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PHOTOCHEMICAL OXIDATION OF PARTIALLY PROTECTED DERIVATIVES OF α-D-GLUCOFURANOSE AND β-D-FRUCTOFURANOSE

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ABSTRACT

An improved procedure for the preparation of 1,2-*O*-isopropylidene-β-D-fructofuranose and its 6-pyruvoylation is described. Photolysis of this ester in benzene furnished 5,6-*O*-isopropylidene-β-D-*lyxo*-hexos-5-ulofuranose, characterised as the *O*-methyloxime diacetate. Similarly, photochemical oxidation of 1,2-*O*-isopropylidene-6-*O*-pyruvoyl-α-D-glucofuranose gave 1,2-*O*-isopropylidene-α-D-*gluco*-hexodialdo-1,4:6,3-difuranose in excellent yield.

INTRODUCTION

During the past three decades, proof of the wholesomeness of irradiated foods has been a major obstacle to the acceptance of food preservation by irradiation as a viable process. Sugars are the main constituents (water excluded) of many foods, and results indicating mutagenicity[1] of irradiated solutions of sugars therefore warranted further investigation. We have paid particular attention to the γ-radiolysis products of D-fructose and D-glucose, the major sugar components of Kent mangoes[2]. However, radiolysis yields complex mixtures of products, some of which are formed in low yields (<1%). The isolation and purification of these products have been achieved only in a few cases. However, studies using g.l.c.–m.s.[3,4] showed alduloses and diuloses to be the main products when aqueous solutions of sugars were irradiated in the presence of oxygen.

We have used known methods for the synthesis of several of the potential radiolysis products of D-glucose and D-fructose for the purpose of mutagenic studies[5]. The synthesis of D-*lyxo*-hexos-5-ulose (6-aldo-D-fructose) (**1**), a potential radiation product of D-fructose, has not been described previously, although it is known as a product of the bacterial dehydrogenation of D-fructose[6]. We now describe the synthesis of **1** and of D-*gluco*-hexodialdose (**2**).

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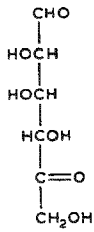

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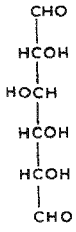

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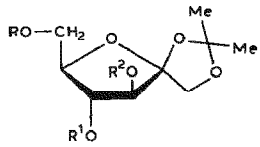
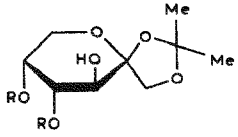
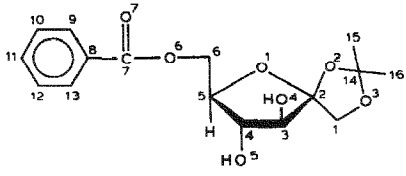


3 R = $R^1 = R^2 = H$
4 R = $R^1 = R^2$ = Ac
8 R = $COCOCH_3$, $R^1 = R^2 = H$



5 R = H
6 R, R = $C(CH_3)_2$



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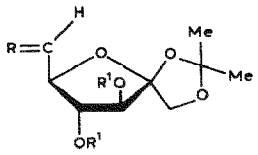
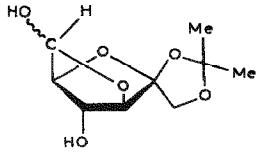


9 R = O, R^1 = H
11 R = NOH, R^1 = H
12 R = $NOCH_3$, R^1 = Ac



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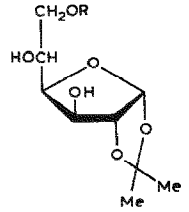
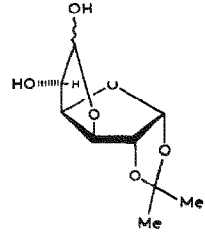


13 R = H
14 R = $COCOCH_3$



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RESULTS AND DISCUSSION

1,2-*O*-Isopropylidene-β-D-fructofuranose (**3**) was chosen as the starting material. Chittenden[7] reported that the tin(II) chloride (10^{-3} mol)-catalysed reaction of D-fructose with 2,2-dimethoxypropane (4 mol. equiv.) in 1,2-dimethoxyethane under reflux (30 min), followed by acetylation, furnished ~25% of 3,4,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-β-D-fructofuranose (**4**). However, we obtained ~8% each of 1,2-*O*-isopropylidene-β-D-fructopyranose (**6**) and 1,2-*O*-isopropylidene-β-D-fructofuranose (**3**) as well as a small proportion of 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**5**), and the total conversion of fructose was low. The presence of even traces of water lowered the yield of **3** and strictly anhydrous conditions were required. The best yield (18%) of **3** was obtained with a reflux time of 20–25 min and a concentration of 2.5×10^{-4} mmol/mL of catalyst. Even under

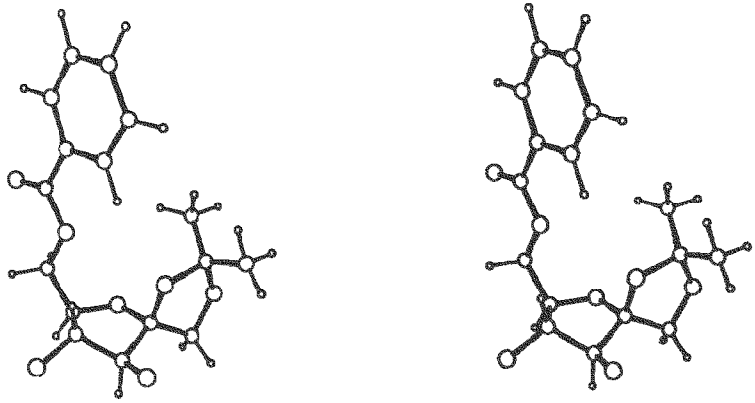

Fig. 1. Stereoview of **7**.

these conditions, the complexity of the mixture of products precluded the direct isolation of **3** and acetylation (→**4**) was required. Compound **3** was not formed when other catalysts [*e.g.*, copper(II) triflate, anhydrous iron(III) chloride, or chlorotrimethylsilane[8]] were used or when acetone was substituted for 2,2-dimethoxypropane.

A significant improvement was obtained on acetalation with 2-methoxypropene. Thus, under optimal conditions, D-fructose with 2-methoxypropene containing 2×10^{-4} mmol/mL of tin(II) chloride (molar ratio, $1:4:10^{-2}$), under reflux for 45 min, reacted quantitatively to furnish ~60% of a mixture of **5** and **3**, isolated by chromatography. The results suggested that **3** was the kinetic product and that, under the reaction conditions, it was partly converted into the thermodynamic product **6**, which in turn was readily converted into **5**. The β-D configuration of **3** was assigned on the basis of indirect evidence[7]. Reaction of **3** with 1 mol. equiv. of benzoyl chloride in pyridine furnished mainly the 6-benzoate (**7**) which was difficult to crystallise; the crystals of several other derivatives of **7** were not suitable for X-ray structure determination. Despite the resulting poor quality of the intensity data. it was possible to solve the structure and confirm the connectivity and relative stereochemistry of **7** and, therefore, of **3**. Fig. 1 shows that the furanoid ring has an E_3 envelope conformation.

The regioselective reaction of pyruvoyl chloride (1 mol) with **3** was effected after activation of the triol with bis(tributyltin) oxide[9]. The use of 0.5 or 1 mol. equiv. of the tin compound yielded 44 and 67%, respectively, of **8**, which required isolation by chromatography at −10°. Compound **8** is extremely sensitive to water and, in addition, readily rearranges (acyl group migration). Photolysis[10,11] (4.5 h) of **8** in oxygen-free dry benzene under nitrogen gave 81% of 5,6-*O*-isopropylidene-β-D-*lyxo*-hexos-5-ulofuranose (**9**).

The ^{1}H-n.m.r. spectrum of **9** lacked the characteristic low-field signal of a formyl group, and the compound had no i.r. absorption for carbonyl, reflecting the

intramolecular hemiacetal formation resulting in the difuranose structure **10**, as in 1,2-*O*-isopropylidene-α-D-*gluco*-hexodialdo-1,4:6,3-difuranose[12] (**15**).

Compound **10** was readily converted into 5,6-*O*-isopropylidene-β-D-*lyxo*-hexos-5-ulofuranose oxime (**11**) and 3,4-di-*O*-acetyl-5,6-*O*-isopropylidene-β-D-*lyxo*-hexos-5-ulofuranose methoxime (**12**). The 500-MHz ^{1}H-n.m.r. spectrum of **12** contained, *inter alia*, the resonance of H-6 as a doublet (J 7.7 Hz) at δ 7.43.

Photochemical oxidation was also applied to the synthesis of **15**. Treatment of 1,2-*O*-isopropylidene-α-D-glucofuranose (**13**) with 1 mol. equiv. of *N*-pyruvoylimidazole in 1,2-dimethoxyethane gave 71% of the 6-pyruvate **14**, isolated by chromatography at −10°. Irradiation of **14** in benzene, as described for **8**, furnished 82% of the hemiacetal **15**. The yield was considerably better than that obtained by oxidation with chromium trioxide[12] or catalytic hydrogen transfer[13], the oxidation of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose with dimethyl sulfoxide[14], and the reduction[15] of 1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone.

The hydrolysis of **15** to D-*gluco*-hexodialdose (**2**) has been described[12]. The hydrolysis of the 1,2-*O*-isopropylidene derivative **10** with 0.5M hydrochloric acid in acetonitrile furnished D-*lyxo*-hexos-5-ulose (**1**) in nearly quantitative yield. H.p.l.c. indicated[5] that **1** is a minor product of the γ-irradiation of solutions of D-fructose.

EXPERIMENTAL

General. — Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra (in chloroform) and optical rotations were measured with a Perkin–Elmer 237 spectrophotometer and a Perkin–Elmer 141 polarimeter, respectively. Unless otherwise stated, ^{1}H-n.m.r. spectra were recorded with a Bruker WP-80 instrument for solutions in $CDCl_3$ (internal Me_4Si). E.i.-mass spectra were obtained with a Varian MAT-212/55-188 mass spectrometer. Column chromatography was performed on Kieselgel 60 (Merck, 60–200 mesh). Silica Gel 60 F_{254} (Merck, 0.25 mm) was used for t.l.c. Pyruvoyl chloride[16], 1,2-*O*-isopropylidene-β-D-fructopyranose[17], 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose[17], and 1,2-*O*-isopropylidene-α-D-glucofuranose[18] were prepared as previously described. Elemental analyses were provided by the Microanalytical Laboratories, CSIR, Pretoria (South Africa).

1,2-O-Isopropylidene-β-D-fructofuranose (**3**). — (*a*) Finely powdered D-fructose (900 mg, 5 mmol) was suspended in dry dimethoxyethane (200 mL), and 2,2-dimethoxypropane (3 mL, 4 mol. equiv.) and tin(II) chloride (10^{-2} mol. equiv., 10 mg) were added. The mixture was heated under reflux for 25 min under dry argon. The reaction was terminated by the addition of pyridine (10^{-2} mol. equiv.) followed by removal of the solvents *in vacuo*. A solution of the residue in water (10 mL) was extracted with chloroform (5 × 50 mL), and the combined extracts were dried (Na_2SO_4), filtered, and concentrated to dryness. The resulting syrup was treated with 1:1 acetic anhydride–pyridine for 12 h, the solvents were removed *in*

vacuo, and a solution of the residue in chloroform (50 mL) was washed with water (2 × 10 mL), dried (Na_2SO_4), and concentrated. Column chromatography (hexane, 4:1 hexane–ethyl acetate, and 3:1 hexane–ethyl acetate) of the resulting oil gave, first, 3-*O*-acetyl-1,2;4,5-di-*O*-isopropylidene-β-D-fructopyranose (190 mg, 12.5%) which, on deacetylation, afforded **5**, m.p. (from ether–hexane) and mixture m.p. 117–119°; lit.[17] m.p. 119°.

Eluted second was 3,4,5-tri-*O*-acetyl-1,2-*O*-isopropylidene-β-D-fructopyranose (328 mg, 19%), m.p. 92–93° (from ether–hexane), which, on deacetylation, gave **6**, m.p. (from ethyl acetate) and mixture m.p. 120–122°; lit.[17] m.p. 121–122°.

Eluted third was 3,4,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-β-D-fructofuranose (**4**; 311 mg, 18%), m.p. 82–84° (from ethyl acetate–hexane), $[\alpha]_D^{20}$ −45° (*c* 1.8, dimethoxyethane); ν_{max} 1740 cm^{-1}. ^{1}H-N.m.r. data (80 MHz, C_6D_6): δ 1.25 and 1.35 (2 s, each 3 H, CMe_2), 1.50, 1.70, and 1.73 (3 s, each 3 H, 3 AcO), 4.00 (ABq, 2 H, J_{AB} 11 Hz, H-1,1′), 4.05 (m, 1 H, H-5), 4.18 (dd, 1 H, $J_{6,6'}$ 11, $J_{5,6}$ 1 Hz, H-6), 4.45 (dd, 1 H, $J_{6,6'}$ 11, $J_{5,6'}$ 5 Hz, H-6′), 5.45 (d, 1 H, $J_{3,4}$ 6.5 Hz, H-3), and 5.55 (dd, 1 H, $J_{3,4}$ 6.5, $J_{4,5}$ 4.5 Hz, H-4). Mass spectrum: *m/z* 331 (M^+ − Me).

A solution of **4** (200 mg) in ice-cold dry methanol (5 mL) was treated with a solution prepared by reacting sodium (2 mg) and dry methanol (2 mL). T.l.c. (ethyl acetate) showed that the reaction was complete after 1.5 h. The mixture was neutralised (solid CO_2) and concentrated *in vacuo*. Column chromatography (100 :1 ethyl acetate–triethylamine) of the residue gave **3** (122 mg, 96%), isolated as a colourless syrup, $[\alpha]_D^{20}$ −38° (*c* 1.7, methanol); lit.[7] $[\alpha]_D^{22}$ −40° (methanol); ν_{max} 3420 (broad) cm^{-1}. ^{1}H-N.m.r. data (80 MHz) δ 1.45 and 1.49 (2 s, each 3 H, CMe_2), 2.75, 3.44, and 3.60 (3 bs, each 1 H, exchangeable with D_2O, 3 OH), 4.05 (ABq, 2 H, *J* 10 Hz, H-1 and H-1′), 3.64–4.9 (m, 5 H, H-3,4,5,6,6′). Mass spectrum: *m/z* 205 (M^+ − Me).

(*b*) A suspension of D-fructose (1.8 g, 10 mmol) in dimethoxyethane (500 mL) was treated with 2-methoxypropene (2.8 g, 40 mmol) and anhydrous tin(II) chloride (20 mg, 10^{-1} mmol) under reflux for 45 min under dry argon. The reaction was terminated by the addition of pyridine (50 μL, 10^{-1} mmol). The solvents were removed *in vacuo*. Column chromatography (hexane–ethyl acetate, 1:1; ethyl acetate) of the residue gave 1,2;4,5-di-*O*-isopropylidene-β-D-fructopyranose followed by **3** (1.32 g, 55%), isolated as a colourless oil.

6-O-Benzoyl-1,2-O-isopropylidene-β-D-fructofuranose (**7**) *and its X-ray structure determination*. — An ice-cold solution of **3** (1 g, 4.5 mmol) in chloroform (10 mL) was treated with pyridine (0.35 mL, 4.5 mmol) and benzoyl chloride (0.53 mL, 4.5 mmol). After 0.5 h at 0°, the solvents were removed *in vacuo*, and a solution of the residue in chloroform (20 mL) was washed with water (2 × 5 mL), dried (Na_2SO_4), and concentrated. Column chromatography (2:1 and then 1:1 hexane–ethyl acetate) of the residue furnished **7** (580 mg, 39.4%). Recrystallisation from ether–hexane gave material having m.p. 83–84°, $[\alpha]_D^{19}$ −14° (*c* 2, methanol). ^{1}H-N.m.r. data (80 MHz, after D_2O exchange): δ 1.30 and 1.40 (2 s, each 3 H,

CMe_2), 3.7–4.4 (m, H-3,4,5), 4.05 (ABq, *J* 10 Hz, 2 H, H-1,1'), 4.50 (m, 2 H, H-6,6'), 7.35–8.15 (m, 5 H, Ph). Mass spectrum: *m/z* 309 (M^+ − Me).

Anal. Calc. for $C_{16}H_{20}O_7$: C, 59.28; H, 6.18. Found: C, 59.11; H, 6.32.

Crystallisation of **7** (ether–hexane) yielded thin plates from which crystals for X-ray diffraction measurements were cut. The crystals were monoclinic, space group $P2_1$ with $a = 8.347(1)$, $b = 5.446(1)$, $c = 18.230(3)$ Å, $\beta = 101.96(1)°$, and $D_{calc.}$ 1.324 g.cm^{-3} for $Z = 2$ ($M_r = 324.32$). The intensity data were measured on an Enraf–Nonius CAD-4 diffractometer (Mo radiation, monochromated, $\omega - 2\theta$ scanning technique). The size of the crystal used was approximately 0.3 × 0.2 × 0.1 mm. The intensities were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SHELXS 84)[19] and refined by the full-matrix least squares method, using weights calculated as $w(hkl) = [\sigma(F_{hkl})]^{-1/2}$ (SHELX-76)[20]. Due to poor crystal quality, only 991 of the 1248 reflections measured were observable ($I > 0$), and only 508 with $I > 4\sigma(I)$ were used in the final refinement. Therefore, it was not possible to refine the non-hydrogen atoms with anisotropic temperature factors or to locate any hydrogen atoms from difference maps. The non-hydrogen atoms were refined with isotropic temperature factors. All the hydrogen atoms, except those in the hydroxyl groups, were included in calculated positions with C–H bond distances constrained to 1.08 Å and with a common isotropic temperature factor which refined to a final value of 0.08(2) Å^2. The methyl groups were refined as rigid groups free to rotate. The short intermolecular distance between O-4 and O-5 of adjacent molecules (2.75 Å) indicates that these hydroxyl groups are involved in hydrogen bonding (for numbering of atoms, see structure **7**). Since the positions of both the hydrogens involved are unknown, it was, however, impossible to calculated their positions. The *R*-factors converged to $R = 0.099$ and $R_w = 0.055$*.

*5,6-O-Isopropylidene-β-*D-lyxo-*hexos-5-ulofuranose* (**9**). — A solution of **3** (1 g, 4.5 mmol) in benzene (80 mL) was heated with bis(tributyltin) oxide (2.8 mL, 1 mol. equiv.) under reflux for 3 h under dry argon, with the azeotropic removal of water, and then allowed to cool to room temperature. Pyruvoyl chloride (480 mg, 4.5 mmol) was added to the stirred solution at 10°. After 1 h, column chromatography (1:1 ethyl acetate–hexane, ethyl acetate) at −10° of the mixture furnished 1,2-*O*-isopropylidene-6-*O*-pyruvoyl-β-D-fructofuranose (**8**; 880 mg, 67%), isolated as a light oil, $[\alpha]_D^{20}$ −26° (*c* 0.2, chloroform). ^{1}H-N.m.r. data (80 MHz): δ 1.45 and 1.35 (2 s, each 3 H, CMe_2), 2.42 (s, 3 H, AcO), 3.7–4.2 (m, 3 H, H-3,4,5), 4.04 (ABq, 2 H, *J* 10 Hz, H-1,1'), 4.34 (m, 2 H, H-6,6'). Mass spectrum: *m/z* 275 (M^+ − Me).

*Tables of F_o and F_c values, fractional coordinates and isotropic temperature factors of all atoms, and bond lengths and bond angles between all the atoms except the hydrogen atoms, which are in calculated positions, have been deposited with, and may be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/356/*Carbohydr. Res.*, 161 (1987) 65–73.

Anal. Calc. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 49.33; H, 6.08.

A solution of **8** (500 mg, 1.7 mmol) in dry benzene (150 mL) was purged with nitrogen for 1 h and then during the Pyrex-filtered irradiation with a 100-W medium-pressure Hanovia mercury lamp. The reaction was monitored by t.l.c. After 4.5 h, the solvent was removed *in vacuo* and column chromatography of the residue yielded **9** (305 mg, 81%), isolated as a light oil, $[\alpha]_D^{20}$ −15° (*c* 0.8, methanol); ν_{max} 3580 and 3500 (broad) cm^{-1}. ^{1}H-N.m.r. data (80 MHz, after D_2O exchange): δ 1.35 and 1.46 (2 s, each 3 H, CMe_2), 3.6–4.4 (m, 5 H, H-1,1′,3,4,5), 5.10 (d, 1 H, $J_{5,6}$ 2.5 Hz, H-6). Mass spectrum: *m/z* 203 (M^+ − Me).

Anal. Calc. for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.31; H, 6.30.

A solution of **9** (100 mg, 0.46 mmol) in pyridine (5 mL) was stirred with hydroxylamine hydrochloride (1 mol. equiv.) at room temperature for 18 h. The solvent was then removed *in vacuo*, and a solution of the residue in chloroform (15 mL) was washed with water (2 × 5 mL), dried (Na_2SO_4), and concentrated, to give 5,6-*O*-isopropylidene-β-D-*lyxo*-hexos-5-ulofuranose oxime (**11**; 98 mg, 92%), which, after recrystallisation from ether–hexane, had m.p. 124–126°, $[\alpha]_D^{20}$ −52° (*c* 1.2, methanol). ^{1}H-N.m.r. data (80 MHz): δ 1.46 and 1.37 (2 s, each 3 H, CMe_2), 7.28 (d, 1 H, $J_{5,6}$ 7.7 Hz, H-6).

Anal. Calc. for $C_9H_{15}N_2O_6$: C, 46.35; H, 6.48; N, 6.01. Found: C, 46.57; H, 6.60; N, 5.82.

The above procedure was repeated with *O*-methylhydroxylamine hydrochloride, and the crude *O*-methyloxime was treated with 1:1 pyridine–acetic anhydride (10 mL) at room temperature for 8 h. The solvents were removed *in vacuo* and column chromatography (2:1 hexane–ethyl acetate) of the residue furnished 3,4-di-*O*-acetyl-5,6-*O*-isopropylidene-β-D-*lyxo*-hexos-5-ulofuranose (**12**; 137 mg, 90%), isolated as a colourless oil, $[\alpha]_D^{20}$ −54° (*c* 2.5, chloroform). ^{1}H-N.m.r. data (500 MHz): δ 1.34 and 1.46 (2 s, each 3 H, CMe_2), 2.06 and 2.10 (2 s, each 3 H, 2 AcO), 3.83 (s, 3 H, NOMe), 4.12 (ABq, 2 H, *J* 9.5 Hz, H-1,1′), 4.43 (dd, 1 H, $J_{4,5}$ 5, $J_{5,6}$ 7.7 Hz, H-5), 5.32 (d, 1 H, $J_{3,4}$ 6.7 Hz, H-3), 5.46 (dd, 1 H, $J_{3,4}$ 6.7, $J_{4,5}$ 5 Hz, H-4), 7.43 (d, 1 H, $J_{5,6}$ 7.7 Hz, H-6). Mass spectrum: *m/z* 316 (M^+ − Me).

Anal. Calc. for $C_{14}H_{21}NO_8$: C, 50.75; H, 6.39; N, 4.23. Found: C, 50.53; H, 6.25; N, 4.11.

D-lyxo-*Hexos-5-ulose (6-aldofructose)* (**1**). — A solution of **9** (50 mg, 0.22 mmol) in acetonitrile (2 mL) was stirred with M HCl (2 mL) at room temperature for 18 h and then filtered through a column of Amberlite IRA-401 (AcO^-) resin (30 mL). Elution with distilled water (2 hold volumes) gave **1** (76 mg, 95%) isolated as a white powder by freeze drying. Crystallisation from ethanol gave material having m.p. 156–158°, $[\alpha]_D^{19}$ −85° (*c* 1, water); lit.[6] m.p. 157–158°, $[\alpha]_D^{20}$ −87° (water).

Anal. Calc. for $C_6H_{10}O_6$: C, 40.45; H, 5.65. Found: C, 40.43; H, 5.43.

1,2-O-Isopropylidene-α-D-gluco-hexodialdo-1,4:6,3-difuranose (**15**). — *N*-Pyruvoylimidazole was prepared by the dropwise addition of pyruvoyl chloride

(0.53 g, 5 mmol) to a stirred cold solution of imidazole (0.68 g, 10 mmol) in chloroform, at such a rate that the reaction temperature remained between 5 and 10°. The precipitated imidazole hydrochloride was then removed, the filtrate was added to a solution of 1,2-*O*-isopropylidene-α-D-glucofuranose (**13**; 1.1 g, 5 mmol) in 1,2-dimethoxyethane (20 mL), and the mixture was stirred at 50° for 2.5 h, then neutralised with glacial acetic acid, and concentrated. Column chromatography (ethyl acetate) of the residue at 0° furnished 1,2-*O*-isopropylidene-6-*O*-pyruvoyl-α-D-glucofuranose (**14**; 1.02 g, 71%), m.p. 110–112° (from ether–hexane), $[\alpha]_D^{20}$ −4° (*c* 1.4, chloroform); ν_{max} 1732 cm^{-1}. ^{1}H-N.m.r. data (80 MHz): δ 1.35 and 1.46 (2 s, each 3 H, CMe_2), 2.45 (s, 3 H, AcO), 3.5–3.7 (m, 2 H, exchangeable with D_2O, 2 OH), 4.0–4.4 (m, 4 H, H-2,3,4,5), 4.50 (m, 2 H, H-6,6'), 6.03 (d, *J* 4.3 Hz, H-1). Mass spectrum: *m/z* 275 (M^+ − Me).

Anal. Calc. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 49.81; H, 6.38.

A solution of **14** (193 mg, 0.66 mmol) in dry oxygen-free benzene (77 mL) was irradiated under nitrogen for 4.5 h as described above, and then concentrated *in vacuo*. Column chromatography (ethyl acetate) of the residue at 0° gave **15** (119 mg, 82%), m.p. 124–125° (from ethyl acetate), $[\alpha]_D^{20}$ +28° (*c* 1.1, methanol); lit.[12] m.p. 125–126°, $[\alpha]_D^{23}$ +27° (*c* 0.5, water). ^{1}H-N.m.r. data (80 MHz): δ 1.30 and 1.47 (2 s, each 3 H, CMe_2), 3.50 (bs, 1 H, exchangeable with D_2O, OH), 4.05 (m, 1 H, changed to t after D_2O exchange, $J_{3,4} = J_{4,5}$ = 5.5 Hz, H-5), 4.30 (bs, 1 H, exchangeable with D_2O, OH), 4.5–4.85 (m, 3 H, H-2,3,4), 5.27 (bt, 1 H, change to d after D_2O exchange, $J_{4,5}$ 5.5 Hz, H-6), 6.05 (d, 1 H, *J* 4 Hz, H-1). Mass spectrum: *m/z* 203 (M^+ − Me).

D-gluco-*Hexodialdose* (**2**). — Hydrolysis[12] of **15**[12] furnished **2** (70 mg, 85%), m.p. 88–90°, $[\alpha]_D^{22}$ −48° (*c* 2, water); lit.[21] m.p. 90–92°, $[\alpha]_D^{25}$ (for **2**·H_2O) +49.6° (*c* 2.3, water). Its bisphenylhydrazone had m.p. 173–174°; lit.[21] m.p. 175°.

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