3.95 (d, 1 H, $J_{2,3}$ 3.6 Hz, H-2), 4.56 (br. s, 1 H, H-1), 4.61, 4.74 (2 d, 2 H, J_{gem} 11.7 Hz, PhCH_2), 4.64, 4.94 (2 d, 2 H, J_{gem} 12.2 Hz, PhCH_2), 7.30–7.42 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{23}N_3O_5$: C, 62.32; H, 6.02; N, 10.90. Found: C, 62.46; H, 5.92; N, 10.85.

Benzyl 2-azido-3-O-benzyl-2-deoxy-6-O-tosyl-β-D-mannopyranoside (**18**).—*p*-Toluenesulfonyl chloride (1.72 g, 9.04 mmol) was added at 0 °C to a solution of **17** (2.32 g, 6.02 mmol) in py (15 mL). The stirred mixture was allowed to warm to rt for 1.5 h, and stirring was continued for the next 2 h. The reaction was quenched by adding water, the resulting mixture was diluted with $CHCl_3$, washed successively with water, M HCl, and water, and concentrated. Column chromatography of the residue (9:1 toluene–EtOAc) yielded **18** (2.86 g, 88%) as a syrup: $[\alpha]_D$ −79.6° (*c* 2, $CHCl_3$). ^{1}H NMR: δ 2.41 (s, 3 H, C$H_3C_6H_4$), 2.47 (br. s, 1 H, OH), 3.39 (dd, 1 H, $J_{3,4}$ 9.1 Hz, H-3), 3.42 (ddd, 1 H, H-5), 3.70 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.94 (d, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 4.23 (dd, 1 H, $J_{5,6a}$ 6.6 Hz, $J_{6a,6b}$ 10.9 Hz, H-6a), 4.43 (dd, 1 H, $J_{5,6b}$ 1.7 Hz, H-6b), 4.48 (s, 1H, H-1), 4.56 (d, 2 H, J_{gem} 11.8 Hz, PhCH_2), 4.73 (d, 1 H, J_{gem} 11.7 Hz, PhCH_2), 4.86 (d, 1 H, J_{gem} 12.0 Hz, PhCH_2), 7.30–7.84 (m, 14 H, 2 Ph, $CH_3C_6$$H_4$). Anal. Calcd for $C_{27}H_{29}N_3O_7S$: C, 60.10; H, 5.42; N, 7.79. Found: C, 59.89; H, 5.57; N, 8.03.

*Benzyl 2-azido-3-*O*-benzyl-2,6-dideoxy-6-iodo-β-*D*-mannopyranoside* (**19**).—A solution of **18** (2.76 g, 5.12 mmol) and sodium iodide (3.84 g, 25.6 mmol) in CH_3CN (30 mL) was heated with stirring at 80–85 °C for 7 h. The solvent was evaporated, and a suspension of the residue in $CHCl_3$ was washed successively with water, M $Na_2S_2O_3$, and water, and then concentrated. The residue was chromatographed (95:5 toluene–EtOAc) to give **19** (2.42 g, 96%) as a syrup: $[\alpha]_D$ −77.3° (*c* 2, $CHCl_3$). ^{1}H NMR: δ 3.22 (dt, 1 H, H-5), 2.46 (d, 1 H, $J_{4,OH}$ 1.5 Hz, OH), 3.30 (t, 1 H, $J_{5,6a}$ 9.1 Hz, $J_{6a,6b}$ 10.4 Hz, H-6a), 3.39 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 3.64 (dt, 1 H, $J_{4,5}$ 8.9 Hz, H-4), 3.65 (dd, 1 H, $J_{5,6b}$ 1.8 Hz, H-6b), 3.97 (d, 1 H, $J_{2,3}$ 3.4 Hz, H-2), 4.53, 4.75 (2 d, 2 H, J_{gem} 11.6 Hz, PhCH_2), 4.54 (s, 1 H, H-1), 4.75, 5.02 (2 d, 2 H, J_{gem} 12.1 Hz, PhCH_2), 7.33–7.45 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{22}IN_3O_4$: C, 48.50; H, 4.48; N, 8.48. Found: C, 48.23; H, 4.47; N, 8.18.

*Benzyl 2-acetamido-3-*O*-benzyl-2,6-dideoxy-β-*D*-mannopyranoside* (**20**).—A solution of **19** (2.50 g, 5.05 mmol) and *N*,*N*-diisopropylethylamine (1.75 mL, 10.1 mmol) in MeOH (25 mL) was stirred with 20% $Pd(OH)_2/C$ (1 g) under hydrogen at 32 °C for 6 h. The catalyst was filtered off through Celite and washed with MeOH, and the combined filtrate and washings were treated with Dowex 1 × 8 (HCO_3^-) anion-exchange resin, filtered, and concentrated. Ac_2O (2.5 mL) was added to a solution of the residue in MeOH (25 mL), and the mixture was kept overnight at rt. The solvent was evaporated, Ac_2O was removed by coevaporation with toluene, and the residue was subjected to column chromatography (85:15 toluene–acetone) to give **20** (1.63 g, 84%) as a foam: $[\alpha]_D$ −116° (*c* 1, $CHCl_3$). ^{1}H NMR: δ 1.49 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 2.08 (s, 3 H, CH_3CO), 3.27 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 3.32 (dq, 1 H, H-5), 3.35 (dd, 1 H, $J_{3,4}$ 9.1 Hz, H-3), 4.39, 4.93 (2 d, 2 H, J_{gem} 10.9 Hz, PhCH_2), 4.54 (s, 1 H, H-1), 4.63, 4.86 (2 d, 2 H, J_{gem} 12.2 Hz, PhCH_2), 4.84 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 5.74 (d, 1 H, $J_{NH,2}$ 9.5 Hz, NH), 7.27–7.39 (m, 10 H, 2 Ph). Anal. Calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.65; H, 7.11; N, 3.52.

*Benzyl 2-acetamido-3-*O*-benzyl-2,6-dideoxy-β-*D*-lyxo-hexopyranoside-4-ulose, oxime* (**22**).—A solution of DMSO (0.97 mL, 13.6 mmol) in CH_2Cl_2 (4 mL) was added at −60 °C to a solution of oxalyl chloride (0.54 mL, 6.19 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 0.5 h while the temperature gradually increased to −30 °C. After cooling to −60 °C, a solution of **20** (1.59 g, 4.13 mmol) in CH_2Cl_2 (15 mL) was added dropwise, the mixture was stirred at −60 °C for 45 min, and then *N*,*N*-diisopropylethylamine (5.3 mL) was added. The mixture was allowed to warm to −20 °C, diluted with $CHCl_3$, washed with M HCl, water, and concentrated. The residue was passed through a short column with silica gel in (85:15) toluene–acetone, and the eluate was concentrated to afford **21**. Hydroxylamine hydrochloride (565 mg, 8.1 mmol) was added to a solution of the ketone **21** in a mixture of CH_2Cl_2 (12 mL) and py (9 mL), and the solution was stirred at rt overnight. The mixture was diluted with $CHCl_3$, and washed with water, and the water phase was extracted twice with $CHCl_3$. The combined organic extract was concentrated, and the residue was chromatographed (3:2 toluene–acetone) to give **22** (1.59 g, 97%) as a mixture of isomers in a ratio of ∼ 8:1. Crystallization from ether–light petroleum gave the major isomer: mp 127–129 °C, $[\alpha]_D$ −35° (*c* 1, $CHCl_3$). ^{1}H NMR: δ 1.64 (d, 3 H, $J_{5,6}$ 7.1 Hz, H-6), 2.00 (s, 3 H, CH_3CO), 4.28 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 4.47 (ddd, 1 H, $J_{2,3}$ 4.3 Hz, H-2), 4.30, 5.01 (2 d, 2 H, J_{gem} 12.0 Hz, PhCH_2), 4.51, 4.67 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 4.92 (d, 1 H, H-3), 5.29 (q, 1 H, H-5), 6.45 (d, 1 H, $J_{NH,2}$ 9.6 Hz, NH), 7.25–7.38 (m, 10 H, 2 Ph). Anal. Calcd for $C_{22}H_{26}N_2O_5$: C, 66.31; H, 6.58; N, 7.03. Found: C, 66.40; H, 6.54; N, 6.88.

*Benzyl 2,4-diacetamido-3-*O*-benzyl-2,4,6-trideoxy-β-*D*-talopyranoside* (**23**) *and benzyl 2,4-diacetamido-3-*O*-benzyl-2,4,6-trideoxy-β-*D*-mannopyranoside* (**24**).—Sodium borohydride (1.55 g, 40.7 mmol) was added portionwise to a solution of **22** (1.62 g, 4.07 mmol) and $NiCl_2 \cdot 6H_2O$ (1.94 g, 8.14 mmol) in MeOH (50 mL) at −35 °C over 0.5 h. The mixture was stirred at the same temperature for 0.5 h and quenched by adding satd aq

$NaHCO_3$ (50 mL). The bulk of the MeOH was evaporated, and the remaining aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined extract was concentrated, and the residue was acetylated with Ac_2O (1.5 mL) in MeOH (20 mL) overnight. The solvent was evaporated, the Ac_2O was coevaporated with toluene, and the residue was subjected to column chromatography (95:5 $CHCl_3$–MeOH) to yield a mixture of **23** and **24**. Individual **23** (1.39 g, 80%) and **24** (130 mg, 8%) were isolated by preparative HPLC on a Zorbax SIL (250 × 21 mm) column (DuPont) in 97:3 EtOAc–MeOH.

Compound **23**: mp 158–159 °C (MeOH–Et_2O), $[\alpha]_D$ −49.4° (*c* 1, $CHCl_3$). ^1H NMR (toluene-d_8, 333 K): δ 1.50 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 1.98, 2.00 (2 s, 6 H, 2 CH_3CO), 3.53 (poorly resolved q, 1 H, H-5), 3.61 (poorly resolved t, 1 H, $J_{2,3}$ ~ $J_{3,4}$ ~ 2 Hz, H-3), 4.60 (s, 1 H, H-1), 4.62 (unresolved, 1 H, H-4), 4.69, 4.98 (2 d, 2 H, J_{gem} 12.0 Hz, $PhCH_2$), 4.79 (unresolved, 1 H, H-2), 4.81 (s, 2 H $PhCH_2$), 6.18 (unresolved, 1 H, NH), 6.44 (unresolved, 1 H, NH), 7.33–7.73 (m, 10 H, 2 Ph). Anal. Calcd for $C_{24}H_{30}N_2O_5$: C, 67.58; H, 7.09; N, 6.57. Found: C, 67.44; H, 7.07; N, 6.56.

Compound **24** was obtained as a foam: $[\alpha]_D$ −109.5° (*c* 1, $CHCl_3$). ^1H NMR (C_6D_6): δ 1.37 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.68, 1.70 (2 s, 6 H, 2 CH_3CO), 3.02 (dq, 1 H, H-5), 3.15 (dd, 1 H, $J_{3,4}$ 10.3 Hz, H-3), 3.94 (q, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 4.35 (s, 1 H, H-1), 4.43, 4.84 (2 d, 2 H, J_{gem} 12.2 Hz, $PhCH_2$), 4.57, 4.94 (2 d, 2 H, J_{gem} 12.2 Hz, $PhCH_2$), 4.86 (d, 1 H, $J_{NH,4}$ 8.9 Hz, NH-4), 5.09 (dd, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 6.29 (d, 1 H, $J_{NH,2}$ 9.7 Hz, NH-2), 7.08–7.39 (m, 10 H, 2 Ph). Anal. Calcd for $C_{24}H_{30}N_2O_5$: C, 67.58; H, 7.09; N, 6.57. Found: C, 66.86; H, 6.96; N, 6.69.

2,4-Diacetamido-2,4,6-trideoxy-D-talose (**25**).—A solution of **23** (1.24 g, 2.91 mmol) in MeOH (20 mL) and water (10 mL) was stirred with 20% $Pd(OH)_2$/C (500 mg) under hydrogen for 6 h at rt. The catalyst was filtered through Celite, and washed with MeOH, (Caution: Extreme fire hazard), the combined filtrate and washings were concentrated, and the residue was subjected to column chromatography (85:15 $CHCl_3$–MeOH) to give **25** (630 mg, 88%) as an amorphous solid: $[\alpha]_D$ + 23.6° → + 15.3° (*c* 1, water). For ^1H and ^{13}C NMR data see Table 1. Anal. Calcd for $C_{10}H_{18}N_2O_5$: C, 48.77; H, 7.37; N, 11.38. Found: C, 48.98; H, 7.57; N, 11.42.

Benzyl 3-O-benzoyl-β-D-fucopyranoside (**27**).—A mixture of **26** (2.22 g, 8.74 mmol) and Bu_2SnO (2.29 g, 9.18 mmol) in benzene (40 mL) was boiled with stirring and azeotropic removal of water for 5 h, then 15 mL benzene was distilled off from the mixture. The remaining solution was cooled to 0 °C and benzoyl chloride (1.12 mL, 9.61 mmol) was added. After stirring at 0–5 °C for 2 h, MeOH (0.5 mL) and py (0.5 mL) were added to destroy the excess benzoyl chloride. After being stirred for 0.5 h at rt, the mixture was concentrated, and the residue was subjected to column chromatography (9:1 toluene–EtOAc) to give **27** (1.90 g, 61%): mp 97–98 °C (EtOAc–light petroleum); $[\alpha]_D$ + 12.5° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.38 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 2.11, 2.34 (2 br. s, 2 H, 2 OH), 3.76 (q, 1 H, H-5), 3.96 (d, 1 H, H-4), 4.03 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2), 4.47 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.65, 4.99 (2 d, 2 H, J_{gem} 11.7 Hz, $PhCH_2$), 5.07 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 7.32–8.11 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 66.92; H, 6.29.

Benzyl 2,4-diazido-3-O-benzoyl-2,4,6-trideoxy-β-D-mannopyranoside (**29**).—Tf_2O (3.10 mL, 18.5 mmol) was added dropwise at 0 °C to a solution of **27** (2.20 g, 6.14 mmol) and py (2.98 mL, 36.8 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred at 0 °C for 1 h, diluted with $CHCl_3$, washed successively with water, M HCl, and water, and concentrated. The crude ditriflate **28** obtained was dissolved in toluene (40 mL) and tetrabutylammoniun azide (10.45 g, 36.8 mmol) was added. The mixture was stirred for 1 h at 65–70 °C and then for 1.5 h at 100–105 °C, cooled, diluted with toluene, washed twice with water, and concentrated. Column chromatography of the residue (7:3 toluene–light petroleum) gave **29** (2.12 g, 85%) as a syrup, $[\alpha]_D$ −46.1° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.59 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 3.40 (dq, 1 H, H-5), 3.77 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 4.36 (d, 1 H, $J_{2,3}$ 3.6 Hz, H-2), 4.77, 5.09 (2 d, 2 H, J_{gem} 12.1 Hz, $PhCH_2$), 4.77 (s, 1 H, H-1), 5.14 (dd, 1 H, $J_{3,4}$ 10.1 Hz, H-3), 7.40–8.23 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{20}N_6O_4$: C, 58.81; H, 4.94; N, 20.58. Found: C, 59.18; H, 5.05; N, 20.61.

Benzyl 2,4-diacetamido-2,4,6-trideoxy-β-D-mannopyranoside (**31**).—A solution of **29** (2.12 g, 5.20 mmol) in MeOH (20 mL) was treated with 2 M sodium methoxide in MeOH (1 mL) for 1 h at rt. The solution was neutralised by adding Amberlite IR-120 (H^+ form) ion-exchange resin, and filtered, and the filtrate was concentrated. A solution of crude **30** in MeOH (30 mL) was stirred with 20% $Pd(OH)_2/C$ (400 mg) at 30 °C under hydrogen for 1.5 h. The catalyst was filtered off through Celite, washed with MeOH, and the combined filtrate and washings were concentrated to a volume of ~20 mL, then Ac_2O (2 mL) was added. After being kept for 1 h at rt, the mixture was evaporated to dryness, and the residue was subjected to column chromatography (97:3 $CHCl_3$–MeOH) to yield **31** (1.51 g, 86%) as a foam: $[\alpha]_D$ −25.2° (*c* 1, $CHCl_3$). ^{1}H NMR ($C_6D_6 + CD_3OD$): δ 1.40 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.86, 1.96 (2 s, 6 H, 2 CH_3CO), 3.32 (dq, 1 H, H-5), 3.83 (dd, 1 H, $J_{3,4}$ 10.5 Hz, H-3), 3.95 (t, 1 H, $J_{4,5}$ 10.1 Hz, H-4), 4.50, 4.80 (2 d, 2 H, J_{gem} 12.0 Hz, PhCH_2), 4.54 (s, 1 H, H-1), 4.73 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 7.07–7.43 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{24}N_2O_5$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.79; H, 7.24; N, 8.36.

2,4-Diacetamido-2,4,6-trideoxy-D-mannopyranose (**32**).—A mixture of **31** (1.35 g, 4.02 mmol) and 20% $Pd(OH)_2/C$ (400 mg) in MeOH (25 mL) was stirred at 32 °C in hydrogen atmosphere for 2 h. The catalyst was filtered through Celite, washed with MeOH, (Caution: Extreme fire hazard), and the combined filtrate and washings were concentrated. The residue was chromatographed (85:15 $CHCl_3$–MeOH) to give **32** (840 mg, 85%) as an amorphous solid: $[\alpha]_D$ +38.1° (*c* 1, water). ^{1}H NMR (D_2O): **32α**, δ 1.19 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6), 2.04, 2.08 (2 s, 6 H, 2 CH_3CO), 3.78 (t, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 3.97 (dq, 1 H, H-5), 4.07 (dd, 1 H, $J_{3,4}$ 10.8 Hz, H-3), 4.30 (dd, 1 H, $J_{2,3}$ 4.6 Hz, H-2), 5.11 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1). **32β**, δ 1.23 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 2.03, 2.12 (2 s, 6 H, 2 CH_3CO), 3.51 (dq, 1 H, H-5), 3.67 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.84 (dd, 1 H, $J_{3,4}$ 10.8 Hz, H-3), 4.47 (dd, 1 H, $J_{2,3}$ 4.3 Hz, H-2), 4.96 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1). The ratio **32α**:**32β** ≈55:45. Anal. Calcd for $C_{10}H_{18}N_2O_5 \cdot 0.5H_2O$: C, 47.05; H, 7.50; N, 10.97. Found: C, 47.21; H, 7.74; N, 11.12.

Benzyl 2,3-O-isopropylidene-β-L-rhamnopyranoside (**33**).—*p*-Toluenesulfonic acid monohydrate (190 mg, 1 mmol) was added to a solution of **5** (6.20 g, 24.4 mmol) and 2,2-dimethoxypropane (18.5 mL, 150 mmol) in acetone (50 mL), and the mixture was kept for 1 h at rt. A few drops of Et_3N were added, the solvent was evaporated, and a solution of the residue in $CHCl_3$ was washed twice with water and concentrated. The residue was crystallized from EtOAc–light petroleum to give 5.77 g of **33**. An additional portion of the product (1.17 g) was obtained by column chromatography (4:1 toluene–EtOAc) of the mother liquor. Total yield of **33** was 6.49 g (97%), mp 97–98 °C, $[\alpha]_D$ +142.6° (*c* 1, $CHCl_3$). ^{1}H NMR: δ 1.38 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 1.40, 1.58 (2 s, 6 H, isopropylidene), 2.61 (d, 1 H, $J_{OH,4}$ 3.1 Hz, OH), 3.27 (dq, 1 H, H-5), 3.56 (ddd, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.99 (t, 1 H, $J_{3,4}$ 6.4 Hz, H-3), 4.20 (dd, 1 H, $J_{2,3}$ 5.6 Hz, H-2), 4.71 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.75, 4.97 (2 d, 2 H, J_{gem} 12.5 Hz, PhCH_2), 7.29–7.40 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.32; H, 7.50.

Benzyl 6-deoxy-2,3-O-isopropylidene-β-L-talopyranoside (**35**).—A solution of DMSO (4.60 mL, 64.7 mmol) in CH_2Cl_2 (10 mL) was added at −60 °C to a solution of oxalyl chloride (2.57 mL, 29.4 mmol) in CH_2Cl_2 (40 mL) and the mixture was stirred for 20 min while the temperature gradually increased to −40 °C. After cooling to −60 °C, a solution of **33** (5.77 g, 19.6 mmol) in CH_2Cl_2 (50 mL) was added dropwise, the mixture was stirred at −60 °C for 45 min, then *N*,*N*-diisopropylethylamine (17.4 mL) was added. The mixture was allowed to warm to −20 °C, diluted with $CHCl_3$, washed with M HCl, water, and concentrated to yield ketone **34**. $NaBH_4$ (760 mg, 20 mmol) was added at 0 °C to a solution of crude **34** in 80% aq EtOH (60 mL) and the mixture was stirred for 20 min. The reduction was quenched by adding acetone, the solvent was evaporated, and a solution of the residue in $CHCl_3$ was washed with M HCl, water, and concentrated. Column chromatography of the residue (85:15 toluene–EtOAc) afforded **35** (5.44 g, 94%), mp 69–70 °C (ether–hexane), $[\alpha]_D$ +108.6° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.40 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.42, 1.63 (2 s, 6 H, isopropylidene), 2.81 (d, 1 H, $J_{OH,4}$ 9.8 Hz, OH), 3.50 (q, 1 H, H-5), 3.60 (dd, 1 H, H-4), 4.16 (dd, 1 H, $J_{2,3}$ 6.3 Hz, H-2), 4.21 (t, 1 H, $J_{3,4}$ 5.6 Hz, H-3), 4.72 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1), 4.77, 4.97 (2 d, 2 H, J_{gem} 12.3 Hz, PhCH_2), 7.30–7.43 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.35; H, 7.47.

Benzyl 6-deoxy-β-L-talopyranoside (**36**).—A solution of **35** (925 mg, 3.15 mmol) in 80% aq AcOH (10 mL) was heated at 40 °C for 1.5 h. The solvent was coevaporated several times with toluene, and the residue was subjected to column chromatography (4:1 toluene–acetone) to give **36** (795 mg, 99%): mp 86–88 °C (EtOAc–light petroleum), $[\alpha]_D$ +89.4° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.40 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6), 3.45 (q, 1 H, H-5), 3.48 (t, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.53 (d, 1 H, H-4), 3.95 (d, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 4.38 (s, 1 H, H-1), 4.68, 4.96 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 7.30–7.38 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.34; H, 7.04.

Benzyl 3-O-benzoyl-6-deoxy-β-L-talopyranoside (**37**).—A mixture of **36** (302 mg, 1.19 mmol) and Bu_2SnO (311 mg, 1.25 mmol) in benzene (20 mL) was boiled with stirring and azeotropic removal of water for 2.5 h, then 10 mL benzene was distilled from the mixture. The remaining solution was cooled to 0 °C, and benzoyl chloride (152 μl, 1.31 mmol) was added. After stirring at 0–5 °C for 45 min, MeOH (0.1 mL) and py (0.1 mL) were added to destroy the excess of benzoyl chloride. After being stirred for 0.5 h at rt, the mixture was concentrated, and the residue was subjected to column chromatography (85:15 toluene–EtOAc) to give **37** (334 mg, 78%): mp 100–102 °C (ether–light petroleum); $[\alpha]_D$ + 27.1° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.43 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.60 (q, 1 H, H-5), 3.78 (d, 1 H, H-4), 4.19 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 4.55 (s, 1H, H-1), 4.73, 4.99 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 4.94 (t, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 7.34–8.15 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 67.19; H, 6.06.

Benzyl 4-azido-4,6-dideoxy-2,3-O-isopropylidene-β-L-mannopyranoside (**41**).—Tf_2O (4.87 mL, 29 mmol) was added dropwise at 0 °C to a solution of **35** (4.27 g, 14.5 mmol) and py (11.7 mL, 145 mmol) in CH_2Cl_2 (40 mL), and the mixture was stirred for 3 h at the same temperature. After dilution with $CHCl_3$, the solution was washed successively with water, M HCl, and water, and concentrated to yield crude triflate **40**. Sodium azide (4.71g, 72.5 mmol) and dibenzo-18-crown-6 (130 mg, 0.36 mmol) were added to a solution of **40** in DMF (40 mL) and the resulting mixture was stirred overnight at rt. Most of the DMF was evaporated, and a suspension of the residue in EtOAc was washed twice with water, then with satd aq NaCl solution. The organic solution was dried with $MgSO_4$, and concentrated, and the residue was chromatographed (95:5 toluene–EtOAc) to give **41** (3.44 g, 74%): mp 95–96 °C (light petroleum); $[\alpha]_D$ +137.2° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.38 (d, 3 H, $J_{5,6}$ 6.0 Hz, H-6), 1.40, 1.62 (2 s, 6 H, isopropylidene), 3.17 (dq, 1 H, H-5), 3.34 (dd, 1 H, $J_{4,5}$ 10.3 Hz, H-4), 4.07 (dd, 1 H, $J_{3,4}$ 7.6 Hz, H-3), 4.17 (dd, 1 H, $J_{2,3}$ 5.5 Hz, H-2), 4.65 (d, 1 H, $J_{1,2}$ 2.1 Hz, H-1), 4.75, 4.97 (2 d, 2 H, J_{gem} 12.5 Hz, PhCH_2), 7.28–7.42 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{21}N_3O_4$: C, 60.17; H, 6.63; N, 13.16. Found: C, 59.92; H, 6.60; N, 13.30.

Benzyl 4-azido-4,6-dideoxy-β-L-mannopyranoside (**42**).—A solution of **41** (3.37 g, 10.56 mmol) in 80% aq AcOH (30 mL) was heated at 40 °C for 5 h. The solvent was evaporated and coevaporated several times with toluene. Column chromatography of the residue (7:3 toluene–EtOAc) gave **42** (2.79 g, 95%): mp 89–91 °C (Et_2O–light petroleum); $[\alpha]_D$ + 85.3° (*c* 1, $CHCl_3$). ^1H NMR: δ 1.41 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 2.71 (br s, 1 H, OH-2), 2.80 (d, 1 H, $J_{3,OH}$ 8.4 Hz, OH-3), 3.15 (dq, 1 H, H-5), 3.29 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.54 (m, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 3.97 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 4.44 (s, 1 H, H-1), 4.64, 4.92 (2 d, 2 H, J_{gem} 11.8 Hz, PhCH_2), 7.33–7.39 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{17}N_3O_4$: C, 55.90; H, 6.14; N, 15.05. Found: C, 56.02; H, 6.38; N, 15.24.

Benzyl 4-azido-3-O-benzoyl-4,6-dideoxy-β-L-mannopyranoside (**43**).—Diol **42** (3.25 g, 11.65 mmol) was subjected to Bu_2SnO-mediated benzoylation as described for **37**. After column chromatography of the reaction mixture (95:5 toluene–EtOAc), the monobenzoate **43** (3.98 g, 89%) was obtained as a syrup: $[\alpha]_D$ +126° (*c* 1, $CHCl_3$). ^{1}H NMR: δ 1.50 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 2.52 (broad s, 1 H, OH), 3.34 (dq, 1 H, H-5), 3.82 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 4.31 (broad s, 1 H, H-2), 4.59 (s, 1 H, H-1), 4.69, 4.94 (2 d, 2 H, J_{gem} 11.9 Hz, PhCH_2), 5.00 (dd, 1 H, $J_{3,4}$ 10.2 Hz, $J_{2,3}$ 2.6 Hz, H-3), 7.32–8.16 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{21}N_3O_5$: C, 62.65; H, 5.52; N, 10.96. Found: C, 62.74; H, 5.51; N, 11.00.

*Benzyl 2,4-diazido-3-*O*-benzoyl-2,4,6-trideoxy-β-*L*-glucopyranoside* (**39**).—Tf_2O (3.36 mL, 20 mmol) was added at 0 °C to a solution of **43** (3.84 g, 10.03 mmol) and py (4.04 mL, 40 mmol) in CH_2Cl_2 (40 mL), and the mixture was stirred at 0–5 °C for 1 h. The solution was diluted with $CHCl_3$, washed successively with water, M HCl, and water, and then concentrated. Crude triflate **44** was dissolved in DMF (30 mL), sodium azide (3.25 g, 50 mmol) was added, and the resulting mixture was stirred at rt overnight. The mixture was diluted with EtOAc, washed thoroughly with water, satd aq NaCl solution, dried with $MgSO_4$ and concentrated. Column chromatography of the residue (9:1 light petroleum–EtOAc) gave **39** (3.82 g, 93%): mp 91–92 °C (Et_2O–light petroleum); $[\alpha]_D$ −1.3° (*c* 1, $CHCl_3$). ^{1}H NMR: δ 1.47 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 3.35 (t, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 3.44 (dq, 1 H, H-5), 3.63 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2), 4.51 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.73, 4.97 (2 d, 2 H, J_{gem} 11.8 Hz, PhCH_2), 5.18 (t, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 7.33–8.15 (m, 10 H, 2 Ph). Anal. Calcd for $C_{20}H_{20}N_6O_4$: C, 58.81; H, 4.94; N, 20.58. Found: C, 58.91; H, 5.06; N, 20.61.

*Benzyl 2,4-diacetamido-2,4,6-trideoxy-β-*L*-glucopyranoside* (**45**).—Lithium aluminum hydride (2.00 g, 52.8 mmol) was added portionwise at 0 °C to a stirred solution of **39** (3.59 g, 8.80 mmol) in THF (60 mL). After completion of the exothermic reaction, the mixture was stirred for 1.5 h at rt. The excess of $LiAlH_4$ was destroyed by careful addition of water, then 5 M NaOH solution (150 mL) was added. The organic layer was separated, the aqueous layer was thoroughly extracted with Et_2O. The combined organic solution was dried with $MgSO_4$ and concentrated. The residue in MeOH (30 mL) was acetylated with Ac_2O (5 mL) overnight at rt. The crystalline precipitate was separated, washed with MeOH, and dried to give **45** (1.28 g). Column chromatography of the mother liquor (9:1 $CHCl_3$–MeOH) gave an additional portion of the product (0.72 g). The total yield of **45** was 2.00 g (68%): mp 302–307 °C (EtOH); $[\alpha]_D$ +55.1° (*c* 1, DMF). ^{1}H NMR ($CDCl_3$ + CD_3OD): δ 1.11 (d, 3 H, $J_{5,6}$ 5.8 Hz, H-6), 1.79, 1.83 (2 s, 6 H, 2 CH_3CO), 3.32 (dq, 1 H, H-5), 3.36 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.38 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.49 (t, 1 H, $J_{3,4}$ 9.9 Hz, H-3), 4.42, 4.71 (2 d, 2 H, J_{gem} 12.0 Hz, PhCH_2), 4.42 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 7.11–7.19 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{24}N_2O_5$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.60; H, 7.21; N, 8.37.

*Benzyl 2,4-diacetamido-2,4,6-trideoxy-3-*O*-mesyl-β-*L*-glucopyranoside* (**46**).—Methanesulfonyl chloride (1.68 mL, 21.7 mmol) was added at 0 °C to a suspension of **45** (1.82 g, 5.42 mmol) in CH_2Cl_2 (30 mL) and py (10 mL), and the mixture was stirred for 2 h at 0 °C, then overnight at rt. Water (100 mL) was added, and the two-phase solution was stirred for 2 h at rt. The organic layer was separated, the aqueous layer was extracted twice with $CHCl_3$, and the combined organic solution was concentrated to give 0.72 g of crude **46**. The aqueous solution was concentrated to a volume of ~30 mL and left at 5 °C overnight. The crystalline precipitate was filtered off and dried to give the second portion of **46**. Both portions of **46** were combined and subjected to column chromatography (95:5 $CHCl_3$–MeOH) to yield pure **46** (2.16 g, 96%): mp 187–189 °C (MeOH); $[\alpha]_D$ +43° (*c* 1, DMF). ^{1}H NMR ($CDCl_3$ + CD_3OD): δ 1.15 (d, 3 H, $J_{5,6}$ 5.7 Hz, H-6), 1.78, 1.83 (2 s, 6 H, 2 CH_3CO), 2.84 (s, 3 H, CH_3SO_2), 3.46–3.59 (m, 3 H, H-2,4,5), 4.45, 4.73 (2 d, 2 H, J_{gem} 12.1 Hz, PhCH_2), 4.64 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 4.85 (t, 1 H, $J_{2,3}$ ~ $J_{3,4}$ ~ 9.8 Hz, H-3), 7.13–7.21 (m, 5 H, Ph). Anal. Calcd for $C_{18}H_{26}N_2O_5S$: C, 52.16; H, 6.32; N, 6.76. Found: C, 52.13; H, 6.46; N, 6.47.

*Benzyl 2,4-diacetamido-2,4,6-trideoxy-β-*L*-allopyranoside* (**47**).—A mixture of **46** (2.10 g, 5.07 mmol) and AcONa (2.08 g, 25.4 mmol) in 95% aq 2-methoxyethanol (50 mL) was boiled under reflux for 2.5 h. The solvent was evaporated and a suspension of the residue in 85:15 $CHCl_3$–MeOH was filtered through a layer of silica gel. The filtrate was concentrated, and the residue was chromatographed (92:8 $CHCl_3$–MeOH) to give **47** (1.62 g, 95%): mp 301–305 °C (EtOH–Et_2O); $[\alpha]_D$ +47.6° (*c* 1, DMF). ^1H NMR ($C_6D_6 + CD_3OD$): δ 1.28 (d, 3 H, $J_{5,6}$ 5.8 Hz, H-6), 1.83, 1.84 (2 s, 6 H, 2 CH_3CO), 3.92 (dq, 1 H, H-5), 3.97 (dd, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 4.02 (t, 1 H, $J_{3,4}$ 2.3 Hz, H-3), 4.16 (dd, 1 H, $J_{2,3}$ 2.8 Hz, H-2), 4.51, 4.82 (2 d, 2 H, J_{gem} 12.0 Hz, $PhCH_2$), 4.87 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 7.08–7.28 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{24}N_2O_5$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.53; H, 7.13; N, 8.29.

2,4-Diacetamido-2,4,6-trideoxy-L-allopyranose (**48**).—20% $Pd(OH)_2/C$ (500 mg) was added to a solution of **47** (1.40 g, 4.17 mmol) in MeOH (50 mL), (Caution: Extreme fire hazard), and the mixture was stirred under hydrogen at 35 °C for 1 h. Water (10 mL) was added until complete dissolution of a white precipitate and formation of a clear solution over the catalyst, then hydrogenolysis was continued for another 1 h. The catalyst was filtered off through Celite, and washed with 80% aq MeOH, and the combined filtrate and washings were concentrated. Crystallization from water–EtOH–Et_2O gave **48** (890 mg, 87%): mp 235–242 °C; $[\alpha]_D$ −3.5° → −15.7° (*c* 1, water). ^1H NMR (D_2O): **48α**, δ 1.20 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 2.04, 2.06 (2s, 6 H, 2 CH_3CO), 3.79 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4), 3.96 (t, 1 H, $J_{3,4}$ 2.8 Hz, H-3), 4.05 (t, 1 H, $J_{2,3}$ 3.3 Hz, H-2), 4.18 (dq, 1 H, H-5), 5.15 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1). **48β**, δ 1.20 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 2.03, 2.04 (2 s, 6 H, 2 CH_3CO), 3.76 (dd, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 3.81 (dd, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 3.92 (dq, 1 H, H-5), 3.97 (t, 1 H, $J_{3,4}$ 2.9 Hz, H-3), 4.94 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1). The ratio **48α**:**48β** ≈ 1:3.3. Anal. Calcd for $C_{10}H_{18}N_2O_5$: C, 48.77; H, 7.37; N, 11.38. Found: C, 48.76; H, 7.41; N, 11.40.

5,7-Diacetamido-3,5,7,9-tetradeoxy-L-glycero-D-galacto- and L-glycero-D-talo-non-2-ulosonic acids (**49** and **50**).—Oxalacetic acid (165 mg, 1.25 mmol) was dissolved in water (4 mL), and the pH of the solution was adjusted to 10.5 by adding 5 M NaOH solution. Sodium tetraborate decahydrate (190 mg, 0.5 mmol) was added, and the pH was adjusted to 10.5 again. Then solid **15** (308 mg, 1.25 mmol) was added, and the resulting mixture was stirred at rt while the pH was maintained at 10.5 as above. More oxalacetic acid (42 mg, 0.31 mmol) was added after 6, 24, and 48 h. After being stirred for 72 h, the mixture was neutralized with Amberlite 420 (H^+), and filtered, and the filtrate was concentrated to a volume of 3–4 mL. The solution was applied to a column of Dowex 1 × 8 ($HCOO^-$), and the column was washed first with water to elute neutral products, then with 0.3 M formic acid. The appropriate fractions were pooled and concentrated, and the residue was subjected to preparative reversed-phase C_{18} HPLC to give **49** (75 mg, 18%), t_R 9.2 min, and **50** (84 mg, 20%), t_R 10.5 min, as amorphous solids. Acid **49** had $[\alpha]_D$ +15.4° (*c* 1.6, water). ESIMS (+): Calcd for $[M+Na]^+$ 357.1. Found 356.8. Compound **50** had $[\alpha]_D$ −19.2° (*c* 1.6, water). ESIMS (+): Calcd for $[M+Na]^+$ 357.1. Found 356.8. For ^1H and ^{13}C NMR data for **49** and **50**, see Tables 2 and 3.

5,7-Diacetamido-3,5,7,9-tetradeoxy-D-glycero-L-altro- and D-glycero-L-manno-non-2-ulosonic acids (**51** and **52**).—Hexose **25** (150 mg, 0.61 mmol) was allowed to react with oxalacetic acid in the presence of sodium tetraborate as described for **15**. Anion-exchange chromatography and reversed-phase HPLC of the condensation products afforded **52** (8 mg, 4%), t_R 8.5 min, $[\alpha]_D$ −39.0° (*c* 0.5, water), and **51** (57 mg, 28%), t_R 14.6 min, $[\alpha]_D$ −14.3° (*c* 1, water). ESIMS (+): Calcd for $[M+Na]^+$ 357.1. Found 357.0 for both **51** and **52**. For ^1H and ^{13}C NMR data see Tables 2 and 3.

5,7-Diacetamido-3,5,7,9-tetradeoxy-D-glycero-D-galacto- and D-glycero-D-talo-non-2-ulosonic acids (**53** and **54**).—Condensation of **32** (375 mg, 1.52 mmol) with oxalacetic acid was performed as described for **15**. After anion-exchange chromatography and reversed-phase HPLC, compounds **53** (36 mg, 7%), t_R 11.2 min, $[\alpha]_D$ +27.2° (*c* 1, water), and **54** (50 mg, 10%), t_R 13.0 min, $[\alpha]_D$ −12.5° (*c* 1, water), were obtained. ESIMS (−): Calcd for

$[M-H]^-$ 333.1. Found 332.9 for **53** and 333.1 for **54**. For ^1H and ^{13}C NMR data, see Tables 2 and 3.

*5,7-Diacetamido-3,5,7,9-tetradeoxy-*L*-glycero-*L*-altro-*, L*-glycero-*L*-manno-, and* L*-glycero-*L*-gluco-non-2-ulosonic acids* (**55**, **56**, and **57**).—Reaction of **48** (308 mg, 1.25 mmol) with oxalacetic acid, followed by anion-exchange chromatography and reversed-phase HPLC, afforded **56** (12 mg, 3%), t_R 8.5 min, $[\alpha]_D$ −56.9° (*c* 1, water), **57** (5 mg, 1%), t_R 12.5 min, $[\alpha]_D$ −76.0° (*c* 0.5, water), and **55** (34 mg, 8%), t_R 13.3 min, $[\alpha]_D$ −48.2° (*c* 1, water). ESIMS (−): Calcd for $[M-H]^-$ 333.1. Found 333.4 for **55** and 333.3 for both **56** and **57**. For ^1H and ^{13}C NMR data see Tables 2 and 3.

*Methyl (5,7-diacetamido-2,4,8-tri-*O*-acetyl-3,5,7,9-tetradeoxynon-2-ulopyranos)onates* (**62**–**65**).—Etheral diazomethane was added to solutions of acids **49**, **51**, **53**, and **55** (15–20 mg of each) in MeOH (0.5–0.7 mL) until a yellow colour in the solutions persisted. A drop of AcOH was added, and the mixtures were taken to dryness. The residues were subjected to reversed-phase C_{18} HPLC in aq MeOH (6–8%) to give esters **58**–**61** as amorphous solids.

Compound **58**: yield 52%; $[\alpha]_D$ +26.0° (*c* 1, water). ^1H NMR: δ 1.15 (d, 3 H, $J_{8,9}$ 6.3 Hz, H-9), 1.89 (dd, 1 H, $J_{3ax,4}$ 11.5 Hz, H-3ax), 1.98, 2.00 (2 s, 6 H, 2 CH_3CO), 2.30 (dd, 1 H, $J_{3eq,4}$ 4.9 Hz, $J_{3ax,3eq}$ 13.1 Hz, H-3eq), 3.71 (t, 1 H, $J_{5,6}$ 10.5 Hz, H-5), 3.83 (dq, 1 H, H-8), 3.86 (s, 3 H, CH_3O), 3.91 (dd, 1 H, $J_{7,8}$ 8.8 Hz, H-7), 3.97 (ddd, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 4.32 (dd, 1 H, $J_{6,7}$ 2.1 Hz, H-6).

Compound **59**: yield 35%; $[\alpha]_D$ −27.7° (*c* 0.4, water). ^1H NMR: δ 1.09 (d, 3 H, $J_{8,9}$ 6.4 Hz, H-9), 1.93 (dd, 1 H, $J_{3ax,4}$ 11.6 Hz, H-3ax), 2.05, 2.06 (2 s, 6 H, 2 CH_3CO), 2.34 (dd, 1 H, $J_{3eq,4}$ 4.7 Hz, $J_{3eq,3ax}$ 13.2 Hz, H-3eq), 3.84 (s, 3 H, CH_3O), 3.85 (t, 1 H, $J_{5,6}$ 10.3 Hz, H-5), 3.92 (dd, 1 H, $J_{6,7}$ 3.0 Hz, H-6), 3.93 (d, 1 H, H-7), 3.99 (ddd, 1 H, $J_{4,5}$ 11.3 Hz, H-4), 4.39 (q, 1 H, H-8).

Compound **60**: yield 57%; $[\alpha]_D$ +33.5° (*c* 1, water). ^1H NMR: δ 1.15 (d, 3 H, $J_{8,9}$ 6.3 Hz, H-9), 1.89 (dd, 1 H, $J_{3ax,4}$ 11.5 Hz, H-3ax), 1.98, 2.00 (2 s, 6 H, 2 CH_3CO), 2.30 (dd, 1 H, $J_{3eq,4}$ 4.9 Hz, $J_{3eq,3ax}$ 13.1 Hz, H-3eq), 3.71 (t, 1 H, $J_{5,6}$ 10.5 Hz, H-5), 3.83 (dq, 1 H, H-8), 3.86 (s, 3 H, CH_3O), 3.91 (dd, 1 H, $J_{7,8}$ 8.8 Hz, H-7), 3.97 (ddd, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 4.32 (dd, 1 H, $J_{6,7}$ 2.1 Hz, H-6).

Compound **61**: yield 49%; $[\alpha]_D$ −55.1° (*c* 1, water). ^1H NMR: δ 1.18 (d, 3 H, $J_{8,9}$ 6.4 Hz, H-9), 1.94 (dd, 1 H, $J_{3ax,4}$ 11.2 Hz, H-3ax), 2.03, 2.07 (2 s, 6 H, 2 CH_3CO), 2.30 (dd, 1 H, $J_{3eq,4}$ 4.6 Hz, $J_{3eq,3ax}$ 13.2 Hz, H-3eq), 3.84 (s, 3 H, CH_3O), 3.88 (t, 1 H, $J_{5,6}$ 10.4 Hz, H-5), 3.94 (ddd, 1 H, $J_{4,5}$ 11.1 Hz, H-4), 3.95 (dd, 1 H, $J_{6,7}$ 3.2 Hz, H-6), 4.04 (quintet, 1 H, H-8), 4.15 (dd, 1 H, $J_{7,8}$ 5.7 Hz, H-7).

Esters **58**–**61** (5–10 mg of each) were acetylated with Ac_2O (0.2 mL) in py (0.4 mL) for 48 h at rt. After concentration and removal of residual Ac_2O and py by coevaporation with toluene, the residues were passed through a Sep Pak Silica cartridge in 96:4 $CHCl_3$–MeOH and the eluates were concentrated to give acetates **62**–**65**, respectively. For ^1H and ^{13}C NMR data, see Table 4.

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