NUCLEOPHILIC DISPLACEMENT REACTIONS IN CARBOHYDRATES

PART XX[1]. DISPLACEMENTS ON ALKYL α-L-TALOPYRANOSIDE 4-SULPHONATE DERIVATIVES*

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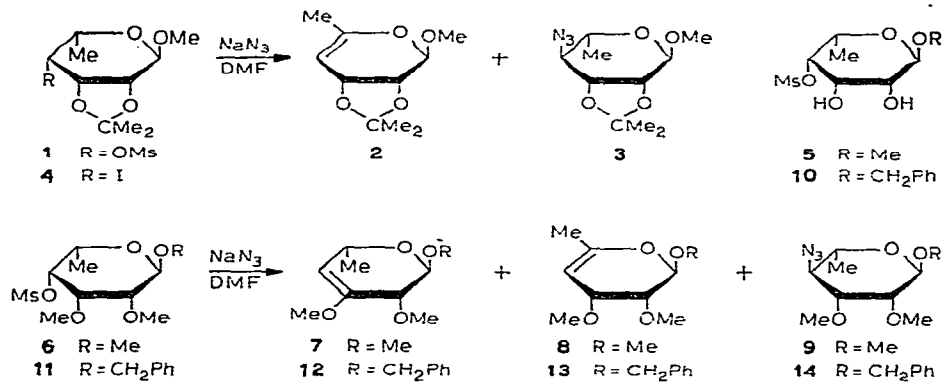
ABSTRACT

The azide displacement reaction on methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (**6**) in *N*,*N*-dimethylformamide yielded methyl 4,6-dideoxy-2,3-di-*O*-methyl-α-L-*threo*-hex-3-enopyranoside (**7**, *ca.* 50%), methyl 4,6-dideoxy-2,3-di-*O*-methyl-β-D-*erythro*-hex-4-enopyranoside (**8**, *ca.* 10%), and methyl 4-azido-4,6-dideoxy-2,3-di-*O*-methyl-α-L-mannopyranoside (**9**, *ca.* 40%). The corresponding azide **14** (20%) and the unsaturated sugars **12** (68%) and **13** (12%) were obtained from a comparable reaction on benzyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (**11**).

INTRODUCTION

In a previous paper[2], it was reported that the reaction of methyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranoside (**1**) with sodium azide in boiling *N*,*N*-dimethylformamide afforded the unsaturated sugar **2**, as the major product, together with the azide **3**. It was suggested that the preference for elimination with the weakly basic, azide ion might be the result of unfavourable interactions developed in the transition state of the displacement reaction. In view of our interest in the displacement reactions of carbohydrate sulphonates, we have examined the displacement reactions of talopyranoside sulphonates which are not conformationally restrained by the fusion of a dioxolane ring, *viz.* methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (**6**) and the corresponding benzyl glycoside **11**. Our interest in these displacements was also stimulated by a report[3] that a compound purported to be methyl 4,6-dideoxy-4-iodo-2,3-*O*-isopropylidene-α-L-talopyranoside (**4**) gave ring-contracted products when treated with sodium azide in boiling *N*,*N*-dimethylformamide. However, the structure originally assigned to the iodide has been proved erroneous and its re-assignment[4–6] as methyl 5,6-dideoxy-5-iodo-2,3-*O*-isopropylidene-β-D-allofuranoside accounts for the differences noted in the displacement reactions.

*Dedicated to Professor M. Stacey, C.B.E., F.R.S., in honour of his 65th birthday.



DISCUSSION

Methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (**6**) was prepared by mild, acid hydrolysis of the 2,3-acetal[2] **1** followed by methylation of the resulting diol **5**. An analogous sequence of reactions on benzyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranoside[7] afforded benzyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (**11**).

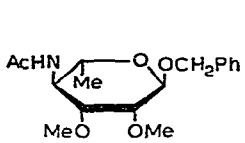
Treatment of the methanesulphonate **6** with sodium azide in boiling *N*,*N*-dimethylformamide gave three products which, after chromatographic separation, were identified as methyl 4,6-dideoxy-2,3-di-*O*-methyl-α-L-*threo*-hex-3-enopyranoside (**7**, *ca.* 50%), methyl 4,6-dideoxy-2,3-di-*O*-methyl-β-D-*erythro*-hex-4-enopyranoside (**8**, *ca.* 10%), and methyl 4-azido-4,6-dideoxy-2,3-di-*O*-methyl-α-L-mannopyranoside (**9**, *ca.* 40%); the yields were determined by gas–liquid chromatography. A partial separation of the three components was achieved by chromatography on silica gel, which gave a fraction containing the azide **9** and the major unsaturated sugar **7**, together with another fraction containing only the unsaturated sugar **8**. Preparative g.l.c. was then used to resolve the mixture of **7** and **9**. Both unsaturated sugars **7** and **8** were unstable, and the samples rapidly deteriorated on storage; we have already commented[1] on the instability of the D-enantiomer of **7**.

The structure of the azide **9** was conveniently established by comparison with an authentic sample obtained by methylation of methyl 4-azido-4,6-dideoxy-α-L-mannopyranoside[2]. Due to the marked instability of both unsaturated sugars, satisfactory elemental analyses could not be obtained, but their structures could be confidently assigned on the basis of chemical and spectroscopic evidence. Both **7** and **8** rapidly decolourised a solution of bromine in carbon tetrachloride, and the presence of an unsaturated linkage in each compound was verified by the presence of an absorption band at *ca.* 1670 cm^{-1} in their infrared spectra. The mass spectrum of **7** was compatible[8] with the structure assigned, exhibiting a peak due to the molecular ion at *m/e* 188 ($C_9H_{16}O_4$), while more pronounced peaks were observed at *m/e* 173 (M^+-Me), 157 (M^+-OMe), and 128 ($M^+-HCOOMe$). The mass spectrum

of the isomeric sugar **8** did not contain a peak due to the molecular ion, but significant peaks were again observed at *m/e* 173 and 157. The abundant ion at *m/e* 128 in the spectrum of **7** provided the first indication of the position of the double bond, since it could arise by a retrodiene fragmentation as noted for other 3,4-unsaturated glycosides[8].

More-compelling evidence for the positions of the olefinic linkage in **7** and **8** was derived from ^{1}H n.m.r. spectroscopy, which also revealed the presence of three methoxyl groups, a CMe group, and four other protons in each compound. The C-5-methyl resonance in the spectrum of **7** appeared as a three-proton doublet ($J_{5,6}$ 6 Hz) at τ 8.70, whereas the corresponding resonance for **8** was observed as a three-proton singlet at τ 8.26, signifying the absence of a proton at C-5.

A comparable azide displacement on benzyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside (**11**) also afforded three products, which were assumed to be **12** (68%), **13** (12%), and **14** (20%); the percentage yields given in parenthesis were determined by g.l.c. Chromatography of the mixture on silica gel yielded a fraction containing **12** and **14**, while a second fraction contained an unsaturated sugar (ν_{max} 1673 cm^{-1}), which was assigned as benzyl 4,6-dideoxy-2,3-di-*O*-methyl-β-D-*erythro*-hex-4-enopyranoside (**13**) from the appearance of the C-5-methyl resonance as a three-proton singlet in its ^{1}H n.m.r. spectrum. A portion of the first fraction [ν_{max} 2100 (N_3) and 1670 cm^{-1} (C=C)] was resolved by preparative g.l.c. to give a sufficient quantity of the azide **14** to effect its characterisation by elemental analysis and by its conversion into crystalline benzyl 4-acetamido-4,6-dideoxy-2,3-di-*O*-methyl-α-L-mannopyranoside (**15**) on reduction and *N*-acetylation. The other unsaturated sugar, **12**, was extremely unstable and it began to decompose shortly after separation. The ^{1}H n.m.r. spectrum of the mixture of **12** and **14**, however, exhibited two closely overlapping doublets ($J_{5,6}$ 6 Hz) at τ *ca.* 8.60, signifiying that both compounds possessed a HCMe group. Thus, the unsaturated sugar was tentatively identified as benzyl 4,6-dideoxy-2,3-di-*O*-methyl-α-L-*threo*-hex-3-enopyranoside (**12**).



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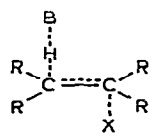

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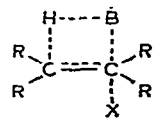

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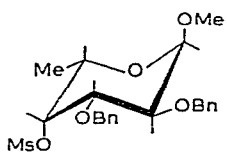
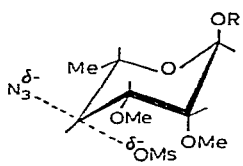
The reactions of the alkyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranosides **6** and **11** with azide ion are analogous to that previously observed[2] with the 2,3-acetal **1**. Formation of the 3,4-unsaturated sugar in the latter reaction is presumably excluded by the strain which would result from the introduction of a double bond between C-3 and C-4 of the bicyclic system. It is also notable that the 3,4-unsaturated sugars **7** and **12** predominate in the eliminations of the methane-

sulphonates **6** and **11**, respectively, which is in agreement with expectations based on the predicted, relative acidities of the protons at C-3 and C-5 (however, see later).

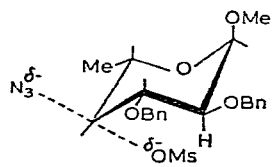
The predominant formation of unsaturated sugars in the reactions of the alkyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranosides **6** and **11** is, at first sight, suprising in view of the weakly basic character of the azide ion and its known[9] predisposition towards S_N2 reactions. There has been some controversy over the mechanism of bimolecular elimination reactions promoted in dipolar, aprotic solvents by anions that are weakly basic towards hydrogen but are strong carbon nucleophiles. One view[10] is that such eliminations occur through the same type of transition state (**16**, designated as E2H) as do normal E2 reactions, whereas another view[9,11] holds that there is some covalent attachment of the nucleophile to the α-carbon atom and to the β-hydrogen atom (**17**, E2C). Many of the arguments hinge on the importance of C_β-H bond breaking and base.....H bond formation in the transition state of the E2 reaction. While these mechanistic considerations are germane to a precise understanding of the way in which the unsaturated sugars are formed from the methanesulphonates **6** and **11**, we have been mainly concerned in obtaining a qualitative appreciation of why unsaturated sugars are formed in this case but not with methyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-methanesulphonyl-α-D-galactopyranoside, which undergoes[12] an essentially quantitative exchange with azide ion in boiling *N,N*-dimethylformamide. If the L-enantiomer **18** of the latter compound is considered for the convenience of comparison, it can be seen that *anti*-elimination of the sulphonate group is not precluded.



18 Bn=CH_2Ph



19 R=Me or CH_2Ph



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It can be assumed that the direct displacement reactions on the methanesulphonates **6**, **11**, and **18** occur from the *1C* (L) conformation in each case, since in the alternative chair conformation the sulphonate group is flanked by vicinal, *axial*-substituents, an arrangement known[13] to hinder or prevent the displacement reaction. In the likely transition state **19** of the azide displacements on the alkyl talopyranoside sulphonates **6** and **11**, it is apparent that unfavourable steric (and perhaps polar) interactions are developed between the leaving sulphonate anion and the C-2 methoxyl group. However, the corresponding interaction in the transition state **20** of the galactose derivative is minimal due to the hydrogen substituted at C-2. Since both elimination and substitution of the alkyl talopyranoside sulphonates occur from the same ground-state conformation, it can be concluded that the higher energy of the transition state **19** of the S_N2 reaction allows the E2 reactions to complete on favourable terms. The double-bond character developed in the C3–C4 and C4–C5 bonds in

the respective E2 transition states produces a flattening of the pyranoid ring along these bonds, with a consequent decrease in the 1,3-diaxial interaction between the substituents at C-2 and C-4.

Similar arguments to those advanced above have been used[1] to explain the formation of a 3,4-unsaturated sugar when methyl 6-deoxy-4-*O*-methanesulphonyl-3-*O*-methyl-2-*O*-toluene-*p*-sulphonyl-α-D-allopyranoside is treated with benzoate ion in *N,N*-dimethylformamide. Moreover, the proclivity of methyl 2,3,5-tri-*O*-toluene-*p*-sulphonyl-β-D-lyxofuranoside towards elimination of the 3-sulphonate group under similar conditions was ascribed[14] to the relief of "steric compression". It is pertinent to point out that only the unsaturated sugars **7** and **8** appeared to be formed when the sulphonate **6** was treated with benzoate ion in boiling *N,N*-dimethylformamide. An awareness of such factors is valuable from a synthetic viewpoint, since it is often useful to be able to predict the reactivity and behaviour of a sulphonate group in a particular environment.

EXPERIMENTAL

General methods. — Thin-layer chromatography (t.l.c.) was performed on silica gel with detection by ethanolic vanillin–sulphuric acid[15]. Infrared spectra were recorded on a Perkin–Elmer 125 or Infracord spectrometer. N.m.r. spectra were usually measured at 60 MHz on deuteriochloroform solutions, with tetramethylsilane as internal reference. Gas–liquid chromatography (g.l.c.) was carried out on a Pye 104 instrument with flame-ionisation detection at the column temperature stated; a column packing of either 10% silicon ester 30 or 10% silicon oil on Celite was usually employed as the stationary phase. Mass spectra were obtained on an A.E.I. MS9 mass spectrometer, using a direct-insertion technique to introduce the sample. Solvents were removed by evaporation at *ca.* 40°.

*Methyl 6-deoxy-4-*O*-methanesulphonyl-α-L-talopyranoside* (**5**). — A solution of the acetal[2] **1** (5 g) in water (400 ml) and acetic acid (200 ml) was heated under reflux on a boiling water-bath for 15 min, after which time t.l.c. (ethyl acetate–hexane, 1:1) showed that removal of the acetal group was complete. Removal of the solvents afforded a syrup, which was crystallised from ethyl acetate–light petroleum (b.p. 80–100°) to give the diol **5** (3.5 g), m.p. 104–105°, $[\alpha]_D$ −99.8° (*c* 1, chloroform) (Found: C, 37.5; H, 6.0; S, 12.6. $C_8H_{16}O_7S$ calc.: C, 37.5; H, 6.2; S, 12.5%). N.m.r. data: τ 6.65 (3-proton singlet, OMe), 6.82 (3-proton singlet, OMs), and 8.68 (3-proton doublet, $J_{5,6}$ 6 Hz, HCMe).

*Methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-L-talopyranoside* (**6**). — To a stirred solution of **5** (5 g) in *N,N*-dimethylformamide (80 ml) was added methyl iodide (30 ml) followed by the gradual addition of sodium hydride (2 g). After 4 h, t.l.c. (ethyl acetate–hexane, 1:1) showed that all of the starting material had reacted. Methanol (50 ml) containing a few drops of acetic acid (*ca.* 0.2 ml) was than added with cooling, the solvents were removed, and the residue was partitioned between water (150 ml) and chloroform (150 ml). The aqueous layer was further extracted

with chloroform (3 × 100 ml), and the combined extracts were washed with water (2 × 200 ml) and dried ($MgSO_4$). Removal of the solvent and recrystallisation of the residue from ethyl acetate–light petroleum (b.p. 40–60°) gave the dimethyl ether **6** (4.4 g), m.p. 109–110°, $[\alpha]_D$ −83 ±0.5° (*c* 1, chloroform) (Found: C, 42.1; H, 7.3; S, 11.6. $C_{10}H_{20}O_7S$ calc.: C, 42.25; H, 7.1; S, 11.25%). N.m.r. data: τ 5.20 (1-proton singlet, H-1), 6.54 and 6.65 (9 protons, each singlets, intensity ratio 2:1, 3 × OMe), 6.85 (3-proton singlet, OMs), and 8.64 (3-proton doublet, $J_{5,6}$ 6 Hz, HCMe).

*Reaction of methyl 6-deoxy-4-*O*-methanesulphonyl-2,3-di-*O*-methyl-α-*L*-talopyranoside* (**6**) *with sodium azide in* N,N-*dimethylformamide*. — A solution of the title sulphonate (2.5 g) in *N,N*-dimethylformamide (250 ml) containing sodium azide (7.5 g) was heated under reflux for 3 h, during which time the reaction was completed. Water (250 ml) was added to the cooled solution, the aqueous solution was extracted with chloroform (3 × 100 ml), and the combined extracts were washed with water (3 × 300 ml) and dried ($MgSO_4$). Removal of the solvents left a syrupy residue, which was shown by g.l.c. (10% silicon oil on Celite, 130°) to contain **8** (*ca.* 10%, retention time 6.1 min), **7** (*ca.* 50%, 12.6 min), and **9** (*ca.* 40%, 25 min), respectively. The mixture of products was partially resolved by chromatography on silica gel [elution with hexane–ether (4:1) containing 0.2% of triethylamine] to give a mixture (1.7 g) of the azide **9** and the unsaturated sugar **7**. Continued elution afforded pure methyl 4,6-dideoxy-2,3-di-*O*-methyl-β-D-*erythro*-hex-4-enopyranoside (**8**) (0.125 g), b.p. 33–35°/0.05 mmHg, $[\alpha]_D$ −288° (*c* 1.2, chloroform), ν_{max}^{film} 1670 cm^{-1} (C=C). N.m.r. data: τ 5.00–6.3 (H-1–H-4), 6.58 and 6.70 (9 protons, each singlets, intensity ratio 2:1, 3 × OMe), and 8.26 (3-proton singlet, C=CMe). The molecular formula was deduced[8] to be $C_9H_{16}O_4$ from the appearance of a top-mass peak at *m/e* 157 (M − 31) in the mass spectrum.

A portion (1.1 g) of the mixture containing the other components was partially separated by preparative g.l.c. to give methyl 4,6-dideoxy-2,3-di-*O*-methyl-α-L-*threo*-hex-3-enopyranoside (**7**) (117 mg), b.p. 40–42°/0.05 mmHg, $[\alpha]_D$ −213° (*c* 1, carbon tetrachloride), ν_{max}^{film} 1670 cm^{-1} (C=C). N.m.r. data: τ 6.45 and 6.57 (9 protons, each singlets, intensity ratio 1:2, 3 × OMe), and 8.70 (3-proton doublet, $J_{5,6}$ 6 Hz, HCMe). The molecular formula was deduced to be $C_9H_{16}O_4$ from the appearance of a top-mass peak at *m/e* 188 (M^+) in the mass spectrum; lit.[1] (D-enantiomer), b.p. 40–42°/0.05 mmHg, $[\alpha]_D$ +208° (*c* 1, carbon tetrachloride). The other component isolated was methyl 4-azido-4,6-dideoxy-2,3-di-*O*-methyl-α-L-mannopyranoside (**9**) (88 mg), b.p. 60–62°/0.05 mmHg, $[\alpha]_D$ −131° (*c* 1, carbon tetrachloride), ν_{max}^{film} 2100 cm^{-1} (N_3) (Found: C, 46.6; H, 7.2; N, 18.1. $C_9H_{17}N_3O_4$ calc.: C, 46.75; H, 7.4; N, 18.2%). N.m.r. data: τ 6.54 and 6.70 (9 protons, each singlets, intensity ratio 2:1, 3 × OMe), and 8.75 (3-proton doublet, $J_{5,6}$ 6 Hz, HCMe). The azide was indistinguishable (i.r. and n.m.r. spectroscopy) from that obtained by methylation[16] of methyl 4-azido-4,6-dideoxy-α-L-mannopyranoside[2].

*Benzyl 6-deoxy-4-*O*-methanesulphonyl-α-L-talopyranoside* (**10**). — A solution of benzyl 6-deoxy-2,3-*O*-isopropylidene-4-*O*-methanesulphonyl-α-L-talopyranoside[7] (6 g) in water (40 ml) and glacial acetic acid (40 ml) was heated under gentle reflux on a

boiling water-bath for 15 min, after which time t.l.c. (acetone–toluene, 1:2) showed that removal of the acetal group was complete. Removal of the solvents, with repeated additions of toluene, afforded the diol **10** (5.1 g), $[\alpha]_D$ −92° (*c* 1, chloroform), ν_{max}^{film} 3500 cm^{-1} (broad, OH), as a syrup, which could not be induced to crystallise.

Acetylation, in the usual manner, gave methyl 2,3-di-*O*-acetyl-6-deoxy-4-*O*-methanesulphonyl-α-L-talopyranoside, m.p. 114–115° (from ethyl acetate–light petroleum, b.p. 80–100°), $[\alpha]_D$ −97° (*c* 1, chloroform) (Found: C, 51.7; H, 5.8; S, 7.7. $C_{18}H_{24}O_9S$ calc.: C, 51.9; H, 5.8; S, 7.7%).

Benzyl 6-deoxy-4-O-methanesulphonyl-2,3-di-O-methyl-α-L-talopyranoside (**11**). — To a solution of **10** (4 g) in dry *N,N*-dimethylformamide (80 ml) containing suspended sodium hydride (2 g) at room temperature was gradually added methyl iodide (20 ml) and, on complete addition, the mixture was set aside for 4 h. Work up, as described previously, gave the dimethyl ether **11** (3.8 g), m.p. 74–75° [from ether–light petroleum (b.p. 80–100°)], $[\alpha]_D$ −6° (*c* 1, chloroform) (Found: C, 53.5; H, 7.1; S, 8.4. $C_{16}H_{24}O_7S$ calc.: C, 53.3; H, 6.7; S, 8.9%).

Reaction of benzyl 6-deoxy-4-O-methanesulphonyl-2,3-di-O-methyl-α-L-talopyranoside (**11**) *with sodium azide in* N,N-*dimethylformamide.* — A solution of the title compound (3 g) in *N,N*-dimethylformamide (300 ml) containing sodium azide (9 g) was heated under reflux for 9 h, after which time t.l.c. (hexane–ethyl acetate, 2:1) showed that no starting material remained. Water (250 ml) was added to the cooled solution, which was then extracted with chloroform (3 × 200 ml), and the combined extracts were washed with water (3 × 300 ml) and dried ($MgSO_4$). G.l.c. (10% silicon ester 30 on Celite, 187°) showed the presence of **12** (68%, retention time 17.5 min), **13** (12%, 12 min), and **14** (20%, 30.4 min). Removal of the solvent left a syrupy residue, which was partially resolved by chromatography on silica gel [elution with hexane–ether (3:1) containing 0.2% of triethylamine] into two main fractions. A portion (0.5 g) of the first fraction (1.5 g) [ν_{max}^{film} 2100 cm^{-1} (N_3) and 1673 cm^{-1} (C=C)] containing both **12** and **14** was separated by preparative g.l.c. to afford benzyl 4,6-dideoxy-2,3-di-*O*-methyl-α-L-*threo*-hex-3-enopyranoside (**12**) (84 mg), ν_{max}^{film} 1673 cm^{-1} (C=C), $[\alpha]_D$ −111.5° (*c* 0.8, chloroform); this material was unstable and deteriorated rapidly on storage. Preparative g.l.c. also gave benzyl 4-azido-4,6-dideoxy-2,3-di-*O*-methyl-α-L-mannopyranoside (**14**) (80 mg), $[\alpha]_D$ −118° (*c* 0.8, chloroform), ν_{max}^{film} 2100 cm^{-1} (N_3) (Found: C, 58.0; H, 7.1; N, 12.8. $C_{15}H_{21}N_3O_4$ calc.: C, 58.6; H, 6.8; N, 13.6%). The second fraction (*ca.* 0.3 g) from the original separation exhibited ν_{max}^{film} 1673 cm^{-1} (C=C), but decomposed before its characterisation could be satisfactorily achieved. It is likely that this unsaturated sugar is benzyl 4,6-dideoxy-2,3-di-*O*-methyl-β-D-*erythro*-hex-4-enopyranoside (**13**), since its n.m.r. spectrum exhibited a three-proton singlet at τ 8.20.

Benzyl 4-acetamido-4,6-dideoxy-2,3-di-O-methyl-α-L-mannopyranoside (**15**). — A mixture (0.45 g) containing **12**, **13**, and **14** from the azide-exchange reaction in dry ether (12 ml) containing lithium aluminium hydride (0.12 g) was heated under gentle reflux for 1 h before ethyl acetate (2 ml) and ether (5 ml) were added, followed by a few drops of water to destroy the excess of reagent. The mixture was heated briefly,

insoluble material was filtered off and washed thoroughly with ether, and the combined filtrate and washings were dried ($MgSO_4$). Removal of the solvent left a residue (*ca.* 0.37 g), which was dissolved in methanol (1 ml) and treated with acetic anhydride (0.5 ml) for 1 h at room temperature, whereupon the solvents were removed with repeated additions of toluene. Part of the residue crystallised from chloroform–ether, giving the amide **15** (0.1 g), m.p. 176–178°, $[\alpha]_D$ −63° (*c* 1, chloroform), ν_{max} 1650 and 1550 cm^{-1} (amide) (Found: C, 63.1; H, 7.5; N, 4.25. $C_{17}H_{25}NO_5$ calc.: C, 63.2; H, 7.7; N, 4.3%). N.m.r. data: τ *ca.* 2.70 (5 aromatic protons), 5.45 (2 protons, AB quartet, *J* 12 Hz, benzyl methylene protons), 6.54 and 6.62 (3-proton singlets, 2 × OMe), 8.05 (3-proton singlet, NAc), and 8.80 (3-proton doublet, $J_{5,6}$ 6 Hz, HCMe).

ACKNOWLEDGMENT

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