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THE SYNTHESIS OF D-*xylo*-HEXOS-4-ULOSE AND SOME DERIVATIVES

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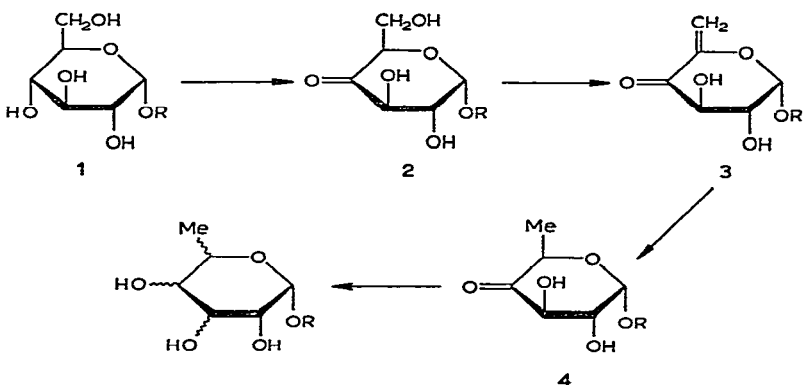
ABSTRACT

D-*xylo*-Hexos-4-ulose has been synthesised, and characterised chromatographically, and methyl α-D-*xylo*-hexopyranosid-4-ulose has been shown to be stable in neutral, aqueous solution, contrary to a previous report. Glycosyl phosphate derivatives are also reported.

INTRODUCTION

In the last ten years, considerable evidence has been accumulated to show that nucleoside 5′-pyrophosphate derivatives of aldopyranos-4-uloses are intermediates in the biosynthesis of 6-deoxyhexoses, 3,6-dideoxyhexoses, aminodeoxyhexoses, and branched-chain sugars, and in the interconversion of some monosaccharides[1,2]. Such derivatives of 6-deoxyhexos-4-uloses have been isolated in micromole quantities and characterised by sequential reduction and hydrolysis to give two epimeric 6-deoxyhexoses[3]. Uridine 5′-(D-*xylo*-hexopyranosyl-4-ulose pyrophosphate) is the likely intermediate in the interconversion of UDP-D-glucose and UDP-D-galactose. The



Scheme 1

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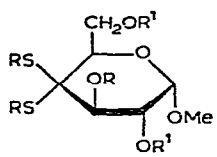
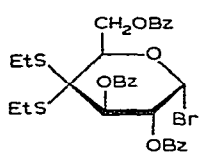
significance of the chemical trapping of this 4-ulose intermediate, by reduction with sodium borohydride, was at first questioned[4a], but the results were later rationalised[4b]. The first steps in the *in vivo* conversion of D-glucose into 6-deoxyhexose are oxidation to the 4-ulose followed by dehydration and reduction (Scheme 1, R = nucleoside 5′-pyrophosphate)[2], and Gabriel has proposed[5], on the basis of model experiments, that the intermediate 4-ulose (**2**) would spontaneously lose water to give the enone **3**. We now report a convenient route for the synthesis of D-*xylo*-hexos-4-ulose and derivatives thereof, and comment on their stability.

RESULTS

In view of the lability[5,6] of the pyranosid-4-ulose (**2**, R = Me), the generation of the ketone function is likely to be the most crucial step, and the synthesis of the methyl glycoside (**2**, R = Me) was first studied in order to establish the feasibility of forming the ketone function from a dithioacetal precursor. The hexosid-4-ulose (**2**, R = Me) had been prepared previously[6], but in very low yield, by oxidation of methyl 6-*O*-trityl-α-D-glucopyranoside. A route was required which could also be used for the biochemicaliy important glycosyl phosphate derivative [**2**, R = $PO(OH)_2$], and oxidation of methyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside[7] was chosen as a convenient route. Oxidation of the galactoside tribenzoate with ruthenium tetraoxide gave the crystalline 4-ulose[8,9], which was converted into the ethylene dithioacetal **5** by reaction with ethane-1,2-dithiol in the presence of boron trifluoride. The dithioacetal was obtained as a syrup contaminated with an aliphatic, sulphur-containing impurity after column chromatography, and this impurity was removed by chloroform extraction after debenzoylation.



5 R = CH_2CH_2, R^1 = Bz
6 R = CH_2CH_2, R^1 = H
7 R = Et, R^1 = H



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Since ethylene dithioacetals containing a hydroxyl-substituted α-carbon atom rearrange under relatively mild conditions (*e.g.*, in the presence of silica gel in chloroform) to unsaturated 1,4-dithianes[10], the structure of the dithioacetal **6** was confirmed by conversion into a crystalline triacetate. Attempts to convert the triacetate of **6** into the 4-ulose were unsuccessful, the compound being recovered unchanged after solutions in aqueous acetone or aqueous ethanol had been boiled in the presence of mercuric chloride and cadmium carbonate. The dithioacetal **6** was also unreactive during four days at room temperature. Cyclic dithioacetals are known to be less reactive than acyclic dithioacetals[11], and indeed the diethyl dithioacetal **7**, prepared

as for the ethylene dithioacetal, was smoothly converted into the 4-ulose (**2**, R = Me) in thirty minutes at room temperature. The 4-ulose was characterised by reduction with sodium borohydride to a mixture of methyl α-D-glucopyranoside and methyl α-D-galactopyranoside. Aqueous solutions of methyl α-D-*xylo*-hexopyranosid-4-ulose were stable at room temperature for ten days as shown by reduction of aliquots removed at intervals. Catalytic hydrogenation of the 4-ulose gave methyl α-D-galactopyranoside and no methyl 6-deoxy-α-D-galactopyranoside. Gabriel's conclusion[5] that the 4-ulose (**2**, R = Me) undergoes spontaneous dehydration was based on the isolation of methyl 6-deoxy-α-D-galactopyranoside after the platinum-catalysed oxidation of methyl α-D-galactopyranoside followed by catalytic hydrogenation. This conclusion clearly refers only to the conditions to which the 4-ulose was exposed, namely a weakly acidic solution at 45–50°. The 4-ulose decomposed slowly when stored as a syrup at room temperature.

Methyl 2,3,6-tri-*O*-benzoyl(or acetyl)-α-D-*xylo*-hexopyranosid-4-ulose diethyl dithioacetal could, in principle, be converted into other derivatives by replacement of the anomeric methoxyl group, but no reaction occurred when the dithioacetal triacetate was treated with hydrogen bromide in glacial acetic acid, and acetolysis at 0° caused decomposition. Since anomeric acyloxy groups are more readily removed than alkoxy groups, 1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose, obtained from D-glucose by selective benzoylation[12a], was used as starting material. Oxidation of the glucose tetrabenzoate with ruthenium tetraoxide gave a crystalline 4-ulose in 70% yield; oxidation with methyl sulphoxide and acetic anhydride gave the 4-acetate. However, the 4-ulose tetrabenzoate could not be converted into the required diethyl dithioacetal under the usual conditions. Rapid formation of a mixture of products occurred, and mass-spectral and n.m.r. analysis suggested that both 2,3,6-tri-*O*-benzoyl-D-*xylo*-hexos-4-ulose bis(diethyl dithioacetal) and ethyl 2,3,6-tri-*O*-benzoyl-1-thio-D-*xylo*-hexopyranosid-4-ulose diethyl dithioacetal were formed. It was then found to be possible to oxidise 2,3,6-tri-*O*-benzoyl-α-D-glucopyranosyl bromide (*cf.* Ref. 12*b*) to the 4-ulose, which was isolated as the crystalline ketone and also as the crystalline, hydrated ketone. The n.m.r. spectrum of the latter compound in acetone-d_6 contained a singlet and doublet for the hydroxyl protons, the doublet presumably being due to long-range coupling (J 1.4 Hz) between the axial hydroxyl proton and the axial H-5 (*cf.* Ref. 13).

The bromide 4-ulose was converted into the crystalline diethyl dithioacetal **8** by reaction with ethanethiol and boron trifluoride. Hydrolysis of **8**, followed by debenzoylation, gave syrupy D-*xylo*-hexos-4-ulose diethyl dithioacetal, which was converted into the free 4-ulose in 90% yield as for the methyl glycoside derivative already described. Reduction of the 4-ulose with sodium borohydride gave D-glucitol and galactitol. Chromatographic mobilities of D-*xylo*-hexos-4-ulose*, the fourth and

*D-*xylo*-Hexos-4-ulose was presumably formed in the recently reported[14], reductive inactivation of UDP-D-galactose 4-epimerase by D-galactose in the presence of uridine 5′-phosphate, but it was not identified.

last D-aldohexosulose to be synthesised that is derived from D-glucose*, are recorded in the experimental section.

The synthesis of glycosyl phosphate derivatives of the 4-ulose was not possible using the selective benzoylation–oxidation sequence. A 2,3,6-tri-*O*-benzoyl derivative could not be isolated starting from α-D-glucopyranosyl (diphenyl phosphate)[16] or from dipyridinium and other phosphate salts. However, the bromide 4-ulose diethyl dithioacetal (**8**) is a convenient intermediate for the synthesis of glycosyl phosphate derivatives. Thus, reaction of the bromide **8** with silver (dibenzyl phosphate) in benzene gave a glycosyl phosphate, which was isolated in 58% yield after column chromatography. The β-configuration was established by the value (8 Hz) of $J_{1,2}$. Reaction of **8** with triethylammonium (diphenyl phosphate) in benzene gave 2,3,6-tri-*O*-benzoyl-α-D-*xylo*-hexopyranosyl-(4-ulose diethyl dithioacetal)(diphenyl phosphate), which was obtained crystalline in 60% yield. In the 100-MHz p.m.r. spectrum of the diphenyl phosphate, H-2 and H-3 were very strongly coupled, and therefore the value (~3 Hz) of $J_{1,2}$, which indicated the α-configuration, was obtained from the 220-MHz spectrum. A long-range coupling of ~3 Hz was also detected between H-2 and phosphorus. All attempts to remove the phenyl protecting groups were unsuccessful. Although successful hydrogenolyses of compounds containing divalent sulphur functions are known[17], no reaction was observed using platinum and a variety of solvents and pressures (1–4 atmospheres).

The key intermediate, the bromide diethyl dithioacetal (**8**), is readily prepared from D-glucose in four steps, and derivatives of this type can, in principle, be used to introduce the protected aldulose moiety into larger molecules. Naturally occurring compounds containing aldulose moieties have been reported in recent years. For example, the monosaccharide component of datiscoside, an antileukemic cucurbitacin glycoside, is a 6-deoxyhexopyranos-3-ulose[18]. The antibiotic cinerubin B contains three monosaccharides, one of which is a 3,6-dideoxyhexopyranos-4-ulose[19]. A 2,3,6-trideoxyhexopyranos-4-ulose has also been found[20] to be a component of cinerubin A and of a macrolide antibiotic[21], B-58941. An example of a naturally occurring 2-ulose is provided by the cardiac glycoside gomphoside[22], which contains a 4,6-dideoxyhexopyranos-2-ulose moiety in a ring-fused hemiacetal form.

EXPERIMENTAL

General. — Solutions were concentrated under reduced pressure below 40°. Melting points were measured on a Kofler hot-stage apparatus, and were uncorrected. N.m.r. spectra were measured on a Varian HA-100 spectrometer, using $CDCl_3$ as solvent unless otherwise stated. First-order coupling constants were measured to ±0.2 Hz. Mass spectra were recorded on an A.E.I. MS-9 spectrometer, and optical rotations were measured with a Perkin–Elmer 141 polarimeter at 20 ±2° with chloroform as solvent unless otherwise stated. G.l.c. was performed with an F and M

*The synthesis of a 3,6-dideoxyaldohexos-4-ulose was recently reported[15].

810 chromatograph and glass columns (240 × 0.4 cm) packed with 10% liquid phase on silanised Chromosorb W (60–80 mesh). Compounds were detected by flame ionization. T.l.c. was performed on Kieselgel G (Merck), spots being detected by spraying with 5% sulphuric acid in ethanol and heating to 120°, or by iodine vapour. Descending paper chromatography was carried out on Whatman No. 1 paper, using the following solvents: *A*, ethyl acetate–acetic acid–water (3:1:3); *B*, ethyl acetate–pyridine–water (8:2:1); *C*, 1-butanol–toluene–pyridine–water (5:1:3:3).

*Methyl 2,3,6-tri-*O*-benzoyl-α-*D*-xylo-hexopyranosid-4-ulose.* — Oxidation of methyl 2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside with ruthenium tetraoxide gave the crystalline 4-ulose (71% yield), m.p. 136–138°, $[\alpha]_D$ +172°; lit.[9] m.p. 137°, $[\alpha]_D$ +173°; lit.[8] m.p. 121°.

Ethylene dithioacetal formation. — The 4-ulose (0.506 g) in chloroform (5 ml) was treated with ethane-1,2-dithiol (0.4 ml) and boron trifluoride etherate (0.2 ml). Further additions of reagents were made as follows: BF_3 etherate (0.2 ml) after 2 and 4.5 h, ethane-1,2-dithiol (0.2 ml) after 4.5 h. After 20 h at room temperature, t.l.c. analysis indicated four products. The solution was washed with 2M sodium hydroxide and water, and then dried ($MgSO_4$). Removal of desiccant and solvent gave a syrup (0.538 g), which was fractionated on silica gel (30 g). Benzene–ether eluted an aliphatic compound (36 mg), followed by the slightly impure, syrupy methyl 2,3,6-tri-*O*-benzoyl-α-D-*xylo*-hexopyranosid-4-ulose ethylene dithioacetal (**5**, 294 mg). N.m.r. data: τ 2.0 (6 H, m, Ar*H*), 2.6 (9 H, m, Ar*H*), 3.5–5.5 (6 H, m), 6.6 (s)+6.4–7.5 (m, 12 H, OMe+$C_2H_4S_2$+impurity).

Sodium methoxide-catalysed debenzoylation followed by partition between water and chloroform gave, from the aqueous layer, syrupy methyl α-D-*xylo*-hexopyranosid-4-ulose ethylene dithioacetal (**6**). N.m.r. data: τ (D_2O) 5.2 (d, *J* 3 Hz, H-1), 5.8–6.4 (m, H-2,3,5,6,6′), 6.6 (s, OMe), 6.75 (m, $C_2H_4S_2$), no integral available. Acetylation with acetic anhydride–pyridine gave a crystalline triacetate (12% overall yield from 4-ulose tribenzoate), m.p. 184–186°. N.m.r. data: τ 4.5 (1 H, d, *J* 9 Hz, H-3), 5.0–5.2 (2 H, m, H-1,2), 5.9–6.7 (3 H, m, H-5,6,6′), 6.6 (3 H, s, OMe), 6.8 (4 H, m, $C_2H_4S_2$), 7.92+7.93+7.95 (3 × 3 H, 3 s, $MeCO_2$). Mass spectrum: *m/e* 394 (~10%), 334 (~1%), 303 (~1%), 292 (3%), 274 (~1%), 232 (9%), 201 (3%), 189 (38%), 176 (30%), 147 (20%), 134 (60%), 43 (100%).

Anal. Calc. for $C_{15}H_{22}O_8S_2$: C, 45.6; H, 5.6. Found: C, 45.1; H, 5.6.

Diethyl dithioacetal formation. — A solution of methyl 2,3,6-tri-*O*-benzoyl-α-D-*xylo*-hexopyranosid-4-ulose (1 g) in chloroform (10 ml) was stirred at room temperature with ethanethiol (2.4 ml) and boron trifluoride etherate (2.4 ml). After 3 h, the reaction solution was processed as above to give a syrupy product (1.2 g) that contained three components. Fractionation on a silica gel column was not satisfactory, only small quantities of two homogeneous compounds being obtained. These were shown by n.m.r. to be a bis(diethyl dithioacetal); τ 1.9–2.8 (15 H, Ar*H*), 3.9–4.15 (3 H, m, H-1,2,3), 4.64 (1 H, q, *J* 12 and 1 Hz, H-6), 4.96 (1 H, q, *J* 9 and 1 Hz, H-5), 5.32 (1 H, q, *J* 12 and 9 Hz, H-6′), 7.02 (4 H, m, $-SCH_2-$), 7.52 (4 H, m, $-SCH_2-$), 8.8 (12 H, m, $-SCH_2CH_3$); and a diethyl dithioacetal; τ 1.9–2.8 (15 H,

Ar*H*), 3.88 (1 H, d, *J* 10 Hz, H-3), 4.17 (1 H, q, *J* 10 and 4 Hz, H-2), 4.70 (1 H, d, *J* 10 Hz, H-5), 4.81 (1 H, d, *J* 4 Hz, H-1), 5.4 (2 H, m, H-6), 6.65 (3 H, s, OMe), 7.08 (4 H, m, $-SCH_2-$), 8.75 (6 H, m, $-SCH_2CH_3$).

The fractions containing the diethyl dithioacetal were combined and debenzoylated with methanolic sodium methoxide to give a syrupy product (0.8 g). Purification by preparative t.l.c. gave methyl α-D-*xylo*-hexopyranosid-4-ulose diethyl dithioacetal (7) (214 mg, 36%). N.m.r. data (pyridine-d_5): τ 4.84 (1 H, d, *J* 3.6 Hz, H-1), 5.1–5.8 (8 H, m, H-2,3,5,6 and OH), 6.50 (3 H, s, OMe), 6.4–6.9 (2 H, m, SCH_2), 7.1–7.4 (2 H, m, SCH_2), 8.8 (6 H, m, SCH_2CH_3). With acetic anhydride and pyridine, 7 gave the dithioacetal triacetate (220 mg, 26% overall yield from the 4-ulose tribenzoate), m.p. 53–54°, $[\alpha]_D$ +125° (methanol). N.m.r. data: τ 4.44 (1 H, d, *J* 10 Hz, H-3), 4.58 (1 H, q, *J* 10 and 3.5 Hz, H-2), 5.05 (1 H, d, *J* 3.5 Hz, H-1), 5.10 (1 H, m, ?), 5.75 (2 H, m, ?), 6.65 (3 H, s, OMe), 7.2 (4 H, m, $-SCH_2-$), 7.92, 7.94, 7.96 (all 3 H, s, $MeCO_2$), 8.8 (6 H, m, $-SCH_2CH_3$).

Anal. Calc. for $C_{17}H_{28}O_8S_2$: C, 48.1; H, 6.6; S, 15.0. Found: C, 48.0; H, 6.4; S, 14.1.

Methyl α-D-xylo-*hexopyranosid-4-ulose and its stability in aqueous medium.* — A solution of the dithioacetal 7 (70 mg) in water (4 ml) was stirred at room temperature with mercuric chloride (100 mg) and cadmium carbonate (200 mg). T.l.c. analysis showed that the reaction was complete in 30 min, the 4-ulose being detected as an orange spot (R_F 0.3; benzene–methanol, 7:3) with phenylhydrazine reagent. The 4-ulose gave a yellow spot (R_{Glc} 2.5, solvent *A*) with *p*-anisidine reagent after analysis by p.c. The reaction mixture was filtered, and a one-tenth aliquot was reduced with sodium borohydride (10 mg) overnight. A dark precipitate was removed by filtration, and the usual work-up gave a mixture of methyl α-D-glucopyranoside and -galactopyranoside, which was hydrolysed to give D-glucose and D-galactose (detected by p.c. and g.l.c.[23]).

The remainder of the 4-ulose solution was deionised by treatment with hydrogen sulphide, filtered, and then rapidly neutralised with Amberlite MB 3 resin. T.l.c. analysis indicated that aqueous solutions of the 4-ulose were unchanged after ten days at room temperature. This was confirmed by the reduction with sodium borohydride, and hydrogenation over platinum, of aliquots removed after 7 and 10 days. Prior to hydrogenation, the aqueous solution was concentrated to dryness, and the syrupy 4-ulose was dissolved in methanol. In each case, sodium borohydride gave only methyl α-D-glucopyranoside and -galactopyranoside, and hydrogenation gave the latter with a trace of the glucoside. A sample of the 4-ulose, which had been stored as a syrup for three days at room temperature, gave on hydrogenation at least four products, three of which corresponded (g.l.c.) to methyl α-glycopyranosides of D-glucose, D-galactose, and D-allose. Methyl 6-deoxy-α-D-galactopyranoside was absent.

*1,2,3,6-Tetra-O-benzoyl-*α-D-xylo-*hexopyranos-4-ulose.* — 1,2,3,6-Tetra-*O*-benzoyl-α-D-glucopyranose[12a] (0.5 g) in acetone (3 ml) was oxidised in the usual way by ruthenium tetraoxide in carbon tetrachloride. Filtration and evaporation of the

solvent gave the crystalline 4-ulose tetrabenzoate. Recrystallisation from chloroform–ether gave the title compound (0.35 g, 70%), m.p. 146–147°, $[\alpha]_D$ +175°. N.m.r. data: τ 1.8–2.2 (8 H, Ar*H*), 2.4–2.8 (12 H, Ar*H*), 2.98 (1 H, d, *J* 3.4 Hz, H-1), 3.70 (1 H, d, *J* 10.8 Hz, H-3), 4.03 (1 H, q, *J* 3.4 and 10.8 Hz, H-2), 5.03 (1 H, m, ?), 5.25 (2 H, m, ?).

Anal. Calc. for $C_{34}H_{26}O_{10}$: C, 66.7; H, 4.4. Found: C, 66.7; H, 4.5%.

*Oxidation of 2,3,6-tri-*O*-benzoyl-α-*D*-glucopyranosyl bromide.* — The bromide[24] (1 g, prepared from 1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose[12]) in the minimum volume of acetone was oxidised with ruthenium tetraoxide (from 3 g of dioxide) in carbon tetrachloride overnight to give a product which crystallised from chloroform–light petroleum (b.p. 60–80°) as the hydrated 4-ulose (500 mg, 50%), m.p. 83–85°, $[\alpha]_D$ +172° (acetone). Yields up to 70% could be obtained by using more oxidant. N.m.r. data (acetone-d_6): τ 1.9–2.7 (15 H, Ar*H*), 2.93 (1 H, d, *J* 3.9 Hz, H-1), 3.85 (1 H, s, OH), 3.99 (1 H, d, *J* 10.2 Hz, H-3), 4.00 (1 H, d, *J* 1.4 Hz, OH), 4.51 (1 H, q, *J* 10.2 and 3.9 Hz, H-2), 5.0–5.6 (3 H, m, H-5,6,6′); OH signals were removed by D_2O exchange.

Anal. Calc. for $C_{27}H_{23}BrO_9$: C, 56.7; H, 4.0. Found: C, 56.1; H, 3.7%.

In another experiment, the product, after chromatography on silica gel, crystallised from chloroform–light petroleum (b.p. 60–80°), as the 4-ulose, m.p. 124–127°.

Anal. Calc. for $C_{27}H_{21}BrO_8$: C, 59.1; H, 4.0. Found: C, 58.6; H, 3.8%.

*2,3,6-Tri-*O*-benzoyl-α-*D*-xylo-hexopyranosyl-(4-ulose diethyl dithioacetal) bromide.* — A solution of the hydrated bromide 4-ulose (150 mg) in chloroform (0.2 ml) containing ethanethiol (0.3 ml) and boron trifluoride etherate (0.15 ml) was kept overnight. The usual work-up gave a foam (135 mg) which, after chromatography on silica gel with toluene, yielded the title compound (80 mg, 46%), m.p. 106–107° [from ether–light petroleum (b.p. 60–80°)], $[\alpha]_D$ +80°. N.m.r. data: τ 1.9–2.8 (15 H, Ar*H*), 3.09 (1 H, d, *J* 4 Hz, H-1), 3.77 (1 H, d, *J* 9.8 Hz, H-3), 4.13 (1 H, q, *J* 9.8 and 4 Hz, H-2), 4.64 (1 H, d, *J* 11.8, H-6), 5.07 (1 H, d, *J* 8.2 Hz, H-5), 5.30 (1 H, q, *J* 11.8 and 8.2 Hz, H-6′), 7.0 (4 H, m, SCH_2), 8.73 (6 H, t, *J* 7 Hz, SCH_2CH_3). In subsequent preparations, the product was obtained crystalline, without chromatography, by seeding.

D-xylo-*Hexos-4-ulose.* — The foregoing bromide dithioacetal was hydrolysed in refluxing, 80% aqueous acetone in the presence of silver carbonate to give 2,3,6-tri-*O*-benzoyl-α,β-D-*xylo*-hexopyranos-4-ulose diethyl dithioacetal, which was isolated as a syrup [acetylation gave a mixture of the 1-acetoxy α- and β-pyranoses, τ 7.97 and 7.99 (3 H, two s, $MeCO_2$)].

Debenzoylation of the pyranose tribenzoate with methanolic sodium methoxide, in the usual way, gave syrupy D-*xylo*-hexos-4-ulose diethyl dithioacetal, which was converted in 1.5 h into the free 4-ulose (90% yield) by the action of mercuric chloride and cadmium carbonate as described above for the methyl α-D-glycopyranoside derivative. D-*xylo*-Hexos-4-ulose was obtained as a homogeneous syrup, $[\alpha]_D$ +38° (water), which could be stored at 0° for several days without decomposition. Re-

duction of a portion of the 4-ulose with sodium borohydride gave a mixture of D-glucitol and galactitol (the latter slightly predominating), which were identified as the peracetates by comparison (g.l.c. on a butane-1,4-diol succinate column, and n.m.r.) with authentic samples. In a few experiments, when the 4-ulose was contaminated with small amounts of other compounds, purification was achieved by preparative t.l.c. using ether–methanol (5:1) as solvent.

The chromatographic mobilities of the 4-ulose were as follows. For t.l.c.: R_{Glc} 1.5, R_{Xyl} 1.0, in ether–methanol (2:1); R_{Glc} 2.15, R_{Xyl} 1.0, in acetone–water (19:1). For paper chromatography: R_{Glc} 1.7, R_{Xyl} 0.63, in solvent *B*; R_{Glc} 1.2, R_{Xyl} 0.7, in solvent *C*. Neutral solvents caused streaking on paper chromatograms.

*2,3,6-Tri-*O*-benzoyl-β-*D*-xylo-hexopyranosyl-(4-ulose diethyl dithioacetal) (dibenzyl phosphate).* — The bromide dithioacetal (200 mg) in dry benzene (5 ml) was heated with silver (dibenzyl phosphate) (300 mg) and Drierite (300 mg) at 50° for 0.5 h, and then refluxed for 1.5 h. Filtration and concentration gave a syrup which was dissolved in chloroform and passed through a small column of silica gel. The β-(dibenzyl phosphate) was obtained as a homogeneous syrup (150 mg, 58%), $[\alpha]_D$ −4°. N.m.r. data: τ 1.95–2.2 (6 H, m, Ar*H*), 2.5–3.1 (19 H, m, Ar*H*), 3.75 (1 H, q, *J* 9.5 and 8 Hz, H-2), 4.12 (1 H, d, *J* 9.5 Hz, H-3), 4.30 (1 H, t, *J* 7.5 Hz, H-1), 4.64 (1 H, m), 4.95–5.65 (6 H, m, PhCH_2 + ?), 6.8–7.2 (4 H, m, SCH_2), 8.66–8.88 (6 H, m, SCH_2CH_3).

*2,3,6-Tri-*O*-benzoyl-α-*D*-xylo-hexopyranosyl-(4-ulose diethyl dithioacetal) (diphenyl phosphate).* — A solution of the bromide dithioacetal (100 mg) in dry benzene (3 ml) containing diphenyl phosphate (170 mg) and triethylamine (0.26 ml) was refluxed for 4 h. The cooled mixture was filtered and concentrated to a syrup which crystallised from ether–light petroleum (b.p. 60–80°) to give the α-(diphenyl phosphate) (75 mg, 60%), m.p. 97–99°, $[\alpha]_D$ +52°. N.m.r. data (at 220 MHz): τ 2.0–2.3 (6 H Ar*H*), 2.5–3.0 (19 H, Ar*H*), 3.63 (1 H, q, *J* 3.3 and 6.5 Hz, H-1), 3.83 (1 H, d, *J* 10.0 Hz, H-3), 3.92 (1 H, two t, *J* 10 and 3 Hz, H-2), 4.69 (1 H, q, *J* 1 and 12 Hz, H-6), 5.18 (1 H, q, *J* 1 and 8 Hz, H-5), 5.40 (1 H, q, *J* 8 and 10 Hz, H-6′), 6.9–7.2 (4 H, m, SCH_2), 8.74 and 8.81 (each 3 H, t, *J* 7 Hz, SCH_2CH_3).

Anal. Calc. for $C_{43}H_{41}O_{11}PS_2$: C, 62.3; H, 4.95. Found: C, 62.1; H, 4.6%.

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