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1,2:3,4-DI-*O*-ISOPROPYLIDENE-α-D-*galacto*-HEXODIALDO-1,5-PYRANOSE AND ITS 6-ALDEHYDROL*†

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ABSTRACT

Oxidation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**1**) with methyl sulfoxide–*N*,*N*′-dicyclohexylcarbodiimide–pyridinium phosphate (Pfitzner–Moffatt reagent) furnishes a preparative route to the title aldehyde **2**. In aqueous solution, **2** exists entirely in the form of its 6-aldehydrol (**8**). In common with a number of other *aldehydo* sugar derivatives, compound **2** exhibits zero spin-coupling between the aldehyde proton and the proton vicinal to it. The aldehyde **2** was characterized as the crystalline 6-oxime (**3**) and 6-(*p*-nitrophenyl)hydrazone (**7**). Compounds **2**, **3**, and **7** are important as potential intermediates in chain-extension reactions leading to 6-amino-6,8-dideoxy-octoses related to lincomycin.

INTRODUCTION

The addition of acetylenic or vinylic Grignard reagents to suitably protected *aldehydo* sugars is a useful method for chain extension in the sugar series[1–6], and similar additions to *keto* sugar derivatives furnish a route to branched-chain sugars[7]. The versatility of the ethynyl and vinyl groups in numerous synthetic transformations provides potential access to a wide variety of modified sugars[1–6]. A program in this laboratory has emphasized the development of high-yielding procedures, based on addition of Grignard reagents, for chain-extension and chain-branching reactions, together with effective methods for separation of the diastereoisomeric products formed. Structural characterization of the separated epimers has been achieved by n.m.r. spectroscopy and by degradation to known, crystalline derivatives[4–6].

Although the addition of unsaturated Grignard reagents to *aldehydo* (and *keto*) sugar derivatives can be effected in high yield[4–7], the number of useful preparative routes to the carbonyl derivatives required is limited. Isopropylidene acetals and

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perbenzoic esters of *aldehydo* sugars can be obtained by way of dialkyl dithioacetals of aldoses, and addition of ethynylmagnesium bromide to the aldehyde group has been studied with such acetals[1,4] and esters[5]. Cleavage of suitable, protected glycols furnishes a further route to protected *aldehydo* sugars. In this laboratory, addition of unsaturated Grignard reagents has been effected with 2,3-*O*-isopropylidene-D-glyceraldehyde[1,2,6] and with 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose[1,2], derived by glycol cleavage from 1,2:5,6-di-*O*-isopropylidene-D-mannitol and 1,2-*O*-isopropylidene-α-D-glucofuranose, respectively. Protected *keto* sugars are readily obtained on a preparative scale by the methyl sulfoxide–acetic anhydride procedure for oxidation of "isolated" secondary alcohols to ketones[8]. However, attempts to prepare a protected *aldehydo* sugar by treating an "isolated" primary alcohol derivative with methyl sulfoxide–acetic anhydride were unsuccessful. Instead of the desired aldehyde, the (methylthio)methyl ether of the alcohol was the principal product[3].

The reagent of Pfitzner and Moffatt[9] (methyl sulfoxide–*N*,*N*′-dicyclohexylcarbodiimide–pyridinium phosphate) can be used for oxidation of nucleosides to the 5′-*aldehydo* derivatives[9], and for oxidation of "isolated" secondary alcohol groups to ketones in sugar derivatives[8,10]. In this laboratory, the use of the Pfitzner–Moffatt oxidant for preparing *aldehydo* sugar derivatives[1] from "isolated" primary alcohol derivatives has presented technical difficulties in preparative-scale work, because separation of the product aldehyde from side-products and excess reagents is not readily achieved.

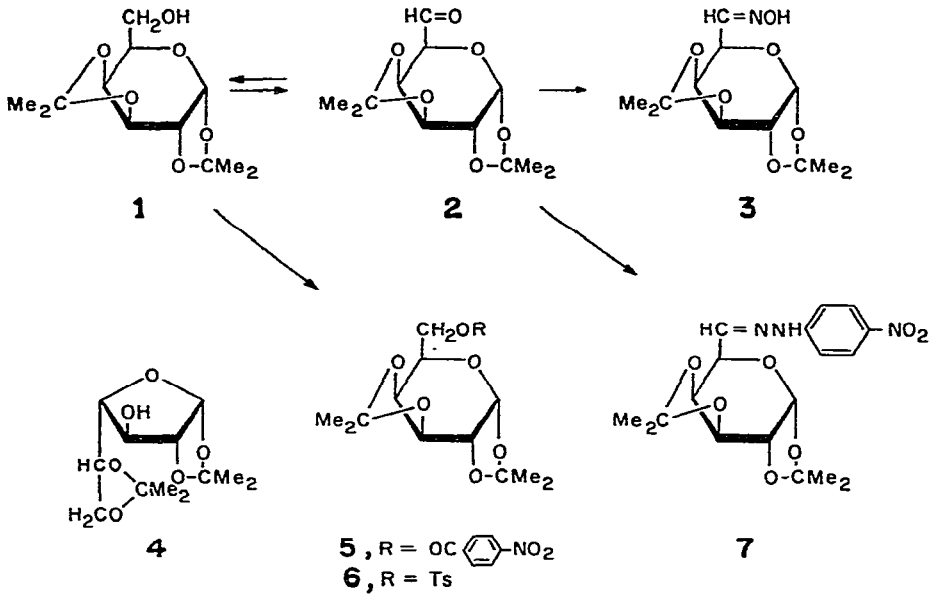
The present report describes the use of the Pfitzner–Moffatt oxidant for preparative conversion of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**1**) into the corresponding 6-aldehyde **2**. This aldehyde was characterized by formation of crystalline derivatives, and by n.m.r. spectroscopic studies on the free aldehyde **2**, its derived aldehydrol (**8**), and related *aldehydo* sugar derivatives.

DISCUSSION

Acetonation of D-galactose by the conventional procedure[11] with copper(II) sulfate and sulfuric acid as catalysts gave 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**1**) as a distilled syrup. It has been pointed out by DeJongh and Biemann[12] that, prepared by this procedure, **1** contains a small proportion (< 3%) of a side product, which they isolated by g.l.c. and formulated on the basis of mass-spectrometric evidence as 1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose (**4**). T.l.c. of the distilled product isolated in the present work revealed the presence of a small proportion of a side product having a mobility greater than that of **1**. Careful fractional distillation gave pure **1**, b.p. 128–129°/0.8 torr, that was chromatographically homogeneous; the side product boiled at 89–91°/1 torr. Unless the acetal **1** was separated in this way from the low-boiling side-product, much difficulty was experienced in isolating the aldehyde **2** derived by oxidation of **1**.

The purified acetal **1** gave a crystalline *p*-nitrobenzoate (**5**). The *p*-toluenesulfo-

nate (6) of 1 had a specific rotation in agreement with literature values[13], and its m.p. corresponded to that reported[14,15] for a high-melting dimorph of 6.



Oxidation of the pure acetal 1 with the Pfitzner–Moffatt reagent gave the crude aldehyde 2 as a syrup in about 80% yield. Careful control of the isolation procedure was required in order to ensure maximum separation of 2 from the reagents and decomposition products. Although the crude aldehyde 2 gave satisfactory results in reactions with unsaturated Grignard reagents[16], t.l.c. revealed that, in addition to 2, this material contained several side-products, including one that gave a positive Schiff test. The aldehyde 2 could be obtained chromatographically homogeneous and analytically pure by careful fractional distillation of the crude product.

The pure aldehyde 2 gave positive Schiff and Tollens reactions, and showed characteristic absorptions for the aldehyde group in its i.r. spectrum. Reduction of 2 with aqueous sodium borohydride regenerated the parent alcohol 1, characterized as its 6-*p*-toluenesulfonate (6). Treatment of 2 with (*p*-nitrophenyl)hydrazine hydrochloride or with hydroxylamine hydrochloride, in aqueous alcohol containing sodium acetate, did not lead to crystalline derivatives, but, when pyridine was used as the acid acceptor and catalyst, the crystalline oxime (3) and (*p*-nitrophenyl)-hydrazone (7) of the aldehyde 2 were readily obtained.

The n.m.r. spectrum of the aldehyde 2 in chloroform-*d* (Fig. 1) shows the signal of the aldehyde proton (H-6) at τ 0.43. This signal is observed as a singlet, indicating that the vicinal coupling ($J_{5,6}$) is approximately zero. Other *aldehydo* sugar derivatives isolated in this laboratory [1,4–6,17] show the signal of the aldehyde proton at similar field, and the coupling of the aldehyde proton with the proton vicinal to it is either very small or zero (see Table I), except in the case of β-unsaturated aldehyde derivatives[1], where a large (7 Hz) vicinal coupling is observed.

The magnitude of the vicinal coupling for the saturated aldehyde derivatives indicates that the dihedral angle of the aldehyde proton and the proton vicinal to

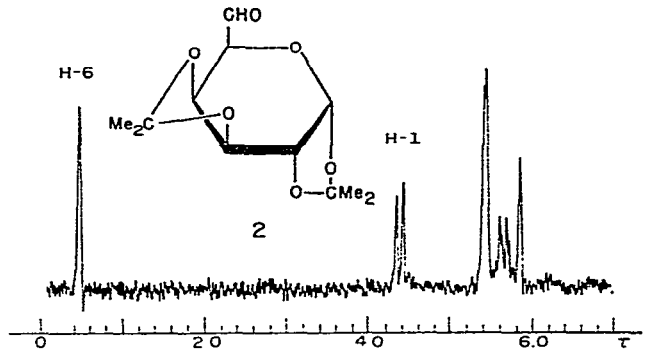
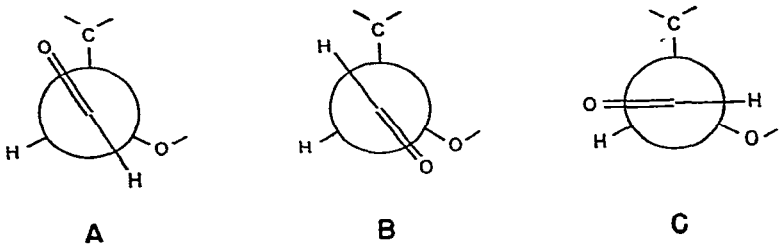


Fig. 1. The low-field portion of the 60-MHz n.m.r. spectrum of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (2) in chloroform-*d*.

it is approximately 90°, if it can be assumed that the Karplus relationship is valid for such systems. This arrangement would require the carbonyl group to be almost eclipsed by a carbon atom (rotamer A) or an oxygen atom (rotamer B) attached to the vi-



cinal carbon atom; the carbonyl group is definitely not eclipsed by the vicinal hydrogen atom (rotamer C), because this arrangement would lead to a large, vicinal coupling-constant. The favored rotamer state for simple aldehydes is considered[20] to be that in which the carbonyl group is eclipsed by a large substituent. The large, vicinal couplings observed with β-unsaturated aldehydes is consistent with the presumed planarity of the conjugated π-system.

In aqueous solution, the aldehyde **2** exists entirely as the aldehydrol (**8**). The n.m.r. spectrum of **8** (see Fig. 2) shows the H-6 signal at τ 4.95 as a one-proton, wide doublet, $J_{5,6}$ 7.1 Hz, and no aldehyde-proton signal is observed. The resonance of the aldehydrol proton is observed at much higher field than that of the parent aldehyde. The chemical shift of this signal is in the "anomeric proton region", and this observation emphasizes that the aldehydrol form should receive consideration as a possible contributor to tautomeric equilibria whenever free sugars in aqueous solution are examined by n.m.r. spectroscopy.

The large, vicinal coupling observed for the aldehydrol is consistent with a favored rotamer state that has the vicinal protons antiparallel (rotamer D). Similar

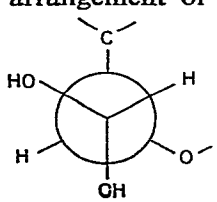
TABLE I

N.M.R. SPECTRAL DATA FOR *aldehydo* SUGAR DERIVATIVES AND RELATED COMPOUNDS[a]

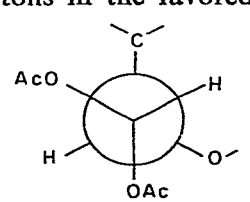
Compound	*Chemical shift of aldehyde[b] proton, τ*	*Coupling of aldehyde[b] proton with vicinal proton, Hz*	*References*
Saturated aldehydes			
4-Acetamido-4,5-dideoxy-2,3-*O*-isopropylidene-*aldehydo*-L-xylose	0.67	0	17
3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose	0.35	3	1,18
2,3:4,5-Di-*O*-isopropylidene-L-arabinose	0.35	0	4[c]
1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (2)	0.43	0	*c*
2,3-*O*-Isopropylidene-D-glyceraldehyde	0.35	1.7	1,6
2,3,4,5-Tetra-*O*-benzoyl-L-arabinose	0.30	0	5
Unsaturated aldehydes			
trans-2,3-Dideoxy-4,5:6,7-di-*O*-isopropylidene-L-*arabino*-hept-2-enose	0.38	7	1
trans-2,3-Dideoxy-4,5-*O*-isopropylidene-D-*glycero*-pent-2-enose	0.55	7	1
Aldehydrols (and acetates)			
1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose 6-aldehydrol[d] (8)	4.95	7.1	*c*
1,1-Di-*O*-acetyl-2,3,4,5-tetra-*O*-benzoyl-L-arabinose aldehydrol	2.80	7	5
1,1-Di-*O*-acetyl-2,3-*O*-iospropylidene-D-glyceraldehyde aldehydrol	3.20	4.7	6
Dithioacetals			
2,3,4,5-Tetra-*O*-acetyl-L-arabinose diethyl dithioacetal	6.13	7.8	19
2,3,4,5-Tetra-*O*-acetyl-L-arabinose diphenyl dithioacetal	5.80	5.6	19
2,3,4,5-Tetra-*O*-benzoyl-L-arabinose diethyl dithioacetal	5.68	6.9	5

[a]For solutions in chloroform-*d*. [b]Proton of the aldehyde, aldehydrol, or dithioacetal group. [c]Present work. [d]In deuterium oxide.

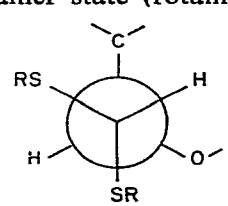
large vicinal couplings have been noted for aldehydrol acetates of sugars, and also for some dialkyl dithioacetals of aldoses (see Table I), again indicating the antiparallel arrangement of protons in the favored rotamer state (rotamers E and F). These



D



E



F

rotamer states (D, E, and F) are the expected, favored conformers, because they correspond to maximum staggering of large groups. In certain systems, interactions with groups on carbon atoms more distant than the vicinal position may influence the favored conformation[21].

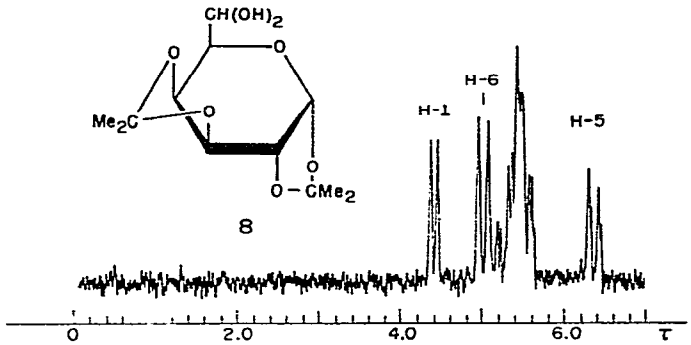


Fig. 2. The low-field portion of the 60-MHz n.m.r. spectrum of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose 6-aldehydrol (**8**) in deuterium oxide.

When the aldehyde **2** is converted into the 6-aldehydrol **8**, a considerable upfield shift of the H-5 signal is observed (see Figs. 1 and 2), with the result that, in **8**, the H-5 signal gives rise to a sharp quartet outside the envelope of signals for H-2, 3, and 4. Since the $J_{5,6}$ coupling is evident from the H-6 doublet, it is possible to measure $J_{4,5}$ (1.7 Hz) directly; the value observed is close to that determined[22,24] for other, related derivatives. This upfield shift of the resonance of the vicinal proton, that occurs when the aldehyde is hydrated, may, in some instances, provide a useful method for obtaining additional conformational information about a ring system.

In moist chloroform, the aldehyde **2** is hydrated to only a small extent.

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Specific rotations were determined in a 2-dm polarimeter tube. Infrared spectra were measured with a Perkin–Elmer Model 137 "Infracord" infrared spectrometer. N.m.r. spectra were measured at 60 MHz with a Varian A-60 n.m.r. spectrometer. Chemical shifts are given on the τ-scale, and spectra were measured at ~30°. Unless otherwise mentioned, spectra were measured for solutions (15–20%) in chloroform-*d*, with tetramethylsilane (τ = 10.00) as the internal standard. Microanalyses were performed by W. N. Rond. X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation; the camera diameter was 114.59 mm. Relative intensities were estimated visually: s, strong; m, moderate; w, weak; v, very. The strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities. T.l.c. was effected on plates coated with a 250-μm layer of Silica Gel G (E. Merck, Darmstadt, Germany), activated at 110°, as the adsorbent. The developers used were: (*A*) 9:1 benzene–methanol; (*B*) 2:3:2:2:1

hexane–benzene–ethyl acetate–tetrahydrofuran–*tert*-butyl alcohol; and (*C*) 7:1:1:1 benzene–chloroform–acetone–methanol. Indication was effected with sulfuric acid, iodine vapor, or Schiff reagent.

*Preparation of 1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**1**). — D-Galactose (20 g) was acetonated with the use of copper(II) sulfate and sulfuric acid as the condensing agents[11]. The resultant oil was found by t.l.c. to contain a major component having R_F 0.23 (*A*) and a minor component having R_F 0.72 (*A*). Fractional distillation of the oil gave the minor component as the first fraction, b.p. 89–91°/1 torr, R_F 0.72 (*A*), 0.90 (*B*), 0.70 (*C*). The pure acetal **1** distilled at 128–129°/0.8 torr as a colorless, chromatographically homogeneous oil; yield 24 g (80%), $[\alpha]_D^{20}$ −59° (*c* 1.4, chloroform) (lit.[11] $[\alpha]_D$ −55° in chloroform); R_F 0.23 (*A*), 0.83 (*B*), 0.36 (*C*); λ_{max}^{film} 2.88 (OH), 7.21, 7.28 μm (CMe_2).

If the low-boiling side-product present in the crude **1** was not removed, the aldehyde **2** derived by oxidation of **1** proved to be very difficult to purify*.

The *6*-p-*toluenesulfonate* (**6**) of **2**, prepared by the usual method[23], was obtained from ethanol as colorless plates in 70% yield; m.p. 99–100°, $[\alpha]_D^{20}$ −66° (*c* 1.0, chloroform); R_F 0.76 (*A*), 0.86 (*B*), 0.79 (*C*); n.m.r. data: τ 2.19, 2.68 (2-proton doublets, A_2B_2 system, $J_{A,B}$ 8.2 Hz, aryl), τ 4.54 (1-proton doublet, $J_{1,2}$ 4.8 Hz, H-1), τ 5.40 (1-proton quartet[23], $J_{2,3}$ 2.1 Hz, $J_{3,4}$ 7.6 Hz, H-3), τ 5.64–5.97 (5-proton multiplet, H-2, 4, 5, 6, 6'), τ 7.57 (3-proton singlet, Me of Ts), τ 8.50, 8.67, 8.69, 8.70 (3-proton singlets, CMe_2); X-ray powder diffraction data: 7.69 w, 6.78 s (1,1), 5.82 w, 5.39 s (1,1), 4.91 w, 4.62 s (1,1), 4.43 w, 4.21 m, 4.10 w, 3.91 vw, 3.78 vw, 3.72 vw, 3.37 m, 3.25 vw.

Various melting points have been recorded for this substance: m.p.[13] 89–91°; m.p.[25] 91–92°; m.p.[14] 102–103°; and m.p.[15] 104–105°. It is probable that there are at least two polymorphs of **6** that have been isolated.

*1,2:3,4-Di-*O*-isopropylidene-6-*O*-p-nitrobenzoyl-α-*D*-galactopyranose* (**5**). —*p*-Nitrobenzoyl chloride (1 g) was added portionwise to a solution of **1** (1 g) in dry pyridine (20 ml), and the solution was kept for 48 h at room temperature. Water was then added[24], and the solvent was evaporated. The residue was dissolved in benzene (30 ml), and the solution was washed successively with cold, 10% sulfuric acid solution, 5% sodium hydrogen carbonate solution, and water. The dried (calcium sulfate) solution was evaporated, and the residue was crystallized from ethanol to give **5** as pale-yellow plates; yield 1.3 g (82%), m.p. 116.5–117.5°, $[\alpha]_D^{20}$ −57° (*c* 1.0, chloroform); R_F 0.80 (*A*), 0.84 (*B*), 0.83 (*C*), λ_{max}^{KBr} 5.79 (C=O), 6.21 (aryl), 6.54, 7.38 (NO_2), 7.24, 7.31 μm (CMe_2); n.m.r. data: τ 1.79 (4-proton singlet, aryl), τ 4.45 (1-proton doublet, $J_{1,2}$ 4.8 Hz, H-1), τ 5.24–5.85 (6-proton multiplet, H-2,3,4,5,6,6'), τ 8.50, 8.51, 8.63 (3-, 3-, and 6-proton singlets, CMe_2); X-ray powder diffraction data:

**Note added in proof.* The side product was identified as 1,2:3,4-di-*O*-isopropylidene-β-L-arabinopyranose by elemental analysis and by comparison of its n.m.r. spectrum with that published for this compound[23]. It was determined that this side product arose because the commercial D-galactose used contained L-arabinose as an impurity.

9.19 vs (1), 7.71 w, 6.99 w, 6.45 w, 5.60 m, 5.23 w, 4.95 s, 4.69 w. 4.40 s, 4.27 vw, 4.08 s, 3.77 w, 3.59 w, 3.52 vw, 3.28 w.

Anal. Calc. for $C_{19}H_{23}NO_9$: C, 55.74; H, 5.66; N, 3.42. Found: C, 55.79; H, 5.57; N, 3.50.

1,2:3,4-Di-O-*isopropylidene*-α-D-galacto-*hexodialdo-1,5-pyranose* (**2**). — To a solution of **1** (10 g) in methyl sulfoxide (35 ml) and benzene (10 ml) were added pyridine (2 ml), phosphoric acid (1 ml), and *N,N'*-dicyclohexylcarbodiimide (25 g). The mixture was stirred for 5 h at room temperature, and filtered to remove *N,N'*-dicyclohexylurea, and a solution of oxalic acid (20 g) in methanol (50 ml) was added to the filtrate. The resulting suspension was stirred for 1 h at room temperature, and then filtered. The filtrate was washed with three 50-ml portions of aqueous sodium hydrogen carbonate. The aqueous extracts were extracted with ethyl acetate (100 ml), and the organic phases were combined, dried (calcium sulfate), and evaporated. The residual syrup was dissolved in acetone (100 ml), whereupon a small amount of *N,N'*-dicyclohexylurea crystallized out. The mixture was filtered, the filtrate was evaporated, and the resultant syrup was treated twice more with acetone in the same way, to give the crude, syrupy aldehyde **2**, yield 8 g (80%). The syrup was distilled twice, and the fraction having b.p. 104–105°/0.5 torr was collected. This fraction was the pure, chromatographically homogeneous aldehyde **2**, yield 4.5 g (46%), $[\alpha]_D^{20}$ −131° (*c* 0.9, chloroform); R_F 0.21 (*A*), 0.69 (*B*), 0.39 (*C*); Schiff and Tollens positive; λ_{max}^{film} 3.70 (CHO), 5.72 (C=O), 7.24, 7.30 μm (CMe_2); n.m.r. data (see Fig. 1): τ 0.43 (1-proton singlet, $J_{5,6}$ ~0 Hz, H-6), τ 4.40 (1-proton doublet, $J_{1,2}$ 4.8 Hz, H-1), τ 5.40–5.83 (4-proton multiplet, H-2,3,4,5), τ 8.50, 8.56, 8.68 (3-, 3-, and 6-proton singlets, CMe_2).

Anal. Calc. for $C_{12}H_{18}O_6$: C, 55.80; H, 7.03. Found: C, 55.43; H, 6.76.

T.l.c. of the crude product showed the presence of five components, having R_F 0.28, 0.35, 0.39, 0.70, and 0.85 (developer *C*). The major component was that having R_F 0.39; it gave a positive reaction with the Schiff reagent, as did the side-product having R_F 0.35. The component having R_F 0.28 was chromatographically indistinguishable from *N,N'*-dicyclohexylurea. Attempts to purify the major component by chromatography on a column of silica gel were not successful.

Reduction of the aldehyde **2** *to the alcohol* **1**. — To a solution of the aldehyde **2** (200 mg) in water (30 ml) was added sodium borohydride (60 mg). The solution was kept for 4 h at room temperature, aqueous acetic acid was then added dropwise to bring the pH to ~5, and the solution was evaporated. T.l.c. of the residue revealed a single component, chromatographically indistinguishable from the alcohol **1**. The residue was dissolved in pyridine (5 ml), and *p*-toluenesulfonyl chloride (200 mg) was added. The product was isolated in the usual way[24] to give the *p*-toluenesulfonate **6**, indistinguishable from an authentic sample of **6**.

1,2:3,4-Di-O-*isopropylidene*-α-D-galacto-*hexodialdo-1,5-pyranose 6-oxime* (**3**). — To a solution of the 6-aldehyde **2** (0.5 g) in methanol (5 ml) was added a solution of hydroxylamine hydrochloride (140 mg) in a mixture of water (1 ml) and pyridine (1 ml). The solution was kept for 18 h at room temperature and then evaporated, and

the resultant syrup was dissolved in benzene (50 ml). The solution was successively washed with water, 10% sulfuric acid, 5% sodium hydrogen carbonate, and water, dried (calcium sulfate), and evaporated. The residue was crystallized from hexane to give **3** as colorless plates, yield 0.35 g (66%), m.p. 107–108°, $[\alpha]_D^{20}$ −116° (*c* 0.35, chloroform); R_F 0.20 (*A*), 0.82 (*B*), 0.54 (*C*); λ_{max}^{KBr} 2.91 (OH), 6.19 (C=N), 7.28, 7.30 μm (CMe_2); X-ray powder diffraction data: 10.77 m, 7.39 vs (1), 6.99 vw, 6.30 w, 5.82 w, 5.26 m, 4.95 s, 4.75 m, 4.51 m, 4.16 vw, 3.94 s, 3.60 vw, 3.31 m, 3.19 w, 3.09 w, 2.92 w.

Anal. Calc. for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.83; H, 7.22; N, 5.25.

1,2:3,4-Di-O-isopropylidene-α-D-galacto-hexodialdo-1,5-pyranose 6-(p-nitrophenyl)hydrazone (**7**). — A solution of (*p*-nitrophenyl)hydrazine hydrochloride (500 mg) in a mixture of water (5 ml) and pyridine (1 ml) was mixed with a solution of the 6-aldehyde **2** (500 mg) in methanol (5 ml). The solution was kept for 20 h at room temperature and then evaporated. The resultant syrup was dissolved in benzene (50 ml), and the solution was washed successively with water, 10% sulfuric acid, 5% sodium hydrogen carbonate solution, dried (calcium sulfate), and evaporated. The residue was crystallized from benzene–ethanol to give **7** as yellow needles, yield 600 mg (82%), m.p. 214–215°, $[\alpha]_D^{22}$ −83.5° (*c* 1.0, chloroform); R_F 0.55 (*A*), R_F 0.85 (*B*), R_F 0.76 (*C*); λ_{max}^{KBr} 3.07 (NH), 6.25 (C=N), 6.53, 7.26 μm (NO_2); X-ray powder diffraction data: 8.00 s (3,3), 7.51 m, 7.10 s, 6.71 m, 6.05 m, 5.80 s (2), 5.01 s, 4.56 vs (1), 4.75 m, 4.19 s, 4.00 s (3,3), 3.84 w, 3.65 w, 3.55 w.

Anal. Calc. for $C_{18}H_{23}N_3O_6$: C, 54.96; H, 5.89; N, 10.68. Found: C, 55.28; H, 6.08; N, 10.43.

1,2:3,4-Di-O-isopropylidene-α-D-galacto-hexodialdo-1,5-pyranose 6-aldehydrol (**8**). — A solution (~10%) of the aldehyde **2** was prepared in deuterium oxide. The n.m.r. spectrum (see Fig. 2) revealed the 6-aldehydrol **8** as the only detectable species in solution, n.m.r. data (internal standard, sodium 4,4-dimethyl-4-silapentane-1-sulfonate, τ = 10.00): τ 4.37 (1-proton doublet, $J_{1,2}$ 4.8 Hz, H-1), τ 4.95 (1-proton doublet, $J_{5,6}$ 7.1 Hz, H-6), τ 5.22 (1-proton quartet, $J_{2,3}$ 2.1 Hz, $J_{3,4}$ 7.6 Hz, H-3), τ 5.37–5.58 (multiplet, HOD, H-2,4), τ 6.33 (1-proton quartet, $J_{4,5}$ 1.7 Hz, H-5), τ 8.43, 8.52, 8.60 (3-, 3-, and 6-proton singlets, CMe_2).

Addition of 2 drops of deuterium oxide to 0.4 ml of a 10% solution of the aldehyde **2** in chloroform-*d* caused the signal at τ 0.43 for the aldehydic proton (H-6) to be diminished to about 33% of its original intensity, and a signal of ~20% of the intensity of one proton appeared at τ 4.95 (H-6 of the aldehydrol).

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