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2,4-*O*-BENZYLIDENE-L-XYLOSE AND 2,4-*O*-METHYLENE-L-XYLOSE: SUGARS WHICH DO NOT READILY FORM PYRANOSE RINGS

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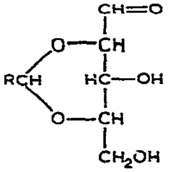
ABSTRACT

Oxidation of 2,4-*O*-benzylidene-D-glucitol with lead tetraacetate, followed by acetylation, gave the two anomers of 1,5-di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-xylitol) (**5**), and a dimeric product (**8**). After periodate oxidation of 2,4-*O*-benzylidene-D-glucitol, only one compound, $1,2_1,3,5$-tetra-*O*-acetyl-2,4-*O*-benzylidene-2-*C*-hydroxymethyl-L-*threo*-pentitol (**9**), could be isolated in very low yield. Most of the oxidation products appear to be dimeric; the *aldehydo* or the pyranoid forms of 2,4-*O*-benzylidene-L-xylose were not obtained.

INTRODUCTION

Oxidation of 2,4-*O*-benzylidene-D-glucitol and 2,4-*O*-methylene-D-glucitol with periodate or lead tetraacetate results in the formation of 2,4-*O*-benzylidene-L-xylose (**1**) and 2,4-*O*-methylene-L-xylose (**2**), respectively. These sugars are usually not isolated but are hydrolyzed to L-xylose[1,2] or reduced to 2,4-*O*-benzylidene-[3] and 2,4-*O*-methylene-xylitol[4]. All of these compounds are obtained in good yield which proves that the 2,4-acetals of L-xylose (or compounds from which it is easily generated) are the main products of the initial oxidation. The 2,4-acetals of L-xylose are, however, not readily isolated. Only once has 2,4-*O*-benzylidene-L-xylose been described[1] as a crystalline compound, but it was isolated in very small yield; its acetate, obtained by acetylation of the crude reaction mixture, was amorphous and melted over a wide range. 2,4-*O*-Methylene-L-xylose was only obtained as a syrup[4]. Our experiments indicate that periodate or lead tetraacetate oxidation of the 2,4-acetals of D-glucitol gives mixtures containing numerous compounds.

At first glance, it might be expected that the 2,4-acetals of L-xylose would exist as mixtures of the α- and β-pyranoid forms. They would then be suitable starting materials for the synthesis of L-xylose derivatives substituted on O-3; we attempted to use them in this way, but without success. On the other hand, the pyranoid form would have to be in the *C1*(L) conformation (**3**) in which O-2, O-3, and O-4 are all axial. This conformation is sterically unfavourable, and the formation of the pyranoid ring would require more than the usual change in free energy. It is possible, therefore, that these xylose derivatives do not form pyranoid rings spontaneously. In the case of 2,4-*O*-benzylidene-L-xylose, there is another circumstance that is unfavourable to the formation of a pyranose ring: the phenyl group, which is equatorially oriented in 2,4-*O*-benzylidene-D-glucitol, will become axial on closing the pyranoid ring (3) or one of the two rings in the pyranose will be in a non-chair form. Both alternatives are unfavourable. This argument does not apply, however, to the 2,4-*O*-methylene derivative.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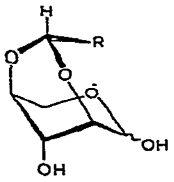
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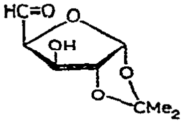
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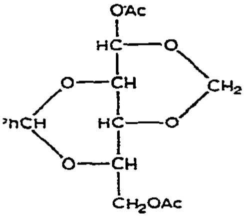
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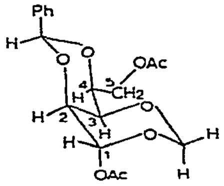
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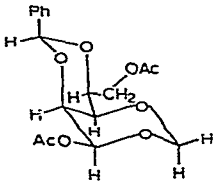
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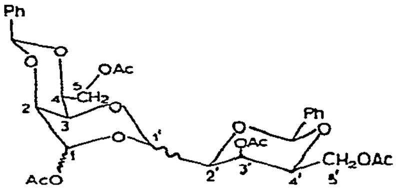
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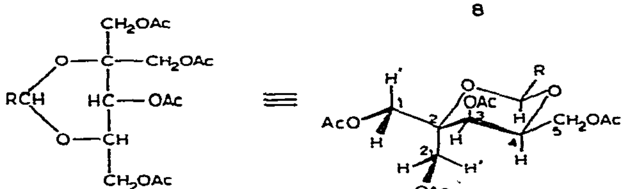
9 R= Ph
10 R= H

If, despite the presence of a free hydroxyl group on C-5, the 2,4-acetals of L-xylose do not cyclize intramolecularly, they would be expected to behave similarly to 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose (4), the compound formed from 1,2-*O*-isopropylidene-α-D-glucofuranose by glycol fission, which has been thoroughly investigated by Schaffer and Isbell[5], and by Inch[6]. This compound is not found as the free aldehyde but forms a dimer, and condenses with formaldehyde, if present, to a 3,5-*O*-methylene derivative. The two reactions are of the same type;

β-hydroxyaldehydes readily and reversibly condense with themselves or with other aldehydes. 2,4-*O*-Ethylidene-D-erythrose (obtained by periodate oxidation of 4,6-*O*-ethylidene-D-glucose) also forms a crystalline dimer[7]. We have found that the 2,4-acetals of L-xylose behave similarly: a dimer, two *O*-methylene derivatives, and also products formed by an aldol condensation with formaldehyde have been isolated.

DISCUSSION

2,4-*O*-Benzylidene-D-glucitol was oxidized with lead tetraacetate and with sodium periodate; in each case, t.l.c. showed that a mixture of at least ten components was obtained, some of which were judged by their low mobility to be dimers. By analogy with Schaffer and Isbell's results[5], the dimers would have (after acetylation) the structure shown by **8**, in which each anomeric carbon atom can have one of two configurations. Therefore, four diastereomeric dimers of this structure are possible. The *aldehydo* form, the aldehydrol, the α- and β-pyranoses, the *O*-methylene derivatives, and the dimers are potentially all in equilibrium with each other. If one of these crystallizes readily, as happened in previous cases[5,7], most of the material is converted into that form. If nothing crystallizes, attempts to separate the components will lead to re-equilibration and will therefore be unsuccessful. No crystalline material was obtained from the periodate oxidation and only a very small amount of crystals from the lead tetraacetate oxidation; these may be identical with those described by von Vargha[1] but were insufficient for further investigation.

To prevent equilibration during separation, the crude reaction mixture was acetylated, and the aldehydrol **5** (28%), the product formed by condensation of 2,4-*O*-benzylidene-L-xylose with formaldehyde (both products of the glycol fission), was thereby obtained. The n.m.r. spectrum showed signals for two acetyl groups and a dioxymethylene group as an AB pattern at δ 5.12 and 4.93 with J 6.0 Hz. This value is consistent with geminal coupling in a dioxymethylene group[8]. The appearance of the anomeric proton at low field (δ 6.11) shows that C-1 carries one of the acetoxy groups. The other hydrogen atoms were located by decoupling. The condensation of formaldehyde with a β-hydroxyaldehyde has already been reported by Inch[6].

From the mother liquors, another compound was isolated (in 1% yield) which had the same analysis as, and a n.m.r. spectrum (Fig. 1) very similar to that of, the preceding compound. It is therefore the anomer of **5**. Inch obtained only one of the anomers from the oxidation of 1,2-*O*-isopropylidene-α-D-glucofuranose[6]. The configuration cannot be assigned to each of the anomers with certainty. The anomeric proton of the major product is at lower field (δ 6.11) than that of the minor one (δ 5.87), and on this basis it is tentatively concluded that the former is equatorial, and that the major compound has the (1*R*) configuration (**6**) and the minor one the (1*S*) configuration (**7**). In accordance with this assignment, the signal for H-3 is at lower field in **6** than it is in **7**, as it should be because of deshielding by a *syn*-axial group[9]. However, the signals for H-2 and for the axial hydrogen atom of the methylene group should also be at lower field in **6** than in **7**, which is not the case. Moreover, the optical rotation of **6** (which has the configuration of α-D-mannose around the

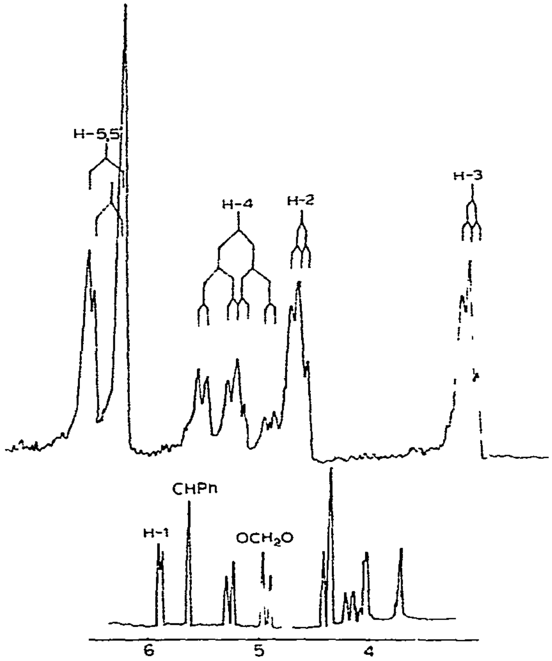

Fig. 1. Part of the n.m.r. spectrum, at 100 MHz in chloroform-*d*, of the acetylated (1*S*)-aldehydrol (**7**).

anomeric carbon atom) should be larger than that of **7** (with a configuration like β-D-mannose); in fact, it is somewhat smaller. The available evidence is therefore contradictory. It is suggested that the anomeric effect, which is large for an acetoxy group in chloroform solution, makes **6** the more stable isomer because it has an axial anomeric group, and that it causes the 1,3-*O*-methylene ring in **7** to be in a twist form in order to avoid having an equatorial anomeric group. This assumption, which could explain the anomalies, will be tested by X-ray crystallographic analysis.

If the methylene derivatives **6** and **7** are formed from 2,4-*O*-benzylidene-L-xylose and formaldehyde, addition of more formaldehyde to the reaction mixture should increase their yield. This proved to be the case; when 2,4-*O*-benzylidene-D-glucitol was oxidized with lead tetraacetate in the presence of paraformaldehyde, and the mixture acetylated, **6** was obtained in 51% and **7** in 3% yield. The reaction mixture appeared to contain fewer components than in the absence of paraformaldehyde, and, after chromatography, a solid but amorphous product was isolated. This was shown by its n.m.r. spectrum to be a dimer, probably of structure **8**. Signals for two benzylic protons were discernible at δ 5.77 and 5.81; one anomeric proton signal showed at low field (δ 6.08), whereas another one was in the region of δ 5.15–5.3. The two moieties of the dimer are therefore not equivalent, and only one of the anomeric carbon atoms carries an acetoxy group. These facts are compatible with the proposed structure **8**, but the configuration of the two anomeric centers could not be deduced from the n.m.r. data.

Extensive and repeated chromatography of the mother liquors obtained from lead tetraacetate oxidations yielded no further crystalline compounds. The n.m.r. spectra of the faster-moving fractions did not show anomeric signals that were compatible with an acetylated pyranose structure.

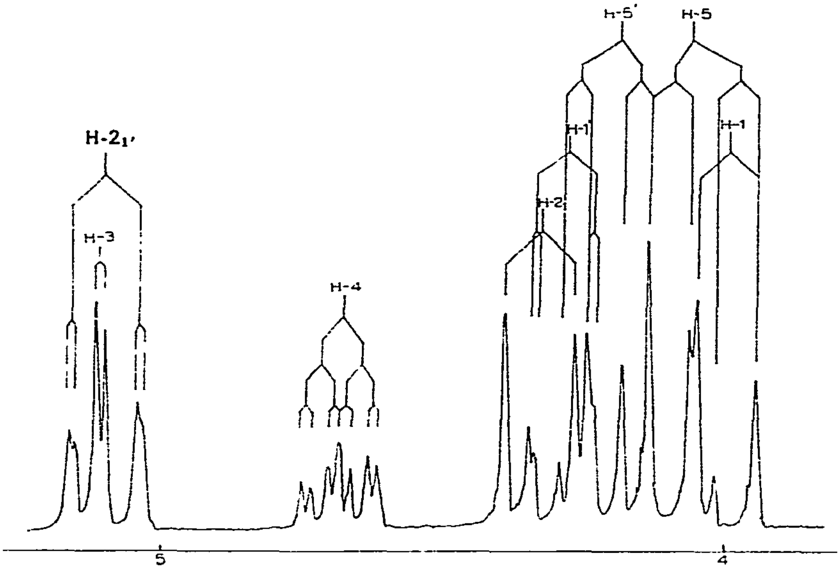

Fig. 2. Part of the n.m.r. spectrum, at 100 MHz in acetone-d_6, of 1,2_1,3,5-tetra-*O*-acetyl-2,4-*O*-benzylidene-2-*C*-hydroxymethyl-L-*threo*-pentitol (9).

When 2,4-*O*-benzylidene-D-glucitol was oxidized with sodium periodate, the two 1,3-methylene acetals, (6) and (7), were not obtained. Working up of the reaction mixture involves the evaporation of water, and the formaldehyde is apparently removed by this procedure. To make sure that all formaldehyde was removed, an additional amount of water was added and evaporated. After acetylation, extensive chromatography yielded only one, unexpected, crystalline product in very small yield (1%). Its n.m.r. spectrum (Fig. 2) shows that it is the tetraacetate of 2,4-*O*-benzylidene-2-*C*-hydroxymethyl-L-*threo*-pentitol (9). Although the spectrum is complex, systematic decoupling established the identity of each signal. There are four acetyl groups and three geminal methylene groups (*J* 11–12.5 Hz), of which two are not coupled to any other proton. Normally, the chemical shifts of two geminal methylene protons are similar, but, in this case, one of the signals is at very much lower field than the others. This is taken to be the signal for the hydrogen atom (H-2_1') of the axial acetoxymethyl group which is directed "inwards", towards the axial hydrogen atoms*. It is interesting to note that, as the wide separation of the signals of the two hydrogen atoms indicates, the axial acetoxymethyl group is preponderantly in one rotational conformation. The proton signal at lower field shows long-range

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*An axial methyl group appears normally at lower field than an equatorial[12], but the difference in chemical shifts is smaller (*ca.* 0.5 p.p.m.) because the observed shift is the average of that of the three equivalent hydrogen atoms.

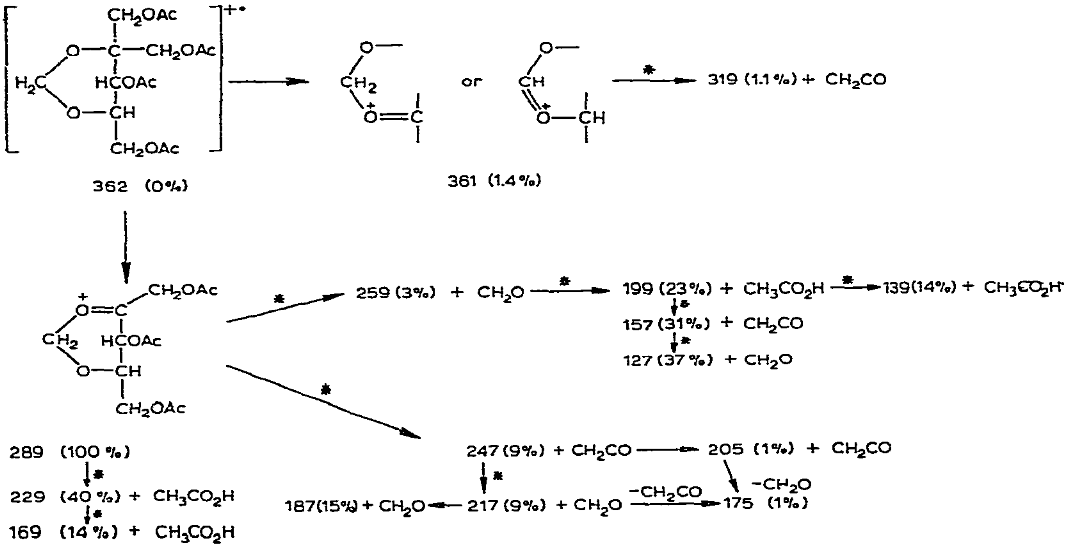
coupling (^4J *ca.* 1 Hz) with one of the methylene protons of the other acetoxymethyl group; therefore, one rotamer preponderates for that group also. The two hydrogen atoms coupled over long range are the ones marked H′ in formula **9**, since these are in the planar W arrangement which gives the largest long-range coupling[10]. One of the possible conformations is shown in the formula; the other would be obtained by interchanging OAc and H at C-1 and C-2_1. The conformations in which the two bonds carrying the acetoxy groups are parallel can be disregarded owing to their unfavourable 1:3 interaction.

The branched-chain compound **9** is evidently formed from 2,4-*O*-benzylidene-L-xylose and formaldehyde by a mixed aldol condensation, followed by a crossed Cannizzaro reaction. A similar reaction was described by Schaffer[11], but with use of a strong base; its occurrence under our almost neutral conditions is surprising.

To prove that **9** was formed from 2,4-*O*-benzylidene-L-xylose, and not by some other reaction, the acetylated (1*R*)-aldehydrol **6** (which generates 2,4-*O*-benzylidene-L-xylose in alkaline solution) was treated with formaldehyde in ethanolic sodium hydroxide solution: the branched-chain compound **9** was obtained in 13% yield.

Despite extensive chromatography, no other crystalline compound could be isolated from the periodate oxidation of 2,4-*O*-benzylidene-D-glucitol. Most of the fractions appeared to contain dimeric material.

2,4-*O*-Methylene-D-glucitol was also oxidized with sodium periodate. After acetylation, g.l.c. analysis showed the presence of the acetates of L-xylose, but most of the other compounds had long retention times, compatible only with dimeric structures. The only crystalline compound obtained, in small yield, was the branched-chain product of the mixed aldol condensation, 2,4-*O*-methylene-2-*C*-hydroxymethyl-L-*threo*-pentitol tetraacetate (**10**). Its n.m.r. spectrum resembles that of the benzylidene



Scheme 1. Ion transitions of compound **10** (* indicates presence of metastable ion).

analogue (9), but it could not be fully analyzed. However, the proposed structure was confirmed by the mass spectrum, recorded by Professor J. S. Shannon on an A.E.I. MS 12 spectrometer. The main ion transitions in the mass spectrometer are shown in Scheme 1. Evidence for the molecular weight is provided by the $M-1$ ion (*m/e* 361). The absence of an observable molecular ion is not surprising in view of the several possible pathways leading to stable oxonium ions. For example, the $M-1$ ion may have one of the two structures shown, while the most-abundant ion at *m/e* 289 may be formed by the loss of one of the tertiary acetoxymethyl groups. The remaining reactions, while not providing direct structural confirmation, are, nevertheless, quite rational for the proposed structure.

Our inability to isolate the pyranoid forms of 2,4-*O*-benzylidene-L-xylose does not prove that these are not present in the reaction mixture. However, the ease of condensation with formaldehyde and of the formation of dimers indicates that the pyranoses are not the stable forms of 2,4-*O*-benzylidene(and methylene-)-L-xylose.

EXPERIMENTAL

Chloroform solutions were dried with $MgSO_4$ before evaporation under reduced pressure. "Light petroleum" refers to the fraction with b.p. 60–80°. In general, t.l.c. was carried out on microscope slides, and column chromatography was performed on Mallinckrodt silicic acid (100 mesh), using ether–light petroleum (6:4), unless otherwise stated.

G.l.c. analysis was carried out by using a 4-foot glass column of LAC-1-R-296 (1.5%) on Chromosorb W (100–200 mesh). Optical rotations were determined with a Bendix automatic polarimeter. N.m.r. spectra were measured with a JNM-4H-100 spectrometer at 100 MHz, chloroform-*d* containing tetramethylsilane being used as the solvent, unless otherwise stated.

*Lead tetraacetate oxidation of 2,4-O-benzylidene-*D*-glucitol.* — Lead tetraacetate (22.5 g) was added to a stirred solution of 2,4-*O*-benzylidene-D-glucitol (13.5 g) in glacial acetic acid (135 ml), and the suspension was stirred for 1 h at ambient temperature. The resulting, clear solution was evaporated under reduced pressure at <40° (bath) to give a clear, viscous oil, which was distributed between ethyl acetate (150 ml) and water (50 ml). The extract was dried ($MgSO_4$) and evaporated to an oil (12.1 g). Addition of chloroform gave a small amount of crystalline material (m.p. 189–192°) which could not be recrystallized satisfactorily (von Vargha[1] obtained crystals, m.p. 184°, in unspecified yield). Since no further crystalline material could be obtained from this oil, and t.l.c. indicated that it was a multiple-component mixture, the oil was acetylated with acetic anhydride in pyridine. The product (18 g) was isolated as an oil by the usual procedures. On addition of ether to this oil, crystals (5.5 g) were obtained. Recrystallization from 95% ethanol gave (1*R*)-1,5-di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-xylitol) (6) (5.0 g, 28%), m.p. 160–161°, $[\alpha]_D^{23}$ +51.4° (*c* 0.84, chloroform) (Found: C, 58.2; H, 5.7. $C_{17}H_{20}O_8$ calc.: C, 57.95; H, 5.7%). N.m.r. data: δ 2.07, 2.15 (3-proton singlets, 2Ac), 3.77 (triplet, H-2, $J_{1,2}$ 1.5 Hz, $J_{2,3}$

1.5 Hz), 3.88 (triplet, H-3, $J_{3,4}$ 1.5 Hz), 4.11 (septet, H-4, $J_{4,5}$ and $J_{4,5'}$ 5.2 and 6.5 Hz), 4.33, 4.34 (two doublets with one peak of each overlapping, nearly degenerate ABX spectrum[13], H-5 and H-5'), 4.93 and 5.12 (doublets, OCH_2O, J_{gem} 6.0 Hz), 5.61 (singlet, CHPh), 6.11 (doublet, H-1), 7.3–7.45 and 7.5–7.65 (Ph).

Evaporation of the ethereal mother liquors left an oil which, on addition of ether, deposited a further amount of crystalline material (0.5 g). Recrystallization from 95% ethanol gave (1*S*)-1,5-di-*O*-acetyl-2,4-*O*-benzylidene-1,3-*O*-methylene-(1-hydroxy-L-xylitol) (7) (0.2 g, 1%), m.p. 144–146°, $[\alpha]_D^{23}$ +64.6° (*c* 0.88, chloroform) (Found: C, 58.15; H, 5.7. $C_{17}H_{20}O_8$ calc.: C, 57.95; H, 5.7%). N.m.r. data (Fig. 1): δ 2.08, 2.16 (3-proton singlets, 2Ac), 3.70 (triplet, H-3, $J_{2,3}$ 1.0 Hz, $J_{3,4}$ 1.5 Hz), 4.01 (triplet, H-2, $J_{1,2}$ 1.5 Hz), 4.14 (septet, H-4, $J_{4,5}$ and $J_{4,5'}$ 5.0 and 6.3 Hz), 4.35, 4.36 (two doublets with one peak of each overlapping[13], H-5 and H-5'), 4.90 and 5.23 (doublets, OCH_2O, J_{gem} 6.5 Hz), 5.61 (singlet, CHPh), 5.87 (doublet, H-1), 7.2–7.45 and 7.5–7.7 (Ph). Irradiation at δ 3.70 causes a collapse at 4.01 to a doublet, at 4.14 to a pair of doublets.

Evaporation of the ethereal mother liquors again gave an oil. T.l.c. of this oil showed no components moving faster than the 1,3-*O*-methylene derivatives, but at least six that were slower moving. A fairly good separation of this material was achieved by chromatography on silicic acid (30 g per 1 g of mixture). The n.m.r. spectra of the fractions eluted from the column all showed two signals in the region of δ 5.5–5.8 that could be attributed to two benzylidene protons; on this basis, these compounds were considered to be dimeric and were not further investigated.

*Lead tetraacetate oxidation of 2,4-*O*-benzylidene-*D*-glucitol in the presence of paraformaldehyde.* — A suspension of lead tetraacetate (22.5 g), 2.4-*O*-benzylidene-D-glucitol (13.5 g), and paraformaldehyde (7.0 g) in glacial acetic acid (135 ml) was stirred for 2 h. The suspension was filtered, and the product was isolated and acetylated by the procedure described above to give an oil (17.5 g). On addition of ether to this oil, the acetylated (1*R*)-aldehydrol **6** (7.5 g) was obtained. Column chromatography of the material left in the ethereal mother liquors, using ether–light petroleum (6:4), gave a further amount of the (1*R*)-derivative (1.5 g), followed by the (1*S*)-isomer **7** (0.5 g); on changing the ether–light petroleum ratio to 8:2, a dimeric material (4.9 g) was obtained. Further column chromatography of the dimer on silicic acid (80 g), using ether–light petroleum (7:3), gave a material (probably **8**) (4.0 g) that was very nearly homogeneous. N.m.r. data in acetone-d_6: δ 2.00, 2.04, 2.10, 2.14 (3-proton singlets, 4Ac), 3.7–4.6 (complex, seven protons), 5.13–5.3 (complex, two protons, probably H-1' and H-3'), 5.77 and 5.81 (singlets, -CHPh-), 6.08 (doublet, H-1, $J_{1,2}$ 1.25 Hz), 7.3–7.7 (complex, ten protons, Ph groups).

*Sodium periodate oxidation of 2,4-*O*-benzylidene-*D*-glucitol.* — A solution of sodium periodate (11.3 g) in water (90 ml) was added to a stirred solution of 2,4-*O*-benzylidene-D-glucitol (13.5 g) in water (50 ml) and ethanol (10 ml). After stirring had been continued for 1.5 h, the precipitated salts were removed, the filtrate was evaporated under reduced pressure, and water (150 ml) was distilled from the residual oil to yield, after final freeze-drying, a foam (13.5 g). Acetylation with acetic anhydride and pyridine gave, after isolation by the usual procedures, an oil which was shown by t.l.c. to be a multiple-component mixture. Initial separation of material (which was assumed, on the basis of the preceding experiment, to be monomeric or polymeric) was achieved on B.D.H. silica gel by using chloroform as the developing solvent to give monomeric material (6.9 g) and polymeric material (11.7 g). T.l.c. of the monomeric material, using ether–light petroleum (6:4), showed five components with R_F 0.1, 0.2, 0.3, 0.35, and 0.5. This material was chromatographed on silicic acid (120 g), using ether–light petroleum (1:1), to yield five fractions, the first three of which were considered from their n.m.r. spectra to be monomeric and the last two dimeric. The first three fractions were combined to give an oil (3.0 g); t.l.c. [20-cm run with benzene–ethyl acetate (9:1)] indicated that five components were present with R_F 0.42, 0.4, 0.35, 0.32, and 0.25. Column chromatography of this oil on silicic acid (90 g), using benzene–ethyl acetate (9:1), gave 22 fractions. Fractions 1 and 2 smelt strongly of benzaldehyde and contained components with R_F 0.42, 0.4, and 0.35; fractions 3 and 4 contained a compound with R_F 0.35, fractions 5–8 a compound with R_F 0.32, and fractions 9–22 a compound with R_F 0.25. Preparative layer chromatography of the fractions gave compounds with R_F 0.42 and 0.35 as chromatographically homogeneous oils, which remain unidentified but did not show a signal at δ *ca.* 6.0 in the n.m.r. spectrum and therefore are not benzylidene derivatives. The material having R_F 0.32 was crystallized from ethanol to yield 2,4-*O*-benzylidene-2-*C*-hydroxymethyl-L-*threo*-pentitol tetraacetate (9) (200 mg), m.p. 102–103°, $[\alpha]_D^{22}$ $-13.4°$ (*c* 1, chloroform) (Found: C, 57.3; H, 6.1. $C_{21}H_{26}O_{10}$ calc.: C, 57.5; H, 6.0%). N.m.r. data in acetone-d_6 (Fig. 2): δ 1.96, 1.98, 2.08, 2.11 (singlets, 4Ac), 3.99, 4.28 (doublets, H-1 and H-1′, $J_{1,1'}$ 11.0 Hz), 4.32, 5.10 (doublets, H-2_1 and H-$2_{1'}$, $J_{2_1,2_{1'}}$ 12.5 Hz), 4.69 (septet, H-4, $J_{3,4}$ 2.0, $J_{4,5}$ 4.15, $J_{4,5'}$ 8.35 Hz), 4.04, 4.19 (2 pairs of doublets each, AB part of an ABX system, H-5 and H-5′, $J_{5,5'}$ 11.65 Hz), 5.12 (doublet, H-3), 6.13 (singlet, CHPh), 7.3–7.6 (Ph).

The assignment of the signals was established by decoupling; *e.g.* irradiation at 5.12 p.p.m. causes the collapse of the signal for H-4 to a pair of doublets and that for H-2_1 to a singlet. Irradiation at 4.69 p.p.m. results in the collapse of the doublet of H-3 to a singlet and causes changes in the region δ 4.0–4.20.

*2,4-*O*-Benzylidene-2-*C*-hydroxymethyl-*L-threo*-pentitol tetraacetate.* — A solution of the acetylated (1*R*)-aldehydrol **6** (6.0 g), sodium hydroxide (3.0 g) in ethanol (45 ml), and formaldehyde solution (4 ml of 34%) was kept at ambient temperature for five days. The solution was neutralized with ion-exchange resin [Zeo-Karb 225(H$^+$)] and evaporated to a viscous oil which was acetylated with acetic anhydride in pyridine. Isolation of the product by the usual procedure gave an oil (7.0 g). Column chromatography of this oil on silicic acid (80 g) with ether–light petroleum (4:6) gave an oil (1.8 g) which, on crystallization from ethanol, yielded the product (1.0 g, 13%), m.p. 101–102°, $[\alpha]_D^{24}$ $-13.2°$ (*c* 1.18, chloroform). The melting point was undepressed by admixture with the material obtained previously.

*Sodium periodate oxidation of 2,4-*O*-methylene-*D*-glucitol.* — A solution of sodium periodate (6.4 g, 30 mmoles) in water (90 ml) at 0° was added to a solution of 2,4-*O*-methylene-D-glucitol (5.0 g, 28 mmoles) in water (50 ml) at 0°. After 40 min, the inorganic salts were precipitated by addition of a slight excess of barium hydroxide. The suspension was filtered, and the filtrate was evaporated under reduced pressure in the presence of barium carbonate. The residue was then extracted with ethanol (3 × 50 ml), and evaporation of the ethanol extract gave a clear, viscous oil (3.0 g). T.l.c. of this oil, using ethyl acetate–ethanol (9:1), revealed a mixture of at least seven compounds. Initial purification of this material was attempted on silicic acid (60 g) with ethyl acetate–methanol (9:1). No real separation was achieved, and so the material was acetylated with acetic anhydride in pyridine. Isolation of the product by normal procedures gave an oil; addition of ethanol gave 2,4-*O*-methylene-2-*C*-hydroxymethyl-L-*threo*-pentitol tetraacetate (**10**) (200 mg, 2%), m.p. 147–148°, $[\alpha]_D^{22.5}$ +1.6° (*c* 1, chloroform) (Found: C, 49.6; H, 6.15. $C_{15}H_{22}O_{10}$ calc.: C, 49.7; H, 6.1%). N.m.r. data: δ 2.01, 2.03, 2.05, 2.07 (3-proton singlets, 4Ac), 4.25, 4.85 (doublets, H-2_1 and H-$2_{1'}$, $J_{2_1,2_{1'}}$ 12.5 Hz), 4.99 and 5.11 (doublets, OCH_2O, J_{gem} 7.0 Hz), 4.99 (doublet, H-3, $J_{3,4}$ 0.9 Hz). The remaining protons appear as a complex between 3.72–4.16.

In the ethanolic mother liquors, the acetates of L-xylose were identified by g.l.c. analysis at 170°. At 230°, a peak corresponding to **10** was found after 15 min, and then material having retention time of 40 min was detected; this was assumed to be dimeric on the basis of its low volatility. However, no material was detected which had a volatility consistent with a compound containing one methylene and two acetate groups.

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