Synthesis of 3-Amino-3,4-dideoxysugars

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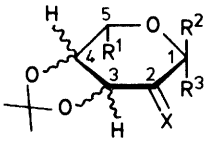
Sequential treatment of methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose (1) with aqueous sodium hydroxide and phenylhydrazine results in elimination of acetone and formation of 2*S*-methoxytetrahydropyran-3,4-dione 4-phenylhydrazone (7) as the main product. Similarly, methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-2-ulose (2) was converted into 2*R*-methoxy-6*S*-methyltetrahydropyran-3,4-dione 4-phenylhydrazone (8). The effect of base on the related uloside, methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (16), resulted in the formation of 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltol) (17). Compounds (7) and (8) have been converted into, respectively, 3-amino-3,4-dideoxy-D-*erythro*-pentopyranose (22) and 3-amino-3,4,6-trideoxy-L-*ribo*-hexopyranose (25).

Methyl glycosiduloses have been used extensively as intermediates in the modification of sugars. Such modification is usually at the site of the hydroxy group in a methyl glycoside at which oxidation has been effected to produce the glycosidulose. In this paper, details are provided of a sequence of reactions which results in modification at C-3 and C-4 of a methyl glycopyranosid-2-ulose derivative.[1] This reaction sequence provides a convenient route for the preparation of aminosugars containing the $-CH_2CHNH_2-$ system, as occurs in some antibiotics.[2]

The 2-ulosides investigated in this work were methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose (1) and methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-2-ulose (2) which were prepared in good yields by well established procedures from, respectively, L-arabinose [3] and L-fucose.[4]



(1) $R^1 = R^2 = H$, $R^3 = OMe$, X = O
Configuration at C-3—C-4, L-*erythro*

(2) $R^1 = Me$, $R^2 = OMe$, $R^3 = H$, X = O
Configuration at C-3—C-4, D-*erythro*

(3) $R^1 = R^2 = H$, $R^3 = OMe$, X = NNHPh
Configuration at C-3—C-4, as in (1)

(4) $R^1 = Me$, $R^2 = OMe$, $R^3 = H$, X = NNHPh
Configuration at C-3—C-4, as in (2)

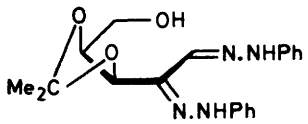
Atom numbering of the compounds in this paper is based on nomenclature and the ^1H n.m.r. data

When compound (1) was treated with phenylhydrazine in ethanol without a catalyst it gave the phenylhydrazone (3): under similar conditions the hexopyranosidulose (2) gave the phenylhydrazone (4). N.m.r. spectral investigation of a freshly isolated sample of phenylhydrazone (3) indicated the presence of two forms in the proportions 1 : 2. When a solution of the compound in deuteriochloroform was stored, the amount of the minor form increased at the expense of the other form until after 18 h it was the sole component. As the aromatic solvent-induced shift (ASIS $\equiv \Delta^{C_6D_6}_{CDCl_3} \equiv \delta^{C_6D_6} - \delta^{CDCl_3}$) of this component is approximately five times greater for 1-H than for 3-H it was concluded that this isomer is the '*syn*' form of the phenylhydrazone (3).[5] (For the convention of assignment of '*syn*' and '*anti*' forms, see ref. 6.) As the phenylhydrazone (4) showed n.m.r. spectral characteristics closely akin to those of compound (3) (*syn*), it also is considered to be the '*syn*' isomer. No '*anti*' isomer was detected at any stage in the formation of phenylhydrazone (4).

The addition of base significantly affects the reaction of either of the glycosiduloses [(1) or (2)] and phenylhydrazine. Dependent on the conditions, besides the phenylhydrazone, the osazone and α-diketone monophenylhydrazone are formed. Thus, three products, (A), (B), and (C), were formed when a hot ethanolic solution of compound (1) was treated with 2M aqueous sodium hydroxide for 0.5 min and then with 1 equiv. of phenylhydrazine for 2 min. After the major product (A) (72%) had been separated as bright yellow crystals, two minor products (B) (10%) and (C) (2%) were isolated by column chromatography. The conditions indicated were the most appropriate to obtain maximum amounts of compound (A). It was shown that compound (C) was the predominant product when an excess of phenylhydrazine was employed with catalytic amounts of base. Also, it was found that compound (B) could be converted into compound (C) by treatment with base and phenylhydrazine. When methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-2-ulose (2) was treated likewise with base and phenylhydrazine it afforded a compound (D) (61%) as the major product: no attempt was made to isolate the minor products. The greater solubility in ethanol of the hexosidulose (2) when compared with the pentosidulose (1) enabled the reaction to be carried out in more concentrated solution, but losses occurred during isolation owing to the extent of solubility of compound (D) in the reaction medium. The 2,4-dinitrophenylhydrazone of compound (1) was prepared [3] but when this compound was treated with sodium hydride in a mixture (1 : 1) of dry 1,2-dimethoxyethane and t-butyl alcohol only starting material (60%) could be recovered.

Compounds (B) and (C) were readily identified as, respectively, the phenylhydrazone (3) and 3,4-*O*-isopropylidene-L-*erythro*-pentosazone (5). The structure of compound (C) was indicated by its spectral characteristics: it showed four strong i.r. absorptions between 1 490 and 1 605 cm^{-1} characteristic of an osazone. Twin peaks at 1 370—1 375 cm^{-1} indicated the presence of geminal methyl groups and so retention of the *O*-isopropylidene residue: this was confirmed by analysis of the ^1H n.m.r. spectrum: the presence of resonances attributable to two sets of aromatic protons, two low-field NH signals,[7] [δ (NH) 12.4 and 10.5], and the absence of a signal for the glycosidic methoxy group were all indicative of the osazone structure. A singlet at δ 7.79 was assigned to 1-H and indicated that the compound was in the open-chain form. Predictably,[8]

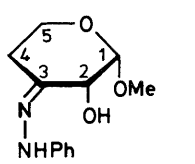
this compound is base-labile and this property probably accounts for the fluctuating yields obtained in reactions for its preparation.



(5)

Compounds (A) and (D) showed analogous behaviour and characteristics. In the i.r. spectrum of compound (A) there were strong absorptions at 1 610 and 1 670 cm^{-1} and corresponding peaks at 1 610 and 1 680 cm^{-1} in the spectrum of compound (D). These were attributed to C=N and conjugated C=O groups in each compound. The u.v. spectra indicate that the C=N and C=O groups are conjugated: maxima were observed at approximately 100 nm higher wavelength than is noted for simple phenylhydrazones including glycosidulose phenylhydrazones.

^{1}H N.m.r. and mass spectral measurements provide evidence that the methyl pyranoside is intact in each compound. In the ^{1}H n.m.r. spectrum of each compound two singlets are observed which can be attributed to the methoxy group and the anomeric proton. The absence of isopropylidene signals indicated that the formation of each compound was accompanied by elimination of acetone. The ^{1}H n.m.r. spectrum of compound (D) contains the signals of three ring protons, additional to the anomeric proton, arising from the methylene and methine protons and compound (A) contains signals for four ring protons (additional to the anomeric proton) and which arise from a $-CH_2CH_2-$ group not coupled to any other protons. This evidence pointed to compound (A) being 2*S*-methoxytetrahydropyran-3,4-dione 3-(or 4-)monophenylhydrazone and (D) being its 2*R*-methoxy-6*S*-methyl analogue. Elemental analyses and mass spectral evidence were in accord with these structures. From the borohydride reduction of compound (A) a single monohydroxylated product was obtained. The hydroxy group was located adjacent to the methoxy group as indicated by its n.m.r. spectrum in which the anomeric proton appeared as a doublet coupled to the added hydrogen. Subsequent work has demonstrated that the reduction product is methyl 4-deoxy-α-D-*glycero*-pentopyranosid-3-ulose phenylhydrazone (6) and its formation indicates that compound (A) is the 4-phenylhydrazone (7) of the 3,4-dione and not the isomeric 3-phenylhydrazone.



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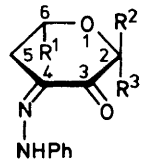
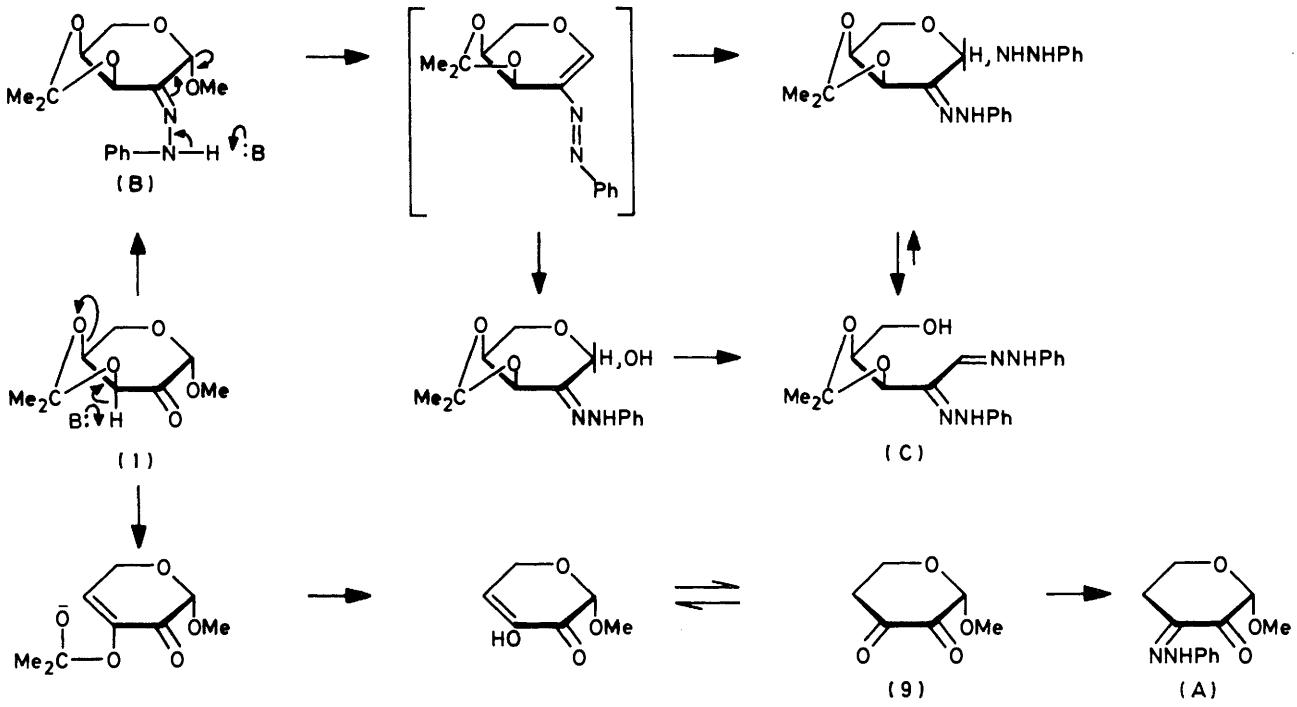


(7) $R^1 = R^2 = H$, $R^3 = OMe$ (Product A)
(8) $R^1 = Me$, $R^2 = OMe$, $R^3 = H$ (Product D)

By analogy, compound (D) is considered to have structure (8), *i.e.* it is 2*R*-methoxy-6-methyltetrahydropyran-3,4-dione 4-phenylhydrazone (alternatively named as a glycoside, it is methyl 4,6-dideoxy-α-L-*glycero*-hexopyranosid-2,3-diulose 3-phenylhydrazone). Further evidence for these structures was obtained from an investigation of the aminosugars which can be derived from compounds (A) and (D) (see later).

Possible routes for the conversion of compound (1) into compounds (3), (5), and (7) (B, C, and A respectively) are shown in Scheme 1. Formation of the phenylhydrazone (B) is straightforward. Previous work in our laboratory [9] and by others [10] has demonstrated that some phenylhydrazones of this type undergo base-catalysed elimination of methanol to give phenylazoalkenes. Production of such an intermediate from phenylhydrazone (B) followed by 1,4-addition of phenylhydrazine to the azoalkene or, less likely, addition of water



Scheme 1.

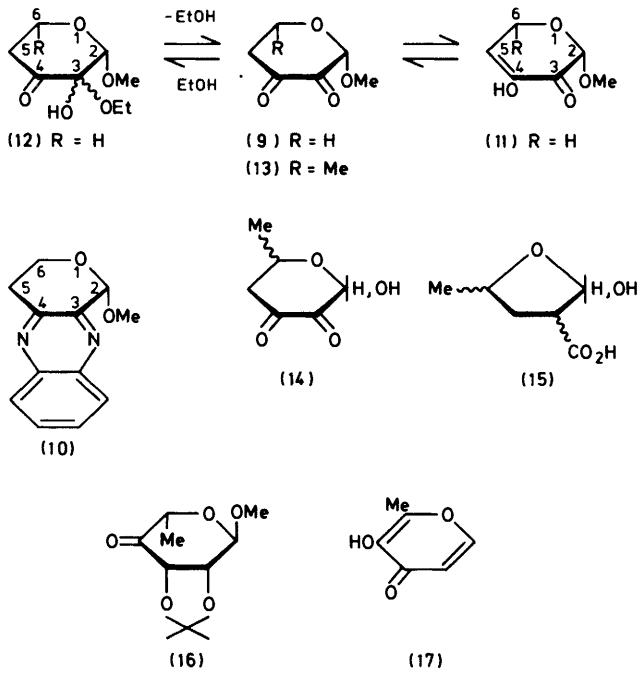
Table. ^{1}H N.m.r. spectral data (δ; *J*/Hz) for compounds (7), (11), and (12) in $CDCl_3$

Compound	2-H	5-H	5'-H	6-H	6'-H	OH	OMe	3-OEt
(7) [a,b]	s, 4.76	ddd, 2.71 ($J_{5,5'}$ 16.0, $J_{5,6}$ 2.5, $J_{5,6'}$ 4.0)	ddd, 3.07 ($J_{5',5}$ 16.0, $J_{5',6}$ 6.0, $J_{5',6'}$ 11.0)	dt, 3.90 ($J_{6,6'}$ 11.0, $J_{6,5}$ 5.25, $J_{6,5'}$ 6.0)	ddd, 4.21 ($J_{6',6}$ 11.0, $J_{6',5}$ 4.0, $J_{6',5'}$ 11.0)	—	s, 3.50	—
(11)	s, 5.03	dd, 6.32 ($J_{5,6}$ 4.5, $J_{5,6'}$ 2.5)		3.9—4.7 [c]			s, 3.52	—
(12)	s, 4.95	2.1—2.7		3.9—4.7 [c]			s, 3.60	t, 1.33; q, 4.32

[a] 100 MHz. [b] δ 7.3—7.0 (5 H, ArH; 1 H, NH). [c] One proton is exchanged in D_2O.

and subsequent condensation of the product with phenylhydrazine would lead to the osazone (C). An intermediate azoalkene was not isolated but this is not surprising when it is recalled that compound (B) is converted into (C) by base and phenylhydrazine and that excess of phenylhydrazine and base convert compound (1) into the osazone (C) as the main product. Moreover, in the example cited by Collins *et al.*[9] the azoalkene intermediate was not isolated. To obtain compound (A) from the glycosidulose (1) it is suggested that base-catalysed elimination of acetone [11-13] affords an intermediate glycosid-diulose which then condenses with 1 equiv. of phenylhydrazine. A similar sequence could account for the conversion of compound (2) into (D). Glycosiduloses (1) and (2) have been shown to form acetals or hemiacetals in alcoholic solutions [14] and it may be that the elimination reaction occurs directly from such a derivative. Masking of the original carbonyl group by acetal formation would lead to the production of the 4-phenylhydrazone (7) (product A) rather than its 3-isomer. Normally, an *O*-isopropylidene acetal is formed when diol protection is needed under basic conditions, but it is known that nearby electron-withdrawing substituents can influence the stability of such acetals. Elimination of the isopropylidene group from compound (1) was demonstrated by boiling the pentopyranosidulose in ethanolic sodium hydroxide and trapping the evolved vapour in 2,4-dinitrophenylhydrazine reagent. Acetone 2,4-dinitrophenylhydrazone was isolated.

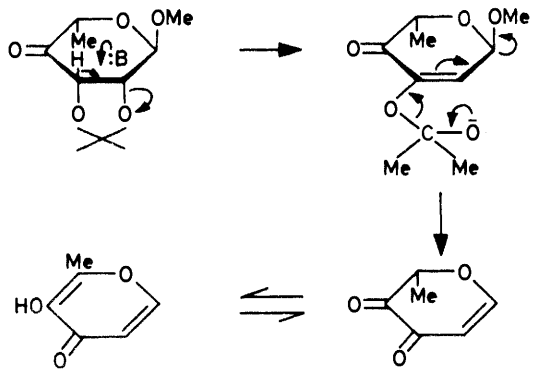
As our earlier investigation [9] of base-catalysed reactions between glycosiduloses and phenylhydrazine had indicated that hydrazone formation preceded elimination of a substituent from a neighbouring ring carbon, evidence was sought that the reactions leading to compounds (5) and (7) were concurrent and that a diulose intermediate (9) was involved in the formation of compound (7). That this was so was demonstrated by intercepting intermediate (9) as its crystalline quinoxaline derivative (10). This was obtained when the glycosidulose (1) was heated under reflux in ethanolic base in the presence of *o*-phenylenediamine and it was identified from its spectral characteristics and elemental analysis. In the ^{1}H n.m.r. spectrum there were signals from four ring protons [apart from the proton at C-2 (pyran numbering)] in a similar arrangement to that of the two sets of methylene protons of compound (7), and four protons from the aromatic residue. The presence of C=N groups was indicated by absorption at 1 570 cm^{-1}. The formation of the diulose having been demonstrated, attempts were made to isolate the compound. Unfortunately, it decomposed rapidly under basic conditions, probably undergoing a benzylic acid-type rearrangement. However, it could be isolated under carefully controlled conditions. The glycosidulose (1) was heated briefly in ethanolic base and the reaction mixture was quickly cooled, neutralised, and concentrated. N.m.r. spectral measurements on a chloroform extract gave a spectrum (see Table) indicative of a mixture of the enolic (11) and hemiacetal (12) forms of the diketone in the ratio *ca.* 30 : 70.



Noteworthy is the relationship of the diuloside (9), and more particularly its analogue (13) which, by analogy, would be formed as an intermediate in the conversion of glycosidulose (2) into compound (8), to actinospectose (14)—a sugar obtained by hydrolysis of the antibiotic spectinomycin [15] and which promptly rearranges to the carboxylic acid derivative (15).

As an extension of this investigation it was of interest to examine the effect of base on methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (16) which contains a carbonyl group adjacent to a diol system protected as the *O*-isopropylidene acetal. In the presence of a small amount of base, a dilute aqueous ethanolic solution of the hexopyranosid-4-ulose (16) gave, at room temperature, a crystalline product which was identified as 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltol) (17). Its physical [16] and spectral [17] characteristics were identical with those of an authentic sample.

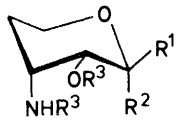
In Scheme 2 there is an indication of the sequence of changes leading to maltol. Elimination of the isopropylidene group from compound (16) is followed by rapid elimination of methanol to afford maltol. Attempts to halt the reaction at the glycosid-diulose stage by forming a quinoxaline or



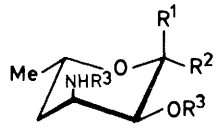
Scheme 2.

phenylhydrazone were unsuccessful. Several examples of similar base-catalysed elimination of the aglycone group from glycopyranosid-3-uloses are known.[18,19]

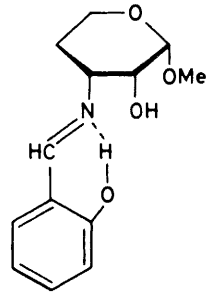
The phenylhydrazones (7) and (8) are useful precursors of 3-amino-3,4-dideoxysugars. When compound (7) in glacial acetic acid was hydrogenated at room temperature over Adams' catalyst and the product was acetylated, the reaction sequence afforded methyl 3-acetamido-2-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-pentopyranoside (18) in good yield. This compound was obtained in lower yield *via* the intermediate (6) by sequential reduction [(i) $NaBH_4$, (ii) PtO_2–H_2] followed by acetylation. Deacetylation of compound (18) with boiling 1M-sodium hydroxide yielded methyl 3-amino-3,4-dideoxy-α-D-*erythro*-pentopyranoside (19) which could be benzoylated to give the *N*,*O*-dibenzoyl derivative (20) and also could be converted into a crystalline *N*-salicylidene derivative (21).



(18) R^1 = H, R^2 = OMe, R^3 = Ac
(19) R^1 = R^3 = H, R^2 = OMe
(20) R^1 = H, R^2 = OMe, R^3 = COPh
(22) R^1,R^2 = H, OH, R^3 = H



(23) R^1 = OMe, R^2 = R^3 = H
(24) R^1 = OMe, R^2 = H, R^3 = Ac
(25) R^1,R^2 = H, OH, R^3 = H



(21)

The aminoglycoside (19) could be obtained readily as its anil by treating the reduction mixture of compound (7) with salicylaldehyde and then separating the anil from *N*-salicylidene-cyclohexylamine by column chromatography. Subsequently this method was used in preference to the acetylation procedure described above. The free 3-amino-3,4-dideoxypentose (22) (isolated as its hydrochloride) was obtained by acid hydrolysis of the aminoglycoside (19), its *N*,*O*-diacetyl derivative (18), or the *N*-salicylidene derivative (21).

The configuration of compounds (18)—(21) follows from the determination of the *X*-ray crystal structure of the *N*-salicylidene (N=Sal) derivative (21) by Palmer and Palmer.[20] They have shown that, in the crystal, the pyranoid ring of the molecule is in the $^4C_1$ chair conformation with the substituents at C-1, C-2, and C-3 (OMe, OH, N=Sal) disposed in the relationship ax, eq, ax, *i.e.* the configuration is α-D-*erythro*. There is a very weak intramolecular hydrogen bond between the nitrogen atom and the hydroxy group attached to the aromatic ring. The n.m.r. spectral data for this series of compounds could be interpreted in a manner consistent with the configuration based on the *X*-ray results. The c.d. spectrum of compound (20) in cuprammonium solution exhibited, as expected [21] for a compound with the D-*erythro* configuration, a negative Cotton effect (θ − 225) at $\lambda_{max.}$ 546 nm.

A single aminoglycoside was obtained from the reduction of compound (8) and it was purified *via* its *N*-acetyl-2-*O*-acetyl derivative and isolated after deacylation as its *N*-salicylidene derivative. A 3-amino-3,4,6-trideoxy-L-hexopyranose, isolated as its crystalline hydrochloride, was obtained by acidic hydrolysis of the *N*-salicylidene derivative. For the following reasons the glycoside and its derivatives are considered to have the α-L-*ribo*-configuration, *i.e.* the glycoside is (23) and its diacetate is (24). The configurations at C-1 and C-5 are known from the nature of the initial hexopyranose and its glycopyranoside. From the c.d. spectrum of the methyl 3-amino-3,4,6-trideoxy-α-L-hexopyranoside in cuprammonium solution a positive Cotton effect (θ + 263; $\lambda_{max.}$ 546 nm) was observed which would be the case if the compound had the L-*ribo* or L-*lyxo* configuration. The magnitude of the $J_{1,2}$ values for the aminoglycoside and its derivatives is characteristic of an ax–eq (or eq–ax depending on the chair conformation assumed) relationship for 1-H and 2-H. As the configuration at C-1 is known this serves to define the configuration at C-2. The disposition of 3-H can be inferred from the values of $J_{2,3}$, $J_{3,4}$, and $J_{3,4}$· and *in toto* the ^{1}H n.m.r. evidence points to the L-*ribo* configuration. Consequently, the 3-amino-3,4,6-trideoxy-L-hexopyranose is considered to have structure (25). It is interesting to note that both aminoglycosides (19) and (23) have the *cis*,*cis* relationship at C-1, C-2, and C-3.

Experimental

Methods.—M.p.s were determined with a Townson and Mercer apparatus and are uncorrected. Optical rotations were measured with either a Bellingham and Stanley polarimeter or with a Bendix type 147 automatic polarimeter on chloroform solutions unless stated otherwise. U.v. spectra were measured on a Perkin-Elmer 402 spectrophotometer for 96% ethanol solutions. I.r. spectra were measured for solids dispersed in potassium bromide discs and for syrups as smears on potassium bromide discs: Perkin-Elmer spectrophotometers 137, 297, and 457 were used. N.m.r. spectra were determined with a Varian A-60D instrument or with a JEOL JNM-MH-100 spectrometer: unless otherwise stated measurements were made on solutions in deuteriochloroform relative to the internal standard tetramethylsilane. Coupling constants were normally obtained by first-order analysis of the spectra. The operating frequency for partially second-order spectra was 100 MHz. It is recognised that in the first-

order analysis, errors will be greater from a 60 MHz spectrum than from a 100 MHz spectrum. Also, it is appreciated that due consideration must be given to the deviation of line spacings from the coupling constants in second-order spectra but this is not critical to our determinations. The J values quoted are not used to deduce detailed conformational features but only to distinguish between possible conformers and dispositions of substituents. Mass spectra were determined by courtesy of the PCMU (Harwell). T.l.c. was performed on microscope slides coated with either Silicagel G (Merck) or Silicagel GF_{254} (Type 60) (Merck) with benzene–ethyl acetate (9 : 1) as developing solvent. Spots were located by spraying with 5% ethanolic sulphuric acid followed by heating the plates at 150 °C for a short time, unless stated to the contrary. Column chromatography was performed on Silicagel 60 (Merck).

Pyridine was dried over P_2O_5 and then distilled. The fraction with b.p. 115 °C was collected and stored over potassium hydroxide pellets. Dimethylformamide, b.p. 57 °C/14 mmHg, was distilled. Light petroleum refers to that fraction boiling in the range 40–60 °C. Organic solutions were dried with anhydrous sodium sulphate unless stated otherwise.

When, for a compound, only nitrogen elemental analysis is quoted the material was shown to be homogeneous by t.l.c.

Treatment of Methyl 3,4-O-*Isopropylidene*-β-L-erythro-*pentopyranosidulose* (1) *with Sodium Hydroxide*.—(a) A solution of methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose [3] (0.4 g) [m.p. 98—99 °C; $[\alpha]_D$ +230° (*c* 0.5), +166° (*c* 1 in EtOH)], aqueous sodium hydroxide (2M; 0.1 ml), and *o*-phenylenediamine (0.2 g) in ethanol (10 ml) was heated on a steam-bath for 10 min. T.l.c. showed one product (R_f 0.18) besides excess of reagent. The reaction mixture was neutralised with dilute hydrochloric acid, concentrated to 3 ml, and extracted with chloroform (3 × 10 ml). The extract was shaken with charcoal, dried, and filtered through a short alumina column. Concentration of the filtrate gave crystals of the *quinoxaline derivative* of 2S-*methoxytetrahydropyran*-3,4-*dione* (10) (0.23 g, 53%), m.p. 117—118 °C (from pentane); $[\alpha]_D$ −30° (*c* 2); $\nu_{max.}$ 3 030 (Ar–H), 2 900 and 2 850 (aliphatic CH), and 1 570 cm^{-1} (C=N); $\lambda_{max.}$ (ε) 214 (11 000), 239 (24 000), and 324 nm (7 000); δ_H * 5.72 (1 H, s, 2-H), 4.6—3.9 (2 H, m, 5-H_2), 3.6—3.1 (2 H, m, 6-H_2), 3.68 (3 H, s, OMe), and 7.68—8.30 (4 H, m, ArH) (Found: C, 66.3; H, 5.7; N, 12.8. $C_{12}H_{12}N_2O_2$ requires C, 66.6; H, 5.6; N, 13.0%).

(b) The pentopyranosid-2-ulose (1) (1 g) was dissolved in hot ethanol (6 ml), the solution was cooled, and aqueous sodium hydroxide (2.5M; 0.5 ml) was added After 30 sec, phenylhydrazine (0.5 ml) was added and the mixture was boiled vigorously for 2 min. As the solution cooled, yellow crystals separated and were collected. After being washed with cold ethanol (1 ml) and air-dried, 2S-*methoxytetrahydropyran*-3,4-*dione* 4-*phenylhydrazone* (product A) (7) (0.85 g, 73%) was obtained, m.p. 157—158 °C; $[\alpha]_D$ −138° (*c* 1); $\nu_{max.}$ 3 250 (NH), 1 670 (CO), and 1 610 cm^{-1} (C=N); $\lambda_{max.}$ (ε) 230 (5 400) and 383 nm (9 000); see Table for n.m.r. spectral parameters; *m/z* 234 (70%, M^+), 204 (20, $M - CH_2O$), 203 (30, M − OMe), 174 (60, $M - HCO_2Me$, confirmed by *m** 129.4), and 173 (100, $M - HCO_2Me - H$, confirmed by *m** 172.0) (Found: C, 61.7; H, 6.2; N, 11.8. $C_{12}H_{14}N_2O_3$ requires C, 61.5; H, 6.0; N, 11.9%).

T.l.c. showed the presence of a further two compounds [R_f values of 0.55 (major component) and 0.29 (minor component)] in the mother liquor. These were isolated by dilution of the mother liquor with water (10 ml) and extraction with benzene (3 × 15 ml). The dried extract was concentrated and separated by column chromatography [elution with benzene–ethyl acetate [9 : 1, v/v)]. Evaporation of the first fraction (50 ml) gave methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose *syn*-phenylhydrazone (product B) (3) (0.15 g, 10%). The second fraction (150 ml) yielded 3,4-*O*-isopropylidene-L-*erythro*-pentosazone (product C) (5) (0.04 g, 2.2%).

Both compounds (3) and (5) had i.r., u.v., and ^1H n.m.r. spectral features and physical properties identical with those obtained for these compounds prepared as described below.

Methyl 3,4-O-*Isopropylidene*-β-L-erythro-*pentopyranosidulose Phenylhydrazone* (3).—Phenylhydrazine (0.5 ml) and aqueous sodium hydroxide (1M; 0.05 ml) were added to a solution of the glycosidulose (1) (1 g) in ethanol (10 ml). After 0.5 h at room temperature, t.l.c. showed that all the starting material had undergone reaction and that the main product was the title compound contaminated with 3,4-*O*-isopropylidene-L-*erythro*-pentosazone (5). On addition of water (20 ml) to the reaction mixture, a red syrup separated. The supernatant liquid was decanted and the residue was triturated with hot water and dissolved in benzene (20 ml), and the solution was dried and filtered through a short column of silica gel to give the title compound (1.2 g, 80%) as a yellow syrup.

Alternatively, the glycosidulose (1) (1 g) was dissolved in ethanol (10 ml) and phenylhydrazine (0.5 ml) was added to the solution. After 20 h, t.l.c. showed conversion into phenylhydrazone was complete and was not accompanied by osazone formation. Evaporation of the solvent afforded a syrup (1.44 g) comprising 63% *anti* and 37% *syn* forms of the phenylhydrazone, as shown by its ^1H n.m.r. spectrum. After 24 h the sample, which had been retained in the n.m.r. tube, was re-examined and it was found that only the *syn* isomer was present. The *syn* form was isolated and showed $[\alpha]_D$ +350° (*c* 0.5); $\nu_{max.}$ 3 380 (NH), 1 590 (C=N), and 1 500 cm^{-1} (PH); $\lambda_{max.}$ (ε) 280 (20 000) and 302sh nm (13 000); δ_H 5.38 (1 H, s, 1-H), 4.90 (1 H, d, $J_{3,4}$ 8 Hz, 3-H), 4.36 (1 H, br d, $J_{4,5} \simeq J_{4,5'} \simeq$ 15 Hz, 4-H), 3.70 (2 H, m, 5-H_2), 3.50 (3 H, s, OMe) 1.36 and 1.52 (6 H, 2 × s, CMe_2), 6.78—7.62 (5 H, m, Ph), and 9.17 (1 H, s, NH, exchangeable with D_2O); δ_H (C_6D_6 5.14 (1-H) and 4.95 (3-H) (Found: C, 61.6; H, 6.8; N, 9.4. $C_{15}H_{20}N_2O_4$ requires C, 61.6; H, 6.9; N, 9.6%).

Signals from the *anti* form included δ_H 5.06 (1 H, s, 1-H), 5.05 (d, $J_{3,4}$ 5.5 Hz, 3-H), 4.21 (1 H, br d, 4-H), 4.01 (2 H, m, 5-H_2), 3.39 (3 H, s, OMe), 1.39 and 1.76 (6 H, 2 × s, CMe_2), and 7.5—6.7 (5 H, m, Ph).

3,4-O-*Isopropylidene*-L-erythro-*pentosazone* (5).—Methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentapyranosidulose (0.2 g) was heated at 100 °C with phenylhydrazine (0.4 ml) and aqueous sodium hydroxide (2M; 0.05 ml) in ethanol (10 ml) for 10 min. Water (10 ml) was added and the precipitate was collected by filtration. Crystallisation from aqueous ethanol yielded the title compound (0.2 g, 52%), m.p. 186—187 °C; $\nu_{max.}$ 3 450 (OH), 3 250 (NH), 1 605, 1 560, 1 530, and 1 490 cm^{-1} (osazone); $\lambda_{max.}$ (ε) 258 (8 600), and 395 nm (8 600), δ_H ([$^2H_6$]DMSO) 7.79 (1 H, s, 1-H), 3.8—5.85 (4 H, m, 3-H, 4-H, and 5-H_2), 3.30 (1 H, s, OH)*, 1.40 and 1.56 (6 H, 2 × s, CMe_2), 10.86 (1 H, s, NH)*, 12.40 (1 H, s, NH)*, and 6.70—7.70 (10 H, m, 2 × Ph) [Signals marked with an asterisk exchange with D_2O) (Found: N, 14.4. $C_{20}H_{24}N_4O_3$ requires N, 15.2%).

When methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosidulose phenylhydrazone (3) (0.2 g) was heated on a steam-bath for 10 min with phenylhydrazine (0.5 ml) in ethanol (5 ml) it afforded the pentosazone (5). At room temperature

* Locants for H atoms correspond to the pyran ring numbering.

the reaction required 18 h for completion. The product (0.16—0.2 g, 40—60%) was isolated in the usual way.

Methyl 6-*Deoxy*-3,4-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-2-*ulose* syn-*Phenylhydrazone* (4).—Phenylhydrazine (0.05 g) was added to a solution of the glycosidulose (2) [22] [m.p. 73—74 °C; $[\alpha]_D$ −106° (*c* 1)] [(0.1 g) in ethanol (5 ml). After 4 h, when t.l.c. indicated that reaction was complete, the solvent was removed under reduced pressure. The residue was crystallised from deuteriochloroform and was recrystallised from ethanol–water to give the syn-*phenylhydrazone* (0.1 g, 70%), m.p. 104—105 °C; $[\alpha]_D$ +256° (*c* 1); $\nu_{max.}$ 3 450 (NH) and 1 610 cm^{-1} (C=N); $\lambda_{max.}$ 283 nm (ε 1 900); δ_H 5.37 (1 H, s, 1-H), 4.88 (1 H, d, $J_{3,4}$ 7.8 Hz, 3-H), 4.18 (1 H, dd, $J_{4,5}$ 1.8 Hz, 4-H), 3.8 (1 H, m, 5-H), 1.2—1.5 (total 9 H, m, 5-Me and CMe_2), 3.50 (3 H, s, OMe), and 6.9—7.4 (total 6 H, m, NH and Ph); δ_H (C_6D_6) 5.2 (1-H) and 4.92 (1 H, d, $J_{3,4}$ 7.8 Hz, 3-H) (Found: C, 62.6; H, 7.3; N, 9.2. $C_{16}H_{22}N_2O_4$ requires C, 62.7; H, 7.2; N, 9.1%).

2R-*Methoxy*-6S-*methyltetrahydropyran*-3,4-*dione* 4-*Phenylhydrazone* (8).—Aqueous sodium hydroxide (2M; 0.2 ml) was added to a solution of methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-2-ulose (2) (0.54 g) in ethanol (3 ml) and after 30 s phenylhydrazine (0.27 ml) was added and the mixture was boiled vigorously for 2 min and then cooled to −5 °C. The precipitate was filtered off, washed with portions (0.5 ml) of cold ethanol, and air-dried. The crude product (0.4 g) was recrystallised from methanol–water (4 : 1) to afford the *title compound* (product D) as yellow needles (0.38 g, 61%), m.p. 143 °C; $[\alpha]_D$ +320° (*c* 0.5); $\nu_{max.}$ 3 300 (NH), 1 680 (CO), and 1 610 cm^{-1} (C=N); $\lambda_{max.}$ 380 nm (ε 12 500); δ_H (100 MHz) 4.68 (1 H, s, 2-H), 2.64 (1 H, dd, $J_{5,5'}$ 16.0 Hz, $J_{5,6}$ 3.0 Hz, 5-H), 2.70 (1 H, s, 5'-H), 4.32 (1 H, dq, $J_{6,Me}$ 6.0 Hz, 6-H), 1.32 (3 H, d, Me), 3.44 (3 H, s, OMe), and 6.98—7.44 (total 6 H, m, NH and Ph) (Found: C, 62.6; H, 6.5; N, 11.4. $C_{13}H_{16}N_2O_3$ requires C, 62.9; H, 6.5; N, 11.3%).

2R-*Methoxy*-6S-*methyltetrahydropyran*-3,4-*dione Alkyl Acetals*.—An ethanolic solution (3 ml) of methyl 6-deoxy-3,4-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-2-ulose (2) (0.1 g) and aqueous sodium hydroxide (2M; 0.1 ml) were heated together at 100 °C for 3 min. The solution was cooled to 0 °C and carefully neutralised with hydrochloric acid (1M). Solvents were evaporated under reduced pressure and the residual diethyl acetal was extracted with deuteriochloroform. The filtered extract showed the following characteristics: δ_H 1.10—1.6 (total 9 H, m, 6-Me and 2 × CH_3CH_2), 2.08 (1 H, dd, $J_{5,6}$ 3.0 Hz, 5-H), 2.20 (1 H, $J_{5,5'}$ 15 Hz, 5'-H), 3.52 (3 H, s, OMe), 3.75 and 4.30 (4 H, 2 × q, 2 × CH_3CH_2), 4.52 (1 H, dq, $J_{6,Me}$ 7.0 Hz, 6-H), and 5.16 (1 H, s, 2-H). If methanol is used instead of ethanol, the methyl analogue is produced: δ_H 5.10 (1 H, s, 2-H), 4.46 (1 H, dq, $J_{6,Me}$ 6.0 Hz, 6-H), 3.80 (3 H, s, OMe), 3.50 (total 6 H, s, 2 × OMe), 2.16 (1 H, m, $J_{5,5'}$ 15.0 Hz, 5'-H), 2.06 (1 H, dd, $J_{5,6}$ 3.0 Hz, 5-H), and 1.30 (3 H, d, $J_{Me,6}$ 6.0 Hz, 6-Me).

Alkaline Treatment of Methyl 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose* (16).—The glycosidulose (16) [23] (b.p. 77—79 °C/0.2 mmHg) (0.1 g) was dissolved in ethanol (5 ml) and aqueous sodium hydroxide (10%; 0.05 ml) was added. After 1 h at room temperature the reaction mixture was neutralised [ion exchange resin IR-120(H^+)] and concentrated to leave a solid residue (60 mg) which was identified as 3-hydroxy-2-methyl-4*H*-pyran-4-one (maltol) (17). When crystallised from benzene–light petroleum it had m.p. 161—162 °C (lit.,[24] 162—164 °C) and gave a positive iron(III) chloride test for enols. In chloroform its n.m.r. spectrum was identical with that of the authentic compound.[17]

Methyl 3-*Acetamido*-2-O-*acetyl*-3,4-*dideoxy*-α-D-erythro-*pentopyranoside* (18).—(a) A solution of 2*S*-methoxytetrahydropyran-3,4-dione 4-phenylhydrazone (7) (2.52 g) in glacial acetic acid (200 ml) was added to pre-reduced Adams' catalyst (0.5 g) in glacial acetic acid (50 ml) and was hydrogenated at room temperature and atmospheric pressure. After 3 h, the theoretical amount of hydrogen had been consumed and the yellow colour of the solution had been discharged. The solution was filtered and concentrated to a syrup which was dissolved in dry pyridine (20 ml) containing acetic anhydride (5 ml). After storage for 24 h at room temperature the solution was concentrated under reduced pressure and toluene (3 × 20 ml) was distilled over the residue. Dissolved in benzene, the residue was fractionated on a column (250 g, silica gel) by graded elution with benzene and ethyl acetate (to 9 : 1, v/v). The products isolated were (i) *N*-acetylcyclohexylamine (1.1 g), m.p. and mixed m.p. 106 °C (lit.,[25] m.p. 104 °C) and (ii) the *title compound* (2 g, 81%) as a white solid, m.p. 90—91 °C (crystallised from diethyl ether–pentane); $[\alpha]_D$ +45° (*c* 1.5); $\nu_{max.}$ 3 300 (NH), 1 730 (ester), 1 630 (amide I), and 1 550 cm^{-1} (amide II); δ_H (100 MHz; CCl_4) 4.50 (1 H, dd, $J_{1,2}$ 3.2, $J_{1,3}$ *ca.* 0.3 Hz, 1-H), 4.90 (1 H, dd, $J_{2,3}$ 4.0 Hz, 2-H), 4.3 (1 H, m, $J_{3,4a}$ 3.5, $J_{3,4eq}$ 3.2 Hz, 3-H), 3.85 (1 H, ddd, $J_{5ax,4ax}$ 8.0, $J_{5ax,4eq}$ 5.0, $J_{5ax,5eq}$ 12.5 Hz, 5-H_{ax}), 3.30 (1 H, dt, $J_{5eq,4ax}$ 3.5, $J_{5eq,4eq}$ 3.5 Hz, 5-H_{eq}), 3.2 (3 H, s, OMe), 1.8—2.0 (2 H, 4-H_2 obscured by acetate signals), 1.90 [3 H, s, MeCO(N or O)], 1.84 [3 H, s, MeCO(O or N)], and 7.05 (1 H, d, $J_{NH,3}$ *ca.* 8.0 Hz, NH) (Found: C, 52.1; H, 7.3; N, 6.0. $C_{10}H_{17}NO_5$ requires C, 51.9; H, 7.3; N, 6.1%).

(b) A solution of sodium borohydride (0.06 g) in water (5 ml) was added to a stirred suspension of 2*S*-methoxytetrahydropyran-3,4-dione 4-phenylhydrazone (7) (0.7 g) in ethanol (40 ml) and t.l.c. indicated that reaction was complete in 10 min. The mixture was neutralised with dilute hydrochloric acid and cooled in an ice-bath to give *methyl* 4-*deoxy*-α-D-glycero-*pentopyranosid*-3-*ulose phenylhydrazone* (6) as white, crystalline granules (0.48 g, 68%), m.p. 156 °C; $[\alpha]_D$ +165° (*c* 1 in EtOH); $\nu_{max.}$ 3 420 (OH), 3 320 (NH), 1 610 (C=N), and 1 530 cm^{-1} (Ph); $\lambda_{max.}$ 278 nm (ε 19 000); δ_H (100 MHz; [$^2H_6$]Me_2CO) 8.70 (1 H, br s, NH)*, 6.65—7.35 (5 H, m, Ph), 4.76 (1 H, d, $J_{1,2}$ 3.3 Hz, 1-H), 4.30 (1 H, d, $J_{2,1}$ 3.3 Hz, 2-H), 3.60—3.85 (2 H, m, 5-H_2), 3.87 (1 H, d, 2-OH)*, 3.36 (3 H, s, OMe), 2.96 (1 H, ddd, $J_{4eq,4ax}$ 15.0, $J_{4eq,5ax}$ 3.0, $J_{4eq,5eq}$ 3.0 Hz, 4-H_{eq}), and 2.30 (1 H, ddd, $J_{4ax,4eq}$ 15.0, $J_{4ax,5ax}$ 10.0, $J_{4ax,5eq}$ 7.5 Hz, 4-H_{ax}) [Signals marked with an asterisk exchange with D_2O] (Found: C, 60.7; H, 6.7; N, 11.7. $C_{12}H_{16}N_2O_3$ requires C, 61.0; H, 6.8; N, 11.8%).

A 2% solution of the phenylhydrazone (6) (1 g) in glacial acetic acid was added to a pre-hydrogenated suspension of Adams' catalyst (0.1 g) in glacial acetic acid (20 ml). The yellow solution absorbed hydrogen (260 ml) (4 mmol H_2/mmol of sugar derivative) and after 24 h the solution was filtered and concentrated. The residue was dissolved in anhydrous pyridine (10 ml) and acetic anhydride (3 ml). After storage for 1 d at room temperature the reaction mixture was poured into ice-water (150 ml) and was extracted with chloroform (3 × 10 ml). The combined dried and concentrated extracts were separated by column chromatography [benzene–ethyl acetate (9 : 1, v/v)] and afforded *N*-acetylcyclohexylamine (0.1 g) and methyl 3-acetamido-2-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-pentopyranoside (18) (0.15 g, 15%) identical with the products described above.

Methyl 3-*Amino*-3,4-*dideoxy*-α-D-erythro-*pentopyranoside* (19).—Methyl 3-acetamido-2-*O*-acetyl-3,4-dideoxy-α-D-*ery*-

thro-pentopyranoside (18) (1 g) was suspended in aqueous sodium hydroxide (1M; 20 ml) and heated under reflux for 2 h, after which t.l.c. showed hydrolysis to be complete. The product was extracted with dichloromethane (50 ml) in a continuous liquid–liquid extractor. The dried organic layer was concentrated to a syrup (0.5 g, 80%); $[\alpha]_D$ +64° (*c* 1.5), +46° (*c* 0.3 in water); $\nu_{max.}$ 3 350br (OH and NH) cm^{-1}. This compound gave a crystalline *N*-salicylidene derivative identical with methyl 3,4-dideoxy-3-salicylideneamino-α-D-*erythro*-pentopyranoside prepared as described below.

Methyl 3,4-*Dideoxy*-3-*salicylideneamino*-α-D-erythro-*pentopyranoside* (21).—The crude concentrate (0.4 g) from the catalytic reduction of 2*S*-methoxytetrahydropyran-3,4-dione 4-phenylhydrazone (0.14 g) in ethanol (5 ml) was heated under reflux for 1 h with salicylaldehyde (0.6 g). The reaction mixture was concentrated to give a syrup and the benzene-soluble part was transferred to a column of silica gel (20 g). Excess of reagent and *N*-salicylidenecyclohexylamine were washed from the column with benzene–ethyl acetate (9 : 1, v/v) (180 ml). The silica gel was then extruded and washed with methanol (3 × 30 ml). The washings were concentrated, diluted with absolute ethanol–diethyl ether (1 : 1, v/v) (10 ml), and filtered. The filtrate was concentrated to leave a residue (0.14 g) which crystallised. After recrystallisation from ethanol, *methyl* 3,4-*dideoxy*-3-*salicylideneamino*-α-D-erythro-*pentopyranoside* was obtained as yellow prisms, m.p. 144 °C; $[\alpha]_D$ +41° (*c* 1.5); $\nu_{max.}$ 3 500, 3 400 (OH), and 1 630 cm^{-1} (C=N); $\lambda_{max.}$ (ε) 255 (8 700), 282 (3 800), 318 (2 400), and 408 nm (1 500); δ_H (100 MHz) 8.39 (1 H, s, CH=N), 6.82—7.35 (4 H, m, ArH), 4.75 (1 H, d, $J_{1,2}$ 3.8 Hz, 1-H), 4.10 (1 H, dt, $J_{5ax,4ax}$ 11.7, $J_{5ax,4eq}$ 2,5, $J_{5ax,5eq}$ 11.7 Hz, 5-H_{ax}), 3.52—3.8 (total 3 H, m, 2-H, 3-H, and 5-H_{eq}), 3.44 (3 H, s, OMe), 2.12 (1 H, m, $J_{4ax,4eq}$ 13.8, $J_{4ax,5ax}$ 11.5, $J_{4ax,3}$ 4.5, $J_{4ax,5eq}$ 3.0 Hz, 4-H_{ax}), and 1.74 (1 H, m, $J_{4eq,4ax}$ 13.8, $J_{4eq,3}$ 2.8, $J_{4eq,5eq}$ 2.8, $J_{4eq,5ax}$ 2.5 Hz, 4-H_{eq}), (Found: C, 61.2; H, 6.8; N, 5.6. $C_{13}H_{17}NO_4$ requires C, 62.1; H, 6.8; N, 5.6%).

Methyl 3-*Benzamido*-2-O-*benzoyl*-3,4-*dideoxy*-α-D-erythro-*pentopyranoside* (20).—Methyl 3-amino-3,4-dideoxy-α-D-*erythro*-pentopyranoside (19) (0.35 g) was benzoylated in dry pyridine (3 ml) with benzoyl chloride (1 ml). After storage at room temperature for 24 h, the product was isolated in the customary manner by pouring the reaction mixture into ice–water (25 ml) and extracting with chloroform (5 × 25 ml). Benzoic acid (0.25 g) was separated from the crude product by addition of pentane to a solution in benzene. From the filtrate a syrup was isolated which was purified by p.l.c. (preparative liquid chromatography) ($CHCl_3$ eluant) to give the O,N-*dibenzoyl derivative* (20) (0.34 g, 41%), $[\alpha]_D$ +32° (*c* 1.5); $\nu_{max.}$ 1 720 (CO) and 1 650 cm^{-1} (C=N); δ_H (220 MHz) 7.2—8.1 (total 10 H, m, 2 × Ph), 5.18 (1 H, t, $J_{2,1}$ 4.0, $J_{2,3}$ 4.0 Hz, 2-H), 5.03 (1 H, d, $J_{1,2}$ 4.0 Hz, 1-H), 4.76 (1 H, m, $J_{3,4ax}$ 4.0, $J_{3,4eq}$ 4.0, $J_{3,NH}$ 7.0 Hz, 3-H), 3.93 (1 H, dt, $J_{5ax,5eq}$ 11.5, $J_{5ax,4eq}$ 4.0, $J_{5ax,4ax}$ 11.5 Hz, 5-H_{ax}), 3.50 (3 H, s, OMe), and 2.10 (2 H, m, 4-H_2) (Found: N, 3.7. $C_{20}H_{21}NO_5$ requires N, 3.9%).

3-*Amino*-3,4-*dideoxy*-D-erythro-*pentopyranose Hydrochloride* (22).—(a) Methyl 3,4-dideoxy-3-salicylideneamino-α-D-*erythro*-pentopyranoside (21) (0.13 g) was dissolved in aqueous hydrochloric acid (1M; 10 ml) and hydrolysis immediately occurred as indicated by fading of the bright yellow colour of the solution. The reaction was monitored by optical rotation measurements and was complete in 3 h. The reaction mixture was concentrated to *ca.* one-third of its original volume, then diluted with water (10 ml), filtered, and reconcentrated. This procedure was repeated ten times to remove excess of hydrogen chloride and salicylaldehyde. The residue was dissolved in ethanol (10 ml) and heated with acid-washed charcoal for 10 min at 60 °C. The colourless filtrate and ethanolic washings were combined and concentrated to 2 ml. Addition of dry diethyl ether led to separation of the *amino sugar hydrochloride* (0.07 g, 80%) as white hygroscopic crystals, m.p. 123—124 °C (decomp.); $[\alpha]_D$ +24° (equilib.) (*c* 1 in water); $\nu_{max.}$ 3 400 and 1 500 cm^{-1} (Found: C, 35.5; H, 6.9. $C_5H_{12}ClNO_3$ requires C, 35.4; H, 7.2%).

(b) Methyl 3-acetamido-2-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-pentopyranoside (18) (0.15 g) was hydrolysed by being heated under reflux with 15% aqueous hydrochloric acid (7 ml). The product was isolated as before in 70% yield.

Methyl 3,4,6-*Trideoxy*-3-*salicylideneamino*-α-L-ribo-*hexopyranoside*.—A solution of 2*R*-methoxy-6*S*-methyltetrahydropyran-3,4-dione 4-phenylhydrazone (8) (1.2 g) in glacial acetic acid (50 ml) was hydrogenated (room temperature and atmospheric pressure) over pre-reduced Adams' catalyst (0.4 g). After 4 h the initial red reaction mixture had become colourless and was filtered. Concentration of the filtrate yielded a syrup which was acetylated in dry pyridine (10 ml) with acetic anhydride (3 ml). After storage for 24 h at room temperature the product was isolated conventionally and separated chromatographically into *N*-acetylcyclohexylamine (0.6 g), m.p. 106 °C, and syrupy methyl 3-acetamido-2-*O*-acetyl-3,4,6-trideoxy-α-L-*ribo*-hexopyranoside (24) (0.92 g), $[\alpha]_D$ −47° (*c* 3.5); $\nu_{max.}$ 3 320 (NH), 1 730 (ester), 1 650 (amide I), and 1 550 cm^{-1} (amide II); δ_H (100 MHz; C_6D_6) 6.85 (1 H, d, $J_{NH,3}$ *ca.* 7 Hz, NH, exchangeable with D_2O), 4.85 (1 H, dd, $J_{2,3}$ 4.5 Hz, 2-H), 4.74 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 4.56 (1 H, m, $J_{3,4}$ 3.5, $J_{3,NH}$ 7.5, $J_{3,4'}$ 3.5 Hz, 3-H), 3.82 (1 H, dsex, $J_{5,4}$ 12.0, $J_{5,4'}$ 2.5, $J_{5,6}$ 6.0 Hz, 5-H), 3.1 (3 H, s, OMe), 1.76 (total 6 H, s, OMe and NMe), 1.2—1.5 (2 H, m, 4-H_2), and 1.02 (3 H, d, $J_{6,5}$ 6.0 Hz, 6-H_3).

This syrup (0.32 g) was deacylated by being heated under reflux for 24 h in suspension in aqueous sodium hydroxide (1M; 10 ml). The reaction mixture was extracted for 24 h with dichloromethane (50 ml) in a continuous liquid–liquid extractor. The organic solution was dried and concentrated to give the amine (23) as a syrup (0.15 g), $[\alpha]_D$ −63.5° (*c* 2 in CH_2Cl_2); $\nu_{max.}$ 3 500—3 200br cm^{-1} (NH and OH); θ + 263 (λ 546 nm).

The N-*salicylidene derivative* (0.15 g) was prepared from the syrup (23) (0.21 g) by treatment in boiling ethanol (5 ml) with salicylaldehyde (0.26 g) for 1 h. After recrystallisation from ethanol the compound had m.p. 131—132 °C; $[\alpha]_D$ −41° (*c* 0.5); $\nu_{max.}$ 3 400 (OH) and 1 625 cm^{-1} (C=N); $\lambda_{max.}$ (ε) 253 (7 800), 280 (4 000), and 315 nm (2 200); δ_H (C_6D_6) 8.4 (1 H, s, C*H*Ph), 6.85—7.40 (4 H, m, ArH), 4.90 (1 H, d, $J_{1,2}$ 4.2 Hz, 1-H), 3.80—4.65 (3 H, m, 2-, 3-, and 5-H), 3.50 (3 H, s, OMe), 1.55—1.77 (2 H, m, 4-H_2), 1.26 (3 H, d, $J_{6,5}$ 6.0 Hz, 5-Me) (Found: C, 63.2; H, 7.2; N, 5.3. $C_{14}H_{19}NO_4$ requires C, 63.4; H, 7.2; N, 5.3%).

3-*Amino*-3,4,6-*trideoxy*-L-ribo-*hexopyranose Hydrochloride* (25).—The salicylidene derivative (0.15 g), prepared as described above, was dispersed in aqueous hydrochloric acid (2M; 5 ml) and heated under reflux for 4 h. Salicylaldehyde and excess of hydrogen chloride were removed by co-distillation with water. The residue was taken up in ethanol (10 ml), and the solution was shaken with decolourising charcoal and filtered. The filtrate was concentrated to 0.5 ml and diethyl ether was added. The *hydrochloride* (0.07 g) of the amino-sugar (25) separated as white hygroscopic crystals, m.p. 109—111 °C after recrystallisation from ethanol–diethyl ether; $[\alpha]_D$ −18° (*c* 3 in water); $\nu_{max.}$ 3 500—3 300 and 1 500 cm^{-1} (Found: N, 7.7. $C_6H_{14}ClNO_3$ requires N, 7.6%).

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