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ACID-CATALYZED ISOPROPYLIDENATION OF SOME HEPTOSES

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ABSTRACT

Acid-catalyzed acetonation of D-*glycero*-D-*galacto*-heptose yields solely the 1,2:3,4:6,7-tri-*O*-isopropylidene pyranoid derivative, whereas D-*glycero*-L-*gluco*- and D-*glycero*-L-*manno*-heptose react in the furanose form to give 1,2:5,6-(major) and 1,2:6,7-di-*O*-isopropylidene-D-*glycero*-L-*gluco*-heptose (minor), and 2,3:5,6-(major) and 2,3:6,7-di-*O*-isopropylidene-D-*glycero*-L-*manno*-heptose (minor), respectively.

INTRODUCTION

Isopropylidene acetals are widely used as protecting groups in carbohydrate chemistry. The structures of the *O*-isopropylidene derivatives of the pentoses and the majority of the hexoses and of their acyclic derivatives are now well-established. Empirical rules have been proposed to correlate the structures of sugars with the arrangement of acetal residues in the corresponding isopropylidene derivatives[1].

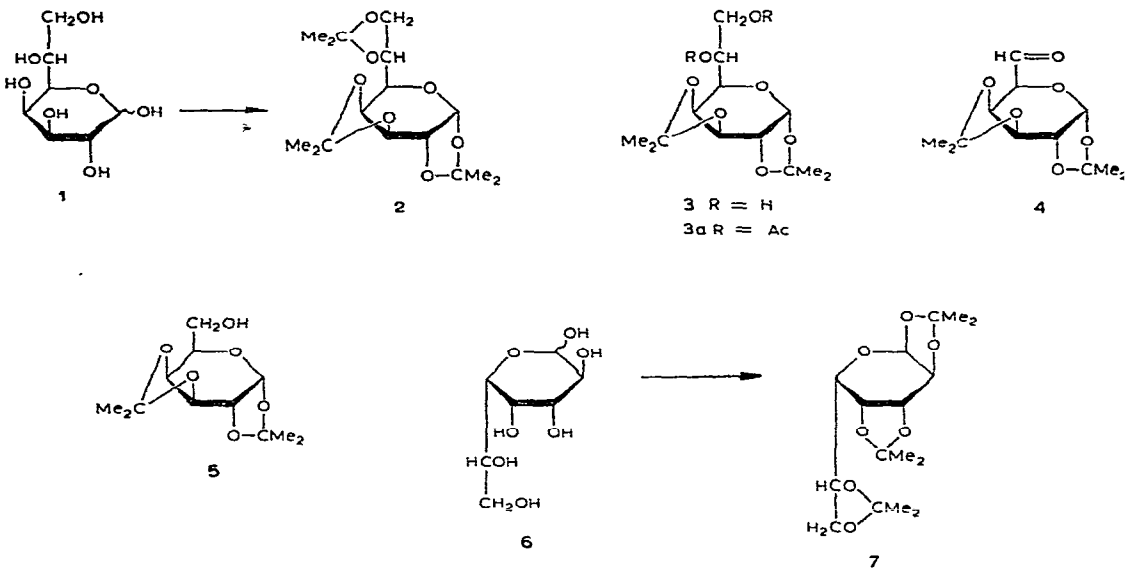
Heptoses offer additional possibilities in condensation reactions with acetone, and we now report on the acetonation of heptoses structurally related to galactose, glucose, and mannose.

RESULTS AND DISCUSSION

Treatment of D-*glycero*-D-*galacto*-heptose[2] (**1**) with dry acetone containing 0.05M sulphuric acid, under conditions of thermodynamic control, was thought to yield the tri-*O*-isopropylidene derivative **2**, as the configuration of **1** is favourable for reaction in the pyranose form. The triacetal **2** is the sole product and its structure was proved by m.s. data[3,4] and by chemical evidence. The mass spectrum of **2** contains an intense peak at *m/e* 315 (M − 15), thus proving the molecular weight to be 330. The other characteristic, primary fragments at *m/e* 229 and 101 were formed by fission of the C-5–C-6 bond.

Mild, acid hydrolysis of the 6,7-acetal group of **2** afforded the diacetal **3** in high yield. The diacetal **3** has also been prepared[5] by ozonolysis of 7,8-dideoxy-1,2:3,4-di-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-oct-7-enopyranose followed by reduction,

though the product was not completely characterized. The structure of **3** was confirmed herein by m.s. and p.m.r. spectral data for the 6,7-diacetate (**3a**). The observed *J* values of the ring protons (Table I) are indicative of a non-chair conformation of a pyranose ring fused *cis–anti–cis* to two dioxolane rings[6]. Oxidation of **3** with lead tetra-acetate gave 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**4**). Reduction of **4** with borohydride afforded known[7] 1,2:3,4-di-*O*-isopropylidene-α-D-galactose (**5**).



The foregoing data establish that **2** has a pyranoid structure and that acetonation of **1** proceeds with preservation of the pyranose ring in a manner analogous to that of galactose. The presence of an additional CH(OH) group allows the formation of a third isopropylidene residue.

The mixture of D-*glycero*-L-*galacto*- and D-*glycero*-L-*ido*-heptose, obtained[8] from D-xylose *via* a Wittig reaction, can be fractionated after acetonation. Acetonation of crystalline D-*glycero*-L-*galacto*-heptose (**6**) yielded, quantitatively, a triacetal (**7**), the mass spectrum of which was identical to that of **2**. The result of acetonation of D-*glycero*-L-*gluco*-heptose[9] (**8**) was difficult to predict, as the formation of di-*O*-isopropylidene pyranoid and furanoid derivatives is theoretically possible, and, in fact, two diacetals (**9** and **10**) were formed (combined yield, 65%). Under the reaction conditions used, **8** appeared to be of low solubility and 20% was recovered. The isomers **9** and **10** were obtained in pure form in yields of 53 and 11%, respectively, after column chromatography.

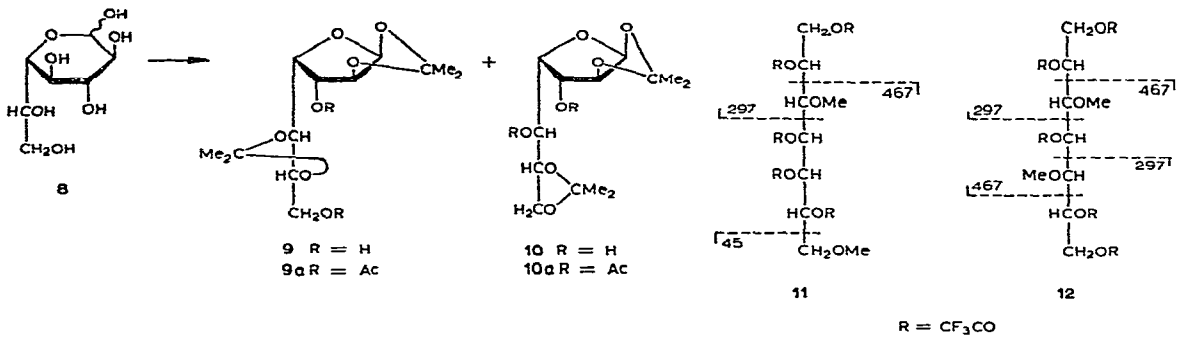
The mass spectra of **9** and **10** contained intense peaks at *m/e* 275 (M−15) and 159 which indicated that each isomer was a diacetal with a furanose ring fused to a 2,2-dimethyl-1,3-dioxolane ring[4]. However, the ratio of intensities for the peaks at

TABLE I

P.M.R. DATA OF HEPTOSE ISOPROPYLIDENE DERIVATIVES[a]

Compound	*Chemical shifts (δ, p.p.m.)*								*Coupling constants (Hz)*				
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*C-CH₃*	*O-Ac*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
3a	5.40d		4.55q	4.31q	3.91q	4.97o	1.29 (×2) 1.39, 1.50	1.98, 1.99	5.0	2.5	8.0	2.0	9.0
9a	5.75d	4.36d	5.15d				1.27, 1.47 1.35 (×2)	2.05 (×2)	3.7	—	2.8	—	—
10a	5.78d	4.33d	5.28d		4.92q		1.27 (×2) 1.34, 1.48	1.98 (×2)	3.7	—	2.8	9.8	3.5
14a	6.00s	5.56d	4.76q				1.30, 1.44 1.36 (×2)	2.0 (×2)	0.5	5.9	2.8	—	—
14b	5.23s	4.47d	4.73q				1.29 1.39 (×2)	2.03	0.5	5.9	2.8	—	—
15a	6.06s	4.56d	4.72q		5.03q		1.30 (×2) 1.37, 1.46	2.03, 2.05	0.5	5.9	3.5	9.0	3.0
15b	5.29s	4.47d	4.68q		5.07q		1.28 (×2) 1.38 (×2)	2.03	0.5	5.9	3.5	9.0	3.0
16a	5.92s	4.50d	4.68q		5.26q		1.21 (×2) 1.27, 1.40	1.94 (×2)	0.5	5.9	3.0	8.0	5.0

[a]Spectra were recorded in CCl_4 solution at 60 MHz: s, singlet; d, doublet; q, quartet; o, octet.



m/e 101 and 131 was 1:4 for **9**, and 8:1 for **10**; the peaks at *m/e* 101 and 131 are due not only to primary fragments but also to secondary ones arising from ions at *m/e* 159 and 189 by the loss of acetone (−58). These data indicate that the isopropylidene residues in **9** and **10** occupy different positions in the exocyclic (C-5,6,7) moiety. The furanoid nature of **9** and **10** was further confirmed by the p.m.r. spectra of the respective diacetates (**9a** and **10a**). The signals of H-1,2,3 were doublets having small coupling constants ($J_{1,2}$ 3.7, $J_{3,4}$ 2.8 Hz), so that a *cis* 1,2-*O*-isopropylidene furanoid-structure[10] could be assigned. Because of the AcO-5 group in **10a**, the signal of H-5 appears as a low-field quartet.

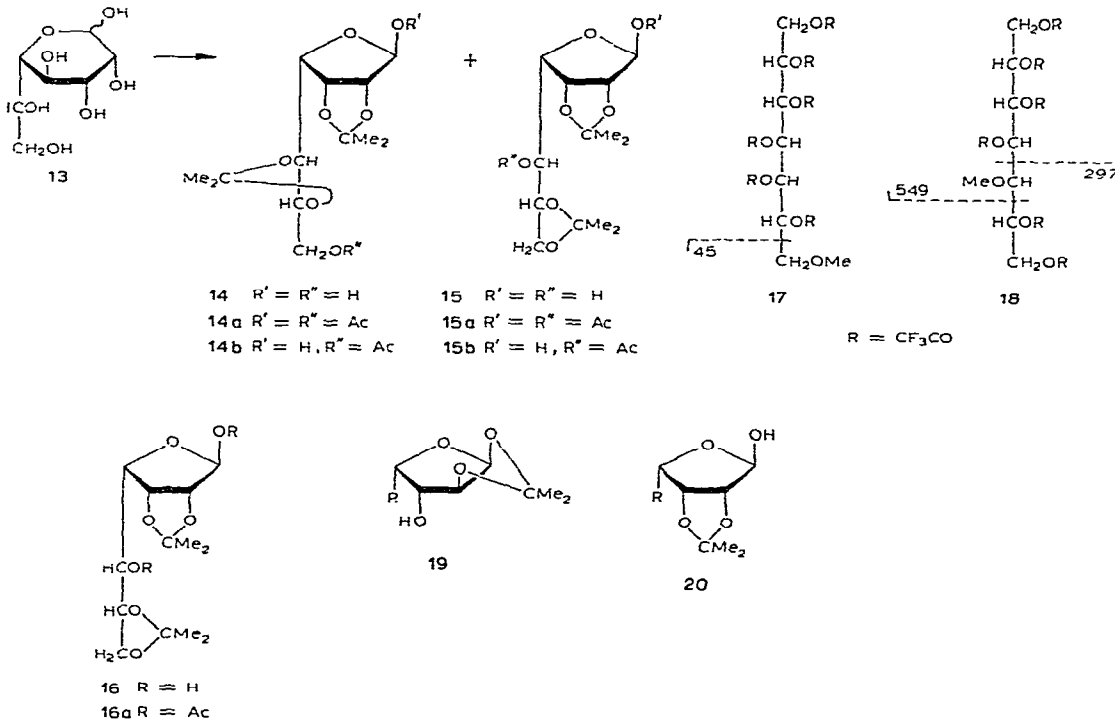
The correlation[11] between the steric environment of the C-methyl groups in 2,2-dimethyl-1,3-dioxolane rings and their chemical shifts also confirmed the structures of **9** and **10**. In the p.m.r. spectrum of **9a**, there were three signals for Me protons in the ratios 1:2:1 at 1.27, 1.35, and 1.47 p.p.m., corresponding to one Me^{α}, two Me^{β}, and one Me^{γ}, respectively; Me^{α}, Me^{β}, and Me^{γ} connote[11] (*cf.* ref. 12) Me groups *cis* to H/H, H/R, and R′/R″, respectively, at positions 4 and 5.

Methylation analysis of **9** and **10** led to 3,7- and 3,5-di-*O*-methylheptitols, which were unequivocally identified by m.s. of the pentakis(trifluoroacetates), **11** and **12**, respectively. The fragmentation of **11** and **12** was analogous to that described for methylated alditol acetates, *i.e.*, fission took place mainly near to CH(OMe) groups. The primary fragments containing methoxyl groups lost molecules of trifluoroacetic acid (−114) to yield more-intense peaks of secondary fragments. Structures **11** and **12** are similar, and the respective mass spectra contained the same series of 5-C and 3-C ions. An abundant peak at *m/e* 45 for **11** was consistent with a terminal methoxyl group. A similar peak, but with half the intensity, was given by **12**, and this could be due to migration of H• to the terminal methoxyl group of the primary fragments followed by further fragmentation to yield $CH_2{=}\overset{+}{O}{-}CH_3$.

Acetonation of D-*glycero*-L-*manno*-heptose[9] (**13**) afforded a mixture of the two isopropylidene derivatives **14** (77%) and **15** (18%), which were isolated by column chromatography.

The structures of **14** and **15** were established on the basis of m.s. and p.m.r. spectroscopy of the diacetates (**14a** and **15a**), and methylation analysis. The fragmentation pattern of **14** and **15** accorded with diacetal structures. Each gave charac-

teristic ions at *m/e* 275 (M−Me), and **15** gave a molecular-ion peak at *m/e* 290. The presence of a substantial peak at *m/e* 159 clearly indicated that each diacetal had a furanoid structure. A peak of low intensity at *m/e* 273 (M−OH) was detected in the spectrum of **15**; this type of ion is given[14] by aldofuranose derivatives having HO-1



unprotected. The ratios of intensities of the peaks at *m/e* 101 and 131 (1:3.5 for **14** and 6.3:1 for **15**) indicated that the isopropylidene residues were differently located in the side chain (C-5,6,7). This conclusion was confirmed by p.m.r. data for the corresponding diacetates (**14a** and **15a**). Acetyl derivatives are useful in studies of furanoid systems that contain unprotected anomeric hydroxyl groups, as acetylation with acetic anhydride in pyridine does not significantly affect the anomeric equilibrium[15]. Moreover[16], furanose rings are stabilised by fusion with dioxolane rings, so that the equilibrium mixture contains <10% of pyranoid forms. The p.m.r. spectrum of the diacetate (**16a**) of 2,3:6,7-di-*O*-isopropylidene-β-D-*glycero*-D-*gulo*-heptofuranose (**16**) was consistent with the furanoid structure deduced by Brimacombe and Tucker[17].

Comparison with the reported data for 2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranose[16] indicated that **14a** and **15a** were furanose derivatives, and the small $J_{1,2}$ values showed them to be β anomers. That the free hydroxyl group in the minor diacetal **15** was at position 5 was supported by the observation that the p.m.r. signal

for one proton of **15a** was a downfield quartet. The chemical shifts and intensity ratios (1:2:1) of the signals for the isopropylidene groups for **14a** indicated Me^{α}, $2Me^{\beta}$, and Me^{γ} groups, and the ratios (2:1:1) for **15a** indicated $2Me^{\alpha}$, Me^{β}, and Me^{γ} groups in agreement with the structures proposed. Methylation (methyl iodide–sodium hydride–*N*,*N*-dimethylformamide) of **14** and **15** under conditions[17] that did not favour mutarotation yielded, after acid hydrolysis and borohydride reduction, 7- and 5-*O*-methylheptitols, respectively, which were identified by m.s. of the hexakis(trifluoroacetates) (**17** and **18**); the principal, primary fragments are shown in the formulae.

On deacetylation of **14a** and **15a** with sodium methoxide in methanol or methanol–chloroform, different rates were observed. AcO-1 was saponified most rapidly and AcO-7 was lost within 30 min, whereas for **15a**, ~16% of the monoacetate **15b** remained after 12 h. These findings may be of use for the selective removal of the protecting groups. The structures of **14b** and **15b** were supported by p.m.r. and m.s. data. The presence of characteristic peaks at *m/e* 317 (M−Me) and abundant peaks at *m/e* 315 (M−OH) were indicative of di-*O*-isopropylidene derivatives having unsubstituted anomeric centres. The p.m.r. spectra of the mono- and di-acetates were very similar (Table I), the only significant difference being the shift of the signal for H-1 to high field by 0.75 p.p.m., reflecting the loss of AcO-1.

The course of isopropylidenation of the heptoses **8** and **13** is parallel to that for glucose and mannose. The formation of a *cis*-fused trioxabicyclo[3.3.0]octane ring-system is typical for the condensation of pentoses and some hexoses with acetone[18], with the minimum number of *endo*-substituents determining fusion at positions 1,2 or 2,3. The favoured structure of the 1,2-acetal **19** is characteristic of the *gluco* configuration, and the 2,3-acetal **20** is typical of the *manno* configuration. The formation of two diacetals from both **8** and **13** probably reflects relatively small differences in the thermodynamic stability of the products. However, the major diacetal of each heptose contains an αT^{12} (5,6)-dioxolane ring which is thermodynamically more-stable than a terminal (α) ring[1].

EXPERIMENTAL

General. — T.l.c. was performed on silica gel KSK, using *A* benzene–methanol (9:1) and *B* chloroform–methanol (94:6). G.l.c. was carried out at 220° on a glass column (1 m × 3 mm) packed with 5% of SE-30 on Chromosorb W (60–80 mesh), using a Pye Unicam 104 chromatograph with a flame-ionization detector and a nitrogen flow-rate of 50 ml/min. Retention times (T_R) of isopropylidene derivatives are given relative to that of tri-*O*-isopropylidene-D-*glycero*-D-*galacto*-heptose (**2**). P.m.r. spectra were recorded on solutions in carbon tetrachloride, using a Varian DA-60-IL (60 MHz) spectrometer with tetramethylsilane and hexamethyldisiloxane (δ 0.05 p.p.m.) as the internal standards. Mass spectrometry was carried out with a Varian CH-6 instrument, using direct insertion and an ionization potential of 70 eV. Optical rotations were determined on a Perkin–Elmer polarimeter Model 141.

Melting points were determined on a Kofler micro hot-stage. Concentrations were carried out under diminished pressure at <40°. Removal of isopropylidene residues was effected by mild hydrolysis with 90% trifluoroacetic acid[19]. Hydrolysis of methyl furanosides was carried out with 0.3M hydrochloric acid at 100° for 16 h. Trifluoroacetyl derivatives of mono- and di-*O*-methylheptitols were prepared by the procedure of Bourne *et al.*[20].

Acetonation of D-glycero-D-galacto-*heptose* (**1**). — A mixture of powdered **1**[2] (0.45 g) in a 50mM solution of sulphuric acid in dry acetone (75 ml) was stirred for 12 h at room temperature, then neutralised with ammonia, and filtered. Removal of the solvent left a syrupy residue which was eluted from silica gel with chloroform to give 1,2:3,4:6,7-tri-*O*-isopropylidene-α-D-*glycero*-D-*galacto*-heptose (**2**) as a syrup (0.61 g, 86%), $[\alpha]_D^{20}$ −62° (*c* 3, chloroform), R_F 0.75 (solvent *A*), T_R 1.00 (6.16 min). Mass spectrum: *m/e* 330 (M^+), 315 (100%), 257 (13), 199 (30), 229 (2.5), 171 (5), 101 (65).

Anal. Calc. for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.32; H, 8.01.

1,2:3,4-Di-O-*isopropylidene*-α-D-glycero-D-galacto-*heptopyranose* (**3**). — A solution of **2** (0.224 g) in acetic acid (9 ml) was diluted with water (18 ml) and kept for 20 h at room temperature. T.l.c. then revealed complete disappearance of starting material and the formation of a new product with R_F 0.3 (solvent *A*). The solution was concentrated, and toluene was distilled from the residue which was then eluted from silica gel with chloroform–methanol (methanol 0→4%) to afford **3** as a syrup (0.189 g, 96%), $[\alpha]_D^{20}$ −48° (*c* 1.9, chloroform). Mass spectrum: *m/e* 275 (72%), 217 (10), 59 (73), 43 (100).

The 6,7-diacetate (**3a**) had m.p. 50–52° (from pentane), $[\alpha]_D^{21}$ −44° (*c* 3.2, chloroform), R_F 0.77 (solvent *A*), T_R 1.94. Mass spectrum: *m/e* 359 (82%), 299 (8), 241 (8), 181 (17), 314 (7), 256 (8), 198 (15), 138 (28), 229 (1), 171 (6), 113 (67), 100 (100).

Anal. Calc. for $C_{17}H_{26}O_9$: C, 54.53; H, 7.00. Found: C, 54.59; H, 6.97.

A solution of **3** (0.65 g) in dry benzene (8 ml) was treated with an excess of lead tetra-acetate for 7 min at room temperature. The oxidant was decomposed with a few drops of ethylene glycol and the mixture was poured into water (20 ml). The benzene layer was washed with water (2 × 5 ml), dried (Na_2SO_4), and concentrated to give syrupy 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**4**, 49 mg), $[\alpha]_D^{20}$ −119° (*c* 1.9, chloroform), *T* (relative to 1,2:3,4-di-*O*-isopropylidene-α-D-galactose) 0.78 at 180°; lit.[21] $[\alpha]_D^{28}$ −111° (*c* 2.3, chloroform).

A solution of **4** (40 mg) in methanol–chloroform (2:1, 6 ml) was treated with sodium borohydride (30 mg) at room temperature for 12 h. The solution was neutralised with KU-2(H^+) resin and concentrated, and methanol was thrice distilled from the residue to give 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**5**, 38 mg), $[\alpha]_D^{21}$ −53° (*c* 1.9, chloroform), indistinguishable (g.l.c.) from an authentic sample.

1,2:3,4:6,7-Tri-O-*isopropylidene*-β-D-glycero-L-galacto-*heptopyranose* (**7**). — Acetonation of D-*glycero*-L-*galacto*-heptose[8] (**6**, 0.14 g) afforded **7** (0.21 g, 95.5%), m.p. 78–79° (from hexane), $[\alpha]_D^{20}$ +65.5° (*c* 1.85, methanol), R_F 0.7 (solvent *A*),

T_R 1.19. Mass spectrum: *m/e* 315 (92%), 257 (30), 199 (20), 229 (4), 171 (10), 101 (100).

Anal. Calc. for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.14; H, 7.86.

Acetonation of D-glycero-L-gluco-*heptose* (**8**). — A suspension of powdered **8**[9] (1.15 g) in the acetonation mixture (225 ml) was stirred for 48 h in the dark. Unreacted heptose (0.24 g, 21%) was collected, and washed with acetone. The combined filtrate and washings were neutralised with ammonia, filtered, and concentrated. The syrupy product contained a major (R_F 0.35, solvent *B*) and a minor component (R_F 0.43). Elution of the mixture from silica gel with benzene–methanol (methanol 1→3%) gave first the minor isomer **10** (0.175 g, 11%) and then the major isomer **9** (0.835 g, 52.7%).

1,2:5,6-Di-*O*-isopropylidene-*β*-D-*glycero*-L-*gluco*-heptofuranose (**9**) was a syrup, $[\alpha]_D^{20}$ +15° (*c* 2.2, chloroform). Mass spectrum: *m/e* 275 (37%), 217 (14), 157 (14), 159 (3), 101 (8), 131 (34), 59 (100), 43 (83).

Anal. Calc. for $C_{13}H_{22}O_7$: C, 53.79; H, 7.64. Found: C, 54.09; H, 7.88.

The 3,7-diacetate (**9a**) of **9** was a syrup, $[\alpha]_D^{20}$ +37° (*c* 2.15, chloroform), T_R 1.75. Mass spectrum: *m/e* 359 (43%), 301 (15), 241 (5), 181 (23), 201 (6), 143 (18), 173 (22), 115 (90).

Anal. Calc. for $C_{17}H_{26}O_9$: C, 54.53; H, 7.00. Found: C, 54.64; H, 7.09.

1,2:6,7-Di-*O*-isopropylidene-*β*-D-*glycero*-L-*gluco*-heptofuranose (**10**) had m.p. 85–87° (from hexane), $[\alpha]_D^{18}$ +9° (*c* 2.2, chloroform). Mass spectrum: *m/e* 275 (37%), 217 (14), 157 (17), 189 (3), 131 (12), 159 (8), 101 (100).

Anal. Calc. for $C_{13}H_{22}O_7$: C, 53.79; H, 7.64. Found: C, 53.89; H, 7.70.

The 3,5-diacetate (**10a**) of **10** had m.p. 114–116° (from heptane), $[\alpha]_D^{18}$ −3° (*c* 2.6, chloroform), T_R 1.58. Mass spectrum: *m/e* 359 (58%), 301 (28), 241 (5), 181 (20), 359 (6), 299 (5), 239 (3), 101 (100).

Anal. Calc. for $C_{17}H_{26}O_9$: C, 54.53; H, 7.00. Found: C, 54.55; H, 6.98.

Acetonation of D-glycero-L-manno-*heptose* (**13**). — A suspension of powdered **13**[9] (0.45 g) in the acetonation mixture (75 ml) was stirred for 12 h at room temperature, then neutralised, filtered, and concentrated. The syrupy residue contained a major (R_F 0.42, solvent *B*) and a minor component (R_F 0.47). Elution of the mixture from silica gel with a benzene–methanol gradient gave first the minor component **15** (0.11 g, 17.8%) and then the major product **14** (0.48 g, 77%).

Syrupy 2,3:5,6-di-*O*-isopropylidene-*β*-D-*glycero*-L-*manno*-heptofuranose (**14**) had $[\alpha]_D^{20}$ +0.5° (*c* 2.1, chloroform). Mass spectrum: *m/e* 275 (39%), 217 (6), 157 (6), 273 (1), 159 (2), 101 (8), 131 (28), 59 (100), 43 (78).

Anal. Calc. for $C_{13}H_{22}O_7$: C, 53.79; H, 7.64. Found: C, 53.91; H, 7.69.

The 1,7-diacetate (**14a**) of **14** was a syrup, $[\alpha]_D^{19}$ −11.5° (*c* 3.25, chloroform), T_R 1.80. Mass spectrum: *m/e* 359 (10%), 301 (5), 241 (2), 181 (8), 315 (1), 257 (6), 199 (6), 173 (3), 115 (21), 101 (8), 43 (100).

Anal. Calc. for $C_{17}H_{26}O_9$: C, 54.53; H, 7.00. Found: C, 54.41; H, 7.09.

2,3:6,7-Di-*O*-isopropylidene-*β*-D-*glycero*-L-*manno*-heptofuranose (**15**) had m.p. 117–119° (from heptane–ether), $[\alpha]_D^{21}$ −15° (*c* 1.3, chloroform). Mass spectrum:

m/e 290 (M^+), 275 (24%), 217 (8), 157 (7), 231 (1), 189 (2), 131 (13), 159 (2.5), 101 (82), 43 (100).

Anal. Calc. for $C_{13}H_{22}O_7$: C, 53.79; H, 7.64. Found: C, 53.88; H, 7.63.

The 1,5-diacetate (**15a**) of **15** had m.p. 85–86° (from pentane–hexane), $[\alpha]_D^{22}$ −17° (*c* 3.4, chloroform), T_R 1.61. Mass spectrum: *m/e* 359 (12%), 301 (8), 241 (1.5), 181 (5), 315 (1), 257 (4), 199 (4), 101 (43), 43 (100).

Anal. Calc. for $C_{17}H_{26}O_9$: C, 54.53; H, 7.00. Found: C, 54.54; H, 6.97.

*7-O-Acetyl-2,3:5,6-di-O-isopropylidene-β-*D-glycero-L-manno-*heptofuranose* (**14b**). — A solution of **14a** (90 mg) in 0.3% methanolic sodium methoxide (7 ml) was stored for 10 min, then neutralised with KU-2(H^+) resin, filtered, and concentrated. The syrupy residue contained two components (R_F 0.36 and 0.58, solvent *B*). Elution of the mixture from silica gel with benzene–methanol (methanol 1→5%) afforded **14** (28 mg, 40%) and syrupy **14b** (39 mg, 49%), $[\alpha]_D^{20}$ +16° (equil.; *c* 1.9, chloroform), T_R 1.48. Mass spectrum: *m/e* 317 (100%), 259 (18), 199 (12), 139 (25), 315 (1), 173 (20), 115 (91), 159 (4), 101 (26).

*5-O-Acetyl-2,3:6,7-di-O-isopropylidene-β-*D-glycero-L-manno-*heptofuranose* (**15b**). — Compound **15** (55 mg) was deacetylated with 0.3% sodium methoxide in methanol–chloroform (2:1, 7 ml) for 1.5 h. The solution was neutralised with KU-2(H^+) resin and then concentrated. The syrupy residue, which had R_F 0.52 (solvent *B*), crystallised from heptane to afford **15b** (40 mg, 79.5%), m.p. 108–109°, $[\alpha]_D^{20}$ +14.5° (equil.; *c* 0.8, chloroform), T_R 1.35. Mass spectrum: *m/e* 317 (21.5%), 259 (8.5), 199 (6), 139 (17), 315 (1), 231 (1), 171 (4), 101 (65), 43 (100).

Anal. Calc. for $C_{15}H_{24}O_8$: C, 54.23; H, 7.28. Found: C, 54,31; H, 7.34.

*1,5-Di-O-acetyl-2,3:6,7-di-O-isopropylidene-β-*D-glycero-D-gulo-*heptofuranose* (**16a**). — Acetylation of **16**[17] with acetic anhydride in pyridine afforded syrupy **16a**, $[\alpha]_D^{20}$ −31° (*c* 2, carbon tetrachloride), T_R 1.82. Mass spectrum: *m/e* 359 (34%), 301 (45), 241 (3), 181 (30), 273 (3), 201 (55), 143 (6), 101 (66), 43 (100).

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