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New and Efficient Synthesis of 6-Deoxy-L-gulose[1]

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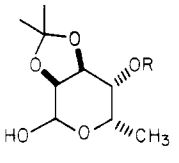
An efficient synthetic procedure for the transformation of D-glucurono-γ-lactone to 6-deoxy-L-gulose (**20**) in five steps and 52% yield is described. The scheme relies on the selective blocking of the 2- (silyl ether) and 3,5- (isopropylidene) hydroxyl groups and then diisobutylaluminum hydride reduction of the lactone carbonyl. An alternate route that relies on the more standard sodium amalgam reduction of the lactone triol was found to be technically inefficient and to result in a poor overall yield.

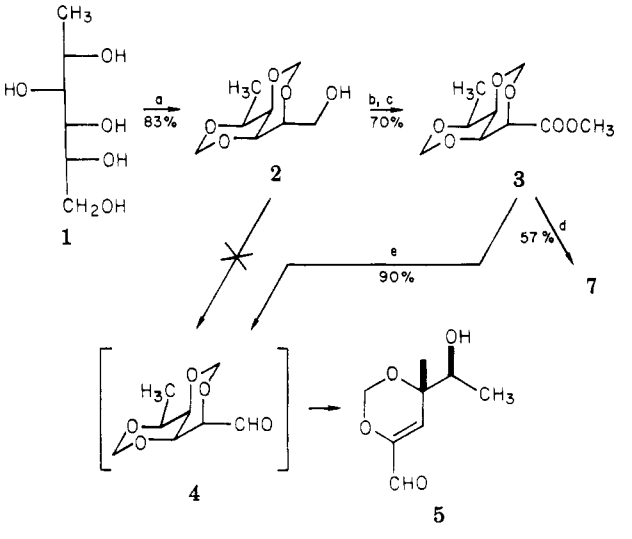
In connection with an ongoing project in this laboratory, a synthetic approach to 4-*O*-alkyl-6-deoxy-2,3-*O*-(1-methylethylidene)-L-gulopyranose derivatives (I) was required. The first preparation of 6-deoxy-L-gulose was accomplished by Müller and Reichstein and began with L-xylose.[2] The stereochemical correspondence between 6-deoxy-L-gulose and D-glucose (Figure 1) suggested that the abundant and inexpensive D-glucose could serve as a practical starting material for the preparation of derivatives related to I. The following experiments were undertaken to evaluate this possibility.



I

The first approach (Scheme I) began with 1-deoxy-D-glucitol (1)[2] which was prepared in 51% yield from D-glucose via reductive desulfurization[3] of the diethyl thioketal.[4] Treatment of this deoxyhexitol with aqueous formaldehyde and hydrogen chloride afforded the primary alcohol **2**[5] in 83% yield, based on unrecovered starting material. The initial plan entailed conversion of this alcohol to aldehyde **4** and removal of the methylene protecting groups to provide the desired 6-deoxy-L-gulose. However, several attempts at partial oxidation, including Collin's reagent,[6] pyridinium chlorochromate,[7] and several variations of the Pfitzner–Moffatt process,[8] failed to provide any of the desired aldehyde. Successful oxidation of alcohol **2** was effected, however, with chromium trioxide in acetic acid, and methylation of the product with diazomethane provided ester **3** in 70% overall yield. Deprotection of this ester with excess boron trichloride afforded the known[2] compound 6-deoxy-L-gulonolactone **7**. Reduction of ester **3** with diisobutylaluminum hydride

Scheme I[a]



[a] a, HCHO-H_2O, HCl; b, CrO_3-AcOH; c, CH_2N_2, Et_2O; d, BCl_3, CH_2Cl_2; e, DIBAL, OH^-.

† Contribution No. 6072.

(1) Grateful acknowledgment is made for the support of this investigation through Public Health Service Research Grant No. HL 21367 from the National Heart and Lung Institute and the Hoffman-LaRoche Foundation.

(2) Müller, H.; Reichstein, K. *Helv. Chim. Acta* **1938**, *21*, 251–62.
(3) Wolfrom, M. L.; Karabinos, J. V. *J. Am. Chem. Soc.* **1944**, *66*, 909–11.
(4) Fischer, E. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 673–9.
(5) Wolfrom, M. L.; Lew, B. W.; Goepp, Jr., R. M. *J. Am. Chem. Soc.* **1946**, *68*, 1443–8.
(6) Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, *30*, 3363–6.
(7) Corey, E. J.; suggs, J. W. *Tetrahedron Lett.* **1975**, *31*, 2647–50.
(8) Pfitzner, K. E.; Moffatt, J. G. *J. Am. Chem. Soc.* **1963**, *85*, 3027–8.

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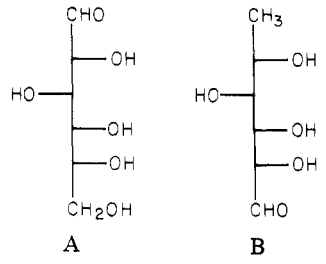
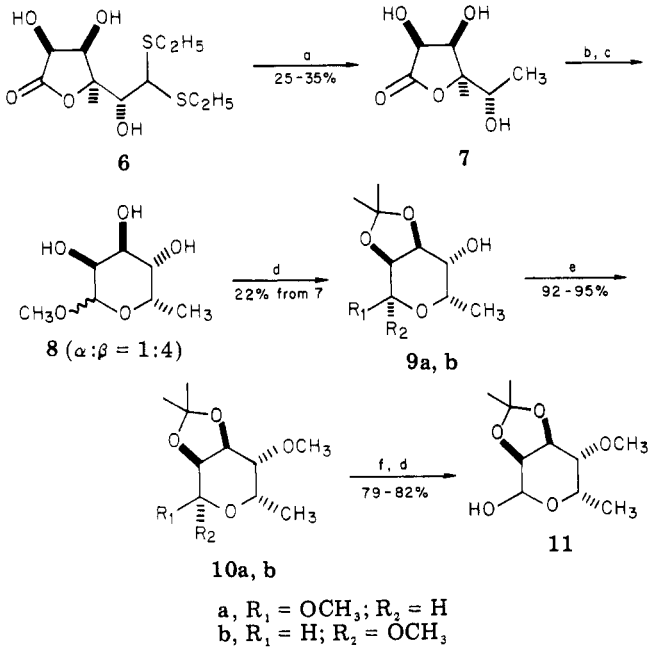


Figure 1. Fischer-type formulas illustrating the relationship between D-glucose (A) and 6-deoxy-L-gulose (B).

Scheme II[a]

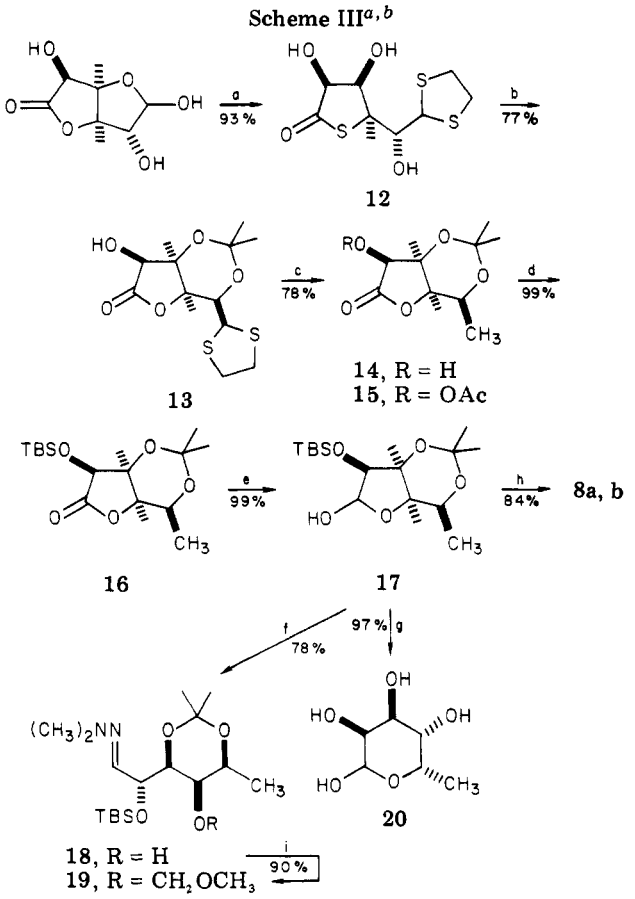


[a] a, Ni(R), 80% Et_2O-H_2O; b, Na(Hg), H_3O^+; c, CH_3OH, H^+; d, $CH_3C(OCH_3)_2CH_3$, H^+, acetone; e, KH, MeI, THF; f, H_3O^+.

(DIBAL), followed by hydrolysis of the excess hydride and intermediate aluminates with anhydrous methanol, gave a 3:1 mixture of aldehyde **4** and enone **5**. The proportion of unsaturated aldehyde **5** (as determined by NMR) steadily increased following dissolution of a portion of this mixture in deuteriochloroform. By treatment of ester **3** with DIBAL and hydrolysis of the reaction mixture with aqueous sodium hydroxide, enone **5** was prepared in 90% yield. The instability of aldehyde **4** precluded the isolation of this key intermediate and caused the abandonment of this approach to 6-deoxy-L-gulose.

An alternate approach to the desired pyranoid derivatives (Scheme II) began with the thioacetal **6**,[9] derived from D-glucurono-γ-lactone. Desulfurization of this thioacetal with Raney nickel catalyst afforded 6-deoxy-L-gulonolactone **7** in 25–35% yield, based on D-glucuronolactone. Reduction of lactone **7** with sodium amalgam and treatment of the crude product with methanol and hydrogen chloride gave a mixture (α:β = 1:4)[10] of the isomeric methyl gulopyranosides **8**. Treatment of this mixture with 2,2-dimethoxypropane and a trace of acid in acetone afforded the isopropylidene derivatives **9a** and **9b**. These isomers were separated by chromatography on silica gel and were isolated in 22% overall yield from lactone **7**. Methylation of these anomeric alcohols produced the gulopyranosides **10a** and **10b**. The lactol **11** was prepared in 79–82% yield from either **10a** or **10b** by hydrolysis with aqueous acid and treatment of the hydrolysate with dimethoxypropane and a trace of acid in acetone. The overall yield of this lactol from D-glucurono-γ-lactone is between 4% and 6%.

Scheme III[a,b]



[a] a, $(CH_2SH)_2$, H_3O^+; b, $CH_3C(OCH_3)_2CH_3$, acetone, H^+; c, Ni(R), EtOH-THF; d, t-$C_4H_9(CH_3)_2SiCl$, DMF; e, DIBAL, THF; f, $CCl_4/P(NMe_2)_3$, $(CH_3)_2NNH_2$, THF; g, H_3O^+, 60 °C; h, H^+, CH_3OH, 60 °C; i, LDA, $ClCH_2OCH_3$. [b] TBS = t-Bu$(CH_3)_2$Si.

While providing the first samples of a derivative of the desired type, the scheme outlined above suffered from several technical deficiencies. Specifically, the amorphous nature of thioacetal **6** prevented convenient large-scale purification of this starting material. Also, the polarity of the triols **6** and **7** required the use of large volumes of polar solvent during the desulfurization and, by adsorbance of these polar molecules onto the catalyst, adversely affected the material balance in this reaction. Furthermore, the reduction of aldono lactones with sodium amalgam requires careful control of pH and temperature and is further complicated by the difficulties encountered in separating water-soluble products from aqueous solutions of inorganic salts.

To overcome these problems, a third approach (Scheme III) was developed. The acid-catalyzed reaction of ethanedithiol with D-glucurono-γ-lactone provided the crystalline thioacetal **12** in 93% yield. This acetal is a more tractable intermediate than is its amorphous analogue **6**. The acetal **12** afforded ketal **13** in 77% yield by treatment

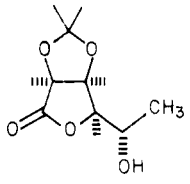
(9) Zinner, H.; Dässler, C.-G.; Rembarz, G. *Chem. Ber.* **1958**, *91*, 427–30.

(10) The anomeric configuration of these products is based upon the known preference for formation of the β-anomer and can be verified by comparison of the optical properties of alcohols **9a** and **9b** with the known rotation for the enantiomorph of **9a**, methyl 6-deoxy-2,3-*O*-(1-methylethylidene)-α-D-gulopyranoside.[11]

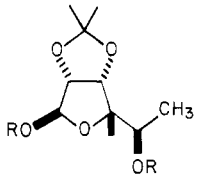
(11) Capek, K.; Tikal, I.; Jary, J.; Masojikova, M. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1973–85.

with acetone, dimethoxypropane, and sulfuric acid. Desulfurization of ketal **13** with Raney nickel catalyst generated, in 78% yield, the deoxy lactone **14**, which was silylated in 99% yield to provide silyl ether **16**. Reduction of lactone **16** with DIBAL afforded lactol **17** in 99% yield.

In principle, ketalization of triol **12** could have generated the 2,3-*O*-isopropylidene isomer which would provide, after desulfurization with Raney nickel, the isomeric hydroxy lactone i. That lactone **14** is indeed the 3,5-*O*-isopropylidene isomer could be shown by acetylation of the free hydroxyl group. The ^1H NMR spectrum of the resulting acetate **15** was found to be similar to that of the hydroxy lactone **14**, except that a doublet (1 H, J = 4 Hz) had shifted downfield 1.1 ppm. This is consistent with acetylation of the hydroxy group in the proposed structure for lactone **14** and inconsistent with the results expected in the event the alternative product, i, had been obtained. The quartet attributed to H-5 in lactone **14** (δ 4.10) moved downfield only 0.07 ppm upon acetylation of the hydroxyl group. This may be compared to the results reported for the hydroxy lactol ii, where acetylation to generate iii results in a 1.1 ppm downfield change in the H-5 quartet resonance.[11]



i



ii, R = H
iii, R = OAc

Several products of value to our investigations may be obtained from lactol **17**. Treatment of lactol **17** with methanolic hydrogen chloride provided, in 80% yield, the mixture of methyl gulopyranosides (**8a,b**) described in Scheme II. The overall yield of these glycosides from 6-deoxy-D-glucurono-γ-lactone is 44%—a significant improvement over the 6–8% yield obtained in Scheme II. Alternatively, treatment of lactol **17** with tris(dimethylamino)phosphine and carbon tetrachloride, followed by dimethylhydrazine, provided hydrazone **18** in 78% yield. This product is of interest because it offers a method for introducing specific protecting groups on the C-4 hydroxyl group, as illustrated by the preparation of the 4-*O*-methoxymethyl ether, **19**.

Finally, aqueous acidic hydrolysis of lactol **17** provided 6-deoxy-L-gulose (**20**) as an amorphous solid, $[\alpha]^{22}_D$ +40.3° (*c* 1.60, H_2O) [lit.[2] $[\alpha]^{21}_D$ +40.8° (*c* 1.615, H_2O)], which was further identified by conversion to the *p*-bromophenylhydrazone, mp 135–136 °C (lit.[2] mp 136 °C), $[\alpha]^{23}_D$ +14.5° (*c* 1.08, EtOH) [lit.[12] $[\alpha]^{25}_D$ +13±2° (*c* 1, EtOH)]. The overall yield of 6-deoxy-L-gulose from D-glucurono-γ-lactone is 52%.

In summary, methods have been developed for the synthesis of furanoid and pyranoid derivatives of 6-deoxy-L-gulose from D-glucurono-γ-lactone. In particular, the last approach is presented as a useful and high-yield route to 6-deoxy-L-gulose, recently reported to be a constituent of antibiotic YA-56.[12]

Experimental Section[13]

1-Deoxy-D-glucitol (6-Deoxy-L-gulitol) (1). A solution of 15.0 g (54 mmol) of glucose diethyl thioketal[3] in 200 mL of 70% ethanol–water was added to a suspension of 120 g of Raney nickel catalyst in 900 mL of 70% ethanol–water at 45 °C and this mixture was stirred for 7.5 h. The catalyst was then removed by filtration through Celite and washed with ten 100-mL portions of hot (~80 °C) 80% ethanol–water. Concentration of the combined filtrates at 45–50 °C under reduced pressure afforded a viscous oil which was taken up in 500 mL of absolute ethanol. Removal of ethanol from this solution under reduced pressure, followed by drying of the residue under vacuum (0.4 mmHg, 18 h), and recrystallization from ethanol afforded 6.45 g (74%) of pentitol **1**, a colorless, crystalline solid, mp 124–126 °C (lit.[5] mp 127–128 °C).

6-Deoxy-2,4:3,5-di-*O*-methylene-L-gulitol (2). A solution of 9 g (54 mmol) of pentitol **1** in 27 mL of 37% formaldehyde–water at 0–2 °C was treated with 25 g of dry HCl. The mixture was then warmed to 75 °C over a 1.6-h period and stirred for 1 h. The cooled reaction mixture was neutralized with solid $NaHCO_3$ and concentrated. Extraction of the residue by trituration with several 100-mL portions of chloroform afforded, after drying ($MgSO_4$) of the combined extracts and removal of solvent under reduced pressure, 10.9 g of a viscous syrup. Chromatography of this syrup on 300 g of silica gel with 100% ethyl acetate provided 6.49 g (63%) of alcohol **2** as colorless crystals: R_f 0.27 (silica gel, 100%

(12) Ohashi, Y.; Kawabe, S.; Kono, T.; Ito, Y. *Agric. Biol. Chem.* **1973**, *37*, 2379–85.

(13) Boiling points are uncorrected. Melting points were determined with a Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were determined on a Perkin-Elmer 237B or 737B infrared spectrometer or on a Beckman 4210 infrared spectrometer. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian T-60 or EM-390 spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane (δ 0.0) as an internal standard. Optical rotations for solutions in 1-dm cells of 1-mL capacity were measured on a Perkin-Elmer Model 141 polarimeter. Chloroform, when used as a solvent for optical rotation determinations or for IR spectra, was filtered through neutral alumina immediately prior to use.

Vapor phase chromatographic (VPC) analyses were performed on a Hewlett-Packard 5750 gas chromatograph, equipped with a flame ionization detector, using helium carrier gas at a flow rate of 60 mL/min. The indicated liquid phase was absorbed on 60–80 mesh Chromosorb W AW DMCS.

Analytical thin-layer chromatography (TLC) was conducted on 2.5 × 10 cm precoated TLC plates (silica gel 60 F-254, layer thickness 0.25 mm) manufactured by E. Merck and Co. Preparative TLC was conducted on 20 × 20 cm glass plates coated in this laboratory with a 0.6-mm thickness of silica gel G "for TLC acc. to Stahl" (5–25 μm) manufactured by E. Merck and Co.

Silica gel columns for chromatography utilized E. Merck "Silica Gel 60", 70–230 mesh ASTM. Acidic silica gel refers to Silicar CC-4 Special "for column chromatography", sold by Mallinckrodt Chemical Works.

"Dry" solvents were distilled shortly before use from an appropriate drying agent. Ether, tetrahydrofuran (THF), and dimethoxyethane were distilled under dry argon from sodium metal in the presence of benzophenone. Benzene and toluene were distilled from calcium hydride. Hexane and dichloromethane were distilled from phosphorus pentoxide. Methanol was distilled from magnesium methoxide. Hexamethylphosphoramide (HMPA) was distilled at ~1.0 mmHg from pulverized calcium hydride.

Triethylamine was distilled under argon from sodium–benzophenone immediately prior to use. Diisopropylamine, pyridine, hexamethyldisilazane, and dimethylhydrazine were all distilled before use from calcium hydride. Ammonia was distilled from the tank and then from a blue lithium solution.

Other reagents were purified as follows: oxalyl chloride was distilled under argon; 1-butanol chloride and 1-propanoyl chloride were heated at reflux for 3 h with phosphorus pentachloride and then distilled, and the distillate was treated with quinoline and redistilled; methyl iodide was distilled from phosphorus pentoxide immediately before use; tris(dimethylamino)phosphine (TDAP) was distilled under argon before use; chloromethyl methyl ether was dried for several hours over anhydrous calcium chloride, decanted, stirred briefly with anhydrous potassium carbonate, and distilled under argon from anhydrous calcium chloride. Ammonium chloride was dried at 75 °C under vacuum (1 mmHg) over phosphorus pentoxide for at least 12 h.

All other reactants and solvents were "Reagent Grade" unless described otherwise. "Ether" refers to anhydrous diethyl ether which is supplied by Mallinckrodt and Baker. "Petroleum ether" refers to the "Analyzed Reagent" grade hydrocarbon fraction, bp 35–60 °C, which is supplied by J. T. Baker Co., and was not further purified.

Reactions were run under an argon atmosphere arranged with a mercury bubbler so that the system could be alternately evacuated and filled with argon and left under a positive pressure.

Mass spectral analyses were performed by Dr. Kai Feng, UCLA, Los Angeles, CA. Elemental combustion analyses were performed by Spang Microanalytical Laboratory.

EtOAc); mp 116–117 °C (lit.[5] mp 117–118 °C); IR ($CHCl_3$) 3600 (OH), 1180, 1090, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, 3 H, J = 7 Hz, $CHCH_3$), 3.5–4.3 (m, 6 H), 4.76 (d, 1 H, J = 6 Hz, $OCH(H)O$), 5.06 (s, 2 H, OCH_2O), 5.14 (d, 1 H, J = 6 Hz, $OCH(H)O$); $[\alpha]^{24}_D$ +17° (c 1.0, $CHCl_3$).

Anal. Calcd for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.45; H, 7.36.

In addition to **2**, the chromatography gave 3.2 g of a mixture of unidentified byproducts. This mixture was dissolved in a solution of 6.8 g of phloroglucinol in 150 mL of 5% hydrochloric acid, and the resulting solution was heated at reflux for 5 h and then set aside for 18 h at room temperature. The resulting red precipitate was removed by filtration and the filtrate was washed with three 50-mL portions of ether and treated with excess silver carbonate. Removal of the silver salts from this solution by filtration and concentration of the filtrate afforded, after recrystallization of the residue from ethanol with decolorizing carbon, 2.2 g of slightly yellow, crystalline starting material (**1**), mp 113–118 °C. On the basis of this recovered material, the overall yield of **2** is 83%.

Methyl 6-Deoxy-2,4:3,5-di-*O*-methylene-L-gulonate (3). A stirred solution of 1.1 g (5.8 mmol) of alcohol **2** in 45 mL of acetone (freshly distilled from $KMnO_4$) at 0 °C was treated dropwise with 3.19 mL (10% excess) of Jones reagent (8 N e^-). After 3.5 h 1.0 mL of 2-propanol was added, and the precipitated salts were removed by filtration through Celite and washed with 100 mL of acetone and 50 mL of dichloromethane. The filtrate was concentrated to an ~6-mL volume, taken up in 300 mL of dichloromethane, and treated with excess ethereal diazomethane. After removal of excess diazomethane under reduced pressure, the solution was dried ($MgSO_4$) and solvents were removed under reduced pressure. Chromatography of the residue on 100 g of silica gel with 100% ethyl acetate afforded 0.87 g (70%) of ester **3**: mp 94–95 °C; R_f 0.54 (silica gel, 100% EtOAc); IR ($CHCl_3$) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (d, 3 H, J = 7 Hz, $CHCH_3$), 3.83 (s, 3 H, OCH_3), 4.82 (d, 1 H, J = 6.5 Hz, $OCH(H)O$); $[\alpha]^{20}_D$ −18° (c 1.12, $CHCl_3$).

Anal. Calcd for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.47; H, 6.40.

(4*S*,4α*S*)-4-(1-Hydroxyethyl)-4*H*-1,3-dioxin-6-carbaldehyde (5). To a solution of 163 mg (0.75 mmol) of ester **3** in 9 mL of dry dichloromethane at −78 °C under an argon atmosphere was added 2.2 mL of a 1 M solution of diisobutylaluminum hydride in hexane. After 1 h 0.5 mL of anhydrous methanol was added, followed by 0.5 mL of 1 N aqueous NaOH. After 30 min at room temperature, the mixture was treated with 1.0 g of anhydrous $MgSO_4$ and filtered through Celite, and the filtrate was dried over $MgSO_4$. Removal of solvent under reduced pressure and chromatography of the residue on 15 g of silica gel with 100% ethyl acetate afforded 106 mg (90%) of the enone **5**. The analytical sample was provided by distillation [Kugelrohr, 85–95 °C (0.001 mmHg)] of a portion of this product: R_f 0.40 (silica gel, 100% EtOAc); IR ($CHCl_3$) 3600 (OH), 1700 (C=O), 1630 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (d, 3 H, J = 7 Hz, $CHCH_3$), 3.87 (dq, 1 H, J = J' = 7 Hz, $CHCH_3$), 4.32 (dd, 1 H, J = 7 Hz, J' = 2 Hz, C=CCH), 5.03 (d, 1 H, J = 6 Hz, $OCH(H)O$), 5.90 (d, 1 H, J = 2 Hz, C=CH), 9.17 (s, 1 H, O=CH); $[\alpha]^{22}_D$ −80° (c 0.84, $CHCl_3$).

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.10; H, 6.43.

6-Deoxy-L-gulono-1,4-lactone (7). A. By Deprotection of Ester 3. To a stirred solution of 100 mg (0.46 mmol) of ester **3** in 4 mL of dry dichloromethane at −78 °C under an argon atmosphere was added 4.25 mL (3.7 mmol) of a 0.9 M solution of boron trichloride in dichloromethane. After 5 min the reaction mixture was warmed to 30–35 °C and the solvent was removed under reduced pressure. Traces of solvent and excess boron trichloride were removed at 0.2 mmHg, and the residual glass foam was heated at 40 °C in a water bath for 15 min. A solution of the cooled residue in 4 mL of 90% methanol–water was stirred for 20 min at room temperature and concentrated to a viscous syrup. Traces of boron were removed from this syrup by several additions and evaporations of dry methanol. Recrystallization from ethanol afforded 45 mg (57%) of the lactone **7**, mp 179–183 °C. (lit.[2] mp 184–185 °C). The analytical sample, obtained by two recrystallizations from ethanol, melted at 183–184 °C.

Anal. Calcd for $C_6H_{10}O_5$: C, 44.44; H, 6.22. Found: C, 44.50; H, 6.17.

B. By Desulfurization of Thioacetal 6. The thioacetal **6** was first prepared by Zinner.[9] The process presented here is a modification of that procedure. A mixture of 14.1 g (0.08 mol) of D-glucurono-γ-lactone, 14.4 mL (0.20 mol) of ethanethiol, and 13.6 mL of concentrated hydrochloric acid, in a tightly stoppered 250-mL round-bottomed flask, was shaken vigorously for 10 min and then cooled and stirred in an ice bath while 52 mL of 3 N aqueous NaOH was slowly added. Stirring was then discontinued, and after 20 min the oil which separated was removed by pipet and dissolved in 200 mL of dichloromethane. The remaining aqueous layer was extracted with two 50-mL portions of dichloromethane and discarded. The combined dichloromethane solutions were washed with 20 mL of saturated aqueous $NaHCO_3$ and 20 mL of saturated aqueous NaCl, dried (Na_2SO_4), and filtered. Concentration of the filtrate under reduced pressure afforded 20 g of a white foam, the crude thioacetal **6**.

A solution of 20 g of crude thioacetal **6** in 300 mL of 60% ethanol–water was added to a stirred suspension of 200 g of freshly prepared Raney nickel catalyst (W-4) in 1800 mL of 60% ethanol–water. After 3 h at room temperature, the catalyst was removed by filtration through powdered cellulose and washed with ten 200-mL portions of hot (~80 °C) 60% ethanol–water. Concentration of the combined filtrates under reduced pressure at 45–50 °C and recrystallization of the residue from ethanol afforded 5.5 g (42%) of the lactone **7** (mp 170–179 °C), suitable for reduction. Further purification by recrystallization provided 4.7 g (38%) of lactone **7**, melting at 180–182°C (lit.[2] mp 184–185 °C).

Reduction of 6-Deoxy-L-gulonolactone 7. To a stirred solution of 5.9 g (36 mmol) of lactone **7** in 140 mL of deionized water at 5–10 °C was added 120 g of 2.5% sodium amalgam (4–8 mesh) while at the same time 20% sulfuric acid was added, as required, to maintain the pH at 3.0–3.5. When no sodium remained, the supernatant was separated from the mercury, filtered, concentrated at 45 °C under reduced pressure to ~50 mL, and the diluted with 1000 mL of absolute ethanol. The precipitated inorganic salts were removed by filtration and washed with absolute ethanol, and the ethanol was removed from the combined filtrates under reduced pressure. The residue was dissolved in 50 mL of water and treated with a saturated solution of barium hydroxide until basic to phenolphthalein. The mixture was diluted with 1000 mL of absolute ethanol, treated with decolorizing charcoal, and filtered. Evaporation of ethanol from the filtrate at reduced pressure gave 3.6 g of a cream-colored, glassy foam, crude 6-deoxy-L-gulose.

Methyl 6-Deoxy-2,3-*O*-(1-methylethylidene)-(α and β)-L-gulopyranoside (9a and 9b). To a stirred solution of 0.8 g of the crude 6-deoxy-L-gulose in 10 mL of dry methanol was added 20 mL of 1% methanolic HCl. After 5 h at room temperature, the reaction was quenched with excess silver carbonate and after filtration, removal of methanol under reduced pressure and chromatography of the residue on 40 g of silica gel afforded 270 mg of **8** as a colorless, water soluble oil: R_f 0.30 (silica gel, 5:1 chloroform–methanol). A solution of this oil in 10 mL of dry acetone with 0.2 mL of 2,2-dimethoxypropane and 5 mg of *p*-toluenesulfonic acid was stirred for 16 h at room temperature, neutralized with solid $BaCO_3$, and filtered. Removal of solvent under reduced pressure and chromatography of the residue on 30 g of silica gel with 50% ethyl acetate–toluene afforded the two isomeric products.

Fraction I, 9b: 225 mg; R_f 0.45 (50% EtOAc–toluene); IR ($CHCl_3$) 3600 (OH), 1375, 1065, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 d, 3 H, J = 7 Hz, $CHCH_3$), 1.35 (s, 3 H, CCH_3), 1.51 (s, 3 H, CCH_3), 3.50 (s, 3 H, OCH_3), 4.40 (dd, 1 H, J = 2 Hz, J' = 6 Hz), 4.59 (d, 1 H, J = 3.5 Hz); $[\alpha]^{23}_D$ +54° (c 1.0, $CHCl_3$).

Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.88; H, 8.31.

Fraction II, 9a: 55 mg; R_f 0.27 (50% EtOAc–toluene); IR ($CHCl_3$) 3600 (OH), 1375, 1060, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (d, 3 H, J = 7 Hz, $CHCH_3$), 1.36 (s, 3 H, CCH_3), 1.53 (s, 3 H, CCH_3), 3.42 (s, 3 H, OCH_3), 4.71 (dd, 1 H, J = 2 Hz, J' = 4 Hz); $[\alpha]^{23}_D$ −57° (c 0.8, $CHCl_3$).

Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.89; H, 8.21.

The combined overall yield of these alcohols from lactone **7** was 16%. For preparative purposes, a modified procedure which omitted the chromatographic purification of **8** was used. Thus, a solution of 2.5 g of crude 6-deoxy-L-gulose in 25 mL of 1.5% methanolic hydrogen chloride was heated at reflux for 80 min and then cooled. Neutralization with excess silver carbonate, filtration of the resulting mixture, and evaporation of the methanol from the filtrate under reduced pressure gave 2.4 g of a brown oil. A solution of this oil in 50 mL of dry acetone with 3.3 mL of 2,2-dimethoxypropane and 20 μL of sulfuric acid was stirred for 16 h at room temperature and then treated with excess barium carbonate and filtered. The crude product which remained after evaporation of acetone from the filtrate under reduced pressure was purified by chromatography on 200 g of silica gel with 40% ethyl acetate–benzene and gave 950 mg of **9b** (R_f 0.31) and 242 mg of **9a** (R_f 0.18). The combined overall yield from lactone **7** was 22%, and the products were identical (IR, NMR, TLC) with the products obtained above.

Methyl 6-Deoxy-2,3-*O*-(1-methylethylidene)-4-*O*-methyl-α-L-gulopyranoside (10a). To a stirred suspension of 50 mg (1.25 mmol) of potassium hydride in 7 mL of dry THF at 0 °C under an argon atmosphere was added 0.44 mL (7.0 mmol) of dry methyl iodide, followed immediately by a solution of 218 mg (1.0 mmol) of alcohol **9a** in 3 mL of dry THF, and the resulting mixture was stirred for 30 min at room temperature. Isolation of the product by dichloromethane extraction ($MgSO_4$), including a base wash,[14] gave 221 mg (95%) of methyl ether **10a**, homogeneous by TLC. Distillation [Kugelrohr, 95 °C (1.0 mmHg)] of a portion of this product gave the analytical sample: R_f 0.33 (40% EtOAc–benzene); IR ($CHCl_3$) 1375, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) 1.22 (d, 3 H, J = 7 Hz, $CHCH_3$), 1.36 (s, 3 H, CCH_3), 1.52 (s, 3 H, CCH_3), 2.29, 2.31 (2 s, 2 × 3 H, 2 OCH_3); $[\alpha]^{23}_D$ −42° (*c* 0.87, $CHCl_3$).

Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.77; H, 8.72.

Methyl 6-Deoxy-2,3-*O*-(1-methylethylidene)-4-*O*-methyl-β-L-gulopyranoside (10b). By the procedure described for the preparation of **10a**, 795 mg (3.42 mmol) of alcohol **9b** in 5 mL of dry THF, with 172 mg (4.28 mmol) of potassium hydride in 1.5 mL (24 mmol) of methyl iodide in 13 mL of dry THF, provided 816 mg (96%) of methyl ether **10b**. Distillation [Kugelrohr, 95 °C (1.0 mmHg)] of a portion of this product gave the analytical sample: R_f 0.42 (40% EtOAc–benzene); IR ($CHCl_3$) 1375, 1160, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (d, 3 H, J = 7 Hz, $CHCH_3$), 1.39 (s, 3 H, CCH_3), 1.52 (s, 3 H, CCH_3), 3.50 (s, 6 H, 2 OCH_3); $[\alpha]^{23}_D$ +127° (*c* 0.81, $CHCl_3$).

Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.94, H, 8.75.

6-Deoxy-2,3-*O*-(1-methylethylidene)-4-*O*-methyl-L-gulopyranose (11). A stirred solution of 195 mg (0.84 mmol) of guloside **10b** in 30 mL of 2% aqueous sulfuric acid was heated at reflux for 16 h and then cooled and treated with 2.4 g of barium carbonate. After 2 h the solution was filtered and the water was removed from the filtrate under reduced pressure at 45–50 °C. After drying under vacuum (1 mmHg), the residue was triturated with 10 mL of dry acetone, the resulting mixture was filtered, and the solids were washed with two 10-mL portions of dry acetone. The combined filtrates were stirred for 2 h with 0.16 mL of 2,2-dimethoxypropane and 1 μL of sulfuric acid and then treated with excess silver carbonate. Filtration of this reaction mixture and evaporation of acetone from the filtrate under reduced pressure gave 140 mg (77%) of **11**, a crystalline solid, mp 93–96 °C. Recrystallization of a portion of this product from *n*-hexane afforded the analytical sample: mp 97–98 °C; R_f 0.19 (40% EtOAc–benzene); IR (CCl_4) 3600 (OH), 1380, 1050, 1030 cm^{-1}; ^1H NMR (CCl_4) δ 1.20 (d, 3 H, J = 6 Hz, $CHCH_3$), 1.29 (s, 3 H, CCH_3), 1.40 (s, 3 H, CCH_3), 3.47 (s, 3 H, OCH_3); $[\alpha]^{23}_D$ +27° (*c* 0.92, $CHCl_3$).

Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.08; H, 8.35.

By the process described above, 250 mg (1.08 mmol) of glycoside **10a** with 30 mL of 2% aqueous sulfuric acid, 2.4 g of barium carbonate, 30 mL of dry acetone, and 0.2 mL (1.6 mmol) of 2,2-dimethoxypropane afforded 195 mg (83%) of **11**, indistinguishable (mp, IR, NMR, TLC) from that obtained from glycoside **10b**.

D-Glucurono-γ-lactone Ethylene Dithioacetal (12). A solution of 40 g (0.23 mol) of D-glucurono-γ-lactone in 60 mL of hot water was cooled to room temperature and then shaken vigorously for 20 min in a sealed flask with 40 mL of (0.48 mol) of 1,2-ethanedithiol and 40 mL of concentrated hydrochloric acid. The mixture was shaken intermittently for 2 h and then set aside for 12 h while the product separated as a white crystalline solid. After dilution of the reaction mixture with 200 mL of ice-cold water, the solid was collected by filtration, washed with four 100-mL portions of cold water and four 100-mL portions of ether, and dried under vacuum (1 mmHg) over P_2O_5 to give 53.7 g (93%) of thioacetal **12**, mp 189–190 °C. A portion of this material was recrystallized twice from 3:2 water–ethanol and dried under vacuum at 80 °C to give analytically pure material: mp 190–191 °C; IR (Nujol) 1740 (C=O), 1160, 1000 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.0–3.5 (m, 4 H, SCH_2CH_2S), 4.56 (dd, 1 H, J = 7 Hz, J = 4 Hz), 5.77 (d, 1 H, J = 7 Hz, SCHS); $[\alpha]^{22}_D$ +14° (*c* 0.95, H_2O).

Anal. Calcd for $C_8H_{12}O_5S_2$: C, 38.08; H, 4.79. Found: C, 38.09; H, 4.78.

3,5-*O*-Isopropylidene-D-glucurono-γ-lactone Ethylene Dithioacetal (13). To a stirred suspension of 10.0 g (0.04 mmol) of finely ground triol **12** and 6.1 mL (0.05 mmol) of 2,2-dimethoxypropane in 1.0 L of acetone at room temperature was added 4 mL of concentrated sulfuric acid. After 10 h the mixture was treated with excess $BaCO_3$ and filtered. Removal of solvent from the filtrate and recrystallization of the residue from acetone–hexane afforded 8.9 g (77%) of ketal **13**, a white, crystalline solid: mp 238–239 °C; IR (Nujol) 3540 (OH), 1780 (C=O) cm^{-1}: ^1H-NMR (Me_2SO-d_6) δ 1.28 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 3.15 (s, 4 H, SCH_2CH_2S), 5.78 (d, 1 H, J = 7 Hz, SCHS); $[\alpha]^{22}_D$ +48° (*c* 0.65, CH_2Cl_2).

Anal. Calcd for $C_{11}H_{16}O_5S_2$: C, 45.19; H, 5.52. Found: C, 45.24; H, 5.48.

6-Deoxy-3,5-*O*-isopropylidene-L-gulono-γ-lactone (14). A solution of 7.8 g (27 mmol) of dithioacetal **13** in a mixture of 200 mL of acetone and 100 mL of dry THF at 60 °C was added to a slurry of 160 mL of Raney nickel (W-4) in 300 mL of absolute ethanol and stirred without external heating for 14 h. The catalyst was then removed by filtration and washed with six 150-mL portions of 60% ethanol–acetone. Removal of solvents from the combined filtrates under reduced pressure afforded a glass foam, which was taken up in 200 mL of CH_2Cl_2. This solution was dried ($MgSO_4$), and filtered, and solvent was removed to afford 4.2 g (78%) of lactone **14**, mp 101–104 °C. VPC analysis (4% SE-30, 140 °C) indicated >99% purity. The analytical sample was obtained by recrystallization from ethyl acetate–hexane: mp 107–107.5 °C; IR ($CHCl_3$) 3600 (OH), 1805 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (d, 3 H, J = 7 Hz, CH_3), 1.43 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 4.10 (dq, 1 H, J = 7 Hz, J = 2 Hz, H-5), 4.51 (d, 1 H, J = 2 Hz, H-2); $[\alpha]^{23}_D$ +76° (*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.47; H, 6.92.

2-*O*-(*tert*-Butyldimethylsilyl)-6-deoxy-3,5-*O*-isopropylidene-L-gulono-γ-lactone (16). To a solution of 5.12 g (25.3 mmol) of hydroxy lactone **14** and 6.88 g (102 mmol) of imidazole (sublimed) in 10.0 mL of dry dimethylformamide at room temperature was added 7.6 g (51 mmol) of *tert*-butyldimethylchlorosilane. The resulting homogeneous solution was stirred for 29 h, during which time it solidified to a colorless, crystalline mass. The solid was then partially dissolved in 350 mL of ether, washed with four 80-mL portions of water, and dried ($MgSO_4$). Removal of ether under reduced pressure afforded a

(14) In cases where reaction intermediates or products were isolated "by solvent extraction (Na_2SO_4)", the procedure followed was to dilute the reaction mixture with the indicated solvent or to extract the aqueous solution with several portions of the indicated solvent; then the combined organic extracts were washed first with several portions of water and then with saturated sodium chloride before being dried over anhydrous sodium sulfate. Drying over anhydrous magnesium sulfate ($MgSO_4$) or anhydrous potassium carbonate (K_2CO_3) is indicated by the appropriate parenthetical substitution. After drying, the solution was filtered and the solvent was evaporated from the filtrate under reduced pressure (water aspirator) using a rotary evaporator. The use of the terms "base wash" or "acid wash" indicates washing of the organic solution with saturated aqueous sodium bicarbonate solution or with 10% aqueous hydrochloric acid, respectively, prior to the aforementioned washing with water.

crystalline residue from which disiloxane was removed by evaporative transfer under vacuum (~1 mmHg) at 40 °C for 14 h. There remained 7.95 g (99%) of siloxy lactone **16** as a white, crystalline solid, mp 108–112 °C. Recrystallization of a portion of this product from *n*-hexane afforded the analytical sample: mp 113.5–114.5 °C; IR ($CHCl_3$) 1800 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6 H, 2 $SiCH_3$), 0.94 (s, 9 H, *t*-Bu), 1.33 (d, 3 H, J = 7 Hz, CH_3), 1.39 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 4.12 (dq, 1 H, J = 7 Hz, J = 2 Hz, H-5), 4.45 (br s, 2 H, H-2 and H-4); $[\alpha]^{22}_D$ +88° (*c* 1.1, $CHCl_3$).

Anal. Calcd for $C_{13}H_{28}O_5Si$: C, 56.93; H, 8.92. Found: C, 56.78; H, 8.97.

2-*O*-(*tert*-Butyldimethylsilyl)-6-deoxy-3,5-*O*-isopropylidene-L-gulofuranose (17). To a stirred solution of 3.24 g (10.2 mmol) of siloxy lactone **16** in 150 mL of dry dichloromethane under an argon atmosphere at −78 °C was added 30 mL (30 mmol) of a 1 M solution of diisobutylaluminum hydride in hexane. After 60 min, the reaction mixture was treated cautiously with 10 mL of methanol and allowed to warm to room temperature. After 30 min, the reaction mixture was diluted with 200 mL of dichloromethane and washed with 100 mL of 1 M sodium potassium tartrate, three 100-mL portions of H_2O, and 50 mL of saturated NaCl. After drying ($MgSO_4$), removal of solvent under reduced pressure afforded 3.21 g (98%) of lactol **17**, a crystalline solid, mp 108–110 °C. Recrystallization from ethyl acetate–hexane provided the analytical sample: mp 110.5–111.5 °C; IR ($CHCl_3$) 3600 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) 0.10 (s, 6 H, 2 $SiCH_3$), 0.92 (s, 9 H, *t*-Bu), 1.20 (d, 3 H, J = 7 Hz, CH_3), 1.39 (s, 6 H, 2 CH_3), 3.28 (dd, 1 H, $J = J'$ = 2 Hz, H-3), 3.56 (d, 1 H, J = 12 Hz, OH), 4.81 (dd, J = 12 Hz, J' = 4 Hz, H-1); $[\alpha]^{23}_D$ +62° (*c* 1.33, $CHCl_3$).

Anal. Calcd for $C_{15}H_{30}O_5Si$: C, 56.57; H, 9.49. Found: C, 56.53; H, 9.48.

2-*O*-Acetyl-6-deoxy-3,5-*O*-isopropylidene-L-gulono-γ-lactone (15). To a stirred solution of 202 mg (1.0 mmol) of hydroxy lactone **14** in 2 mL of dry pyridine at room temperature, under an argon atmosphere, was added 0.4 mL (4.0 mmol) of acetic anhydride. After 28 h the reaction mixture was diluted with 10 mL of H_2O and extracted with two 30-mL portions of dichloromethane. The combined extracts were washed with 30 mL of 10% HCl, 20 mL of 1 N $CuSO_4$, and 20 mL of saturated $NaHCO_3$ and dried ($MgSO_4$). Removal of solvent under reduced pressure and recrystallization of the residue from ethyl acetate–hexane provided 238 mg (97%) of acetate **15**: mp 130.5–131.5 °C; IR ($CHCl_3$) 1750, 1880 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) 1.32 (d, 3 H, J = 7 Hz, CH_3), 1.38 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 4.17 (dq, 1 H, J = 7 Hz; J' = 2 Hz, H-5), 5.38 (d, 1 H, J = 4 Hz, H-2); $[\alpha]^{22}_D$ +156° (*c* 1.14, $CHCl_3$).

Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.14; H, 6.53.

2-*O*-(*tert*-Butyldimethylsilyl)-6-deoxy-3,5-*O*-isopropylidene-L-gulose *N,N*-Dimethylhydrazone (18). To a stirred solution of 2.7 g (8.5 mmol) of lactol **17** and 1.23 mL (12.8 mmol) of carbon tetrachloride in 18 mL of dry THF at −78 °C under an argon atmosphere was added 1.70 mL (9.35 mmol) of tris(dimethylamino)phosphine and, after 30 min, 5.2 mL (68 mmol) of *unsym*-dimethylhydrazine. Cooling was then discontinued, and, after 4 h at room temperature, ether extraction ($MgSO_4$)[14] and chromatography of the crude product on 100 g of silica gel with 50% ether–petroleum ether provided 2.4 g (78%) of hydrazone **18**, a colorless oil. Distillation [Kugelrohr, 110–120 °C (0.01 mmHg)] of a portion of this product afforded the analytical sample: IR ($CHCl_3$) 3600 (OH), 1620 (C=N), 840 (OSi) cm^{-1}; ^1H NMR (CCl_4) 0.03 (s, 3 H, $SiCH_3$), 0.10 (s, 3 H, $SiCH_3$), 0.87 (s, 9 H, *t*-Bu) 1.13 (d, 3 H, J = 7 Hz, CCH_3), 1.32 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 2.72 (s, 6 H, CH_3NCH_3), 6.20 (d, 1 H, N=CH); *m/e* calcd 360.2444, *m/e* found 360.2439 ± 0.0018; $[\alpha]^{25}_D$ +11° (*c* 1.1, $CHCl_3$).

Anal. Calcd for $C_{17}H_{36}O_4N_2Si$: C, 56.63; H, 10.06. Found: C, 56.83; H, 10.22.

2-*O*-(*tert*-Butyldimethylsilyl)-6-deoxy-4-*O*-(methoxymethyl)-3,5-*O*-isopropylidene-L-gulose *N,N*-Dimethylhydrazone (19). To a solution of 1.25 g (3.5 mmol) of hydroxy hydrazone **18** in 7 mL of dry THF at −78 °C under an argon atmosphere was added 5.8 mL (3.9 mmol) of a 0.66 M solution of lithium diisopropylamide in THF, followed by 4 mL of dry hexamethylphosphoramide and 0.60 mL (7.8 mmol) of dry chloromethyl methyl ether. Cooling was then discontinued, and after 2 h at room temperature, ether extraction ($MgSO_4$), including a base wash,[14] afforded the crude product, which was further purified by filtration through 15 g of silica gel and elution with 100 mL of 70% ethyl acetate–hexane. Removal of solvents from the eluate provided 1.27 g (90%) of **19**, a colorless oil. Distillation [Kugelrohr, 120–130 °C (0.005 mmHg)] of a portion of this product afforded the analytical sample: IR ($CHCl_3$) 1620 (C=N), 840 (OSi) cm^{-1}; ^1H NMR (CCl_4) 0.03, 0.11 (2 s, 6 H, 2 $SiCH_3$), 0.90 (s, 9 H, *t*-Bu), 1.21 (d, 3 H, J = 7 Hz, CCH_3), 1.33, 1.36 (2 s, 6 H, CH_3CCH_3), 2.78 (s, 6 H, CH_3NCH_3), 3.40 (s, 3 H, OCH_3), 4.56 (d, 1 H, J = 7 Hz, OC**H**(H)O), 4.73 (d, 1 H, J = 7 Hz, OCH(**H**)O), 6.23 (d, 1 H, J = 7 Hz, N=CH); $[\alpha]^{23}_D$ +23° (*c* 0.90, $CHCl_3$).

Anal. Calcd for $C_{19}H_{40}O_5N_2Si$: C, 56.40; H, 9.96. Found: C, 56.46; H, 10.00.

Methanolysis of Lactol 17. Methyl 6-Deoxy-(α and β)-L-gulopyranoside (8a and b). A solution of 318 mg (1.0 mmol) of lactol **17** in 10 mL of 3% dry methanolic hydrogen chloride was heated at reflux under argon for 20 h. The reaction mixture was then treated with excess silver carbonate and filtered. Removal of methanol from the filtrate afforded a residue, chromatography of which on 20 g of silica gel with 9% methanol–chloroform provided 150 mg (84%) of a mixture of pyranosides **8a** and **8b**, as described above. The ratio of anomers could be determined by ^1H NMR spectroscopy: ^1H NMR δ 1.3 (d, 3 H, J = 7 Hz, CH_3), 3.47 and 3.63 (2 s, 1:4 ratio, 3 H, α-OCH_3;β-OCH_3).

Hydrolysis of Lactol 17. 6-Deoxy-L-gulose (20). A suspension of 1.2 g (3.8 mmol) of lactol **17** in 10 mL of 2% aqueous sulfuric acid was heated at 60 °C for 4 h, during which time the mixture first became homogeneous and then *tert*-butyldimethyldisiloxane separated. The aqueous reaction mixture was then cooled, washed with two 15-mL portions of ether, and neutralized with excess $BaCO_3$. The resulting suspension was then filtered, and removal of water from the filtrate by lyophilization provided 658 mg (105%) of a fluffy white solid. A portion of this material (55 mg) was converted to the *p*-bromophenylhydrazone as described by Reichstein.[2] The hydrazone was recrystallized from ethanol: mp 135–136 °C [(lit.[2] mp 136 °C; lit.[12] mp 135–137 °C)]; $[\alpha]^{23}_D$ +14.5° (*c* 1.1, EtOH) [lit.[12] $[\alpha]^{25}_D$ +13.2° (*c* 1, EtOH)]. The remainder of the product was dissolved in 5 mL of water, and a small amount of insoluble material was removed by filtration through a fine glass frit. Removal of water from the filtrate by lyophilization provided 555 mg (97%, corrected) of 6-deoxy-L-gulose, $[\alpha]^{22}_D$ +40.3° (*c* 1.60, H_2O) [lit.[2] $[\alpha]^{21}_D$ +40.8° (*c* 1.615, H_2O)].

Registry No. 1, 18545-96-5; **2**, 72251-88-8; **3**, 72251-89-9; **5**, 72251-90-2; **6**, 4258-11-1; **7**, 29217-83-2; **8**, α-isomer, 72274-54-5; **8**, β-isomer, 72274-55-6; **9a**, 72251-91-3; **9b**, 72251-92-4; **10a**, 72251-93-5; **10b**, 72251-94-6; **11**, 72050-25-0; **12**, 72251-95-7; **13**, 72251-96-8; **14**, 72251-97-9; **15**, 72251-98-0; **16**, 72251-99-1; **17**, 72252-00-7; **18**, 72252-01-8; **19**, 72252-02-9; **20**, 35867-45-9; glucose diethyl thioketal, 1941-52-2; D-glucurono-γ-lactone, 32449-92-6; ethanethiol, 75-08-1; *tert*-butyldimethylchlorosilane, 18162-48-6; *unsym*-dimethylhydrazine, 540-73-8; chloromethyl methyl ether, 107-30-2; 1,2-ethanedithiol, 540-63-6.