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NUCLEOPHILIC DISPLACEMENT REACTIONS IN CARBOHYDRATES PART XII[1]. THE REACTION OF 6-DEOXY-2,3-*O*-ISOPROPYLIDENE-4-*O*-METHANESULPHONYL-α-L-TALOPYRANOSE WITH SODIUM METHOXIDE

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ABSTRACT

Oxidation of benzyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside (**3**) with ruthenium tetroxide in carbon tetrachloride gave benzyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (**4**) in excellent yield. Ketone **4** was reduced stereospecifically, with sodium borohydride in methanol, to yield benzyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (**5**), which was converted into the crystalline 4-methanesulphonate **6**. Catalytic debenzylation of methanesulphonate **6** gave 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranose (**7**), which, on solvolysis with sodium methoxide in methanol at room temperature, was converted into 1,4-anhydro-6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranose (1,5-anhydro-6-deoxy-2,3-*O*-isopropylidene-β-L-mannofuranose) (**9**, 58%), methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**12**, 26%), and methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannofuranoside (**14**, 12%). The mechanisms of formation of these products are discussed.

INTRODUCTION

In a previous paper[2], we reported that 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-mannopyranose (**1**) was converted smoothly into 1,4-anhydro-6-deoxy-2,3-*O*-isopropylidene-β-L-talopyranose (**2**) on treatment with sodium methoxide in methanol at room temperature. Although details of the mechanism of this intramolecular displacement were not ascertained, it was suggested[2] that formation of the 1,4-anhydro ring-system was favoured by the fact that the C-Me group and the 1,3-dioxolane ring adopted an *exo*-configuration in the transition state with respect to the dioxabicyclo[2.2.1]heptane ring-system under formation. In a continuation of these studies, we have examined the products resulting from similar treatment of 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranose (**7**). This reaction is particularly interesting, since, although the C-1 alkoxide ion has free access to the methanesulphonate group in the boat conformation **8**, both the C-Me group and the 1,3-dioxolane ring are required to assume an *endo*-configuration with respect to the bicyclic ring-system under formation. It was of interest to establish

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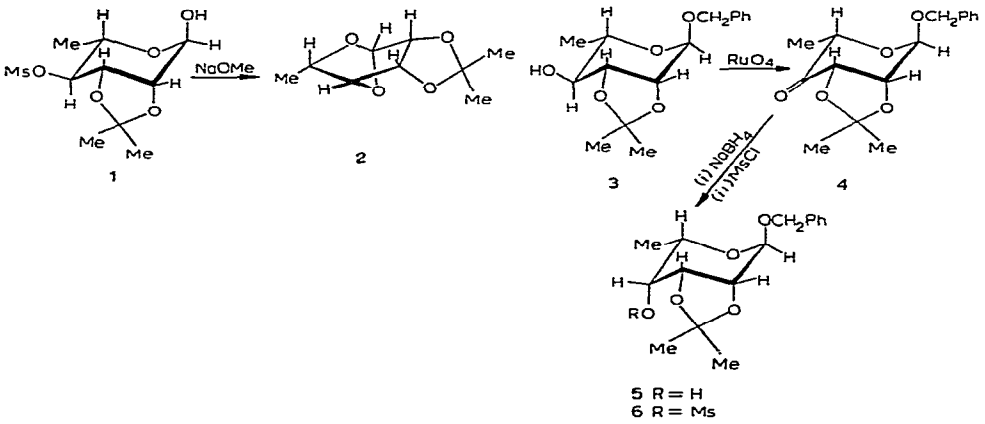
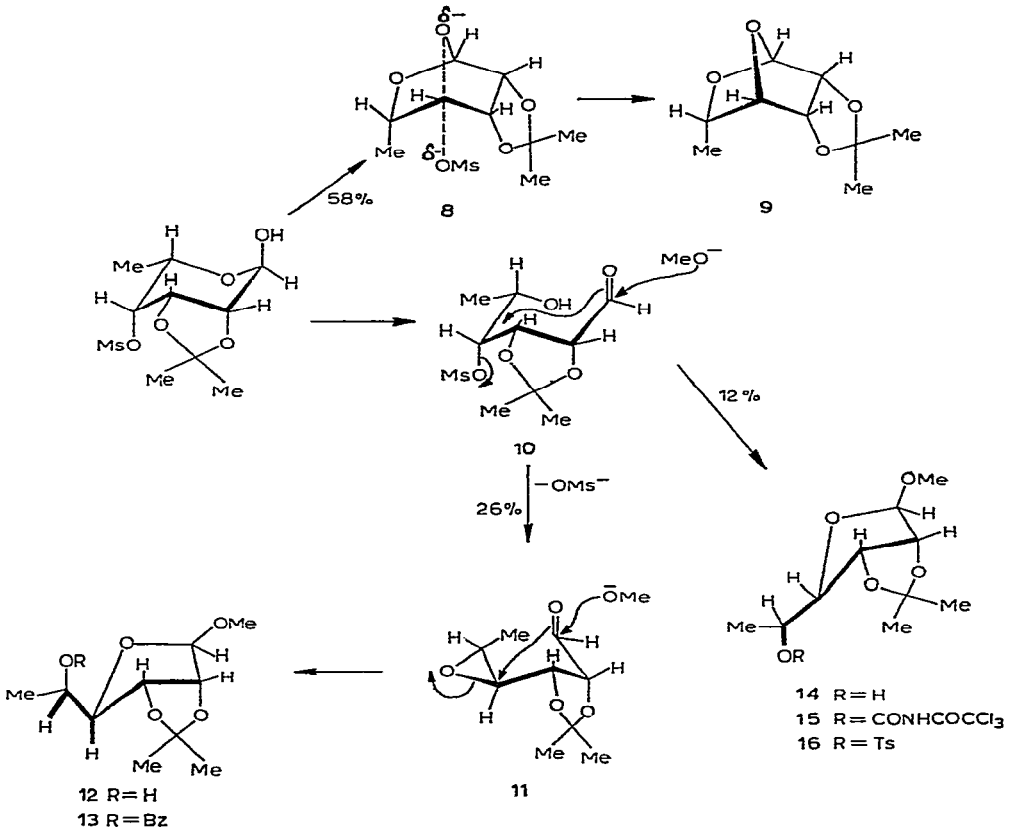
whether the non-bonded interactions developed in the transition state between the *endo*-substituents were of sufficient magnitude to divert the reaction to alternative pathways involving the *aldehydo*-form **10**. This information is important to a fuller understanding of the solvolysis of related sulphonates with sodium methoxide in methanol.

DISCUSSION

Oxidation of benzyl 6-deoxy-2,3-*O*-isopropylidene-α-L-manno pyranoside[2] (**3**) with ruthenium tetroxide[3] gave the syrupy ketone **4** in nearly quantitative yield. Reduction of ketone **4** with sodium borohydride in methanol proceeded stereospecifically to give a crystalline alcohol that was readily distinguishable from compound **3** (by g.l.c., physical constants, etc.) and which is, therefore, benzyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talopyranoside (**5**). The stereochemical course of this reduction was anticipated, since metal hydride reductions of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose and its oxime are highly stereoselective in favour of the L-*talo* epimer[4-7], and Collins and Overend[4] have pointed out the preference for attacking nucleophiles to approach the carbonyl group from the direction remote from the axial substituent at C-2. Treatment of **5** with methanesulphonyl chloride in pyridine afforded benzyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranoside (**6**), which, on catalytic debenzylation, afforded crystalline 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranose (**7**).



The reaction of methanesulphonate **7** with sodium methoxide in methanol at room temperature yielded a mixture which was shown by g.l.c. (Fig. 1) and t.l.c. to contain one major component, together with at least three minor components. Although these products could not be resolved completely by either preparative g.l.c. or chromatography on silica gel, it was possible, nevertheless, by a combination of these methods to obtain sufficient quantities of three of the components to effect their identification. The major product (58%, estimated by g.l.c.) was separated



from the mixture by preparative g.l.c. and was purified by sublimation. Its molecular formula was determined as $C_9H_{14}O_4$ by elemental analysis and by accurate mass measurement of the top peak[8] at *m/e* 171 (M−15) in its mass spectrum. Absorptions attributable to either C = C, OH, or sulphonic ester groups were absent from its infrared spectrum, and, on acid hydrolysis, it gave a single, reducing sugar which was indistinguishable from 6-deoxy-L-mannose on paper chromatograms. These data are compatible with the structure 1,4-anhydro-6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranose (1,5-anhydro-6-deoxy-2,3-*O*-isopropylidene-β-L-mannofuranose) (**9**), and this assignment of structure was supported by n.m.r. spectroscopy. In addition to verifying the presence of the isopropylidene and C-Me groups, the n.m.r. spectrum showed a narrow doublet (*J* 2Hz) at low field which was ascribed to the bridgehead proton H-1. The size of the coupling between the *exo*-proton at C-2 and the vicinal, bridgehead proton is the same as that found[9] between similar protons in 1,4-anhydro-2,3-*O*-isopropylidene-α-D-lyxopyranose, although it is less than that (3.2–6.0 Hz) found[10,11] in bicyclo[2.2.1]heptane derivatives. Although the coupling between these protons may be small, it is evidently indicative of the *exo*-configuration of the non-bridgehead proton, since the coupling of *endo*-protons with vicinal, bridgehead

protons is zero in bornane[10], norbornane[11], and structurally related carbohydrate derivatives[2,12].

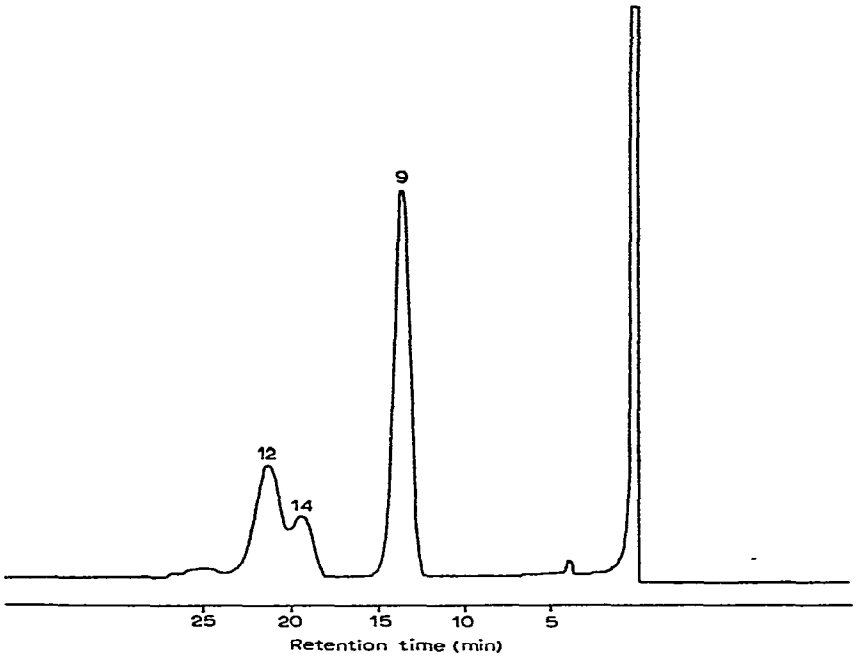


Fig. 1. Gas–liquid chromatogram of the solvolysis products from 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranose (**7**). The percentages of the products formed were estimated as **9** (58%), **12** (26%), **14** (12%), and unidentified components (4%).

One of the minor components (*ca.* 26%) was obtained as a chromatographically homogeneous syrup, and it liberated 6-deoxy-L-talose (chromatographic identification) on acid hydrolysis. A clear indication of its structure was provided by the presence of a resonance attributable to a methoxyl group at τ 6.52 in its n.m.r. spectrum. Mechanistic considerations (see below) suggest that this compound is probably methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**12**); confirmation of this assignment was provided by comparison of its chromatographic and spectroscopic properties with those of an authentic sample[13] and by formation of the known, crystalline 5-benzoate[13] **13**. An essentially similar approach was used to characterise another minor component (12%) which was shown to give 6-deoxy-L-mannose (chromatographic identification) on acid hydrolysis. Accurate mass measurement of the top mass peak[8] at *m/e* 203 (M−15) showed that the compound is isomeric with **12**. Again, a salient feature of the n.m.r. spectrum (Fig. 2) was the presence of a methoxyl resonance at τ 6.70, and the general structure of this component was deduced from its n.m.r. spectrum and that of the derived trichloroacetylcarbamate (see inset, Fig. 2). The latter derivative was formed rapidly *in situ* by the addition of trichloroacetyl isocyanate to a solution of the compound in deuteriochloroform; complete reaction was discerned by the appearance of a resonance, corresponding to one proton, at

low field (τ *ca.* 1.80) due to the presence of the NH proton. The multiplet centre at τ 5.95 (Fig. 2) is shifted well downfield (τ 4.78) in the derived carbamate (see inset, Fig. 2), and, on this evidence, it can be assigned to the proton residing on the same carbon atom as the hydroxyl group[14]. It is also clear from the spectrum that this proton is coupled to the C-Me group and is, therefore, located at C-5. This required the compound to be a methyl 6-deoxyhexofuranoside and, furthermore, the appearance of the anomeric proton as a singlet (at τ 5.09) signified[15] a *trans*-relationship of H-1 and H-2. The combined chemical and spectroscopic evidence indicate that this compound is methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannofuranoside (**14**), and this assignment was established by comparison of the n.m.r. spectrum with that of an authentic sample, prepared by gas–liquid chromatographic separation of the anomeric furanosides obtained by acid-catalysed acetonation of 6-deoxy-L-mannose in the presence of methanol[16a], and by formation of the known[16b] 5-toluene-*p*-sulphonate **16**. The other minor component(s) (*ca.* 4%) were not isolated in a sufficiently pure form to permit meaningful characterisation.

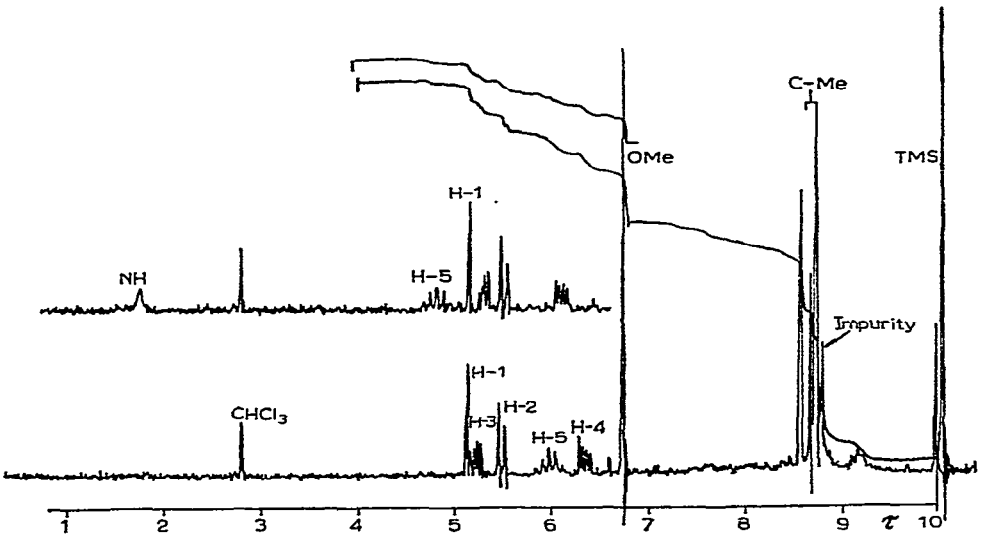
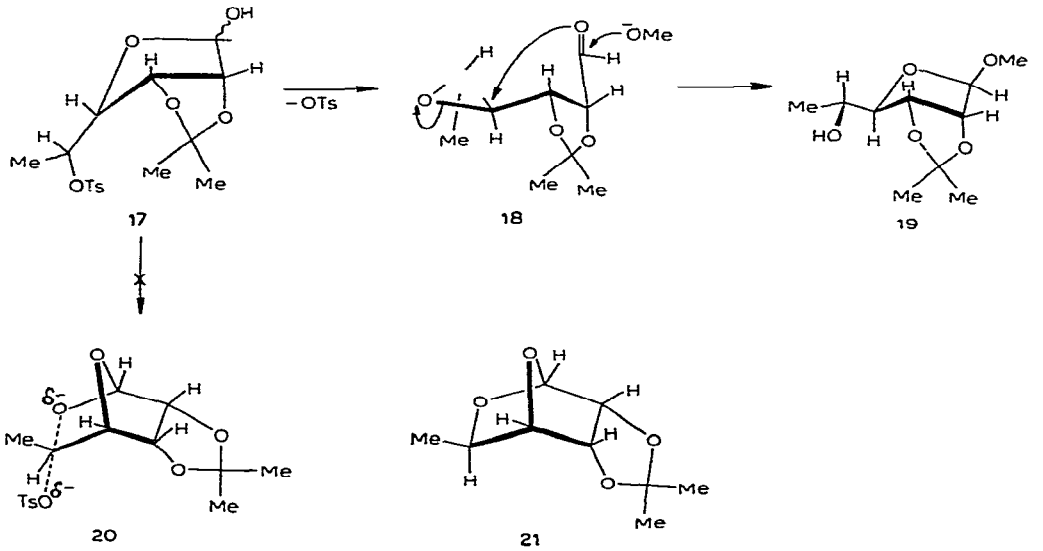


Fig. 2. N.m.r. spectrum ($CDCl_3$) at 100 MHz of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannofuranoside (**14**) and the lower region of the spectrum of the derived trichloroacetylcarbamate **15**. The following coupling constants were derived for **15** by first-order methods and by ignoring the slight second-order perturbation shown by H-3 and H-2: $J_{1,2} \sim 0.5$, $J_{2,3}$ 6, $J_{3,4}$ 3.7, $J_{4,5}$ 7.5, and $J_{5,6}$ 6.7 Hz.

It is clear from the preponderance of anhydro sugar **9** among the products of solvolysis that non-bonded interactions engendered in the transition state between the *endo*-substituents, while undoubtedly having an influence on the course of the reaction, are not sufficiently severe to divert the reaction completely to other routes. This result has a bearing on previous observations[2] regarding the rearrangement of 6-deoxy-2,3-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-L-mannofuranose (**17**) with

sodium methoxide. This reaction yields[9,17] principally methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside (**19**) *via* the acyclic epoxide **18**, but the anhydro sugar **21** is not observed as a product of the solvolysis. Its absence was attributed[2] either to steric and/or electronic interactions preventing the approach of the C-1 alkoxide ion from within the *V*-shape formed by the trioxabicyclo[3.3.0]octane ring-system, or to adverse steric interactions, which would be introduced in the transition state **20**, between the *endo*-hydrogen atom and the dioxolane ring. The geometry of the transition state **20**, which would result in the formation of anhydro sugar **21**, closely resembles that which gives rise to anhydro sugar **9** and which also contains the more unfavourable interactions between *endo*-substituents, due to the *endo*-configuration of the C-Me group. Hence, it is reasonable to assume that the formation of anhydro sugar **21** from the rhamnose sulphonate **17** is prevented more by factors affecting the nucleophile's approach to the rearside of the sulphonate group than to unfavourable interactions between the *endo*-substituents in the transition state of the displacement reaction.



It is significant that both of the minor products contain a glycosidic methoxyl group which must have been introduced by way of the acyclic form **10**. In the formation of taloside **12**, loss of the methanesulphonyloxy group occurs with retention of configuration and ring contraction. There are several analogies[9,12,17,18] to indicate that this compound arises by aldehyde-group participation in the opening of an intermediate epoxide **11**, in the manner shown. Formation of the rhamnoside **14**, on the other hand, involves both a ring contraction and an inversion of configuration at C-4. This can be achieved by neighbouring-group participation by the aldehyde group in displacing the methanesulphonyloxy group (*i.e.*, **10**→**14**). An analogous mechanism rationalises[19] the ready solvolysis of 2,3,5-tri-*O*-benzyl-4-*O*-toluene-*p*-sulphonyl-*aldehydo*-D-ribose, in sodium methoxide–methanol, to give a mixture of

the anomeric methyl 2,3,5-tri-*O*-benzyl-L-lyxofuranosides. In our case, the presence of the isopropylidene ring probably accounts for the preferential formation of the α-glycoside **14**.

EXPERIMENTAL

Thin-layer chromatography (t.l.c.) was performed on silica gel, and detection was effected with vanillin–sulphuric acid[20]. Paper chromatography was performed by downward irrigation with ethyl acetate–pyridine–water (8:2:1), and the components were detected with aniline hydrogen phthalate[21]. N.m.r. spectra were measured in deuteriochloroform (tetramethylsilane as internal reference) at 60 and 100 MHz with either a Varian A-60 or Perkin–Elmer R-14 spectrometer, respectively; infrared spectra were recorded for Nujol mulls with a Perkin–Elmer 257 spectrometer. Analytical gas–liquid chromatography (g.l.c.) was carried out on a Pye 104 instrument at a column temperature of 130°, and preparative g.l.c. on a Pye 105 instrument with flame-ionisation detection at a column temperature of 160°; a column packing of 10% silicon ester-30 on Celite was used in both cases. Molecular weights were measured on an A.E.I. MS-9 mass spectrometer by using a direct-insertion technique.

Benzyl 6-deoxy-2,3-O-isopropylidene-α-L-lyxo-hexopyranosid-4-ulose (**4**). — Ruthenium dioxide dihydrate[3] (4.3 g) was added to a solution of sodium metaperiodate (60 g) in water (600 ml), and the mixture was shaken vigorously until conversion into the tetroxide was complete. The aqueous solution was extracted with carbon tetrachloride (4 × 200 ml), and the combined extracts were added gradually to a stirred solution[2] of **3** (7 g) in carbon tetrachloride (100 ml). On complete addition, the solution was stirred for 1 h, whereupon t.l.c. (acetone–toluene, 3:7) showed that all of the starting material had reacted, and isopropyl alcohol (140 ml) was then added. Solid material was filtered off after 30 min, and the solvents were removed to yield ketone **4** (6.8 g), $[\alpha]_D$ −113° (*c* 1, chloroform), ν_{max} 1740 cm^{-1}, as a chromatographically homogeneous syrup (Found: C, 65.2; H, 6.6. $C_{16}H_{20}O_5$ calc.: C, 65.7; H, 6.9%).

Benzyl 6-deoxy-2,3-O-isopropylidene-α-L-talopyranoside (**5**). — To a solution of ketone **4** (6.7 g) in methanol (140 ml) sodium borohydride (1.35 g) was gradually added, and, on complete addition, the solution was stirred for 30 min at room temperature. Ethyl acetate (40 ml) was then added, the solvents were removed, and the residue was partitioned between water (250 ml) and ether (500 ml). The aqueous layer was extracted further with ether (2 × 100 ml), and the combined organic layers were dried ($MgSO_4$) and filtered. Removal of the solvent and distillation of the residue gave taloside **5** (6.6 g), b.p. 135–140°/0.1–0.2 mmHg, which crystallised on standing and, on recrystallisation from light petroleum (b.p. 80–100°), had m.p. 45–47°, $[\alpha]_D$ −74° (*c* 1, chloroform) (Found: C, 65.6; H, 7.4. $C_{16}H_{22}O_5$ calc.: C, 65.3; H, 7.5%). Compound **5** was readily distinguished from the mannoside **3** by g.l.c. (column temperature, 200°), the retention times of the components being 10.4 and 9.5 min, respectively; g.l.c. also demonstrated the absence of **3** in the original

reduction. N.m.r. data: τ 2.70 (5 aromatic protons); 4.90 (1-proton singlet, H-1); 5.38 (AB quartet, J 12 Hz, benzyl methylene protons); 8.44, 8.65 (3-proton singlets, CMe_2); 8.68 (3-proton doublet, $J_{5,6}$ 6 Hz, CMe).

Hydrolysis of **5** (50 mg) with N sulphuric acid (2 ml) on a boiling water-bath for 2 h, with paper chromatography of the neutralised hydrolysate, revealed that 6-deoxy-L-talose[4] was the only reducing sugar formed.

Benzyl 6-deoxy-2,3-O-isopropylidene-4-O-methanesulphonyl-α-L-talopyranoside (**6**).—A solution of compound **5** (6.6 g) in pyridine (150 ml) was treated with methanesulphonyl chloride (10.8 ml) for 24 h at room temperature, and methane sulphonate **6** (6.8 g), m.p. 138–139° [from ethyl acetate–light petroleum (b.p. 40–60°)], $[\alpha]_D$ −46° (*c* 1, methanol), was then isolated in the usual way (Found: C, 54.6; H, 6.4; S, 8.8. $C_{17}H_{24}O_7S$ calc.: C, 54.8; H, 6.5; S, 8.6%). N.m.r. data: τ 2.70 (5 aromatic protons); 4.93 (1-proton singlet, H-1); 5.38 (AB quartet, J 12 Hz, benzyl methylene protons); 6.94 (3-proton singlet, OMs); 8.43, 8.65 (3-proton singlets, CMe_2); 8.64 (3-proton doublet, $J_{5,6}$ 6 Hz, CMe).

6-Deoxy-2,3-O-isopropylidene-4-O-methanesulphonyl-α-L-talopyranose (**7**). — A solution of the glycoside **6** (4.2 g) in methanol (400 ml) containing 10% palladium–calcium carbonate (8.4 g) was shaken in the presence of a slight overpressure of hydrogen for 24 h at room temperature, and t.l.c. (acetone–toluene, 3:7) then showed that all of the starting material had reacted. The catalyst and solvent were removed, and the residue was extracted with chloroform (100 ml). Evaporation of the solvent, with recrystallisation of the residue from chloroform–light petroleum (b.p. 40–60°), gave compound **7** (2.3 g), m.p. 124–125°, $[\alpha]_D$ +13° (*c* 1, chloroform), ν_{max} 3400 cm^{-1} (OH) (Found: C, 43.0; H, 6.5; S, 11.3. $C_{10}H_{18}O_7S$ calc.: C, 42.6; H, 6.4; S, 11.3%). N.m.r. data: τ 4.63 (broad, 1-proton singlet, H-1, α-D anomer); 6.88 (3-proton singlet, OMs); 8.42, 8.60 (3-proton singlets, CMe_2); 8.63 (3-proton doublet, $J_{5,6}$ 6 Hz, CMe).

Treatment of 6-deoxy-2,3-O-isopropylidene-4-O-methanesulphonyl-α-L-talopyranose (**7**) *with sodium methoxide in methanol.* — A solution of methanesulphonate **7** (2.5 g) in N sodium methoxide in methanol (50 ml) was set aside at room temperature for 4 h, during which time complete reaction had occurred. The solution was neutralised with carbon dioxide, the solvent was removed, and the residue was extracted with ether (50 ml) which was dried ($MgSO_4$). Concentration of the filtered extract afforded a syrup (1.72 g) which g.l.c. (Fig. 1) showed to contain at least four components; the amounts of the products formed were estimated from the gas–liquid chromatogram as **9** (58%), **12** (26%), **14** (12%), and unidentified product(s) (4%). These compounds had retention times of 13.8, 21.7, 19.4, and 25.1 min, respectively.

A portion (0.4 g) of the product mixture was subjected to preparative g.l.c., and this gave 1,4-anhydro-6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranose (**9**) (0.15 g) which was sublimed at 75°/15 mmHg to give the pure compound, m.p. 39–41°, $[\alpha]_D$ +128.5° (*c* 1, in chloroform) (Found: C, 58.1; H, 7.7. $C_9H_{14}O_4$ calc.: C, 58.05; H, 7.5%). The mass spectrum of **9** contained a top mass peak at *m/e* 171 (M−15) (ref. 8) which was shown by accurate mass measurement to correspond to the

molecular formula $C_8H_{11}O_4$ (Found: 171.067551; Calc.: 171.065728). N.m.r. data: τ 4.57 (1-proton doublet, $J_{1,2}$ 2 Hz, H-1); 5.20–6.00 (H-2, H-3, H-4, and H-5); 8.36 (3-proton doublet, $J_{5,6}$ 7 Hz, CMe); 8.37, 8.66 (3-proton singlets, CMe_2). Hydrolysis of **9** (50 mg) in *p*-dioxane (0.3 ml) and 2N sulphuric acid (0.3 ml) on a boiling water-bath for 2 h gave a reducing sugar which was indistinguishable from 6-deoxy-L-mannose on paper chromatograms.

A second portion (0.4 g) of the product mixture was chromatographed over silica gel (acetone–toluene, 3:7) to give, *inter alia*, a fraction containing anhydro sugar **9** and a small proportion of compound **12**. Preparative g.l.c. afforded a pure sample (20 mg), $[\alpha]_D$ −50° (*c* 1, methanol), of the minor component which was identified as methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**12**) by comparison of its n.m.r. and i.r. spectra with those of an authentic sample[13]; n.m.r. data: τ 4.99 (1-proton singlet, H-1); 5.76 (1-proton doublet, $J_{2,3}$ 3.5 Hz, H-2); 6.52 (3-proton singlet, OMe); 8.52, 8.68 (3-proton singlets, CMe_2); 8.78 (3-proton doublet, $J_{5,6}$ 6 Hz, CMe). Benzoylation[13] of **12** (50 mg) gave methyl 5-*O*-benzoyl-6-deoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (**13**) (25 mg), m.p. and mixed m.p. 93–95° (lit.[13] m.p. 93.5–95°); the i.r. spectrum of the benzoate was indistinguishable from that of an authentic sample.

The foregoing separation on silica gel also yielded a fraction containing only the glycosides **12** and **14**, which was subjected to preparative g.l.c. This procedure gave a small amount of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannofuranoside (**14**) (8 mg) as a chromatographically homogeneous syrup. Accurate mass measurement of the top mass peak at *m/e* 203 (M−15) (ref. 8) in the mass spectrum gave a molecular formula of $C_9H_{15}O_5$ for this ion (Found: 203.089021; calc.: 203.091941) which signified the molecular formula $C_{10}H_{18}O_5$ for compound **14**. The n.m.r. spectrum of compound **14** is shown in Fig. 2, and it was identical with that of an authentic sample separated (by g.l.c.) from a mixture of methyl 6-deoxy-2,3-*O*-isopropylidene-α- and β-L-mannofuranosides[16a].

Acid hydrolysis of compound **14**, as previously described, afforded a reducing sugar which was indistinguishable from 6-deoxy-L-mannose on paper chromatograms. Toluene-*p*-sulphonate **16**, prepared from **14** in the usual way, had m.p. 83–84° which was not depressed on admixture with an authentic sample (lit[16b] m.p. 83–84°).

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