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The synthesis of L-gulose and L-xylose from D-gluconolactone

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Abstract—L-Gulose, an essential component for the antibiotic and antitumor activities of bleomycin A_2, was synthesized in 47% yield from D-glucono-1,5-lactone. The effective cleavage of acetonides by $SnCl_2$ in the presence of *tert*-butyldimethylsilyl ethers was of importance in the course of synthesis. Elaboration of D-glucono-1,5-lactone that includes a step of oxidative degradation by Dess–Martin periodinane also afforded a respectable yield of L-xylose.

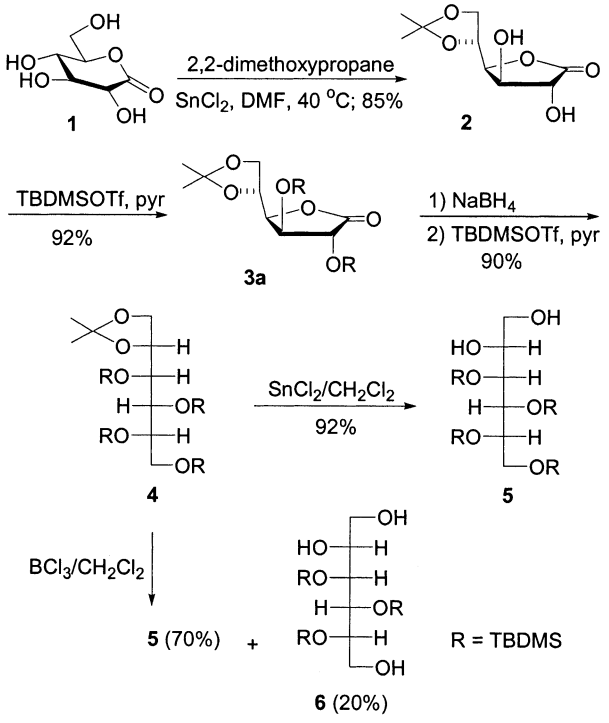
1. Introduction

The use of aldonolactones in the preparation of biologically interesting molecules, such as *C*-glycosides, carbasugars and azasugars, has been documented in several reports.[1] These studies mainly focus on the manipulation of lactone functionality.[2,3] In comparison with common sugars (e.g. glucose and galactose), sugar lactones are seldom used directly as the starting materials in organic syntheses, though many of them are commercially available at low cost. This consequence may be partly due to the low pK_a of their C-2 hydrogens that often cause problems of elimination under basic conditions. The preference for the formation of 1,4-lactones over 1,5-lactones may also limit their synthetic applications.[4] As a continuation of our study of sugar lactones, we demonstrate herein the synthesis of L-xylose and L-gulose (less available in nature) from a common precursor, D-gluconolactone. A Lewis acid $SnCl_2$ is found to be an especially effective promoter in the protection of diol functionalities, and in the deprotection of the acetonides.

2. Results and discussion

Chittenden has reported a two-step synthesis of acetonide **2** (less than 40% yield) from D-glucono-1,5-lactone (**1**) via the intermediacy of D-glucono-1,4-lactone.[5] We devised an improved procedure[6] for the direct formation of acetonide **2** as shown in Scheme 1. In the presence of $SnCl_2$, the sugar lactone **1** in DMF solution was treated with 2,2-dimethoxypropane at 40°C for 15 h. After DMF and excess 2,2-dimethoxypropane were removed, acetonide **2** was obtained in 85% yield by chromatography on a silica gel column. In order to ensure a high and reproducible yield, the acetalization should be conducted under anhydrous conditions, and prolonged chromatography should be avoided.

In case the moisture was not rigorously excluded, two diacetonide esters **7a** and **7b** (Fig. 1) were also obtained as the side products. When D-glucono-1,5-lactone was treated with acetone in the presence of iodine, diacetonide **7c** and triacetonide **7d** were obtained instead of the desired



Scheme 1.

Keywords: L-gulose; L-xylose; lactone; oxidation; tin(II) chloride.
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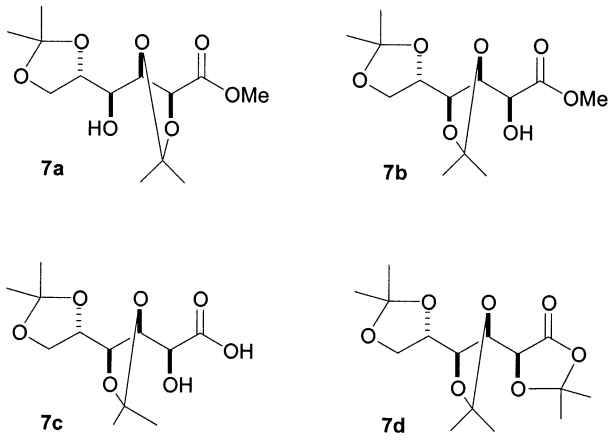


Figure 1.

acetonide **2**. The structures of **7a**–**d** were determined by comparison of their ^{1}H and ^{13}C NMR spectra with those reported in literature.[7] The structure of **7c** was confirmed by an X-ray diffraction analysis, as shown in Fig. 2.

Acetonide **2** was subjected to silylation with *tert*-butyldimethylsilyl (trifluoromethane)sulfonate (TBDMSOTf), giving lactone **3a** in 92% yield. Reduction of lactone **3a** with $NaBH_4$, followed by silylation, afforded compound **4** in 90% yield. Deprotection of the acetonide moiety was achieved in a chemoselective manner by using $SnCl_2$ as the promoter to give diol **5** in 92% yield. When BCl_3 was used to replace $SnCl_2$, the reaction gave diol **5** (70%) and a side product of triol **6** (20%) derived from a concurrent cleavage of the primary silyl ether.[6b] The beneficial effect of $SnCl_2$ was also applicable to the related reactions (Fig. 3). The acetonide moieties in compounds **3b** and **9** were removed without interference with the silyl and ester groups (OTBDMS and CO_2Me). A selective cleavage of the less hindered acetonide of 1,2:5,6-*O*-isopropylidene-α-D-glucofuranose (**11**) was also realized by treatment with $SnCl_2$ in CH_2Cl_2 solution.

At this stage, compound **5** played a pivotal role in the synthesis of L-xylose and L-gulose (Scheme 2). The vicinal diol underwent an oxidative degradation on treatment with Dess–Martin periodinane[8] to give aldehyde **13** in 73%

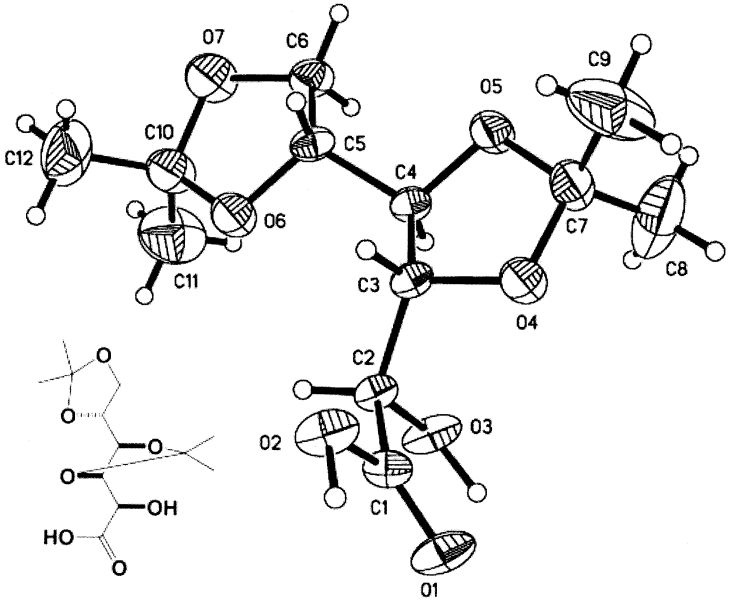


Figure 2.

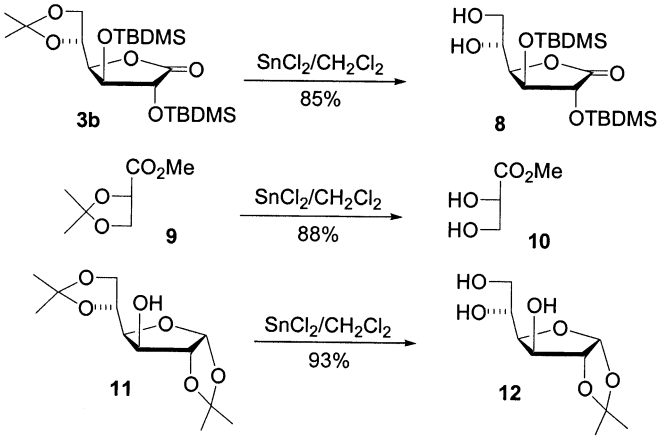
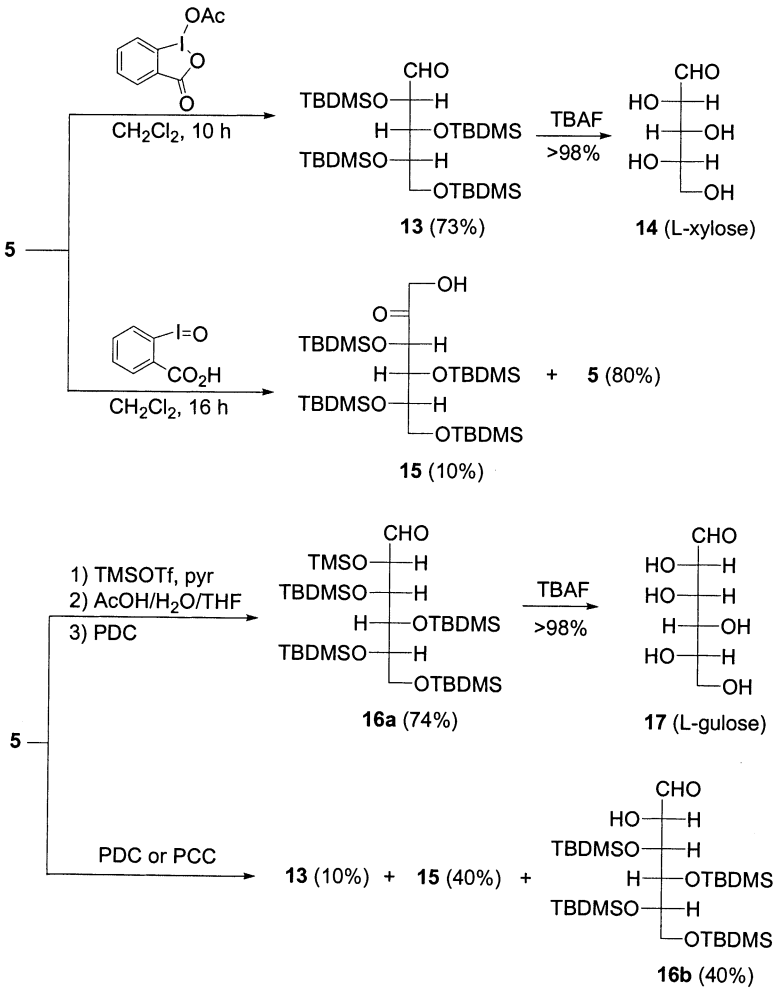


Figure 3.



Scheme 2.

yield. Removal of the TBDMS groups resulted in a levorotatory product **14**, $[\alpha]_D^{24}=-19.8°$ (*c* 5.0, H_2O), which was determined to be L-xylose by comparison of its ^1H NMR spectrum with that of D-xylose. The reactivity of *o*-iodosobenzoic acid (IBX)[9] toward diol **5** was rather low. When diol **5** was stirred with IBX at 22°C for 16 h, a 10% yield of hydroxy ketone **15** was obtained accompanied by an 80% recovery of the diol. The ketose **15** may serve as a precursor for the synthesis of L-ascorbic acid, providing that the CH_2OH group can be elaborated to CHO or COOH groups.[10] This investigation will be conducted in due course.

On the other hand, diol **5** was treated with trimethylsilyl (trifluoromethane)sulfonate (TMSOTf), followed by selective cleavage of the primary TMS ether under mild acidic conditions (AcOH/THF/H_2O=1/4/1 at 0°C for 1 h).[11] The subsequent oxidation with pyridinium dichromate (PDC) produced aldehyde **16a** in 74% overall yield. Deprotection of compound **16a** with tetrabutylammonium fluoride (TBAF) gave a quantitative yield of L-gulose having the optical rotation $[\alpha]_D=+21.0°$ (*c* 0.95, H_2O) in agreement with the literature value,[12] $[\alpha]_D=+21.3°$ (*c* 4.58, H_2O). The ^1H and ^{13}C NMR spectra of the synthetic sample were identical with those of authentic sample. When diol **5** was subjected to oxidation with PDC or pyridinium chlorochromate (PCC), compounds **13**, **15** and **16b** were obtained in 10, 40 and 40% yields, respectively.[13] Removal of the TBDMS groups in **16b** also led to L-gulose.

Thus, our present method has the advantage of the built-in absolute configurations of D-gluconolactone to provide an efficient synthesis of L-gulose by inversion of the two terminal groups (at C_1 and C_6).[14] The previous preparations[12,15] of L-gulose are less practical because these procedures often require creating new stereocenters by various reactions. In many cases, perfect stereoselectivity is hardly achieved.

3. Conclusion

In summary, pure L-xylose and L-gulose were prepared from D-gluconolactone in reasonable yields by relatively short sequences. The selective deprotection of acetonides, in the presence of esters and silyl ethers, was realized by using $SnCl_2$ as the promoter. This finding is significant because it is generally applicable to carbohydrate chemistry.

4. Experimental

4.1. General

Melting points are uncorrected. Optical rotations were measured on a digital polarimeter with a cuvette of 10 cm length. ^{1}H NMR spectra were recorded at 400 or 500 MHz with $CHCl_3$ (δ_H 7.24) or CD_3OD (δ_H 3.30 (central line of quintet)) as the internal standard; ^{13}C NMR spectra were recorded at 100 or 125 MHz with $CDCl_3$ (δ_C 77.0 (central line of triplet)) or CD_3OD (δ_C 49.0 (central line of septet)) as the internal standard. Mass spectra were recorded at an ionizing voltage of 70 or 20 eV. Column chromatography was performed on silica gel (70–230 mesh); gradients of EtOAc and hexanes as well as gradients of MeOH and $CHCl_3$ were used as eluents.

4.1.1. 5,6-*O*-Isopropylidene-D-glucono-1,4-lactone (2).[5] Finely powdered D-glucono-1,5-lactone (1.78 g, 10 mmol) was dissolved in an anhydrous DMF solution (10 mL) containing 2,2-dimethoxypropane (4.16 g, 4.91 mL, 40 mmol) and tin (II) chloride (300 mg, 1.6 mmol). The mixture was stirred at 40°C under Ar for 15 h. The solvent was then removed under reduced pressure and the residue was purified by chromatography on a silica gel column with hexanes/EtOAc (2/1) to give the desired product (1.85 g, 85% yield) as a white solid. IR (KBr, cm^{-1}) 3445 (broad, OH), 1756, 1369, 1212, 1067, 992, 847; ^{1}H NMR (400 MHz, CD_3OD) δ 1.34 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 3.94 (dd, 1H, J=8.7, 5.9 Hz, H-6a), 4.05 (d, 1H, J=2.7 Hz, H-2), 4.10 (dd, 1H, J=8.7, 6.5 Hz, H-6b), 4.23 (dd, 1H, J=4.4, 2.7 Hz, H-3), 4.43 (ddd, 1H, J=6.5, 6.1, 5.9 Hz, H-5), 4.62 (dd, 1H, J=6.1, 4.4 Hz, H-4), 4.85 (br s, 2H, OH×2); ^{13}C NMR (100 MHz, CD_3OD) δ 25.43, 26.80, 66.91, 73.87, 74.39, 75.25, 83.19, 110.36, 177.03. MS FAB m/z (rel. intensity): 219 ($M+H^+$, 100), 203 (78), 161 (24), 115 (29). HRMS (FAB) calcd for $C_9H_{15}O_6$ ($M+H^+$) 219.0869, found 219.0858.

4.1.2. 2,3-Di-*O*-*tert*-butyldimethylsilyl-5,6-*O*-isopropylidene-D-glucono-1,4-lactone (3a). To a stirred solution of compound **2** (360 mg, 1.3 mmol) in anhydrous DMF (5 mL) at room temperature (20°C) were added pyridine (2.7 mL, 36 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf, 785 mg, 0.68 mL, 2.6 mmol). The mixture was stirred at 20°C for 20 h, and then evaporated under reduced pressure. The resulting residue was purified by silica gel chromatography with hexanes/EtOAc (5/1) to give 662 mg of **3a** in 92% yield as a white solid. Mp 43–44°C; $[\alpha]_D^{18}$=+38.4° (c 5, $CHCl_3$); R_f=0.35 (EtOAc/hexanes=1/20); IR (KBr, cm^{-1}) 1800, 1472, 1372, 1257, 1124, 1073, 1051, 839, 782; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H, CH_3), 0.10 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.86 (s, 9H, $C(CH_3)_3$), 0.87 (s, 9H, $C(CH_3)_3$), 1.32 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 3.94 (d, 1H, J=1.4 Hz, H-2), 3.96 (dd, 1H, J=8.8, 5.5 Hz, H-6a), 4.11 (dd, 1H, J=8.8, 6.0 Hz, H-6b), 4.12 (dd, 1H, J=3.2, 1.4 Hz, H-3), 4.31 (ddd, 1H, J=8.2, 6.0, 5.5 Hz, H-5), 4.46 (dd, 1H, J=8.2, 3.2 Hz, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.16 (2×), −4.89, −4.81, 18.03, 18.05, 25.21, 25.54, 25.60, 26.76, 67.13, 71.67, 74.40, 75.28, 82.93, 109.44, 174.03; FAB-MS m/z (rel. intensity): 447 ($M+H^+$, 8), 431 (18), 389 (27), 331 (16), 74 (100); HRMS (FAB) calcd for $C_{21}H_{43}O_6Si_2$ ($M+H^+$) 447.2598, found 447.2605.

4.1.3. 1,2,3,4-Tetra-*O*-*tert*-butyldimethylsilyl-5,6-*O*-isopropylidene-D-glucitol (4). To a solution of compound **3a** (500 mg, 1.12 mmol) in THF/H_2O (10 mL, 9/1) was added sodium borohydride (200 mg, 5.2 mmol). After stirring at room temperature for 2 h, the reaction was quenched by addition of acetic acid (2 mL). The reaction mixture was stirred for an additional 30 min, and extracted with EtOAc (20 mL×3). The collected organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The resulting residue was purified by chromatography on a silica gel column with hexanes/EtOAc (5/1) to give the diol product (504 mg) in a quantitative yield. ESI-MS ($C_{21}H_{46}O_6Si_2$) m/z (rel. intensity) 451 ($M+H^+$, 100), 411 (31), 393 ([$M-57$]$^+$, 90).

To a solution of the above product (500 mg, 1.11 mmol) in anhydrous CH_2Cl_2 (15 mL) were added TBDMSOTf (722 mg, 0.7 mL, 6.6 mmol) and pyridine (1.86 g, 2.3 mL, 22.2 mmol) at room temperature (24°C). After stirring for 15 h, the mixture was quenched with water, and extracted with EtOAc (20 mL×3). The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue (750 mg) was purified by silica gel chromatography with hexanes/EtOAc (100/1) to give 680 mg of product **4** in 90% yield. R_f=0.75 (EA/hexanes=1/5); $[\alpha]_D^{20}$=+10° (c 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 6H, $SiCH_3$), 0.03 (s, 3H, $SiCH_3$), 0.06 (s, 3H, $SiCH_3$), 0.08 (s, 6H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.88 (s, 18H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.26 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 3.56 (dd, 1H, J=9.9, 6.5 Hz, H-6a), 3.73 (dd, 1H, J=9.9, 4.4 Hz, H-6b), 3.80 (dd, 1H, J=7.5, 7.2 Hz, H-1a), 3.82 (dd, 1H, J=6.6, 3.6 Hz, H-4), 3.85 (dt, 1H, J=6.6, 4.4 Hz, H-5), 3.99 (dd, 1H, J=7.5, 4.6 Hz, H-1b), 4.00 (dd, 1H, J=3.6, 5.0 Hz, H-3), 4.30 (ddd, 1H, J=7.2, 5.0, 4.6 Hz, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.28, −5.17, −4.44, −4.32, −3.89, −3.70, −3.28, −3.17, 18.19, 18.30, 18.40 (2×), 24.97, 26.02 (2×), 26.06, 26.14, 26.47, 64.20, 66.48, 72.68, 73.08, 74.90, 75.42, 107.83. $C_{33}H_{74}O_6Si_4$ ESI-MS m/z (rel. intensity): 679 ($M+H^+$, 10), 677 (28), 563 (40), 447 (100), 391 (54).

4.1.4. 1,2,3,4-Tetra-*O*-*tert*-butyldimethylsilyl-D-glucitol (5). Compound **4** (100 mg, 0.15 mmol) and tin(II) chloride (70 mg, 0.37 mmol) were mixed in anhydrous CH_2Cl_2 (5 mL) and stirred at room temperature for 0.5 h. The reaction progress was monitored by TLC with hexanes/EtOAc (5/1). The undissolved tin chloride was removed by filtration, and the filtrate was neutralized with saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4, and concentrated. The resulting residue was subjected to silica gel chromatography with hexanes/EtOAc (10/1) to give 88 mg of diol **5** in 92% yield as a white solid. R_f=0.7 (EtOAc/hexanes=1/4), mp 82–83°C; $[\alpha]_D^{20}$=+31.3° (c 1, $CHCl_3$); IR (KBr, cm^{-1}) 3508 (broad, OH), 1472, 1254, 1084, 836, 777; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.03 (s, 6H, $SiCH_3$), 0.06 (s, 3H, $SiCH_3$), 0.09 (s, 9H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.14 (s, 3H, $SiCH_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 2.08 (dd, 1H, J=4.9, 7.9 Hz, OH),

3.47–3.63 (m, 3H, H-6a, H-6b, H-4), 3.66 (ddd, 1H, J=11.0, 4.9, 3.0 Hz, H-5), 3.76 (dd, 1H, J=9.2, 4.5 Hz, H-1a), 3.91 (dt, 1H, J=9.2, 4.5 Hz, H-2), 3.95 (s, 1H, OH), 4.00 (d, 1H, J=4.5 Hz, H-1b), 4.05 (t, 1H, J=7.5 Hz, H-3); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.25, −5.25, −5.20, −5.09, −4.21, −3.91, −3.63, −3.63, 17.82, 18.06, 18.20, 18.47, 25.74, 25.85, 25.89, 26.08, 62.79, 63.57, 69.36, 70.14, 73.09, 73.70; ESI-MS m/z (rel. intensity): 639 ($M+H^+$, 100), 507 (7); HRMS (FAB) calcd for $C_{30}H_{71}O_6Si_4$ ($M+H^+$) 639.4328, found 639.4329.

4.1.5. 2,3,4-Tri-*O*-*tert*-butyldimethylsilyl-D-glucitol (6). Boron trichloride (0.1 mL of 1 M solution in CH_2Cl_2) was added to a CH_2Cl_2 solution (5 mL) of compound **4** (100 mg, 0.15 mmol) at −78°C. The reaction progress was monitored by TLC with hexanes/EtOAc (5/1). The reaction was stirred at −78°C for 5 min, after which the reaction mixture was neutralized with saturated $NaHCO_3$ solution. The resulting mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, and concentrated. The residue was subjected to silica gel chromatography with hexanes/EtOAc (5/1) to give 67 mg of diol **5** in 70% yield and 17 mg of triol **6** in 20% yield. Compound **6**: R_f=0.45 (EtOAc/hexanes=1/4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$), 0.09 (s, 9H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.11 (s, 3H, $SiCH_3$), 0.12 (s, 3H, $SiCH_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 2.29 (br s, 1H, OH), 3.03 (br s, 1H, OH), 3.47 (br s, 1H, OH), 3.56 (dd, 1H, J=10.2, 4.7 Hz, H-1a), 3.63 (dd, 1H, J=11.2, 5.5 Hz, H-6a), 3.65 (dd, 1H, J=11.2, 3.7 Hz, H-1b), 3.70 (dd, 1H, J=8.7, 5.6 Hz, H-3), 3.76 (dd, 1H, J=10.2, 5.6 Hz, H-1b), 3.80 (m, 1H, H-5), 3.88 (t, 1H, J=5.6 Hz, H-4), 3.93 (ddd, 1H, J=8.7, 5.6, 4.7 Hz, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.52, −5.43, −4.68, −4.62, −4.26, −3.98, 18.12, 18.18, 18.30, 25.85, 25.91, 25.93, 63.60, 65.39, 71.79, 72.83, 73.04, 73.82; ESI-MS m/z (rel. intensity): 525.2 ($M+H^+$, 100), 393.2 (5); HRMS (FAB) calcd for $C_{24}H_{57}O_6Si_3$ ($M+H^+$) 525.3463, found 525.3485.

4.1.6. Methyl 2,3:5,6-di-*O*-isopropylidene-D-gluconate (7a)[16] and methyl 3,4:5,6-di-*O*-isopropylidene-D-gluconate (7b).[17] As previously mentioned in the main text, compounds **7a** and **7b** were obtained as the side products in the reaction of D-glucono-1,5-lactone with 2,2-dimethoxypropane and tin(II) chloride. Compound **7a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.15 (d, J=9.4 Hz, 1H, OH), 3.63 (ddd, J=9.4, 8.5, 1.9 Hz, 1H, H-4), 3.76 (s, 3H, OMe), 4.03–3.98 (m, 1H, H-5), 4.10–4.05 (m, 2H, H-6), 4.39 (dd, J=1.9, 7.7 Hz, 1H, H-3), 4.53 (d, J=7.7 Hz, 1H, H-2). Compound **7b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 2.99 (d, J=9.1 Hz, 1H, OH), 3.81 (s, 3H, OMe), 3.96 (dd, J=3.9, 8.2 Hz, 1H, H-6), 4.03 (d, 1H, J=7.5 Hz, 1H, H-2), 4.06 (ddd, J=3.9, 5.6, 9.0 Hz, 1H, H-5), 4.12 (dd, J=5.6, 8.2 Hz, 1H, H-6), 4.19 (dd, J=1.5, 7.5 Hz, 1H, H-3), 4.31 (dd, J=1.5, 9.0 Hz, 1H, H-4); ^{13}C NMR (100 MHz, $CHCl_3$) δ 25.25, 26.51, 26.65, 27.14, 52.64, 67.87, 69.44, 76.48, 77.27, 80.89, 109.85, 110.06, 172.97.

4.1.7. 3,4:5,6-Di-*O*-isopropylidene-D-glucuronic acid (7c) and 1,2:3,4:5,6-tri-*O*-isopropylidene-D-gluconate (7d).[18] Finely powdered D-glucono-1,5-lactone (1.78 g, 10.0 mmol) was dissolved in an acetone solution (50 mL) containing I_2 (507.6 mg, 2.0 mmol). The reaction was stirred at 45°C for 24 h. The solvent was removed under reduced pressure to give a residue, which was chromatographed by a silica gel column with EtOAc/hexanes (1/1) to give a mixture of compounds **7c** and **7d**. Compound **7c** was crystallized, and its structure was confirmed by an X-ray diffraction analysis. The mother liquor was further subjected to chromatography on a silica gel column (EtOAc/hexanes=1/3) to afford pure compounds **7c** and **7d**. Compound **7c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 3.98 (dd, J=3.7, 8.0 Hz, 1H, H-6), 4.01 (dd, J=7.9, 8.0 Hz, 1H, H-4), 4.09 (ddd, J=2.1, 3.7, 8.0 Hz, 1H, H-5), 4.13 (dd, J=2.1, 8.0 Hz, 1H, H-6), 4.29 (dd, J=1.4, 7.9 Hz, 1H, H-3), 4.40 (d, J=1.4 Hz, 1H, H-2). Crystallographic data of **7c** have been deposited with the Cambridge Crystallographic Data Center as the deposition number CCDC 173783. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Compound **7d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 3.92 (t, J=8.4 Hz, 1H, H-4), 3.96 (dd, J=3.9, 8.2 Hz, 1H, H-6), 4.07 (ddd, J=3.9, 6.0, 8.4 Hz, 1H, H-5), 4.12 (dd, J=6.0, 8.2 Hz, 1H, H-6), 4.25 (dd, J=1.5, 8.4 Hz, 1H, H-3), 4.60 (d, J=1.5 Hz, 1H, H-2).

4.1.8. 2,3-Di-*O*-*tert*-butyldimethylsilyl-D-glucono-1,4-lactone (8),[19] methyl L-glycerate (10),[20] and 1,2-*O*-isopropylidene-α-D-glucofuranose (12).[21] Compound **3b** (35.2 mg, 0.079 mmol) and tin(II) chloride (70 mg, 0.37 mmol) were mixed in anhydrous CH_2Cl_2 (2 mL), and stirred at room temperature. The reaction progress was monitored by TLC with $CHCl_3$/MeOH (5/1). After 48 h, the mixture was evaporated and purified by silica gel chromatography with $CHCl_3$/MeOH (5/1) to give 27.3 mg of diol **8** in 85% yield as a white solid. R_f=0.6 ($CHCl_3$/MeOH=5/1); $[\alpha]_D^{25}$=+34.0° (c 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.15 (s, 6H, $SiCH_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 2.59 (d, J=5.4 Hz, 1H, OH), 3.76 (dd, J=4.9, 11.3 Hz, 1H, H-6), 3.87 (dd, J=2.4, 11.3 Hz, 1H, H-6), 3.99 (m, 1H, H-5), 4.09 (d, J=2.9 Hz, 1H, H-2), 4.30 (dd, J=2.9, 4.0 Hz, 1H, H-3), 4.50 (dd, J=4.0, 8.9 Hz, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.03, −5.01, −4.72, −4.65, 17.96, 18.08, 25.59, 25.61, 63.71, 68.63, 74.70, 74.94, 79.88, 173.69. HRMS (FAB) calcd for $C_{18}H_{39}O_6Si_2$ ($M+H^+$) 407.2285, found 407.2282. By similar procedures, deprotection of compounds **9** and **11** gave compounds **10** and **12** in 88 and 93% yields, respectively. Compound **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (bs, 1H), 3.96–3.77 (m, 2H), 3.76 (s, 3H, –OMe), 3.34 (bs, 1H, –OH), 2.63 (bs, 1H, –OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.64, 64.01, 71.79, 173.41; ^{13}C NMR (100 MHz, CD_3OD) δ 51.29, 63.72, 71.99, 173.29. FAB-MS calcd for $C_4H_9O_4$ ($M+H^+$) 121.0, found 121.1. Compound **12**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.21 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 3.34 (m, 1H, H-6), 3.55 (ddd, J=3.0, 5.4, 11.2 Hz, 1H, H-6), 3.68 (m, 1H, H-5), 3.82 (dd, J=2.4, 8.5 Hz, 1H, H-4), 4.02 (bs, 1H, H-3), 4.36 (d, J=3.6 Hz, 1H, H-2), 4.48 (m,

1H, OH), 4.66 (d, J=5.9 Hz, 1H, OH), 5.16 (d, J=4.6 Hz, 1H, OH), 5.78 (d, J=3.6 Hz, 1H, H-1); ^{1}H NMR (400 MHz, CD_3OD) δ 1.33 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.63 (dd, J=6.0, 11.5 Hz, 1H, H-6), 3.79 (dd, J=3.1, 11.5 Hz, 1H, H-6), 3.93 (ddd, J=3.1, 6.0, 8.3 Hz 1H, H-5), 4.05 (dd, J=2.6, 8.3 Hz, 1H, H-4), 4.24 (d, J=2.6 Hz, 1H, H-3), 4.51 (d, J=3.6 Hz, 1H, H-2) 5.90 (d, J=3.6 Hz, 1H, H-1); ^{13}C NMR (100 MHz, DMSO-d_6) δ 26.22, 26.77, 63.82, 68.57, 73.43, 80.19, 84.79, 104.57, 110.59.

4.1.9. 2,3,4,5-Tetra-*O*-*tert*-butyldimethylsilyl-L-xylose (13). Diol **5** (186 mg, 0.30 mmol) dissolved in anhydrous CH_2Cl_2 (20 mL) was mixed with Dess–Martin periodinane (247 mg, 0.58 mmol) at room temperature. The reaction mixture was stirred for 10 h. The TLC analysis (EtOAc/hexanes=1/5) showed a new spot. The reaction was quenched with saturated $NaHCO_3$ (2 mL) to give a clear solution. After stirring for 5 min, the mixture was extracted with CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The collected organic layers were evaporated under reduced pressure to give 310 mg of crude product. Further purification on a silica gel column with EtOAc/hexanes (1/40) afforded 136 mg of the desired aldehyde **13** in 73% yield. The compound can also be obtained as a minor product from the PCC or PDC oxidation. R_f=0.7 (EtOAc/hexanes=1/5); $[\alpha]_D^{20}$=+23.8° (c 0.8, $CHCl_3$); IR (KBr, cm^{-1}) 1738, 1730, 1471, 1361, 1255, 1148, 1091, 1005, 836, 777; ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.02 (s, 6H, $SiCH_3$), −0.01 (s, 3H, $SiCH_3$), 0.02 (s, 3H, $SiCH_3$), 0.03 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.08 (s, 3H, $SiCH_3$), 0.83 (s, 9H, $C(CH_3)_3$), 0.86 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 3.52 (dd, 1H, J=9.9, 5.6 Hz, H-5a), 3.67 (dd, 1H, J=9.9, 7.3 Hz, H-5b), 3.83 (ddd, 1H, J=7.3, 5.6, 2.6 Hz, H-4), 3.99 (d, 1H, J=5.4 Hz, H-2), 4.06 (dd, 1H, J=5.4, 2.6 Hz, H-3), 9.77 (s, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.34, −5.30, −5.22, −4.84, −4.62, −4.60, −3.88 (2×), 18.02 (2×), 18.18, 18.34, 25.74 (2×), 25.92 (2×), 62.59, 72.38, 73.89, 77.42, 202.24; ESI-MS m/z (rel. intensity) 635 ($M+H^+$, 4), 432 (100); HRMS (FAB) calcd for $C_{30}H_{67}O_6Si_4$ ($M+H^+$) 635.4006, found 635.4015.

4.1.10. L-Xylose (14). A solution of compound **13** (63 mg, 0.1 mmol) in THF (5 mL) was treated with 0.5 mL (0.5 mmol) of tetrabutylammonium fluoride (1.0 M in THF), and stirred at 0°C for 2 h. The mixture was concentrated, and purified by silica gel chromatography ($CHCl_3$/MeOH=5/1) to give 15 mg of compound **14** (>98% yield). $[\alpha]_D^{24}$=−19.8° (c 5.0, H_2O). Compound **14** exhibited the ^{1}H and ^{13}C NMR spectra compatible to that of D-xylose.[22]

4.1.11. 3,4,5,6-Tetra-*O*-*tert*-butyldimethylsilyl-L-xylo-hexulose (15) and 3,4,5,6-tetra-*O*-*tert*-butyldimethylsilyl-L-gulose (16b). A mixture of diol **5** (63 mg, 0.1 mmol), pyridinium dichromate (119 mg, 0.3 mmol) and Celite (200 mg) in anhydrous CH_2Cl_2 (10 mL) was stirred at 25°C for 20 h. The reaction mixture was filtered through Pyrex 3G3 filter, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel chromatography (EtOAc/hexanes=1/40) to afford aldopentose **13** (6 mg, 10%), ketohexose **15** (26 mg, 40%) and aldohexose **16b** (25 mg, 40%). Products **15** and **16b** were also obtained by Jones' oxidation of diol **5**. Compound **15**: R_f=0.6 (EtOAc/hexanes=1/10). IR (KBr, cm^{-1}) 3508 (broad –OH), 1720, 1473, 1257, 1088, 837, 778; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.03 (s, 3H, $SiCH_3$), −0.02 (s, 3H, $SiCH_3$), 0.01 (s, 6H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$), 0.06 (s, 3H, $SiCH_3$), 0.08 (s, 3H, $SiCH_3$), 0.86 (s, 9H, $C(CH_3)_3$), 0.87 (s, 9H, $C(CH_3)_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.94 (s, 9H, $C(CH_3)_3$), 3.03 (t, 1H, J=4.8 Hz, OH), 3.58 (dd, 1H, J=9.2, 3.7 Hz, H-6a), 3.83 (dd, 1H, J=9.2, 3.9 Hz, H-6b), 3.84 (ddd, 1H, J=4.3, 3.9, 3.7 Hz, H-5), 3.90 (dd, 1H, J=4.3, 3.1 Hz, H-4), 4.30 (dd, 1H, J=19.7, 4.8 Hz, H-1a), 4.42 (d, 1H, J=3.1 Hz, H-3), 4.55 (dd, 1H, J=19.7, 4.8 Hz, H-1b); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.40, −5.18, −4.84 (2×), −4.78, −4.70, −4.67, −4.39, 17.98, 18.02, 18.16 (2×), 25.83, 25.94, 25.96, 26.01, 63.78, 67.91, 75.39, 75.64, 76.81, 212.01; ESI-MS m/z (rel. intensity) 659.6 ($M+Na^+$, 100), 637.4 ($M+H^+$, 20), 505.4 (25), 373.3 (45). Compound **16b**: R_f=0.7 (EtOAc/hexanes=1/10); IR (KBr, cm^{-1}) 3453 (broad, OH), 1739.5, 1472, 1255, 1094, 836, 776; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 6H, $SiCH_3$), 0.06 (s, 6H, $SiCH_3$), 0.09 (s, 6H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.86 (s, 9H, $C(CH_3)_3$), 0.87 (s, 18H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 3.56 (dd, 1H, J=9.9, 6.6 Hz, H-6a), 3.73 (dd, 1H, J=9.9, 4.7 Hz, H-6b), 3.80 (dd, 1H, J=6.6, 5.8 Hz, H-3), 3.84 (ddd, 1H, J=9.2, 6.6, 4.7 Hz, H-5), 3.99 (dd, 1H, J=9.2, 6.6 Hz, H-4), 4.30 (dd, 1H, J=7.2, 5.8 Hz, H-2), 9.77 (s, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.28, −5.17, −4.44, −4.32, −3.89, −3.69, −3.29, −3.17, 18.00, 18.13, 18.27, 18.40, 26.02 (2×), 26.06, 26.13, 64.19, 66.47, 72.68, 73.08, 75.42, 202.25. ESI-MS m/z (rel. intensity): 637 ($M+H^+$, 100), 619 (20), 565 (40), 507 (55), 415 (45), 373 (40).

4.1.12. Jones' oxidation of diol 5. Jones' reagent was freshly prepared by dissolving CrO_3 (1.33 g) in H_2SO_4/H_2O (1.5 mL/5 mL). An excess of Jones reagent (0.035 mL) was added dropwise to a solution of diol **5** (25 mg, 0.039 mmol) in acetone (1 mL) at 0°C until the orange color of Jones' reagent persisted. The reaction mixture was stirred at 0°C for 0.5 h. Water (2 mL) was added, and the reaction mixture was extracted with CH_2Cl_2, washed with brine, and dried over anhydrous Na_2SO_4. The combined organic layers were evaporated under reduced pressure to give 23 mg of crude product. Further purification on a silica gel column with EtOAc/hexanes (1/40) afforded the desired aldehyde **16b** (7.5 mg, 30% yield) and ketohexose **15** (13 mg, 50% yield).

4.1.13. 3,4,5,6-Tetra-*O*-*tert*-butyldimethylsilyl-2-*O*-trimethylsilyl-L-gulose (16a). Diol **5** (64 mg, 0.1 mmol) was treated with TMSOTf (89 mg, 72 μL, 0.4 mmol) and pyridine (158 mg, 162 μL, 2.0 mmol) at 25°C for 15 h to give the corresponding bis(trimethylsilyl) ether. After purification, 78 mg of di-TMS derivative was obtained in 99% yield. The primary TMS ether was selectively cleaved by treatment with AcOH/H_2O/THF (1 mL/1 mL/4 mL) at 0°C for 1 h. The mixture was purified to give 44 mg of the deprotected product (78% yield). The resulting primary alcohol (35.5 mg, 0.05 mmol) was stirred with a mixture of pyridinium dichromate (37.6 mg, 0.1 mmol) and Celite (37.6 mg) in anhydrous CH_2Cl_2 (3 mL) at 25°C for 20 h. The solids were removed by filtration (Pyrex 3G3), and the filtrate was concentrated. The residue was purified by silica gel chromatography with hexanes/EtOAc (20/1) to

give **16a** (33 mg, 95% yield) as a colorless syrup. The overall yield was 74% starting from diol **5**. R_f=0.55 (EtOAc/hexanes=1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.02 (s, 3H, $SiCH_3$), 0.03 (s, 3H, $SiCH_3$), 0.03 (s, 3H, $SiCH_3$), 0.04 (s, 3H, $SiCH_3$), 0.06 (s, 3H, $SiCH_3$), 0.07 (s, 3H, $SiCH_3$), 0.08 (s, 3H, $SiCH_3$), 0.09 (s, 9H, $SiCH_3$), 0.10 (s, 3H, $SiCH_3$), 0.84 (s, 9H, $C(CH_3)_3$), 0.85 (s, 9H, $C(CH_3)_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$), 3.56 (dd, 1H, J=9.8, 6.8 Hz, H-6a), 3.78 (dd, 1H, J=9.8, 4.8 Hz, H-6b), 3.80–3.94 (m, 2H, H-3, H-4), 3.98 (ddd, 1H, J=6.8, 4.8, 2.2 Hz, H-5), 4.65 (s, 1H, H-2), 9.68 (s, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.41, −5.30, −4.54, −4.13 (2×), −4.03, −3.91, −3.46, 0.28, 18.18, 18.32 (3×), 25.98, 26.02, 26.09, 26.16, 63.98, 73.14, 75.36, 78.35, 78.43, 202.52; ESI-MS *m/z* (rel. intensity) 851 ($M+H^+$, 5), 637 (7), 531 (70), 494 (90).

4.1.14. L-Gulose (17).[15a,h] A solution of **16a** (71 mg, 0.1 mmol) in THF (5 mL) was treated with 0.6 mL (0.6 mmol) of tetrabutylammonium fluoride (1.0 M in THF) at 0°C for 2 h, by the procedure similar to that for L-xylose, to give L-gulose in >98% yield. The TBDMS groups of **16b** were also removed by a similar procedure to give L-gulose. Colorless amorphous solid. $[\alpha]_D^{23}$= +21.0° (*c* 0.9, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 3.65 (dt, 1H, J=8.3, 2.5 Hz, H-5), 3.74–3.79 (m, 2H, H-6a, H-6b), 3.83 (m, 1H, H-3), 4.02 (dd, 1H, J=6.0, 2.5 Hz, H-4), 4.09 (dd, 1H, J=6.0, 2.5 Hz, H-2), 4.90 (dd, 1H, J=8.4, 2.5 Hz, H-1); ^{13}C NMR (100 MHz, D_2O) δ 60.56, 68.64, 68.98, 70.72, 73.37, 93.39; HRMS (FAB) calcd for $C_6H_{13}O_6$ 181.0712, found 181.0746.

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