The Deamination of Methyl 4-Amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talo- and -manno-pyranosides with Nitrous Acid [1]

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The deamination of methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (5) with nitrous acid in 90% acetic acid gives methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9) and the corresponding 4-acetate (10) as final products. Similar deamination of methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (2) gives compounds (9) and (10) together with the ring-contracted products methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (11) and the corresponding 5-acetate (12). The stereospecificity observed in the latter deamination is ascribed to solvent attack on an intermediate bicyclic oxonium ion (18) arising from participation of the ring-oxygen atom during heterolysis of the intermediate diazonium ion. Comparison is made with certain displacement reactions of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L(D)-mannopyranoside 4-sulphonates.

THE deamination of carbohydrate amines offers a potentially useful method of structure elucidation and synthesis despite the fact that complex mixtures of products can result from rearrangements accompanying decomposition of the intermediate diazonium ion.[2,3] A more complete knowledge of the factors which control the rearrangements is desirable, and such studies are in progress in this and other laboratories.[3] The activation energy for heterolysis of the diazonium ion is low,[4] and the reaction products can usually be correlated with the ground-state conformations of the starting amine; there are many examples in carbohydrate chemistry [2,3] and other areas [4,5] which illustrate the dependence of such reactions on ground-state conformation. Factors particularly relevant to carbohydrate chemistry have been noted [3,6] recently and will not be elaborated here. Our interest in the deamination of methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (2) was stimulated by the observation that ring-contracted products are derived from displacement reactions between anionic

[1] Preliminary communication, A. K. Al-Radhi, J. S. Brimacombe, and L. C. N. Tucker, *Chem. Comm.*, 1970, 1250.

[2] P. W. Austin, J. G. Buchanan, and R. M. Saunders, *Chem. Comm.*, 1965, 146; *J. Chem. Soc.* (*C*), 1967, 372; S. Inoue and H. Ogawa, *Chem. and Pharm. Bull.* (*Japan*), 1960, **8**, 79; B. C. Bera, A. B. Foster, and M. Stacey, *J. Chem. Soc.*, 1956, 4531; E. J. Reist, D. F. Calkins, and L. Goodman, *J. Amer. Chem. Soc.*, 1968, **90**, 3852.

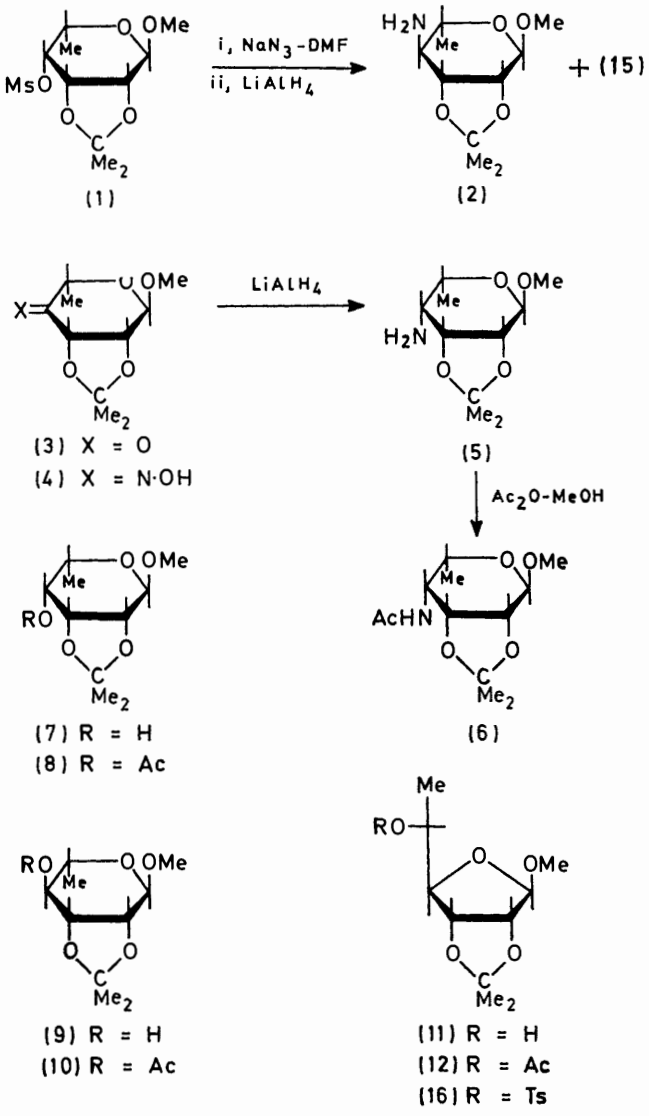
[3] N. M. K. Ng Ying Kim, J. M. Williams, and A. Horsington, *J. Chem. Soc.* (*C*), 1971, 1578.

[4] (*a*) H. Zollinger, ' Azo and Diazo Chemistry,' Interscience, New York, 1961, p. 126, and references cited therein; (*b*) J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

[5] D. J. Cram and J. E. McCarty, *J. Amer. Chem. Soc.*, 1957, **79**, 2866; B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *ibid.*, p. 6160.

[6] J. S. Brimacombe, *Fortschr. Chem. Forsch.*, 1970, **14**, 367.

nucleophiles and methyl 6-deoxy-2,3-*O*-isopropylidene-α-L(D)-mannopyranoside 4-sulphonates.[7-9] In view of certain similarities (but see ref. 4*b*) that have been noted [6] between the products obtained on deamination



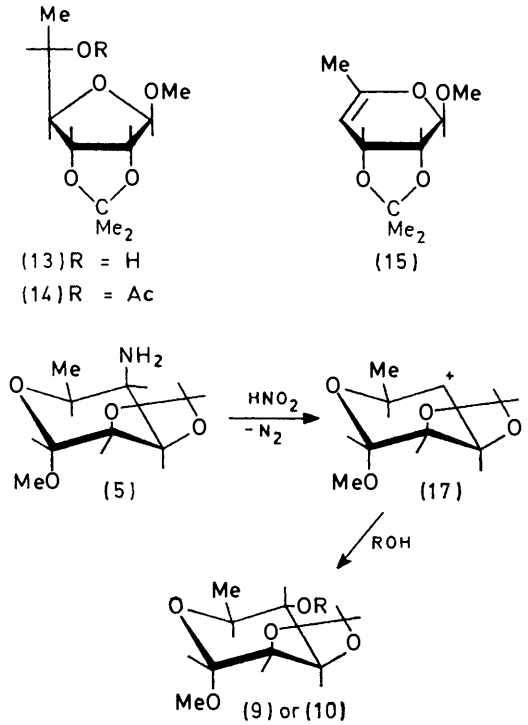
of pyranose amines and those resulting from unimolecular solvolysis of the corresponding sulphonates, it would be useful to effect a comparison in this case. In particular, it was hoped that such a comparison might enable the intervention of ion-pair intermediates to be discerned in the displacement reactions on the mannoside sulphonates. Deamination of the epimeric amine methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (5) was also studied for the purpose of comparison.

Methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (2) was prepared from methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methylsulphonyl-α-L-talopyranoside (1) essentially as described in ref. 10; the L-*talo*-amine (5) was obtained by oximation of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (3) [10,11] followed by reduction of the oxime (4) with lithium aluminium hydride in tetrahydrofuran. Reduction gave only one amine (as evidenced by g.l.c.), which was assigned the L-*talo*-configuration on the basis of similar experiments performed [12] on the enantiomeric ketone. This assignment was corroborated by conversion into methyl 4-acetamido-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (6), whose physical constants showed the expected correspondence with those of the crystalline D-enantiomer.[12] The following known compounds were prepared by literature procedures for use in g.l.c.: methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talopyranoside [10] (7), methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside [13] (9), methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside [14] (11), and methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside [15] (13). The corresponding acetates (8), (10), (12), and (14), respectively, were prepared by acetylation of the alcohols with acetic anhydride in pyridine, and were purified either by distillation or recrystallisation. The conditions used for g.l.c. (see Experimental section for details) did not permit the two acetates (10) and (12) to be distinguished, neither were the two alcohols (7) and (11) separated. Fortunately, in these cases, the corresponding pairs of alcohols and acetates, respectively, were resolved by g.l.c., so that the products of the deaminations in 90% acetic acid could at least be qualitatively assayed. For example, the presence of both acetates (10) and (12) in the acetylated fraction could be inferred when the chromatograms also showed the presence of both alcohols (9) and (11). Perhaps the most important aspect of the analysis by g.l.c. was that it permitted certain of the compounds (7)—(14) to be definitely excluded as products of the deaminations.

Methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (5) was deaminated in 90% acetic acid at *ca.* 0° to give three products, two of which were identified (g.l.c.) as methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9) (32%) and the corresponding 4-acetate (10) (57%). The third component (11%) was not identified, but it was distinguishable from the other standard compounds used for g.l.c. and also from methyl 4,6-dideoxy-2,3-*O*-isopropylidene-β-D-*erthryo*-hex-4-eno-pyranoside [10] (15), which might have been

[7] C. L. Stevens, R. P. Glinski, K. G. Taylor, P. Blumbergs, and F. Sirokman, *J. Amer. Chem. Soc.*, 1966, **88**, 2073.
[8] S. Hanessian, *Chem. Comm.*, 1966, 796.
[9] (*a*) C. L. Stevens, R. P. Glinski, G. E. Gutowski, and J. P. Dickerson, *Tetrahedron Letters*, 1967, 649; (*b*) L. N. Owen, *Chem. Comm.*, 1967, 526.
[10] J. S. Brimacombe, O. A. Ching, and M. Stacey, *J. Chem. Soc.* (*C*), 1969, 1270.
[11] P. M. Collins and W. G. Overend, *J. Chem. Soc.*, 1965, 1912.
[12] C. L. Stevens, R. P. Glinski, and K. G. Taylor, *J. Org. Chem.*, 1968, **33**, 1586.
[13] (*a*) P. A. Levene and I. E. Muskat, *J. Biol. Chem.*, 1934, **105**, 431; (*b*) J. Jarý, K. Čapek, and J. Kovář, *Coll. Czech. Chem. Comm.*, 1963, **28**, 2171.
[14] P. A. Levene and J. Compton, *J. Biol. Chem.*, 1936, **116**, 169.
[15] E. J. Reist, L. Goodman, R. R. Spencer, and B. R. Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 3962.

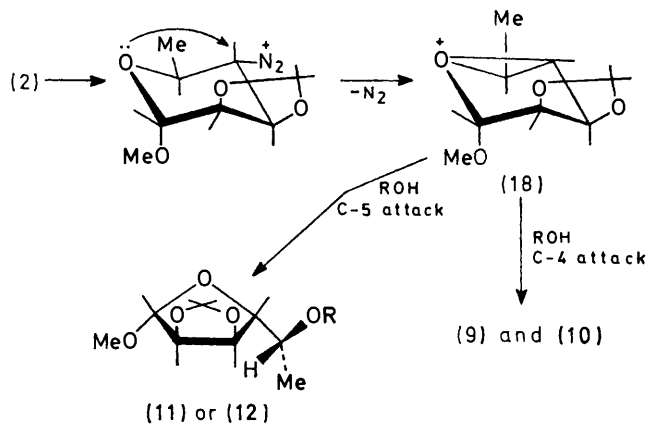
formed by an elimination. Acetylation of the deamination products gave the crystalline 4-acetate (10), with no other acetates being detected by g.l.c. The acetate (10) was identified by comparison (i.r. spectrum, m.p. and mixed m.p.) with an authentic material.



Similar deamination of methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (2) gave four products, which were adduced from g.l.c. to be methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9), the corresponding 4-acetate (10), methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (11), and the corresponding 5-acetate (12). Deacetylation of the products gave a mixture of the alcohols (9) (30%) and (11) (70%), which were identified by comparison with authentic samples [13,14] after separation on silica gel. The latter alcohol was further characterised by conversion into crystalline methyl 6-deoxy-2,3-*O*-isopropylidene-5-*O*-*p*-tolylsulphonyl-β-D-allofuranoside [15] (16), whereas acetylation of (9) afforded crystalline methyl 4-*O*-acetyl-6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (10) (identified by mixed m.p., *etc.* with an authentic sample).

The striking feature of the results is the stereospecificity shown in both deaminations. In the deamination of the axial L-*talo*-amine (5), the inverted products (9) and (10) must largely arise either by an S_N2 mechanism [16] (involving solvent participation in the heterolysis of the $C-\overset{+}{N}_2$ bond), or, more likely, by an S_Ni process [4] involving the solvated carbonium ion (17). The stereospecific attack of solvent on the carbonium ion (17) can presumably be attributed to steric factors. However, it is realised that deaminations are complex reactions, and this is testified to by the fact that deamination of *cis*- and *trans*-4-t-butylcyclohexylamine proceeds [17] by a combination of S_Ni, S_N2, and $E2$ mechanisms and mechanisms involving an intermediate solvated carbonium ion.

The stereospecific formation of the compounds (9)—(12) on deamination of the equatorial L-*manno*-amine (2) is considered to be due to participation of the ring-oxygen atom in the heterolysis of the $C-\overset{+}{N}_2$ bond leading to the bicyclic oxonium ion (18). This participation presumably involves direct interaction



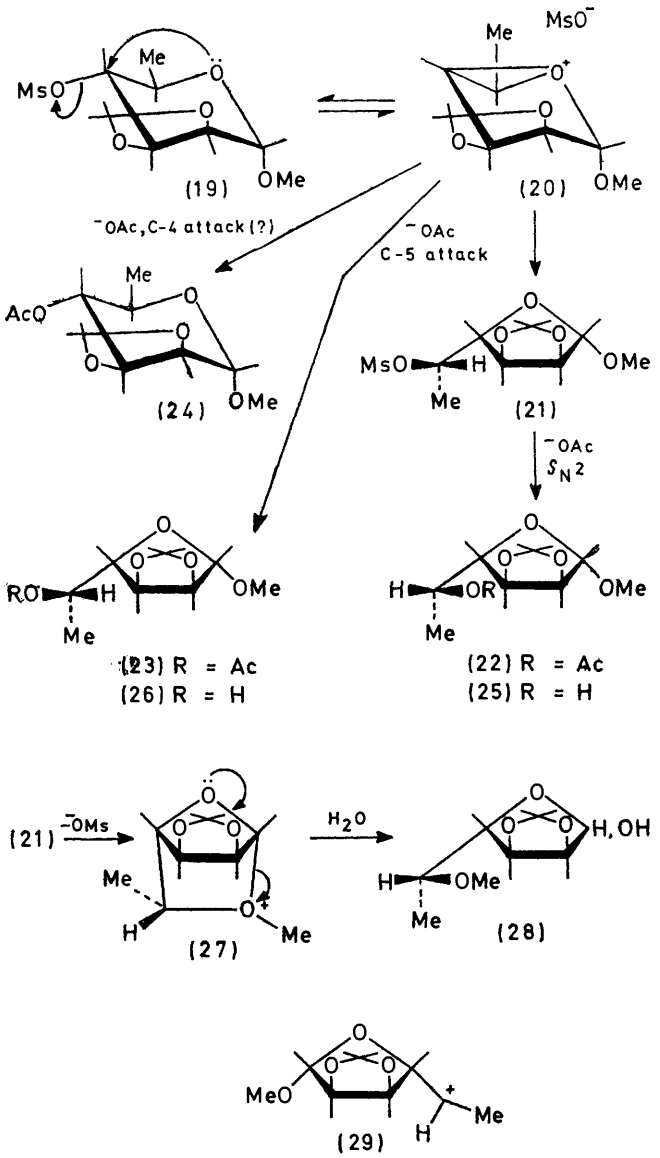
between a developing *p*-orbital at C-4 and one of the lone pair orbitals on the ring-oxygen atom, similar to that suggested [18] in the acetolysis of *endo*-9-oxabicyclo-[4,2,1]nonan-2-yl *p*-bromobenzenesulphonate. Attack of solvents on the oxonium ion (18) at C-4 would yield the L-mannopyranoside derivatives (9) and (10), whereas attack at C-5 would give the D-allofuranosides (11) and (12). There are compelling stereoelectronic reasons why these reactions should preferably occur with inversion of configuration at the relevant carbon atoms on opening of the three-membered ring. Attack at C-1 of the oxonium ion (18) is also possible but any products from such attack may have been lost in processing the deamination mixture. It would be predicted that this mode of attack would be relatively unimportant, since nucleophilic attack should greatly favour opening of the strained, three-membered ring of the bicyclic oxonium ion (18). However, this mode of opening occurs to a small extent with a related bicyclic oxonium ion resulting from deamination of methyl 4-amino-4-deoxy-α-D-glucopyranoside, as shown by the fact that one of the products was 4,5-anhydro-D-galactose.[3]

Bimolecular displacements on methyl 6-deoxy-2,3-*O*-isopropylidene-α-L(D)-mannopyranoside 4-sulphonates are severely impeded by the β-*trans*-axial substituent at C-2,[19] so that these sulphonates undergo a unimolecular displacement presumably involving participation by the ring-oxygen atom. One of the most

[16] C. W. Shoppee, R. E. Lack, and P. Ram, *J. Chem. Soc.* (*C*), 1966, 1018.
[17] C. W. Shoppee, C. Culshaw, and R. E. Lack, *J. Chem. Soc.* (*C*), 1969, 506.
[18] L. A. Paquette and P. C. Storm, *J. Amer. Chem. Soc.*, 1970, **92**, 4295.
[19] A. C. Richardson, *Carbohydrate Res.*, 1969, **10**, 395.

thoroughly studied reactions is that of methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methylsulphonyl-α-D-mannopyranoside (19) with acetate ion in refluxing *NN*-dimethylformamide, which yields [7] the rearranged products methyl 5-*O*-acetyl-6-deoxy-2,3-*O*-isopropylidene-α-D-talofuranoside (22) and the epimeric β-L-allofuranoside (23) in a ratio of 7 : 1, respectively. A related displacement on the enantiomeric methanesulphonate with azide ion yielded [8] methyl 5-azido-5,6-dideoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (34%). The most striking difference between the products of the displacement and the deamination reactions described above is the formation of significant proportions of products having the *talo*-configuration in the former reactions. While it is entirely reasonable to invoke [6,20] the bicyclic oxonium ion (20) as an intermediate in the displacements, direct nucleophilic attack on this ion cannot, for stereoelectronic reasons, lead to the α-D-talofuranoside 5-acetate (22), although the β-L-allofuranoside 5-acetate (23) and methyl 4-*O*-acetyl-6-deoxy-2,3-*O*-isopropylidene-α-D-mannopyranoside (24) might be expected to be formed in this way. This pathway appears to be of minor importance, judging from the small proportion of (23) formed [7] and from the failure to detect any of compound (24), although the latter could conceivably have been overlooked. The possibility that ion pairs might be involved in these displacements has been alluded to by others [7,9b,20] and we feel offers the best explanation for the formation of the talofuranosides by a double inversion at C-5 leading to overall retention of configuration at this position. Ion pair return to the oxonium ion (20) would lead either to the original methanesulphonate (19) or to methyl 6-deoxy-2,3-*O*-isopropylidene-5-*O*-methylsulphonyl-β-L-allofuranoside (21), by an essentially irreversible process. There are many precedents [15,21] to show that the rearranged sulphonate (21) would undergo S_N2 displacement of the sulphonate group with acetate ion to give the inverted acetate (22). An ion pair intermediate almost certainly intervenes in the solvolysis [7] of methanesulphonate (19) in aqueous dioxan in the presence of sodium hydrogen carbonate to give compounds (25) and (26) and 6-deoxy-2,3-*O*-isopropylidene-5-*O*-methyl-D-talofuranoside (28), in the ratio of 1 : 2 : 6. In this case, intramolecular participation by the glycosidic methoxy-group [leading to (27)] is able to complete with solvent in displacements on the rearranged methanesulphonate (21). Supporting evidence was derived from the fact that the *p*-bromobenzenesulphonate analogous to (21) yielded compounds (28) (89%), (25) (9%), and (26) (2%) on solvolysis under the same reaction conditions. The use of aqueous dioxan as the solvolytic medium might explain the presence of both the alcohols (25) and (26), since racemisation is encountered [22] in solvolyses of 1-methylheptyl sulphonates in aqueous dioxan originating from a stereospecific double inversion involving the 'inert' component of the solvent mixture.

Finally, stereospecific attack of iodide ion on the oxonium ion (18) has recently been proposed [23] to



account for the formation of methyl 4,6-dideoxy-4-iodo-2,3-*O*-isopropylidene-α-L-mannopyranoside and methyl 5,6-dideoxy-5-iodo-2,3-*O*-isopropylidene-β-D-allofuranoside on treatment of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9) with triphenyl phosphite methiodide in benzene. However, the suggestion that the small proportion of methyl 5,6-dideoxy-5-iodo-2,3-*O*-isopropylidene-α-L-talofuranoside formed might be ascribed to rearrangement of the oxonium ion (18) to the open-chain carbonium ion (29) seems unnecessary, since it could equally well arise from iodide exchange

[20] B. Capon, *Chem. Rev.*, 1969, **69**, 471.
[21] D. H. Ball and F. W. Parrish, *Adv. Carbohydrate Chem. and Biochem.*, 1969, **24**, 139.
[22] H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, 1965, **87**, 287.
[23] N. K. Kochetkov, A. I. Usov, and K. S. Adamyants, *Tetrahedron*, 1971, **27**, 549.

on methyl 5,6-dideoxy-5-iodo-2,3-*O*-isopropylidene-β-D-allofuranoside.

EXPERIMENTAL

Kieselgel G (Merck) was used for t.l.c.; spots were detected with vanillin–sulphuric acid.[24] G.l.c. was carried out on a Pye 104 chromatograph (10% silicone oil on Celite at *ca.* 160°). I.r. spectra were recorded for either Nujol mulls or liquid films using a Perkin-Elmer 'Infracord' spectrometer. Optical rotations were measured at ambient temperature with a Perkin-Elmer 141 polarimeter.

Preparation of Authentic Compounds for G.l.c.—The following compounds were prepared essentially as described in the literature: methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talopyranoside [10] (7), methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside [13] (9), methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside [14] (11), and methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside [15] (13). Acetylation of the foregoing alcohols with acetic anhydride in pyridine gave *methyl* 4-O-*acetyl*-6-*deoxy*-2,3-O-*isopropylidene*-α-L-*talopyranoside* (8), b.p. 118—119° at *ca.* 0·1 mmHg, $[\alpha]_D$ −38° (*c* 1 in $CHCl_3$) (Found: C, 55·7; H, 7·9. $C_{12}H_{20}O_6$ requires C, 55·4; H, 7·7%); *methyl* 4-O-*acetyl*-6-*deoxy*-2,3-O-*isopropylidene*-α-L-*mannopyranoside* (10), m.p. 68—69° (from aqueous ethanol), $[\alpha]_D$ −16° (*c* 1 in $CHCl_3$) (Found: C, 55·6; H, 7·2%); *methyl* 5-O-*acetyl*-6-*deoxy*-2,3-O-*isopropylidene*-β-D-*allofuranoside* (12), b.p. 127—128° at *ca.* 0·1 mmHg, $[\alpha]_D$ −67·5° (*c* 1 in $CHCl_3$) (Found: C, 55·5; H, 7·2%), and *methyl* 5-O-*acetyl*-6-*deoxy*-2,3-O-*isopropylidene*-α-L-*talofuranoside* (14), b.p. 105° at *ca.* 1 mmHg, $[\alpha]_D$ −59·5° (*c* 1 in $CHCl_3$) (Found: C, 55·5; H, 7·4%).

Methyl 4-*Amino*-4,6-*dideoxy*-2,3-O-*isopropylidene*-α-L-*mannopyranoside* (2).—This compound, b.p. 98—100° at 0·05 mmHg, $[\alpha]_D$ −54° (*c* 1 in MeOH), was prepared as previously described,[10] although it was not then isolated by distillation (Found: C, 55·0; H, 8·8; N, 6·2. Calc. for $C_{10}H_{19}NO_4$: C, 53·3; H, 8·7; N, 6·4%); g.l.c. retention time 13·1 min; i.r. spectrum identical with that of a sample obtained previously.

Acetylation of the amine (2) (60 mg) with acetic anhydride in methanol yielded methyl 4-acetamido-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (55 mg), m.p. 92—93° [from ethyl acetate–light petroleum (b.p. 40—60°)], $[\alpha]_D$ −23° (*c* 1 in MeOH) {lit.,[10] m.p. 82—84°, $[\alpha]_D$ −23° (*c* 1·8 in MeOH)}.

Methyl 6-*Deoxy*-2,3-O-*isopropylidene*-α-L-lyxo-*hexopyranosid*-4-*ulose Oxime* (4).—A solution of the ketone (3) [10] (4 g) in pyridine–ethanol (1 : 1; 40 ml) containing hydroxylamine hydrochloride (5 g) was heated for 2 h under gentle reflux. The cooled solution was evaporated and the residual syrup crystallised upon the addition of water (40 ml). Recrystallisation from ether–n-hexane yielded the oxime (4) (3·8 g), m.p. 129—129·5°, $[\alpha]_D$ −156° (*c* 1 in MeOH) {lit.,[12] (D-enantiomer) m.p. 124·5—126°, $[\alpha]_D$ +155·3° (*c* 1·54 in MeOH)}.

Methyl 4-*Amino*-4,6-*dideoxy*-2,3-O-*isopropylidene*-α-L-*talopyranoside* (5).—A solution of the oxime (4) (3·8 g) in dry tetrahydrofuran (8 ml) was added dropwise during 1 h to a stirred suspension of lithium aluminium hydride (2 g) in tetrahydrofuran (40 ml). The mixture was heated under reflux for 20 h, then cooled to room temperature, and the excess of hydride was decomposed with ethyl acetate and water. Solids were filtered off and washed with chloroform, and the solvents were removed. Distillation of the residue gave the L-*talose amine* (5) (2·85 g), b.p. 70—71° at 0·01 mmHg, $[\alpha]_D$ −66·5° (*c* 1·2 in MeOH) (Found: C, 55·3; H, 8·8; N, 6·2. $C_{10}H_{19}NO_4$ requires C, 55·3; H, 8·7; N, 6·4%). G.l.c. showed the presence of only one component, retention time 9·5 min [*cf.* the L-mannose amine (2), retention time 13·1 min].

Acetylation of the amine (5) (0·1 g) with acetic anhydride in methanol gave methyl 4-acetamido-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (6) (50 mg), m.p. 155—156°, $[\alpha]_D$ −27° (*c* 1 in MeOH) {lit.,[12] (D-enantiomer) m.p. 149—150°, $[\alpha]_D$ +27·1° (*c* 0·5 in MeOH)}.

Deamination of Methyl 4-*Amino*-4,6-*dideoxy*-2,3-O-*isopropylidene*-α-L-talopyranoside (5).—A solution of sodium nitrite (0·35 g) in water (0·5 ml) was added during 30 min to a cooled (0°) solution of the amino-sugar (5) (0·5 g) in 90% acetic acid (8 ml), and the solution was set aside for 1 h at 0°; t.l.c. then showed that all the starting material had reacted. Water (10 ml) and chloroform (20 ml) were added and the separated organic layer was washed with a cold solution of sodium hydrogen carbonate, then with water, and dried ($MgSO_4$). Removal of the solvent left a syrup (0·5 g), which g.l.c. showed to contain three components: methyl 4-*O*-acetyl-6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (10) (57%; retention time 11 min), methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9) (32%; 7·25 min), and an unidentified component (11%; 4·5 min). The identities of compounds (9) and (10) were confirmed by co-injection with authentic samples.

Acetylation of the product mixture with acetic anhydride in pyridine and distillation (b.p. 70—75° at 0·01 mmHg) of the residue gave the acetate (10) (0·12 g), which slowly crystallised. The recrystallised material had m.p. 68—69°, $[\alpha]_D$ −16° (*c* 1 in $CHCl_3$), and the m.p. was not depressed on admixture with an authentic sample. G.l.c. of the acetylated products showed that no other acetates were present.

Deamination of Methyl 4-*Amino*-4,6-*dideoxy*-2,3-O-*isopropylidene*-α-L-*mannopyranoside* (2).—A cooled (0°) solution of the amino-sugar (2) (0·5 g) in 90% acetic acid (8 ml) was treated with a solution of sodium nitrite (0·5 g) in water (0·5 ml) as described in the previous experiment. G.l.c. after processing the reaction mixture indicated that four products had been formed: methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9) (16·5%; 7·3 min), methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (11) (32·5%; 6·9 min), and the corresponding acetates (10) and (12) (51% combined; 10·9 min), respectively. The identities of the products were substantiated by co-injection with authentic samples.

The products of deamination (*ca.* 0·5 g) in methanol (20 ml) were deacetylated on heating with N-sodium methoxide for 2 h under gentle reflux. After work-up of the neutralised solution, g.l.c. of the residual syrup (0·44 g) showed the presence of the alcohols (9) (30%) and (11) (70%), respectively; although the alcohol (11) could not be separated from the isomeric alcohol (7) by g.l.c., the presence of the latter pyranoside could be excluded on the grounds that the corresponding acetate (8) was not observed in the original mixture. The deacetylated products were chromatographed on silica gel [elution with n-hexane–ether (4 : 1) containing 0·2%

[24] 'Chromatography,' E. Merck AG, Darmstadt, 2nd edn., p. 30.

triethylamine] to give first methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (11) (0·2 g), b.p. 73—74° at *ca.* 0·1 mmHg, $[\alpha]_D$ −78° (*c* 1 in MeOH) {lit.,[15] b.p. 74—76° at 0·7 mmHg, $[\alpha]_D$ −73·8° (*c* 2·3 in MeOH)}; i.r. and n.m.r. spectra indistinguishable from those of an authentic sample. The 5-tosylate (16), m.p. 95—96° (from methanol), $[\alpha]_D$ −47° (*c* 1 in MeOH) {lit.,[15] m.p. 91—92°, $[\alpha]_D$ −41·1 ± 4° (*c* 0·34 in MeOH)}, showed no depression of m.p. on admixture with an authentic sample. Continued elution yielded methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (9) (*ca.* 0·1 g), b.p. 98—100° at *ca.* 0·1 mmHg, $[\alpha]_D$ −17 ± 2° (*c* 0·9 in MeOH) {lit.,[13] b.p. 110—112° at 1 mmHg, $[\alpha]_D$ −14·1° (*c* 1·5 in H_2O); an authentic sample had $[\alpha]_D$ −14° (*c* 1 in MeOH)}. The 4-acetate (10) had m.p. and mixed m.p. 68—69° (from aqueous ethanol), $[\alpha]_D$ −16° (*c* 1 in $CHCl_3$).

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