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THE DEAMINATION OF METHYL 5-AMINO-5,6-DIDEOXY-2,3-*O*-ISOPROPYLIDENE-α-L-TALO- AND -β-D-ALLO-FURANOSIDE WITH NITROUS ACID*[1]

JOHN S. BRIMACOMBE, JONATHAN MINSHALL, AND LESLIE C. N. TUCKER
Chemistry Department, The University, Dundee DD1 4HN (Great Britain)
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ABSTRACT

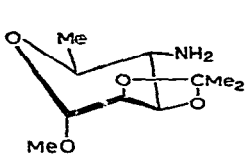
Deamination of methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**6**) with sodium nitrite in 90% acetic acid at ~0° gave methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**8a**) and methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**9a**) (combined yield, 12.3%), the corresponding 5-acetates **8b** (2.9%) and **9b** (26.4%), and the unsaturated sugar methyl 5,6-dideoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hex-5-enofuranoside (**10**) (43.5%). Similar deamination of methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**7**) gave **8a** and **9a** (combined yield, 20.4%), **8b** (12.5%), **9b** (25.8%), **10** (7.7%), and the rearranged products 6-deoxy-2,3-*O*-isopropylidene-5-*O*-methyl-L-talofuranose (**13a**, 17.5%) and the corresponding 1-acetate **13b** (14.1%). A synthesis of **13a** was accomplished by successive methylation and debenzylation of the conveniently prepared benzyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**15b**). Differences between the two sets of deamination products can be rationalized by assuming that the carbonium-ion intermediate reacts in the initial conformation assumed, before significant interconversion to other conformations occurs.

INTRODUCTION

There has recently been a resurgence of interest in the deamination of amino sugars, and systematic studies have attempted to unravel the multifarious rearrangements that occur[2]. The stereochemistry of the products resulting from deamination of methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (**1**) in 90% acetic acid requires[3] the intermediacy of the bicyclic oxonium ion **2**, and it was possible to exclude the intervention of the open carbonium ion **3**, which could arise from 'leakage' from the oxonium ion **2**. In foreseeing the need to differentiate between the reactions of the intermediates **2** and **3**, we sought to prepare the carbonium ion **3** by deamination of both methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**6**) and the diastereoisomeric β-D-allofuranoside amine **7**. Since deamina-

*Dedicated to Dr. Horace S. Isbell, in honour of his 75th birthday.

tive reactions are subject to ground-state control, different sets (or proportions) of products are invariably encountered in the deamination of diastereoisomeric, acyclic amines[4]. Thus, it is advisable to examine the behaviour of both **6** and **7** towards deamination.



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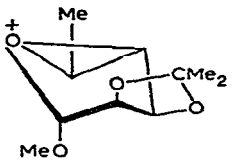

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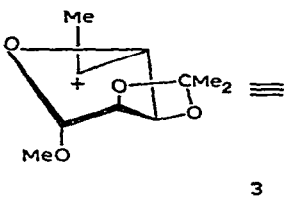

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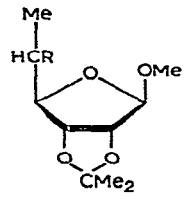

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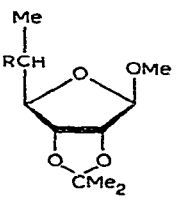
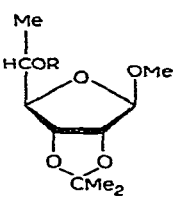
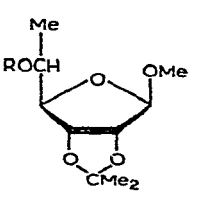
6 R = NH_2



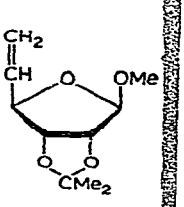
5 R = N_3
7 R = NH_2



8a R = H
8b R = Ac



9a R = H
9b R = Ac
9c R = Ts
9d R = BS



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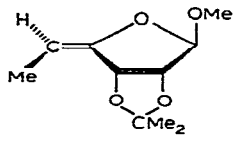
RESULTS

Methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**6**) was prepared by reduction of the azide **4**[5] with lithium aluminium hydride; minor impurities were removed by preparative g.l.c. Similar reduction of the isomeric azide **5**[6] gave chromatographically homogeneous methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**7**).

Treatment of the L-*talo*-amine **6** with sodium nitrite in 90% acetic acid at ~0° gave **8a** and **9a** (combined yield, 12.3%)*, **8b** (2.9%), **9b** (26.4%), and **10** (43.5%). The identification of compounds **8ab** and **9ab** was achieved by g.l.c.–m.s. (see Experimental), whereas a rigorous characterisation of the unsaturated sugar **10** required its isolation as detailed below. Deacetylation of the deamination products with sodium methoxide, followed by chromatography on silica gel, enabled methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**9a**, characterized as the crystalline toluene-*p*-sulphonate **9c**[7]) to be isolated, but the epimeric derivative **8a** was not recovered in amounts sufficient for characterisation. This chromatographic procedure also gave the unsaturated sugar methyl 5,6-dideoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hex-5-enofura-

*Judging from the small proportion of **8b** produced in the deamination of **6**, it seems safe to assume that this mixture contains mainly **9a**, although it was not possible to separate **8a** and **9a** on the chromatographic columns used.

noside (**10**), which is the principal product of the deamination. The gross composition of the unsaturated sugar **10** was indicated by elemental analysis and mass spectrometry [*m/e* 185 (M−15)], while the presence of a C=C bond was revealed by a weak i.r. absorption at 1650 cm^{-1}. A solution of bromine in carbon tetrachloride was rapidly decolourized by **10**. The n.m.r. spectrum of **10** was distinct from that of the isomeric unsaturated sugar **11**[8] ($J_{5,6}$ 7 Hz) and clearly showed the presence of three olefinic protons as a modified ABX pattern. This evidence locates the double bond at the terminal position, and the other spectral characteristics are consistent with the structure assigned. It is notable that such terminal olefins as **10** are not significant products in displacement reactions on the corresponding sulphonates[5,7], although the isomer **12** has recently been identified[8] amongst the products of displacement reactions on methyl 6-deoxy-2,3-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-α-L-mannofuranoside.



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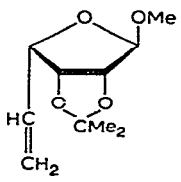

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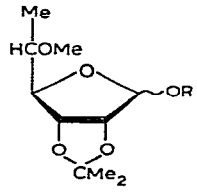
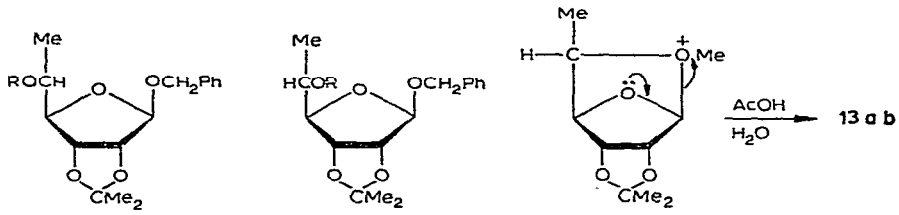


13a R = H
13b R = Ac

Similar deamination of methyl 5-amino-5,6-dideoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**7**) afforded **8a** and **9a** (combined yield, 20.4%), **8b** (12.5%), **9b** (25.8%), **10** (7.7%), **13a** (17.5%), and **13b** (14.1%). Compounds **8a–10** were identified by comparison with available standards, whereas characterization of the rearranged product **13a** (and by inference **13b**) required the synthesis of an authentic sample of 6-deoxy-2,3-*O*-isopropylidene-5-*O*-methyl-α-L-talofuranose. This was achieved either by solvolysis in aqueous *p*-dioxane of methyl 5-*O*-(*p*-bromobenzenesulphonyl)-6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside[9] (**9d**), in which participation and migration of the glycosidic methoxyl-group occurs, or by the following procedure. Benzyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside[10] (**14a**) was converted into the sulphonate **14b** and then into benzyl 5-*O*-benzoyl-6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**15a**) by treatment with sodium benzoate in *N,N*-dimethylformamide. Debenzoylation of **15a** gave the crystalline alcohol **15b**, which was transformed into **13a** following methylation and debenzylation. The latter compound proved to be identical (m.s. and g.l.c.) with the product obtained[9] by solvolysis of **9d**. Although the solvolytic route is shorter, careful chromatography is required to isolate the product, which is obtained in only modest yield when **9d** is solvolysed in boiling, aqueous *p*-dioxane; the temperature used in this solvolysis is lower than that (170°) reported in the literature[9] and presumably accounts for the low yields of **13a** obtained as a result of incomplete reaction.



DISCUSSION

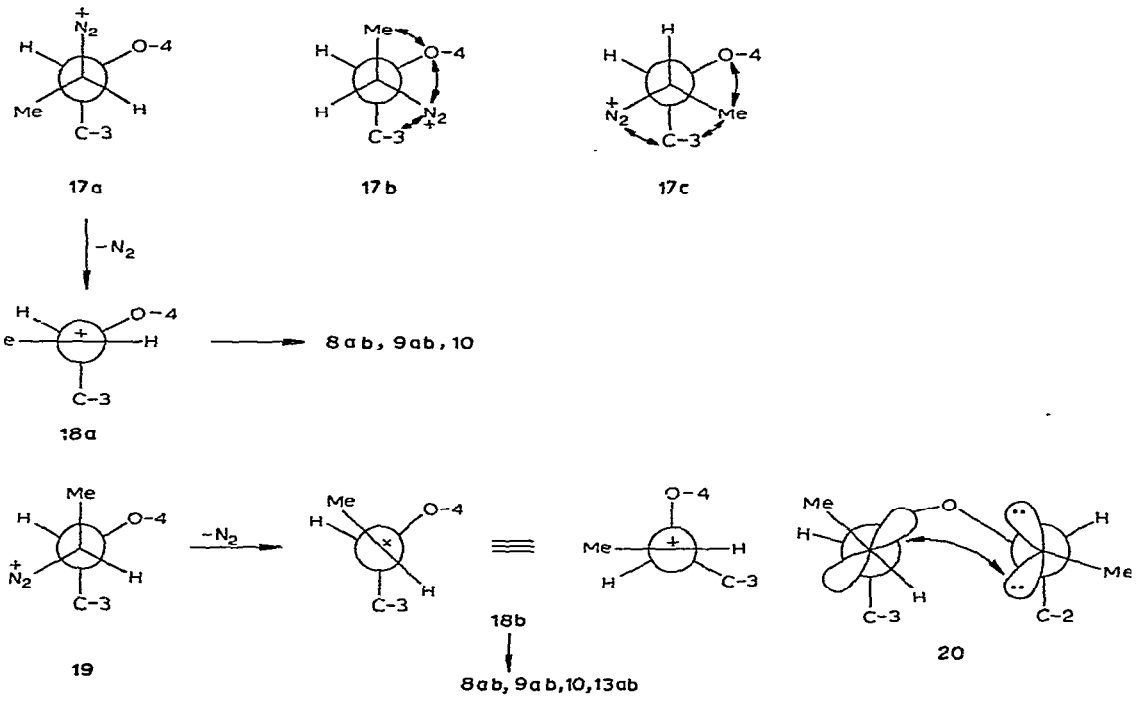
Despite the long-standing interest in the deamination of primary aliphatic amines, the mechanism of the decomposition is not completely understood, and several competing pathways, each with its own characteristic stereochemistry, have been proposed[4] to account for the stereochemical outcome of the reactions*. In view of the mechanistic uncertainty, anything more than a qualitative treatment of the results of the deaminations of **6** and **7** would not be justified. Nevertheless, certain clear-cut differences between the two sets of deamination products can be noted. For example, the terminal unsaturated sugar **10** is only a minor product of deamination of the D-*allo*-amine **7**, whereas it is formed in significant proportions on deamination of the L-*talo*-amine **6**. A further point to note is that the rearranged products **13ab** are formed only in the deamination of the D-*allo*-amine **7**, presumably by a mesomerically assisted opening of the oxonium ion **16**.

The formation of different sets of products from the deamination of diastereoisomeric amines can be anticipated if the initially formed carbonium ion reacts before significant interconversion between the individual conformers occurs by rotation about the adjacent carbon–carbon bond[4]. Heterolysis of the C-N_2^+ bond requires little activation energy, so that deamination primarily occurs from the most-populated conformation of the diazonium ion[4]. The most stable conformation about the C-4–C-5 bond of the L-*talo*-diazonium ion would be expected to be **17a**, since the bulky groups are each flanked by a hydrogen atom on one side (*cf.* conformations **17b** and **17c**). The relatively large value of 9 Hz for $J_{4,5}$ in the parent amine **6** is compatible[11] with a predominantly antiparallel arrangement of H-4 and H-5, and it is reasonable to assume that a similar situation holds for the derived diazonium ion. Heterolysis of the C-N_2^+ bond will give the carbonium ion assuming the conformation **18a**, which will be transformed into products by attack of solvent (to give **8ab** and **9ab**) or by elimination of a proton from the terminal methyl group (to give **10**). The solvolytic

*Although the reaction pathway $RNH_2 \rightarrow RNHNO \rightarrow RN{:}NOH(Ac) \rightarrow \overset{+}{R}N_2 \rightarrow [R^+]_{SOH} \rightarrow$ products is generally accepted for the deamination of primary amines in aqueous or acetic acid solutions, opinions vary as to whether product formation occurs simultaneously with, or subsequent to, the loss of the nitrogen from the alkyldiazonium ion[4].

products of deamination of **6** have preponderantly the inverted (D-*allo*) configuration at C-5, although there is no obvious reason why these should be formed preferentially from the carbonium ion **18a**.

In applying similar considerations to the D-*allo*-amine **7**, the conformation **19** is assumed to be the most stable conformation of the diazonium ion; the $J_{4,5}$ value of 8 Hz for the amine **7** implies[11] that H-4 and H-5 assume a predominantly antiparallel arrangement. In this case, the products will result from solvolytic, elimination, and



rearrangement reactions of the carbonium-ion intermediate in the conformation **18b**. In this conformation, the vacant p-orbital at C-5 and one of the lone-pair orbitals on the glycosidic oxygen atom are suitably oriented (see **20**) for overlap to form the oxonium-ion intermediate **16**. A mesomerically assisted opening of the oxonium ion **16** and attack of solvent on the resulting carboxonium ion would yield the rearranged products **13ab**; in this respect, deamination of the amine **7** resembles the solvolysis[3,9,12] of the corresponding bromobenzenesulphonate **9d**. In neither deamination was there evidence for participation by the oxygen atom of the furanose ring, as judged by the absence of pyranosidic products.

Although secondary carbonium ions have been proposed[4] in most mechanistic schemes for the diazotisation of *sec*-alkyl amines, Friedman[4c] has opined "... that a more internally plausible and consistent picture can be made if both secondary carbonium ions and diazonium ions are considered as product- or intermediate-

forming precursors, the extent of each dependent on reaction conditions and structural and conformation factors". As there is no information relating to the partitioning between these pathways in the diazotisation of amino sugars **6** and **7**, we have considered only secondary carbonium ions as intermediates, but recognize that the true situation is probably more complex.

EXPERIMENTAL

Kieselgel G (Merck) was used for t.l.c., and spots were detected with vanillin–sulphuric acid[13]. 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% 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. was carried out on a Pye 104 chromatograph (nitrogen carrier gas, 7 p.s.i., flame-ionization detector), using a column of 25% silicone gum on Celite at an operating temperature of 160°. Preliminary identification of products from the deaminations was achieved by g.l.c., by co-injection with authentic samples. Light petroleum refers to the fraction having b.p. 60–80°.

Authentic compounds for g.l.c. — Methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**8a**) and methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**9a**), and the corresponding acetates **8b** and **9b**, were prepared as described previously[3]. 6-Deoxy-2,3-*O*-isopropylidene-5-*O*-methyl-L-talofuranose (**13a**) was obtained either by solvolysis of methyl 5-*O*-(*p*-bromobenzenesulphonyl)-6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside[9] (**9d**) in boiling, aqueous *p*-dioxane, or by the route described below. The compounds were all stable under the conditions used for g.l.c.

Benzyl 6-deoxy-2,3-O-isopropylidene-α-L-talofuranoside (**15b**). — A solution of the benzyl allofuranoside **14a**[10] (3.1 g) in dry pyridine (5 ml) was treated at 0° with a solution of toluene-*p*-sulphonyl chloride (8.3 g) in chloroform (15 ml) for 12 h. Work-up in the usual manner, with chromatography on silica gel (elution with light petroleum–chloroform, 2:1), gave the sulphonate **14b** (~4 g), $[\alpha]_D$ −63 ±2° (*c* 1, chloroform), as a syrup. N.m.r. data: τ 2.40 (*m*, 4 aromatic protons, OTs); 2.60 (*s*, 5 aromatic protons, $PhCH_2O$); 4.85 (*s*, 1 proton, H-1); 5.40 (*q*, 2 protons, J_{AB} 12 Hz, CH_2Ar); 7.60 (*s*, 3 protons, Ar-Me); 8.60 and 8.78 (2*s*, 6 protons, CMe_2); and 8.75 (*d*, 3 protons, $J_{5,6}$ 6 Hz, C-5–Me).

A solution of the sulphonate **14b** (0.88 g) in *N*,*N*-dimethylformamide (25 ml) containing sodium benzoate (1.5 g) was heated under reflux for 12 h, water (25 ml) was then added, and the solution was extracted with ether (3 × 50 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated to give the L-talofuranoside benzoate **15a** (0.46 g), ν_{max}^{film} 1730 cm^{-1}. A solution of the benzoate (0.44 g) in methanol (5 ml) containing M sodium methoxide (1 ml) was set aside at room temperature for 3 h, after which time the solution was neutralized with dilute acetic acid and evaporated to dryness. The residue was extracted with ether (3 × 25 ml), and the dried ($MgSO_4$) extracts were

evaporated to give the L-talofuranoside **15b** (0.4 g), m.p. 85–86° (from ether–light petroleum), $[\alpha]_D$ −71° (*c* 0.35, chloroform) (Found: C, 64.9; H, 7.6. $C_{16}H_{22}O_5$ calc.: C, 65.3; H, 7.5%). N.m.r. data: τ 2.70 (*s*, 5 aromatic protons, *Ph*CH_2O); 4.92 (*s*, 1 proton, H-1); 5.40 (*q*, 2 protons, J_{AB} 12 Hz, CH_2Ph); 8.55 and 8.70 (2*s*, 6 protons, CMe_2); and 8.80 (*d*, 3 protons, $J_{5,6}$ 6 Hz, C-5–Me).

Benzyl 6-*deoxy*-2,3-O-*isopropylidene*-5-O-*methyl*-α-L-*talofuranoside* (**15c**). — To a solution of **15b** (0.15 g) in ether (5 ml) containing sodium hydride (0.5 g) was added methyl iodide (5 ml), and the mixture was set aside for 2 h; t.l.c. (light petroleum–ethyl acetate, 3:1) then showed that the methylation was complete. Methanol (5 ml) was added to destroy the excess of reagents and, after 30 min, the solvents were evaporated. The residue was partitioned between chloroform and water, and the organic layer was washed with dilute hydrochloric acid and water, and dried ($MgSO_4$). Removal of the solvents afforded syrupy **15c** (0.13 g), $[\alpha]_D$ −81 ±2° (*c* 0.6, chloroform) (Found: C, 66.2; H, 8.3. $C_{17}H_{24}O_5$ calc.: C, 66.2; H, 7.9%). N.m.r. data: τ 2.65 (*s*, 5 aromatic protons, *Ph*CH_2O); 4.85 (*s*, 1 proton, H-1); 5.30 (*q*, 2 protons, J_{AB} 12 Hz, PhCH_2); 6.65 (*s*, 3 protons, OMe); 8.55 and 8.73 (each *s*, 6 protons, CMe_2); and 8.85 (*d*, 3 protons, $J_{5,6}$ 6 Hz, C-5–Me).

6-*Deoxy*-2,3-O-*isopropylidene*-5-O-*methyl*-L-*talofuranose* (**13a**). — To a solution of the benzyl glycoside **15c** (70 mg) in tetrahydrofuran (2 ml) and liquid ammonia (6 ml), cooled in a bath of dry-ice, small pieces of sodium were added until a blue colour persisted in the solution for 30 min[14]. The ammonia was then allowed to evaporate and, after the addition of methanol, the solvents were evaporated to give **13a** (20 mg), $[\alpha]_D$ *ca.* +1° (*c* 0.5, chloroform), as an oil. This material was indistinguishable (t.l.c., g.l.c., m.s.) from a sample prepared according to the literature procedure[9]. The highest peak in the mass spectrum of **13a** had *m/e* 203 (M−15), and accurate mass measurement gave the molecular formula of this fragment as $C_9H_{15}O_5$ (Found: 203.09217; calc.: 203.09194), signifying a molecular formula of $C_{10}H_{18}O_5$ for **13a**.

Methyl 5-*amino*-5,6-*dideoxy*-2,3-O-*isopropylidene*-α-L-*talofuranoside* (**6**). — A solution of the azide[5] **4** (1.2 g) in dry ether (60 ml) containing a suspension of lithium aluminium hydride (0.45 g) was gently boiled under reflux for 1 h. Ethyl acetate (20 ml) and water (4 ml) were then added carefully to decompose the excess of reagent. The mixture was boiled for 10 min and then filtered, and solids were washed thoroughly with ether. Concentration of the combined and dried ($MgSO_4$) filtrate, with distillation of the residue, afforded a product (1 g) that still contained traces of impurities. A pure sample of the L-*talo*-amine **6**, b.p. 68–70° (bath)/0.5 mmHg, $[\alpha]_D$ −54° (c 1, methanol) (Found: C, 54.3; H, 8.5; N, 6.0. $C_{10}H_{19}NO_4$ calc.: C, 55.3; H, 8.7; N, 6.4%), was obtained by preparative g.l.c. using a Pye 105 chromatograph equipped with a column of 25% silicone gum on Celite at an operating temperature of 160°. N.m.r. data: τ 5.00 (*s*, 1 proton, H-1); 5.40 (*s*, 2 protons, H-2,3); 6.14 (*d*, 1 proton, $J_{4,5}$ 9 Hz, H-4); 6.60 (*s*, 3 protons, OMe); 7.15 (*m*, 1 proton, H-5); 8.50 and 8.67 (2*s*, 6 protons, CMe_2); and 8.85 (*d*, 3 protons, $J_{5,6}$ 6 Hz, C-5-Me); it is notable that H-2 and H-3 have coincident chemical shifts, as observed with other talofuranosides[6].

Methyl 5-amino-5,6-dideoxy-2,3-O-isopropylidene-β-D-allofuranoside (**7**). — Reduction of the azide[6] **5** (1.9 g) in ether (40 ml) with lithium aluminium hydride (0.6 g), as described in the preceding experiment, gave the D-*allo*-amine **7** (1.3 g), b.p. 48–50° (bath)/0.35 mmHg, $[\alpha]_D$ −72° (*c* 1, chloroform) (Found: C, 55.2; H, 8.7; N, 6.4%). N.m.r. data: τ 5.05 (*s*, 1 proton, H-1); 5.16 and 5.43 (2*d*, 2 protons, $J_{2,3}$ 6 Hz, H-2,3); 6.11 (*d*, 1 proton, $J_{4,5}$ ~8 Hz); 6.65 (*s*, 3 protons, OMe); 7.02 (*m*, 1 proton, H-5); 8.51 and 8.68 (2*s*, 6 protons, CMe_2); and 8.85 (*d*, 3 protons, $J_{5,6}$ 6 Hz, C-5–Me). The amine was homogeneous on examination by t.l.c. and g.l.c.

Deamination of methyl 5-amino-5,6-dideoxy-2,3-O-isopropylidene-α-L-talofuranoside (**6**). — To a cooled (0°) solution of **6** (0.82 g) in 90% acetic acid (12 ml) was gradually added a solution of sodium nitrite (0.82 g) in water (0.8 ml), and the solution was set aside for 1 h at 0°; t.l.c. (toluene–acetone, 3:1) then showed that all the starting material had reacted. Water (20 ml) and chloroform (20 ml) were added, and the separated organic layer was washed with aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Removal of the solvent left a syrup (~8 g) which contained (g.l.c.) **10** (43.5%, retention time 9.2 min), **8a** and **9a** (combined yield, 12.3%; 17 min), **9b** (26.4%, 30.2 min), and **8b** (2.9%, 31.6 min); three minor unidentified products were also detected. The unsaturated sugar **10** could not be identified unequivocally at this stage (see below), but g.l.c.–m.s. revealed the highest mass peak at *m/e* 185 (M − 15), indicating that an olefinic linkage was present. The structures of compounds **8ab** and **9ab** were confirmed by g.l.c.–m.s., using a Pye 104 gas chromatograph (7 ft column, 20% silicone gum on Celite at 160°) coupled to a MS 902 mass spectrometer.

A solution of the foregoing products (~0.8 g) in methanol (25 ml) containing M sodium methoxide (2 ml) was gently boiled for 2 h under reflux, and the neutralized (solid carbon dioxide) solution was evaporated to dryness. The residue was chromatographed on silica gel (elution with toluene–acetone, 4:1) to give first methyl 5,6-dideoxy-2,3-O-isopropylidene-β-D-*ribo*-hex-5-enofuranoside (**10**, 0.125 g), b.p. 41–43° (bath)/0.15 mmHg, $[\alpha]_D$ −58 ±1° (*c* 1, chloroform), ν_{max}^{film} 1650 cm^{-1} (weak, C=C); lit.[6] $[\alpha]_D$ −53° (chloroform) (Found: C, 59.7; H, 7.9. $C_{10}H_{16}O_4$ calc.: C, 60.0; H, 8.05%). N.m.r. data: τ 4.07 (*m*, 1 proton, H-5); 4.55–5.00 (*m*, 2 protons, H-6,6′); 4.98 (*s*, 1 proton, H-1); 8.65 (*s*, 3 protons, OMe); and 8.50 and 8.67 (2*s*, 6 protons, CMe_2). The product rapidly decolourized a solution of bromine in carbon tetrachloride. Continued elution gave methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**9a**, 0.16 g), b.p. 70–72° (bath)/0.2 mmHg, $[\alpha]_D$ −68 ±1° (*c* 1, methanol), the n.m.r. and i.r. spectra of which were identical to those of an authentic sample; lit.[7] b.p. 74–76°/0.7 mmHg, $[\alpha]_D$ −73.8° (*c* 2.3, methanol). The derived toluene-*p*-sulphonate **9c** had m.p. and m.m.p. 91–92° (from methanol), $[\alpha]_D$ −48 ±1° (*c* 1, methanol); lit.[7] m.p. 91–92°, $[\alpha]_D$ −41 ±4° (*c* 0.34, methanol).

Deamination of methyl 5-amino-5,6-dideoxy-2,3-O-isopropylidene-β-D-allofuranoside (**7**). — A cooled (0°) solution of the amino sugar **7** (1.1 g) in 90% acetic acid (17 ml) was treated with a solution of sodium nitrite (1.1 g) in water (1.1 ml), as described in the previous experiment. The following components were revealed by g.l.c. after work-up of the reaction mixture: **10** (7.7%), **8a** and **9a** (combined yield,

20.4%), **13a** [17.5%, 24.2 min, *m/e* 203 (M−15)], **9b** (25.8%), **8b** (12.5%), and **13b** [14.1%, 43.8 min, *m/e* 245 (M−15)].

The deamination products were deacetylated as described previously, and the components were partially resolved by chromatography of part of the residue (~0.3 g) on silica gel (elution with light petroleum–acetone, 23:1). This gave first the unsaturated sugar **10** (24 mg), which was identical (n.m.r. and i.r. spectroscopy) with that obtained previously. Continued elution gave the D-allofuranoside **9a** (44 mg) that was identical (n.m.r. and i.r. spectroscopy) with an authentic sample[7]; the derived toluene-*p*-sulphonate[7] **9c** had m.p. and m.m.p. 86–87°. Finally, a chromatographically pure sample of the rearranged product **13a** (25 mg) was obtained, and this could not be distinguished (g.l.c. and m.s.) from an authentic material, the synthesis of which is described above.

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