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Large scale synthesis of the acetonides of L-glucuronolactone and of L-glucose: easy access to L-sugar chirons

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ABSTRACT

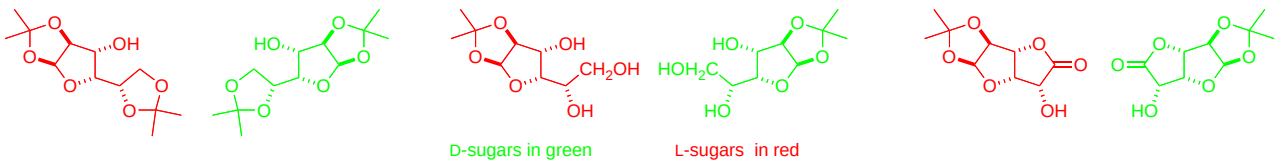
1,2-*O*-Isopropylidene-α-L-glucurono-3,6-lactone may be synthesized on a 100–200 g scale from cheaply available D-glucoheptonolactone in an overall yield of 94% in four steps via L-glucuronolactone. Subsequent elaboration to L-glucose, diacetone-L-glucose (1,2:5,6-di-*O*-isopropylidene-α-L-glucofuranose), and monoacetone-L-glucose (1,2-*O*-isopropylidene-α-L-glucofuranose) allows easy access to a range of L-sugar chirons.

1. Introduction

Diacetone glucose **1D** (with the C3–OH group free) and monoacetone glucose **2D** have long been used as the most common chirons derived from carbohydrates.[1] The acetonide **3D** from D-glucuronolactone (with only the C5–OH group unprotected) has also been widely used as a chiron for the synthesis of iduronic acid,[2] inositols,[3] vitamin C,[4] sugar amino acids[5], fluoro-,[6] amino-,[7] and higher[8] monosaccharides, oxetanes,[9] imino sugars,[10] gonofurone and related compounds,[11] and many other homochiral targets.[12] The use of these acetonides depends on the low prices of D-glucose **4D** (the cheapest monosaccharide) and of D-glucuronolactone **12D**. However, the cost of L-glucose **4L** makes the use of the enantiomers **1L** and **2L** prohibitive as starting materials for homochiral synthesis; L-glucuronolactone **12L** is simply not commercially available. Accessibility to the L-enantiomers of such building blocks[13] would allow access to a range of targets not approachable at present from the chiral pool. Additionally, this would allow the preparation of enantiomers of biologically active compounds;[14] the enantiomers of natural products have significant and different biological activity.[15]

This Letter describes the conversion of D-glucoheptonolactone **9D** on a 100–200 g scale into the acetonide of L-glucuronolactone **12L** in an overall yield of 94% in four steps without chromatography; subsequent reduction by sodium borohydride affords monoacetone-L-glucose **2L** and then conversion into either diacetone-L-glucose **1L** or L-glucose **4L**. There are many published syntheses of L-glucose, such as chemical syntheses from diacetone glucose **1D** or L-arabinose,[16] D-gulonolactone,[17] ab initio asymmetric syntheses[18] and enzymatic[19] or biotechnological[20] procedures; however, none of these approaches provide substantial amounts of L-sugars cheaply. L-Glucose tastes as sweet as D-glucose and has potential as a food substitute and for other uses.[21]

Two strategies for the isomerization of D-glucose **4D** to L-glucose **4L** are shown in Scheme 1. Lundt reported a procedure by which inversion of configuration at all four chiral carbon atoms in the lactone from D-gluconic acid **7D** [obtained by oxidation of glucose] formed L-gluconic acid **8L**. The conversion involves reaction with



1L **1D** **2L** **2D** **3L** **3D**

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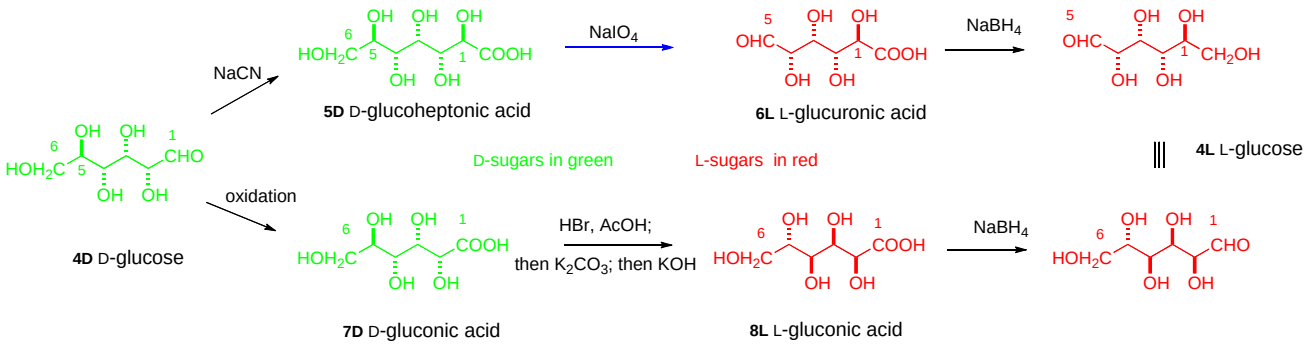


Scheme 1. Strategies for the conversion of D-glucose **4D** into L-glucose **4L** (numbering applies to carbons in D-glucose; aldonic acids are usually handled as their lactones).

hydrogen bromide in acetic acid followed by a series of base-induced epimerisations and Payne rearrangements in which no protecting groups are used. Subsequent borohydride reduction of the lactone of **8L** yields L-glucose **4L**. This work has only appeared in a preliminary form with no indication of yield.[22] A second approach depends on the highly Felkin-Ahn diastereoselective Kiliani cyanide reaction of D-glucose **4D** to give D-glucoheptononic acid **5D** (both salts of **5D** and the corresponding lactone, glucoheptonolactone **9D** are cheaply available). Suitable protection allows selective oxidative cleavage of the original C5–C6 bond of glucose to afford L-glucuronic acid **6L**; subsequent reduction of a protected derivative of **3L** by borohydride gives L-glucose **4L**. This strategy was demonstrated long ago by Sowa[23] but not developed into a scalable procedure.

Reaction of glucoheptonolactone **9D** with benzaldehyde and concentrated aqueous hydrochloric acid gave the highly crystalline benzylidene derivative **10D** in 96% yield (Scheme 2). Periodate cleavage of the diol **10D** afforded the protected L-glucuronic acid **11L** which, without purification, was treated with aqueous trifluoroacetic acid to give L-glucuronolactone **12L** in 99% yield. Reaction of **12L** with acetone in the presence of concentrated sulfuric acid formed the crystalline acetonide **3L** in 99% yield. The overall yield of L-glucuronolactone acetonide **3L** from **9D** is 94% and may readily be performed on a 100–200 g scale. Reduction of the protected lactone **3L** by sodium borohydride in water gave L-glucose monoacetonide **2L** in 60% yield. Treatment of the crude product **2L** from the borohydride reduction of **3L** with acetone in the presence of sulfuric acid afforded diacetone L-glucose **1L** [39% yield over two steps]; alternatively, hydrolysis of crude **2L** gave L-glucose **4L** in 41% yield over the two steps. The ^{13}C and ^{1}H NMR spectra of all the L-sugars **1L**, **2L**, **3L**, **4L**, and **12L** were identical with those of authentic samples of their enantiomers.

In summary, this Letter reports an efficient large scale preparation of the acetonide of L-glucuronolactone **3L** from glucoheptonic acid and further elaboration to the mono-**2L** and di-**1L** acetonides of L-glucose. These procedures provide a family of readily available L-sugar chirons which may be of value for the synthesis of complex targets from the chiral pool. Full experimental details are given.

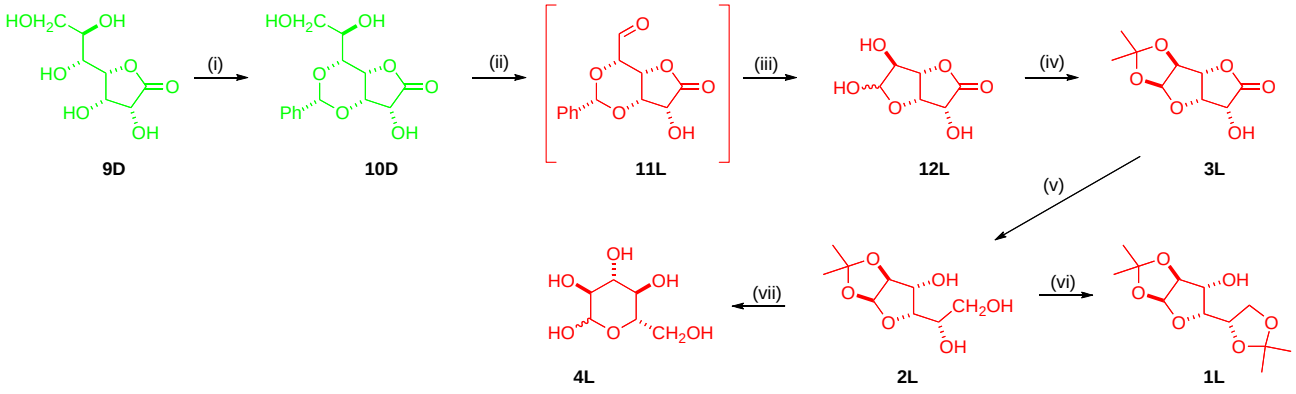
2. Experimental

2.1. 3,5-*O*-Benzylidene-D-glucoheptono-1,4-lactone 10D

D-Glucoheptonolactone **9D** (200 g, 0.962 mol) was added to a mixture of benzaldehyde (600 mL) and concentrated aqueous hydrochloric acid (32%, 60 mL) in a 4-L-jacketed glass reactor fitted with a mechanical overhead stirrer. The reaction mixture was stirred at room temperature for 2 h, after which the reaction was judged complete by TLC analysis (EtOAc:EtOH:H_2O, 45:5:1), with the formation of a major product (R_f 0.44) observed. Petroleum-ether (40–60; 1600 mL) was added to the mixture and the resulting crystalline mass was stirred for 30 min and collected by filtration. The filter cake was washed with ether (500 mL) and then dried under vacuum to give the benzylidene acetal 9D (273 g, 96%), [mp 202–206 °C; $[\alpha]_D^{25}$ −57.0 (c, 1.01 in MeOH), lit.[24] mp 188–191 °C; $[\alpha]_D^{20}$ −56.1 (*c*, 1.0 in MeOH)], which was used in the next step without further purification.

2.2. L-Glucurono-3,6-lactone 12L

A suspension of the benzylidene lactone **10D** (100 g, 0.338 mol) in THF:water (10:1, 770 mL) was warmed to 40 °C to give a clear solution. Sodium periodate (75 g, 0.35 mol) was added portionwise to the stirred reaction mixture over 35 min in order to control



Scheme 2. Reagents: (i) PhCHO, HCl, 96%; (ii) $NaIO_4$, THF/H_2O; (iii) CF_3COOH/H_2O, 99% over two steps; (iv) Me_2CO, H_2SO_4, 99%; (v) $NaBH_4$, H_2O, 60%; (vi) Me_2CO, H_2SO_4, 39% from 3L; (vii) H^+, H_2O, 41% from 3L.

the exotherm and maintain the reaction temperature below 45 °C. TLC analysis (EtOAc:EtOH:H_2O, 45:5:1) after a further 30 min showed complete consumption of starting material (R_f 0.44) and clean conversion into aldehyde **11L** (R_f 0.67). The thick precipitate was removed by filtration and the filter cake washed with THF:water (10:1, 250 mL). The combined filtrates were concentrated in vacuo to give the aldehyde **11L** as a residue which was used for the following step without further purification. A suspension of the crude aldehyde **11L** in trifluoroacetic acid:water (9:1, 200 mL) was stirred at room temperature for 30 min; the reaction mixture was then warmed to 45 °C for 30 min by which time a clear solution formed. TLC analysis (EtOAc:EtOH:H_2O, 45:5:1) showed clean conversion into the deprotected lactone **12L** (R_f 0.51). Trifluoroacetic acid was evaporated under reduced pressure following co-evaporation with toluene (2 × 100 mL). Water (250 mL) and ethyl acetate (100 mL) were added to the oily residue; the aqueous layer was collected and the organic phase extracted with water (50 mL). The combined aqueous layers were then washed with ethyl acetate (50 mL) and concentrated to give a viscous oil, which crystallized on standing to afford L-glucuronolactone **12L** (59 g, 99% over two steps), mp 164–168 °C; $[\alpha]_D^{25}$ initial: −17.8; equilibrium: −21.5 (c, 1.05 in H_2O) [lit.[22] mp 165–167 °C; $[\alpha]_D^{22}$ −18 (c, 2.0 in H_2O); for enantiomer **12D** lit.[25] mp 168–170 °C; $[\alpha]_D^{25}$ +18.7 (c, 1.0 in H_2O)].

2.3. 1,2-*O*-Isopropylidene-α-L-glucurono-3,6-lactone 3L

A solution of concentrated sulfuric acid (50 mL, 0.96 mol) in acetone (1.5 L) was added to L-glucuronolactone **12L** (169 g, 0.960 mol) in a 3-L round-bottomed flask and the mixture stirred at 20 °C for 3 h. TLC analysis (petroleum-ether 40–60:acetone, 7:3) revealed the formation of a major product (R_f 0.28) and the reaction mixture was quenched by the addition of solid sodium bicarbonate (~900 g). The resulting precipitate was removed by filtration and the filter cake washed with acetone (500 mL). The combined organic filtrates were evaporated to give the acetonide **3L** (206 g, 99%), [mp 118–120 °C; $[\alpha]_D^{25}$ −56.9 (c, 1.09 in $CHCl_3$); lit.[22] mp 122–123 °C; $[\alpha]_D^{20}$ −68 (c, 1.2 in H_2O); for the enantiomer **3D** lit.[5a] mp 120.5–121.5 °C; $[\alpha]_D^{20}$ +52.5 (c, 1.95 in $CHCl_3$)].

2.4. 1,2-*O*-Isopropylidene-α-L-glucose 2L

A solution of sodium borohydride (13.2 g, 0.349 mol) in water (230 mL) was added over 5 min to a chilled (10 °C) solution of the lactone **3L** (116 g, 0.537 mol) in water (700 mL). The reaction mixture was stirred for 90 min at 10 °C and then quenched by the addition of acetic acid (20 mL, 0.348 mol). The reaction mixture was concentrated under reduced pressure and the water co-evaporated with methanol (3 × 500 mL) at 40 °C to give the crude monoacetonide **2L** (162 g) [R_f 0.49 (EtOAc:EtOH:H_2O, 45:5:1)] containing salts which was used for subsequent reactions without further purification. An aliquot of the crude product 2L (32.4 g, assumed 0.107 mol) was purified by column chromatography [0–2% water in acetone] to afford the pure monoacetonide **2L** (14.2 g, 60%), [mp 156–158 °C; $[\alpha]_D^{25}$ +11.4 (c, 1.07 in H_2O), lit.[26] mp 160–161 °C; $[\alpha]_D^{19}$ +11.4 (c, 1 in H_2O)].

2.5. 1,2;5,6-Di-*O*-isopropylidene-α-L-glucose 1L

A stirred suspension of crude monoacetonide **2L** (64.8 g, assumed 0.215 mmol) in acetone (500 mL) was adjusted to, pH 2, by addition of concentrated sulfuric acid and stirred for 2 h at room temperature after which time the reaction mixture was neutralized by the addition of triethylamine (10 mL) and the solution concentrated to dryness in vacuo. The residual syrup was dissolved in ethyl acetate (200 mL) and the resulting solution was washed successively with aqueous hydrochloric acid (1 N, 100 mL), water (100 mL), saturated aqueous sodium bicarbonate (200 mL) and water (100 mL). The organic layer was then dried (magnesium sulfate) and concentrated under reduced pressure. Crystallization of the residue from hot cyclohexane (60 mL) gave the pure diacetonide **1L** (22 g, 39% over two steps) [mp 108–110 °C; $[\alpha]_D^{25}$ +17.0 (c, 1.03 in H_2O). For the enantiomer **1D** lit.[27] mp 110–111 °C; $[\alpha]_D^{15}$ −18.4 (c, 1.2 in H_2O)].

2.6. L-Glucose 4L

Trifluoroacetic acid (25 mL) was added to a solution of the crude monoacetonide 2L (64.8 g, assumed 0.215 mol) in water (400 mL) and the reaction mixture stirred at 40 °C. TLC analysis (BuOH:EtOH:H_2O, 5:3:2) after 1 h showed the formation of a major product (R_f 0.51). The reaction mixture was concentrated to 75 mL and loaded onto an IR120 column (H^+ form, 500 g), eluting with water. The fractions containing L-glucose were combined and concentrated to 75 mL before being loaded onto a Dowex 1 × 4 column (HO^- form, 500 g), eluting with water, and the product fractions concentrated to yield L-glucose 1L (15.9 g, 41% over two steps) [mp 138–146 °C; $[\alpha]_D^{25}$ initial: −107.4; equilibrium: −53.0 (c, 1.05 in H_2O), lit.[28] mp 128–142 °C; $[\alpha]_D^{23}$ −52 (c, 0.8 in H_2O)].

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