Synthesis of (L)-Daunosamine and Related Amino Sugars

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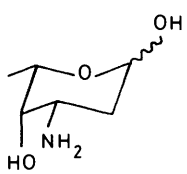
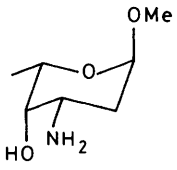
1-(2-Furyl)ethanol (**6**) has been converted into methyl (±)-daunosaminide (**1**) and methyl (±)-ristosaminide (**3**) by use of an intramolecular cyclisation of a trichloroacetimidate group. (±)-Daunosamine (**1**) has been obtained more directly from the alcohol (**10**) by use of a modified Mitsunobu reaction; the scope of the latter reaction has been explored using cyclohex-2-en-1-ol as a model substrate.

Asymmetric reduction of 2-acetylfuran (**5**) has given (*S*)-1-(2-furyl)ethanol (**46**) in good enantiomeric excess, thus providing a short route to the L-enantiomers of the amino sugars (**1**), (**2**), and (**3**) from a cheap, non-carbohydrate precursor.

L-Daunosamine (**1**)[1] is the sugar component of the anthracycline antibiotics daunomycin (**4a**) and adriamycin (**4b**)[2] which exhibit a broad spectrum of activity on solid tumours and soft-tissue sarcomas.[3] There have been several syntheses of the amino sugar (**1**) starting from both carbohydrate precursors and non-sugar substrates; a recent review describes most of these.[4] The importance of the antitumour agents and the need for large quantities in order to make analogues has given rise to renewed activity for short, efficient routes to the amino sugar (**1**).[5]



(**1**)



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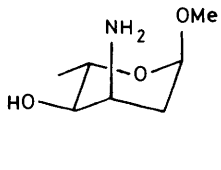
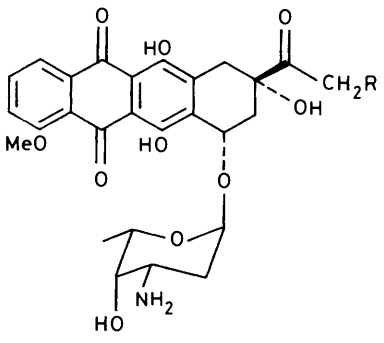


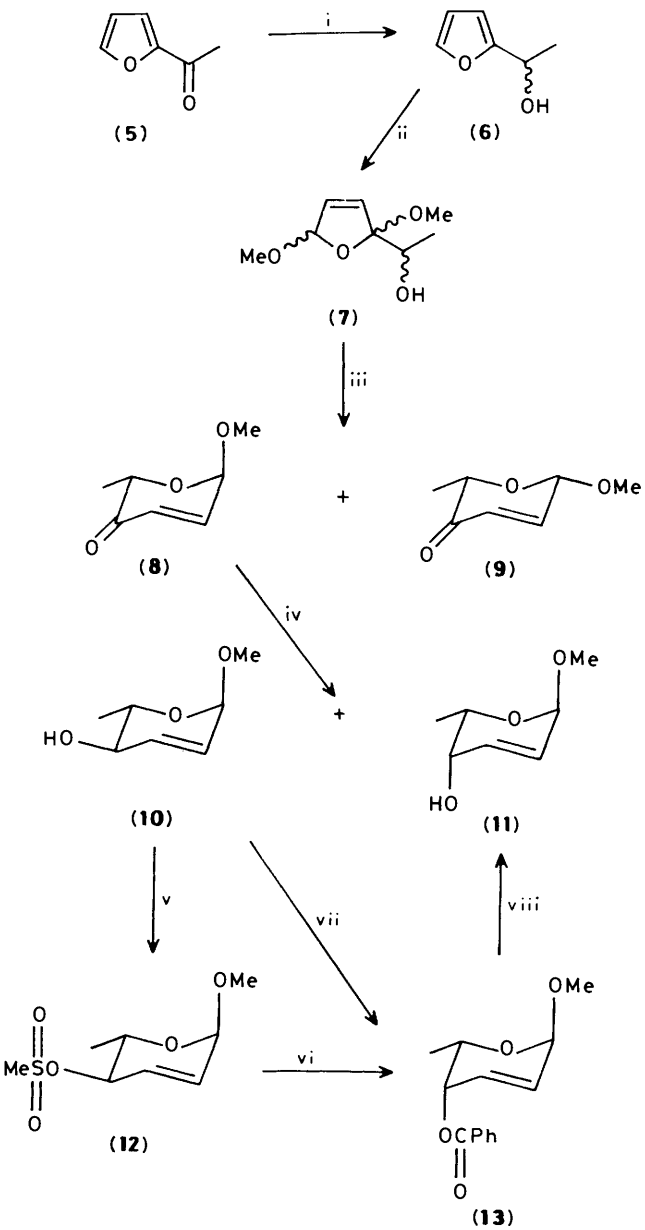
(**3**)



R = H (**4a**)
R = OH (**4b**)

In our recent communication,[6] a non-chiral route to daunosamine (**1**) and a related amino sugar, methyl ristosaminide (**3**), was reported. In this paper, full details of these routes including extension leading to the optically active amino sugars (**1**) and (**3**) are given.

2-Acetylfuran (**5**) was reduced to the furan alcohol (**6**) in quantitative yield. There are several methods for the conversion of furfuryl alcohols into protected pyranuloses such as (**8**) in the literature.[7] In this particular case, the routes of Achmatowicz[8]



Scheme 1. *Reagents and conditions:* i, LAH; ii, Br_2, MeOH, −35 °C; iii, HCO_2H, MeOH; iv, $NaBH_4$; v, $MeSO_2Cl$, pyridine; vi, NaOCOPh; vii, PPh_3, DEAD, $PhCO_2H$; viii, NaOMe

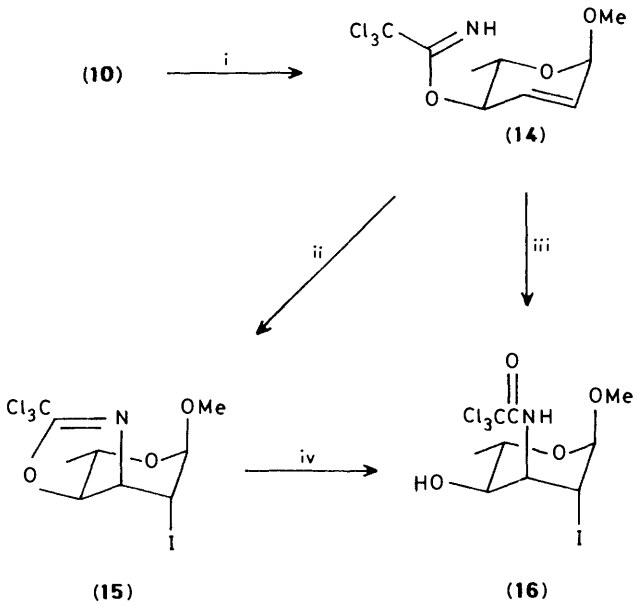
and Weeks[9] gave the best results. The furan alcohol (**6**) was therefore oxidised to the dimethyloxydihydrofuran (**7**) in 93% yield by use of bromine in methanol. Acid treatment of the dihydrofuran (**7**), under strictly anhydrous conditions, gave the pyranuloses (**8**) and (**9**) in a 3:1 (α:β) anomer ratio and an overall yield of 83%. These anomers were easily separated using column chromatography on silica. The major pyranulose product (**8**) was reduced using sodium borohydride to give the epimeric allylic alcohols (**10**) and (**11**) in a 13:1 ratio.[8,10]

The alcohol (**10**) was now available in 54% overall yield from 2-acetylfuran (**5**) and provided a good model system in the search for a route to daunosamine (**1**); the alcohol (**10**) was converted into several ristosamine derivatives in the model investigations.

The trichloroacetimidate (**14**) was obtained from the alcohol (**10**) by Overman's method.[11] The imidate functionality provided a nucleophilic nitrogen atom which was capable of cyclising to the olefinic carbon centre vicinal to the one attached to the imidate group.

Two reagents were used to effect cyclisation of the imidate (**14**). On treatment with iodonium dicollidine tetrafluoroborate[12,*] in acetonitrile, the imidate (**14**) was converted into the iodo-oxazoline (**15**) in 70% yield. Alternatively, in the presence of *N*-iodosuccinimide (NIS)[13] in chloroform, the imidate (**14**) gave the iodo amide alcohol (**16**) in 79% yield. The different products isolated resulted from the differences in work-up procedures. In the latter reaction, it was thought that acid was present in the work-up. Elimination of the acidic conditions enabled us to isolate the iodo-oxazoline (**15**) from the NIS reaction mixture, and further proof was gained by its conversion into the iodo amide alcohol (**16**), using aqueous acid, as shown in Scheme 2.

In an attempt to replace the iodine atom with hydrogen, the oxazoline (**15**) was hydrogenated over 5% palladium–carbon



Scheme 2. *Reagents:* i, CCl_3CN, NaH; ii, $I^+(sym\text{-collidine})_2\ BF^{4-}$; iii, NIS, $CHCl_3$; iv, PTSA, pyridine, water

* Sodium tetrafluoroborate was used instead of sodium perchlorate in the preparation of the iodonium complex.

catalyst in ethyl acetate. Two products, identified as the iodo amide alcohol (**16**) and the dichloroacetamide (**17**), were isolated in 42 and 37% yield respectively.

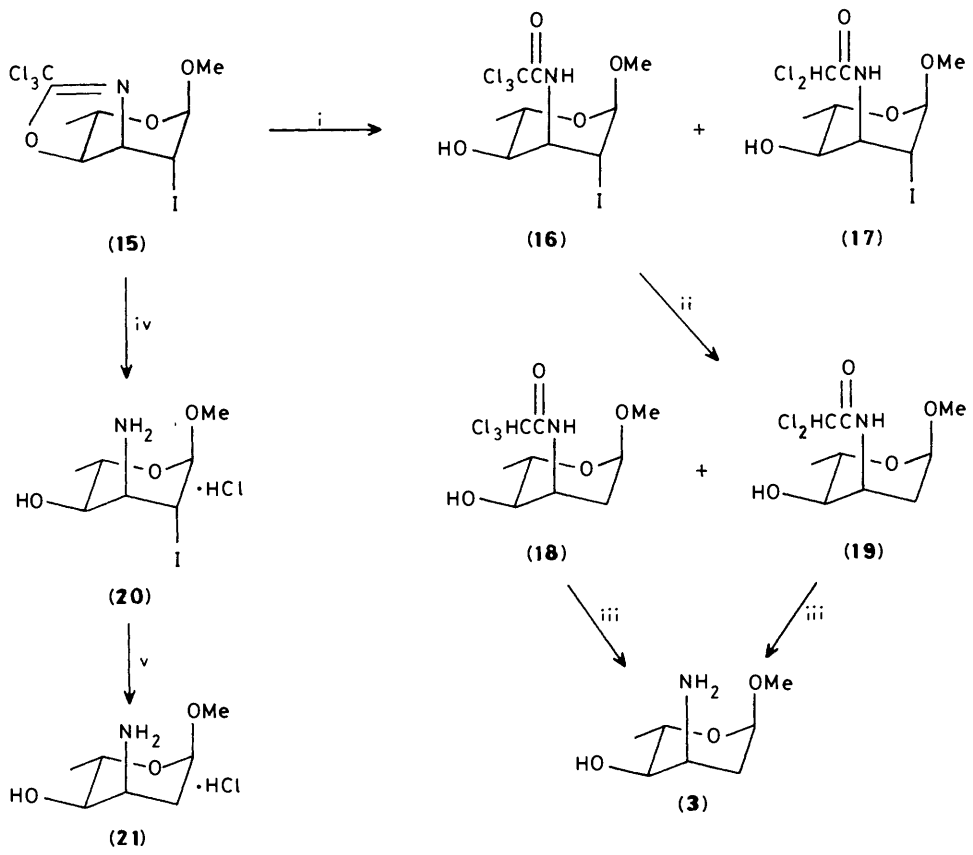
Our attention then turned to a report that Fraser-Reid had used tri-n-butyltin hydride (Bu_3SnH) to replace iodine with hydrogen in a similar route to methyl ristosaminide (**3**).[14] The iodo amide alcohol (**16**) was treated with 1.5 equiv. of tri-n-butyltin hydride in the presence of a catalytic amount of α,α′-azoisobutyronitrile (AIBN) to give the trichloroacetamide (**18**) and dichloroacetamide (**19**) in 84% overall yield. Hydrolysis of the amide functions with aqueous sodium hydroxide gave the *cis*-amino alcohol, methyl α-DL-ristosaminide (**3**), as shown in Scheme 3. The oxazoline (**15**) was also converted into the hydrochloride salt (**21**) of the amino sugar (**3**) by a method outlined by Cardillo.[15] Acid hydrolysis of the oxazoline (**15**) gave the iodo amine hydrochloride (**20**) in 85% yield. Deiodination using tri-n-butyltin hydride afforded the amine hydrochloride (**21**) in 78% yield.

In order to obtain the daunosamine series of derivatives, the minor allylic alcohol (**11**) had to be used. Since this was obtained as a minor product in the reduction of the ketone (**8**), investigations centred on using more hindered reducing agents in order to increase the yield of the alcohol (**11**). However, metal hydride reducing agents such as lithium tri-t-butoxyaluminium hydride, L-Selectride ($LiBHBu^s_3$), or di-isopinocampheylborane had little or no effect in altering the ratio of alcohols (**10**) and (**11**) to give greater amounts of the axial alcohol (**11**).

An alternative approach to this problem was to use the major product alcohol (**10**) and invert the C-4 stereochemistry to give the axial alcohol (**11**). However, these methods increase the number of steps in the route to daunosamine (**1**). The classical method[16] for inversion of the hydroxy centre involved, first, mesylation of the equatorial alcohol (**10**) to give the methanesulphonate (**12**), then displacement of the mesyloxy group with sodium benzoate to give the inverted ester (**13**), followed by solvolysis of the ester group (using sodium methoxide) to give the axial alcohol (**11**) in 26% overall yield. This method proved inefficient when compared with the Mitsunobu reaction.[17] For this method, the alcohol (**10**) was converted directly into the benzoate ester (**17**) in 96% yield by reaction with triphenylphosphine (PPh_3), diethyl azodicarboxylate (DEAD), and benzoic acid.[18] The ester (**13**) was then simply solvolysed to the axial alcohol (**11**) in 98% yield as shown in Scheme 1. All that remained was to synthesize daunosamine (**1**), from the alcohol (**11**), by the routes outlined for the synthesis of methyl α-DL-ristosaminide (**3**).

The alcohol (**11**) was converted into the trichloroacetimidate (**22**).[11] On reaction with NIS, the imidate (**22**) was cyclised to the iodo-oxazoline (**24**) in 71% yield. This cyclisation step took 12 h which is significantly longer than the time taken for the ristosamine derivative (**14**) to cyclise (5 h). This observation can be explained by the fact that the nitrogen atom in the imidate group attacks the double bond preferentially from an axial position. In the ristosamine series, the trichloroacetimidate (**14**) adopts a preferred conformation bearing an 'equatorial' imidate substituent, so the nitrogen atom can only attack the double bond in an axial sense. In the daunosamine series, the trichloroacetimidate (**22**) has an 'axial' imidate substituent so the nitrogen atom will only be able to attack the double bond in an equatorial sense. Since this is not favoured, the imidate (**22**) must change conformation to the conformer (**23**), to make the substituent 'equatorial', before the nitrogen atom is in a position for axial attack on the double bond. From the reaction time, it would seem that the equilibrium between the two conformers (**22**) and (**23**) lies well over to the former conformer.

Reduction of the iodo-oxazoline (**24**) with 5 equiv. of Bu_3SnH gave the oxazoline (**25**) in 78% yield. If 1.5 equiv. of Bu_3SnH were used, then the oxazolines (**26**) and (**27**) were obtained in 43



Scheme 3. *Reagents and conditions:* i, H_2, Pd, EtOAc; ii, Bu_3SnH, AIBN, room temperature; iii, 5M-NaOH; iv, 6M-HCl; v, Bu_3SnH, AIBN, 80 °C

and 44% yield respectively. Treatment of the oxazoline (**25**) with toluene-4-sulphonic acid (PTSA) in a pyridine–water buffer gave the daunosamine derivative (**28**) as shown in Scheme 4. Under the same conditions, the oxazoline (**26**) gave the trichloroacetamide (**29**) in 62% yield.

The oxazoline (**26**) was converted into methyl α-DL-daunosaminide (**2**) on reaction with 5M-sodium hydroxide. The oxazoline (**27**) can also be converted into the amine (**2**) by a similar reaction. Acetylation of the amino alcohol (**2**) gave the amido ester (**30**). Using Cardillo's method,[15] we converted the oxazoline (**24**) into the iodo amine (**31**) as shown in Scheme 5. Subsequent treatment of the amine (**31**) with Bu_3SnH gave methyl α-DL-daunosaminide hydrochloride (**32**), in 63% overall yield from the oxazoline (**24**).

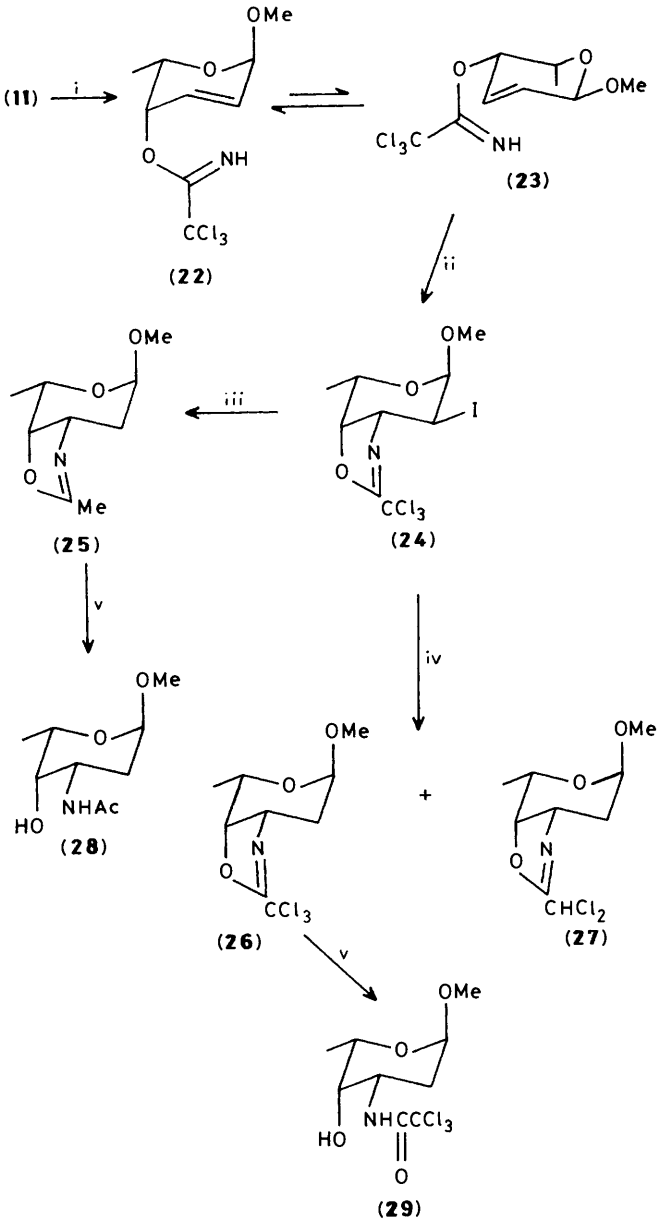
Although methyl α-DL-daunosaminide (**2**) was obtained in 23% overall yield by a 10-step synthesis, it was argued that the route could be improved by using the Mitsunobu reaction on the alcohol (**10**) to generate an axial substituent containing a nucleophilic nitrogen atom. Our attention was therefore focused on a modified Mitsunobu reaction[17] in which cyclic and acyclic imides can be alkylated, as shown by the examples in the Figure, by a process involving an S_N2 displacement about the hydroxy-bearing atom.

With the secondary alcohol (±)-cyclohex-2-en-1-ol (**33**) as a model and in the presence of dibenzamide,[19] the imidate (**34**) was obtained in 93% yield from the modified Mitsunobu reaction. Cyclisation of the nitrogen atom of the imidate (**34**) to the double bond of the cyclohexene ring was achieved using halogenating reagents. Treatment of the imidate (**34**) with NIS in chloroform and ethanol gave the iodo amide ester (**35**) in only 42% yield. However, the imidate (**34**) could be converted into the orthoamide (**36**), upon treatment with *N*-bromosuccinimide (NBS), and on acidic work-up. This gave the bromo amide ester (**37**) in 85% yield, as shown in Scheme 6.

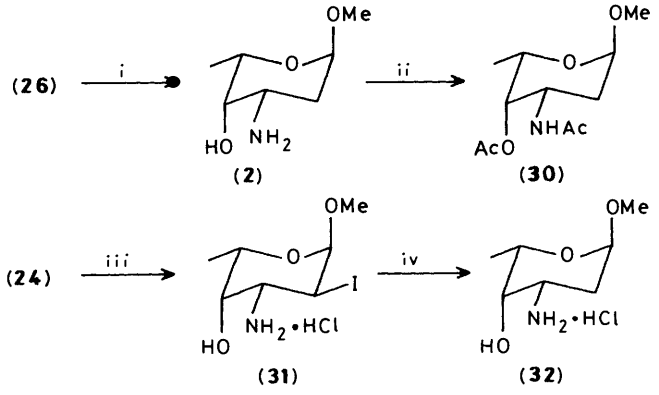
Removal of the bromine atom of the amide (**37**) with Bu_3SnH gave the amide ester (**38**). Base-catalysed solvolysis then gave the amido alcohol (**39**). Acid hydrolysis of the amido alcohol (**39**) gave the *cis*-1,2-amino alcohol,[20] isolated as its hydrochloride salt (**40**). The conversion of the alcohol (**33**) into the *cis*-1,2-amino alcohol salt (**40**) in 5 steps and 62% overall yield was then applied to the synthesis of daunosamine (**1**) from the alcohol (**10**).

Conversion of the alcohol (**10**) into the imidate (**41**), under the modified Mitsunobu reaction conditions, proceeded in 86% yield. After careful investigation of the cyclisation reaction, the imidate (**41**) was converted into the bromo amide ester (**42**) in 91% yield on treatment with 3 equiv. of NBS in chloroform–ethanol. If less than 2 equiv. of NBS was used in the reaction, the imidate (**41**) was simply solvolysed to give the alcohol (**11**), as shown in Scheme 7. The bromo amide ester (**42**) was treated with Bu_3SnH to give the amide ester (**43**) in 96% yield. Base solvolysis of the amide ester (**43**) gave the amido alcohol (**44**) in 94% yield. The amido alcohol (**44**) was also obtained, in 95% yield, from the bromo amide ester (**42**) and lithium aluminium hydride. Thus, methyl *N*-benzoyl-α-DL-daunosamine (**44**) can be prepared in 7 steps from 2-acetylfuran (**5**) in 40% overall yield. Acid hydrolysis of the amide (**44**) gave DL-daunosamine hydrochloride (**45**) in 45% yield.

A short synthetic route to DL-daunosamine (**1**) in good overall yield having now been established an asymmetric



Scheme 4. *Reagents and conditions:* i, CCl_3CN, NaOH; ii, NIS, $CHCl_3$; iii, 5 equiv. Bu_3SnH, AIBN, 111 °C; iv, 1.5 equiv. Bu_3SnH, AIBN, room temperature; v, PTSA, pyridine, water



Scheme 5. *Reagents and conditions:* i, 5M-NaOH; ii, Ac_2O, pyridine; iii, 6M-HCl; iv, Bu_3SnH, AIBN, room temperature

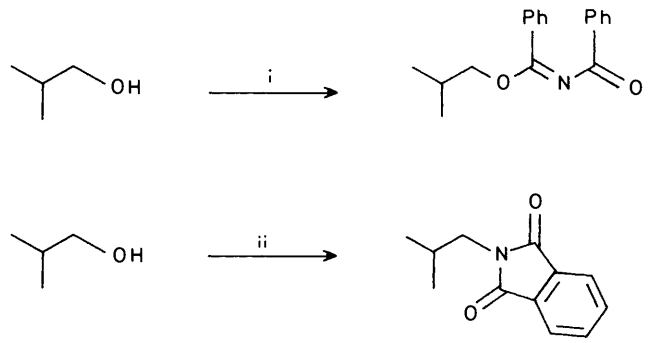
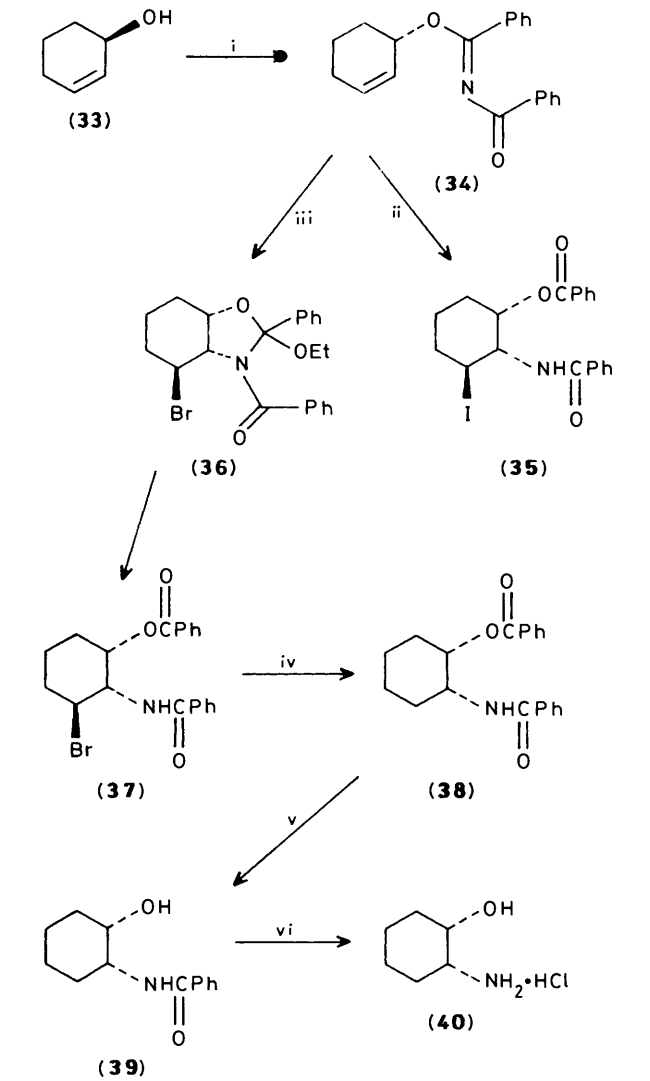


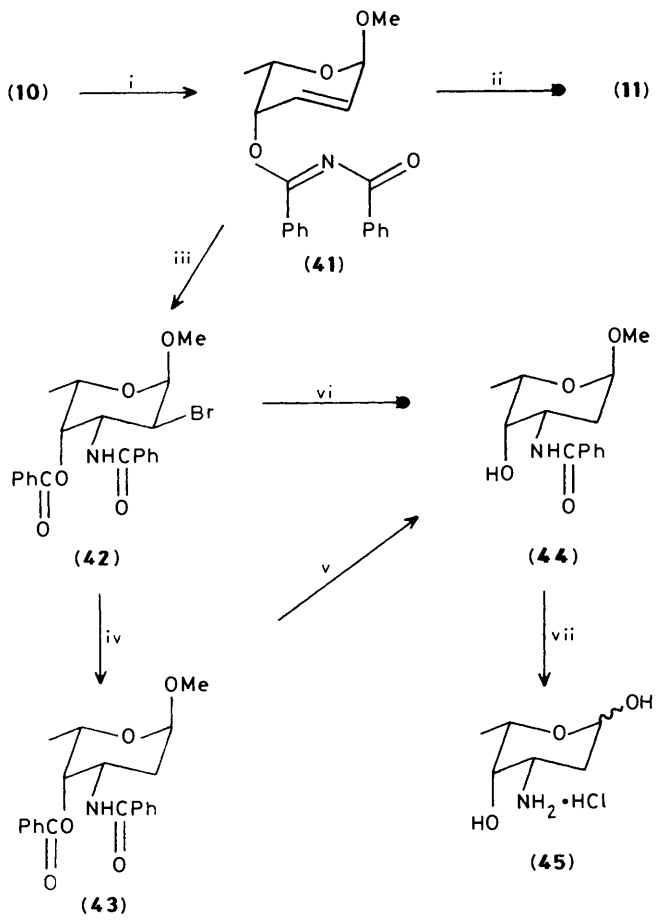
Figure. *Reagents:* i, PPh_3, DEAD, PhCONHCOPh; ii, DEAD, phthalimide



Scheme 6. *Reagents:* i, PPh_3, DEAD, PhCONHCOPh; ii, NIS, EtOH, $CHCl_3$; iii, NBS, EtOH, $CHCl_3$; iv, Bu_3SnH, AIBN; v, NaOMe; vi, 6M-HCl

synthesis was desirable. It was argued that introduction of chirality to the synthetic route would be best achieved by the asymmetric reduction of the ketone (**5**) to give the (*S*)-enantiomer (**46**) of the alcohol (**6**).

Precedent for an asymmetric yeast reduction is well estab-

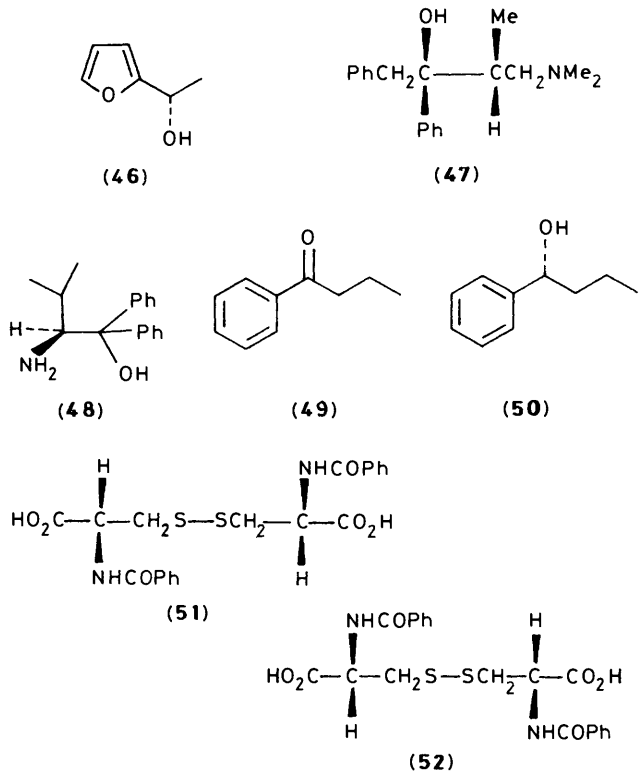


Scheme 7. *Reagents and conditions:* i, PPh_3, DEAD, PhCONHCOPh, room temperature: ii, 2 equiv. NBS, EtOH, $CHCl_3$; iii, 3 equiv. NBS, EtOH, $CHCl_3$; iv, Bu_3SnH, AIBN, 111 °C; v, NaOMe; vi, LAH; vii, HCl, MeOH, water

lished for ketones[21] and α-keto esters.[22] However, several attempts to effect the asymmetric reduction of the ketone (**5**) with baker's yeast failed.

Recently, there have been many publications on the asymmetric reduction of aromatic ketones[23] and even simple aliphatic ketones[24] by metal hydrides in the presence of chiral templates. Most of the methods employ an acidic work-up to isolate the product alcohol from metal complexes. In the present instance, since the furfuryl alcohol (**6**) is very acid-sensitive, these methods cannot be used. For example, reduction of the ketone (**5**) with lithium aluminium hydride in the presence of the chiral template (+)-(2*S*,3*R*)-4-dimethylamino-3-methyl-1,2-diphenylbutan-2-ol (Chirald) (**47**),[23a] gave a polymer of the furan alcohol (**6**) after the acidic work-up. The same result was obtained when the ketone (**5**) was reduced with diborane in the presence of (−)-(*S*)-2-amino-3-methyl-1,1-diphenylbutan-1-ol (**48**).[23e]

More recently, however, Soai *et al.*[25] reduced phenyl propyl ketone (**49**) to (+)-(*R*)-1-phenylbutan-1-ol (**50**) in 90% enantiomeric excess (e.e.) with lithium borohydride[26] in tetrahydrofuran (THF) and t-butyl alcohol in the presence of (*RR*)-*N*,*N*′-dibenzoylcystine (**51**).[27] The work-up procedure involves a base wash which allows one to use this procedure for acid-sensitive products. Since the (*RR*)-enantiomer of the chiral template gives the (*R*)-enantiomer alcohol, it follows that using (*SS*)-*N*,*N*′-dibenzoylcystine (**52**) with lithium borohydride, on the reduction of ketones, will give the (*S*)-enantiomer alcohol.



The chiral template (**52**) was prepared from D-cystine by the known procedure.[27] Following the method of Soai,[25] we reduced the ketone (**5**) to the (*S*)-alcohol (**46**) in 82% yield. The optical rotation of the alcohol (**46**) (was $[\alpha]_D$ −15.8° (*c* 1 in EtOH), which corresponds to a 95% e.e. when compared with the literature value.[28]

A chiral synthesis of the alcohol (**46**) having been found, it only remained for us to test whether the above described route could be used to convert it into daunosamine (**1**) without any racemisation.[29] The alcohol (**46**) was converted into the (5*S*)-pyranulose (**8**) without racemisation. Comparison of the optical rotation of the pyranulose (**8**), $[\alpha]_D$ −16.2° ($CHCl_3$), with the literature value, $[\alpha]_D$ −16.6° ($CHCl_3$), showed that the pyranulose (**8**) contained a 98% e.e. of the required (*S*)-isomer.[30]

The ketone (**8**) was converted into the amino sugars methyl α-L-ristosamine (**3**) and L-daunosamine hydrochloride (**45**) by the methods outlined above (see Experimental section) and their optical rotations were in close agreement with the literature values.[31]

Experimental

General Techniques.—M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 1420 Ratio Recording spectrophotometer, either on film or for solids in chloroform solution. Optical rotation measurements were obtained on a Thorn NPL 243 automatic polarimeter. ^1H N.m.r. spectra were recorded on a Varian EM 360A (60 MHz) spectrometer, a Perkin-Elmer R32 (90 MHz), a Jeol FX 90Q (90 MHz), a Bruker AM 250 (250 MHz), or a Bruker AM 400 (400 MHz) spectrometer and are quoted in p.p.m. relative to tetramethylsilane (TMS) (internal reference) for solutions in deuteriochloroform or as stated. ^1H N.m.r. assignments are as follows: H_a = axial hydrogen, H_e = equatorial hydrogen. Mass spectra were obtained with a Kratos MS 25 instrument. Accurate mass determinations were obtained with an AEI-Kratos MS 9/50 machine. For

compounds containing chlorine or bromine, accurate masses are given for the ^{35}Cl and ^{79}Br isotopes only. Microanalytical determinations were performed by the University of Leeds, School of Chemistry, Microanalytical Department. High-pressure liquid chromatography (h.p.l.c.) was performed on silica using a Jobin Yvon Chromatospec prep 100 column. T.l.c. was carried out on glass plates precoated with Merck Kieselgel 60 GF_{254}. Column chromatography was carried out either on MN-Kieselgel 60 (CAMLAB) or on Kieselgel 60G (Merck) and columns were generally packed and run under pressure. Solvents used for chromatography were distilled before use and solvent ratios are described in ratios of volumes before mixing. Light petroleum refers to that fraction with boiling range 60—80 °C, and ether refers to diethyl ether throughout.

Extracts of organic compounds, unless otherwise stated, were dried over anhydrous sodium sulphate. Solvents were dried using the methods given by Perrin.[32] Chloroform was made ethanol-free by passing the solvent through an activated alumina column (basic) immediately before use. Formic acid was dried by heating to reflux with phthalic anhydride for 6 h before distillation. NBS was freshly recrystallised from hot water and dried over phosphorus pentaoxide, *in vacuo*, before use. AIBN was recrystallised from ether and stored at −10 °C in the dark.

1-(2-*Furyl*)*ethanol* (**6**).[8]—Lithium aluminium hydride (7.58 g, 200 mmol) was added portionwise to a vigorously stirred solution of 2-acetylfuran (**5**) (20 g, 182 mmol) in dry THF (150 ml) at 0 °C. After complete addition, the mixture was stirred for 1h at room temperature, then methanol was added in small amounts until no more effervescence was observed signifying that all the excess of hydride was destroyed. The mixture was poured into ice–water (400 ml) and extracted with ether (4 × 200 ml). The extract was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give a pale yellow oil. Distillation of the yellow oil afforded the oily alcohol (**6**) (19.8 g, 97%), b.p. 90—95 °C at 26 mmHg; $\nu_{max.}$ 3 600—3 200, 1 150, 1 070, 1 010, and 740 cm^{-1}; δ 1.56 (3 H, d, *J* 7 Hz, Me), 2.3 (1 H, br, s, exch. with D_2O, OH), 4.85 [1 H, br m, (after D_2O shake, q, *J* 7 Hz), C*H*Me], 6.24 (1 H, d, *J* 3.5 Hz, 3-H), 6.34 (1 H, dd, *J* 3.5, 1.2 Hz, 4-H), and 7.31 (1 H, d, *J* 1.2 Hz, 5-H); *m/z* 112 ($M^{+\bullet}$, 57.1%), 97 (100), 94 (60), 69 (20.5), and 65 (25.3) (Found: C, 64.3; H, 7.3%; $M^{+\bullet}$, 112.0525. Calc. for $C_6H_8O_2$: C, 64.3; H, 7.1%; *M*, 112.0524).

1-(2,5-*Dihydro*-2,5-*dimethoxy*-2-*furyl*)*ethanol* (**7**).[8]—A solution of bromine (29.2 g, 183 mmol) in methanol (70 ml) was added slowly to a stirred solution of 1-(2-furyl)ethanol (**6**) (20 g, 178 mmol) in a mixture of dry ether (50 ml) and methanol (70 ml) at −35 °C. After complete addition, the dark red solution was stirred for −35 °C for 30 min. The solution was then saturated with gaseous NH_3 to pH *ca.* 8 and then allowed to warm to room temperature. The precipitated NH_4Br was filtered off and the solvents were removed under reduced pressure. The residues were dissolved in ether (200 ml) and the solution was filtered again to remove the remaining NH_4Br. The solvent was removed under reduced pressure and the residue was dissolved in benzene (15 ml). The solution was filtered through an alumina (active:neutral) column. The solvent was removed under reduced pressure to give a pale yellow oil, which was distilled to give the oily dihydrofuran (**7**) (28.9 g, 93%), b.p. 78—81 °C at 1.5 mmHg; $\nu_{max.}$ 3 600—3 200, 1 380, 1 095, and 1 030 cm^{-1}; δ 1.12 (3 H, m, Me), 2.37 (1 H, d, *J* 4.2 Hz, exch. with D_2O, OH), 3.19—3.54 (6 H, m, OMe), 3.86 (1 H, m, C*H*Me), 5.48 (1 H, dt, *J* 13.3, 2.7 Hz, 3-H), 5.95 (1 H, m, 4-H), and 6.14 (1 H, m, 5-H); *m/z* 143 ($M^{+\bullet} - OCH_3$, 7.5%), 129 (64.6), 101 (50.2), 99 (34.6), 83 (29.7), 71 (28.6), and 43 (100) (Found: $M^{+\bullet}$ − H, 173.081 64. Calc. for $C_8H_{13}O_4$: *m/z*, 173.081 38) (Found: C, 55.3; H, 8.1. Calc. for $C_8H_{14}O_4$: C, 55.2; H, 8.1%).

Methyl 2,3,6-*Trideoxy*-α-DL-glycero-*hex*-2-*enopyranosid*-4-*ulose* (**8**)[9] *and Methyl* 2,3,6-*Trideoxy*-β-DL-glycero-*hex*-2-*enopyranosid*-4-*ulose* (**9**).[8]—A solution of the dihydrofuran (**7**) (20 g, 115 mmol) in dry methanol (8.5 ml) was added dropwise, during 15 min, to a vigorously stirred solution of dry formic acid (85 ml) in dry methanol (4.5 ml) at room temperature under nitrogen. The mixture was stirred for 5 min and then poured into a mixture of water (220 ml) and chloroform (100 ml). The mixture was shaken quickly and carefully. The chloroform was separated and the aqueous phase was extracted with chloroform (2 × 100 ml). The combined organic solution was washed successively with saturated aqueous sodium hydrogen carbonate (50 ml) and saturated aqueous sodium chloride (50 ml) and then dried, and the solvent was removed under reduced pressure to give a pale yellow oily mixture of the pyranuloses (**8**) and (**9**). H.p.l.c. of the oil on silica with 1:20 ethyl acetate–light petroleum as eluant gave the less polar α-anomer (**8**) (10.12 g, 62%) before the more polar β-anomer (**9**) (3.42 g, 21%). The α-anomer (**8**) was obtained as an oil, b.p. 40—42 °C at 1 mmHg; $\nu_{max.}$ 1 700, 1 090, and 1 045 cm^{-1}; δ 1.39 (3 H, d, *J* 7 Hz, Me), 3.54 (3 H, s, OMe), 4.56 (1 H, q, *J* 7 Hz, 5-H), 5.09 (1 H, d, *J* 3.6 Hz, 1-H), 6.08 (1 H, d, *J* 10 Hz, 3-H), and 6.84 (1 H, dd, *J* 10, 3.6 Hz, 2-H); *m/z* 142 ($M^{+\bullet}$, 0.6%), 111 (32.2), 98 (100), 83 (51.5), and 70 (21.4) (Found: C, 59.1; H, 7.0%; $M^{+\bullet}$, 142.0626. Calc. for $C_7H_{10}O_3$: C, 59.1; H, 7.1%; *M*, 142.0629).

The β-anomer (**9**) was obtained as an oil, b.p. 39—43 °C at 1 mmHg; $\nu_{max.}$ 1 700, 1 245, and 1 050 cm^{-1}; δ 1.46 (3 H, d, *J* 7 Hz, Me), 3.57 (3 H, s, OMe), 4.22 (1 H, q, *J* 7 Hz, 5-H), 5.25 (1 H, dd, *J* 2, 1.5 Hz, 1-H), 6.12 (1 H, dd, *J* 10.5, 1.5 Hz, 3-H), and 6.9 (1 H, dd, *J* 10.5, 2 Hz, 2-H); *m/z* 142 ($M^{+\bullet}$, 1.0%), 128 (1.4), 111 (22.5), 98 (100), and 83 (31.5) (Found: $M^{+\bullet}$, 142.063 25).

Methyl 2,3,6-*Trideoxy*-α-DL-erythro-*hex*-2-*enopyranoside* (**10**) *and Methyl* 2,3,6-*Trideoxy*-α-DL-threo-*hex*-2-*enopyranoside* (**11**).[8]—A solution of the pyranulose (**8**) (10 g, 70 mmol) in THF (20 ml) was added dropwise to a stirred solution of sodium borohydride (1.33 g, 35 mmol) in water (100 ml) at 0 °C. The mixture was stirred for 30 min at 0 °C and then neutralised with dil. acetic acid. Water (30 ml) was added to the solution which was then extracted with ether (3 × 100 ml). The extract was dried ($MgSO_4$), and the ether was removed under reduced pressure to give a pale yellow oily mixture of the epimeric alcohols (**10**) and (**11**). Column chromatography of the oil on silica with 1:10 ethyl acetate–light petroleum as eluant gave successively the *erythro* alcohol (**10**) and then the *threo* alcohol (**11**). The *erythro* alcohol (**10**) (9.33 g, 92%), had b.p. 70—72 °C at 1 mmHg; $\nu_{max.}$ 3 550 and 1 050 cm^{-1}; δ 1.35 (3 H, d, *J* 6 Hz, Me), 2.1 (1 H, br s, exch. with D_2O, OH), 3.44 (3 H, s, OMe), 3.69 (1 H, dq, *J* 9, 6 Hz, 5-H), 3.84 [1 H, br d, *J* 9 Hz (after D_2O shake, dd, *J*, 9, 2.3 Hz), 4-H], 4.84 (1 H, dd, *J* 1.6, 0.9 Hz, 1-H), 5.74 (1 H, ddd, *J* 10, 2.3, 1.6 Hz, 2-H), and 5.94 (1 H, d, *J* 10 Hz, 3-H); *m/z* 144 ($M^{+\bullet}$, 0.6%), 113 (25.3), and 100 (100) (Found: $M^{+\bullet}$, 144.078 551. Calc. for $C_7H_{12}O_3$: *M*, 144.078 638).

The *threo* alcohol (**11**) (0.71 g, 7%) was identical with the material described below.

Methyl 2,3,6-*Trideoxy*-4-O-*Trichloroacetimidoyl*-α-DL-erythro-*hex*-2-*enopyranoside* (**14**).[15]—A solution of the *erythro* alcohol (**10**) (3 g, 21 mmol) in dry THF (10 ml) was added dropwise to a stirred suspension of sodium hydride (0.16 g, 60% dispersion in mineral oil, previously washed with hexane; 4 mmol) in dry THF (3 ml) at 0 °C under nitrogen. The solution was stirred for 1 h at 0 °C and was then added dropwise to a stirred solution of trichloroacetonitrile (3.1 g, 21 mmol) in dry THF (10 ml) at 0 °C under nitrogen. The solution was stirred at

0 °C for 2 h, and then the solvent was removed under reduced pressure. A mixture of methanol (0.5 ml) in hexane (30 ml) was added to the vigorously stirred residues. The solution was filtered, and the solvents were removed under reduced pressure to give a yellow oil. Column chromatography of the oil on silica with 1:1 ethyl acetate–light petroleum afforded the oily imidate (**14**) (3.61 g, 60%); $\nu_{max.}$ 3 338, 1 730, 1 663, 1 295, and 1 050 cm^{-1}; δ 1.33 (3 H, d, *J* 6 Hz, Me), 3.46 (3 H, s, OMe), 4.13 (1 H, dq, *J* 9.2, 6 Hz, 5-H), 4.92 (1 H, d, *J* 1.5 Hz, 1-H), 5.21 (1 H, dd, *J* 9.2, 4.1 Hz, 4-H), 5.85 (1 H, ddd, *J* 10.2, 4.1, 1.5 Hz, 2-H), 6.07 (1 H, d, *J* 10.2 Hz, 3-H), and 8.43 (1 H, br s, C=NH); *m/z* 256 ($M^{+\cdot}$ − OCH_3, 2.5%), 243 (47.3), 214 (9.1), 111 (17.8), and 100 (100) (Found: $M^{+\cdot}$, 286.9888. Calc. for $C_9H_{12}Cl_3NO_3$: *M*, 286.9883).

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2-*iodo*-2′-*trichloromethyl*-(*methyl* α-DL-*altropyranosido*)[3,4-d]*oxazole* (**15**).[15]—Iodonium di-*sym*-collidine tetrafluoroborate [12] (6.25 g, 14 mmol) was added to a stirred solution of the imino ether (**14**) (2.5 g, 9 mmol) in acetonitrile (75 ml). The solution was stirred for 8 h at room temperature and then the solvent was removed under reduced pressure. The collidine complex residue was washed with ethyl acetate (3 × 50 ml) to remove all the soluble organic products. The filtered organic extract was washed with water (3 × 30 ml) and dried, and the solvent was removed under reduced pressure to give a yellow oil, which was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give a white solid. Recrystallisation of the solid from an ether–light petroleum mixture gave white, needle-like crystals of the iodo-oxazoline (**15**) (3.6 g, 70%), m.p. 80—82 °C; $\nu_{max.}$ 1 655, 1 108, 1 066, 1 033, and 955 cm^{-1}; δ 1.39 (3 H, d, *J* 6.1 Hz, Me), 3.44 (3 H, s, OMe), 3.85—4.15 (2 H, m), 4.5—4.7 (2 H, m), and 5.03 (1 H, d, *J* 6.2 Hz, 1-H); *m/z* 413 ($M^{+\cdot}$, 0.6%), 382 (6.1), 353 (3.7), 348 (3.3), 296 (44.0), 286 (68.0), 242 (15.3), 226 (17.4), 184 (100), 168 (50.3), 125 (19.9), and 117 (15.7) (Found: C, 25.9; H, 2.5; N, 3.3; Cl, 25.3; I, 30.4%; $M^{+\cdot}$, 412.884 37. Calc. for $C_9H_{11}Cl_3INO_3$: C, 26.1; H, 2.7; N, 3.4; Cl, 25.6; I, 30.6%; *M*, 412.885 11).

Methyl 2,3,6-*Trideoxy*-2-*iodo*-3-*trichloroacetamido*-α-DL-*altropyranoside* (**16**).*—*Method A*. NIS (1.8 g, 8 mmol) was added to a stirred solution of the imino ether (**14**) (2.0 g, 7 mmol) in chloroform (70 ml). The solution was stirred for 5 h at room temperature and then Amberlyst A26 (Cl^-) resin (treated with dil. HCl, washed with acetone, and dried) (15 g) was added. After being stirred for 5 min the solution was filtered, and the solvent was removed under reduced pressure. The residue was subjected to chromatography on a silica column with 1:4 ethyl acetate–light petroleum as eluant to give a foamy gum. Trituration of the gum with hexane gave a white solid, which was recrystallised in an ether–hexane mixture to give white cubic crystals of the *amide* (**16**) (2.37 g, 79%), m.p. 103.5—104 °C; $\nu_{max.}$ 3 600—3 300, 3 370, 1 710, 1 512, 1 142, and 1 050 cm^{-1}; δ 1.39 (3 H, d, *J* 6.2 Hz, Me), 2.17 (1 H, d, *J* 3.9 Hz, exch. with D_2O, OH), 3.45 (3 H, s, OMe), 3.79 (1 H, dq, *J* 9.5, 6.2 Hz, 5-H), 4.24 (1 H, dd, *J* 3.0, 1.25 Hz, 2-H), 4.27 (1 H, dd, *J* 9.5, 4.05 Hz, 4-H), 4.52 (1 H, ddd, *J* 8.2, 4.05, 3.0 Hz, 3-H), 4.93 (1 H, d, *J* 1.25 Hz, 1-H), and 8.31 (1 H, br d, *J* 8.2 Hz, exch. with D_2O, NH); *m/z* 399 ($M^{+\cdot}$ − OCH_3, 18.9%), 371 (22.2), 354 (5.0), 314 (16.3), 272 (30.6), 230 (44.0), 184 (34.1), 119 (31.8), and 99 (100) (Found: C, 25.0; H, 3.1; N, 3.2; Cl, 29.2; I, 24.3%; $M^{+\cdot}$, 430.895 55. $C_9H_{13}Cl_3INO_4$ requires C, 25.0; H, 3.0; N, 3.2; Cl, 29.3; I, 24.6%; *M*, 430.895 66).

Method B. PTSA (0.1 g, 0.5 mmol) was added to a stirred solution of the iodo-oxazoline (**15**) (0.159 g, 0.4 mmol) in a mixture of pyridine (4 ml) and water (1 ml). The solution was stirred for 2.5 h at 100 °C and then extracted with ether (3 × 10 ml). The combined extract was dried, and the solvent was removed under reduced pressure. The residue was eluted down a column of silica with 1:1 ethyl acetate–light petroleum to give white crystals of the amide (**16**) (0.113 g, 68%), m.p. 103—104 °C. Spectroscopic and analytical data were identical with those described for (**16**) above.

Methyl 2,3,6-*Trideoxy*-2-*iodo*-3-*trichloroacetamido*-α-DL-*altropyranoside* (**16**) *and Methyl* 2,3,6-*Trideoxy*-2-*iodo*-3-*dichloroacetamido*-α-DL-*altropyranoside* (**17**).—The iodo-oxazoline (**15**) (0.5 g, 1.2 mmol) was hydrogenated under a hydrogen atmosphere (1 atm) using 5% palladium–carbon catalyst (0.1 g) in ethyl acetate (20 ml), at room temperature, for 24 h. The solution was filtered through a Celite pad to remove the catalyst, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica with 1:4 ethyl acetate–light petroleum as eluant to give the less polar iodo amide (**16**) (0.22 g, 42%) before the more polar *iodo amide* (**17**) (0.17 g, 37%). Iodo amide (**16**) had m.p. 102—104 °C and identical spectroscopic and analytical data as described above for this compound.

Iodo amide (**17**) had m.p. 48—50 °C; $\nu_{max.}$ 3 600—3 200, 3 360, 1 685, 1 515, 1 130, and 1 050 cm^{-1}; δ 1.38 (3 H, d, *J* 6.1 Hz, Me), 2.5 (1 H, br s, exch. with D_2O, OH), 3.46 (3 H, s, OMe), 3.78 (1 H, dq, *J* 9.4, 6.1 Hz, 5-H), 4.2 (1 H, dd, *J* 3.1, 1.3 Hz, 2-H), 4.23 (1 H, dd, *J* 9.3, 3.9 Hz, 4-H), 4.52 (1 H, ddd, *J* 8, 3.9, 3.1 Hz, 3-H), 4.92 (1 H, d, *J* 1.3 Hz, 1-H), 5.9 (1 H, s, $CHCl_2$), and 8.1 (1 H, br d, *J* 8 Hz, exch. with D_2O, NH); *m/z* 365 ($M^{+\cdot}$ − CH_3OH, 11.4%), 337 (7.7), 280 (9.4), 238 (20.3), 196 (25.9), 184 (15.2), 83 (56.0), and 57 (100) (Found: $M^{+\cdot}$, 396.934 49. $C_9H_{14}Cl_2INO_4$ requires *M*, 396.934 64).

Methyl 2,3,6-*Trideoxy*-3-*trichloroacetamido*-α-DL-ribo-*hexopyranoside* (**18**)[14,*] *and Methyl* 2-*Dichloroacetamido*-2,3,6-*trideoxy*-α-DL-ribo-*hexopyranoside* (**19**).—Tributyltin hydride (Bu_3SnH) (0.19 g, 0.65 mmol) was added to a stirred solution of the iodo amide (**16**) (0.19 g, 0.4 mmol) and AIBN (0.003 g, catalyst) in toluene (1 ml). The solution was stirred at room temperature for 1 h after which the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica with 1:4 ethyl acetate–light petroleum as eluant to give the less polar amido alcohol (**18**) before the more polar *amido alcohol* (**19**) in 84% combined yield. The amido alcohol (**18**) (0.07 g, 50%) had m.p. 174—176 °C; $\nu_{max.}$ 3 600—3 300, 3 350, 1 695, 1 510, 1 125, and 1 050 cm^{-1}; δ 1.3 (3 H, d, *J* 5.9 Hz, Me), 1.95—2.1 (2 H, m, CH_2), 2.52 (1 H, br d, *J* 2.7 Hz, exch. with D_2O, OH), 3.42 (3 H, s, OMe), 3.5 (1 H, ddd, *J* 9.8, 3.2, 2.7 Hz, 4-H), 3.75 (1 H, dq, *J* 9.8, 5.9 Hz, 5-H), 4.39 (1 H, m, 3-H), 4.78 (1 H, dd, *J* 2.5, 2.2 Hz, 1-H), and 8.55 (1 H, br s, exch. with D_2O, NH); *m/z* 274 ($M^{+\cdot}$ − OCH_3, 0.4%), 212 (0.2), 203 (4.2), 156 (3.3), 113 (17.5), 86 (56.7), 69 (13.8), and 59 (100) (Found: $M^{+\cdot}$ − OCH_3, 273.981 82. $C_8H_{11}Cl_3NO_3$ requires *m/z*, 273.980 64).

The amido alcohol (**19**) (0.041 g, 34%) had m.p. 143—145 °C; $\nu_{max.}$ 3 600—3 300, 3 455, 1 685, 1 520, 1 125, and 1 060 cm^{-1}; δ 1.3 (3 H, d, *J* 5.9 Hz, Me), 1.98—2.06 (2 H, m, CH_2), 2.74 (1 H, br d, *J* 2.7 Hz, exch. with D_2O, OH), 3.42 (3 H, s, OMe), 3.5 (1 H, ddd, *J* 9.6, 3.6, 2.7 Hz, 4-H), 3.74 (1 H, dq, *J* 9.6, 5.9 Hz, 5-H), 4.41 (1 H, m, 3-H), 4.76 (1 H, dd, *J* 2.4, 2.2 Hz, 1-H), 5.95 (1 H, s, $CHCl_2$), and 8.3 (1 H br s, exch. with D_2O, NH); *m/z* 272 ($M^{+\cdot}$, 4.7%), 240 (43.2), 227 (8.9), 204 (1.8), 197 (4.1), 169 (91.1), 113 (49.9), and 86 (100) (Found: C, 39.7; H, 5.6; N, 4.9; Cl, 26.2%; $M^{+\cdot}$, 272.045 51. $C_9H_{15}Cl_2NO_4$ requires C, 39.7; H, 5.6; N, 5.1; Cl, 26.1%; *M*, 272.045 63).

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-DL-ribo-*hexopyranoside* (*Methyl* α-DL-*Ristosaminide*) (**3**).[15]—The amido alcohol (**18**)

* Compounds marked thus have been cited in the literature but full spectroscopic and analytical data were not included.

(0.3 g, 0.98 mmol) was heated to 60 °C for 2 h in a mixture of aqueous 5M-sodium hydroxide (1 ml) and methanol (2 ml). The solvents were removed under reduced pressure and the residue was extracted with chloroform (3 × 10 ml). The extract was dried and the solvent was removed under reduced pressure. The crude yellow solid obtained was recrystallised in ether to give white crystals of the amine (**3**) (0.13 g, 82%), m.p. 71—73 °C; $\nu_{max.}$ 3 620, 3 590, 3 600—3 400, 1 360, 1 121, and 1 045 cm^{-1}; δ 1.28 (3 H, d, *J* 6.5 Hz, Me), 1.67 (2 H, m, CH_2), 1.82 (3 H, br s, exch. with D_2O, OH, and NH_2), 3.28 (1 H, m, 3-H), 3.37 (3 H, s, OMe), 3.45 (1 H, dd, *J* 9.4, 3.2 Hz, 4-H), 3.94 (1 H, dq, *J* 9.4, 6.5 Hz, 5-H), and 4.76 (1 H, dd, *J* 2.4, 2.2 Hz, 1-H); *m/z* 161 ($M^{+\bullet}$, 0.3%), 144 (3.1), 130 (25.3), 104 (35.8), 86 (60.3), and 59 (100) (Found: $M^{+\bullet}$, 161.105 56. Calc. for $C_7H_{15}NO_2$: $M^{+\bullet}$, 161.105 19).

Methyl 3-*Amino*-2,3,6-*trideoxy*-2-*iodo*-α-DL-*altropyranoside Hydrochloride* (**20**).[15]—6M-Hydrochloric acid solution (3 ml) was added to a solution of the iodo-oxazoline (**15**) (1.0 g, 2.4 mmol) in methanol (3 ml). The solution was stirred at room temperature for 24 h, and then the solvents were removed under reduced pressure at < 35 °C. The yellow solid residue was washed with ether to give white, needle-like crystals of the amine (**20**) (0.66 g, 85%), m.p. 167—168 °C (decomp.); $\nu_{max.}$ 3 600—3 200, 1 595, 1 580, and 1 520 cm^{-1}; δ(CD_3OD) 1.3 (3 H, d, *J* 5.8 Hz, Me), 3.4 (3 H, s, OMe), 3.7 (1 H, m, 3-H), 3.85 (1 H, dq, *J* 9.6, 5.8 Hz, 5-H), 4.09 (1 H, dd, *J* 9.6, 4.2 Hz, 4-H), 4.41 (1 H, dd, *J* 2.6, 1.5 Hz, 2-H), and 4.9 (1 H, d, *J* 1.5 Hz, 1-H); *m/z* 288 ($M^{+\bullet}$, 3.9%), 256 (11.9), 230 (23.9), 212 (12.7), 198 (33.0), 184 (17.4), 170 (100), 142 (25.9), 128 (28.0, 116 (49.7), and 100 (66.0) (Found: $M^{+\bullet}$, 288.009 77. Calc. for $C_7H_{14}INO_3$: *M*, 288.009 85).

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-DL-ribo-*hexopyranoside Hydrochloride* (**21**).[15]—Bu_3SnH (0.58 g, 2 mmol) was added to a stirred solution of the hydrochloride salt of the iodo amine (**20**) (0.5 g, 1.55 mmol) and AIBN (0.004 g) in a mixture of methanol (1 ml) and toluene (1 ml). The solution was stirred at 80 °C for 8 h, and then the solvents were removed under reduced pressure. The residue was chromatographed on a column of silica with 3:7 methanol–ethyl acetate as eluant to give the amine hydrochloride (**21**) (0.24 g, 78%) as a white solid, m.p. 167—168 °C; $\nu_{max.}$ 3 600—3 300, 3 150—2 800, 1 590, and 1 190 cm^{-1}; δ(CD_3OD) 1.22 (3 H, d, *J* 5.9 Hz, Me), 1.85—1.95 (2 H, m, CH_2), 3.32 (3 H, s, OMe), 3.4—3.6 (2 H, m, 4- and 3-H), 3.7 (1 H, dq, *J* 9.3, 5.9 Hz, 5-H), and 4.7 (5 H, br s, 1-H, OH, and NH_3); *m/z* 162 ($M^{+\bullet}$ 25.0%), 143 (12.9), 130 (48.1), 104 (35.8), 86 (70.8), 72 (71.2), and 59 (100) (Found: $M^{+\bullet}$ + H, 162.113 04. Calc. for $C_7H_{16}NO_3$: *m/z*, 162.113 01).

Methyl 2,3,6-*Trideoxy*-4-O-*methylsulphonyl*-α-DL-erythro-*hex*-2-*enopyranoside* (**12**).[33]—Mesyl chloride (2.06 g, 18 mmol) was added to a stirred solution of the *erythro* alcohol (**10**) (1.4 g, 9.7 mmol) in pyridine (18 ml) at 0 °C. The solution was stirred at room temperature for 12 h and then water (15 ml) was added. The solution was extracted with chloroform (3 × 20 ml). The extract was dried, and the solvent was removed under reduced pressure. The resultant red oil was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give the mesyl ester (**12**) (0.94 g, 44%) as an oil having $\nu_{max.}$ 1 380, 1 260, 1 180, and 965 cm^{-1}; δ 1.35 (3 H, d, *J* 6 Hz, Me), 3.05 (3 H, s, OSO_2Me), 3.42 (3 H, s, OMe), 4.2 (1 H, dq, *J* 9, 6 Hz, 5-H), 4.85 (2 H, m, 1- and 4-H), 5.85 (1 H, ddd, *J* 10, 3.5, 1.5 Hz, 2-H), and 6.02 (1 H, dd, *J* 10, 0.5 Hz, 3-H); *m/z* 191 ($M^{+\bullet}$ − OCH_3, 5.2%), 178 (11.3), 99 (100), and 95 (24.1) (Found: $M^{+\bullet}$ H, 221.048 64. Calc. for $C_8H_{13}O_5S$: *m/z* 221.048 36) (Found: C, 42.9; H, 6.3; S, 14.4. Calc. for $C_8H_{14}O_5S$: C, 43.2; H, 6.3; S, 14.4%).

Methyl 4-O-*Benzoyl*-2,3,6-*trideoxy*-α-DL-threo-*hex*-2-*enopyranoside* (**13**).[10]—*Method A*.[17] A solution of DEAD (14.5 g, 93 mmol) in dry THF (5 ml) was added dropwise to a solution of the *erythro* alcohol (**10**) (6 g, 42 mmol), triphenylphosphine (21.9 g, 93 mmol), and benzoic acid (10.18 g, 93 mmol) in dry THF (55 ml) at 0 °C. The mixture was stirred at room temperature for 2 h, and then the solvent was removed under reduced pressure. Ether (60 ml) was added to the residues and a white solid (triphenylphosphine oxide and diethyl hydrazinedicarboxylate) precipitated. The solid was filtered off and the solvent was removed under reduced pressure. The crude product was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give, as an oil, the benzoate (**13**) (10 g, 96%); $\nu_{max.}$ 1 715, 1 270, 1 108, 1 042, and 965 cm^{-1}; δ 1.33 (3 H, d, *J* 6.8 Hz, Me), 3.46 (3 H, s, OMe), 4.33 (1 H, qd, *J* 6.8, 2.6 Hz, 5-H), 4.96 (1 H, d, *J* 2.2 Hz, 1-H), 5.13 (1 H, dd, *J* 4.8, 2.6 Hz, 4-H), 6.02 (1 H, dd, *J* 10, 2.2 Hz, 2-H), 6.2 (1 H, dd, *J* 10, 4.8 Hz, 3-H), and 7.35—8.2 (5 H, m, Ph); *m/z* 217 ($M^{+\bullet}$ − OCH_3, 1.3%), 204 (14.8), 105 (100), 95 (13.9), and 77 (22.1) (Found: C, 67.6; H, 6.4%; $M^{+\bullet}$ 248.104 61. Calc. for $C_{14}H_{16}O_4$: C, 67.7; H, 6.5%; *M*, 248.104 85).

Method B.[10] The methanesulphonate (**12**) (0.73 g, 3.3 mmol) and sodium benzoate (1.41 g, 10 mmol) were heated to 100 °C for 3 h in dry dimethylformamide (100 ml). Benzene (100 ml) was added and then the solution was filtered. Water (100 ml) was added to the solution and the organic phases were separated. The aqueous phase was extracted with ether (3 × 100 ml). The combined organic phases were washed with water (50 ml) and dried, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica using 1:10 ethyl acetate–light petroleum as eluant to give the oily ester (**13**) (0.49 g, 60%), which gave identical spectroscopic and analytical data with those described above.

Methyl 2,3,6-*Trideoxy*-α-DL-threo-*hex*-2-*enopyranoside* (**11**).[10]—Sodium metal (1 g, 45 mmol) was dissolved in a solution of the benzoate (**13**) (10 g, 41 mmol) in methanol (100 ml) at 0 °C. The solution was stirred at room temperature for 3 h after which the volume of solvent was reduced to *ca.* 10 ml under reduced pressure. Water (50 ml) was added and the solution was extracted with chloroform (3 × 50 ml). The combined extracts were dried, and the solvent was removed under reduced pressure. The crude product was chromatographed on a column of silica with 1:1 ethyl acetate–light petroleum as eluant to give the *threo* alcohol (**11**) as an oil (5.8 g, 98%), b.p. 80—84 °C at 1.5 mmHg; $\nu_{max.}$ 3 600—3 300, 1 090, and 1 045 cm^{-1}; δ 1.32 (3 H, d, *J* 6.8 Hz, Me), 2.0 (1 H, br s, exch. with D_2O, OH), 3.41 (3 H, d, OMe), 3.61 (1 H, dd, *J* 6, 2 Hz, 4-H), 4.1 (1 H, qd, *J* 6.8, 2 Hz, 5-H), 4.83 (1 H, d, *J* 2.6 Hz, 1-H), 5.85 (1 H, dd, *J* 10, 2.6 Hz, 2-H), and 6.17 (1 H, dd, *J* 10, 6 Hz, 3-H); *m/z* 144 ($M^{+\bullet}$, 0.6%), 113 (25.3), and 100 (100) (Found: C, 58.3; H, 8.6%; $M^{+\bullet}$, 144.0781. Calc. for $C_7H_{12}O_3$: C, 58.3; H, 8.4%; *M*, 144.0786).

Methyl 2,3,6-*Trideoxy*-4-O-*trichloroacetimidoyl*-α-DL-threo-*hex*-2-*enopyranoside* (**22**).[33]—A solution of the *threo* alcohol (**11**) (5.8 g, 40 mmol) in dry THF (10 ml) was added dropwise to a stirred suspension of sodium hydride (0.1 g, 4 mmol) in dry THF (5 ml) at 0 °C under nitrogen. The solution was stirred for 1 h at 0 °C and was then added dropwise to a stirred solution of trichloroacetonitrile (5.9 g, 41 mmol) in dry THF (20 ml) at 0 °C under nitrogen. The solution was stirred for 2 h at 0 °C, and then the solvent was removed under reduced pressure. A mixture of methanol (1 ml) and hexane (40 ml) was added to the vigorously stirred residues and the resultant solution was filtered. The solvents were removed under reduced pressure, and column chromatography of the oily residue on silica with 1:1 ethyl acetate–light petroleum as eluant afforded the trichloroacetimidate (**22**) as an oil (9.5 g, 82%); $\nu_{max.}$ 3 335, 1 657, 1 290, and

1 050 cm^{-1}; δ 1.38 (3 H, d, *J* 6.9 Hz, Me), 3.47 (3 H, s, OMe), 4.31 (1 H, qd, *J* 6.5, 2.4 Hz, 5-H), 4.97 (1 H, d, *J* 2.95 Hz, 1-H), 5.03 (1 H, dd, *J* 5.7, 2.4 Hz, 4-H), 6.07 (1 H, dd, *J* 10, 2.95 Hz, 2-H), 6.27 (1 H, dd, *J* 10, 5.7 Hz, 3-H), and 8.34 (1 H, br s, NH); *m/z* 287 ($M^{+\bullet}$, 1.1%), 256 (4.8), 243 (33.2), 199 (18.9), 186 (18.2), 164 (13.4), 150 (16.5), 125 (32.3), 117 (24.8), 111 (43.3), and 100 (100) (Found: C, 37.4; H, 4.3; N, 4.9; Cl, 37.0%; $M^{+\bullet}$, 286.988 66. Calc. for $C_9H_{11}Cl_3NO_3$: C, 37.5; H, 4.2; N, 4.9; Cl, 36.9%; *M*, 286.988 26).

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2-*iodo*-2′-*trichloromethyl*-(*methyl* α-DL-*galactopyranosido*)[3,4-d]*oxazole* (**24**).[33]—NIS (11.55 g, 51 mmol) was added to a stirred solution of the trichloroacetimidate (**22**) (5.0 g, 17 mmol) in chloroform (70 ml). The mixture was stirred for 12 h at at room temperature and then the solution was washed with 1M-aqueous sodium thiosulphate (30 ml) and dried, and the solvent was removed under reduced pressure to give a yellow oil. Column chromatography of this oil on silica with 1:1 ethyl acetate–light petroleum as eluant afforded a white solid. Recrystallisation of the solid from ethyl acetate–hexane gave white, needle-like crystals of the iodo-oxazoline (**24**) (5.1 g, 71%), m.p. 112—113 °C; $\nu_{max.}$ 1 658, 1 116, 1 060, 1 030, and 960 cm^{-1}; δ 1.43 (3 H, d, *J* 6.3 Hz, Me), 3.5 (3 H, s, OMe), 3.91 (1 H, dd, *J* 7.8, 3.6 Hz, 2-H), 4.42 (1 H, qd, *J* 6.3, 2.4 Hz, 5-H), 4.57 (1 H, dd, *J* 7.6, 2.4 Hz, 4-H), 4.60 (1 H, d, *J* 3.6 Hz, 1-H), and 4.74 (1 H, t, *J* 7.8 Hz, 3-H); *m/z* 413 ($M^{+\bullet}$, 0.8%), 382 (1.5), 353 (1.8), 296 (18.7), 286 (13.7), 226 (11.0), 184 (79.1), 168 (28.2), and 125 (100) (Found: C, 25.9; H, 2.7; N, 3.3; Cl, 25.4; I, 30.5%; $M^{+\bullet}$, 412.885 21. Calc. for $C_9H_{11}Cl_3INO_3$: C, 26.1; H, 2.7; N, 3.4; Cl, 25.6; I, 30.6%; *M*, 412.885 10).

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2′-*methyl*-(*methyl* α-DL-lyxo-*hexopyranosido*)[3,4-d]*oxazole* (**25**).[4]—Bu_3SnH (3.1 g, 10.6 mmol) was added to a stirred solution of the iodo-oxazoline (**24**) (0.9 g, 2.1 mmol) and AIBN (0.003 g, catalyst) in benzene (20 ml). The solution was heated to reflux for 3 h and then the solvent was removed under reduced pressure. The crude product was dissolved in acetonitrile (10 ml) and the solution was washed with light petroleum (6 × 2 ml) to remove unwanted tin residues. The acetonitrile was removed under reduced pressure to give the oily *oxazoline* (**25**) (0.31 g, 78%); $\nu_{max.}$ 1 673, 1 242, 1 091, and 1 041 cm^{-1}; δ 1.27 (3 H, d, *J* 6.7 Hz, 5-Me), 1.74 (1 H, ddd, *J* 15, 8.3, 3.8 Hz, 2-H_a), 2.0 (3 H, d, *J* 1.4 Hz, N=CMe), 2.33 (1 H, ddd, *J* 15, 5.9, 1.4 Hz, 2-H_e), 3.38 (3 H, s, OMe), 3.93 (1 H, qd, *J* 6.7, 1.2 Hz, 5-H), 4.32 (1 H, dddd, *J* 10.5, 3.8, 1.4, 1.4 Hz, 3-H), 4.39 (1 H, dd, *J* 10.5, 1.2 Hz, 4-H), and 4.69 (1 H, dd, *J* 8.3, 5.9 Hz, 1-H); *m/z* 185 ($M^{+\bullet}$, 4.1%), 154 (32.0), 141 (6.5), and 61 (100) (Found: $M^{+\bullet}$, 185.2238. $C_9H_{15}NO_3$ requires *M*, 185.2230).

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2′-*trichloromethyl*-(*methyl* α-DL-lyxo-*hexopyranosido*)[3,4-d]*oxazole* (**26**) *and* 2,3,4,6-*Tetradeoxy*-2′-*dichloromethyl*-4′,5′-*dihydro*-(*methyl*-α-DL-lyxo-*hexopyranosido*)[3,4-d]*oxazole* (**27**).—Bu_3SnH (0.97 g, 3.3 mmol) was added to a stirred solution of the iodo-oxazoline (**24**) (1.0 g, 2.4 mmol) and AIBN (0.004 g, catalyst) in toluene (5 ml). An exothermic reaction was observed. The solution was stirred at room temperature for 30 min after which the solvent was removed under reduced pressure. Pentane (5 ml) was added to the residues and the precipitated orange solid was filtered off. The solution was extracted with acetonitrile (2 × 5 ml). The combined extract was washed with more pentane (5 × 2 ml) and the solvent was then removed under reduced pressure. The residue was eluted from a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give successively the oxazolines (**26**) and (**27**). The *oxazoline* (**26**) was a white solid, which was recrystallised from ether–hexane to give white, needle-like crystals (0.3 g, 43%), m.p. 85—86.5 °C; $\nu_{max.}$ 1 660, 1 246, 1 126, and 1 080 cm^{-1}; δ 1.33 (3 H, d, *J* 6.5 Hz, Me), 1.81 (1 H, ddd, *J* 15.3, 7.9, 4.8 Hz, 2-H_a), 2.5 (1 H, ddd, *J* 15.3, 5.9, 3.1 Hz, 2-H_e), 3.39 (3 H, s, OMe), 3.99 (1 H, qd, *J* 6.5, 1.5 Hz, 5-H), 4.6 (1 H, ddd, *J* 9.9, 4.8, 3.1 Hz, 3-H), 4.73 (1 H, dd, *J* 7.9, 5.9 Hz, 1-H), and 4.8 (1 H, dd, *J* 9.9, 1.5 Hz, 4-H); *m/z* 286 ($M^{+\bullet}$, 0.7%), 256 (4.6), 251 (1.2), 243 (4.4), 170 (2.5), 150 (2.0), 117 (2.9), and 95 (100) (Found: C, 37.4; H, 4.1; N, 4.9; Cl, 36.9%; $M^{+\bullet}$ 286.987 07. $C_9H_{12}Cl_3NO_3$ requires C, 37.5; H, 4.2; N, 4.9; Cl, 36.9%; *M*, 286.988 26).

The *oxazoline* (**27**) was a white solid, which was recrystallised from ether–hexane to give white, needle-like crystals (0.27 g, 44%), m.p. 68—69 °C; $\nu_{max.}$ 1 651, 1 241, 1 083, 1 030, and 1 000 cm^{-1}; δ 1.32 (3 H, d, *J* 6.5 Hz, Me), 1.78 (1 H, ddd, *J* 13.3, 6.8, 4.2 Hz, 2-H_a), 2.41 (1 H, ddd, *J* 13.3, 5.3, 2.7 Hz, 2-H_e), 3.39 (3 H, s, OMe), 3.98 (1 H, qd, *J* 6.5, 1.5 Hz, 5-H), 4.5 (1 H, ddd, *J* 8.7, 4.2, 2.7 Hz, 3-H), 4.67 (1 H, dd, *J* 8.7, 1.5 Hz, 4-H), 4.69 (1 H, dd, *J* 6.8, 5.3 Hz, 1-H), and 6.23 (1 H, s, $CHCl_2$); *m/z* 253 ($M^{+\bullet}$, 1.0%), 240 (9.6), 227 (5.1), 170 (70.5), 154 (11.5), 113 (40.4), 100 (18.0), and 86 (100) (Found: $M^{+\bullet}$, 253.027 89. $C_9H_{13}Cl_2NO_3$ requires *M*, 253.027 24).

*Methyl*3-*Acetamido*-2,3,6-*trideoxy*-α-DL-lyxo-*hexopyranoside* (**28**).[4]—PTSA (0.6 g, 3.2 mmol) was added to a stirred solution of the oxazoline (**25**) (0.3 g, 1.6 mmol) in a mixture of pyridine (4 ml) and water (1 ml). The solution was stirred at 100 °C for 2 h and was then extracted with chloroform (3 × 20 ml). The combined extract was dried, and the solvent was removed under pressure. The residue was chromatographed on a column of silica with 1:1 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ether–hexane to give white, needle-like crystals of the acetamido alcohol (**28**) (0.24 g, 72%), m.p. 153—155 °C; $\nu_{max.}$ 3 440, 3 281, 1 632, and 1 534 cm^{-1}; δ 1.25 (3 H, d, *J* 7 Hz, Me), 1.69 (1 H, td, *J* 13, 13, 3.5 Hz, 2-H_a), 1.87 (1 H, ddt, *J* 13, 6, 0.5 Hz, 2-H_e), 1.98 (3 H, s, NAc), 2.05 (1 H, br s, exch. with D_2O, OH), 3.33 (3 H, s, OMe), 3.56 (1 H, br s, 4-H), 4.02 (1 H, q, *J* 7 Hz, 5-H), 4.36 (1 H, m, 3-H), 4.74 (1 H, dd, *J* 3.5, 0.5 Hz, 1-H), and 5.93 (1 H, br, *J* 8 Hz, exch. with D_2O, NH); *m/z* 204 ($M^{+\bullet}$ + H, 2.1%), 185 (10.5), 172 (23.7), 153 (10.3), 129 (12.6), 113 (17.9), 101 (66.6), and 59 (100) (Found: $M^{+\bullet}$ + H, 204.123 92. Calc. for $C_9H_{18}NO_4$: *m/z* 204.123 57)[34] (Found: C, 53.3; H, 8.5; N, 6.8. Calc. for $C_9H_{17}NO_4$: C, 53.2; H, 8.5; N, 6.9%).

Methyl 2,3,6-*Trideoxy*-3-*trichloroacetamido*-α-DL-lyxo-*hexopyranoside* (**29**).—PTSA (0.1 g, 0.5 mmol) was added to a stirred solution of the oxazoline (**26**) (0.105 g, 0.25 mmol) in a mixture of pyridine (4 ml) and water (1 ml). The solution was heated to 100 °C for 2 h and was then extracted with chloroform (3 × 10 ml). The combined extract was dried, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica with 1:1 ethyl acetate–light petroleum as eluant to give a gum. Trituration of the gum in ether–hexane gave white, rhombic crystals of the *amido alcohol* (**29**) (0.068 g, 62%), m.p. 93—94 °C; $\nu_{max.}$ 3 600—3 200, 3 500, 1 712, and 1 500 cm^{-1}; δ 1.26 (3 H, d, *J* 6.9 Hz, Me), 1.79 (1 H, td, *J* 13, 13, 3.9 Hz, 2-H_a), 1.98 (1 H, ddt, *J* 13, 5.2 1 H, 2-H_e), 2.05 (1 H, d, *J* 9.5 Hz, exch. with D_2O, OH), 3.36 (3 H, s, OMe), 3.65 (1 H, dd, *J* 9.5, 2.5 Hz, 4-H), 4.05 (1 H, q, *J* 6.9 Hz, 5-H), 4.34 (1 H, m, 3-H), 4.79 (1 H, dd, *J* 3.9, 1 Hz, 1-H), and 7.09 (1 H, d, *J* 8 Hz, exch. with D_2O, NH); *m/z* 306 ($M^{+\bullet}$ + H, 7.5%), 274 (100), and 240 (4.7) (Found: C, 35.3; H, 4.7; N, 4.3; Cl, 34.8%; $M^{+\bullet}$, 304.998 88. $C_9H_{14}Cl_3NO_4$ requires C, 35.3; H, 4.6; N, 4.5; Cl, 37.4%; *M*, 304.998 83).

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-DL-lyxo-*hexopyranoside* (*Methyl* α-DL-*Daunosaminide*) (**2**).[4]—A solution of the oxazoline (**26**) (0.5 g, 1.7 mmol) in methanol (5 ml) was stirred at 50 °C with 5M-aqueous sodium hydroxide (1 ml) for 2 h. The volume

of solvent was reduced to *ca.* 2 ml and the residue was extracted with chloroform (6 × 5 ml). The combined extract was dried, and the solvent was removed under reduced pressure to give a yellow solid. The solid was recrystallised from ethyl acetate–hexane to give white, needle-like crystals of the amine (**2**) (0.25 g, 88%), m.p. 91—94 °C; $\nu_{max.}$ 3 630, 3 600—3 460, 1 360, 1 121, 1 045, and 978 cm^{-1}; δ 1.27 (3 H, d, *J* 6.7 Hz, Me), 1.67 (2 H, m, CH_2), 1.76 (3 H, br s, exch. with D_2O, OH and NH_2), 3.25 (1 H, ddd, *J* 9.8, 8, 3.1 Hz, 3-H), 3.35 (3 H, s, OMe), 3.42 (1 H, d, *J* 3.1 Hz, 4-H), 3.89 (1 H, q, *J* 6.7 Hz, 5-H), and 4.74 (1 H, dd, *J* 3.3, 2.1 Hz, 1-H); *m/z* 161 ($M^{+\bullet}$, 32.5%), 146 (5.8), 144 (5.9), 130 (100), and 104 (18.0) (Found: C, 52.1; H, 9.4; H, 8.6%; $M^{+\bullet}$, 161.105 04. Calc. for $C_7H_{15}NO_3$: C, 52.1; H, 9.4; N, 8.7%; *M*, 161.105 19).[34]

Methyl 3-*Acetamido*-4-O-*acetyl*-2,3,6-*trideoxy*-α-DL-lyxo-*hexopyranoside* (**30**).[33]—Acetic anhydride (2 ml) and pyridine (1 ml) was added to methyl α-DL-daunosaminide (**2**) (0.1 g, 0.6 mmol). The mixture was stirred for 4 h at room temperature and was then poured into ice–water (10 ml). The solution was extracted with chloroform (4 × 10 ml) and the extract was washed successively with aqueous sodium hydrogen carbonate (10 ml) and water (10 ml), then dried, and the solvent was removed under reduced pressure. The pale yellow solid obtained was recrystallised in ether to give white, needle-like crystals of the amide ester (**30**) (0.135 g, 90%), m.p. 166—167 °C; $\nu_{max.}$ 3 310, 1 740, 1 650, and 1 535 cm^{-1}; δ 1.11 (3 H, d, *J* 6.8 Hz, Me), 1.80 (2 H, m, CH_2), 1.94 (3 H, s, NAc), 2.18 (3 H, s, OAc), 3.34 (3 H, s, OMe), 4.05 (1 H, qd, *J* 6.8, 2.1 Hz, 5-H), 4.55 (1 H, m, 3-H), 4.8 (1 H, t, *J* 2.1 Hz, 4-H), 5.09 (1 H, d, *J* 2.4 Hz, 1-H), and 5.45 (1 H, br d, *J* 7.9 Hz, exch. with D_2O, NH); *m/z* 245 ($M^{+\bullet}$, 2.0%), 214 (100), 201 (3.0), and 155 (11.6) (Found: C, 54.0; H, 7.7; N, 5.7%; $M^{+\bullet}$, 245.126 85. Calc. for $C_{11}H_{19}NO_5$: C, 53.9; H, 7.8; H, 5.7%; *M*, 245.126 31).[34]

Methyl 3-*Amino*-2,3,6-*trideoxy*-2-*iodo*-α-DL-*galactopyranoside Hydrochloride* (**31**).[33]—6M-Hydrochloric acid (3.3 ml) was added to a stirred solution of the iodo-oxazoline (**24**) (4.6 g, 11 mmol) in methanol (33 ml). The solution was stirred at room temperature for 24 h after which the solvents were removed under reduced pressure (< 35 °C). The yellow solid obtained was then washed with ether to give white crystals of the amine hydrochloride (**31**) (3.45 g, 96%), m.p. 197—199 °C (decomp.); $\nu_{max.}$ 3 600—3 200, 1 595, 1 582, 1 522, and 988 cm^{-1}; δ(CD_3OD), 1.35 (3 H, d, *J* 6.5 Hz, Me), 3.54 (3 H, s, OMe), 3.87 (1 H, dd, *J* 11.5, 3.4 Hz, 2-H), 3.95 (1 H, br s, 4-H), 4.2 (1 H, qd, *J* 6.5, 1.2 Hz, 5-H), 4.5 (1 H, ddm, *J* 11.5, 3.3 Hz, 3-H), 4.9 (4 H, s, OH and NH_3), and 4.95 (1 H, d, *J* 3.4 Hz, 1-H); *m/z* 288 ($M^{+\bullet}$, 7.1%), 256 (5.5), 212 (4.1), 198 (8.0), 184 (15.0), 169 (29.6), 128 (33.5), and 100 (100) (Found: C, 26.0; H, 4.6; N, 4.3; Cl, 10.7; I, 39.6%; $M^{+\bullet}$, 288.009 18. Calc. for $C_7H_{15}ClINO_3$: C, 26.0; H, 4.6; N, 4.3; Cl, 10.9; I, 39.2%; *M*, 228.009 85).

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-DL-lyxo-*hexopyranoside Hydrochloride* (**32**).[33]—Bu_3SnH (3.37 g, 11.6 mmol) was added to a stirred solution of the iodo amine hydrochloride (**31**) 2.5 g, 7.7 mmol) and AIBN (0.003 g, catalyst) in a mixture of methanol (10 ml) and toluene (20 ml). The solution was stirred for 1 h at room temperature and then the solvents were removed under reduced pressure. The residue was chromatographed on a column of silica with 7:3 ethyl acetate–methanol as eluant to give the amine hydrochloride (**32**) as a white solid (0.91 g, 65%), m.p. 171—173 °C; $\nu_{max.}$(Nujol) 3 650—3 300, 3 200—2 800, 1 595, 1 575, 1 190, and 985 cm^{-1}; δ(CD_3OD) 1.38 (3 H, d, *J* 6.8 Hz, Me), 1.95—2.2 (2 H, m, CH_2), 3.47 (3 H, s, OMe), 3.65—3.85 (2 H, m, 4- and 3-H), 4.05 (1 H, q, *J* 6.8 Hz, 5-H), and 4.95 (5 H, br s, 1-H, OH, and NH_3); *m/z* 162 ($M^{+\bullet}$, 17.7%), 143 (11.0), 131 (38.4), 104 (31.0), 86 (62.1), 72 (66.7), and 59 (100) (Found: C, 42.5; H, 8.1; N, 7.0; Cl, 17.9%; $M^{+\bullet}$, 162.113 15. Calc. for $C_7H_{16}ClNO_3$: C, 42.5; H, 8.1; N, 7.1; Cl, 17.9%; *M*, 162.113 01).

Cyclohex-2-enyl N-*Benzoylbenzimidate* (**34**).—DEAD (1.25 g, 7.2 mmol) was added dropwise to a stirred solution of cyclohex-2-en-1-ol (**33**) (0.65 g, 6.6 mmol), PPh_3 (1.92 g, 7.3 mmol), and dibenzamide[19] (1.5 g, 6.6 mmol) in dry THF (25 ml) at 0 °C. The solution was stirred for 15 min at room temperature and then the solvent was removed under reduced pressure. Ether (30 ml) was added to the residue and the precipitated white solid, containing triphenylphosphine oxide and diethyl hydrazinedicarboxylate, was filtered off. The solvent was removed under reduced pressure and the residue was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give a gum. Trituration of this gum in ether–hexane gave a white solid, which was recrystallised from ether–hexane to give white, needle-like crystals of the *imidate* (**34**) (1.88 g, 93%), m.p. 92—94 °C; $\nu_{max.}$(Nujol) 1 660, 1 635, 1 600, 1 580, 1 270, 1 150, and 1 065 cm^{-1}; δ 1.7—2.3 (6 H, m, CH_2), 5.6 (1 H, br s, 1-H), 6.0 (2 H, m, 2- and 3-H), and 7.1—8.1 (10 H, m, Ph); *m/z* 305 ($M^{+\bullet}$, 1.6%), 225 (10.6), 200 (11.7), and 105 (100) (Found: C, 78.6; H, 6.2; N, 4.5%; $M^{+\bullet}$, 305.141 05. $C_{20}H_{19}NO_2$ requires C, 78.6; H, 6.3; N, 4.6%; *M*, 305.141 57).

1,2-cis-2,3-trans-2-*Benzamido*-3-*iodocyclohexyl Benzoate* (**35**).—NIS (0.405 g, 1.8 mmol) was added to a stirred solution of the imidate (**34**) (0.5 g, 1.6 mmol) in chloroform (30 ml) containing ethanol (0.5 ml). The solution was stirred at room temperature for 1 h after which it was washed with 1M-aqueous sodium thiosulphate (15 ml) and dried, and the solvent was removed under reduced pressure. The residue was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ether–hexane to give white, needle-like crystals of the *amide ester* (**35**) (0.304 g, 42%), m.p. 148—150 °C; $\nu_{max.}$ 3 400, 1 723, 1 665, 1 604, 1 510, 1 490, 1 270, and 1 110 cm^{-1}; δ 1.5—2.4 (6 H, m, CH_2), 4.3—4.75 (2 H, m, 2- and 3-H), 5.55 (1 H, br s, 1-H), 6.2 (1 H, br, d, *J* 8 Hz, exch. with D_2O, NH), and 7.3—8.1 (10 H, m, Ph); *m/z* 322 ($M^{+\bullet}$ − I, 0.9%), 216 (20.0), 199 (45.3), 171 (15.9), and 105 (100) (Found: $M^{+\bullet}$ − I, 322.143 61. $C_{20}H_{20}NO_3$ requires *m/z* 322.144 31) (Found: C, 53.3; H, 4.5; N, 3.1; I, 28.0. $C_{20}H_{20}INO_3$ requires C, 53.4; H, 4.5; N, 3.1; I, 28.2%).

1,2-cis-2,3-trans-2-*Benzamido*-3-*bromocyclohexyl Benzoate* (**37**).—NBS (0.7 g, 4 mmol) was added to a stirred solution of the imidate (**34**) (1 g, 3.2 mmol) and propylene oxide (0.1 g, 2.5 mmol) in chloroform (40 ml) containing ethanol (0.5 ml). The solution was stirred for 1 h at room temperature and was then washed with 1M-aqueous sodium thiosulphate (15 ml). The aqueous phase was back-extracted with chloroform (30 ml) and the combined chloroform phases were dried. The solvent was removed under reduced pressure and the resultant yellow oil was subjected to column chromatography on silica with 1:4 ethyl acetate–light petroleum as eluant to give *orthoamide* (**36**) as a gum which had $\nu_{max.}$ 1 650, 1 450, 1 370, 1 355, and 1 060 cm^{-1}; δ 1.15 (3 H, t, *J* 7 Hz, OCH_2Me), 1.5—2.4 (6 H, m, ring CH_2), 3.47 (2 H, q, *J* 7 Hz, OCH_2Me), 4.5—5.05 (3 H, m, 1-, 2-, and 3-H), and 7.2 (10 H, br s, Ph).

The orthoamide (**36**) was dissolved in methanol (30 ml), and dil. hydrochloride acid (5 ml) was added to the stirred solution. The solution was stirred for 30 min at room temperature and then solvents were removed under reduced pressure to give a white solid, which was dissolved in chloroform (30 ml) and the solution was washed with water (10 ml). The organic phase was dried, and the solvent was removed under reduced pressure to give a white solid, which was recrystallised from ethyl acetate–light petroleum to give white, needle-like crystals of the *bromo*

amide ester (**37**) (1.12 g, 85%), m.p. 160—162 °C; $\nu_{max.}$ 3 450, 1 723, 1 665, 1 510, 1 495, 1 270, and 1 110 cm^{-1}; δ 1.6—2.7 (6 H, m, CH_2), 4.2—4.7 (2 H, m, 2- and 3-H), 5.63 (1 H, br s, 1-H), 6.26 (1 H, br d, *J* 8 Hz, exch. with D_2O, NH), and 7.3—8.1 (10 H, m, Ph); *m/z* 322 ($M^{+\bullet}$ − Br, 3.5%), 296 (0.2), 280 (0.4), 216 (38.4), 199 (95.1), 171 (35.8), 122 (6.9), and 105 (100) (Found: C, 59.7; H, 5.0; N, 3.7; Br, 20.1%; $M^{+\bullet}$, 401.063 14. $C_{20}H_{20}BrNO_3$ requires C, 59.7; H, 5.0; N, 3.5; Br, 19.9%; *M*, 401.062 70).

The bromoamide ester (**37**) can be prepared directly from the imidate (**34**). using the reaction conditions but without propylene oxide and then washing the chloroform extract with dil. hydrochloric acid after the thiosulphate wash.

cis-2-*Benzamidocyclohexyl Benzoate* (**38**).[20]—Bu_3SnH (1.59 g, 5.5 mmol) was added to a stirred solution of the bromo amide ester (**37**) (2.0 g, 5 mmol) and AIBN (0.004 g, catalyst) in toluene (20 ml) containing methanol (2 ml). The solution was stirred at reflux for 1 h and then the solvents were removed under reduced pressure. The residue was chromatographed on a column of silica with 1:1 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ether–light petroleum to give white, needle-like crystals of the amide ester (**38**) (1.5 g, 96%), m.p. 149—150 °C; $\nu_{max.}$ 3 450, 1 725, 1 665, 1 510, 1 490, and 1 268 cm^{-1}; δ 1.55—2.2 (8 H, m, CH_2), 4.3 (1 H, m, 2-H), 5.4 (1 H, m, 1-H), 6.38 (1 H, br d, *J* 7.8 Hz, exch. with D_2O, NH), and 7.3—8.1 (10 H, m, Ph); *m/z* 323 ($M^{+\bullet}$, 2.0%), 226 (3.0), 218 (6.9), 201 (23.0), 173 (2.4), 122 (16.7), and 105 (100) (Found: $M^{+\bullet}$, 323.152 28. Calc. for $C_{20}H_{21}NO_3$: *M*, 323.152 13).

N-(cis-2-*Hydroxycyclohexyl*)*benzamide* (**39**).[20]—Sodium (0.079 g, 3.4 mmol) was dissolved in methanol (10 ml). The solution of sodium methoxide was then added to a stirred solution of the amide ester (**38**) (1.0 g, 3.1 mmol) in methanol (20 ml). The solution was stirred at room temperature for 30 min and then water (20 ml) was added. The mixture was extracted with chloroform (3 × 50 ml). The extract was dried, and the solvent was removed under reduced pressure. The resultant yellow gum was chromatographed on a column of silica with 1:1 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ethyl acetate–benzene to give white, needle-like crystals of the amido alcohol (**39**) (0.64 g, 94%), m.p. 185—186 °C; $\nu_{max.}$ 3 550—3 250, 3 440, 1 645, 1 545, and 1 490 cm^{-1}; δ 1.35—1.95 (8 H, m, CH_2), 2.04 (1 H, br s, exch. with D_2O, OH), 3.95—4.2 (2 H, m, 1- and 2-H), 6.55 (1 H, br d, *J* 8 Hz, exch. with D_2O, NH), and 7.3—7.8 (5 H, m, Ph); *m/z* 219 ($M^{+\bullet}$, 1.4%), 201 (2.0), 191 (2.6), 162 (2.6), 148 (11.2), 122 (66.3), and 105 (100) (Found: C, 71.1; H, 7.8; N, 6.3%; $M^{+\bullet}$, 219.125 75. Calc. for $C_{13}H_{17}NO_2$: C, 71.2; H, 7.8; N, 6.4%; *M*, 219.125 92).

cis-2-*Aminocyclohexanol Hydrochloride* (**40**).[20]—6M-Hydrochloric acid (8 ml) was added to a stirred solution of the amido alcohol (**39**) (0.5 g, 2.3 mmol) in methanol (8 ml). The solution was stirred at reflux for 24 h, after which the solvents were removed under reduced pressure. The resultant pale yellow solid was recrystallised from acetone to give white, needle-like crystals of the *cis*-1,2-aminoalcohol hydrochloride (**40**) (0.26 g, 82%), m.p. 182—184 °C; $\nu_{max.}$(Nujol) 3 600—3 250, 3 200—2 800, 1 610, 1 590, 1 505, 1 380, 1 030, and 990 cm^{-1}; δ(CD_3OD) 1.5—2.1 (8 H, m, CH_2), 3.35 (1 H, m, 1-H), 4.12 (1 H, m, 2-H), and 4.95 (4 H, br s, OH and NH_3); *m/z* 115 ($M^{+\bullet}$, 21.3%), 97 (1.9), 86 (3.5), 72 (13.2), and 56 (100) (Found: $M^{+\bullet}$, 115.099 67. Calc. for $C_6H_{13}NO$: *M*, 115.099 71) (Found: C, 47.5; H, 9.4; N, 9.0; Cl, 23.4. Calc. for $C_6H_{14}ClNO$: C, 47.5; H, 9.3; N, 9.2; Cl, 23.4%).

Methyl 4-O-(N-*Benzoylbenzimidoyl*)-2,3,6-*trideoxy*-α-DL-threo-*hex*-2-*enopyranoside* (**41**).—A solution of DEAD (1.73 g, 10 mmol) in dry THF (2 ml) was added to a stirred solution of the alcohol (**10**) (1.03 g, 7.1 mmol), PPh_3 (2.6 g, 10 mmol), and dibenzamide[19] (2.03 g, 10 mmol) in dry THF (25 ml) at 0 °C. The mixture was stirred for 2 h at room temperature after which the solvent was removed under reduced pressure. Ether (50 ml) was added and the white precipitate was filtered off. The solvent was removed under reduced pressure and the residue was chromatographed on a column of silica with 1:8 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ether–hexane mixture to give white, needle-like crystals of the *imidate* (**41**) (2.16 g, 86%), m.p. 87—89 °C; $\nu_{max.}$(Nujol) 1 670, 1 640, 1 270, 1 060, 955, and 700 cm^{-1}; δ 1.46 (3 H, d, *J* 6.6 Hz, Me), 3.48 (3 H, s, OMe), 4.36 (1 H, qd, *J* 6.6, 2.5 Hz, 5-H), 4.99 (1 H, d, *J* 3 Hz, 1-H), 5.18 (1 H, dd, *J* 5.2, 2.5 Hz, 4-H), 6.1 (1 H, dd, *J* 10, 3 Hz, 2-H), 6.45 (1 H, dd, *J* 10, 2.5 Hz, 3-H), and 7.25—8.0 (10 H, m, Ph); *m/z* 351 ($M^{+\bullet}$, 0.5%), 225 (17.9), 197 (5.3), 105 (100), and 77 (52.0) (Found: C, 71.8; H, 6.0; N, 4.0%; $M^{+\bullet}$, 351.147 57. $C_{21}H_{21}NO_4$ requires C, 71.8; H, 6.0; N, 4.0%; *M*, 351.147 05).

Methyl 3-*Benzamido*-4-O-*benzoyl*-2-*bromo*-2,3,6-*trideoxy*-α-DL-*galactopyranoside* (**42**).—NBS (1.9 g, 11 mmol) was added to a stirred solution of the imidate (**41**) (1.5 g, 4.2 mmol) in chloroform (25 ml) containing ethanol (1 ml). The solution was stirred for 6 h at room temperature and was then washed with 1M-aqueous sodium thiosulphate (20 ml). The aqueous phase was back-extracted with chloroform (25 ml). The combined chloroform phases were dried, and the solvent was removed under reduced pressure to give a pale yellow solid. The solid was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ethyl acetate–hexane to give white needle-like crystals of the *bromo amide ester* (**42**) (1.71 g, 91%), m.p. 211.5—213.5 °C; $\nu_{max.}$(Nujol) 3 395, 3 340, 1 720, 1 700, 1 645, 1 530, 1 270, 1 050, 1 030, and 715 cm^{-1}; δ 1.18 (3 H, d, *J* 6.6 Hz, Me), 3.52 (3 H, s, OMe), 4.36 (1 H, dd, *J* 12.1, 3.15 Hz, 2-H), 4.38 (1 H, qd, *J* 6.6, 1.25 Hz, 5-H), 4.99 (1 H, d, *J* 3.15 Hz, 1-H), 5.05 (1 H, ddd, *J* 12.1, 8.4, 3.1 Hz, 3-H), 5.66 (1 H, dd, *J* 3.1, 1.25 Hz, 4-H), 6.02 (1 H, br d, *J* 8.4 Hz, exch. with D_2O, NH), and 7.3—8.1 (10 H, m, Ph); *m/z* 447 ($M^{+\bullet}$ + H, 0.9%), 416 (0.8), 387 (1.3), 368 (14.1), 342 (1.6), 246 (7.6), 226 (4.1), 190 (4.2), and 105 (100) (Found: $M^{+\bullet}$ + H, 447.067 26. $C_{21}H_{23}BrNO_5$ requires *m/z*, 447.068 18) (Found: C, 56.2; H, 5.0; N, 2.9; Br, 17.9. $C_{21}H_{22}BrNO_5$ requires C, 56.2; H, 5.0; N, 3.1; Br, 17.8%).

Methyl 3-*Benzamido*-4-O-*benzoyl*-2,3,6-*trideoxy*-α-DL-lyxo-*hexopyranoside* (**43**).—Bu_3SnH (0.21 g, 0.7 mmol) was added to a stirred solution of the bromo amide ester (**42**) (0.29 g, 0.65 mmol) and AIBN (0.004 g, catalyst) in toluene (10 ml) containing methanol (1 ml). The solution was stirred at reflux for 30 min, after which the solvents were removed under reduced pressure. The residue was subjected to column chromatography on silica with 1:1 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ethyl acetate–light petroleum mixture to give white crystals of the *amide ester* (**43**) (0.23 g, 96%), m.p. 181—183 °C; $\nu_{max.}$ 3 450, 1 730, 1 665, 1 510, 1 490, and 1 270 cm^{-1}; δ 1.21 (3 H, d, *J* 6.6 Hz, Me), 1.96—2.1 (2 H, m, CH_2), 3.42 (3 H, s, OMe), 4.24 (1 H, q, *J* 6.6 Hz, 5-H), 4.85 (1 H, m, 3-H), 4.92 (1 H, d, *J* 2.7 Hz, 4-H), 5.42 (1 H, d, *J* 2.6 Hz, 1-H), 6.15 (1 H, br d, *J* 8 Hz, exch. with D_2O, NH), and 7.3—8.2 (10 H, m, Ph); *m/z* 369 (M^+, 0.1%), 338 (2.0), 325 (0.2), 267 (0.7), 247 (7.7), 215 (6.7), 190 (9.6), 142 (6.7), and 105 (100) (Found: C, 68.2; H, 6.3; N, 3.9%; $M^{+\bullet}$, 369.157 76. $C_{21}H_{23}NO_5$ requires C, 68.3; H, 6.3; N, 3.8%; *M*, 369.157 61).

Methyl 3-*Benzamido*-2,3,6-*trideoxy*-α-DL-lyxo-*hexopyranoside* (**44**)[35].—*Method A*. A solution of the amide ester (**43**) (0.2 g, 0.54 mmol) in methanol (5 ml) was added to a stirred solution of sodium (0.02 g, 0.8 mmol) in methanol (15 ml). The solution was

stirred at room temperature for 1 h, and then the volume of solvent was reduced under reduced pressure to *ca.* 5 ml. Water (10 ml) was added to the solution which was then extracted with chloroform (3 × 20 ml). The extract was dried, and the solvent was removed under reduced pressure. The yellow solid residue was chromatographed on a column of silica with 1:1 ethyl acetate–light petroleum as eluant to give a white solid, which was recrystallised from ethyl acetate–light petroleum mixture to give white, plate-like crystals of the amide (**44**) (0.135 g, 94%), m.p. 171—172 °C; $\nu_{max.}$ 3 600—3 200, 3 440, 1 655, 1 510, 1 490, 1 125, and 980 cm^{-1}; δ 1.25 (3 H, d, *J* 6.6 Hz, Me), 1.75—2.1 (3 H, m, CH_2 and OH), 3.36 (3 H, s, OMe), 3.66 (1 H, dd, *J* 8.65, 2.6 Hz, 4-H), 4.07 (1 H, q, *J* 6.6 Hz, 5-H), 4.55 (1 H, m, 3-H), 4.78 (1 H, d, *J* 2.7 Hz, 1-H), 6.48 (1 H, br d, *J* 8 Hz, exch. with D_2O, NH), and 7.3—7.8 (5 H, m, Ph); *m/z* 266 ($M^{+\cdot}$ + H, 0.2%), 247 (2.7), 233 (7.2), 221 (0.5), 191 (4.8), 163 (13.4), 122 (14.3), and 105 (100) (Found: C, 63.3; H, 7.2; N, 5.1%; $M^{+\cdot}$, 265.131 21. Calc. for $C_{14}H_{19}NO_4$: C, 63.4; H, 7.2; N, 5.3%; *M*, 265.131 40).

Method B. Lithium aluminium hydride (LAH) (0.058 g, 1.5 mmol) was added to a stirred solution of the bromo amide ester (**42**) (0.2 g, 0.44 mmol) in dry THF (10 ml). The solution was stirred for 30 min at room temperature, then water (1 ml) was added to destroy the excess of LAH. The white precipitate was filtered off and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica with 1:9 methanol–ethyl acetate as eluant to give the white solid amide (**44**) (0.112 g, 95%), m.p. 170—172 °C, having identical spectroscopic and analytical properties with those outlined above.

3-*Amino*-2,3,6-*trideoxy*-DL-lyxo-*hexopyranoside Hydrochloride* (DL-*Daunosamine Hydrochloride*) (**45**).[35]—12M-Hydrochloric acid (2 ml) was added to a stirred solution of the amide (**44**) (0.3 g, 1.1 mmol) in a mixture of methanol (1 ml) and water (5 ml). The solution was stirred at reflux for 24 h. The solvents were removed under reduced pressure to give a yellow oil, which was eluted down a column of silica with 1:4 methanol–ethyl acetate as eluant to give a white, hygroscopic solid, which was recrystallised from acetone to give white, needle-like crystals of the amine hydrochloride (**45**) (0.093 g, 45%), m.p. 148—150 °C; $\nu_{max.}$(Nujol) 3 450—3 300, 3 150—2 800, 1 605, 1 590, 1 505, and 1 030 cm^{-1}; *m/z* 147 ($M^{+\cdot}$, 0.5), 130 (0.7), and 94 (10.1) (Found: $M^{+\cdot}$ + H, 148.097 35. Calc. for $C_6H_{14}NO_3$: *m/z*, 148.097 36) (Found: C, 39.4; H, 7.7; N, 7.6. Calc. for $C_6H_{14}ClNO_3$: C, 39.3; H, 7.7; N, 7.6%).

(−)-(S)-1-(2-*Furyl*)*ethanol* (**46**).[28]—Lithium borohydride (2.14 g, 98 mmol) was added to a solution of (*SS*)-*N*,*N*′-dibenzoylcystine (**52**) (14.66 g, 32.7 mmol) and t-butyl alcohol (3.23 g, 43.6 mmol) in dry THF (70 ml). The solution was stirred at reflux for 12 h, and was then cooled to −78 °C and a solution of 2-acetylfuran (**5**) (3 g, 27 mmol) in dry THF (5 ml) was added dropwise to the stirred borohydride solution. The solution was stirred at −78 °C for 3 h and was then allowed to warm to room temperature. The solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and the solution was washed with 2M-sodium hydroxide (3 × 100 ml). The organic layer was dried and the solvent was removed to give a yellow oil, which was chromatographed on a column of silica with 1:4 ethyl acetate–light petroleum as eluant to give the oily alcohol (**46**) (2.508 g, 82%); $[\alpha]_D$ −15.8° (*c* 1 in EtOH) {lit.,[28] $[\alpha]_D$ −17.0° (*c* 6 in EtOH)}. When the aqueous phase was left overnight under air, (*SS*)-*N*,*N*′-dibenzoylcystine (**52**) (11.139 g, 76%) was recovered. Repetition of the reaction sequences outlined above, but starting from the optically active alcohol (**46**), gave the following optically active products (structures as shown in the Schemes).

(−)-1-(2,5-*Dihydro*-2,5-*dimethoxy*-2-*furyl*)*ethanol* (**7**).—$[\alpha]_D^{22}$ −15.4° (*c* 1 in $CHCl_3$).

Methyl 2,3,6-*Trideoxy*-α-L-glycero-*hex*-2-*enopyranosid*-4-*ulose* (**8**).—M.p. 56—58 °C; $[\alpha]_D^{21}$ −16.2° (*c* 2 in $CHCl_3$) {lit.,[30] $[\alpha]_D^{24}$ −16.6 (*c* 1 in $CHCl_3$)}.

Methyl 2,3,6-*Trideoxy*-α-L-erythro-*hex*-2-*enopyranoside* (**10**).—$[\alpha]_D^{21}$ −89.6° (*c* 1 in $CHCl_3$) {lit.,[36] $[\alpha]_D$ −−94° (*c* 1 in $CHCl_3$)}.

Methyl 2,3,6-*Trideoxy*-4-O-*trichloroacetimidoyl*-α-L-erythro-*hex*-2-*enopyranoside* (**14**).—$[\alpha]_D^{21}$ −154.2° (*c* 1 in $CHCl_3$) {lit.,[15] $[\alpha]_D$ −150.4° (*c* 1 in CH_2Cl_2)}.

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2-*iodo*-2′-*trichloromethyl*-(*methyl* α-L-*altropyranosido*)[3,4-d]*oxazole* (**15**).—M.p. 136—138 °C; $[\alpha]_D^{21}$ +30.7° (*c* 1 in $CHCl_3$) {lit.,[15] $[\alpha]_D$ +30.8° (*c* 1 in CH_2Cl_2)}.

Methyl 3-*Amino*-2,3,6-*trideoxy*-2-*iodo*-α-L-*altropyranoside Hydrochloride* (**20**).—M.p. 165—166 °C; $[\alpha]_D^{22}$ −31.7° (*c* 1 in CH_3OH) {lit.,[15] $[\alpha]_D$ −31.8° (*c* 1 in CH_3OH)}.

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-L-ribo-*hexopyranoside Hydrochloride* (*Methyl* α-L-*Ristosaminide Hydrochloride*) (**21**).—M.p. 165—168 °C; $[\alpha]_D^{20}$ −122.8° (*c* 1 in CH_3OH) {lit.,[31c] $[\alpha]_D$ −123.8° (*c* 1 in water)}.

Methyl 4-O-*Benzoyl*-2,3,6-*trideoxy*-α-L-threo-*hex*-2-*enopyranoside* (**13**).—$[\alpha]_D^{21}$ +189.6° (*c* in $CHCl_3$).

Methyl 2,3,6-*Trideoxy*-α-L-threo-*hex*-2-*enopyranoside* (**11**).—M.p. 58—60 °C; $[\alpha]_D^{22}$ +144.3° (*c* 1 in $CHCl_3$) {lit.,[33] $[\alpha]_D$ +139° (*c* 2 in MeOH)}.

Methyl 2,3,6-*Trideoxy*-4-O-*trichloroacetimidoyl*-α-L-threo-*hex*-2-*enopyranoside* (**22**).—$[\alpha]_D^{21}$ +106.2° (*c* 1 in $CHCl_3$) {lit.,[33] $[\alpha]_D$ +95° (*c* in CH_2Cl_2)}.

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2-*iodo*-2′-*trichloromethyl*-(*methyl* α-L-*galactopyranosido*)[3,4-d]*oxazole* (**24**).—M.p. 150—152 °C; $[\alpha]_D^{21}$ −132.8° (*c* 2 in $CHCl_3$).

2,3,4,6-*Tetradeoxy*-4′,5′-*dihydro*-2′-*trichloromethyl*-(*methyl* α-L-lyxo-*hexopyranosido*)[3,4-d]*oxazole* (**26**).—M.p. 132—134 °C; $[\alpha]_D^{20}$ −27.3° (*c* 1 in CHl_3).

2,3,4,6-*Tetradeoxy*-2′-*dichloromethyl*-4′,5′-*dihydro*-(*methyl* α-L-lyxo-*hexopyranosido*)[3,4-d]*oxazole* (**27**).—M.p. 120—122 °C; $[\alpha]_D^{21}$ −66.9° (*c* 1 in $CHCl_3$).

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-L-lyxo-*hexopyranoside* (*Methyl* α-L-*Daunosaminide*) (**2**).—M.p. 114—115 °C (lit.,[31a] 109—110 °C); $[\alpha]_D^{20}$ −197.4° (*c* 1 in CH_3OH) {lit.,[31a] $[\alpha]_D$ −210° (*c* 1 in $CHCl_3$)}.

Methyl 3-*Amino*-2,3,6-*trideoxy*-2-*iodo*-α-L-*galactopyranoside Hydrochloride* (**31**).—M.p. 204—205 °C (lit.,[33] 210—213 °C); $[\alpha]_D^{22}$ −100.2° (*c* 1 in MeOH) {lit.,[33] $[\alpha]_D$ −104° (*c* 0.15 in MeOH)}.

Methyl 3-*Amino*-2,3,6-*trideoxy*-α-L-lyxo-*hexopyranoside Hydrochloride* (*Methyl* α-L-*Daunosaminide Hydrochloride*) (**32**).—M.p. 194—197 °C (lit.,[37] 188—189 °C); $[\alpha]_D^{21}$ −135.8° (*c* 1 in MeOH) {lit.,[37] $[\alpha]_D$ −140° (*c* 1 in MeOH)}.

Methyl 4-O-(N-*Benzoylbenzimidoyl*)-2,3,6-*trideoxy*-α-L-

threo-*hex*-2-*enopyranoside* (**41**).—M.p. 103—105 °C; $[\alpha]_D^{22}$ +226.7° (*c* 1 in $CHCl_3$).

Methyl 3-*Benzamido*-4-O-*benzoyl*-2-*bromo*-2,3,6-*trideoxy*-α-L-*galactopyranoside* (**42**).—M.p. 95—97 °C; $[\alpha]_D^{22}$ −297.4° (*c* 1 in $CHCl_3$).

Methyl 3-*Benzamido*-4-O-*benzoyl*-2,3,6-*trideoxy*-α-L-lyxo-*hexopyranoside* (**43**).—M.p. 143—144 °C; $[\alpha]_D^{21}$ −222.8° (*c* 1 in $CHCl_3$).

Methyl 3-*Benzamido*-2,3,6-*trideoxy*-α-L-lyxo-*hexopyranoside* (*Methyl* N-*Benzoyl*-L-*daunosamine*) (**44**).—M.p. 160—162 °C (lit.,[34] 155—156 °C); $[\alpha]_D^{21}$ −189.4° (*c* 1 in $CHCl_3$) {lit.,[34] $[\alpha]_D$ −167° (*c* 0.4 in MeOH)}.

3-*Amino*-2,3,6-*trideoxy* L-lyxo-*hexopyranoside Hydrochloride* (L-*Daunosamine Hydrochloride*) (**45**).—M.p. 156—158 °C (lit.,[38] 168—170 °C); $[\alpha]_D^{21}$ −63.2° (*c* 1 in water) {lit.,[38] $[\alpha]_D^{25}$ −65.4° (*c* 1.3 in water)}.

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