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NUCLEOPHILIC DISPLACEMENTS OF METHYL 2,3-*O*-ISOPROPYLIDENE-4-*O*-TOLUENE-*p*-SULPHONYL-α-D-LYXO- AND -β-L-RIBO-PYRANOSIDES, AND DEAMINATION OF THE CORRESPONDING 4-AMINO SUGARS*

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ABSTRACT

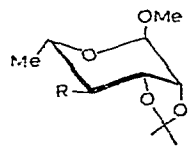
Reinvestigation of the reaction of methyl 2,3-*O*-isopropylidene-4-*O*-toluene-*p*-sulphonyl-α-D-lyxopyranoside (**4**) with azide ion has shown that methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*erythro*-pent-4-enopyranoside (**8**, ~51.5%) is formed, as well as the azido sugar **7** (~48.5%) of an S_N2 displacement. The unsaturated sugar **8** was more conveniently prepared by heating the sulphonate **4** with 1,5-diazabicyclo-[5.4.0]undec-5-ene. An azide displacement on methyl 2,3-*O*-isopropylidene-4-*O*-toluene-*p*-sulphonyl-β-L-ribopyranoside (**12**) furnished methyl 4-azido-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**13**, ~66%) and the unsaturated sugar **14** (~28.5%), which was also prepared by heating the sulphonate with 1,5-diazabicyclo[5.4.0]undec-5-ene. Deamination of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**5**), prepared by reduction of **13**, with sodium nitrite in 90% acetic acid at ~0°, yielded methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside (**10a**, 26.2%), methyl 2,3-*O*-isopropylidene-β-L-ribofuranoside (**21a**, 18.4%), and the corresponding acetates **10b** (34.5%) and **21b** (21.3%). These products are considered to arise by solvolysis of the bicyclic oxonium ion **29**, formed as a consequence of participation by the ring-oxygen atom in the deamination reaction. Similar deamination of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-β-L-ribopyranoside (**6**) afforded, exclusively, the products **10a** (34.4%) and **10b** (65.6%) of inverted configuration. Deamination of methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**20**) gave **22ab**, but no other products. An alternative synthesis of the amino sugars **5** and **6** is available by conversion of **10a** into methyl 2,3-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-4-ulose (**11**), followed by reduction of the derived oxime **15** with lithium aluminium hydride.

INTRODUCTION

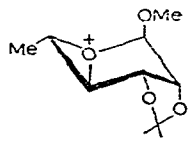
A recent investigation[3] has shown that the deamination of methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (**3**) requires the intermediacy

*Nucleophilic Displacements in Carbohydrates: Part XXIII[1]. For Part XXII, see Ref. 2.

of the bicyclic oxonium ion **2**; the products arise from stereospecific solvolysis of this ion at both C-4 and C-5. The bicyclic oxonium ion **2** also accounts[3,4] for the formation of ring-contracted products in displacements on methyl 6-deoxy-2,3-*O*-isopropylidene-L(or D)-mannopyranoside 4-sulphonates (**1**) with ionic nucleophiles[5] (*e.g.*, N_3^-), although internal-return phenomena need to be invoked to explain some of the other products. It was of interest to examine related displacement and deamination reactions of an analogous pair of compounds, *viz.* methyl 2,3-*O*-isopropylidene-4-*O*-toluene-*p*-sulphonyl-α-D-lyxopyranoside (**4**) and the 4-amino sugar **5**, since, although a similar steric situation is encountered, there is clear evidence[6,7] that the sulphonate **4** undergoes nucleophilic displacements (*e.g.*, with N_3^- and BzS^-) without the formation of ring-contracted products. For example, Reist and his co-workers[6] reported that the enantiomeric sulphonate L-**4**, although possessing a



1 R = OMs or OTs
3 R = NH_2



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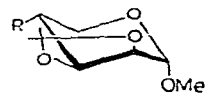
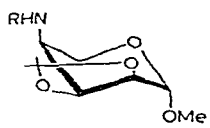
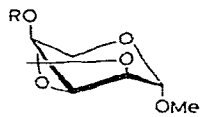


4 R = OTs
5 R = NH_2
16 R = NHAc



6 R = H
17 R = Ac



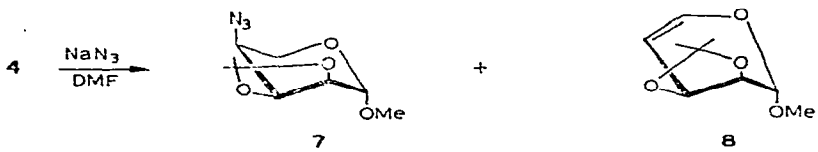
9a R = H
9b R = Ac

β-axial substituent in the preferred $^1C_4$ conformation, yields the inverted azide D-**7** (30%) when treated with sodium azide in *N*,*N*-dimethylformamide. This azide was characterized by conversion into derivatives of 4-acetamido-4-deoxy-D-ribose, which were also prepared by an unequivocal route. While the displacements on D-**4** presumably take place by way of a conformation other than the $^4C_1$ conformation (to alleviate the *β-trans*-axial effect[8]), the deamination of the corresponding amino sugar **5** should be subject to ground-state control[9], so that ring-contracted products might result. For comparison, the deaminations of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-β-L-ribopyranoside (**6**) and methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**20**) have also been studied.

RESULTS

The amino sugars **5** and **6** used in this study were each prepared by two independent methods. An azide displacement on methyl 2,3-*O*-isopropylidene-4-*O*-

toluene-*p*-sulphonyl-α-D-lyxopyranoside[10] (**4**) in *N*,*N*-dimethylformamide at 140° was shown (g.l.c.) to yield two products (*cf.* Ref. 7), which were identified as methyl 4-azido-4-deoxy-2,3-*O*-isopropylidene-β-L-ribopyranoside (**7**, ~48.5%) and methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*erythro*-pent-4-enopyranoside (**8**, ~51.5%). These components could be separated with some difficulty by chromatography over silica gel. The component eluted first from the column exhibited a strong absorption band at 2100 cm^{-1} in its i.r. spectrum, and was assigned as the azide **7** by analogy with the work of Reist *et al.*[6]. The i.r. spectrum of the second component contained a band at 1650 cm^{-1}, indicative of a carbon–carbon double-bond; the presence of an unsaturated linkage was confirmed when it rapidly decolourized a solution of bromine



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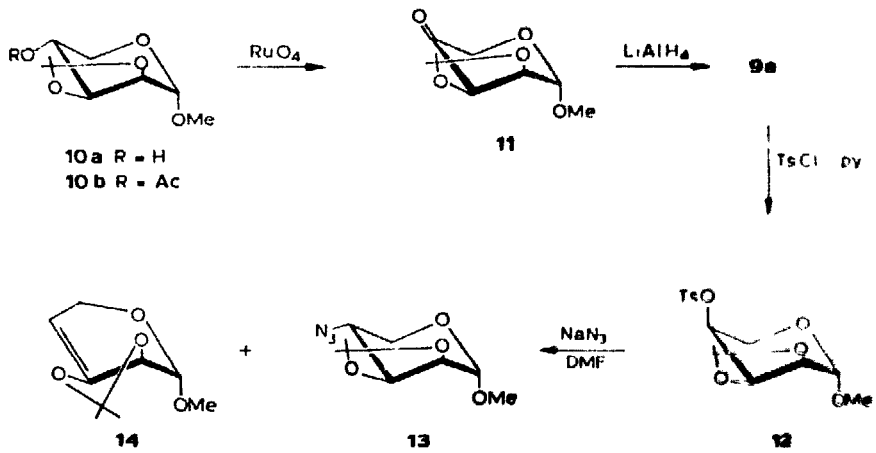
in carbon tetrachloride. The structure **8** of this component was revealed by its n.m.r. spectrum, which showed the presence of *two* olefinic protons at τ 3.34 (d) and 4.64 (q, $J_{3,4}$ ~4, $J_{4,5}$ ~6 Hz), assigned to H-5 and H-4, respectively. The azide **7** furnished methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-β-L-ribopyranoside (**6**) on reduction with lithium aluminium hydride in ether. In large-scale preparations of **6**, no attempt was made to separate the unsaturated sugar **8** until after the azide **7** had been reduced.

Treatment of the sulphonate **4** with sodium benzoate in *N*,*N*-dimethylformamide at 140° gave principally the unsaturated sugar **8** (92%), although a small proportion of methyl 2,3-*O*-isopropylidene-β-L-ribopyranoside[11] (**9a**, 8%) was detected (g.l.c.) and characterized following treatment of the reaction products with sodium methoxide. Predictably, the sulphonate **4** was converted into the unsaturated sugar **8** only when heated with the non-nucleophilic base 1,5-diazabicyclo[5.4.0]undec-5-ene.

Since the benzoate-exchange reaction on sulphonate **4** could not be used as the first step in effecting a double inversion of configuration at C-4, the following route was used to prepare methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**5**). Oxidation of methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside[10] (**10a**) with ruthenium tetraoxide in carbon tetrachloride furnished the pentopyranosid-4-ulose **11**, which was reduced stereoselectively[11] to methyl 2,3-*O*-isopropylidene-β-L-ribopyranoside (**9a**) with lithium aluminium hydride in ether*. Treatment of the derived toluene-*p*-sulphonate **12** with sodium azide in *N*,*N*-dimethylformamide at 140° yielded (g.l.c. evidence) a mixture of the azide **13** (~66%) and an unsaturated sugar (~28.5%), which was subsequently identified as methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*glycero*-pent-3-enopyranoside (**14**). Chromatographic separation

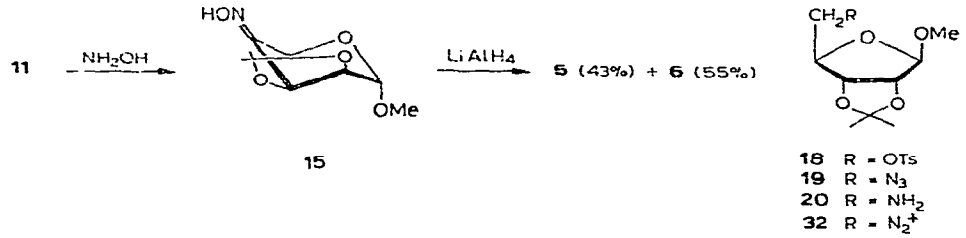
*Reduction with this reagent gives[11] a mixture of **9a** and **10a** in a ratio of 27:1. No attempt was made to separate these alcohols, since the toluene-*p*-sulphonate **12** obtained from **9a** was readily crystallized.

of these compounds proved to be extremely difficult and tedious, but sufficient of the azide **13** was obtained to characterize it by elemental analyses and by i.r. and n.m.r spectroscopy (see Experimental). The unsaturated sugar **14** could not be isolated in amounts sufficient to effect its characterization, but it was indistinguishable (g.l.c and mass spectrometry) from the only product formed when the sulphonate **12** was heated with 1,5-diazabicyclo[5.4.0]undec-5-ene. Treatment of the foregoing mixture



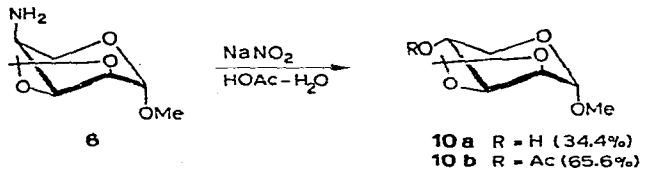
with lithium aluminium hydride produced a separable mixture of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**5**) and the unsaturated sugar **14**. Accurate mass measurement of the molecular ion gave the molecular formula of **14** as $C_9H_{14}O_4$, and **14** was readily distinguishable from the isomeric unsaturated sugar **8** by both g.l.c. and n.m.r. spectroscopy. The n.m.r. spectrum of **14** revealed the presence of only *one* olefinic proton, the signal for which was an ill-defined multiplet at τ 5.20 which can be assigned to H-4; other signals in the spectrum were compatible with the structure assigned.

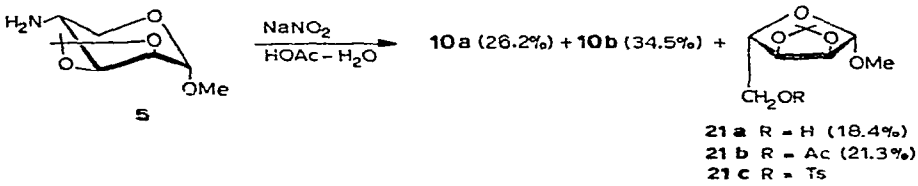
The formation of the unsaturated sugars **8** and **14** decreases the efficiency of the displacement reactions as a means of preparing the amino sugars **5** and **6**. An alternative preparation of one, or as it transpired both, of these amino sugars was sought by reduction of the oxime **15** prepared from the pentopyranosid-4-ulose **11**. With lithium aluminium hydride in tetrahydrofuran, the oxime **15** gave a mixture of **5** and **6**, which were isolated in 43% and 55% yield, respectively, following preparative thin-layer chromatography. Characterization of the amino sugars was effected by conversion into the *N*-acetyl derivatives **16** and **17**, which were identical with those obtained by *N*-acetylation of the amino sugars **5** and **6** prepared *via* azide exchange. The formation of both **5** and **6** on reduction of the oxime **15** is surprising in view of the highly stereoselective reduction that the parent pentopyranosidulose **11** undergoes. It may be that the delivery of hydride ion from the sterically less-favoured direction (*i.e.*, *endo* with respect to the bicyclic ring-system) is aided by the formation of a complex between the reagent and the hydroxyl group of the oxime

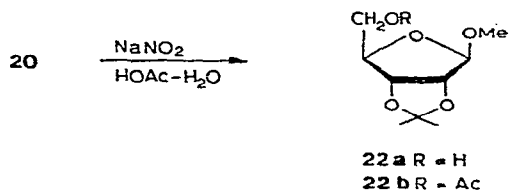


Methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**20**) was prepared from the sulphonate **18**[12] by an azide displacement, followed by reduction of the resulting azide **19** with lithium aluminium hydride. The amino sugar **20** has been obtained previously *via* displacement of the sulphonyloxy group from **18** with potassium phthalimide[12a]. The n.m.r. spectrum of methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**19**) was distinct from that of the isomeric azide **7**, thereby substantiating the conclusion[6,7] that displacements on the lyxopyranoside sulphonate **4** occur without ring contraction.

Deamination of the amino sugars **5**, **6**, and **20** was performed with sodium nitrite in 90% acetic acid at ~0°, and preliminary identification of the products was achieved by g.l.c. using authentic compounds (prepared as described in the Experimental) for comparison. Deamination of the L-ribopyranoside amine **6** gave methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside (**10a**, 34.4%) and the corresponding 4-acetate **10b** (65.6%). Following treatment of the product mixture with sodium







methoxide, **10a**[10] (identified by i.r. and n.m.r. spectroscopy) was obtained by distillation, and this compound was also characterized by conversion into the crystalline toluene-*p*-sulphonate **4**[10].

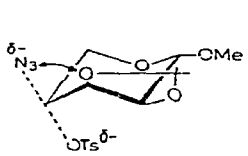
Deamination of the D-lyxopyranoside amine **5** yielded four products that were identified as methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside[10] (**10a**, 26.2%), methyl 2,3-*O*-isopropylidene-β-L-ribofuranoside (**21a**, 18.4%), and the monoacetates **10b** (34.5%) and **21b** (21.3%). Acetylation of the products afforded a mixture containing **10b** (66%) and **21b** (34%), whose n.m.r. spectrum was virtually superimposable on that of a mixture comprising **10b** and **22b** (*i.e.*, D-**21b**) in the appropriate proportions. Deacetylation of the monoacetates gave, after preparative chromatography, **21a** (identified by spectroscopic comparison with the D enantiomer[12]) and **10a**[10] (identified by i.r. and n.m.r. spectroscopy). In each case, the crystalline toluene-*p*-sulphonate (**21c**[12] or **4**[10]) was prepared.

A mixture of **22a** and **22b** was obtained when methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**20**) was deaminated as already described. Deacetylation and distillation furnished **22a**[12] (identified by i.r. and n.m.r. spectroscopy), which was also characterized by conversion into the toluene-*p*-sulphonate **18**[12].

DISCUSSION

^{1}H-N.m.r. spectroscopy indicated that the D-*lyxo*-sulphonate **4** preferentially adopts a $^4C_1$(D) conformation in the ground-state conformational equilibrium. Since the stereochemistry of **4** is analogous to that of the homologous L-*manno*-sulphonate **1**, the *β-trans*-axial substituent[8] should prevent the displacement with azide ion in the $^4C_1$(D) conformation. The displacement yielding the azide **7** must therefore take place by way of either the $^1C_4$(D) conformation or a skew-chair conformation in which the effect of the *β-trans*-axial substituent is alleviated. Although the transition state **23** for the azide displacement in the $^1C_4$(D) conformation contains an unfavourable interaction[8] between the incoming nucleophile and the *cis*-axial substituent at C-3, an examination of molecular models showed that other skew-chair and boat conformations also contain unfavourable interactions. The competing β-elimination yielding the 4,5-unsaturated sugar **8** will amost certainly occur from the $^1C_4$(D) conformation of **4**, as most eliminations induced by weak bases proceed by an *anti* stereochemistry[13]. Since azide ion is also a good carbon-nucleophile in S_N2 reactions, the β-elimination yielding **8** may occur by way of an E2C-like[13,14] transition state **24***. As there is a partitioning of the reaction between the S_N2 and E2C pathways, adverse steric interactions engendered in the transition state (*e.g.*, **23**) of the displace-

*A brief word of explanation is needed on the non-linearity of the transition state **24** involved in the concerted elimination induced by azide ion on **4**. It is generally accepted that the transition states in concerted β-eliminations promoted by weak or moderately weak bases, which are invariably good carbon-nucleophiles, differ significantly from those promoted by conventionally strong bases. In the E2C-like mechanism originally proposed by Parker et al.[14], it was suggested that there is covalent orbital overlap between the weak base (B^-) and C_α in the transition state (*A*). More recently, a



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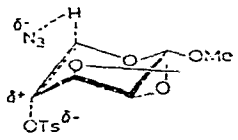

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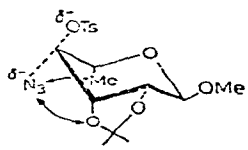

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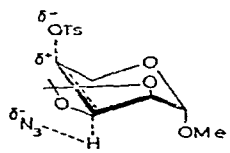

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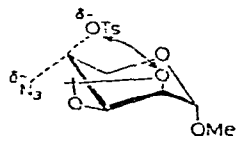

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ment reaction would favour the elimination pathway. It is also possible to explain why the L-*manno*-sulphonate **1** follows an entirely different course in its displacement reaction with azide[5]. The (conceptualized) transition state **25** for displacement by way of the $^4C_1$(L) conformation would not only contain an unfavourable 1,3-interaction between the axial substituents at C-3 and C-5, but the approach of the nucleophile to C-4 is now impeded by *both* of these substituents. In this case, unimolecular displacement of the sulphonyloxy group, to yield the oxonium ion **2** in the $^1C_4$(L) conformation, offers an energetically viable alternative[5].

The reaction of the D-*lyxo*-sulphonate **4** with benzoate ion in *N*,*N*-dimethylformamide yielded principally the unsaturated sugar **8** (92%) and only a small proportion of the displacement product. Since benzoate ion is more basic than azide ion, a higher proportion of the unsaturated sugar **8** is to be expected; the reaction with benzoate ion is also likely to proceed by way of an E2H-like mechanism[14], which must necessarily operate in the reaction of **4** with the non-nucleophilic base 1,5-diazabicyclo[5.4.0]undec-5-ene.

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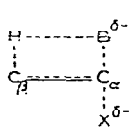
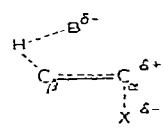
revised transition-state spectrum *B* has been suggested[15], which differs from the original proposals insofar as the π-bond



A

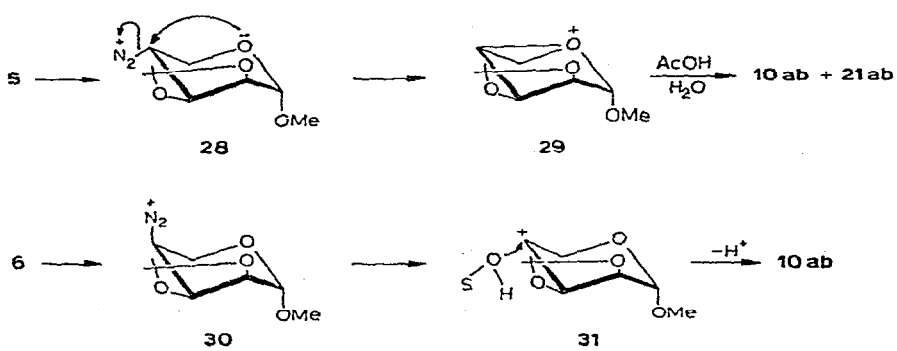


B

is less well-developed because the weak base has not gained control of the β-proton to any great extent. This proposal assumes a non-linear arrangement of B ... H ... C_β in the proton-transfer step, for which the energy loss may be compensated by a stabilizing *electrostatic* interaction between the electron-deficient centre (C_α) and hardly neutralized base. Since the revised transition state *B* for the E2C-like mechanism is claimed[15] to accommodate all the facts for this type of reaction, it has been adopted in the transition states **24** and **26** of the azide-induced eliminations. The transition states of reactions of the moderately basic azide ion in dipolar aprotic solvents are thought[14b] to be more E2C-like than E2H-like for substrates with good leaving-groups.

Azide ion reacted with the L-*ribo*-sulphonate **12** to yield the azide **13** (66%) and the 3,4-unsaturated sugar **14** (28.5%). The concerted *β*-elimination yielding **14** presumably occurs in the $^4C_1$(L) conformation, possibly *via* an E2C-like transition state **26**. It is also tempting to suggest that the S_N2 displacement yielding **13** also takes place by way of the $^4C_1$(L) conformation, despite the unfavourable interaction generated between the departing sulphonyloxy group and the axial C-2 substituent in the transition state **27** (corollary of the *β-trans*-axial effect[8]). This interaction would destabilize the transition state, thereby allowing the *β*-elimination to compete on more-favourable terms. An analogous explanation has been invoked[16] to account for the high proportion of 4,5-unsaturated sugar obtained in the reaction of azide ion with methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-*α*-L-talopyranoside, which has a related stereochemistry. The exclusive formation of the 3,4-unsaturated sugar **14** in the reaction of the L-*ribo*-sulphonate **12** with azide ion presumably reflects differences in the kinetic acidities of H-5_{ax} and H-3.

Deaminations of alkyl amines are usually controlled by the ground-state conformational equilibrium[9] (corollary of the Curtin–Hammett principle[17]), in contrast to the reactions of alkyl sulphonates which may occur by way of conformations that are unimportant in the ground state. The latter point is nicely illustrated by the reaction of the D-*lyxo*-sulphonate **4** with azide ion. Another characteristic feature of deaminations is that rearrangements occur to a greater extent than in related solvolytic and other displacement reactions due to the low activation-energies involved in converting the diazonium ion into products[9,18]. The deamination of the D-*lyxo*-amine **5** with nitrous acid in 90% aqueous acetic acid parallels that of the L-*manno*-amine **3**[3], in that ring-contracted products are formed. The ^{1}H-n.m.r. spectrum of **5** in deuteriochloroform revealed only a small coupling ($J_{1,2}$ ~2 Hz) between H-1 and H-2, compatible with a preference for the $^4C_1$(D) conformation in the ground-state conformational equilibrium. The results of the deamination show that this conformation is also adopted by the amine **5** and, by inference, the corresponding diazonium ion **28** in aqueous acetic acid. In the $^4C_1$(D) conformation of the diazonium ion **28**, one of the lone pairs of electrons on the ring-oxygen atom can interact with the vacant p-orbital developed at C-4 on heterolysis of the C–N_2^+ bond. Solvent attack at C-4 and C-5 of the resulting bicyclic oxonium ion **29** furnishes the



D-lyxopyranosides **10ab** (~60%) of retained configuration and the L-ribofuranosides **21ab** (~40%), respectively. The proportion of furanosides obtained in this case is significantly less than that (70%) resulting from deamination of the L-*manno*-amine **3** under comparable conditions. The extent of primary and secondary C–O bond cleavage presumably reflects the abilities of C-4 and C-5 to sustain a positive charge in the transition states leading from the oxonium ion **29** to products, particularly in highly ionizing solvents, such as aqueous acetic acid, where the solvolysis would tend to become more limiting in character[19]. Steric factors should favour attack of solvent at C-5 (less substituted) of the oxonium ion **29**, whereas electronic factors should favour attack at the secondary position C-4. The subtle interplay between steric and electronic factors will obviously differ for the solvolysis of the oxonium ion **2**, where both C-4 and C-5 are secondary carbon atoms.

The absence of a large coupling between H-1 and H-2 (J ~4 Hz) in the ^{1}H-n.m.r. spectrum of the L-*ribo*-amine **6** indicated that the $^4C_1$(L) conformation predominates in the ground-state conformational equilibrium in deuteriochloroform. This preference is also evident from the absence of ring-contracted and other products (*vide infra*) that would be expected if the amine **6** reacted by way of the alternative chair conformation in forming the diazonium ion. The stereospecific formation of the α-D-lyxopyranosides **10ab** on deamination of **6** in 90% acetic acid might result either from an S_N2 solvolysis of the intermediate diazonium ion **30**[9] and/or from preferential solvation of the carbocation **31** from the side opposite to that of the departing nitrogen molecule. An analogous stereospecificity is observed when methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talopyranoside is deaminated under comparable conditions[3].

The products **22ab** obtained on deamination of methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside **20** presumably arise from S_N2 solvolysis of the intermediate diazonium ion **32**, since the formation of a primary carbocation is unlikely in view of the high energy associated with the formation of such species. It is interesting to compare this deamination with the solvolysis of benzyl 5-*O*-(*p*-bromobenzenesulphonyl)-2,3-*O*-isopropylidene-β-D-ribofuranoside in aqueous methanol, which yields, *inter alia*, products arising from participation and migration of the glycosidic benzyloxy group[20]. The absence of rearrangement products in the deamination of the D-ribofuranoside amine **20** may be related to the conformation that the diazonium ion **32** adopts about the C-4–C-5 bond.

EXPERIMENTAL

Kieselgel G (Merck) was used for t.l.c., and detection was effected with vanillin–sulphuric acid[21]. I.r. spectra were recorded for either Nujol mulls or liquid films, using a Perkin–Elmer "Infracord" spectrophotometer, and n.m.r. spectra were measured for solutions in deuteriochloroform (1% of tetramethylsilane as an internal standard) with a Perkin–Elmer R-10 spectrometer. Optical rotations were measured at ambient temperature with a Perkin–Elmer 141 automatic polarimeter. Analytical

g.l.c. for the displacement reactions was carried out on a Pye 104 chromatograph (nitrogen carrier gas, 7 p.s.i., flame-ionization detector) using a column of 25% of silicone gum on Celite at an operating temperature of 160°; peaks were calibrated against an internal standard. Preliminary identification of products from the deaminations was achieved by g.l.c. (Perkin–Elmer F11 chromatograph, nitrogen carrier gas at 7 p.s.i., using a column of 15% of Carbowax on Chromosorb W at 170°) by co-injection with authentic materials. Light petroleum refers to the fraction having b.p. 60–80°.

*Reactions of methyl 2,3-O-isopropylidene-4-O-toluene-*p*-sulphonyl-α-*D*-lyxopyranoside* (**4**). — (*a*) *With sodium azide.* A solution of the sulphonate **4**[10] (1 g) in *N,N*-dimethylformamide (10 ml) containing sodium azide (1 g) was heated at ~140° (oil bath) for 10 h, after which time t.l.c. (light petroleum–acetone, 4:1) showed that no starting material remained. Chloroform (50 ml) and water (50 ml) were added to the cooled reaction mixture, and the separated aqueous layer was further extracted with chloroform (2 × 50 ml). The combined organic extracts were washed with water (50 ml) and dried ($MgSO_4$), and the solvent was evaporated to leave an oil (0.6 g), which g.l.c. showed to contain two components in approximately equal proportions. Chromatography on silica gel (elution with light petroleum–acetone, 15:1) gave first a mixture (0.43 g) of both components, followed by methyl 4-azido-4-deoxy-2,3-*O*-isopropylidene-β-L-ribopyranoside (**7**, 0.14 g), b.p. 60–62° (bath) at 0.3 mmHg, $[\alpha]_D$ +29 ±1° (*c* 2.6, chloroform), ν_{max}^{film} 2100 cm^{-1}(str., N_3); lit. (D enantiomer)[6], b.p. 76–78° at 0.3 mmHg. Accurate mass measurement gave the molecular formula for **7** as $C_9H_{15}N_3O_4$ (Found: 229.2381; calc.: 229.2385 for M^+). N.m.r. data: τ 5.43 (d, 1 H, $J_{1,2}$ 4 Hz, H-1); 6.55 (s, 3 H, OMe); and 8.42 and 8.58 (2 s, 6 H, CMe_2).

Further chromatography of the mixture of components (0.43 g) gave methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*erythro*-pent-4-enopyranoside (**8**, 0.13 g), b.p. 61–63° (bath) at 12 mmHg, $[\alpha]_D$ +180 ±3° (*c* 1.95, chloroform), ν_{max}^{film} 1650 cm^{-1} (str., C=C) (Found: C, 58.3; H, 7.3. $C_9H_{14}O_4$ calc.: C, 58.05; H, 7.6%). N.m.r. data: τ 3.34 (d, 1 H, $J_{5,4}$ 6 Hz, H-5); 4.64 (q, 1 H, $J_{4,5}$ 6, $J_{4,3}$ 4 Hz, H-4); 5.17 (d and q, 2 H, $J_{1,2}$ 6 Hz, H-1 and H-3); 5.73 (t, 1 H, $J_{2,3} = J_{1,2}$ ~6 Hz, H-2); 6.15 (s, 3 H, OMe); and 8.49 and 8.61 (2 s, 6 H, CMe_2).

(*b*) *With sodium benzoate.* A solution of the sulphonate **4**[10] (2 g) in *N,N*-dimethylformamide (20 ml) containing sodium benzoate (2.5 g) was heated at 140° (oil bath) for 60 h; t.l.c. (light petroleum–acetone, 3:1) then showed that two products had been formed. Water (25 ml) was added to the cooled reaction mixture, which was then extracted with ether (3 × 25 ml). The combined ethereal extracts were washed with aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Removal of the solvent left an oil (1.54 g), which was dissolved in dry methanol (50 ml) containing M sodium methoxide (5 ml); after standing overnight at room temperature, the excess of base was neutralized (solid CO_2) and the solvent was removed. The residue was extracted with ether (3 × 50 ml), and the combined extracts were washed with water (25 ml) and dried ($MgSO_4$). Removal of the solvent afforded an oil (0.85 g), shown (g.l.c.) to contain a major component (~92%) and a minor com-

ponent (~8%), in addition to methyl benzoate. Chromatography on silica gel (elution with light petroleum–ether, 6:1) furnished methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*erythro*-pent-4-enopyranoside (**8**, 0.13 g), b.p. 38–40° (bath) at 1 mmHg, $[\alpha]_D$ +185 ±1° (*c* 1.2, chloroform), having an n.m.r. spectrum indistinguishable from that of the material obtained in (*a*). Continued elution gave methyl 2,3-*O*-isopropylidene-β-L-ribopyranoside (**9a**, 20 mg), b.p. 55–57° (bath) at 0.1 mmHg, $[\alpha]_D$ + 62° (*c* 0.2, ethanol); lit.[11] b.p. 95–96° at 1 mmHg, $[\alpha]_D$ +68° (*c* 0.9, ethanol). G.l.c. showed that this material was indistinguishable from that obtained by reduction of the keto sugar **11** (see later).

(*c*) *With 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).* The sulphonate **4**[10] (1 g) in DBU (2 ml) was heated at 140° (oil bath) for 6 h, after which time t.l.c. (light petroleum–ether, 5:1) showed that all the starting material had been consumed with the formation of a single product. Water (20 ml) was added to the cooled solution, and the aqueous solution was extracted with chloroform (2 × 25 ml); the combined extracts were washed with M sulphuric acid (20 ml) and water (20 ml), and dried ($MgSO_4$). Removal of the solvent and distillation of the residue gave methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*erythro*-pent-4-enopyranoside (**8**; 0.32 g, 62%), b.p. 60–62° (bath) at *ca.* 12 mmHg, $[\alpha]_D$ +173 ±3° (*c* 2.6, chloroform) (Found: C, 57.9; H, 7.8. $C_9H_{14}O_4$ calc.: C, 58.05; H, 7.6%). The n.m.r. and i.r. spectra of this material were indistinguishable from those of the unsaturated sugar **8** obtained in the displacement reactions described above. A solution of bromine in carbon tetrachloride was rapidly decolorized by **8**.

*Methyl 2,3-*O*-isopropylidene-β-*L*-*erythro*-pentopyranosid-4-ulose* (**11**). — To a stirred solution of the acetal **10a** (24.4 g) in carbon tetrachloride (300 ml) at room temperature was added a solution of ruthenium tetraoxide in carbon tetrachloride [prepared by treating ruthenium dioxide dihydrate (8.6 g) in water (1.5 l) with sodium periodate (120 g) and extraction of the solution with carbon tetrachloride (4 × 200 ml)]. The reaction mixture was vigorously stirred for 12 h, after which time t.l.c. (light petroleum–acetone, 3:1) revealed that a significant quantity of starting material remained. The mixture was filtered and the recovered ruthenium dioxide was reconverted into the tetraoxide (as above), which was added to the filtrate (reduced in volume to ~300 ml). This process was repeated three times, the oxidation being allowed to proceed for 4 h at room temperature after each addition. Propan-2-ol (400 ml) was then added and, after stirring for 30 min, the mixture was filtered and the solvent was removed. Distillation of the residue gave the methyl pentosidulose **11** (18.3 g, 76%), b.p. 60–65° at 0.3 mmHg, $[\alpha]_D$ +79° (*c* 1.2, ethanol), ν_{max}^{film} 1730 cm^{-1} (str., C=O); lit.[11] b.p. 76–78° at 0.7 mmHg, $[\alpha]_D$ +71° (*c* 1.3, ethanol).

*Methyl 2,3-*O*-isopropylidene-β-*L*-ribopyranoside* (**9a**). — A solution of the pentosidulose **11** (8.3 g) in dry ether (80 ml) containing lithium aluminium hydride (4 g) was heated under reflux for 3 h, whereupon ethyl acetate (30 ml) and water (2 ml) were cautiously added to decompose the excess of reagent. After heating under reflux for 15 min, solids were filtered off and washed thoroughly with ether, and the combined filtrate and washings were dried ($MgSO_4$). Removal of the solvent and

distillation of the residue afforded the L-ribopyranoside derivative **9a** (5 g, 60%), b.p. 56–58° at 0.15 mmHg, $[\alpha]_D$ +76° (*c* 1.2, ethanol); lit.[11] b.p. 95–96° at 1 mmHg, $[\alpha]_D$ +68° (*c* 0.9, ethanol). The i.r. spectrum of **9a** showed an absorption band at 3400 cm^{-1} (OH), but no band at ~1730 cm^{-1} due to carbonyl absorption. This material was probably contaminated with a small proportion of **10a**[11].

*Methyl 2,3-O-isopropylidene-4-O-toluene-*p*-sulphonyl-β-L-ribopyranoside* (**12**). — The L-ribopyranoside **9a** (8 g) in pyridine (150 ml) was treated with a solution of toluene-*p*-sulphonyl chloride (26 g) in chloroform (100 ml) at ~0° and then at room temperature for 12 h. Work-up in the usual manner gave the sulphonate **12** (8.4 g, 60%), m.p. 105–106° (from ethyl acetate–light petroleum), $[\alpha]_D$ +27° (*c* 1.2, chloroform) (Found: C, 53.75; H, 6.1; S, 8.9. $C_{16}H_{22}O_7S$ calc.: C, 53.6; H, 6.2; S, 8.9%). N.m.r. data: τ ~2.30 (m, 4 H, aromatic); 4.98 (narrow m, 1 H, H-4); 5.45 (d, 1 H, $J_{1,2}$ ~3 Hz, H-1); 6.55 (s, 3 H, OMe); 7.54 (s, 3 H, Ar*Me*); and 8.48 and 8.72 (2 s, 6 H, CMe_2).

*Reactions of methyl 2,3-O-isopropylidene-4-O-toluene-*p*-sulphonyl-β-L-ribopyranoside* (**12**). — (*a*) *With sodium azide.* A solution of the sulphonate **12** (14 g) in dry *N*,*N*-dimethylformamide (250 ml) containing sodium azide (14 g) was heated at 140° overnight, during which time complete reaction had occurred. Work-up (as before) gave an oil, shown (g.l.c.) to consist of **13** [66%; retention time, 28.4 min; *m/e* 214 ($M^+ - 15$)] and **14** [28.5%; retention time, 9.3 min; *m/e* 186 ($M^+ - 15$)]; the minor component could not be distinguished by g.l.c. and mass spectrometry from an authentic sample of **14** [see (*b*)]. Chromatography of a part (~3 g) of the mixture on silica gel (elution with carbon tetrachloride–ether, 9:1) failed to separate a pure sample of the unsaturated sugar **14**, but afforded pure methyl 4-azido-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**13**, 0.82 g), b.p. 40–42° (bath) at 0.2 mmHg, $[\alpha]_D$ +35° (*c* 2, chloroform), ν_{max}^{film} 2100 cm^{-1} (str., N_3) (Found: C, 47.5; H, 6.6; N, 18.6. $C_9H_{15}N_3O_4$ calc.: C, 47.2; H, 6.6; N, 18.3%). N.m.r. data: τ 5.13 (broad s, 1 H, H-1); 5.85 and 6.39 (2 m, 5 H, H-2–H-5′); 6.57 (s, 3 H, OMe); and 8.43 and 8.62 (2 s, 6 H, CMe_2).

A mixture (1.52 g) of **13** and **14** was also eluted from the column.

(*b*) *With DBU.* The sulphonate **12** (1 g) in DBU (2 ml) was heated for 2 h at 140° (oil bath); water (15 ml) was added to the cooled solution, which was then extracted with ether (2 × 10 ml). The extracts were dried (Na_2SO_4), and removal of the solvent left an oil (0.47 g, 90%), which was distilled to give methyl 4-deoxy-2,3-*O*-isopropylidene-β-L-*glycero*-pent-3-enopyranoside (**14**), b.p. 68–70° (bath) at ~12 mmHg, $[\alpha]_D$ −35° (*c* 1.15, chloroform), ν_{max}^{film} 1700 cm^{-1} (str., O–C=C). Accurate mass measurement gave the molecular formula as $C_9H_{14}O_4$ (Found: 186.08872; calc.: 186.08920). N.m.r. data: τ 5.20 (ill-defined m, 1 H, H-4); 5.64 (m, 4 H); 6.42 (s, 3 H, OMe); 8.50 (s, 6 H, CMe_2). A sample of **14** rapidly decolourized a solution of bromine in carbon tetrachloride.

*Methyl 2,3-O-isopropylidene-β-L-*erythro*-pentopyranosid-4-ulose oxime* (**15**). — A solution of the pentosidulose **11** (5 g) in pyridine–ethanol (1:1, 50 ml) containing hydroxylamine hydrochloride (5 g) was heated under reflux for 4 h, whereafter it was

evaporated to dryness and water (50 ml) was added. The aqueous solution was extracted with chloroform (3 × 50 ml), and the combined extracts were dried ($MgSO_4$) and concentrated to give the impure product (5 g, 93%). Several recrystallisations from ether–light petroleum gave the pure oxime **15**, m.p. 96–97°, $[\alpha]_D$ +81° (*c* 1.1, chloroform) (Found: C, 49.6; H, 6.7; N, 6.3. $C_9H_{15}NO_5$ calc.: C, 49.75; H, 7.0; N, 6.45%). N.m.r. data: τ 5.28–5.78 (5 H, H-1–H-5′); 6.57 (s, 3 H, OMe); and 8.48 and 8.62 (2 s, 6 H, CMe_2).

*Methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-β-*L*-ribopyranoside* (**6**). — A solution of the azide **7** (0.15 g) in dry ether (25 ml) containing lithium aluminium hydride (50 mg) was heated under reflux for 2 h, after which the excess of reagent was decomposed by the careful addition of ethyl acetate (10 ml) and water (2 ml). The mixture was then heated under reflux for 15 min and filtered. Removal of the solvents from the dried ($MgSO_4$) filtrate furnished the amine **6** (81 mg, 61%), b.p. 55–60° (bath) at 0.2 mmHg, $[\alpha]_D$ +75° (*c* 1.75, chloroform), ν_{max}^{film} 3300 cm^{-1} (broad, NH_2) (Found: C, 53.0; H, 8.2; N, 6.6. $C_9H_{17}NO_4$ calc.: C, 53.2; H, 8.4; N, 6.9%). N.m.r. data: τ 5.55 (d, 1 H, $J_{1,2}$ ~4 Hz, H-1); 6.53 (s, 3 H, OMe); 8.38 (s, 2 H, NH_2); and 8.48 and 8.62 (2 s, 6 H, CMe_2).

In large-scale preparations of the amine **6**, chromatographic removal of the unsaturated sugar **8** formed in the reaction on the sulphonate **4** was not attempted until after the mixture had been treated with lithium aluminium hydride to reduce the azide **7**.

*Methyl 4-acetamido-4-deoxy-2,3-*O*-isopropylidene-β-*L*-ribopyranoside* (**17**). — Treatment of the amino sugar **6** (0.2 g) in methanol containing acetic anhydride in the usual way gave the *N*-acetyl derivative **17** (0.2 g, 83%), b.p. 74–76° (bath) at 0.2 mmHg, $[\alpha]_D$ +16° (*c* 1.9, ethanol), ν_{max}^{film} 1650 and 1550 cm^{-1} (str. NHAc) (Found: C, 53.6; H, 7.9; N, 5.6. $C_{11}H_{19}NO_5$ calc.: C, 53.9; H, 7.8; N, 5.7%), as a viscous syrup. N.m.r. data: τ 5.55–6.35 (6 H, H-1–H-5′); 6.51 (s, 3 H, OMe); 7.97 (s, 3 H, NAc); and 8.45 and 8.61 (2 s, 6 H, CMe_2).

*Methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-*D*-lyxopyranoside* (**5**). — A mixture (3.5 g) of **13** and **14** (resulting from an azide-exchange reaction on the sulphonate **12**) in dry ether (200 ml) containing lithium aluminium hydride (0.75 g) was heated under reflux for 2 h. Work-up in the usual way and chromatography on silica gel (elution with carbon tetrachloride–acetone, 5:1) gave first the unsaturated sugar **14** (0.4 g), b.p. 36–38° (bath) at 0.6 mmHg, $[\alpha]_D$ −32 ±1° (*c* 3, chloroform); the n.m.r. and i.r. spectra of this material were identical to those obtained previously. Continued elution afforded the amino sugar **5** (2.4 g), b.p. 58–60° (bath) at 0.6 mmHg, $[\alpha]_D$ +59° (*c* 0.8, chloroform), ν_{max}^{film} 3400 cm^{-1} (broad, NH_2) (Found: C, 52.8; H, 8.5; N, 6.6. $C_9H_{17}NO_4$ calc.: C, 53.2; H, 8.4; N, 6.9%). N.m.r. data: τ 5.25 (narrow d, 1 H, $J_{1,2}$ ~2 Hz, H-1); 6.56 (s, 3 H, OMe); and 8.50 and 8.65 (2 s, 6 H, CMe_2).

*Methyl 4-acetamido-4-deoxy-2,3-*O*-isopropylidene-α-*D*-lyxopyranoside* (**16**). — This compound (87%), m.p. 133–134° (from chloroform–light petroleum), $[\alpha]_D$ +86° (*c* 1.3, chloroform), ν_{max} 1650 and 1545 cm^{-1} (NHAc), was prepared by *N*-acetylation

of the amino sugar **5** in the usual way (Found: C, 54.2; H, 7.9; N, 5.9. $C_{11}H_{19}NO_5$ calc.: C, 53.9; H, 7.8; N, 5.7%). N.m.r. data: τ 5.42 (d, 1 H, $J_{1,2}$ ~3.5 Hz, H-1); 6.48 (s, 3 H, OMe); 7.99 (s, 3 H, NAc); and 8.45 and 8.63 (2 s, 6 H, CMe_2).

*Reduction of methyl 2,3-O-isopropylidene-β-*L*-erythro-pentopyranosid-4-ulose oxime* (**15**) *to give the amino sugars* **5** *and* **6**. — A solution of the oxime **15** (2.5 g) in dry tetrahydrofuran (100 ml) containing lithium aluminium hydride (1.14 g) was gently boiled under reflux overnight; t.l.c. (light petroleum–acetone, 7:3) then revealed the formation of two products. Work-up in the usual manner and chromatography on silica gel gave first methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**5**; 1 g, 43%), b.p. 59–60° (bath) at 0.2 mmHg, $[\alpha]_D$ +54° (*c* 2.2, chloroform); the *N*-acetyl derivative **16** had m.p. and mixture m.p. 131–132°, $[\alpha]_D$ +87° (*c* 0.8, chloroform). Continued elution gave methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-β-L-ribopyranoside (**6**; 1.3 g, 55%), b.p. 48–50° (bath) at 0.2 mmHg, having n.m.r. and i.r. spectra indistinguishable from those of the material previously prepared; the *N*-acetyl derivative **17**, $[\alpha]_D$ +16° (*c* 1, chloroform), was also indistinguishable (i.r. and n.m.r. spectra) from an authentic material.

*Methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-*D*-ribofuranoside* (**19**). — A solution of methyl 2,3-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-β-D-ribofuranoside[12] (**18**, 1 g) in dry *N*,*N*-dimethylformamide (15 ml) containing sodium azide (1 g) was heated at 140° (oil bath) for 2.5 h; work-up (as before) gave the azide **19** (0.6 g, 94%), b.p. 40–41° (bath) at 0.25 mmHg, $[\alpha]_D$ −58° (*c* 3, chloroform), ν_{max}^{film} 2100 cm^{-1} (N_3) (Found: C, 47.6; H, 6.6; N, 18.2. $C_9H_{15}N_3O_4$ calc.: C, 47.2; H, 6.6; N, 18.3%). N.m.r. data: τ 4.98 (s, 1 H, H-1); 5.37 (s, 2 H, H-2 and H-3); 5.68 (t, 1 H, $J_{4,3}$ 7 Hz, H-4); 6.62 (s, 3 H, OMe); and 8.51 and 8.68 (2 s, 6 H, CMe_2).

*Methyl 5-amino-5-deoxy-2,3-*O*-isopropylidene-β-*D*-ribofuranoside* (**20**). — The azide **19** (3.4 g) in dry ether (50 ml) containing lithium aluminium hydride (0.7 g) was heated under reflux for 3 h; work-up in the usual manner furnished the 5-amino sugar **20** (2.8 g, 92%), b.p. 65–67° at 0.2 mmHg, $[\alpha]_D$ −71° (*c* 2.7, chloroform); lit.[12a] $[\alpha]_D$ −71.6° (*c* 0.8, chloroform).

Authentic compounds for g.l.c. — Methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside[10] (**10a**) and methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside[12a] (**22a**) were prepared by using the literature procedures; the preparation of methyl 2,3-*O*-isopropylidene-β-L-ribopyranoside[11] (**9a**) has been described earlier.

The monoacetates of **10a**, **22a**, and **9a** were obtained in yields of 75–86% by acetylation using acetic anhydride in pyridine in the usual way. Methyl 4-*O*-acetyl-2,3-*O*-isopropylidene-α-D-lyxopyranoside (**10b**) had b.p. 58–60° (bath) at 0.4 mmHg, $[\alpha]_D$ +25° (*c* 1.3, chloroform) (Found: C, 54.0; H, 7.6. $C_{11}H_{18}O_6$ calc.: C, 53.6; H, 7.4%). N.m.r. data: τ 4.95 (q, 1 H, $J_{4,5a} = J_{4,3}$ ~10 Hz, $J_{4,5e}$ ~5 Hz, H-4); 5.30 (d, 1 H, $J_{1,2}$ 3 Hz, H-1); 6.53 (s, 3 H, OMe); 7.90 (s, 3 H, OAc); and 8.46 and 8.65 (2 s, 6 H, CMe_2).

Methyl 5-*O*-acetyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (**22b**) had b.p. 58–60° (bath) at 0.25 mmHg, $[\alpha]_D$ −60° (*c* 2.4, chloroform) (Found: C, 53.9; H, 7.5%); the n.m.r. spectrum was identical with that published[22] in the literature.

Methyl 4-*O*-acetyl-2,3-*O*-isopropylidene-β-L-ribopyranoside (**9b**) had b.p. 51–53° (bath) at 0.25 mmHg, $[\alpha]_D$ +43° (*c* 0.9, chloroform), ν_{max}^{film} 1740 cm^{-1} (OAc) (Found: C, 53.9; H, 7.7%). N.m.r. data: τ 5.50, 5.93, and 6.20 (3 m, 6 H, H-1–H-5'); 6.53 (s, 3 H, OMe); 7.89 (s, 3 H, OAc); and 8.43 and 8.63 (2 s, 6 H, CMe_2). The compounds were all stable under the conditions used for g.l.c.

*Deamination of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-β-*L*-ribopyranoside* (**6**). — To a cooled (0°) solution of **6** (0.6 g) in 90% acetic acid (10 ml) was gradually added a solution of sodium nitrite (0.6 g) in water (0.6 ml), and the solution was set aside for 3 h at 0°; t.l.c. (light petroleum–acetone, 4:1) then showed that all the starting material had reacted. Water (10 ml) and chloroform (30 ml) were added and the separated organic layer was washed with cold, aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Removal of the solvent left a syrup (~0.45 g) which g.l.c. showed to contain **10a** (34.4%) and **10b** (65.6%).

A solution of the products (0.45 g) in methanol (15 ml) containing M sodium methoxide (2 ml) was heated under reflux for 2 h, whereafter the excess of base was neutralized (solid CO_2) and the solvent was removed. Water (10 ml) and chloroform (25 ml) were added, and the aqueous layer was further extracted with chloroform (25 ml). Concentration of the dried ($MgSO_4$) extracts yielded an oil (~0.19 g), shown (g.l.c.) to contain a single component. Distillation gave methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside (**10a**), b.p. 84–86° (bath) at 0.2 mmHg, $[\alpha]_D$ +45° (*c* 1.6, ethanol); lit.[10] b.p. 65° at 0.02 mmHg, $[\alpha]_D$ +42.7° (*c* 0.8, ethanol)*. The n.m.r. and i.r. spectra of this material were indistinguishable from those of an authentic sample. The derived toluene-*p*-sulphonate **4** had m.p. and mixture m.p. 105–106° (from ethanol), $[\alpha]_D$ −9.7° (*c* 1.8, ethanol); lit.[10] m.p. 96–97°, $[\alpha]_D$ −10.2° (*c* 1.9, ethanol); m.p. 104.5–105° and $[\alpha]_D$ +11.5° (*c* 1, chloroform) have been recorded[7] for the L enantiomer.

*Deamination of methyl 4-amino-4-deoxy-2,3-*O*-isopropylidene-α-*D*-lyxopyranoside* (**5**). — A cooled (0°) solution of **5** (1.4 g) in 90% acetic acid (20 ml) was treated with a solution of sodium nitrite (2.8 g) in water (5 ml) as described in the previous experiment. The following components were revealed by g.l.c. after work-up of the reaction mixture: **10a** (26.2%; retention time, 21.4 min), **21a** (18.4%; 17.2 min), **10b** (34.5%; 14.9 min), and **21b** (21.3%; 14.8 min).

Acetylation of a portion (0.29 g) of the products in pyridine (10 ml) containing acetic anhydride (10 ml), with work-up in the usual manner, afforded a mixture (0.27 g) of **10b** (~66%) and **21b** (~34%) (g.l.c. examination). The n.m.r. spectrum of this mixture was superimposable on that of a synthetic mixture containing **10b** and **22b**[22] (*i.e.*, the D enantiomer) in the proportions indicated.

Deacetylation of the mixture of **10b** and **21b** (0.7 g) with methanolic sodium methoxide (as previously described) gave an oil (0.63 g), which was partially resolved by chromatography on silica gel (elution with carbon tetrachloride–acetone, 9:1) to give methyl 2,3-*O*-isopropylidene-β-L-ribofuranoside (**21a**, 50 mg), $[\alpha]_D$ +72°

*The L enantiomer of **10a** is reported[7] to have m.p. 51.5–52.5°, $[\alpha]_D$ −47° (c 1, ethanol).

(*c* 0.8, chloroform); lit. (D-enantiomer)[12a] $[\alpha]_D$ −82.2° (*c* 2, chloroform); the n.m.r. and i.r. spectra of the isolated material were indistinguishable from those of the D enantiomer. The derived toluene-*p*-sulphonate **21c** had m.p. 82–83° (from ether–light petroleum), $[\alpha]_D$ +33° (*c* 0.7, ethanol); lit. (D enantiomer)[12b] m.p. 83–84°, $[\alpha]_D$ −35.5° (*c* 1, ethanol). Continued elution gave methyl 2,3-*O*-isopropylidene-α-D-lyxopyranoside (**10a**, 0.18 g), $[\alpha]_D$ +51° (*c* 1.2, chloroform), whose n.m.r. and i.r. spectra were identical with those of an authentic sample; lit.[10] $[\alpha]_D$ +42.7° (*c* 0.8, ethanol). The derived toluene-*p*-sulphonate **4** had m.p. and mixture m.p. 105–106° (from ethanol), $[\alpha]_D$ −13° (*c* 2, ethanol); lit.[10] m.p. 96–97°, $[\alpha]_D$ −10.2° (*c* 1.9, ethanol). An unresolved mixture (0.4 g) of **21a** and **10a** was also eluted from the column.

Deamination of methyl 5-amino-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside (**20**). — A cooled (0°) solution of **20** (2.3 g) in 90% acetic acid (40 ml) was treated with sodium nitrite (3 g) in water (2 ml) as previously described. The oil (2.2 g) containing **22ab**, obtained on work-up, was deacetylated (M sodium methoxide in methanol) to give methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**22a**, 1.5 g), b.p. 50–56° (bath) at 0.25 mmHg, $[\alpha]_D$ −75° (*c* 2, chloroform), the n.m.r. and i.r. spectra of which were identical with those of an authentic sample; lit.[12a] $[\alpha]_D$ −82.2° (*c* 2, chloroform). The derived toluene-*p*-sulphonate **18** had m.p. and mixture m.p. 83–84° (from ether–light petroleum); lit.[12] m.p. 83–84°.

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