Carbohydrate Research
Elsevier Publishing Company, Amsterdam
Printed in Belgium

A RE-EXAMINATION OF THE ACETONATION OF AN EQUILIBRIUM MIXTURE OF D-ALTROSE AND 1,6-ANHYDRO-β-D-ALTROPYRANOSE AND A SYNTHESIS OF 1,2:5,6-DI-*O*-ISOPROPYLIDENE-β-D-MANNOFURANOSE

J. S. BRIMACOMBE* AND (MISS) P. A. GENT
Chemistry Department, P. O. Box 363, The University, Birmingham 15 (Great Britain)
(Received May 27th, 1969)

ABSTRACT

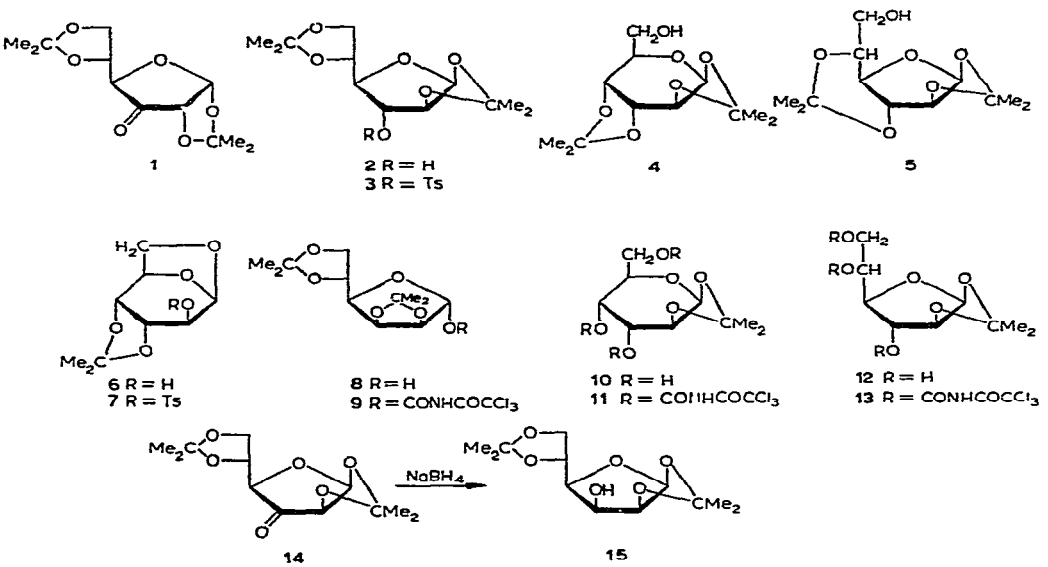
Acid-catalysed acetonation of an equilibrium mixture of D-altrose and 1,6-anhydro-β-D-altropyranose was shown by g.l.c. to yield 1,6-anhydro-3,4-*O*-isopropylidene-β-D-altropyranose (**6**, 60%), 1,2:5,6-di-*O*-isopropylidene-β-D-altrofuranose (**2**, 23%), and 1,2:3,4-di-*O*-isopropylidene-β-D-altropyranose (**4**, 17%). Evidence is presented in support of the structure **4** for the latter diacetal which has been obtained in crystalline form. Oxidation of the diacetal **2** with acetic anhydride–methyl sulphoxide afforded 1,2:5,6-di-*O*-isopropylidene-β-D-*arabino*-hexofuranos-3-ulose (**14**), which was reduced stereospecifically, with sodium borohydride, to 1,2:5,6-di-*O*-isopropylidene-β-D-mannofuranose (**15**).

INTRODUCTION

The ketone **1**, which is obtained[1–3] by oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, has proved to be a versatile intermediate in the synthesis of a number of sugars of biological interest. Syntheses of 3-acetamido-3-deoxy-D-glucose[3], 3-acetamido-3-deoxy-D-galactose[4], 3-amino-3-deoxy-D-xylose[3], 3-amino-3-deoxy-L-arabinose[5], 3-deoxy-3-fluoro-D-glucose[6], 3-deoxy-3-fluoro-D-galactose[7], D-allose[8], and D-gulose[9] have been initiated from the ketone **1**. The general procedures adopted in the foregoing syntheses should be applicable to other 1,2:5,6-di-*O*-isopropylidene-hexofuranos-3-uloses, and, in this connection, we sought to prepare the ketone **14** by oxidation of 1,2:5,6-di-*O*-isopropylidene-β-D-altrofuranose (**2**). The diacetal **2** is obtained, *inter alia*, by acid-catalysed acetonation of D-altrose[10] or the equilibrium mixture of D-altrose and 1,6-anhydro-β-D-altropyranose resulting from acid hydrolysis of methyl 4,6-*O*-benzylidene-α-D-altropyranoside[11]. The structure **2** is reasonably founded[10] on the unreactivity of the diacetal towards oxidation by alkaline permanganate. The latter acetonation also yielded 1,6-anhydro-3,4-*O*-isopropylidene-β-D-altropyranose (**6**) and a second, syrupy diacetal to which the structure 1,2:3,4-di-*O*-isopropylidene-β-D-altropyranose (**4**) was tentatively assigned[11], since, on oxidation with alkaline permanganate, it afforded a carboxylic acid derivative. However, it was pointed out[11] that the structure **5**, although less likely, would also fit the available

*To whom enquiries should be addressed at The Chemistry Department, The University, Dundee DD1 4HN, Scotland.

evidence. We now present evidence in favour of the structure **4** and report on a synthesis of 1,2:5,6-di-*O*-isopropylidene-β-D-mannofuranose (**15**) from diacetal **2**.



DISCUSSION

The diacetal **2** was prepared according to the literature procedures[10,11] and was isolated from the acid-catalysed acetonation of D-altrose by chromatography on silica gel. A comprehensive analysis of the products of acetonation was not attempted in this case, but the percentage composition of the acetals formed by acetonation of D-altrose–1,6-anhydro-β-D-altropyranose was given as **6** (60%), **2** (23%), and **4** (17%) by g.l.c. Chromatography of these products on silica gel afforded a fraction containing both the diacetals **2** and **4**, together with a second fraction which yielded 1,6-anhydro-3,4-*O*-isopropylidene-β-D-altropyranose (**6**) (characterised as the crystalline 2-toluene-*p*-sulphonate **7**)[11]. 1,2:5,6-Di-*O*-isopropylidene-β-D-altrofuranose (**2**) could be crystallised directly from the mixture of diacetals, whereafter preparative g.l.c. of the mother liquors was used to separate 1,2:3,4-di-*O*-isopropylidene-β-D-altropyranose (**4**), which was obtained in crystalline form. Comparison of the physical constants (see Experimental) of the crystalline diacetal **4** with those reported[11] for a syrupy preparation suggested that the latter was probably heavily contaminated with the strongly laevorotatory acetal **6**.

The chemical evidence[10] for the structure of diacetal **2** was confirmed by mass spectrometry. In addition to the highest mass peak at *m/e* 245 (M − 15), the mass spectrum of **2** exhibited a prominent peak at *m/e* 101 (M − 159) which is characteristic[12] in these compounds for fragmentation of the C-4–C-5 bond. The mass spectrum of the isomeric diacetal **4** contained a peak at *m/e* 245 (M − 15), and it also exhibited other mass peaks (see Experimental) that were compatible with[12], but not definitive for, the structure assigned.

More-compelling evidence for the structure **4** accrued from n.m.r. spectroscopy of the monoacetals formed on graded, acid hydrolysis; complete, acid hydrolysis liberated D-altrose as the only reducing sugar. Attempts to selectively remove one of the isopropylidene groups by brief treatment of diacetal **4** with hot 1% nitric acid in ethyl acetate gave a fairly complex product mixture, although these conditions selectively removed[13] the 3,4-acetal group from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose. Treatment of diacetal **4** with 80% acetic acid for 2 h at 50° gave a small proportion of a monoacetal fraction that was isolated by chromatography on silica gel. N.m.r. spectroscopy (see Fig. 3) and g.l.c. of this fraction showed that it consisted of two monoacetals in the ratio of *ca.* 4:1. The major component (*A*) was readily distinguished from 1,2-*O*-isopropylidene-β-D-altrofuranose[14] (**12**) by n.m.r. spectroscopy (*cf.* Figs. 2 and 3) and by comparison of the derived tris-*O*-(trimethylsilyl) derivatives by g.l.c. A choice between other possible structures for *A* was based on n.m.r. spectroscopy of the tris(trichloroacetylcarbamate) which was rapidly formed, *in situ*, by the addition of a slight excess of trichloroacetyl isocyanate[15] to a solution of *A* in deuterioacetone. Characteristic downfield shifts of carbinol protons are observed[16] upon formation of the trichloroacetylcarbamoyl derivative, and related shifts have been of immense value in assigning structures to partially esterified carbohydrates[17]. The effect on the n.m.r. spectrum of adding trichloroacetyl isocyanate to a solution of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**8**) in deuteriochloroform is clearly seen from Fig. 1. The H-1 resonance of **8** appears at τ 4.64 as a narrow doublet ($J_{H,OH}$ 2.5 Hz) due to coupling with the hydroxylic proton. Conversion into the trichloroacetylcarbamate **9** removes this coupling, and the H-1 resonance now appears as a singlet at τ 3.82, a downfield shift of *ca.* 0.8 p.p.m.

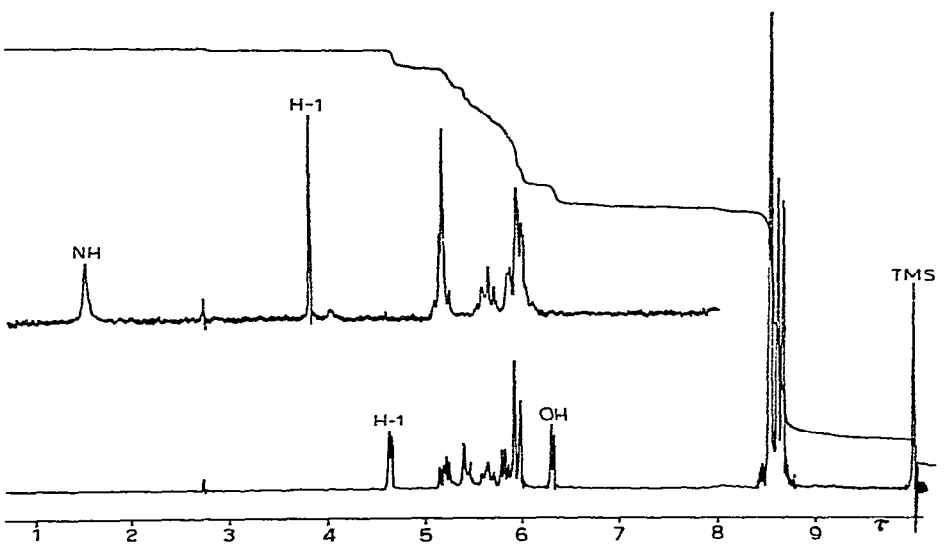


Fig. 1. The n.m.r. spectrum (100 MHz, $CDCl_3$) of 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**8**), and the partial spectrum of the derived trichloroacetylcarbamate (**9**).

By contrast, the H-1 resonance observed as a narrow doublet at τ 4.20 in the n.m.r. spectrum of the 1,2-acetal **12** suffers only a minor shift on formation of the tris-(trichloroacetylcarbamoyl) derivative **13** (see Fig. 2). Marked shifts to lower field can be noted, however, for other resonances in the spectrum, which is now amenable to analysis. Treatment of monoacetal *A* with trichloroacetyl isocyanate caused (Fig. 3)

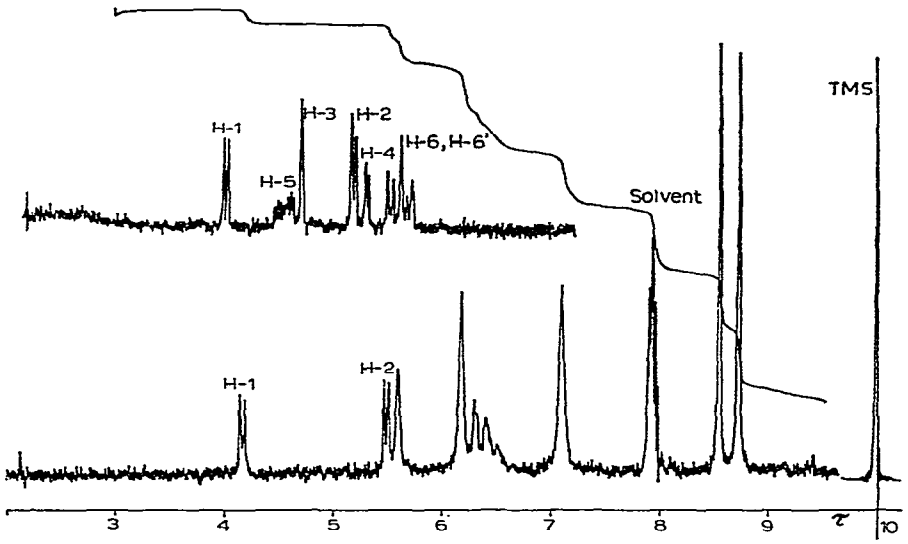


Fig. 2. The n.m.r. spectrum (100 MHz, Me_2CO-d_6) of 1,2-*O*-isopropylidene-β-D-altrofuranose (**12**) and the partial spectrum of the tris(trichloroacetylcarbamoyl) derivative (**13**). The coupling constant obtained for **13** were $J_{1,2}$ 4; $J_{2,3} \sim J_{3,4}$ <0·5; $J_{4,5}$ 2·5; $J_{5,6}$ 5; $J_{5,6'} \sim$10 Hz.

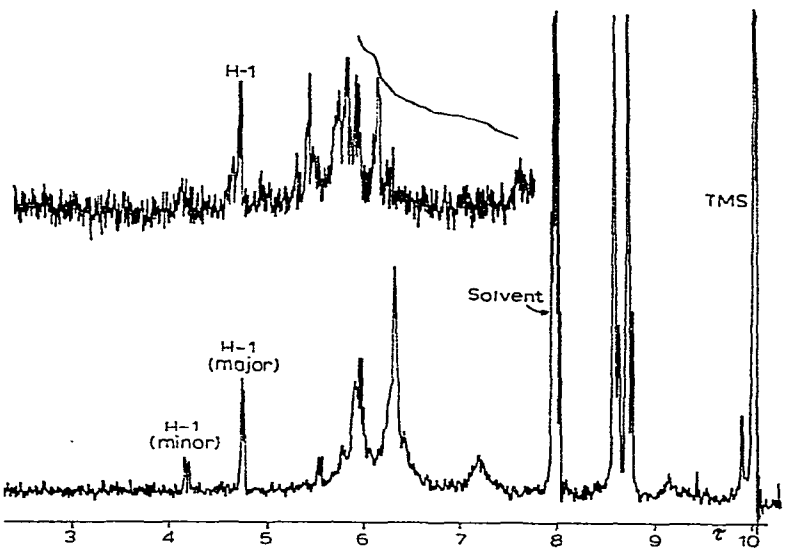


Fig. 3. The n.m.r. spectra (100 MHz, Me_2CO-d_6) of the monoacetals resulting from graded hydrolysis of diacetal **4** before and after (inset) the addition of trichloroacetyl isocyanate.

no change in the chemical shift of the H-1 resonance, which appears as a narrow doublet ($J_{1,2}$ *ca.* 2 Hz) centred at τ 4.75. This implies that the acetal group must involve C-1 and C-2, and hence that *A* is 1,2-*O*-isopropylidene-β-D-altropyranose (**10**). This information, combined with the chemical evidence[11], precludes structures other than **4** for the original diacetal.

The diacetal **2** was oxidised with acetic anhydride–methyl sulphoxide[18] to give, principally, 1,2:5,6-di-*O*-isopropylidene-β-D-*arabino*-hexofuranos-3-ulose (**14**), which gave 1,2:5,6-di-*O*-isopropylidene-β-D-mannofuranose (**15**) on reduction with sodium borohydride in aqueous ethanol. The stereospecificity of this reduction parallels that observed[3,19] with the ketone **1**, and, in each case, the approach of the nucleophile to the carbonyl group is clearly favoured from an *exo*-direction with respect to the trioxabicyclo[3.3.0]octane ring-system. The structure of diacetal **15** was proved by elemental analyses, by the formation of D-mannose (characterised as the phenylhydrazone[20]) on complete acid hydrolysis, and from the presence of a peak at *m/e* 101 (M − 159) in its mass spectrum[12]. The mass spectrum of **15** was generally similar to that of the isomeric diacetal **8**, but it was significant that the latter spectrum contained a more intense peak at *m/e* 243 (M − 17) due to the attachment of the hydroxyl group to C-1 rather than to C-3. This difference was also apparent[21] in the mass spectra of the isomeric D-talofuranose diacetals having 2,3:5,6- and 1,2:5,6-arrangements of the isopropylidene groups. These results lend weight to a suggestion of De Jongh and Biemann[12] that differences of this sort may prove useful in assigning structures to isomeric di-*O*-isopropylidenehexofuranoses.

EXPERIMENTAL

Thin-layer chromatography (t.l.c.) was performed on Kieselgel G, and detection was effected with vanillin–sulphuric acid[22]. Paper chromatography was performed on Whatman No. 1 paper by downward irrigation with ethyl acetate–pyridine–water (8:2:1, solvent *a*) or butyl alcohol–pyridine–water (6:4:3, solvent *b*), and detection with aniline hydrogen phthalate[23]. Analytical g.l.c. was carried out by using a Pye 104 gas chromatograph, and preparative separations were effected on a Pye 105 gas chromatograph (column, 30′ × 3/8″); a column packing of 10% silicon ester-30 on Celite was used in both cases, at the stated temperature. Infrared spectra were recorded with a Perkin–Elmer 257 spectrometer, and, unless otherwise indicated, n.m.r. spectra were obtained with a Perkin–Elmer R-14 spectrometer for deuteriochloroform solutions with tetramethylsilane as internal reference. Mass spectra were measured with an A.E.I. MS9 spectrometer using a direct-insertion technique. Trimethylsilylations were achieved by using bis(trimethylsilyl)acetamide according to the manufacturer's instructions.

Acetonation of D-*altrose.* — A solution of syrupy D-altrose[24] (0.72 g) in dry acetone (50 ml) containing anhydrous copper(II) sulphate (3.6 g) and conc. sulphuric acid (0.05 ml) was shaken for 48 h at room temperature, and the reaction mixture was then processed as described by Steiger and Reichstein[10]. A partial separation

of the diacetal fraction was obtained by chromatography of the syrupy products (0.88 g) on silica gel (elution with 15% of acetone in toluene). Two recrystallisations from ether–light petroleum (b.p. 40–60°) gave the diacetal **2** (0.13 g), m.p. 89–90°, $[\alpha]_D$ +25° (*c* 0.49, acetone); lit., m.p. 89°, $[\alpha]_D$ +28.3° (*c* 2, acetone) (ref. 10); m.p. 87–88°, $[\alpha]_D$ +28.7° (*c* 1.04, acetone) (ref. 11). The derived 3-toluene-*p*-sulphonate[14] **3**, prepared in the usual manner, had m.p. 101–102° (from ethanol), $[\alpha]_D$ +29° (*c* 0.5, chloroform). The mass spectrum of diacetal **2** showed prominent peaks at *m/e* 245 (M−15), 187, 159, 127, 101, 59, and 43, in agreement[12] with the structure originally assigned[11]. N.m.r. data: τ 4.10 (1-proton doublet, $J_{1,2}$ 4 Hz, H-1); 8.50, 8.58, 8.65, 8.68 (singlets, each 3 protons, isopropylidene groups).

Acetonation of an equilibrium mixture of D-*altrose and 1,6-anhydro-β-*D-*altropyranose.* — A mixture[11] of the title compounds (18 g) was shaken with acetone (280 ml) containing conc. sulphuric acid (1.6 ml) for 24 h at room temperature, whereafter the solution was neutralised with conc. ammonia, and solids were filtered off. Evaporation of the solvent left a syrup which was extracted with ether (6 × 50 ml), and the combined extracts were evaporated to give the products (13.8 g). G.l.c. (column temperature, 151°) showed that the mixture contained **6** (60%), **2** (23%), and **4** (17%), with retention times of 13.2, 25.8, and 21.6 min, respectively. A portion (6 g) of the mixture was chromatographed on silica gel (elution with ethyl acetate–hexane, 2:1) to yield a crystalline mixture of the diacetals **2** and **4** (1.65 g) and, after washing the column with acetone, the acetal **6** (*ca.* 3.4 g). The latter compound was characterised as the crystalline 2-toluene-*p*-sulphonate **7** which had m.p. 178–178.5°, $[\alpha]_D$ −153° (*c* 0.57, chloroform); lit.[11], m.p. 176–177°, $[\alpha]_D$ −150.8° (*c* 2.24, chloroform). The remainder of the original acetonation products was chromatographed in the same way to give a total of 5.5 g of diacetals **2** and **4**. Fractional crystallisation from ether–light petroleum (b.p. 60–80°) gave diacetal **2** (1.8 g), m.p. and mixed m.p. 87–88°, $[\alpha]_D$ +29° (*c* 0.7, acetone). G.l.c. of the mother liquors at this stage revealed the predominance of diacetal **4**. Concentration of the mother liquors left a crystalline residue (3.1 g) which was dissolved in ether to give an approximately 50% solution, which was subjected, in several aliquot portions (200 μl), to preparative g.l.c. (column temperature, 182°; nitrogen flow-rate, 120 ml/min). Collection of the appropriate fractions (retention time, 1.7 h) afforded a crystalline material which was sublimed at 15 mmHg to give diacetal **4** (0.2 g), m.p. 64–65°, $[\alpha]_D$ +68° (*c* 0.96, chloroform), ν_{max} 1379 (CMe_2) and 3507 cm^{-1} (OH) (Found: C, 55.1; H, 7.8. $C_{12}H_{20}O_6$ calc.: C, 55.4; H, 7.7%). The mass spectrum contained characteristic[12] peaks at *m/e* 245 (M−15), 187, 171, 127, 113, 100, 99, 85, 71, 69, 59, and 43. N.m.r. data: τ 4.73 (1-proton doublet, $J_{1,2}$ 2.5 Hz, H-1); 8.49, 8.55, 8.62, 8.65 (singlets, each 3 protons, isopropylidene groups). Newth and Wiggins[11] reported $[\alpha]_D$ −13.1° (*c* 1.3, chloroform) for a syrupy preparation which was probably contaminated with the acetal **6**.

Hydrolysis of diacetal **4** in a small quantity of methanol containing an equal volume of N sulphuric acid on a boiling water-bath for 2 h liberated D-altrose (chromatographic identification in solvent *a*) as the only reducing component.

1,2-O-Isopropylidene-β-D-altrofuranose (**12**). — This compound, m.p. 129–130°, $[\alpha]_D$ +23° (*c* 0.64, methanol), was prepared as described by Newth[14] who reported m.p. 125–126°, $[\alpha]_D$ +25.8° (*c* 1.01, methanol). The n.m.r. spectrum of monoacetal **12** in deuterioacetone and that of the tris(trichloroacetylcarbamate) **13** (prepared by the addition of a slight excess of trichloroacetyl isocyanate[15]) are shown in Fig. 2.

Graded hydrolysis of 1,2:3,4-di-O-isopropylidene-β-D-altropyranose (**4**). — A solution of diacetal **4** (0.16 g) in 80% acetic acid (5 ml) was heated for 2 h at 50°, after which time t.l.c. (methanol–ethyl acetate, 9:1) revealed the presence of the free sugar, a monoacetal fraction, and unreacted material. The solvents were removed, and the residue was chromatographed on silica gel (elution with methanol–ethyl acetate, 19:1) to give a crystalline fraction (30 mg), m.p. 128–129° (from ethyl acetate), containing monoacetal **10** and a second monoacetal, presumably 3,4-*O*-isopropylidene-D-altropyranose, in the ratio of *ca.* 4:1; further recrystallisations failed to remove the minor component (Found: C, 49.1; H, 7.0. $C_9H_{16}O_6$ calc.: C, 49.1; H, 7.3%). The monoacetals **10** and **12** were distinguished by g.l.c. (column temperature, 190°) of their tris-*O*-(trimethylsilyl) derivatives which had retention times of 18.4 and 21.6 min, respectively. The m.p. of the crystalline fraction containing **10** was depressed to 113–117° on admixture with compound **12**, and the X-ray powder photographs of the two materials showed them to be different.

The n.m.r. spectrum (deuterioacetone) of the mixture of monoacetals resulting from graded hydrolysis of diacetal **4** is shown in Fig. 3, together with part of the spectrum after the addition of trichloroacetyl isocyanate.

1,2:5,6-Di-O-isopropylidene-β-D-mannofuranose (**15**). — A solution of diacetal **2** (0.31 g) in methyl sulphoxide (24 ml) and acetic anhydride (3 ml) was stirred for 15 h at room temperature, whereupon t.l.c. (acetone–toluene, 1:4) showed that all of the starting material had reacted. The solvents were removed under diminished pressure at 50° to give a syrup which was distilled to give the ketone **14** (0.22 g), b.p. 102–108° (bath)/0.7 mmHg, $[\alpha]_D$ −25° (*c* 0.9, acetone), ν_{max} 1778 (C = O) and 1375 cm^{-1} (CMe_2). T.l.c. showed that this material contained a small proportion of a faster-moving component, but it was used in subsequent experiments without further purification (Found: C, 55.1; H, 6.7. $C_{12}H_{18}O_6$ calc. : C, 55.8; H, 7.0%).

Sodium borohydride (0.2 g) was gradually added to the ketone **14** (0.2 g) in 75% aqueous methanol (5 ml) and, on complete addition, the solution was kept for 1.5 h at room temperature. It was then extracted with chloroform (3 × 5 ml), and the combined extracts were washed with water (5 ml) and dried ($MgSO_4$). G.l.c. (column temperature, 172°) of the trimethylsilyl ether of the product (retention time, 22.8 min) showed that negligible amounts of diacetal **2** were formed; trimethylsilylation of **2** gave a product having a retention time of 20.4 min. Removal of the solvent left a syrupy residue (0.19 g) which still contained a faster-moving impurity. Preparative t.l.c. [acetone–toluene (1:4) as the mobile phase] and distillation gave the pure diacetal **15** (0.12 g), b.p. 120–125°(bath)/0.05 mmHg, which crystallised on standing. The crystalline material had m.p. 51–53.5° [from ether–light petroleum (b.p. 40–60°)], $[\alpha]_D$ +3 ±1° (*c* 1.27, acetone), ν_{max} 3500 (OH) and 1377 cm^{-1} (CMe_2) (Found:

C, 55.1; H, 7.8. $C_{12}H_{20}O_6$ calc.: C, 55.4; H, 7.7%). N.m.r. data: τ 4.33 (1-proton doublet, $J_{1,2}$ 4 Hz, H-1); 5.30–6.30 (6 protons, H-2–H-6); 8.41, 8.56, 8.60, 8.63 (singlets, each 3 protons, isopropylidene groups). The mass spectrum of **15** exhibited peaks at *m/e* 245 (M − 15), 187, 159, 127, 113, 101, 85, 59, and 43, in accord[12] with the structure assigned.

Hydrolysis of **15** (80 mg) in 50% aqueous methanol (5 ml) for 5 h at 66° with an excess of Amberlite IR-120 (H^+) afforded D-mannose (*ca.* 50 mg) (chromatographic identification, solvent *b*) as the only reducing sugar. D-Mannose phenylhydrazone, prepared in the usual way[20], had m.p. 195–196° (dec.), and its X-ray powder photograph was indistinguishable from that of an authentic sample; lit.[20] m.p. 199–200°.

ACKNOWLEDGMENTS

The authors thank Professor M. Stacey, C. B. E., F. R. S., for his interest, Dr. E. F. Mooney for measuring the n.m.r. spectra, and Dr. J. R. Majer for obtaining the mass spectra. The Science Research Council is gratefully acknowledged for the award of a studentship (to P. A. G.).

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