Total Syntheses of Enantiomerically Pure D- and L-Glycosyl Donors as Components of Sannamycin-type Aminoglycoside Antibiotics

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Both enantiomers of purpurosaminides C (*ent*-**7b**, **13a–c**), of a 2-azido analogue (*ent*-**16b**) and of 2-azido epimers (*ent*-**26b**, *ent*-**29b**), suitably protected for their direct use as glycosyl donors, are prepared from racemic 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer, *rac*-1). The latter has been resolved on a preparative scale through the diastereoisomeric trifluoroacetylated 1'-amines obtained with (1*R*)- and (1*S*)-1-phenylethylamine, which allowed the combination of optical resolution with the introduction of the glycosyl 6-amino function.

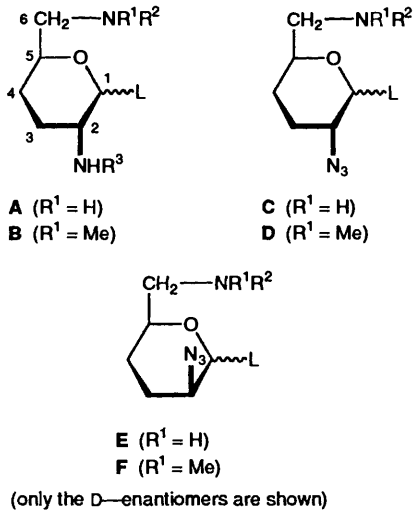
Fortimicins,[1] sannamycins[2] and sporaricins[3] are members of a relatively young family of aminoglycoside antibiotics of which one (Fortimicin A) has been used commercially since 1985.[4] Their broad antibacterial activity, combined with reduced side effects, and their relatively simple binuclear structure made them attractive targets for chemical modification and total synthesis.[5]

With the greater part of the respective aglyca—fortamines,[6] *epi*-fortamines,[7] sannamines,[8] sporamines[9]—now available to us not only as racemates but also as natural and non-natural enantiomers, suitably protected as glycosyl acceptors,[10,11] the total synthesis of glycosides in all possible combinations of the sugar and aglycon enantiomers—particularly the mirror images of the natural antibiotics—became the central theme of this project.[12]

In this paper we detail our activities as they were directed towards the synthesis of the glycosyl donors utilized in the construction of variously modified antibiotics, again in the form of both enantiomers: D-/L-**A**/**B**, the purpurosaminides C (as D-enantiomers found in the sannamycins); D-/L-**C**/**D**, the 2-azido analogues, and D-/L-**E**/**F**, the 2-epimers of the donors **C**/**D**. The decision in making the choice of the leaving group L and of the protecting groups R^1–R^3 was dictated by the glycosylation methodology to be ultimately applied; for reasons which will be commented upon in subsequent papers devoted to the ultimate aminoglycoside antibiotics,[12,13] acetate as leaving group (L = OAc) became the first choice. Protection at 2-N (R^3) was generally provided by either a DNP (2,4-dinitrophenyl) group or in form of the N_3 substituent, and at 6-N (R^1, R^2) by a DNP or an alkyl group.

A short recollection of the most pertinent reported syntheses of purpurosamines is appropriate for putting our contribution into proper context. For enantiopure D-methylpurpurosaminides C,[14–18] B and 6-*epi*-B[19–24] a number of syntheses had been accomplished,[14] some of them exploiting various natural sources. Except for a few,[23,24] they do not directly lead to purpurosaminides appropriately protected to be used as glycosyl donors. Above all, no L-enantiomer of any such purpurosamine B or C has so far been described, to the best of our knowledge. Closely related to the subject of this paper is the synthesis developed by Brimacombe *et al.* for racemic purpurosaminides C (and 2-epimers) which is based on dimeric acrolein.[25]

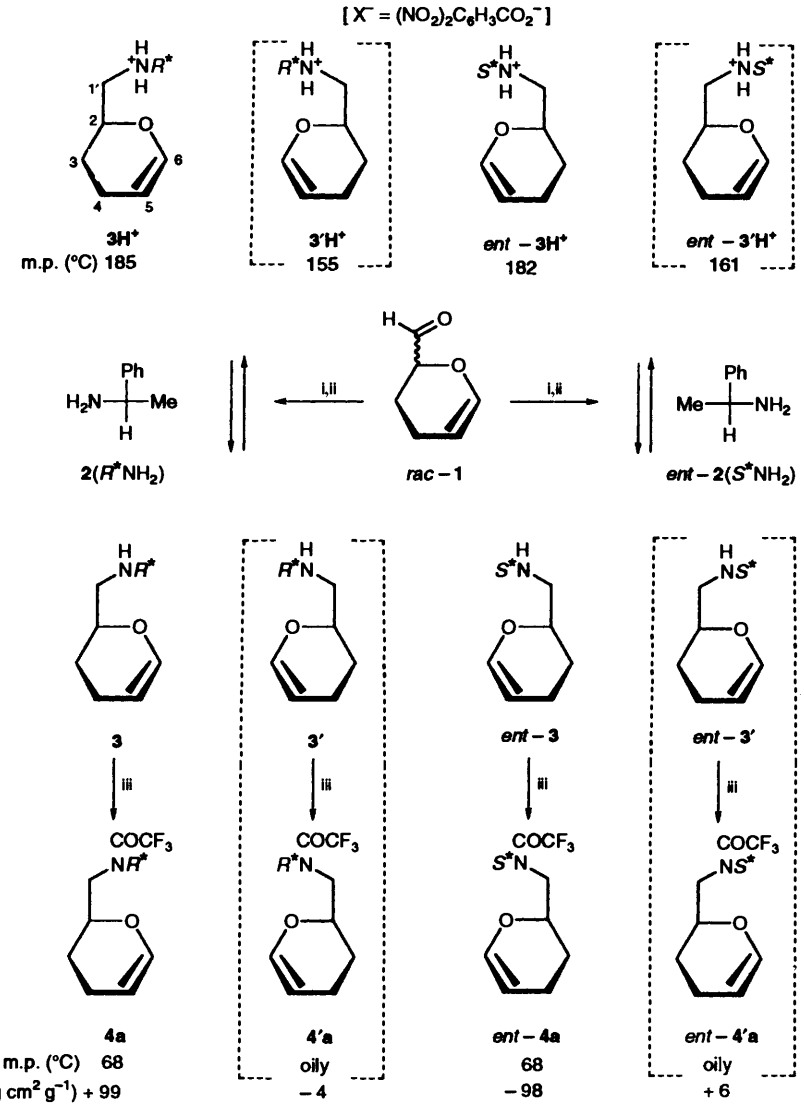
† Degussa Co. has kindly provided us with kg quantities of *rac*-**1**.



Results and Discussion

N-Protected (2R/2S)-2-*Aminomethyl*-3,4-*dihydro*-2H-*pyrans*.[26]—The general strategy in our venture for enantiomerically pure glycosyl donors of type **A**–**F** was patterned after the Brimacombe synthesis for racemic methylpurpurosaminide C[25] insofar as the racemic 3,4-dihydro-2*H*-pyran-2-carbaldehyde **1** (as acrolein dimer, a cheap industrial product)† serves as starting material, into which the 2-amino group of the ultimate glycone is introduced by addition of NOCl.[27] Our essential modification is concerned with the way in which the installation of the 1'-amino group into rac-**1**—the 6-amino group of the glycone—is combined with the optical resolution. Scheme 1 presents the main steps of this approach, which in principle consists in the formation of diastereoisomeric 1'-methylamino pyrans with the (1*R*)/(1*S*) 1-phenylethylamines **2**/*ent*-**2** as chiral sources (**3**/**3'**, *ent*-**3**/*ent*-**3'**) and their separation.

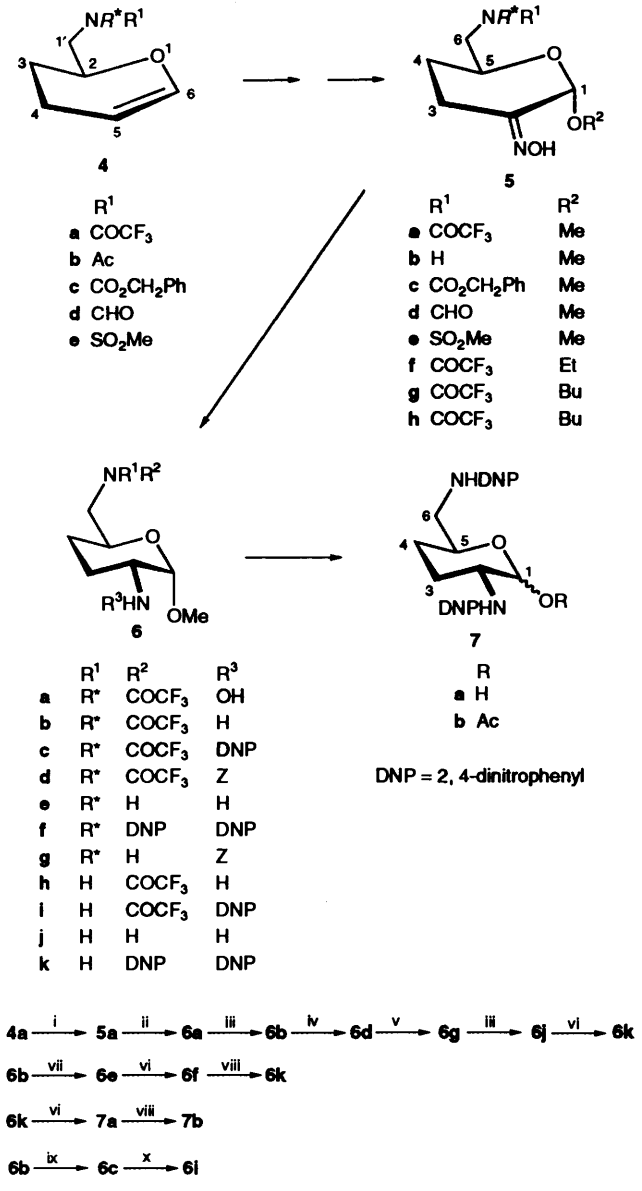
Condensation of *rac*-**1** with (1*R*)-1-phenylethylamine **2** in dry ethanol, reduction of the resulting imines with sodium boranuide and distillative work-up led to an oily mixture of the diastereoisomeric amines **3** (D*R*) and **3'** (L*R*) in an averaged 76% yield on a 0.85 molar scale. When the separation of these amines by fractional crystallization from various solvents had turned out to be impractical, when separation by distillation (difference in boiling points ~ 10 °C) had failed because of formation of an



Scheme 1 *Reagents:* i, (1*R*)/(1*S*)-1-phenylethylamine; ii, $NaBH_4$; iii, $(CF_3CO)_2O$, pyridine. Throughout the paper, the substituents *R**NH and *S**NH are used to represent (1*R*)- and (1*S*)-phenylethylamino, respectively.

azeotrope and insufficient stability, and when chromatographic separation had been satisfactory only on a small scale (g), resort was made to the differing basicity of diastereoisomers **3** and **3'**. After addition of 0.5 mole equivalent of 3,5-dinitrobenzoic acid to the original mixture of compounds **3**/**3'** (135.5 g, 0.62 mol), as hot, appropriately concentrated solutions in MeCN, it was, however, not a single (D*R* or L*R*) salt but a mixture of the salts $3H^+/3'H^+$ which deposited as a brownish solid after slow cooling to 5 °C. For the material filtered off under reduced pressure after 3 h—the composition can be qualitatively monitored by TLC—^1H NMR analysis (based on the well separated 1'-H/2-H signals) confirmed a ratio in favour of the D*R* salt $3H^+$ of up to 6:1. Treatment of this mixture with base provided the respective mixture of the amines (57.4 g, 76%). Small quantities of pure oily compounds **3** and **3'** were obtained by chromatography; they were characterized by their optical rotation, NMR and mass spectra and analysed as crystalline 3,5-dinitrobenzoates. Since for the subsequent NOCl addition (Scheme 2) protection of the amino group and high purity of the glycal were needed, the search went next for a protecting group at 1'-NH_2 of compounds **3**/**3'** (R^1), which would provide solid derivatives which are sufficiently stable to allow the large-scale separation of the enriched 6:1 mixture by fractional crystallization. Out of several tested alternatives (**4a–e**[26]), the trifluoroacetamides **4a**/**4'a** proved superior with respect to separability and yield along the way to the respective 2-(hydroxyimino)glycosides **5a–e**. In fact, fractional crystallization of a batch (40 g) of the respective mixture **4a**/**4'a** from methanol provided an averaged 46 g (77%) yield of practically pure **4a** {m.p. 68 °C, $[\alpha]_D^{20}$ +99 × 10^{-1} deg cm^2 g^{-1} (*c* 0.99, CH_2Cl_2); the absolute configuration has previously been confirmed[26]}. Samples of pure oily compound **4'a**, not accessible through crystallization of the ~1:9 enriched oily residue, were obtained for characterization through chromatography {$[\alpha]_D^{20}$ −4 × 10^{-1} deg cm^2 g^{-1} (*c* 1.55, CH_2Cl_2)}. In line with this finding, unsurmountable difficulties were met in our attempts to secure by crystallization the greater part of compound **4'a** from the complex oily mixture of compounds **3**/**3'** and $3H^+/3'H^+$ left after the crystallization from MeCN.

Access to crystallizable, pure derivatives of the L-series were sought instead through condensation of *rac*-**1** with (1*S*)-1-phenylethylamine (*ent*-**2**). As expected, it was the L*S*-amide *ent*-**4a** {$[\alpha]_D^{20}$ −98 × 10^{-1} deg cm^2 g^{-1} (*c* 0.02, CH_2Cl_2)}, which as the less soluble diastereoisomer, could be secured analogously to its enantiomer **4a** and with comparable yield *via* the enriched mixture of amines *ent*-**3**/*ent*-**3'**. Pure samples of *ent*-**3'** and *ent*-**4'a** {$[\alpha]_D^{20}$ +6 × 10^{-1} deg cm^2 g^{-1} (*c* 0.02, CH_2Cl_2)} were again collected chromatographically for characterization.

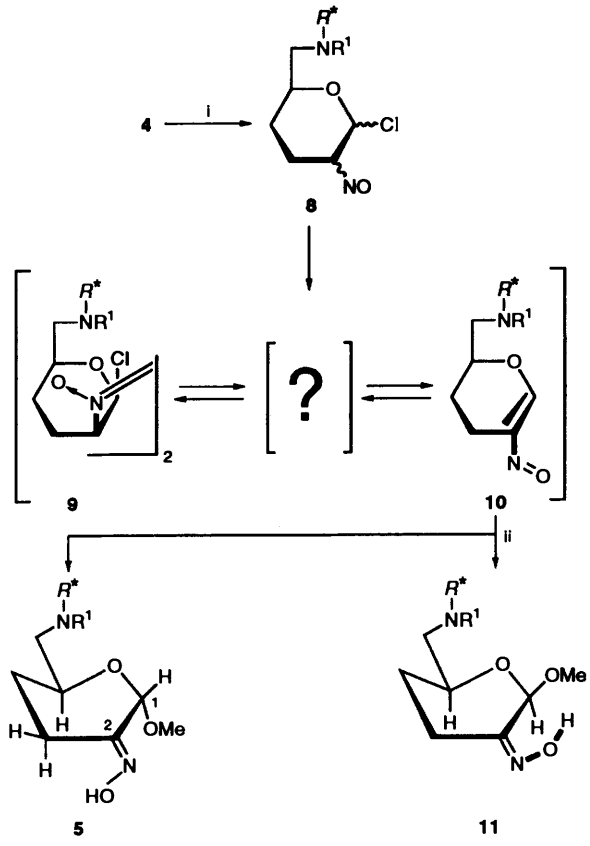


Scheme 2 *Reagents:* i, NOCl, MeOH; ii, $NaCNBH_3$; iii, Pd–C, H_2; iv, Z-Cl; v, $NaBH_4$; vi, DNP-F, $NaHCO_3$; vii, $NaBH_4$, MoO_3; viii, CF_3CO_2H; ix, AcOH–1 mol dm^{-3} H_2SO_4 (1.3:1); x, Ac_2O, pyridine

Clearly, this way to 'resolve' *rac*-**1** on a large scale in the form of the enantiomers **4a** and *ent*-**4a**, with loss of amines **4'a** and *ent*-**4'a**, is costly as well as time consuming. In addition, fractional crystallization of the diastereoisomeric dinitrobenzoates was found to be somewhat critical in that reproduction of the stated degree of enrichment (6:1) and of the average yield requires some experience. For the repeated preparation of compound **4a** (*ent*-**4a**) a shortening of the preparative protocol by omission of the enrichment step at a slightly reduced yield was elaborated. To this end, the 1:1 mixture (0.5 mol) of the amines **3**/**3'** (*ent*-**3**/*ent*-**3'**) was directly transformed into the 1:1 mixture of amides **4a**/**4'a** (*ent*-**4a**/*ent*-**4'a**). Fractional crystallization from methanol allowed the collection of an average 49.4 g of pure compound **4a** (*ent*-**4a**) corresponding to 63% of the theoretical yield.

D-/L-*Purpurosamine C Donors* **A**.—In the planning stage, the procedure from the 6-aminomethyl glycals **4** to appropriately protected glycosyl donors of type **A** (*e.g.*, **7**, Scheme 2) had implied protection of the 1'-amino group, regiospecific addition of NOCl to the C=C double bond, tautomerization with subsequent elimination of HCl (see structure **10**), efficient and highly α-selective glycosylation with methanol, stereospecific reduction of the oximes to give α-hydroxylamines, and, after appropriate group manipulations, expeditious transformation of the methyl glycosides into the glycosyl donors.

Given the lack of the stabilizing as well as stereodirecting O-functionalities at C-3/C-4 in glycals **4**, present in the pioneering study of Lemieux *et al.*,[27] and the different substitution at C-1' compared with the Brimacombe substrates,[25] most of the above stated assumptions and expectations were, however, risky. And, indeed, there were surprises all along this route. An exploratory NMR study of the course of the addition of NOCl to compounds **4a–e** (standardized conditions, 10–50 mg samples, not detailed in the Experimental section) made it rapidly clear that neither the primary NOCl adducts **8a–e**—independent of the nature of R^1 group—nor the nitrosoenes **10a–e** were stable enough to be directly observed (−70 °C) and that at low-temperature nitro sodimers (*cis*/*trans*-isomers, *e.g.*, **9**) were formed,[28] which underwent configurational changes as the temperature was raised (Scheme 3). After concentration of the



Scheme 3 *Reagents and conditions:* i, NOCl, CH_2Cl_2, −78 °C; ii, MeOH, 2,4,6-collidine, DMF, −78 °C ⟶ room temp.

CH_2Cl_2 solutions at −70 °C, and treatment of the bluish solids (**8a**, **e**) or oils (**8b–d**) with 1.2 mole equivalents of dry methanol in the presence of 1,3,5-trimethylpyrazole, the 2-(hydroxyimino)-D-glycosides **5a–e** were obtained in yields, depending on the R^1 group, ranging from good (67%, **5c**) to nearly quantitative (94%, **5a**).

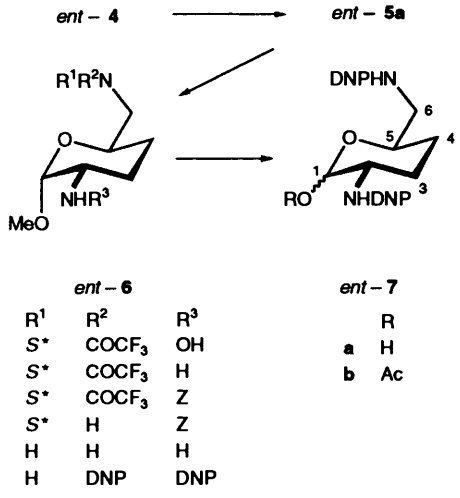
Complications came with the increase in scale. Dosage in the addition of NOCl, complete expulsion of the eventual excess of NOCl from the syrupy product, low stationary concentration of the nitrosoenes and the latter's rapid interception, were practical problems, which only after intensive optimization efforts could be overcome in a satisfactory manner. In a prototypical experiment with glycal **4a** (4 g), protection at 6-N with $COCF_3$,

replacement of CH_2Cl_2 by dimethylformamide (DMF) and trimethylpyrazole [pK_a (Me_2SO) ~ 0.8] by the stronger base 2,4,6-collidine [pK_a (Me_2SO) ~ 4.5][29] and strict timing in the addition of reagent provided, after chromatography, an oily, ~ 5:1 mixture of the hydroxyimino α-/β-glycosides **5a**/**11a** in yields up to 75%. For full spectroscopic characterization (IR, ^1H and ^{13}C NMR, MS) pure samples of compounds **5a** (52%) and **11a** (11%) were collected chromatographically, the respective *E*- and *Z*-configuration being derived from the NOEs indicated in the formula. The hydrogenative reduction of oximes was described as unproblematic in model cases;[30] under standard conditions ($Pd/C/H_2$) concomitant loss of the phenylethyl group (*R**) was envisaged. Yet, presumably with participation of the geminal trifluoroacetyl group, catalytic hydrogenation (Pd/C) and several other reduction procedures (*inter alia* B_2H_6, $TiCl_3$–$NaBH_4$)[31] ended in total decomposition. With $NaBH_4$ as reducing agent, the CF_3CO group was preferably lost (49% **5b**), with $NaBH_4$–MoO_3 (ethanol, room temp.)[32] reduction of the imine and elimination of CF_3CO occurred concurrently (**6e**, identified as **6f**, 41%). $NaCNBH_3$ (acetic acid) turned out to be the reagent of choice in spite of an unexpected complication which could not be avoided. *E*-oxime **5a** was neatly and stereospecifically reduced to the 2-hydroxylamine **6a**, yet the H-bonded *Z*-isomer **11a** remained intact even under more forcing conditions and thus was lost for the synthesis. Chromatographic separation of compounds **6a**/**11a**—in contrast to that of isomers **5a**/**11a**—was unproblematic, hydrogenolysis of the hydroxylamine **6a** to amine **6b** being straightforward. The latter was highly air sensitive and was therefore directly transformed into DNP- or benzyloxy (Z)-protected, spectroscopically characterized compound **6c** (yellow crystals, m.p. 123 °C) or **6d** (crystals, m.p. 107 °C).

For the decision not to proceed with compounds **5b** and **6c** and to prepare the 2-*N*,6-*N* DNP-protected glycosyl donor **7b** along the reaction sequence **6b** ⟶ **6d** ⟶ **6g** ⟶ **6j** ⟶ **6k** ⟶ **7a** ⟶ **7b**, which meant temporary protection of the 2-amino group in compound **6b** as the benzyl carbamate **6d**, several prior findings, detailed in the Experimental section, were decisive: (i) Dealkylation (*R**) of amide **6b** to give compound **6h** or likewise of **6e** to give free amine **6j** could not be brought about by catalytic hydrogenation, at least not with sufficient selectivity, complexation of the catalyst by the 2-NH_2 group being a probable cause for this. (ii) Dealkylation (*R**) of compound **6f**, obtained from 2-amine **6e** and DNPF, was quantitative (to give compound **6k**) after short exposure to dry CF_3CO_2H (TFA) at 60 °C. (iii) Compound **6c** reacted again only sluggishly with TFA and provided dealkylated (*R**) compound **6i** in only moderate yield (62%) under more vigorous conditions.

In practice, a time-saving upscaled version for the preparation of the intermediate **6d** from glycal **4a** was applied by which the crude reaction mixture of the addition of NOCl to **4a** (mainly **5a**/**11a**) was transformed into compound **6d** without isolation of any intermediate. Crystallization of the crude reaction mixture from methanol afforded pure compound **6d** in 31% yield [~ 8 g from **4a** (15 g)]. Of the three protecting groups in compound **6d** first the $COCF_3$ group was removed [as in oxime **5a** ($NaBH_4$)], in compound **6g** subsequently the *R** and Z groups by one-pot catalytic hydrogenation. The reaction of diamine **6j** with DNPF gave the bis-DNP-protected **6k** {68%, $[\alpha]_D^{20}$ +38 × 10^{-1} deg cm^2 g^{-1} (*c* 0.08, CH_2Cl_2)}. For the hydrolysis **6k** ⟶ **7a**, addition of nitromethane to the standard mixture of 1 mol dm^{-3} H_2SO_4–acetic acid[33] was essential for solubility reasons; the free sugar **7a** was directly transformed into the donor **7b** with acetic anhydride–pyridine (68%), and the latter was isolated in form of yellow crystals (m.p. 94 °C). Compound **7b** turned out to be a 5.5:1 mixture of α and β anomers ($\delta_{1\text{-H}}$ 6.30 and 5.67, $J_{1,2}$ 3.5 and 10.0 Hz, $\delta_{C\text{-}1}$ 89.7 and 96.0 respectively).

The enantiomeric L-donor *ent*-**7b** (Scheme 4) was made



Scheme 4 *Reagents:* see Scheme 2

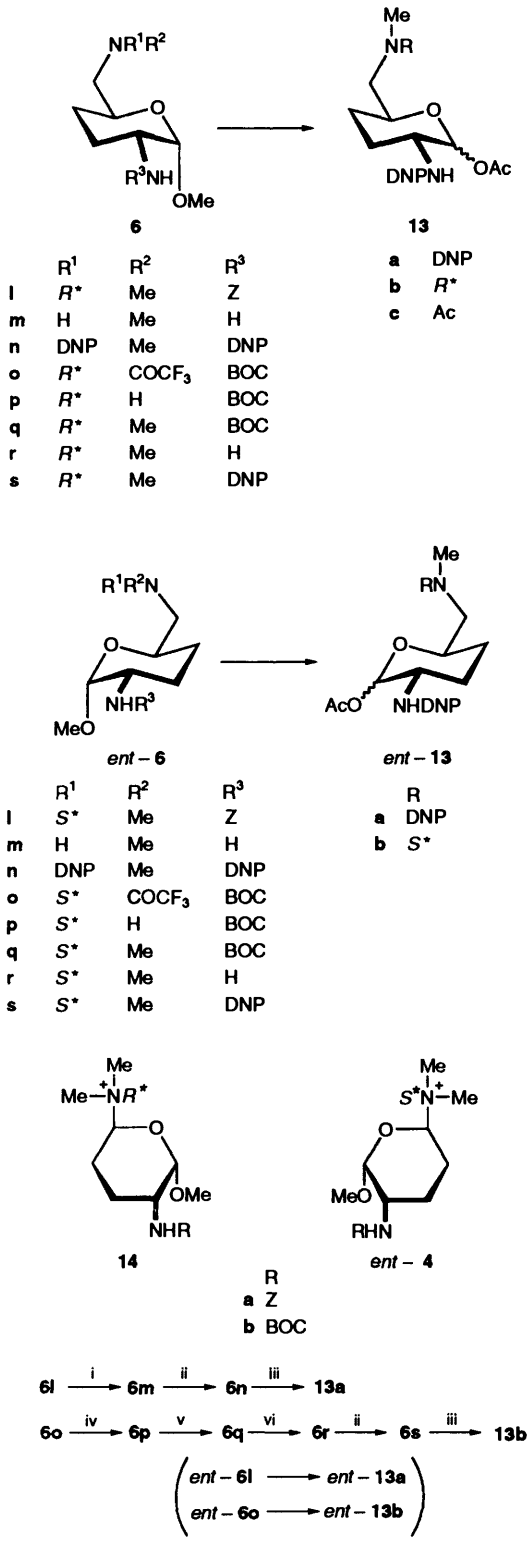
available by taking the glycal *ent*-**4a** through the same sequence of addition of NOCl (5.4:1 mixture of α:β hydroxyiminoglycosides *ent*-**5a**), reduction with $NaBH_3CN$ (*ent*-**6a**), catalytic hydrogenation (*ent*-**6b**), Z-protection (*ent*-**6d**, 59% based on *ent*-**6a**), treatment with $NaBH_4$ (*ent*-**6g**), and catalytic reduction (*ent*-**6j**) followed by protection with DNP {68% *ent*-**6k** $[\alpha]_D^{20}$ −41 × 10^{-1} deg cm^2 g^{-1} (*c* 0.16, CH_2Cl_2)}. The sugar *ent*-**7a** was again directly transformed into the yellowish crystalline donor *ent*-**7b** (66%, 5:1 anomeric mixture).

D-/L-6-N-*Methylpurpurosamine C Donors* **B**.—The introduction of the 6-*N*-methyl group which distinguishes donors **B** from donors **A** (*cf.* the sannamycins A) originally had been envisaged at the stage of the glycals **3**. However, as observed for the 6:1 mixture of *ent*-**3**/*ent*-**3'**, the mixture of their 6-*N*-Me derivatives *ent*-**12**/**12'**, obtained after standard methylation (Scheme 5), was an oil and effective separation by

Scheme 5 *Reagents:* i, MeI, $NaHCO_3$

fractional crystallization was not possible. Since, on the other hand, the protocol for the subsequent formation of oxime (addition of NOCl) again had been found to be productive only with glycals of a purity attainable by crystallization, this route was not pursued any further.

As an alternative, 6-*N*-methylation was postponed to the stage of the suitably protected methylpurpurosaminides **6** (*ent*-**6**). When standard methylation conditions (~ 2.5 mole equivalents MeI–K_2CO_3 in MeOH or MeCN) were applied to substrate **6g** (or **6p**, Scheme 6) at room temperature, exclusive methylation at 6-N was first observed. Yet, with increasing conversion into compound **6l** (or **6q**) the latter's quaternization at 6-N to form the ammonium salt **14a** (or **14b**) became unavoidable. After total conversion (in the presence of *tert*-butylammonium iodide as catalyst) besides ~ 60% of the



Scheme 6 *Reagents:* i, Pd–C, H_2; ii, DNP-F; iii, AcOH–1 mol dm^{-3} H_2SO_4 (1.3:1), Ac_2O, pyridine; iv, $NaBH_4$; v, MeI, K_2CO_3; vi, 2 mol dm^{-3} HCl

desired product **6l** (**6q**), ~30% of the yellowish salts **14a** (**14b**) were present. Intensive efforts to demethylate the salt **14b** back to compound **6q** with the help of ethanolamine,[34] with sulfur[35] or selenium reagents,[36] or reductively with $LiAlH_4$,[37] induced mainly decomposition. In going ahead with substrate **6l**, the elimination of the *R**- and Z-group could again be conveniently conducted as a one-pot hydrogenation experiment. The resulting crude diamine **6m** was directly twice protected with DNPF, and compound **6n** was crystallized from $CHCl_3$ (84%). Prepared analogously to compound **7b**, the yellowish solid donor **13a** was isolated as a 4:1 α:β-anomeric mixture [$\delta_{1\text{-H}}$ 6.15 and 5.51, $J_{1,2}$ 3.0 and 6.0 Hz, respectively; *m/z* (*inter alia*) 534 (M^+, 10%)].

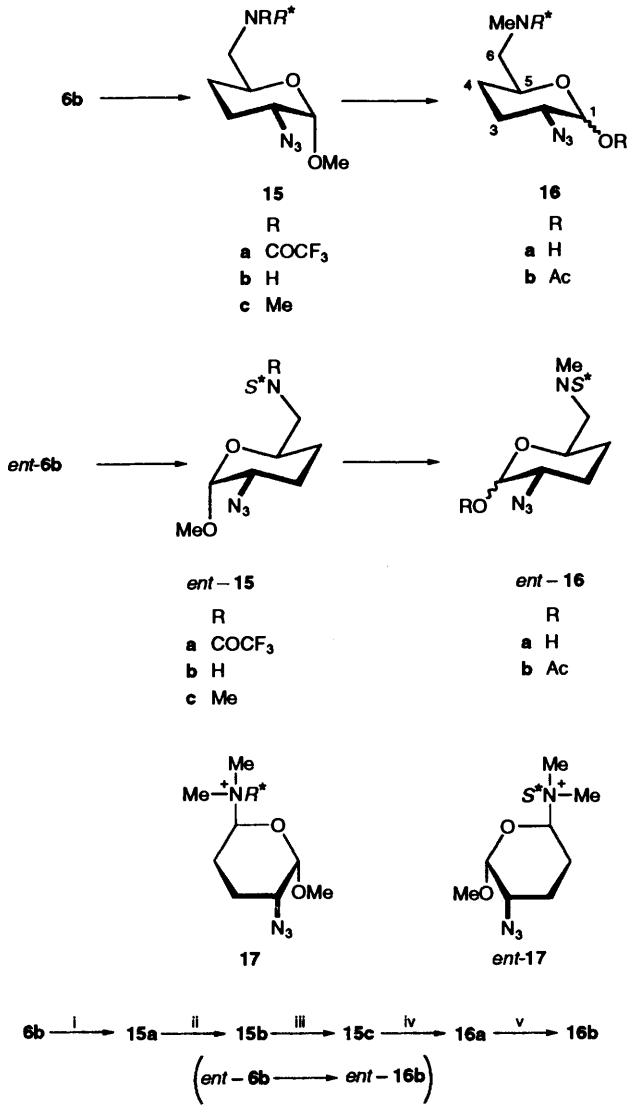
The non-natural donor *ent*-**13a** (α:β ratio 5:1) was made from substrate *ent*-**6g** *via* the same sequence of group manipulations (*ent*-**6g** ⟶ *ent*-**6l** ⟶ *ent*-**6m** ⟶ *ent*-**6n** ⟶ *ent*-**13a**).

When, at a later stage of the project, evidence had accumulated that the phenylethyl group (*R**, *S**) at 6-N can be cleanly eliminated after the glycosylation step under sufficiently mild conditions, the donors **13b** and *ent*-**13b** became attractive. Preparation of acetate **13b** from compound **6b** was supposed to follow closely that of acetate **13a** (⟶ **6r** ⟶ **6s**). Yet it turned out that the *R** group necessitated other protecting measures when the Z-group at 2-N in compound **6l** could not be replaced by the DNP group by the proven hydrogenation procedure. When it was found that various alternative methodologies for Z-deprotection [BBr_3, $AlCl_3$, TFA, Me_3SiI (TMSI)] were not helpful, compound **6s** was approached *via* the 2-*N*-Boc-protected precursors [**6b** ⟶ **6o** (65%) ⟶ **6p** (78%) ⟶ **6q** (70%) ⟶ **6r** ⟶ **6s** (79%)]. Hydrolysis of compound **6s** was performed as with its analogue **6n**; the yield of donor **13b** was comparable (63%), yet the α:β-ratio of 9.3:1 was significantly higher [$\delta_{1\text{-H}}$ 6.24 and 5.50; $J_{1,2}$ 3.0 and 7.0 Hz, $\delta_{C\text{-}1}$ 90.0 and 96.8, respectively; *m/z* (*inter alia*) 472 (M^+, 100%)].

Enantiomeric donor *ent*-**13b** was generated from compound *ent*-**6b** by the same five-steps sequence (*ent*-**6b** ⟶ *ent*-**6o** ⟶ *ent*-**6p** ⟶ *ent*-**6q** ⟶ *ent*-**6r** ⟶ *ent*-**6s** ⟶ *ent*-**13b**), with similar yields for the individual transformations and an α:β-ratio of 7:1 ($J_{1,2}$ 3.7 and 8.2 Hz, respectively).

D-/L-2-*Azidopurpurosamine C Donors* **D**.—Depending on the kind of protection of the 2-amino group (R^3), the reactivity of the glycosyl donors of type **A**/**B** can be profoundly diminished.[12,13] A proven way to circumvent such limitations is the replacement in compounds **A**/**B** of the NHR^3 group by the sterically less demanding, non-participating N_3 function (**C**/**D**). There was the additional advantage that, at the very end of the total syntheses, the catalytic reduction of the N_3 function could be conveniently combined with the deprotection of other functionalities. Two routes to such 2-azido sugars have been selected with the intention to make use of enantiomerically pure precursor substrates prepared in this study: Azidonitration of glycals **4** (*ent*-**4**) to be discussed in the next section, and diazo transfer[38] to the 2-amino function in the methyl glycoside **6b** (*ent*-**6b**). We had applied this methodology of amine ⟶ azide transformation in a different context with great success by making use of *in situ*-generated trifluoromethanesulfonyl azide (TfN_3).[39] Recent examples in the sugar area are the 2-azido-2-deoxyaldols reported by Vasella *et al.*[40]

In an unoptimized synthetic procedure developed for the 2α-azido-D-glycosyl donor **16b** (Scheme 7), air-sensitive amine **6b** was introduced as the crude oily material arising from the catalytic reduction of the hydroxylamine **6a**. To a methanolic solution of crude **6b** the CH_2Cl_2 solution of TfN_3 (~1.2 mol equiv.) was added dropwise at room temperature. After total conversion (TLC) and chromatographic work-up of the complex reaction mixture, the azide **15a** was isolated in the form of low melting crystals, in a so-far moderate yield of 35–50%; ν_{max}/cm^{-1} (N_3) 2176; NMR (*inter alia*) $J_{1,2}$ 3.0 Hz; and *m/z* (%) (*inter alia*) 386 (M^+, 6), 355 ($M^+ - OCH_3$, 10), 313 ($M^+ - OCH_3 - N_3$, 12) and 216 ($M^+ - OCH_3 - N_3 - COCF_3$, 21) confirm the structure, particularly the *erythro*-configuration $[\alpha]_D^{20}$ +73 × 10^{-1} deg cm^2 g^{-1} (*c* 0.33, CH_2Cl_2). Deprotection



Scheme 7 *Reagents:* i, TfN_3; ii, $NaBH_4$; iii, MeI, K_2CO_3; iv, AcOH–1 mol dm^{-3} H_2SO_4 (1.3:1); v, Ac_2O, pyridine

of compound **15a** with $NaBH_4$ to give amine **15b** was nearly quantitative ($J_{1,2}$ 3.0 Hz); *m/z* (%) (*inter alia*) 290 (M^+, 2), 259 ($M^+ - OCH_3$, 3), 248 ($M^+ - N_3$, 36). Methylation of compound **15b** at 6-N posed the problem already met with compounds **6g** and **6p**. Compromising between conversion and quaternization, a typical experiment (~1.5 mol equiv. of MeI) provided methylated compound **15c** in 55% yield [*m/z* (*inter alia*) 304 (M^+, 2%), 289 ($M^+ - CH_3$, 1)] after separation from compound **15b** and quaternary salt **17**. After hydrolysis in 1 mol dm^{-3} H_2SO_4–acetic acid–$MeNO_2$ solution, the crude oily pyranose **16a** consisted of a ~3:1 mixture of α:β-anomers. For characterization, samples were purified by flash chromatography [α: $\delta_{1\text{-H}}$ 5.29; $J_{1,2}$ 3.0 Hz; β: $\delta_{1\text{-H}}$ 4.51; $J_{1,2}$ 7.0 Hz; *m/z* (%) (*inter alia*) 290 (M^+, 3), 275 ($M^+ - CH_3$, 8) and 248 ($M^+ - N_3$, 3)]. Standard installation of the OAc leaving group provided, after flash chromatographic work-up, an oily 3:1 mixture of α:β-acetates **16b** (in ~55% yield) [α: $\delta_{1\text{-H}}$ 6.14; $J_{1,2}$ 3.0 Hz; β: $\delta_{1\text{-H}}$ 4.46; $J_{1,2}$ 8.2 Hz; *m/z* (%) (*inter alia*) 332 (M^+, 28), 317 ($M^+ - CH_3$, 8) and 290 ($M^+ - N_3$, 5)].

Taking advantage of the experience with compound **16b**, the L-donor *ent*-**16b** was built up from compound *ent*-**6b** (Scheme 7) in a strictly analogous fashion (⟶ *ent*-**15a** ⟶ *ent*-**15b** ⟶ *ent*-**15c** ⟶ *ent*-**16a** ⟶ *ent*-**16b**) with similar individual yields and α:β ratios.

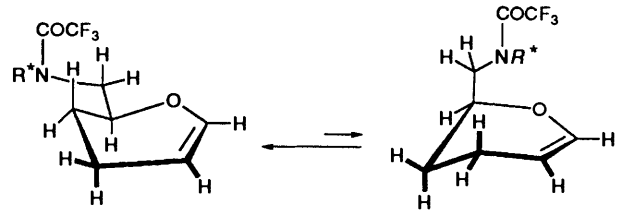
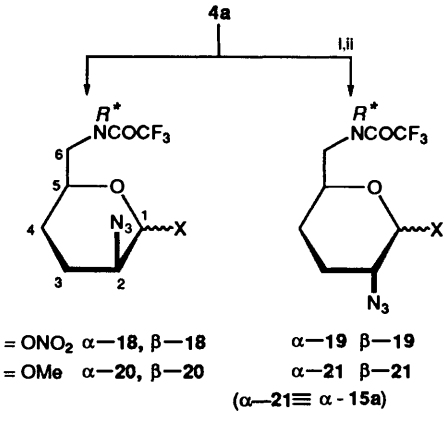


Fig. 1 Conformational preference in glycal **4a**

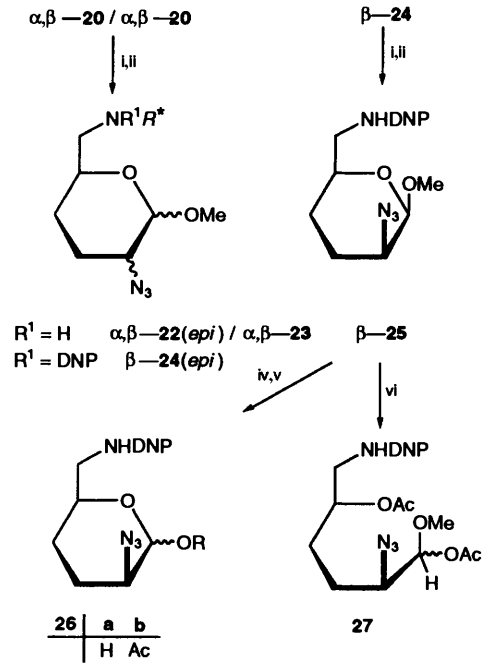
D-/L-2-epi-*Purpurosamine C Donors* **E**/**F**.—Derivatives of *rac*-2-*epi*-purpurosamine C (2,6-diamino-2,3,4,6-tetradeoxy-D,L-*threo*-hexose)—part of *inter alia* dihydrosisomicin[41]—have been synthesized by Brimacombe *et al.* exploiting the procedure developed for the *rac*-purpurosamines C.[25] Again, with our eyes on both enantiomers of this sort of glycosyl donor, the efficiency and stereochemical outcome of the azidonitration methodology[42,43] as applied to the glycals **4** (*ent*-**4**) were investigated. For several D-hexose glycals, the influence of the orientation and nature of functionalities at C-3 and C-4, of promoter, solvent and temperature, upon the *erythro*/*threo* ratio had been analysed.[44] In the 3,4-dideoxy glycal **4a** (*ent*-**4a**) such stereodirecting groups were not present; for its highly populated half-chair-like conformation with the substituent being quasi-equatorially oriented (^{1}H NMR, X-ray[45]) a preference for the desired addition of N_3 from the β-side seemed probable; a high α:β ratio, however, was rather questionable (see Fig. 1).

Exposure of compound **4a** to cerium(IV) ammonium nitrate (CAN) and sodium azide in MeCN at −40 °C (carefully dried components or eventually in the presence of molecular sieves[43]) led nearly quantitatively to a mixture of all four possible azido nitrates α,β-**18** and α,β-**19** (Scheme 8), but the composition,



Scheme 8 *Reagents and conditions:* i, $Ce(NH_4)_2(NO_3)_6$ (CAN), NaN_3, MeCN, −40 °C; ii, MeOH, −40 ⟶ 0 °C

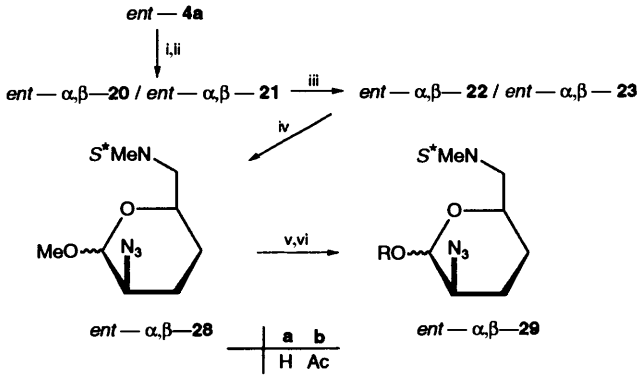
found as 5.3:1:1.4:1 by integration of the ^{1}H NMR signals, amounted to a ~2.6:1 preference for the desired 2-*epi*-azides **18**. When the nitrates proved relatively stable under the conditions of the extractive work-up (diethyl ether–water), rapid chromatography could be applied for separation and provided the main component α-**18** in pure form besides a mixture of nitrate α-**19** with some epimer α-**18**, both fractions as oils. Fully analysed ^{1}H and ^{13}C NMR spectra confirmed the stereochemical assignments, particularly for α-**18**, the 1a,2a,5e chair-like conformation ($J_{C\text{-}1,H}$ 180.0 Hz,[46] $\delta_{C\text{-}3}$ 22.7, γ-effect of



Scheme 9 *Reagents:* i, $NaBH_4$; ii, DNP-F, $NaHCO_3$; iii, AcOH; iv, AcOH–1 mol dm^{-3} H_2SO_4 (1 : 1); v, Ac_2O, pyridine, DMAP; vi, Ac_2O, conc. H_2SO_4

the axially disposed nitrate substituent). Quenching of the crude mixture of the four azido nitrates with methanol at different temperatures (−20 to +20 °C) led in each case quantitatively to mixtures (2.8 : 5.8 : 2.8 : 1) of the four methyl glycosides α,β-**20** and α, β-**21** (α-**21** ≡ **15a**). Their distinction was based on the ^1H and ^{13}C NMR analyses of enriched mixtures and of the prevailing pure 2-*epi*-isomer β-**20** as the result of rapid chromatography. After amidic cleavage ($NaBH_4$) from the mixture of the four amines α,β-**22** and α,β-**23** (92%) the two main components β-**22** [42%, *m/z* (%) (*inter alia*) 290 (M^+, 10), 275 ($M^+ - CH_3$, 54); $\delta_{1\text{-H}}$ 4.43; $J_{1,2}$ 1.5 Hz] and α-**23** ≡ **15b** (37%, $\delta_{1\text{-H}}$ 4.70; $J_{1,2}$ 3.0 Hz) were separated by column chromatography. Protection of oily compound β-**22** as DNP derivative β-**24**, a yellowish foamy material, was straightforward [96%, *m/z* (*inter alia*) 456 (M^+, 1), 441 ($M^+ - CH_3$, 1); $\delta_{1\text{-H}}$ 4.22, $J_{1,2}$ 1.5 Hz; $\delta_{C\text{-}1}$ 102.3, $\delta_{C\text{-}2}$ 57.0] (Scheme 9). Pure 2-*epi-threo*-isomer β-**24**, was cleanly dealkylated by keeping it in solution in acetic acid at 85 °C for 4 h, whereupon compound β-**25** ($\delta_{1\text{-H}}$ 4.58, $J_{1,2}$ 1.5 Hz) was isolated after crystallization from ethyl acetate as yellow needles {92%, $[\alpha]_D^{20}$ +93 (*c* 1, CH_2Cl_2)}. If pure compound β-**25**, as a dilute solution, was exposed to hydrolysis (1 mol dm^{-3} H_2SO_4–acetic acid–$MeNO_2$) and work-up conditions, the yellowish pyranose **26a** was obtained in up to 85% and characterized as a ~1.7 : 1 anomeric mixture [$\delta_{1\text{-H}}$ 5.22 (s) and 4.94 (*J* 1.5 Hz); $\delta_{C\text{-}1}$ 95.0 and 91.9; *m/z* (*inter alia*) 338 (M^+, 36), 196 (82) and 179 (100)]. In acetic anhydride–pyridine, transformation into donor **26b** was practically quantitative [α : β ratio ~1.7 : 1, *m/z* (*inter alia*) 380 (M^+, 100); $\delta_{1\text{-H}}$ 6.08 (s) and 5.84 (d, *J* 1.5 Hz); $\delta_{C\text{-}1}$ 93.9 and 91.3, respectively]. It should be added that in this case the fate of compound β-**25** under standard hydrolysis conditions (1 mol dm^{-3} H_2SO_4–acetic anhydride) could be clarified to the extent that the open-chain tetradeoxy-D-*threo*-hexose derivative **27** was the only isolable monomeric product (38%).[47]

By exploitation of the procedure leading from glycal **4a** *via* azides α,β-**20** and β-**24** to the donor **26b**, the differently 6-N-protected donor *ent*-**29b** was approached with *ent*-**4a** as starting material (Scheme 10). The latter's reaction with CAN–methanol yielded a mixture of the four possible methyl glycosides *ent*-α,β-**20** and *ent*-α,β-**21** in 91% yield. After treatment of this



Scheme 10 *Reagents:* i, CAN, NaN_3; ii, MeOH; iii, $NaBH_4$; iv, MeI, K_2CO_3; v, AcOH–1 mol dm^{-3} H_2SO_4 (1 : 1); vi, Ac_2O, pyridine, DMAP

mixture with $NaBH_4$ the composition of 2.8 : 5.9 : 1 : 1 (^1H NMR spectroscopy) attested to a somewhat reduced side differentiation of the CAN reaction. Chromatographic separation yielded pure samples of *ent*-α-**23** (13%), *ent*-β-**22** (33%), and *ent*-α-**22** (15%) besides a mixture of *ent*-α-**22**/*ent*-β-**22** and *ent*-β-**23** (20%). Methylation of pure free amine *ent*-β-**22** as described for compound **6g** gave crystalline *ent*-β-**28** (65% yield). Methylation of *ent*-α-**22** gave oily *ent*-α-**28** (62% yield). Through hydrolysis with 1 mol dm^{-3} H_2SO_4–acetic acid–$MeNO_2$ the pyranose *ent*-**29a** was obtained in an α : β ratio of 2.0 : 1, and in a yield varying between 60 and 80%. The transformation into donor *ent*-**29b**, an oily α : β mixture of 2.0 : 1 was again nearly quantitative [$\delta_{1\text{-H}}$ 5.98 and 5.76, $J_{1,2}$ < 1 and 1.8 Hz, $\delta_{C\text{-}1}$ 91.9 and 94.1, respectively; *m/z* (*inter alia*) 332 (M^+, 20%) and 317 ($M^+ - CH_3$)].

Comments.—A main feature of the protocols presented in this paper for the synthesis of various purpurosamine-type glycosyl donors is their applicability to both enantiomers. There are obvious drawbacks: The relatively expensive chiral 'auxiliaries' become part of the structures and are lost to a greater extent in the form of the non-crystallizable diastereoisomers (**4'a**, *ent*-**4'a**), at least for the time being. This limitation was acceptable as long as only small quantities of aminoglycosides as the ultimate synthetic targets were needed for biological tests. Still, there are good reasons, particularly in the case of the azido donors **C**–**F**, to look for synthetic alternatives.[48] Separations through biocatalytic methodologies as successfully applied in the aglyca area,[10,11] are being explored at various stages. Hydrolysis–amidation experiments involving various racemic esters and amides derived from *rac*-**1** are indeed promising.[49]† Present efforts[51] are also directed to the resolution of racemic glycals of type **4** *via* the glycosides prepared with enantiopure glycosyl acceptors.[52]

Experimental

M.p.s were measured on a Monoskop IV (Fa. Bock) and are uncorrected. Elemental analyses were performed by Analytische Abteilung des Chemischen Laboratoriums Freiburg i.Br. IR spectra were measured with a Philips 9706, and ^1H NMR spectra with a Bruker AC 250, AM 400 spectrometer (250 MHz, when not specified otherwise; values marked with an asterisk * are interchangeable); *J* values are in Hz. ^{13}C NMR spectra were measured on a Bruker AM 400 spectrometer. Mass spectra were run on a Finnigan MAT 44S spectrometer, EI 70 eV, if not specified differently. Optical rotations were measured on a PE

† Racemic 3,4-dihydro-2*H*-pyran-2-carboxylic acid and *rac*-6-aminomethyl-3,4-dihydro-2*H*-pyran have recently been resolved [with dehydroabiethylamine and (+)-tartaric acid respectively].[50]

241 polarimeter; specific rotation values are given in units of 10^{-1} deg cm^2 g^{-1}. TLC was performed on silica gel 60 F-254 (E. Merck, Darmstadt). The silica gel used for column chromatography was MN 60 (Macherey-Nagel, Düren). The purity of the oily compounds has generally been confirmed by TLC.

General Procedure for Acetylation.—An alcohol (1.00 mmol) was dissolved in a mixture of acetic anhydride (1 cm^3) and pyridine (1 cm^3) and the solution was kept at room temperature for 3 h with a catalytic amount of 4-(dimethylamino)pyridine (DMAP). After total conversion (TLC control), the mixture was evaporated and the residue was chromatographed.

(2S)/(2R)-2-[(1R)-*Phenylethylaminomethyl*]-3,4-*dihydro*-2H-*pyran* **3**/**3'**.—To a solution of (1*R*)-phenylethylamine (99.4 g, 0.82 mol) in dry ethanol (200 cm^3) was added at 0 °C dropwise within 2.5 h racemic acrolein dimer *rac*-**1** (95.5 g, 0.85 mol). After the mixture had been stirred at room temperature for 15 h there was total conversion (TLC, R_f imine 0.56, ethyl acetate). To the solution was added in portions $NaBH_4$ (12.8 g, 0.32 mol); after 3 h (total conversion, TLC, R_f **3** 0.36, R_f **3'** 0.44, ethyl acetate), excess of $NaBH_4$ was destroyed with acetic acid (pH 7). The reaction mixture was evaporated, and the residue was dissolved in water and extracted with diethyl ether. The organic phase was dried ($MgSO_4$) and evaporated, the oily residue was distilled (95 °C, 10^2 Pa) to give compounds **3**/**3'** (135.5 g, 76%) as an oil.

Separation of Diastereoisomers **3**/**3'**.—To a solution of compounds **3**/**3'** (135.5 g, 0.62 mol) in boiling, dry acetonitrile (1000 cm^3) was added a solution 3,5-dinitrobenzoic acid (65.7 g, 0.31 mol) in boiling, dry acetonitrile (1000 cm^3). The mixture was cooled to 5 °C within 3 h. The crystalline precipitate was collected, treated with diethyl ether (350 cm^3) and cold aq. 0.5 mol dm^{-3} NaOH (700 cm^3) was added. After extraction of the aqueous phase (Et_2O), the combined organic phase was dried ($MgSO_4$) and evaporated to give compounds **3**/**3'** ~ 6:1 (57.4 g, 76%, TLC, ethyl acetate) as an oil. For analytical purposes, a small amount (1.0 g) was chromatographed (silica gel, deactivated with triethylamine, ethyl acetate). Compound **3**H$^+$ 3,5-*dinitrobenzoate*, m.p. 185 °C (from MeCN) (Found: C, 58.6; H, 5.0; N, 9.2. $C_{21}H_{23}N_3O_7$ requires C, 58.74; H, 5.40; N, 9.87%); isomer **3'**H$^+$ 3,5-dinitrobenzoate had m.p. 155 °C (from MeCN).

Compound **3**. R_f 0.36 (ethyl acetate); $[\alpha]_D^{20}$ +60 (*c* 2.0, C_6H_6); ν_{max}(KBr)/cm^{-1} 3334w (NH) and 3040w (CH); δ_H(CD_3CN) 7.25 (5 H, m, ArH), 6.32 (1 H, dt, 6-H), 4.63 (1 H, m, 5-H), 3.84 (1 H, m, 2-H), 3.75 (1 H, q, 1″-H), 2.55/2.46 (2 H, dd, 1'-H_2), 2.00 (2 H, m, 4-H), 1.77/1.62 (2 H, m, 3-H) and 1.27 (3 H, d, 2″-H_3); $J_{2,3\alpha}$ 3, $J_{2,3\beta}$ 10.8, $J_{3\alpha,4\alpha}$ 6, $J_{3\beta,4\alpha}$ 10.5, $J_{4\alpha,6}$ 1.2, $J_{4\beta,6}$ 1.2. $J_{5,6}$ 6, $J_{2,1'a}$ 4.5, $J_{2,1'b}$ 6.8 and $J_{1'a,1'b}$ 12; δ_C(CD_3CN) 144.4 (C-6), 129.3 (C-*m*), 127.5 (C-*p*), 118.3 (C-*o*), 101.5 (C-5), 75.5 (C-2), 58.8 (C-1″), 52.4 (C-1'), 26.5 (C-4), 24.9 (C-3) and 20.3 (C-2″).

Compound **3'**. R_f 0.44 (ethyl acetate); $[\alpha]_D^{20}$ +2 (*c* 2.0, C_6H_6); ν_{max}(KBr)/cm^{-1} 3334w (NH) and 3020w (CH); δ_H(CD_3CN) 7.28 (5 H, m, ArH), 6.34 (1 H, dt, 6-H), 4.64 (1 H, m, 5-H), 3.81 (1 H, m, 2-H), 3.74 (1 H, q, 1″-H), 2.59/2.39 (2 H, dd, 1'-H_2), 2.00 (2 H, m, 4-H_2), 1.72/1.52 (2 H, m, 3-H_2) and 1.27 (3 H, d, 2″-H_3); $J_{2,3\alpha}$ 2.3, $J_{2,3\beta}$ 9.3, $J_{3\alpha,3\beta}$ 15, $J_{3\beta,4\alpha}$ 10.5, $J_{4\alpha,6}$ 1.3, $J_{4\beta,6}$ 1.3, $J_{5,6}$ 6, $J_{2,1'a}$ 4.5, $J_{2,1'b}$ 6.8 and $J_{1'a,1'b}$ 12; δ_C(CD_3CN) 144.3 (C-6), 129.3 (C-*m*), 127.6 (C-*p*), 118.3 (C-*o*), 101.5 (C-5), 75.8 (C-2), 59.1 (C-1″), 52.6 (C-1'), 26.6 (C-4), 25.0 (C-3) and 20.1 (C-2″); *m*/*z* (*inter alia*) 217 (M^+, 8%) and 202 ($M^+ - CH_3$, 4).

(2R)/(2S)-2-[(1S)-*Phenylethylaminomethyl*]-3,4-*dihydro*-2H-*pyran* ent-**3**/ent-**3'**.—Generation of *ent*-**3**/*ent*-**3'** with *rac*-**1** and (1*S*)-phenylethylamine and separation as described above for compounds **3**/**3'** gave compounds *ent*-**3**/*ent*-**3'** ~ 6:1 (58.3 g, 76%, TLC, ethyl acetate). Compound *ent*-**3**H$^+$ 3,5-dinitrobenzoate had m.p. 182 °C (from MeCN); compound *ent*-**3'**H$^+$ 3,5-dinitrobenzoate had m.p. 161 °C (from MeCN).

ent-**3**. $[\alpha]_D^{20}$ −88 (*c* 0.01, MeCN); ^{1}H, ^{13}C NMR, IR data are identical with those of compound **3**.

ent-**3'**. $[\alpha]_D^{20}$ +15 (*c* 0.03, MeCN); ^{1}H, ^{13}C NMR, IR data are identical with those of compound **3'**.

(2S)/(2R)-2-{N-*Trifluoroacetyl*-N-[(R)-*phenylethyl*]*aminomethyl*}-3,4-*dihydro*-2H-*pyran* **4a**/**4'a**.—To a solution of the 6:1 mixture of amines **3**/**3'** (40.3 g, 0.19 mol) in a dry mixture of CH_2Cl_2 (360 cm^3) and pyridine (75.1 g, 0.95 mol) was added dropwise at 0 °C during 30 min trifluoroacetic anhydride (TFAA) (42.0 g, 0.20 mol). After the mixture had been stirred for 1 h [total conversion, TLC, R_f **4a** 0.40, R_f **4'a** 0.32 light petroleum (60–70 °C)–diethyl ether (5:1)], saturated aq. $NaHCO_3$ (300 cm^3) was added. The aqueous phase was thoroughly extracted with CH_2Cl_2 and dried ($MgSO_4$), and the organic phase was evaporated. Fractional crystallization from MeOH (150 cm^3) at room temperature gave pure amide **4a** (average 46.0 g, 77%) as crystals. Evaporation of the mother liquor gave an oily residue consisting of a ~1:9 mixture of isomers **4a** and **4'a**, which could not be crystallized from a large number of solvents (light petroleum, ethanol, CCl_4) to afford pure compound **4'a**. For analytical purposes pure compound **4'a** was obtained by chromatography [light petroleum (60–70 °C)–diethyl ether (5:1)] as an oil.

Practical Version.—Treatment of a 1:1 mixture of compounds **3**/**3'** (107.8 g, 0.5 mol) with pyridine (200 cm^3, 0.95 mol) and TFAA (70 cm^3, 0.51 mol) as described above gave, after fractional crystallization from MeOH (200 cm^3) at room temperature, pure compound **4a** (average 36.5 g, 45%) as crystals. Fractional crystallization (three times) of the mother liquor from MeOH (100 cm^3) at 0 °C gave a total yield of pure compound **4a** (average 49.4 g, 63%) as crystals. Evaporation of the mother liquor gave an oily residue consisting of a ~1:2.5 mixture of isomers **4a** and **4'a**, which could not be crystallized.

Compound **4a** had m.p. 68 °C (MeOH) (Found: C, 61.2; H, 5.8; N, 4.6. $C_{16}H_{18}F_3NO_2$ requires C, 61.34; H, 5.79; N, 4.47%); $[\alpha]_D^{20}$ +99 (*c* 0.99, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 2986w (CH) and 1678s (C=O); δ_H($CDCl_3$) 7.35 (5 H, m, ArH), 6.33 (1 H, dt, 6-H), 5.31 (1 H, q, 1″-H), 4.64 (1 H, m, 5-H), 4.10 (1 H, dddd, 2-H), 3.31/2.82 (2 H, dd, 1'-H_2), 2.00 (2 H, m, 4-H_2), 1.79/1.42 (2 H, m, 3-H_2), 1.73 (3 H, d, 2″-H_3); $J_{2,3\alpha}$ 2.8, $J_{2,3\beta}$ 11.3, $J_{3\alpha,4\alpha}$ 6, $J_{4\alpha,6}$ 1.4, $J_{4\beta,6}$ 1.4, $J_{5,6}$ 6, $J_{2,1'a}$ 2.5, $J_{2,1'b}$ 8.3 and $J_{1'a,1'b}$ 14.8; δ_C($CDCl_3$) 157.7 (C=O), 143.0 (C-6), 138.0 (C-*ipso*), 128.9 (C-*m*), 128.3 (C-*p*), 127.3 (C-*o*), 118.5 (CF_3), 100.7 (C-5), 71.7 (C-2), 55.5 (C-1″), 47.2 (C-1'), 25.9 (C-4), 19.3 (C-3) and 17.6 (C-2″); J(CF_3, F) 284.75.

Compound **4'a** had $[\alpha]_D^{20}$ −4 (*c* 1.55, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 2980w (CH) and 1686s (C=O); δ_H($CDCl_3$) 7.40 (5 H, m, ArH), 5.95 (1 H, dt, 6-H), 5.40 (1 H, q, 1″-H), 4.65 (1 H, m, 5-H), 3.60 (1 H, dddd, 2-H), 3.37/3.24 (2 H, dd, 1'-H_2), 1.90 (2 H, m, 4-H_2), 1.75/1.50 (2 H, m, 3-H_2) and 1.68 (3 H, d, 2″-H_3); $J_{4\alpha,6}$ 1.5, $J_{4\beta,6}$ 1.5, $J_{5,6}$ 6, $J_{2,1'a}$ 3.5, $J_{2,1'b}$ 6.8 and $J_{1'a,1'b}$ 12; δ_C($CDCl_3$) 143.0 (C-6), 138.0 (C-*ipso*), 128.7 (C-*m*), 128.5 (C-*p*), 127.8 (C-*o*), 118.5 (CF_3), 100.3 (C-5), 72.2 (C-2), 55.3 (C-1″), 47.2 (C-1'), 25.6 (C-4), 19.1 (C-3) and 17.6 (C-2″); J(CF_3, F) 286.76.

(2R)/(2S)-2-{N-*Trifluoroacetyl*-N-[(1S)-*phenylethyl*]*aminomethyl*}-3,4-*dihydro*-2H-*pyran* ent-**4a**/ent-**4'a**.—Generation of isomers *ent*-**4a**/*ent*-**4'a** as described for isomers **3**/**3'** gave *ent*-**4a** (51.0 g, 86%) as crystals and *ent*-**4'a** as an oil.

Compound ent-**4a** had m.p. 68 °C (from MeOH) (Found: C, 61.1; H, 5.75; N, 4.45. $C_{16}H_{18}F_3NO_2$ requires C, 61.34; H, 5.79; N, 4.47%); $[\alpha]_D^{20}$ −98 (*c* 0.02, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **4a**.

Compound *ent*-**4'a** had $[\alpha]_D^{20}$ +6 (*c* 0.02, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **4'a**.

Methyl 2,3,4,6-*Tetradeoxy*-2-*hydroxyimino*-6-{*trifluoroacetyl*-[(1R)-*phenylethyl*]*amino*}-α/β-D-glycero-*hexopyranoside* **5a**/**11a** (α:β 5:1).—Compound **4a** (4.00 g, 12.80 mmol), dried *in vacuo* for 12 h, was placed in a flame-dried, 250 cm^3 flask fitted with gas inlet tube, Teflon valve and serum cap. The apparatus was evacuated three times *via* the Teflon valve and was vented with N_2. Against a stream of N_2, compound **4a** was dissolved in stirred CH_2Cl_2 (70 cm^3, freshly distilled and filtered through basic Al_2O_3, activity I). The solution was cooled to −78 °C. With introduction of NOCl (Fluka, A6), the colourless solution became blue and then green. When the green colour persisted after intensive stirring of the mixture, introduction of NOCl was stopped. The reaction mixture was concentrated to dryness (T_{max} 25 °C) to give a colourless solid residue. A small amount (20 mg) was immediately analysed by ^1H and ^{13}C NMR spectroscopy as pure diimine derivative **9a**; after 6 h, compound **9a** had almost totally rearranged (95%).

The solid residue **9a** was cooled to −78 °C and was dissolved in dry DMF (20 cm^3). At −40 °C dry methanol (5.3 cm^3, 140 mmol) was added and after 5 min dry 2,4,6-collidine (2,4,6-trimethylpyridine) (1.7 cm^3, 12.80 mmol). The reaction mixture was stirred at −40 °C for 10 min and then at room temperature for 40 min. Concentration to dryness and chromatography of the oily residue {R_f **5a** 0.39, R_f **11a** 0.30 [cyclohexane–ethyl acetate (2:1)]} gave isomers **5a** (2.50 g, 52%) and **11a** (500 mg, 10%) as oils.

Compound **5a**: (Found: C, 54.4; H, 5.8; N, 7.0. $C_{17}H_{21}F_3N_2O_4$ requires C. 54.54; H, 5.65; N, 7.48%); $[\alpha]_D^{20}$ +20 (*c* 1.0, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3400w (OH), 2980w (CH), 1725s (C=N) and 1672s (C=O); δ_H(400 MHz; $CDCl_3$) 8.20 (1 H, s, OH), 7.30 (5 H, m, ArH), 5.30 (1 H, q, 1'-H), 4.83 (1 H, s, 1-H), 4.43 (1 H, m, 5-H), 3.34 (3 H, s, OMe), 3.25/2.71 (2 H, dd, 6-H_2), 3.15/2.15 (2 H, m, 3-H), 1.74 (3 H, d, 2'-H) and 1.69/1.21 (2 H, m, 4-H_2); $J_{3\alpha,3\beta}$ 15, $J_{3\alpha,4\alpha}$ 6, $J_{3\alpha,4\beta}$ 15, $J_{3\beta,4\alpha}$ 6, $J_{3\beta,4\beta}$ 5, $J_{4\alpha,4\beta}$ 12, $J_{4\alpha,5}$ 3, $J_{4\beta,5}$ 12, $J_{5,6a}$ 8 and $J_{6a,6b}$ 14; δ_C($CDCl_3$) 157.4 (C=O), 154.3 (C-2), 128.8 (C-*m*), 128.3 (C-*p*), 127.1 (C-*o*), 116.7 (CF_3), 98.3 (C-1), 65.3 (C-5), 55.4 (C-1'), 54.4 (OMe), 49.0 (C-6), 28.3 (C-4), 18.6 (C-3) and 17.7 (C-2'); J(CF_3, F) 287.76.

Compound **11a**: $[\alpha]_D^{20}$ +33 (*c* 0.76, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3380w (OH), 2980w (CH), 1760s (C=N) and 1678s (C=O); δ_H(400 MHz; $CDCl_3$) 8.50 (1 H, s, OH), 7.20 (5 H, m, ArH), 4.85 (1 H, s, 1-H), 4.80 (1 H, q, 1'-H), 4.00 (1 H, m, 5-H), 3.49 (3 H, s, OMe), 3.35/2.90 (2 H, dd, 6-H_2), 2.90 (1 H, m, 3α-H), 2.20 (1 H, m, 3β-H), 1.75 (3 H, d, 2'-H_3) and 1.75/1.50 (2 H, m, 4-H_2); $J_{3\alpha,3\beta}$ 15, $J_{3\alpha,4\alpha}$ 5, $J_{3\alpha,4\beta}$ 15, $J_{3\beta,4\alpha}$ 6.5, $J_{3\beta,4\beta}$ 5, $J_{4\alpha,4\beta}$ 15, $J_{4\alpha,5}$ 6, $J_{4\beta,5}$ 12, $J_{5,6a}$ 3, $J_{5,6b}$ 7.5 and $J_{6a,6b}$ 14; δ_C($CDCl_3$) 157.8 (C=O), 153.4 (C-2), 128.9 (C-*m*), 128.4 (C-*p*), 127.2 (C-*o*), 115.4 (CF_3), 99.3 (C-1), 71.7 (C-5), 55.9 (C-1'), 55.5 (OMe), 49.9 (C-6), 25.6 (C-4), 20.4 (C-3) and 18.04 (C-2'); J(CF_3, F) 288.77; *m/z* (*inter alia*) 374 (M^+, 10%) and 343 ($M^+ - OCH_3$, 14).

Methyl 2,3,4,6-*Tetradeoxy*-2-*hydroxyimino*-6-{*trifluoroacetyl*-[(1S)-*phenylethyl*]*amino*}-β/α-L-glycero-*hexopyranoside* ent-**5a**/ent-**11a** (α:β 5.4:1).—Treatment of compound *ent*-**4a** as described above for compound **4a** yielded products *ent*-**5a** (2.85 g, 60%) and *ent*-**11a** (510 mg, 11%) as oils.

Compound *ent*-**5a**: $[\alpha]_D^{20}$ −23 (*c* 0.04, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of compound **5a**.

Compound *ent*-**11a**: $[\alpha]_D^{20}$ −43 (*c* 0.09, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of compound **11a**.

Methyl 2,3,4,6-*Tetradeoxy*-2-*hydroxyimino*-6-[(1R)-*phenylethylamino*]-α-D-glycero-*hexopyranoside* **5b**.—To a solution of amide **5a** (100 mg, 0.27 mmol) in dry ethanol (5 cm^3) was added in portions $NaBH_4$ (200 mg, 5.30 mmol) at room temperature within 3.5 h (total conversion, TLC, R_f **5b** 0.57, ethyl acetate). Excess of $NaBH_4$ was destroyed with acetic acid (pH 7), and the mixture was evaporated. After addition of water, the mixture was extracted with ethyl acetate, and the organic phase was dried ($MgSO_4$) and evaporated. The oily residue was chromatographed (ethyl acetate) to give title compound **5b** (36 mg, 49%) as an oil; $[\alpha]_D^{20}$ +15 (*c* 0.2, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3338s (OH) and 2922w (CH); δ_H(400 MHz; $CDCl_3$) 7.30 (5 H, m, ArH), 4.85 (1 H, s, 1-H), 4.20 (1 H, dddd, 5-H), 3.80 (1 H, q, 1'-H), 3.40 (3 H, s, OMe), 3.20/2.20 (2 H, dd, 6-H_2), 3.15/2.50 (2 H, m, 3-H_2), 1.70/1.50 (2 H, m, 4-H) and 1.30 (3 H, d, 2'-H_3); $J_{3\alpha,3\beta}$ 15, $J_{3\alpha,4\alpha}$ 6, $J_{3\alpha,4\beta}$ 13, $J_{3\beta,4\alpha}$ 5.5, $J_{4\alpha,4\beta}$ 15, $J_{4\alpha,5}$ 3, $J_{4\beta,5}$ 11.5, $J_{5,6a}$ 3, $J_{5,6b}$ 8 and $J_{6a,6b}$ 12; δ_C($CDCl_3$) 154.0 (C-2), 128.6 (C-*m*), 128.2 (C-*p*), 126.6 (C-*o*), 98.8 (C-1), 68.0 (C-5), 58.1 (C-1'), 54.4 (OMe), 51.7 (C-6), 28.1 (C-4) and 18.7 (C-2'); *m/z* (*inter alia*) 278 (M^+, 4%), 246 ($M^+ - OCH_3$, 4) and 231 ($M^+ - OCH_3 - OH$, 2).

Methyl 2-*Benzyloxycarbonylamino*-2,3,4,6-*tetradeoxy*-6-{*trifluoroacetyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6d**.—To a solution of oxime **5a** (1.46 g, 3.90 mmol) in acetic acid (15 cm^3) was added, at 15 °C, $NaBH_3CN$ (500 mg, 8.00 mmol). After 1.5 h (total conversion, TLC, R_f **6a** 0.39, ethyl acetate), the mixture was neutralized with $NaHCO_3$, and extracted with diethyl ether, and the organic phase was dried ($MgSO_4$) and evaporated. The oily residue was filtered (silica gel, ethyl acetate) to give compound **6a** (1.35 g).

The crude oily hydroxylamine **6a** was dissolved in acetic acid (100 cm^3) and hydrogenated in the presence of 10% Pd–C (1.00 g) at room temperature for 3 h (10^5 Pa). The catalyst was removed by filtration, and washed with hot acetic acid; the combined organic phases were evaporated to give free amine **6b** (1.10 g) as a crude oil.

This was dissolved in acetone–water (1:1) (50 cm^3) and solid $NaHCO_3$ (4.00 g, 48.00 mmol) and Z–Cl (520 mg, 3.10 mmol) were added at room temperature. After 2 h the mixture was evaporated, the residue was diluted with water, the water phase was extracted with ethyl acetate, and the organic phase was dried ($MgSO_4$). Evaporation and chromatography (R_f **6d** 0.64, ethyl acetate) gave title compound **6d** (1.23 g, 64%) as crystals, m.p. 107 °C (from MeOH).

Short Path to Compound **6d**.—Reaction of compound **4a** (15.0 g, 48.0 mmol) with NOCl as described above, careful extraction of the residue with ethyl acetate (200 cm^3) and evaporation gave isomeric mixture **5a**/**11a** as a crude oil. This was treated with $NaBH_3CN$ (4.20 g, 66.4 mmol). After work-up the oily residue was chromatographed to give oily compound **6a** (7.26 g, 38%). Hydrogenation of the hydroxylamine **6a** gave amine **6b**, which was directly treated with Z–Cl (5.0 g, 29.0 mmol). After crystallization [from ethyl acetate–cyclohexane (1:1)] pure *title compound* **6d** (7.94 g, 31% based on conversion of substrate **4a**) was obtained (Found: C, 60.3; H, 5.9; N, 5.6. $C_{25}H_{29}F_3N_2O_5$ requires C, 60.72; H, 5.91; N, 5.66%); $[\alpha]_D^{20}$ +111 (*c* 0.1, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 2938w (CH) and 1716s (C=O); δ_H($CDCl_3$) 7.30 (10 H, m, ArH), 5.60 (1 H, q, 1'-H), 5.10 [2 H, s, CH_2(Z)], 4.90 (1 H, d, 2-NH), 4.48 (1 H, d, 1-H), 4.00 (1 H, dddd, 5-H), 3.70 (1 H, m, 2-H), 3.30 (3 H, s, OMe), 3.20/2.60 (2 H, dd, 6-H_2), 1.70 (3 H, d, 2'-H_3), 1.60–1.10 (4 H, m, 3- and 4-H_2); $J_{1,2}$ 3, $J_{2.NH}$ 9, $J_{3\alpha,3\beta}$ 14, $J_{3\alpha,4\beta}$ 14, $J_{4\alpha,4\beta}$ 14, $J_{4\alpha,5}$ 1.5, $J_{4\beta,5}$ 12, $J_{5,6a}$ 3, $J_{5,6b}$ 8.3 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 157.8 [C=O(Ac)], 155.7 [C=O(Z)], 128.9–127.3 (Ar), 118.4 (CF_3), 98.3 (C-1), 66.8 [CH_2(Z)], 64.8 (C-5), 55.4 (C-1'), 54.7 (OMe), 49.5 (C-2), 49.3 (C-6), 28.4 (C-4), 25.1 (C-3) and 17.9 (C-2'); J(CF_3, F) 297.83.

Methyl 2-*Benzyloxycarbonylamino*-2,3,4,6-*tetradeoxy*-6-{*trifluoroacetyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranoside* ent-**6d**.—Treatment of oxime *ent*-**5a** as described above for compound **5a** gave *title compound ent*-**6d** (1.15 g, 59%) as crystals, m.p. 107 °C (from MeOH) (Found: C, 60.8; H, 5.9; N, 5.55%); $[\alpha]_D^{20}$ −102 (*c* 0.02, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6d**.

Methyl 2,3,4,6-*Tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-{*trifluoroacetyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6c**.—To a solution of compound **6b** (500 mg, 1.30 mmol) in acetone–water (1:1) (50 cm^3) were added solid $NaHCO_3$ (1.10 g, 13.00 mmol) and 2,4-dinitrofluorobenzene (240 mg, 1.30 mmol). The reaction mixture was refluxed for 4.5 h and evaporated. After addition of water, the mixture was extracted with ethyl acetate. The organic phase was dried ($MgSO_4$) and evaporated. The residue was chromtographed (R_f **6c** 0.60, ethyl acetate) to give *title compound* **6c** (600 mg, 87%) as yellow crystals, m.p. 123 °C (from MeOH) (Found: C, 52.5; H, 4.8; N, 10.6. $C_{23}H_{25}F_3N_4O_7$ requires C, 52.48; H, 4.82; N, 10.39%); R_f 0.33 [cyclohexane–ethyl acetate (2:1)]; $[\alpha]_D^{20}$ +88 (*c* 0.08, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3300s (CH), 3096w (CH), 1710s (C=O) and 1585s (N=O); δ_H($CDCl_3$) 9.20 (1 H, d, DNP 3-H), 8.70 (1 H, m, 2-NH), 8.20 (1 H, dd, DNP 5-H), 7.30 (5 H, m, Ph), 6.80 (1 H, d, DNP 6-H), 5.30 (1 H, q, 1′-H), 4.75 (1 H, d, 1-H), 4.10 (1 H, dddd, 5-H), 3.70 (1 H, m, 2-H), 3.40 (3 H, s, OMe), 3.40/2.70 (2 H, dd, 6-H_2), 1.90–1.30 (4 H, m, 3- and 4-H_2) and 1.70 (3 H, d, 2′-H_3); $J_{1,2}$ 4.5, $J_{2,NH}$ 9, $J_{2,3\alpha}$ 11, $J_{4\beta,5}$ 11 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 157.0 (C=O), 130.4 (DNP C-5), 129.0 (C-*m*), 128.4 (C-*p*), 127.3 (C-*o*), 124.4 (DNP C-3), 118.4 (CF_3), 113.6 (DNP C-6), 97.1 (C-1), 65.1 (C-5), 55.4 (C-1′), 54.4 (OMe), 49.1 (C-6), 28.0 (C-4), 24.0 (C-3) and 17.1 (C-2′).

Methyl 2,3,4,6-*Tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-{[2,4-*dinitrophenyl*-(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6f**.—To a solution of compound **5a** (1.00 g, 2.70 mmol) in dry MeOH (10 cm^3) were added Mo^{VI} oxide (460 mg, 3.20 mmol) and $NaBH_4$ (1.00 g, 26.00 mmol) at 0 °C within 5 h (total conversion, TLC). The reaction mixture was neutralized with acetic acid, filtered (Celite), and evaporated and the residue was diluted with water; the dried ($MgSO_4$) organic phase was evaporated to give a syrup (620 mg, ~65%, the $COCF_3$ group was not totally lost). The latter was dissolved in dry ethanol (10 cm^3) and $NaBH_4$ (500 mg, 13.00 mmol) was added (TLC control, R_f 0.80, MeOH). Work-up as above provided compound **6e** (300 mg) as an oil.

The crude oil **6e** was treated with $NaHCO_3$ (290 mg, 3.30 mmol) and 2,4-dinitrofluorobenzene (420 mg, 2.30 mmol) to give *title compound* **6f** (280 mg, 41%, based on substrate **5a**) as yellow crystals, m.p. 82 °C (from EtOH) (Found: C, 54.0; H, 4.4; N, 14.3. $C_{27}H_{28}N_6O_{10}$ requires C, 54.36; H, 4.73; N, 14.08%); R_f 0.28 [ethyl acetate–cyclohexane (2:1)]; ν_{max}(KBr)/cm^{-1} 3340w (NH), 2920w (CH) and 1590s (N=O); δ_H($CDCl_3$) 9.10 (2 H, d, 2 × DNP 3-H), 8.67 (1 H, d, 2-NH), 8.20 (2 H, dd, 2 × DNP 5-H), 7.20 (5 H, m, Ph), 6.84 (2 H, d, 2 × DNP 6-H), 4.89 (1 H, q, 1′-H), 4.64 (1 H, d, 1-H), 3.74 (1 H, dddd, 5-H), 3.70 (1 H, m, 2-H), 3.69 (3 H, s, OMe), 3.31/3.00 (2 H, dd, 6-H_2), 1.96/1.79 (2 H, m, 3-H_2), 1.94/1.34 (2 H, m, 4-H_2) and 1.72 (3 H, d, 2′-H_3); $J_{1,2}$ 3.5, $J_{2,NH}$ 9 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 130.7 (C-*m*), 130.3 (DNP C-5) 128.8 (C-*p*), 127.4 (DNP C-5), 127.1 (C-*o*), 124.6/123.0 (2 × DNP C-3), 121.0/113.9 (2 × DNP C-6), 97.3 (C-1), 65.2 (C-5), 62.7 (C-1′), 55.1 (OMe), 51.4 (C-2), 50.1 (C-6), 27.4 (C-4), 24.0 (C-3) and 16.3 (C-2′).

Methyl 2-*Benzyloxycarbonylamino*-2,3,4,6-*tetradeoxy*-6-[(1R)-*phenylethylamino*]-α-D-erythro-*hexopyranoside* **6g**.—To a solution of compound **6d** (2.30 g, 4.60 mmol) in dry ethanol (100 cm^3) was added $NaBH_4$ in portions (500 mg, 13.00 mmol) at room temperature within 4 h. Additional $NaBH_4$ (200 mg, 5.20 mmol) was added and the reaction mixture was stirred for 1 h (~90% conversion, TLC control, R_f **6g** 0.40, ethyl acetate). Excess of $NaBH_4$ was destroyed with acetic acid (pH 7) and the mixture was evaporated. After addition of water, it was extracted with ethyl acetate and the organic phase was dried ($MgSO_4$). Evaporation and chromatography (ethyl acetate) gave title compound **6g** (1.10 g, 70% based on conversion) as an oil; $[\alpha]_D^{20}$ −7 (*c* 0.50 CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3300w (NH), 2924w (CH) and 1714s (C=O); δ_H($CDCl_3$) 7.20 (10 H, m, ArH), 5.10 [2 H, s, CH_2(Z)], 5.00 (1 H, d, 2-NH), 4.60 (1 H, s, 1-H), 3.80 (2 H, m, 2- and 5-H), 3.78 (1 H, q, 1′-H), 3.38 (3 H, s, OMe), 2.55/2.45 (2 H, dd, 6-H_2), 1.84–1.45 (4 H, m, 3- and 4-H_2) and 1.36 (3 H, d, 2′-H_3); $J_{1,2}$ 3.5, $J_{2,NH}$ 9, $J_{5.6a}$ 3, $J_{5.6b}$ 9 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 155.7 (C=O), 128.5–126.5 (Ar), 98.3 (C-1), 67.1 (C-5), 66.7 [CH_2(Z)], 57.9 (C-1′), 54.9 (OMe), 51.9 (C-6), 49.7 (C-2), 28.0 (C-4), 25.0 (C-3) and 24.3 (C-2′); *m/z* (*inter alia*) 398 (M^+, 30%) and 383 ($M^+ - CH_3$, 22).

Methyl 2-*Benzyloxycarbonylamino*-2,3,4,6-*tetradeoxy*-6-[(1S)-*phenylethylamino*]-α-L-erythro-*hexopyranoside* ent-**6g**.—Treatment of amide *ent*-**6d** as described above for compound **6d** gave title compound *ent*-**6g** (1.20 g, 71% based on conversion) as an oil; $[\alpha]_D^{20}$ +27 (*c* 0.07, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6g**.

Methyl 2,3,4,6-*Tetradeoxy*-2,6-*bis*-(2,4-*dinitrophenylamino*)-α-D- *and* -α-L-erythro-*hexopyranoside* **6k** *and* ent-**6k**.—*Method* (a). A solution of compound **6g** (1.00 g, 2.50 mmol) in MeOH (100 cm^3) was hydrogenated in the presence of 10% Pd–C (2.50 g) at room temperature for 24 h (50 × 10^5 Pa). The catalyst was removed by filtration, and washed with hot MeOH; the filtrates were evaporated to give free diamine **6j** (400 mg). The crude diamine **6j** was treated with solid $NaHCO_3$ (2.60 g, 30 mmol) and 2,4-dinitrofluorobenzene (930 mg, 5.00 mmol) to give title compound **6k** (1.10 g, 68%) as yellow crystals, m.p. 109 °C (from EtOH).

Method (b). A solution of compound **6f** (100 mg, 0.17 mmol) in TFAA (10 cm^3) was heated at 65 °C for 10 min. After evaporation and filtration (silica gel, R_f 0.64, ethyl acetate) the title compound **6k** (78 mg, 94%) was obtained as yellow crystals.

Treatment of compound *ent*-**6g** as described for compound **6g** (method a) gave compound *ent*-**6k** (1.10 g, 68%) as yellow crystals, m.p. 109 °C (from EtOH).

Compound **6k** had $[\alpha]_D^{20}$ +38 (*c* 0.08, CH_2Cl_2); ν_{max}-(KBr)/cm^{-1} 3348w (NH), 3010w (CH) and 1586s (N=O); δ_H($CDCl_3$) 9.15 (2 H, d, 2 × DNP 3-H), 8.88 (1 H, t, 6-NH), 8.79 (1 H, d, 2-NH), 8.31/8.21 (2 H, dd, 2 × DNP 5-H), 6.96 (2 H, d, 2 × DNP 6-H), 4.90 (1 H, d, 1-H), 4.20 (1 H, dddd, 5-H), 3.89 (1 H, m, 2-H), 3.59 (3 H, s, OMe), 3.61/3.45 (2 H, m, 6-H_2), 2.11/2.00 (2 H, m, 3-H) and 1.91/1.74 (2 H, m, 4-H_2); $J_{1,2}$ 3, $J_{2,NH}$ 9, $J_{3\alpha,3\beta}$ 14, $J_{4\alpha,4\beta}$ 14, $J_{4\alpha,5}$ 1.5, $J_{4\beta,5}$ 12, $J_{5.6a}$ 3, $J_{5.6b}$ 8.3 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 130.4 (2 × DNP C-5), 124.6/124.3 (2 × DNP C-3), 113.9/113.6 (2 × DNP C-6), 97.6 (C-1), 66.6 (C-5), 55.9 (OMe), 51.5 (C-2), 47.3 (C-6), 27.4 (C-4) and 23.8 (C-3); *m/z* (*inter alia*) 492 (M^+, 5%), 461 ($M^+ - OCH_3$, 5) and 415 ($M^+ - OCH_3 - NO_2$, 6).

Compound *ent*-**6k** had $[\alpha]_D^{20}$ −41 (*c* 0.16, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6k**.

1-O-*Acetyl*-2,3,4,6-*tetradeoxy*-2,6-*bis*-(2,4-*dinitrophenylamino*)-D- and -L-erythro-*hexopyranose* **7b** (α:β 5.5:1) and *ent*-**7b** (α:β 3:1).—A solution of glycoside **6k** (450 mg, 0.91 mmol) in $MeNO_2$ (46 cm^3), acetic acid (75 cm^3) and 1 mol dm^{-3} H_2SO_4 (58 cm^3) was refluxed for 3 h [total conversion, TLC control, R_f **6k** 0.70, R_f **7a** 0.60 ($CHCl_3$–MeOH (10:1)]. After

addition of CH_2Cl_2 at 0 °C the stirred reaction mixture was neutralized and cooled with aq. NaOH (57.12 g in 300 cm^3). The aqueous phase was extracted with CH_2Cl_2, and washed successively with saturated aq. $NaHCO_3$ and water; the combined organic phases were dried ($MgSO_4$) and evaporated. The residue was chromatographed [$CHCl_3$–MeOH (10:1)] to give not totally pure (TLC) compound **7a** (350 mg) as a yellow oil. The latter was acetylated under standard conditions (3 h). Evaporation and chromatography (R_f **7b** 0.58, ethyl acetate) gave the acetate **7b** (340 mg, 68%) as a yellow crystalline mixture (α:β = 5.5:1), m.p. 94 °C (from acetone).

Treatment of compound *ent*-**6k** as described for isomer **6k** gave title product *ent*-**7b** (310 mg, 66%) as a yellow crystalline mixture (α:β = 5:1), m.p. 94 °C (from acetone).

Acetate **7b**: (Found: C, 46.2; H, 3.9; N, 16.15. $C_{20}H_{20}N_6O_{11}$ requires C, 46.16; H, 3.76; N, 16.14%); ν_{max}(KBr)/cm^{-1} 3364w (NH), 2952w (CH), 1751s (C=O) and 1580s (N=O); δ_H($CDCl_3$) 9.15 (2 H, d, 2 × DNP 3-H), 8.72 (1 H, t, 6-NH), 8.60 (1 H, d, 2-NH), 8.31/8.28 (2 H, dd, 2 × DNP 5-H), 6.96/6.94 (2 H, 2 × DNP 6-H), 6.30 (d, α-**7b**, 1-H) and 5.67 (d, β-**7b**, 1-H) (together 1H), 4.20 (1 H, dddd, 5-H), 3.85 (1 H, m, 2-H), 3.61/3.45 (2 H, dd, 6-H), 2.22 (s, α-**7b**, Ac) and 1.95 (3 H, s, β-**7b**, Ac) (together 3 H), 2.11/2.00 (2 H, m, 3-H_2) and 1.91/1.74 (2 H, m, 4-H_2); $J_{1,2}$ (α-**7b**) 3.5, $J_{1,2}$ (β-**7b**) 10, $J_{2,NH}$ 9, $J_{2,3\alpha}$ 11, $J_{4\beta,5}$ 11, $J_{5,6a}$ 4.5, $J_{5,6b}$ 7.5, $J_{6a,6b}$ 13.5 and $J_{6,NH}$ 4.5; δ_C($CDCl_3$) 169.1/168.6 (C=O), 130.7/130.4 (2 × DNP C-5), 124.5/124.2 (2 × DNP C-3), 113.9/113.7 (2 × DNP C-6), 96.0 (C-1, β-**7b**), 89.7 (C-1, α-**7b**), 68.8 (C-5), 50.2 (C-2), 47.0 (C-6), 27.1 (C-4), 24.4/23.9 (CO*Me*) and 20.7 (C-3).

Compound ent-**7b**: (Found: C, 46.2; H, 3.9; N, 16.15%); ^1H, ^{13}C NMR, IR data are identical with those of isomer **7b**.

Methyl 2-*Benzyloxycarbonylamino*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6l**.—To a solution of compound **6g** (220 mg, 0.54 mmol) in dry acetonitrile (10 cm^3) were added K_2CO_3 (74 mg, 5.40 mmol) and MeI (8 mg, 0.58 mmol) at room temperature within 2 h. Additional K_2CO_3 (74 mg, 5.40 mmol) and MeI (220 mg, 0.54 mmol) were added to the mixture, which was stirred for 1 h (~70% conversion, TLC, R_f **6e** 0.48, ethyl acetate). Excess of MeI was destroyed by stirring with 3% aq. NaOH for 15 min. After evaporation, and addition of water, the mixture was extracted with ethyl acetate, and the organic phase was dried ($MgSO_4$) and chromatographed (ethyl acetate) to give title compound **6l** (165 mg, 71% based on conversion) as an oil, $[\alpha]_D^{20}$ +73 (*c* 0.2, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3438w (NH), 2934w (CH) and 1721s (C=O); δ_H($CDCl_3$) 7.28 (10 H, m, ArH), 5.10 [2 H, s, CH_2(Z)], 5.00 (1 H, d, 2-NH), 4.60 (1 H, d, 1-H), 3.77 (2 H, m, 2- and 5-H), 3.70 (1 H, q, 1′-H), 3.38 (3 H, s, OMe), 2.60/2.40 (2 H, dd, 6-H_2), 2.23 (3 H, s, NMe), 1.80–1.64 (4 H, m, 3- and 4-H_2) and 1.35 (3 H, d, 2′-H_3); $J_{1,2}$ 3.5, $J_{2,NH}$ 9 and $J_{5,6a}$ = $J_{5,6b}$ 6, $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 155.8 (C=O), 128.6–126.8 (Ar), 98.5 (C-1), 66.8 [C-5, CH_2(Z)] 63.1 (C-1′), 58.3 (OMe), 55.1 (C-6), 49.8 (C-2), 39.8 (NMe), 29.0 (C-4), 25.4 (C-3) and 17.4 (C-2′); *m/z* (*inter alia*) 412 (M^+, 5%) and 398 ($M^+ - CH_3$, 2).

Methyl 2-*Benzyloxycarbonylamino*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranoside* ent-**6l**.—Treatment of compound *ent*-**6g** as described for isomer **6g** gave title compound *ent*-**6l** (300 mg, 63% based on conversion) as an oil; $[\alpha]_D^{20}$ −85 (*c* 0.3, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6l**.

Methyl 2,3,4,6-*Tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-[(2,4-*dinitrophenyl*)*methylamino*]-α-D- *and* -α-L-erythro-*hexopyranoside* **6n** *and* ent-**6n**.—Hydrogenation of compound **6l** (560 mg, 1.34 mmol) gave compounds **6m**/*ent*-**6m** as a crude oil; the oily residue was treated with $NaHCO_3$ (1.76 g, 20.00 mmol) and 2,4-dinitrofluorobenzene (500 mg, 2.72 mmol) as described for compound **6j** to give title compound **6n** (580 mg, 84%) as yellow crystals, m.p. 209 °C (from $CHCl_3$).

Compound *ent*-**6n** (570 mg, 82%) was obtained from compound *ent*-**6l** as yellow crystals, m.p. 209 °C (from $CHCl_3$).

Compound **6n**: R_f 0.60 (ethyl acetate); $[\alpha]_D^{20}$ +52 (*c* 0.26, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3322s (NH), 2928s (CH) and 1762s (N=O); δ_H($CDCl_3$) 9.16/8.70 (2 H, d, 2 × DNP 3-H), 8.74 (1 H, d, 2-NH), 8.25 (2 H, dd, 2 × DNP 5-H), 7.18/6.90 (2 H, d, 2 × DNP 6-H), 4.74 (1 H, d, 1-H), 4.14 (1 H, dddd, 5-H), 3.80 (1 H, m, 2-H), 3.60 (2 H, dd, 6-H_2), 3.43 (3 H, s, OMe), 3.10 (3 H, s, NMe) and 2.05–1.50 (4 H, m, 3- and 4-H); $J_{1,2}$ 3.5, $J_{2,NH}$ 9, $J_{5,6a}$ = $J_{5,6b}$ = 3.7 and $J_{6a,6b}$ 7.5; δ_C($CDCl_3$) 130.5/127.6 (2 × DNP C-5), 124.7/124.0 (2 × DNP C-3), 118.0/113.6 (2 × DNP C-6), 97.5 (C-1), 66.7 (C-5), 58.3 (OMe), 55.9 (C-2), 51.6 (C-6), 42.2 (NMe), 27.7 (C-4) and 24.0 (C-3); *m/z* (*inter alia*) 506 (M^+, 42%) and 475 ($M^+ - OCH_3$, 36).

Compound *ent*-**6n**: $[\alpha]_D^{20}$ −40 (*c* 0.01, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6n**.

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-{*trifluoroacetyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6o**.—To a solution of crude compound **6b** (2.90 g, 8.00 mmol) in MeOH (40 cm^3) were added $NaHCO_3$ (2.00 g, 8.00 mmol) and di-*tert*-butyl dicarbonate (1.73 g, 8.00 mmol) and the mixture was kept in an ultrasonic bath at 10 °C for 3 h (total conversion, TLC, R_f **6b** = 0.60, MeOH). The mixture was evaporated, the residue was diluted with water and extracted with ethyl acetate, and the organic phase was dried ($MgSO_4$) and evaporated. The residue was filtered (silica gel, R_f **60** 0.60, ethyl acetate) to give title compound **6o** (3.00 g, 65%) as crystals, m.p. 79 °C (from hexane) (Found: C, 56.7; H, 6.6; N, 6.0. $C_{22}H_{31}F_3N_2O_5$ requires C, 57.38; H, 6.78; N, 6.08%); $[\alpha]_D^{20}$ +77 (*c* 0.2, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3332w (NH), 2972s (Bu^t), 2940w (CH) and 1679s (C=O); δ_H($CDCl_3$) 7.28 (5 H, m, Ph), 5.28 (1 H, q, 1′-H), 4.70 (1 H, d, 2-NH), 4.50 (1 H, d, 1-H), 4.00 (1 H, dddd, 5-H), 3.63 (1 H, m, 2-H), 3.28 (3 H, s, OMe), 3.21/2.62 (2 H, dd, 6-H_2), 1.70 (3 H, d, 2′-H_3), 1.50–1.10 (4 H, m, 3- and 4-H_2) and 1.50 (9 H, s, Bu^t); $J_{1,2}$ 3.7, $J_{2,NH}$ 9, $J_{3\alpha,3\beta}$ 14, $J_{4\alpha,4\beta}$ 14, $J_{4\alpha,5}$ 1.7, $J_{4\beta,5}$ 11, $J_{5,6a}$ 3, $J_{5,6b}$ 8 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 157.2 [C=O(Ac)], 155.3 [C=O(Boc)], 128.6 (C-*m*), 128.3 (C-*p*), 127.3 (C-*o*), 118.4 (CF_3), 98.4 (C-1), 77.4 [C(Boc)], 64.4 (C-5), 55.4 (C-1′), 54.7 (OMe), 49.3 (C-6), 40.0 (C-2), 28.4 [Me(Boc)], 28.3 (C-4), 25.1 (C-3) and 17.9 (C-2′); $J(CF_3,F)$ 293.54.

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-{*trifluoroacetyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranoside* ent-**6o**.—Treatment of compound *ent*-**6b** as described for isomer **6b** gave *title compound ent*-**6o** (3.30 g, 73%) as crystals, m.p. 79 °C (from hexane) (Found: C, 57.2; H, 6.8; N, 5.8%); $[\alpha]_D^{20}$ −78 (*c* 0.99, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6o**.

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-[(1R)-*phenylethylamino*]-α-D-erythro-*hexopyranoside* **6p**.—Treatment of amide **6o** (2.40 g, 5.20 mmol) with $NaBH_4$ (750 mg, 20.00 mmol) as described for compound **6d** gave title product **6p** (1.10 g, 78% based on conversion) as an oil; R_f 0.30 (ethyl acetate); $[\alpha]_D^{20}$ +31 (*c* 0.48, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3432w (NH), 2970w (CH), 2930s (Bu^t) and 1706s (C=O); δ_H($CDCl_3$) 7.28 (5 H, m, Ph), 4.73 (1 H, d, 2-NH), 4.50 (1 H, d, 1-H), 3.77 (2 H, m, 5- and 1′-H), 3.63 (1 H, m, 2-H), 3.30 (3 H, s, OMe), 2.71 (1 H, t, 6-NH), 2.50 (2 H, dd, 6-H_2), 1.60–1.40 (4 H, m, 3- and 4-H_2), 1.40 (9 H, s, Bu^t) and 1.24 (3 H, d, 2′-H); $J_{1,2}$ 3.5, $J_{2,NH}$ 9, $J_{5,6a}$ 3, $J_{5,6b}$ 9 and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 155.2 (C=O), 128.5 (C-*m*), 126.9 (C-*p*), 126.6 (C-*o*), 98.5 (C-1), 79.3 [C(Boc)], 67.1 (C-5), 57.9 (C-1′), 54.9 (OMe), 51.8 (C-6), 40.3 (C-2), 28.4

[Me(Boc)], 28.2 (C-4), 25.1 (C-3) and 24.2 (C-2'); *m/z* (*inter alia*) 364 (M^+, 5%), 337 ($M^+ - OCH_3$, 7) and 307 ($M^+ - Bu^t$, 4).

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-[(1S)-*phenylethylamino*]-α-L-erythro-*hexopyranoside* ent-**6p**.—Treatment of amide *ent*-**6o** as described for isomer **6o** gave title product *ent*-**6p** (950 mg, 66% based on conversion) as an oil; $[\alpha]_D^{20}$ −36 (*c* 0.31, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6p**.

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6q**.—Treatment of compound **6p** (1.15 g, 3.20 mmol) with K_2CO_3 (880 mg, 6.30 mmol) and MeI (450 mg, 3.20 mmol), and after 2 h further addition of K_2CO_3 (880 mg, 6.30 mmol) and MeI (450 mg, 3.20 mmol) as described for compound **6g** gave title product **6q** (610 mg, 70% based on conversion) as an oil; R_f 0.44 (ethyl acetate); $[\alpha]_D^{20}$ +40 (*c* 0.1, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3442w (NH), 2970w (CH), 2930s (Bu^t) and 1707s (C=O); δ_H($CDCl_3$) 7.24 (5 H, m, Ph), 4.76 (1 H, d, 2-NH), 4.55 (1 H, d, 1-H), 3.70 (3 H, m, 2-, 5- and 1'-H), 3.35 (3 H, s, OMe), 2.38 (2 H, dd, 6-H_2), 2.21 (3 H, s, NMe), 1.77–1.42 (4 H, m, 3- and 4-H_2), 1.42 (9 H, s, Bu^t) and 1.30 (3 H, d, 2'-H_3); $J_{1,2}$ 3.7, $J_{2,NH}$ 9, $J_{5,6a} = J_{5,6b} = 6$ and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 155.3 (C=O), 128.1 (C-*m*), 127.8 (C-*p*), 126.8 (C-*o*), 98.7 (C-1), 70.3 [C(Boc)], 66.7 (C-5), 63.1 (C-1'), 58.4 (C-6), 55.0 (OMe), 49.4 (C-2), 39.7 (NMe), 29.1 (C-4), 28.5 [Me(Boc)], 25.4 (C-3) and 17.4 (C-2'); *m/z* (*inter alia*) 378 (M^+, 1%) and 346 ($M^+ - OCH_3 - H$, 2).

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranoside* ent-**6q**.—*Method* (a). Treatment of compound *ent*-**6p** as described for isomer **6p** gave title compound *ent*-**6q** (610 mg, 70% based on conversion) as an oil.

Method (b). To a solution of substrate *ent*-**6p** (1.90 g, 5.22 mmol) in dry propanonitrile (60 cm^3) were added K_2CO_3 (1.50 g, 10.90 mmol), MeI (1.11 g, 7.30 mmol) and a catalytic amount of *tert*-butylammonium iodide at room temperature. After 1.5 h, additional MeI (370 mg, 2.60 mmol) was added (total conversion after 2 h, TLC). Work-up as above gave compounds *ent*-**6q** (1.20 g, 61%) and *ent*-**14b** (640 mg, 24%) as yellowish crystals, m.p. 109 °C (from MeOH).

Product *ent*-**6q** had $[\alpha]_D^{20}$ −59 (*c* 0.12, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6q**.

Methyl 2,3,4,6-*Tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **6s**.—*Method* (a). A solution of carbamate **6q** (870 mg, 2.30 mmol) in $MeNO_2$ (220 cm^3) and 2 mol dm^{-3} HCl (5 cm^3) was heated to 75 °C for 2 h (total conversion, TLC, R_f **6q** 0.44, ethyl acetate). The mixture was evaporated, the residue was dissolved in acetone–water (1:1) (50 cm^3), 2,4-dinitrofluorobenzene (470 mg, 2.50 mmol) and solid $NaHCO_3$ (2.00 g, 23.00 mmol) were added, and the mixture was refluxed for 2 h. After evaporation, and addition of water, the mixture was extracted with ethyl acetate, and the organic phase dried ($MgSO_4$) and evaporated. The residue was chromatographed [R_f **6s** 0.61, $CHCl_3$–MeOH (10:1)] to give title compound **6s** (810 mg, 79%) as a yellow oil.

Method (b). A solution of carbamate **6l** (160 mg, 0.40 mmol) and TMSI (83 mg, 0.40 mmol) in dry acetonitrile (10 cm^3) was stirred at room temperature (N_2) for 5 min (TLC control, R_f **6l** 0.48, ethyl acetate). After conventional work-up, the residue was treated with 2,4-dinitrofluorobenzene (7 mg, 0.40 mmol) and $NaHCO_3$ (330 mg, 4.00 mmol) as described above to give title compound **6s** (38 mg, 22%) as a yellow oil; $[\alpha]_D^{20}$ +16 (*c* 2.0, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3338w (NH), 2932s (CH) and 1614s (N=O); δ_H($CDCl_3$) 9.10 (1 H, d, DNP 3-H), 8.80 (1 H, dd, DNP 5-H), 8.72 (1 H, d, 2-NH), 7.27 (5 H, m, Ph), 6.86 (1 H, d, DNP 6-H), 4.75 (1 H, d, 1-H), 3.90 (1 H, dddd, 5-H), 3.73 (2 H, m, 2- and 1'-H), 3.50 (3 H, s, OMe), 2.53/2.43 (2 H, dd, 6-H_2), 2.27 (3 H, s, NMe), 1.90/1.83 (2 H, m, 3-H_2), 1.80/1.22 (2 H, m, 4-H_2) and 1.36 (3 H, d, 2'-H_3); $J_{1,2}$ 3.7, $J_{2,NH}$ 9, $J_{3\alpha,3\beta}$ 15, $J_{5,6a} = J_{5,6b} = 6$ and $J_{6a,6b}$ 13.5; δ_C($CDCl_3$) 130.4 (DNP C-5), 128.2 (C-*m*), 127.9 (C-*p*), 127.0 (C-*o*), 124.7 (DNP C-3), 113.7 (DNP C-6), 97.6 (C-1), 67.1 (C-5), 63.3 (C-1'), 58.1 (C-6), 55.5 (OMe), 52.1 (C-2), 40.0 (NMe), 28.5 (C-4), 24.5 (C-3) and 17.3 (C-2'); *m/z* (*inter alia*) 445 (M^+, 18).

Methyl 2,3,4,6-*Tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranoside* ent-**6s**.—Treatment of compound *ent*-**6q** as described for isomer **6q** (method *a*) gave title product *ent*-**6s** (830 mg, 81% based on conversion) as a yellow oil; $[\alpha]_D^{20}$ −27 (*c* 0.01, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **6s**.

(2S)/(2R)-2-{*Methyl*-[(1S)-*phenylethyl*]*aminomethyl*}-3,4-*dihydro*-2H-*pyran* ent-**12**/**12'**.—*Method* (a). To a solution of amine *ent*-**3**/**3'** (5:1) (200 mg, 0.92 mmol) in dry acetonitrile (3.5 cm^3) were added formaldehyde (138 mg, 4.60 mmol) and $NaBH_3CN$ (167 mg, 2.60 mmol) at room temperature. After the mixture had been stirred for 15 min, acetic acid (pH 7), and after 45 min, 2 mol dm^{-3} KOH (6.7 cm^3) were added. The mixture was extracted with diethyl ether, and the organic phase washed successively with 0.5 mol dm^{-3} KOH and 1 mol dm^{-3} HCl, dried ($MgSO_4$) and evaporated. The oily residue was chromatographed (ethyl acetate) to give title amines *ent*-**12**/**12'** (6 mg, 29%) as an oil.

Method (b). To a solution of amines *ent*-**3**/**3'** (5:1) (200 mg, 0.92 mmol) in dry MeOH (10 cm^3) were added solid $NaHCO_3$ (76 mg, 0.99 mmol) and MeI (140 mg, 0.99 mmol) at room temperature. After the mixture had been stirred for 36 h [~50% conversion, TLC, R_f *ent*-**12**/**12'** 0.52, ethyl acetate–cyclohexane (1:1)], excess of MeI was destroyed with 3% aq. NaOH (15 min stirring). After concentration, and addition of water, the mixture was extracted with ether, and the organic phase was dried ($MgSO_4$) and chromatographed [ethyl acetate–cyclohexane (1:1)] to give title compounds *ent*-**12**/**12'** (5:1) (310 mg, 72% based on conversion) as an oil; ν_{max}(KBr)/cm^{-1} 2965w (CH) and 1642s (C=C); δ_H($CDCl_3$) 7.28 (5 H, m, Ph), 6.35 (1 H, dt, 6-H), 4.60 and 3.93 (1 H, m, 2-H), 3.67 (1 H, q, 1''-H), 2.60/2.42 (2 H, dd, 1'-H_2), 2.27/2.25 (3 H, s, NMe), 2.00 (2 H, m, 4-H_2), 1.84/1.50 (2 H, m, 3-H_2) and 1.39/1.35 (3 H, d, 2''-H_3); $J_{2,3\alpha}$ 2.5, $J_{2,3\beta}$ 7.5, $J_{3\alpha,3\beta}$ 15, $J_{3\beta,4\alpha}$ 10, $J_{3\beta,4\beta}$ 4, $J_{4\alpha,4\beta}$ 15, $J_{5,6}$ 6, $J_{6,4\alpha}$ 1.5, $J_{4\beta,6}$ 1.5, $J_{2,1'a}$ 6, $J_{2,1'b}$ 6.8 and $J_{1'a,1'b}$ 13.5; δ_C($CDCl_3$) 143.7 (C-6), 128.1 (C-*m*), 127.9 (C-*p*), 126.8 (C-*o*), 100.4 (C-5), 73.1 (C-2), 63.6 (C-1''), 57.7 (C-1'), 39.9 (NMe), 26.2 (C-4), 19.6 (C-3) and 18.0 (C-2''); *m/z* (*inter alia*) 231 (M^+, 8%).

1-O-*Acetyl*-2,3,4,6-*tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-[2,4-*dinitrophenylmethyl*)*amino*]-D- and L-erythro-*hexopyranose* **13a** (α:β 4:1) *and* ent-**13a** (α:β 5:1).—Cleavage of compound **6n** (470 mg, 0.95 mmol) and acetylation as described for compound **6k** gave product **13a** (400 mg, 88%) as a yellow crystalline mixture (α:β 4:1), m.p. 88 °C (from EtOH).

Compound *ent*-**6n** analogously gave product *ent*-**13a** (340 mg, 75%) as a yellow crystalline mixture (α:β 5:1), m.p. 88 °C (from EtOH).

Compound **13a** had R_f 0.14 (Et_2O); ν_{max}(KBr)/cm^{-1} 3342w (NH), 2944 (CH), 1750s (C=O) and 1587s (N=O); δ_H($CDCl_3$) 9.13/8.64 (2 H, d, 2 × DNP 3-H), 8.50 (1 H, d, 2-NH), 8.24 (2 H, dd, 2 × DNP 5-H), 7.10/7.00 (2 H, d, 2 × DNP 6-H), 6.15 and 5.51 (d, α-**13a**, 1-H) and (d, β-**13a**, 1-H) (together 1 H), 4.14 (1 H, m, 5-H), 4.00 (1 H, m, 2-H), 3.76/3.63 (2 H, d, 6-H_2), 3.00 (3 H, s, NMe), 2.17 (β-**13a**) and 2.14 (α-**13a**) (together 3 H, 2 s, Ac) and

2.00–1.65 (4 H, m, 3- and 4-H_2); $J_{1,2}$ (α-**13a**) 3, $J_{1,2}$ (β-**13a**) 6, $J_{2,NH}$ 9, $J_{3\alpha,3\beta}$ 12, $J_{4\alpha,4\beta}$ 12, $J_{6a,6b}$ 6; δ_C($CDCl_3$) 169.2 (C=O), 130.7/127.7 (2 × DNP C-5), 124.6 (2 × DNP C-3), 123.8/113.7 (2 × DNP C-6), 89.5 (C-1), 68.9 (C-5), 58.1 (C-2), 50.2 (C-6), 41.7 (NMe), 29.7/27.4 (CO*Me*), 24.5 (C-4) and 20.8 (C-3); *m/z* (*inter alia*) 534 (M^+, 10%) and 475 (M^+ − Ac, 8).

Compound *ent*-**13a**: ^1H, ^{13}C NMR, IR data are identical with those of isomer **13a**.

1-O-*Acetyl*-2,3,4,6-*tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-D-erythro-*hexopyranose* **13b** (α : β 9.3 : 1).—Cleavage of glycoside **6s** (430 mg, 0.96 mmol) and acetylation as described for compound **6k** gave title product **13b** (300 mg, 63%) as a yellow oil (α : β 9.3 : 1); R_f 0.47 (ethyl acetate); ν_{max}(KBr)/cm^{-1} 3340s (NH), 2966w (CH), 1749s (C=O) and 1615s (N=O); δ_H($CDCl_3$) 9.10 (1 H, d, DNP 3-H), 8.50 (1 H, d, 2-NH), 8.25 (1 H, dd, DNP 5-H), 7.32 (5 H, m, Ph), 7.00 (1 H, d, DNP 6-H), 6.24 (d, α-**13b** 1-H) and 5.50 (d, β-**13b**, 1-H) (together 1 H), 4.00 (2 H, m, 2- and 5-H), 3.73 (1 H, q, 1′-H), 2.59/2.41 (2 H, dd, 6-H_2), 2.25 (s, α-**13b**, Ac) and 2.06 (s, β-**13b**, Ac) (together 3 H), 2.19 (1 H, s, NMe), 2.00–1.50 (4 H, m, 3- and 4-H_2) and 1.35 (3 H, d, 2′-H_3); $J_{1,2}$ (α-**13b**) 3, $J_{1,2}$ (β-**13b**) 7, $J_{2,NH}$ 9, $J_{4\alpha,4\beta}$ 13.5, $J_{5,6a}$ = $J_{5,6b}$ = 6 and $J_{6a,6b}$ = 13.5; δ_C($CDCl_3$) 169.6/147.4 (C=O), 130.7 (DNP C-5), 128.2 (C-*m*), 128.0 (C-*p*), 127.1 (C-*o*), 124.6 (DNP C-3), 113.8 (DNP C-6), 96.8 (C-1, β-**13b**), 90.0 (C-1, α-**13b**), 69.4 (C-5), 63.5 (C-1′), 57.6 (C-2), 50.8 (C-6), 39.8 (NMe), 28.5/28.3 [Me (Ac)], 24.9 (C-4), 20.9 (C-3) and 17.0 (C-2′); *m/z* (*inter alia*) 472 (M^+, 100%) and 309 (M^+ − $C_6H_3N_2O_4$, 20).

1-O-*Acetyl*-2,3,4,6-*tetradeoxy*-2-(2,4-*dinitrophenylamino*)-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-L-erythro-*hexopyranose* ent-**13b** (α : β 7 : 1).—Cleavage of glycoside *ent*-**6s** and acetylation as described for compound **6s** gave title compound *ent*-**13b** (300 mg, 63%) as a yellow oil (α : β 7 : 1); ^1H, ^{13}C NMR, IR data are identical with those of isomer **13b**.

Methyl 2-(tert-*Butoxycarbonylamino*)-2,3,4,6-*tetradeoxy*-6-{*dimethyl*-[(1S)-*phenylethyl*]*ammonio*}-α-L-erythro-*hexopyranoside Iodide* ent-**14b**.—$[\alpha]_D^{20}$ +2 (*c* 0.2, MeOH); ν_{max}(KBr)/cm^{-1} 3440w (NH), 2966w (CH, Bu^t) and 1695s (C=O); δ_H($CDCl_3$) 7.70–7.50 (5 H, m, Ph), 5.43 (1 H, q, 1′-H), 4.73 (1 H, d, 2-NH), 4.61 (1 H, d, 1-H), 4.40/4.22 (2 H, dd, 6-H_2), 3.65 (2 H, m, 2- and 5-H), 3.48 (3 H, s, OMe), 3.40/3.25 (6 H, s, 2 × NMe), 1.95 (3 H, d, 2′-H_3), 1.75–1.35 (4 H, m, 3- and 4-H_2) and 1.39 (9 H, s, Bu^t); $J_{1,2}$ 3, $J_{2,NH}$ 8.25 and $J_{5,6a}$ 7.5; δ_C($CDCl_3$) 155.1 (C=O) 132.3–129.0 (Ar), 99.2 (C-1), 80.0 [C(Boc)], 74.5 (C-5), 65.2 (C-6), 63.8 (C-1′), 57.1 (OMe), 49.2 (C-2), 48.6/48.1 (2 × NMe), 28.5 (C-4), 28.4 [Me(Boc)], 23.1 (C-3) and 15.63 (C-2′); *m/z* (*inter alia*) 378 (M^+ − Me, 1.5%), 363 (M^+ − 2 × CH_3, 1), 348 (M^+ − 3 × CH_3, 1), 347 (M^+ − OCH_3 − CH_3, 1), 332 (M^+ − OCH_3 − 2 × CH_3, 1), 317 (M^+ − OCH_3 − 3 × CH_3, 1) and 277 (M^+ − CH_3 − Boc, 1).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{[(1R)-*phenylethyl*]-(*trifluoroacetyl*)*amino*}-α-D-erythro-*hexopyranoside* **15a**.—To a solution of NaN_3 (8.00 g, 0.12 mol) in water (20 cm^3)–CH_2Cl_2 (25 cm^3) was added, under N_2, trifluoromethanesulfonic anhydride (4.1 cm^3) at 0 °C within 30 min. After being stirred at room temperature for 2 h, the mixture was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 cm^3); the combined organic phase was washed successively with saturated aq. $NaHCO_3$, 1 mol dm^{-3} NaOH, and water, and dried ($MgSO_4$). The TfN_3 solution (~0.26 mol dm^{-3}) was stored at 4 °C.

To a solution of compound **6b** (2.04 g, 5.40 mmol) in dry MeOH (100 cm^3) were added $NaHCO_3$ (2.00 g, 24 mmol) and the TfN_3 solution (45 cm^3, 0.26 mol dm^{-3}) at room temperature. After being stirred for 36 h, the mixture was evaporated. After addition of water, the mixture was extracted with ethyl acetate and the organic phase was dried ($MgSO_4$). Evaporation and chromatography [R_f **15a** 0.50, cyclohexane–ethyl acetate (1 : 1)] gave title compound **15a** (1.10 g, 35–50%) as crystals, m.p. 25–28 °C (from EtOAc) (Found: C, 51.75; H, 5.5; N, 14.5. $C_{17}H_{21}F_3N_4O_3$ requires C, 52.85; H, 5.48; N, 14.5%); $[\alpha]_D^{20}$ +73 (*c* 0.33, CH_2Cl_2); ν_{max}(CCl_4)/cm^{-1} 3056s (CH), 2176s (N_3) and 1721s (C=O); δ_H($CDCl_3$) 7.45–7.30 (5 H, m, Ph), 5.30 (1 H, q, 1′-H), 4.66 (1 H, d, 1-H), 4.03 (1 H, dddd, 5-H), 3.37 (3 H, s, OMe), 3.24/2.68 (2 H, dd, 6-H_2), 3.08 (1 H, dddd, 2-H), 2.00 (1 H, dddd, 3α-H), 1.70 (3 H, d, 2′-H_3), 1.85–1.60 (2 H, m, 3β- and 4β-H) and 1.14 (1 H, dddd, 4α-H); $J_{1,2}$ 3, $J_{2,3\alpha}$ 12, $J_{2,3\beta}$ 5, $J_{4\alpha,4\beta}$ 12.7, $J_{4\alpha,5}$ 4.5, $J_{4\beta,5}$ 12.5, $J_{5,6a}$ 2.5, $J_{5,6b}$ 7.5, $J_{6a,6b}$ 12; δ_C($CDCl_3$) 161.6 (C=O), 128.9–127.2 (Ar), 118.2 (CF_3), 98.8 (C-1), 64.9 (C-5), 57.2 (C-2), 55.4 (C-1′), 54.8 (OMe), 49.0 (C-6), 28.4 (C-4), 22.6 (C-3) and 17.9 (C-2′); *m/z* (*inter alia*) 386 (M^+, 6%), 355 (M^+ − OCH_3, 10), 313 (M^+ − OCH_3 − N_3, 12) and 216 (M^+ − N_3 − OCH_3 − $COCF_3$, 21).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{[(1S)-*phenylethyl*](*trifluoroacetyl*)*amino*}-α-L-erythro-*hexopyranoside* ent-**15a**.—Treatment of compound *ent*-**6b** as described for compound **6b** gave title compound *ent*-**15a** (1.10 mg, 35–50%) as crystals, m.p. 25–28 °C (from EtOAc); $[\alpha]_D^{20}$ −71 (*c* 0.21, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **15a**.

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-[(1R)-*phenylethyl*-*amino*]-α-D-erythro-*hexopyranoside* **15b**.—To a solution of amide **15a** (1.10 g, 2.80 mmol) in dry ethanol (50 cm^3) was added, in portions, $NaBH_4$ (26 mg, 7.00 mmol) at room temperature within 2 h (total conversion, TLC, R_f **15b** 0.30, ethyl acetate). After conventional work-up, the residue was chromatographed (ethyl acetate) to give title compound **15b** (805 mg, 95%) as an oil; $[\alpha]_D^{20}$ +32 (*c* 0.12, CH_2Cl_2); ν_{max}(CCl_4)/cm^{-1} 3058s (CH) and 1965s (N_3); δ_H($CDCl_3$) 7.38–7.26 (5 H, m, Ph), 4.67 (1 H, d, 1-H), 3.99 (1 H, dddd, 5-H), 3.78 (1 H, q, 1′-H), 3.46 (3 H, s, OMe), 3.15 (1 H, dddd, 2-H), 2.57/2.45 (2 H, dd, 6-H_2), 2.04 (1 H, dddd, 3α-H), 1.85 (1 H, m, 3β-H), 1.64/1.51 (2 H, m, 4-H_2) and 1.35 (3 H, d, 2′-H_3); $J_{1,2}$ 3, $J_{2,3\alpha}$ 12, $J_{2,3\beta}$ 4.5, $J_{3\beta,4\alpha}$ 3.75, $J_{3\beta,4\beta}$ 4.5, $J_{4\alpha,4\beta}$ 12, $J_{4\alpha,5}$ 3, $J_{4\beta,5}$ 10.5, $J_{5,6a}$ 3.5, $J_{5,6b}$ 7.5, $J_{6a,6b}$ 12; δ_C($CDCl_3$) 126.9–126.5 (Ar), 98.7 (C-1), 66.9 (C-5), 58.2 (C-1′), 57.9 (C-2), 55.0 (OMe), 51.6 (C-6), 28.0 (C-4), 24.3 (C-3) and 22.5 (C-2′); *m/z* (*inter alia*) 290 (M^+, 2%), 259 (M^+ − OCH_3, 3) and 248 (M^+ − N_3, 36).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-[(1S)-*phenylethyl*-*amino*]-α-L-erythro-*hexopyranoside* ent-**15b**.—Treatment of compound *ent*-**15a** as described for isomer **15a** gave title compound *ent*-**15b** (800 mg, 94%) as an oil; $[\alpha]_D^{20}$ −35 (*c* 0.38, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **15b**.

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranoside* **15c**.—Treatment of compound **15b** (500 mg, 1.72 mmol) with K_2CO_3 (0.70 g, 5.00 mmol) and MeI (0.35 g, 2.58 mmol) as described for compound **6g**. Chromatography [R_f **15c** 0.27, cyclohexane–ethyl acetate (3 : 1)] gave title compound **15c** (312 mg, 55% based on conversion) as an oil; $[\alpha]_D^{20}$ +58 (*c* 0.01, CH_2Cl_2); ν_{max}(CCl_4)/cm^{-1} 3074s (CH), 2836m (CH_3) and 2174s (N_3); δ_H($CDCl_3$) 7.36–7.18 (5 H, m, Ph), 4.69 (1 H, d, 1-H), 3.86 (1 H, dddd, 5-H), 3.69 (1 H, q, 1′-H), 3.46 (3 H, s, OMe), 3.14 (1 H, dddd, 2-H), 2.50/2.34 (2 H, dd, 6-H_2), 2.25 (3 H, s, NMe), 2.01 (1 H, dddd, 3α-H), 1.90–1.24 (3 H, m, 3β-H and 4-H_2) and 1.36 (3 H, d, 2′-H_3); $J_{1,2}$ 3, $J_{2,3\alpha}$ 11.5, $J_{2,3\beta}$ 7, $J_{3\alpha,4\beta}$ 12, $J_{5,6a}$ 6, $J_{5,6b}$ 6 and $J_{6a,6b}$ 12.7; δ_C($CDCl_3$) 128.1–126.5 (Ar), 98.9 (C-1), 66.6 (C-5), 63.1 (C-1′), 58.4 (C-6), 58.1 (C-2), 55.1 (OMe), 39.9 (NMe), 29.0 (C-4), 22.7 (C-3) and 17.3 (C-2′); *m/z* (*inter alia*) 304

(M^+, 2%), 289 ($M^+ - CH_3$, 1), 262 ($M^+ - N_3$, 3) and 247 ($M^+ - N_3 - CH_3$, 5).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranoside* ent-**15c**.—Treatment of compound *ent*-**15b** as described for compound **15b** gave title compound *ent*-**15c** (312 mg, 55% based on conversion) as an oil; $[\alpha]_D^{20}$ −46 (*c* 0.81, CH_2Cl_2); ^1H, ^{13}C NMR, IR data are identical with those of isomer **15c**.

2-*Azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranose* **16a** (α:β 3:1).—A solution of compound **15c** (93 mg, 0.3 mmol) in $MeNO_2$ (3 cm^3), acetic acid (21 cm^3) and 1 mol dm^{-3} H_2SO_4 (21 cm^3) was refluxed for 4 h (total conversion, TLC, R_f **16a** 0.12, ethyl acetate). After conventional work-up, compound **16a** (84 mg) was obtained as a crude oil (α:β 3:1); $\nu_{max}(CCl_4)/cm^{-1}$ 3376w (OH), 2964w (CH) and 2094 (N_3); $\delta_H(CDCl_3)$ 7.41–7.13 (5 H, m, Ph), 5.29 (α-**16a**) and 4.51 (β-**16a**) (each d, together 1 H, 1-H), 4.13 (α-**16a**) and 3.58 (each m, together 1 H, 5-H), 3.67 (1 H, m, 1′-H), 3.21 (α-**16a**) and 3.07 (β-**16a**) (each dddd, together 1 H, 2-H), 2.72–2.54 (2 H, m, 6-H_2), 2.52 (3 H, s, NMe), 2.51–1.80 (2 H, m, 3-H_2), 1.73–1.17 (2 H, m, 4-H) and 1.45 (α-**16a**) and 1.38 (β-**16a**) (together 3 H, each d, 2′-H_3); $J_{1,2}$ (α-**16a**) 3, $J_{1,2}$ (β-**16a**) 7 and $J_{2,3\beta}$ 4.5; $\delta_C(CDCl_3)$ 128.9–127.2 (Ar), 98.2 (C-1, β-**16a**), 91.8 (C-1, α-**16a**), 73.9/64.2 (C-5), 64.1/63.7 (C-1′), 62.0/58.2 (C-2), 57.5/57.2 (C-6), 40.1/39.7 (NMe), 29.1/28.6 (C-4), 27.8/22.0 (C-3) and 18.7/17.1 (C-2′); *m/z* (*inter alia*) 290 (M^+, 3%), 275 ($M^+ - CH_3$, 8) and 248 ($M^+ - N_3$, 3).

2-*Azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranose* ent-**16a** (α:β 3:1).—Treatment of compound *ent*-**15c** as described for isomer **15c** gave title compound *ent*-**16a** (84 mg) as a crude oil (α:β 3:1); ^1H, ^{13}C NMR, IR data are identical with those of isomer **16a**.

1-O-*Acetyl*-2-*azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1R)-*phenylethyl*]*amino*}-α-D-erythro-*hexopyranose* **16b** (α:β 3:1).—The crude oily compound **16a** (84 mg) was acetylated under standard conditions (12 h). Evaporation and flash chromatography [R_f **16b** 0.09, cyclohexane–ethyl acetate (3:1)] gave acetate **16b** (42 mg, 55% based on conversion) as an oil (α:β 3:1); ν_{max}(KBr)/cm^{-1} 3022m (CH), 2220s (N_3) and 1806s (C=O); $\delta_H(CDCl_3)$ 7.38–7.18 (5 H, m, Ph), 6.14 (d, α-**16b**, 1-H) and 5.46 (d, β-**16b**, 1-H) (together 1 H), 3.87 (m, α-**16b**, 5-H) and 3.73–3.60 (m, β-**16b**, 5- and 1′-H) (together 2 H), 3.41–3.24 (1 H, m, 2-H), 2.57–1.73 (4 H, m, 3- and 6-H_2), 2.24 (3 H, s, NMe), 2.17 (3 H, s, Ac), 1.60–1.14 (2 H, m, 4-H_2) and 1.36 (d, α-**16b**, 2′-H_3) and 1.33 (d, β-**16b**, 2′-H_3) (together 3 H); $J_{1,2}$ (α-**16b**) 3 and $J_{1,2}$ (β-**16b**) 8.2; $\delta_C(CDCl_3)$ 169.4/169.2 (C=O), 128.2–126.5 (Ar), 95.1 (C-1, β-**16b**), 91.1 (C-1, α-**16b**), 75.2/69.2 (C-5), 63.4/63.1 (C-1′), 57.6/57.2 (C-2), 57.5/57.2 (C-6), 39.9/39.8 (NMe), 28.4/28.2/28.1/21.1 [Me(Ac), C-4], 22.6/21.5 (C-3) and 17.1/16.1 (C-2′); *m/z* (*inter alia*) 332 (M^+, 28%), 317 ($M^+ - CH_3$, 8) and 290 ($M^+ - N_3$, 5).

1-O-*Acetyl*-2-*azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α-L-erythro-*hexopyranose* ent-**16b** (α:β 3:1).—Treatment of compound *ent*-**16a** as described for isomer **16a** gave title compound *ent*-**16b** (42 mg, 55% based on conversion) as an oil (α:β 3:1); ^1H, ^{13}C NMR, IR data are identical with those of isomer **16b**.

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{[(1R)-*phenylethyl*](*trifluoroacetyl*)*amino*}-α(β)-D-threo(erythro)-*hexopyranoside* α(β)-**20** *and* α(β)-**21**.—To a mixture of $Ce(NH_4)_2(NO_3)_6$ (32.0 g, 60.00 mmol), NaN_3 (3.20 g, 48.00 mmol) and dry compound **4a** (10.0 g, 32.00 mmol) was added dry acetonitrile (100 cm^3) at −40 °C (N_2). The reaction mixture was stirred at −40 °C for 2 h [total conversion, α,β-**18**/α,β-**19**, TLC, diethyl ether–cyclohexane (1:1)], then dry MeOH (30 cm^3, 0.74 mol) was added. After being stirred at 0 °C for 2 h [total conversion; four components, TLC, diethyl ether–cyclohexane (1:3)], the homogeneous mixture was evaporated. After addition of water, the mixture was extracted with ethyl acetate (2 × 150 cm^3), and the organic phase was washed with water (2 × 40 cm^3), dried ($MgSO_4$), and evaporated. The yellowish oil consisting of isomers α,β-**20** and α,β-**21** (α-**21** ≡ **15a**) (12.10 g, 98%) in average proportions 2.8:5.8:2.8:1 (determined by integration of the 1-H signals in the 250 MHz ^1H NMR spectra, $CDCl_3$) was chromatographed [diethyl ether–light petroleum (60–70 °C) (1:3)]. Compound β-**20** was obtained in pure oily form; the other three were identified as a mixture. Data for compounds **20** and **21** are given in the next subsection.

2-*Azido*-2,3,4,6-*tetradeoxy*-6-{[(1R)-*phenylethyl*](*trifluoroacetyl*)*amino*}-α-D-threo(erythro)-*hexopyranosyl Nitrates* α,β-**18** *and* α,β-**19**.—These were formed in average proportions 5.3:1:1.4:1 (integration of the ^1H signals in the 250 MHz NMR spectra, $CDCl_3$). The mixture could not be separated by rapid chromatography [diethyl ether–light petroleum (60–70 °C) (1:3)]; isomers α-**18** and α-**19** could be enriched, however, to such an extent as to allow their identification by ^1H NMR spectroscopy.

Compound α-**18**: ν_{max}(KBr)/cm^{-1} 2930w (CH), 2095s (N_3) and 1670s (C=O); $\delta_H(CDCl_3)$ 7.40–7.24 (5 H, m, Ph), 6.07 (1 H, s, 1-H), 5.27 (1 H, q, 1′-H), 4.15 (1 H, dddd, 5-H), 3.64 (1 H, m, 2-H), 3.26/2.79 (2 H, dd, 6-H_2), 1.92 (2 H, m, 3-H_2), 1.65 (3 H, d, 2′-H_3) and 1.58/1.47 (2 H, m, 4-H_2); $J_{5,6a}$ 2, $J_{5,6b}$ 8 and $J_{6a,6b}$ 14; $\delta_C(CDCl_3)$ 157.4 (C=O), 138.0–127.1 (Ar), 116.6 (CF_3), 97.6 (C-1), 69.0 (C-5), 55.3 (C-1′), 53.7 (C-2), 48.9 (C-6), 23.1 (C-4), 22.7 (C-3) and 17.5 (C-2′); $J_{C1,H}$ 180, $J_{C2,H}$ 148, $J_{C3,H}$ 132, $J_{C4,H}$ 130, $J_{C5,H}$ 150, $J_{C6,H}$ 140 and $J(CF_3,F)$ 285.

Compound α-**19**: $\nu_{max}(CCl_4)/cm^{-1}$ 2930w (CH), 2095s (N_3) and 1670s (C=O); $\delta_H(CDCl_3)$ 7.40–7.24 (5 H, m, Ph), 5.71 (1 H, d, 1-H), 5.28 (1 H, q, 1′-H), 4.04 (1 H, dddd, 5-H), 3.77 (1 H, m, 2-H), 3.31/2.80 (2 H, dd, 6-H_2), 2.10–1.24 (4 H, m, 3- and 4-H_2) and 1.61 (3 H, d, 2′-H_3); $J_{1,2}$ 2, $J_{2,3\beta}$ 3.5, $J_{3\alpha,3\beta}$ 12, $J_{3\beta,4\beta}$ 4, $J_{5,6a}$ 2, $J_{5,6b}$ 8 and $J_{6a,6b}$ 14.

Compound α-**20**: ν_{max}(KBr)/cm^{-1} 2930w (CH), 2095s (N_3) and 1680s (C=O); $\delta_H(CDCl_3)$ 7.40–7.24 (5 H, m, Ph), 5.30 (1 H, q, 1′-H), 4.56 (1 H, s, 1-H), 4.11 (1 H, dddd, 5-H), 3.45 (1 H, m, 2-H), 3.32 (3 H, s, OMe), 3.22/2.73 (2 H, dd, 6-H_2), 2.03 (1 H, dddd, 3α-H), 1.77 (1 H, dddd, 3β-H), 1.75 (3 H, d, 2′-H_3) and 1.35/1.31 (2 H, m, 4-H_2); $J_{1,2}$ < 1.0, $J_{5,6a}$ 2.0, $J_{5,6b}$ 8.0 and $J_{6a,6b}$ 14.0; $\delta_C(CDCl_3)$ 157.4 (C=O), 138.4 (C-*ipso*), 128.8 (C-*m*), 128.1 (C-*p*)*, 127.1 (C-*o*)*, 116.6 (CF_3), 98.4 (C-1), 64.7 (C-5), 56.5 (C-2)*, 55.2 (C-1′)*, 54.5 (OMe)*, 48.9 (C-6), 23.3 (C-4), 22.4 (C-3) and 17.7 (C-2′); $J(CF_3,F)$ 285.

Compound β-**20**: (Found: C, 52.7; H, 5.5; N, 14.4. $C_{17}H_{21}N_4O_3$ requires C, 52.58; H, 5.48; N, 14.50%); ν_{max}-$(CCl_4)/cm^{-1}$ 2930w (CH), 2095s (N_3) and 1680s (C=O); $\delta_H(CDCl_3)$ 7.40–7.24 (5 H, m, Ph), 5.29 (1 H, q, 1′-H), 4.38 (1 H, d, 1-H), 3.86 (1 H, dddd, 5-H), 3.56 (4 H, 2-H and OMe), 3.27/2.85 (2 H, dd, 6-H_2), 1.92–1.37 (4 H, m, 3- and 4-H_2) and 1.76 (3 H, d, 2′-H_3); $J_{1,2}$ 1.5, $J_{2,3\beta}$ 3.5, $J_{2,3\alpha}$ 3.5, $J_{3\alpha,3\beta}$ 14.0, $J_{3\beta,4\beta}$ 4.0, $J_{3\beta,4\alpha}$ 4.0, $J_{3\beta,4\beta}$ 4.0, $J_{3\alpha,4\alpha}$ 14.0, $J_{4\alpha,4\beta}$ 13.5, $J_{4\alpha,5}$ 2.5, $J_{4\beta,5}$ 11.0, $J_{5,6a}$ 2.5, $J_{5,6b}$ 8.0, $J_{6a,6b}$ 14.5 and $J_{1',2'}$ 7.0; $\delta_C(CDCl_3)$ 157.4 (C=O), 138.3 (C-*ipso*), 128.9 (C-*m*), 128.3 (C-*p*), 127.3 (C-*o*), 116.6 (CF_3), 102.6 (C-1), 72.6 (C-5), 57.3 (C-2)*, 56.7 (OMe)*, 55.5 (C-1′)*, 49.4 (C-6), 27.3 (C-4), 23.6 (C-3) and 18.1 (C-2′); $J(CF_3,F)$ 285.

Compound β-**21**: ν_{max}(KBr)/cm^{-1} 2930w (CH), 2095s (N_3) and 1680 (C=O); $\delta_H(CDCl_3)$ 7.40–7.24 (5 H, m, Ph), 5.31 (1 H, q, 1′-H), 4.10 (1 H, d, 1-H), 3.78 (1 H, dddd, 5-H), 3.56 (3 H, s, OMe), 3.24/2.80 (2 H, dd, 6-H_2), 3.10 (1 H, ddd, 2-H), 2.00 (1 H,

dddd, 3α-H), 1.76 (3 H, d, 2'-H_3) and 1.84–1.00 (3 H, m, 3β-H and 4-H_2); $J_{1,2}$ 8.5.

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-[(1R)-*phenylethylamino*]-β(α)-D-threo(erythro)-*hexopyranoside* α(β)-**22** *and* α(β)-**23**.—To a homogeneous solution of amides α,β-**20**/α,β-**21** (7.32 g, 18.90 mmol) in ethanol (100 cm^3) was added in portions $NaBH_4$ (1.00 g, 26.50 mmol) at room temperature. After being stirred for 12 h [total conversion, TLC, $CHCl_3$–MeOH (10:1)], the mixture was evaporated. After addition of water, the residue was extracted with ethyl acetate, the extract was washed with water, and the organic phase was dried ($MgSO_4$) and evaporated. The crude mixture of α,β-**22**/α,β-**23** (α-**23** ≡ **15b**) (5.06 g, 92%) was chromatographed to give pure compounds β-**22** (2.33 g, 42%) and α-**23** (2.00 g, 37%) as oils.

Compound β-**22**: R_f 0.45 [$CHCl_3$–MeOH (10:1)]; ν_{max}(KBr)/cm^{-1} 3482w (NH), 2950w (CH) and 2094m (N_3); δ_H($CDCl_3$) 7.35–7.14 (5 H, m, Ph), 4.43 (1 H, d, 1-H), 3.76 (1 H, q, 1'-H), 3.59 (2 H, m, 2- and 5-H), 3.50 (3 H, s, OMe), 2.60 (2 H, m, 6-H_2), 1.94 (1 H, dddd, 3α-H), 1.78–1.39 (3 H, m, 3β-H and 4-H_2) and 1.35 (3 H, d, 2'-H_3); $J_{1,2}$ 1.5, $J_{2,3\beta}$ 3, $J_{3\alpha,3\beta}$ 13.5, $J_{3\beta,4\alpha} = J_{3\beta,4\beta}$ = 3 and $J_{1',2'}$ 6.7; *m/z* (*inter alia*) 2.90 (M^+, 10%), 275 ($M^+ - CH_3$, 54) and 134 (54).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-[(1S)-*phenylethylamino*]-β(α)-L-threo(erythro)-*hexopyranoside* ent-α(β)-**22** *and* ent-α(β)-**23**.—Treatment of dry amide *ent*-**4a** (2.00 g, 6.40 mmol) with $Ce(NH_4)_2(NO_3)_6$ (6.40 g, 12.00 mmol), NaN_3 (640 mg, 9.60 mmol) and dry MeOH (6 cm^3, 0.15 mol) as described for compound **4a** gave compounds *ent*-α,β-**20**/*ent*-α,β-**21** (2.20 g, 91%) as a yellowish oil. This oil was treated with $NaBH_4$ (1.00 g, 26.50 mmol) as described for compounds α,β-**20**/α,β-**21** to give title compounds *ent*-α,β-**22**/*ent*-α,β-**23** (1.51 g, 82%) in average proportions 2.8:5.9:1:1 (determined by integration of the 1-H signals in the 250 MHz ^1H NMR spectra, $CDCl_3$). The crude mixture was chromatographed [$CHCl_3$–MeOH (10:1) and then with ethyl acetate] to give pure products *ent*-α-**23** (≡ *ent*-**15b**) (280 mg, 15%), *ent*-β-**22** (610 mg, 33%), *ent*-α-**22** (240 mg, 13%) and a mixture of *ent*-α-**22**/*ent*-β-**22**/*ent*-β-**23** (370 mg, 20%) as oils. Compound *ent*-β-**23** could not be separated, but it was enriched to such an extent as to allow identification by ^1H NMR.

Compound *ent*-α-**22**: R_f 0.33 (ethyl acetate); $[\alpha]_D^{20}$ −73 (*c* 1.1, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 2952s (CH), 2100s (N_3) and 1493w (NH); δ_H($CDCl_3$) 7.23 (5 H, m, Ph), 4.50 (1 H, br s, 1-H), 3.85 (1 H, m, 5-H), 3.70 (1 H, q, 1'-H), 3.43 (1 H, m, 2-H), 3.32 (3 H, s, OMe), 2.48 (2 H, m, 6-H_2), 2.05 (1 H, dddd, 3α-H), 1.97 (1 H, ddd, 3β-H), 1.72/1.58 (2 H, m, 4-H_2) and 1.30 (3 H, d, 2'-H_3); $J_{1,2}$ < 1, $J_{3\alpha,3\beta} = J_{4\alpha,4\beta}$ = 13.5, $J_{3\alpha,4\alpha}$ 3.0, $J_{3\alpha,4\beta}$ 13.5, $J_{3\beta,4\alpha}$ 3, $J_{3\beta,4\beta}$ 4.5, $J_{4\alpha,5}$ 6, $J_{4\beta,5}$ 13.5, $J_{5,6a} = J_{5,6b}$ = 6, $J_{1',2'}$ 6; δ_C($CDCl_3$) 145.6–126.7 (Ar), 98.6 (C-1), 67.7 (C-5), 58.0 (C-1'), 57.2 (OMe)*, 55.0 (C-2)*, 52.1 (C-6)*, 24.3 (C-4), 23.4 (C-3) and 22.8 (C-2').

Compound *ent*-β-**22**: R_f 0.33 (ethyl acetate); $[\alpha]_D^{20}$ +51 (*c* 0.2, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 2950s (CH), 2100s (N_3) and 1493w (NH); δ_H($CDCl_3$) 7.30 (5 H, m, Ph), 4.93 (1 H, d, 1-H), 3.78 (1 H, q, 1'-H), 3.61 (2 H, m, 2- and 5-H), 3.51 (3 H, s, OMe), 2.61 (2 H, m, 6-H_2), 2.00–1.56 (4 H, m, 3- and 4-H_2) and 1.35 (3 H, d, 2'-H_3); $J_{1,2}$ 1.5, $J_{2,3\alpha}$ 6, $J_{2,3\beta}$ 3, $J_{3\alpha,3\beta} = J_{4\alpha,4\beta}$ = 13.5, $J_{3\alpha,4\alpha}$ 3.5, $J_{3\alpha,4\beta}$ 13.5, $J_{3\beta,4\alpha}$ 3, $J_{3\beta,4\beta}$ 3, $J_{4\beta,5}$ 13 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 145.5–126.5 (Ar), 102.5 (C-1), 75.5 (C-5), 58.0 (C-1' and OMe)*, 56.5 (C-2)*, 51.9 (C-6), 27.2 (C-4), 24.0 (C-3) and 23.4 (C-2'); *m/z* (*inter alia*) 290 (M^+, 20%), 275 ($M^+ - CH_3$, 68) and 248 ($M^+ - N_3$, 90).

Compound *ent*-β-**23**: R_f 0.22 (ethyl acetate); ν_{max}(KBr)/cm^{-1} 2954s (CH), 2098s (N_3), 1490w (NH) and 1449s (CH); δ_H($CDCl_3$) 7.23 (5 H, m, Ph), 4.20 (1 H, d, 1-H), 3.70 (1 H, q, 1'-H), 3.58 (3 H, s, OMe), 3.51 (1 H, m, 5-H), 3.24 (1 H, m, 2-H), 2.60 (2 H, m, 6-H_2), 1.96–1.40 (4 H, m, 3- and 4-H_2) and 1.29 (3 H, d, 2'-H_3); $J_{1,2}$ 8.5.

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{2,4-*dinitrophenyl*-[(1R)-*phenylethyl*]*amino*}-β-D-threo-*hexopyranoside* β-**24**.—Treatment of amine β-**22** (1.14 g, 3.93 mmol) with $NaHCO_3$ (500 mg, 6.00 mmol) and 2,4-dinitrofluorobenzene (1.10 g, 5.90 mmol) in acetone (50 cm^3) gave, after filtration {silica gel, R_f β-**24** 0.75 [$CHCl_3$–MeOH (10:1)]}, title compound β-**24** 1.72 g, 96%) as a yellow foam; ν_{max}(KBr)/cm^{-1} 2920m (CH), 2094s (N_3) and 1523s (N=O); δ_H($CDCl_3$) 8.59 (d, DNP 3-H), 8.24 (dd, DNP 5-H), 7.37–7.25 (m, 6 H, Ph and DNP 6-H), 4.88 (1 H, q, 1'-H), 4.22 (1 H, d, 1-H), 3.52 (1 H, m, 2-H), 3.44 (1 H, ddd, 5-H), 3.38 (3 H, s, OMe), 3.25/3.04 (2 H, dd, 6-H_2), 1.93 (1 H, ddd, 3α-H), 1.73 (3 H, d, 2'-H_3), 1.62 (1 H, dddd, 3β-H) and 1.34/1.23 (2 H, m, 4-H_2); $J_{1,2}$ 1.5, $J_{2,3\alpha}$ 3.5, $J_{2,3\beta}$ 3, $J_{3\alpha,3\beta}$ 14.5, $J_{3\alpha,4\alpha}$ 4.5, $J_{3\alpha,4\beta}$ 13, $J_{3\beta,4\alpha}$ 3.5, $J_{3\beta,4\beta}$ 6.5, $J_{4\alpha,4\beta}$ 13, $J_{4\alpha,5}$ 5, $J_{4\beta,5}$ 8.5, $J_{5,6a}$ 3, $J_{5,6b}$ 9, $J_{6a,6b}$ 15.5 and $J_{1',2'}$ 7; δ_C($CDCl_3$) 148.1 (DNP C-1), 140.2 (DNP C-2)*, 138.3 (DNP C-4)*, 128.6 (C-*m*), 127.8 (C-*p*), 127.2 (DNP C-5), 126.9 (C-*o*), 122.8 (DNP C-3), 121.0 (DNP C-6), 102.3 (C-1), 72.6 (C-5), 62.4 (C-1'), 57.0 (C-2), 56.2 (OMe), 50.3 (C-6), 26.9 (C-4), 22.9 (C-3) and 16.1 (C-2'); *m/z* (*inter alia*) 456 (M^+, 0.8%) and 441 ($M - CH_3$, 0.6).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-(2,4-*dinitrophenylamino*)-β-D-threo-*hexopyranoside* β-**25**.—A solution of compound β-**24** (2.91 g, 6.38 mmol) in acetic acid (20 cm^3) was heated at 85 °C for 4 h. The mixture was evaporated, the residue was diluted with ethyl acetate, and the organic phase was washed successively twice with 1 mol dm^{-3} NaOH and water, dried ($MgSO_4$), and evaporated to give the *product* β-**25** (2.07 g, 92%) as yellow crystals, m.p. 142 °C (from ethyl acetate) (Found: C, 43.9; H, 4.6; N, 23.85. $C_{17}H_{21}N_4O_3$ requires C, 44.32; H, 4.58; N, 23.85%); $[\alpha]_D^{20}$ +93 (*c* 1.0, CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3358w (NH), 2950w (CH), 2096s (N_3), 1618m (NH) and 1523s (N=O); δ_H($CDCl_3$) 9.16 (1 H, d, DNP 3-H), 8.98 (1 H, m, NH), 8.29 (1 H, dd, DNP 5-H), 6.96 (1 H, d, DNP 6-H), 4.58 (1 H, d, 1-H), 3.86 (1 H, dddd, 5-H), 3.74 (1 H, m, 2-H), 3.61 (3 H, s, OMe), 3.58/3.54 (2 H, dd, 6-H_2), 2.10 (1 H, ddd, 3α-H), 1.86 (1 H, ddd, 3β-H) and 1.79–1.50 (2 H, m, 4-H_2); $J_{1,2}$ 1.5, $J_{2,3\alpha}$ 4.5, $J_{2,3\beta}$ 3, $J_{3\alpha,3\beta}$ 13.5, $J_{4\alpha,5}$ 3, $J_{4\beta,5}$ 9, $J_{5,6a}$ 9 and $J_{5,6b}$ 3.75.

2-*Azido*-2,3,4,6-*tetradeoxy*-6-(2,4-*dinitrophenylamino*)-D-threo-*hexopyranose* **26a** (α:β 1.7:1).—To a solution of glycoside β-**25** (800 mg, 2.27 mmol) in $MeNO_2$ (16 cm^3) were added acetic acid (160 cm^3) and 1 mol dm^{-3} H_2SO_4 (160 cm^3) and the mixture was refluxed for 1 h (TLC control). After addition of water (100 cm^3) and CH_2Cl_2 (100 cm^3), it was neutralized with aq. NaOH (120.00 g in 200 cm^3 of water) at 0 °C. The mixture was extracted with CH_2Cl_2, and the organic phase was washed twice with 0.5 mol dm^{-3} NaOH, dried ($MgSO_4$), and evaporated. The oily residue was chromatographed [$CHCl_3$–MeOH (10:1)] to give title compound **26a** (583 mg, 81%) as a yellow oil (α:β 1.7:1); ν_{max}(KBr)/cm^{-1} 3470s (OH), 3098w (CH), 2926w (CH), 2098s (N_3) and 1520s (N=O); δ_H($CDCl_3$) 9.03 (1 H, m, DNP 3-H), 8.85/8.79 (1 H, m, NH), 8.23 (1 H, dd, DNP 5-H), 6.94/6.93 (1 H, d, DNP 6-H), 5.22 (s, α-**26a**, 1-H) and 4.94 (d, β-**26a**, 1-H) (together 1 H), 4.38/3.93 (1 H, m, 5-H), 4.10 (1 H, m, OH), 3.79/3.66 (1 H, m, 2-H), 3.65–3.39 (2 H, m, 6-H_2) and 2.23–1.59 (4 H, m, 3- and 4-H_2); $J_{1,2}$ (α-**26a**) ~ 0 and $J_{1,2}$ (β-**26a**) 1.5; δ_C($CDCl_3$) 148.4 (DNP C-1), 136.0/135.9 (DNP C-2), 130.4/130.3 (DNP C-4), 124.2 (DNP C-3), 114.2/114.2 (DNP C-5), 95.0/91.9 (C-1), 73.8/66.6 (C-5), 58.7/57.1 (C-2), 47.7/47.5 (C-6) and 26.4/23.2/22.7/21.6 (C-3 and -4); *m/z* (*inter alia*) 338 (M^+, 36).

1-O-*Acetyl*-2-*azido*-2,3,4,6-*tetradeoxy*-6-(2,4-*dinitrophenylamino*)-D-threo-*hexopyranose* **26b** (α:β 1.7:1).—Compound **26a** (400 mg, 1.18 mmol) was acetylated under standard conditions (2 h). Evaporation and filtration (silica gel, ethyl acetate) gave title compound **26b** (435 mg, 97%) as a yellow oil (α:β 1.7:1) (Found: C, 44.7; H, 4.2; N, 21.7. $C_{14}H_{16}N_4O_3$ requires C, 44.22; H, 4.24; N, 22.10%); R_f 0.68 [$CHCl_3$–MeOH (10:1)]; ν_{max}(KBr)/cm^{-1} 3100w (CH), 2948w (CH), 2098s (N_3), 1749s (C=O), 1519s (N=O) and 1372s (N=O); δ_H($CDCl_3$) 9.17 (1 H, d, DNP 3-H), 8.81/8.73 (1 H, dd, NH), 8.28/8.27 (1 H, dd, DNP 5-H), 6.96/6.95 (1 H, d, DNP 6-H), 6.08 (s, α-**26b**, 1-H), 5.84 (d, β-**26b**, 1-H) (together 1 H), 4.20/4.00 (1 H, dddd, 5-H), 3.80/3.66 (1 H, ddd, 2-H), 3.54 (2 H, m, 6-H_2), 2.20/2.15 (3 H, s, Ac), 2.16 (1 H, m, 3α-H), 2.03/1.66 (1 H, dddd, 3β-H) and 1.91/1.79 (2 H, dddd, 4-H); $J_{1,2}$ (α-**26b**) ~ 0, $J_{1,2}$ (β-**26b**) 1.5; δ_C($CDCl_3$) 168.7/168.6 (C=O), 148.4/148.3 (DNP C-1), 136.4 (DNP C-2), 130.3/130.2 (DNP C-4), 124.3 (DNP C-3), 114.1/114.0 (DNP C-6), 93.9/91.3 (C-1), 74.7/69.3 (C-5), 56.8/55.7 (C-2), 47.6/47.4 (C-6) and 26.7/22.8/22.7/22.4 (C-3 and -4); *m/z* (*inter alia*) 380 (M^+, 100%), 338 ($MH^+ - CH_3CO$, 30) and 321 ($M^+ - CH_3CO_2$, 50).

5-*Acetoxy*-2-*azido*-6-(2,4-*dinitrophenylamino*)-1-*methoxyhexyl Acetate* **27**.—To a solution of compound β-**25** (20 mg, 0.06 mmol) in acetic anhydride (2 cm^3) was added one drop of conc. H_2SO_4 at −15 °C and the mixture was stirred for 30 min before being diluted with saturated aq. $NaHCO_3$ and extracted with CH_2Cl_2; the organic phase was dried ($MgSO_4$) and evaporated. The residue was chromatographed [R_f 0.61, cyclohexane–ethyl acetate (1:3)] to give title acetal **27** (10 mg, 38%) as a yellow oil; ν_{max}(KBr)/cm^{-1} 3350w (CH), 2926m (CH), 2100s (N_3) and 1784s (C=O); δ_H($CHCl_3$) 9.17 (1 H, d, DNP 3-H), 8.74 (1 H, t, NH), 8.33 (1 H, dd, DNP 5-H), 7.04/7.03 (1 H, d, DNP 6-H), 5.75/5.73 (1 H, d, 1-H), 5.15 (1 H, m, 5-H), 3.52/3.50 (3 H, s, OMe), 3.41 (1 H, m, 2-H), 2.62 (2 H, m, 6-H_2), 2.19–2.16 (3 H, s, 1-OAc), 2.12 (3 H, s, 5-OAc) and 1.96–1.44 (4 H, 3- and 4-H_2); $J_{1,2}$ 4.5; *m/z* (*inter alia*) 452 (M^+, 2%).

Methyl 2-*Azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-α(β)-L-threo-*hexopyranoside* ent-α(β)-**28**.—Treatment of compound *ent*-β-**22** (150 mg, 0.52 mmol) with K_2CO_3 (200 mg, 1.45 mmol) and MeI (142 mg, 1.04 mmol), and after 2 h with additional MeI (71 mg, 0.52 mmol), as described for compound **6g**, gave title compound *ent*-β-**28** (83 mg, 65% based on conversion) as an oil. Treatment of compound *ent*-α-**22** as described above for isomer *ent*-β-**22** gave title compound *ent*-α-**28** (82 mg, 62% based on conversion).

Compound *ent*-α-**28** had R_f 0.59 (ethyl acetate); ν_{max}-(KBr)/cm^{-1} 2961s (CH), 2090s (N_3) and 1439s (CH); δ_H($CDCl_3$) 7.25 (5 H, m, Ph), 4.57 (1 H, br s, 1-H), 3.88 (1 H, m, 5-H), 3.70 (1 H, q, 1'-H), 3.50 (1 H, m, 2-H), 3.38 (3 H, s, OMe), 2.56/2.42 (2 H, m, 6-H_2), 2.23 (3 H, s, NMe), 2.04 (1 H, dd, 3α-H), 1.80 (1 H, m, 3β-H), 1.50 (2 H, m, 4-H_2) and 1.38 (3 H, d, 2'-H_3); $J_{1,2}$ < 1, $J_{2,3\alpha}$ = $J_{2,3\beta}$ = 2.3, $J_{3\alpha,3\beta}$ 15, $J_{3\beta,4\alpha}$ = $J_{3\beta,4\beta}$ = 3, $J_{5,6a}$ = $J_{5,6b}$ = 6, $J_{6a,6b}$ 13.5 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 128.0–126.8 (Ar), 98.6 (C-1), 67.3 (C-5), 63.2 (C-1'), 58.6 (OMe), 57.3 (C-6), 54.9 (C-2), 39.8 (NMe), 24.2 (C-4), 22.9 (C-3) and 17.3 (C-2').

Compound *ent*-β-**28** had m.p. 48 °C (from $CHCl_3$); $[\alpha]_D^{20}$ +62 (*c* 0.6, $CHCl_3$); R_f 0.30 (ethyl acetate); ν_{max}(KBr)/cm^{-1} 2964s (CH), 2094s (N_3) and 1447s (CH); δ_H($CDCl_3$) 7.29 (5 H, m, Ph), 4.42 (1 H, d, 1-H), 3.72 (1 H, q, 1'-H), 3.63 (1 H, m, 5-H), 3.58 (1 H, m, 2-H), 3.54 (3 H, s, OMe), 2.61 (2 H, m, 6-H_2), 2.28 (3 H, s, NMe), 1.98 (1 H, dd, 3α-H), 1.70 (1 H, m, 3β-H), 1.48 (2 H, m, 4-H_2) and 1.40 (3 H, d, 2'-H_3); $J_{1,2}$ 1.5, $J_{3\alpha,3\beta}$ = $J_{4\alpha,4\beta}$ = 13.5, $J_{3\alpha,4\beta}$ 3, $J_{3\alpha,4\alpha}$ 3 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 143.8–126.8 (Ar), 102.3 (C-1), 75.5 (C-5), 63.2 (C-1'), 58.1 (OMe), 57.9 (C-6), 56.3 (C-2), 39.7 (NMe), 27.1 (C-4), 24.2 (C-3) and 16.8 (C-2'); *m/z* (*inter alia*) 304 (M^+, 20%), 289 ($M^+ - CH_3$, 3) and 262 ($M^+ - N_3$, 8).

2-*Azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-L-threo-*hexopyranose* ent-**29a** (α:β 2.0:1).—To a solution of glycoside *ent*-β-**28** (130 mg, 0.43 mmol) in $MeNO_2$ (3 cm^3) were added acetic acid (30 cm^3) and 1 mol dm^{-3} H_2SO_4 (30 cm^3) and the mixture was refluxed for 5 h. Work-up as described for **26a** and chromatography (R_f *ent*-**29a** 0.21, ethyl acetate) gave title compound *ent*-**29a** (74 mg, 60%) as an oil (α:β 2.0:1).

Treatment of glycoside *ent*-α-**28** (130 mg, 0.43 mmol) as described above for its isomer *ent*-β-**28** gave compound *ent*-**29a** (99 mg, 80%) as an oil (α:β 2.0:1).

Compound *ent*-α-**29a** had ν_{max}(KBr)/cm^{-1} 2974s (CH), 2102s (N_3) and 1454w (CH); δ_H($CDCl_3$) 7.30 (5 H, m, Ph), 5.15 (1 H, br s, 1-H), 4.20 (1 H, m, 5-H), 3.70 (1 H, q, 1'-H), 3.52 (1 H, dd, 2-H), 2.68/2.36 (2 H, m, 6-H_2), 2.22 (3 H, s, NMe), 2.10–1.51 (4 H, m, 3- and 4-H_2) and 1.41 (3 H, d, 2'-H_3); $J_{1,2}$ < 1 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 142.7–127.1 (Ar), 92.0 (C-1), 65.5 (C-5), 63.7 (C-1'), 57.9 (C-2), 57.8 (C-6), 39.9 (NMe), 24.3 (C-4), 22.6 (C-3) and 14.2 (C-2'); *m/z* (*inter alia*) 290 (M^+, 0.6%), 275 ($M^+ - CH_3$, 0.2), 248 ($M^+ - N_3$, 1.4) and 273 ($M^+ - COCH_3$, 10).

Compound *ent*-β-**29a** had ν_{max}(KBr)/cm^{-1} 2974s (CH), 2102s (N_3) and 1454w (CH); δ_H($CDCl_3$) 7.30 (5 H, m, Ph), 4.78 (1 H, d, 1-H), 3.70 (3 H, m, 2-, 5- and 1'-H), 2.68/2.50 (2 H, m, 6-H_2), 2.22 (3 H, s, NMe), 2.10–1.51 (4 H, m, 3- and 4-H_2) and 1.38 (3 H, d, 2'-H_3); $J_{1,2}$ 1.8 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 142.7–127.1 (Ar), 94.9 (C-1), 74.6 (C-5), 63.5 (C-1'), 59.3 (C-2), 58.0 (C-6), 39.9 (NMe), 26.3 (C-4), 24.0 (C-3) and 17.3 (C-2').

1-O-*Acetyl*-2-*azido*-2,3,4,6-*tetradeoxy*-6-{*methyl*-[(1S)-*phenylethyl*]*amino*}-L-threo-*hexopyranose* ent-**29b** (α:β 2.0:1).—Compound *ent*-**29a** (70 mg, 0.24 mmol) was acetylated under standard conditions (3 h). Evaporation and chromatography [R_f *ent*-α-**29b** 0.52, $CHCl_3$–MeOH (10:1)] gave compound *ent*-α,β-**29b** (74 mg, 93%) as an oil (α:β 2.0:1). Compound *ent*-α-**29b** had ν_{max}(KBr)/cm^{-1} 2972s (CH), 2104s (N_3) and 1756s (C=O); δ_H($CDCl_3$) 7.29 (5 H, m, Ph), 5.98 (1 H, br s, 1-H), 3.95 (1 H, m, 5-H), 3.68 (1 H, q, 1'-H), 3.54 (1 H, dd, 2-H), 2.58/2.40 (2 H, m, 6-H_2), 2.22 (3 H, s, NMe), 2.10 (3 H, s, OAc), 2.02 (1 H, m, 3α-H), 1.90 (1 H, dddd, 3β-H), 1.55 (2 H, m, 4-H_2) and 1.35 (3 H, d, 2'-H_3); $J_{1,2}$ < 1, $J_{2,3\alpha}$ = $J_{2,3\beta}$ = 2.3, $J_{3\alpha,3\beta}$ 15, $J_{3\beta,4\alpha}$ = $J_{3\beta,4\beta}$ = 3, $J_{5,6a}$ = $J_{5,6b}$ = 6, $J_{6a,6b}$ 13.5 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 169.0 (C=O), 143.5–126.8 (Ar), 91.9 (C-1), 69.9 (C-5), 63.3 (C-1'), 58.0 (C-2), 56.2 (C-6), 39.8 (NMe), 23.7 (C-4)*, 22.6 (C-3)*, 21.1 [Me(Ac)] and 17.3 (C-2'); *m/z* (*inter alia*) 332 (M^+, 20%), 317 ($M^+ - CH_3$, 2), 290 ($M^+ - N_3$, 2) and 273 ($M^+ - COCH_3$, 10).

Compound *ent*-β-**29b** had R_f 0.45 [$CHCl_3$–MeOH (10:1)]; ν_{max}(KBr)/cm^{-1} 2972s (CH), 2104s (N_3) and 1756s (C=O); δ_H($CDCl_3$) 7.29 (5 H, m, Ph), 5.76 (1 H, d, 1-H), 4.20 (1 H, m, 5-H), 3.70 (m, 2 H, 1'- and 2-H), 2.58/2.40 (2 H, m, 6-H_2), 2.22 (3 H, s, NMe), 2.18 (3 H, s, OAc), 2.10–1.50 (4 H, m, 3- and 4-H_2) and 1.35 (3 H, d, 2'-H_3); $J_{1,2}$ 1.8, $J_{5,6a}$ = $J_{5,6b}$ = 6, $J_{6a,6b}$ 13.5 and $J_{1',2'}$ 6; δ_C($CDCl_3$) 169.0 (C=O), 143.2–126.8 (Ar), 94.1 (C-1), 76.1 (C-5), 63.2 (C-1'), 57.5 (C-2)*, 57.3 (C-6)*, 39.4 (NMe), 23.7 (C-4)*, 22.8 (C-3)*, 21.0 [Me (Ac)] and 16.6 (C-2').

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