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HETEROCYCLIC AMINO SUGAR DERIVATIVES

PART VII.* SYNTHESIS OF 2-DEOXY-2-METHYLAMINO-D-GULOSE AND OF ITS 4-METHYL AND 4,6-DIMETHYL ETHERS*

HAZRAT M. NOORZAD AND PAUL H. GROSS

Department of Chemistry, University of the Pacific, Stockton, California 95204 (U. S. A.)

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ABSTRACT

Benzyl 2-deoxy-α-D-gulopyranosido[2,3:4′,5′]-2′-oxazolidinone (**10**) was synthesized from benzyl 3-*O*-acetyl-2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-glucopyranoside (**1**) *via* the 4-*O*-methylsulfonyl-6-*O*-trityl derivative and 3,4-anhydro-α-D-galactopyranoside derivatives. Compound **10** and its 6-*O*-trityl and 4,6-*O*-benzylidene derivatives were permethylated with methyl iodide–barium oxide in *N*,*N*-dimethylformamide, the protective groups split off, and the resulting compounds acetylated to give the benzyl glycosides as well characterized, stable compounds that could be hydrolyzed to give the title compounds.

INTRODUCTION

A number of antibiotics contain *N*-methylated amino sugars as part of their structures[2]. Van Tamelen *et al.*[3] isolated 2-amino-2-deoxy-D-gulose from streptothricin, and in anticipation of the isolation of 2-deoxy-2-methylamino-D-gulose (**13**), this sugar and its 4-methyl and 4,6-dimethyl ethers were synthesized. Compound **13** has indeed been found in two streptothricin-like antibiotics[4,5], and an independently synthesized sample[6] proved to be identical with the product described in this paper. Thus, it appeared desirable to devise a general procedure for the mono-*N*-methylation of amino deoxy sugars, based on the hypothesis that cyclic amides, in contrast to *N*-acetyl derivatives, can be *N*-methylated easily with methyl iodide–barium oxide in *N*,*N*-dimethylformamide[7].

RESULTS AND DISCUSSION

A more convenient synthesis of benzyl 4,6-*O*-benzylidene-2-deoxy-α-D-gulopyranosido [2,3:4′,5′]-2′-oxazolidinone[8] (**6**) was devised, namely, removal of the trityl

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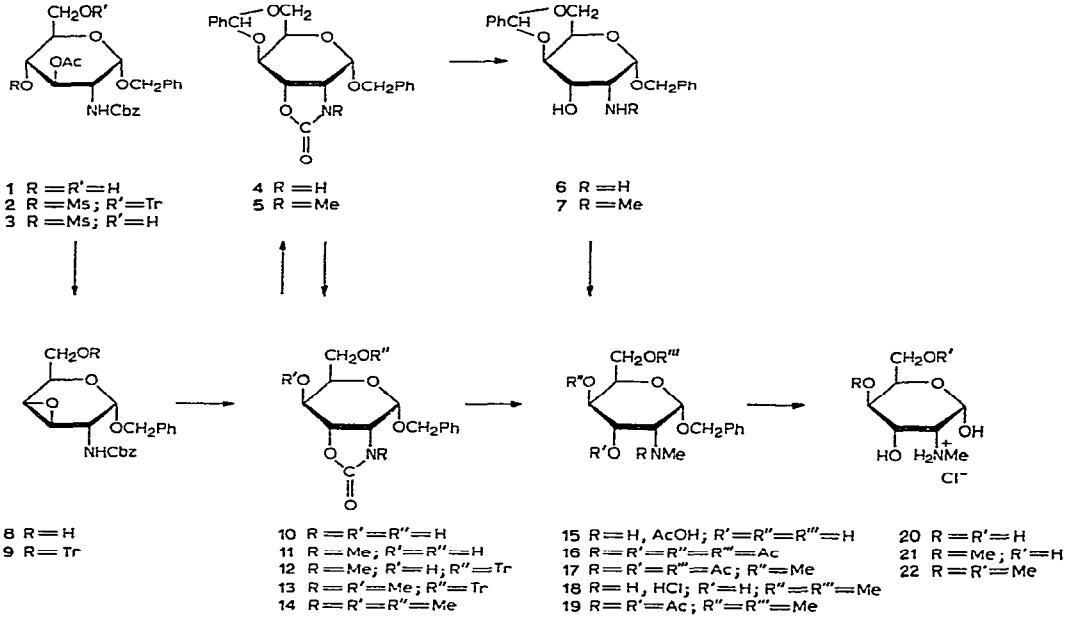
group of the 4-methylsulfonyl-6-trityl derivative (**2**) of benzyl 3-*O*-acetyl-2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-glucopyranoside (**1**) gave **3**, which was transformed by alkali treatment into the epoxide[9] (**8**). Opening of the epoxide ring in aqueous acetic acid with anchimeric assistance of the benzyloxycarbonyl group gave the oxazolidinone (**10**) as reported earlier[8]. This route avoided the experimental difficulties of the selective substitution in a 4,6-dimethylsulfonyl derivative of a sulfonyloxy group at C-6, with an acetate ion[9].

An even simpler synthesis of **10** from **1** was obtained by direct transformation of **2** into the trityl epoxide **9**. Subsequent acid cleavage of the trityl and epoxide groups gave **10**, without purification of the intermediates.

The hydroxyl groups at C-4 and C-6 of **10** were blocked with a benzylidene group, and the resulting **4** was treated with alkali to give the amino alcohol **6** that may serve as a starting material for the preparation of different *N*-substituted benzyl glycosides of 2-amino-2-deoxy-D-gulose, in analogy to the corresponding D-gluco compounds[10]. *N*-Acetylation and subsequent de-*O*-benzylidenation gave benzyl 2-acetamido-2-deoxy-α-D-gulopyranoside, identical with the compound previously described[11].



Methylation with methyl iodide–barium oxide[7] resulted in the quantitative *N*-methylation of **4**, with conservation of the oxazolidinone structure, as shown in the i.r. spectrum by the absence of the NH stretching band and amide II band, and the presence of an amide I band. Alkaline hydrolysis of the resulting **5** gave the amino alcohol **7**, the benzylidene group of which was hydrolyzed and acetylated to give **16**. Acid hydrolysis of the latter compound afforded the amino sugar **20**. Protection of

the hydroxyl group at C-6 of the oxazolidinone **10** with a trityl group gave **12** which was methylated to give the methyl ether **13**, and direct methylation of **10** gave **14**.

In all cases, complete *O*- and *N*-methylation could be observed. After simultaneous or sequential removal of the trityl and carbamate groups of **13** and **14**, acetylation gave the stable, well characterized acetylated derivatives **17** and **19** which could be conveniently hydrolyzed into the free amino sugar methyl ethers **21** and **22**. They were characterized by their i.r. spectrum, optical rotation, and paper chromatography.

Since the synthesis of oxazolidinones has been successfully extended to compounds where the hydroxyl and amino groups at C-3 and C-2 have a *trans*-diequatorial arrangement[12], the synthesis of mono-*N*-methylhexosamines reported here is of general interest. Some of the derivatives described may prove useful in the synthesis of modified antibiotics.

EXPERIMENTAL

General. — Melting points were determined on a Thomas–Hoover melting-point apparatus, model No. 6404 H, and are uncorrected. Optical rotations were measured with a Rudolph polarimeter, model No. 956. Infrared spectra were recorded with a Perkin–Elmer Spectrophotometer, model 337, on potassium bromide pellets. All compounds, unless otherwise mentioned, were found to be homogeneous and different from their precursors by thin-layer chromatography on Silica Gel GF (Merck) with chloroform containing a sufficient proportion of ethanol or hexane to produce R_F-values between 0.2 and 0.7. The spots were visualized by spraying the plates with sulfuric acid (10–15%) in methanol, and heating them at 120°. The microanalyses were performed by Alfred Bernhardt of the Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mühlheim (Germany).

Benzyl 3-O-acetyl-2-[(benzyloxycarbonyl)amino]-2-deoxy-4-O-methylsulfonyl-α-D-glucopyranoside (**3**). — A solution of benzyl 3-*O*-acetyl-2-[(benzyloxycarbonyl)-amino]-2-deoxy-α-D-glucopyranoside[13] (**1**) (22.3 g, 0.05 mole) in absolute pyridine (80 ml) was treated with chlorotriphenylmethane (14 g) for 1 h at 80°, and then for 72 h at room temperature. Methanesulfonyl chloride (21 g) was added at −5° with stirring during 30 min. The reaction mixture was stored at −5° for 36 h, and then poured into ice–water. The resulting precipitate, presumably crude **2**, was filtered off, washed with water, and dissolved in glacial acetic acid (100 ml). Water (100 ml) was added with stirring, during 1 h at 95°. The solution was kept for 12 h at 0°, and the precipitated triphenylmethanol was filtered off. The filtrate was evaporated, and the residue dissolved in chloroform. The solution was washed with sodium hydrogen carbonate solution and water, dried (sodium sulfate), and evaporated *in vacuo*. Recrystallization from 2-propanol gave 17.3 g (70%) of **3**, m.p. 112–3°, $[\alpha]_D^{30}$ +101° (*c* 1, pyridine).

Anal. Calc. for $C_{24}H_{29}NO_{10}S$: C, 55.04; H, 5.58; N, 2.67; O, 30.56; S. 6.13. Found: C, 54.84; H, 5.68; N, 2.35; O, 30.92; S, 5.81.

Benzyl 3,4-anhydro-2-[(benzyloxycarbonyl)amino]-2-deoxy-α-D-galactopyranoside (**8**). — This compound was prepared as previously described[9], except that compound **3** was used instead of its 6-*O*-acetyl derivative.

Benzyl 2-deoxy-α-D-gulopyranosido[2,3:4',5']-2'-oxazolidinone (**10**). — Crude **2**, prepared from **1** (2.2 g, 5 mmol) as described for the preparation of **3**, was treated with sodium 2-propoxide (0.3 g sodium in 20 ml 2-propanol) in *p*-dioxane (20 ml) for 16 h at 5°. Water (1 ml) was added, and the solution was neutralized with solid carbon dioxide. The solids were filtered off, and the filtrate was evaporated *in vacuo* The viscous residue was treated four times with distilled water (20 ml each), which was decanted. The resulting semisolid material was dissolved in glacial acetic acid (20 ml), and water (25 ml) was added dropwise during 2 h at 90°. The mixture was kept for 3 h at 0°, the precipitate (triphenylmethanol) filtered off, and the filtrate evaporated *in vacuo*. The residue was extracted twice with hot distilled water (2 × 20 ml). The solution was evaporated and the residue dried by addition and distillation of toluene–ethanol. It was recrystallized from 1,2-dichloroethane, from water, and from a small amount of methanol–2-isopropoxypropane (1.1 g, 75%), m.p. 114°. The compound was shown to be identical, by i.r. spectrum and mixed m.p., with an authentic sample[8].

Benzyl 4,6-O-benzylidene-2-deoxy-α-D-gulopyranosido[2,3:4',5']-2'-oxazolidinone (**4**). — Compound[10] **10** (5.9 g, 0.02 mol) was dissolved in benzaldehyde (60 ml). Fused, powdered zinc chloride (6 g) was added and the mixture was shaken for 72 h at room temperature, and then poured with stirring into 3:1:3 ether–hexane–(ice–water) (140 ml). The precipitate was filtered off and recrystallized from ethanol to give 7 g (95%) of **4**, m.p. 210–1°, $[\alpha]_D^{30}$ −9° (*c* 1, pyridine).

Anal. Calc. for $C_{21}H_{21}NO_6$: C, 65.78; H, 5.52; N, 3.66; O, 25.04. Found: C, 65.66; H, 5.39; N, 3.81; O, 25.25.

Benzyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-gulopyranoside (**6**). — A solution of compound **4** (7.7 g, 0.02 mol) in ethanolic potassium hydroxide (15%, 115 ml) was heated for 3 h under reflux. Water (100 ml) was added, and the solution was evaporated *in vacuo*. After addition of water (100 ml), the suspension was kept overnight in the refrigerator. The precipitate was filtered off, washed with iced water, and recrystallized from 2-propanol to give 6 g (84%) of **6**, m.p. 125–6°, $[\alpha]_D^{30}$ +105° (*c* 1, pyridine).

Anal. Calc. for $C_{20}H_{23}NO_5$: C, 67.24; H, 6.49; N, 3.92; O, 22.39. Found: C, 67.35; H, 6.46; N, 4.10; O, 22.61.

A solution of **6** (0.36 g, 1 mmol) in methanol (4 ml) was treated with acetic anhydride (0.2 ml) at room temperature for 5 h. Pyridine (0.1 ml) was added, and the solution was kept at room temperature for 1 h, and then evaporated *in vacuo*. The residue was dissolved in glacial acetic acid (5 ml) and water (5 ml) added dropwise during 2 h at 80°. The solution was evaporated *in vacuo*, and the remaining acetic acid removed by addition and distillation of water. The residue was dried by addition and distillation of abs. ethanol, and recrystallized from ethanol to give benzyl 2-acetamido-

2-deoxy-α-D-gulopyranoside (0.25 g, 82%), m.p. 152–3°, identical by mixed m.p. and i.r. spectrum with the compound previously described[11].

Benzyl 4,6-O-benzylidene-2-deoxy-α-D-gulopyranosido[2,3:4',5']-3'-methyl-2'-oxazolidinone (**5**). — Compound **4** (7.7 g, 0.02 mol) was stirred with *N,N*-dimethylformamide (35 ml), methyl iodide (7 ml), barium oxide (15 g), and barium hydroxide octahydrate (0.1 g) for 48 h. The mixture was filtered, and the solids were washed with *N,N*-dimethylformamide (5 ml). The filtrate was poured into water (100 ml), and the product extracted with chloroform (5 × 20 ml). The chloroform layer was washed with water, dried (sodium sulfate), and evaporated *in vacuo*. The residue was crystallized from 2-propanol to give 7 g (80%) of **5**, m.p. 140–2°, $[\alpha]_D^{30}$ +60° (*c* 1, pyridine).

Anal. Calc. for $C_{22}H_{23}NO_6$: C, 66.47; H, 5.84; N, 3.53; O, 24.16. Found: C, 66.66; H, 5.81; N, 3.63; O, 23.97.

Benzyl 2-deoxy-α-D-gulopyranosido[2,3:4',5']-3'-methyl-2'-oxazolidinone (**11**). — Compound **5** (4 g, 0.01 mol) was dissolved in glacial acetic acid (140 ml), and water (80 ml) was added dropwise for 3 h at 90°. The solution was evaporated *in vacuo* at 40°, and the residual solvents removed by addition and distillation of ethanol and toluene. The residue was recrystallized from 2-propanol to give 1.5 g (50%) of **11**, m.p. 75–6°, $[\alpha]_D^{30}$ +88° (*c* 1, pyridine).

Anal. Calc. for $C_{15}H_{19}NO_6 \cdot H_2O$: C, 55.02; H, 6.46; N, 4.28; *N*-Me, 4.60; O, 34.21. Found: C, 55.24; H, 6.61; N, 4.20; *N*-Me, 4.71; O, 34.09.

Benzyl 4,6-O-benzylidene-2-deoxy-2-methylamino-α-D-gulopyranoside (**7**). — A solution of **5** (4 g, 0.01 mol) in ethanolic potassium hydroxide (8%, 100 ml), was heated for 4 h under reflux. Water (200 ml) was added, and the solution was concentrated *in vacuo* to 50 ml and kept for 5 h at 0°. The precipitate was filtered off, washed with ice water, and recrystallized from 2-propanol to give 2.9 g (79%) of **7**, m.p. 133–4°, $[\alpha]_D^{30}$ +133.5° (*c* 1, pyridine).

Anal. Calc. for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.78; O, 21.54. Found: C, 67.95; H, 6.86; N, 3.74; O, 22.50.

Benzyl 2-deoxy-2-methylammonium-α-D-gulopyranoside acetate (**15**). — Water (80 ml) was added dropwise with stirring for 3 h, at 90°, to a solution of **7** (2.2 g, 6 mmol) in glacial acetic acid (140 ml). The solvents were evaporated *in vacuo*, and the residue was dried by addition and distillation of ethanol and toluene. Crystallizations from 2-propanol–2-isopropoxypropane and from 2-propanol gave 1.65 g (80%) of **15**, m.p. 60–1°, $[\alpha]_D^{30}$ +81° (*c* 1, pyridine).

Anal. Calc. for $C_{16}H_{25}NO_7$: C, 55.96; H, 7.34; N, 4.07; O, 32.61. Found: C, 55.74; H, 7.39; N, 4.26; O, 32.61.

Benzyl 3,4,6-tri-O-acetyl-2-deoxy-2-(N-methylacetamido)-α-D-gulopyranoside (**16**). — A solution of **5** (0.34 g, 1 mmol) in pyridine (2 ml) was treated with acetic anhydride (1 ml) for 36 h at room temperature. Addition of ice produced a crystalline precipitate which was filtered off and recrystallized from 2-propanol (0.36 g, 80%), m.p. 155–6°, $[\alpha]_D^{30}$ +49° (*c* 1, chloroform).

Anal. Calc. for $C_{22}H_{29}NO_9$: C, 58.52; H, 6.48; N, 3.10; O, 31.90. Found: C, 57.93; H, 5.88; N, 3.62; O, 32.55.

2-Deoxy-2-methylamino-D-gulose hydrochloride (**20**). — Compound **16** (0.45 g, 1 mmol) was hydrolyzed with 2M hydrochloric acid (90 ml) for 3 h at 50° and for 2 h under reflux. The solution was treated with charcoal and evaporated at 50° *in vacuo*. The residue was dried by addition and distillation *in vacuo* of ethanol, and it was crystallized from methanol–ethanol–ether to give 0.185 g (80%) of **20**, m.p. 175°, $[\alpha]_D^{30}$ −24° (after 24 h, *c* 5.06, water); descending chromatography on Whatman No. 1 paper in 5:6:3 pyridine–acetic acid–water: R_F 0.69, $R_{GN\cdot HCl}$ 1.13, and $R_{2amino-2-deoxy-D-gulose.HCl}$ 1.10. Direct comparison (n.m.r., i.r., g.l.c., and t.l.c.) with the compound prepared by Ito *et al.*[6] showed that both compounds are identical.

Benzyl 2-deoxy-6-O-triphenylmethyl-α-D-gulopyranosido[2,3:4′,5′]-2′-oxazolidinone (**12**). — Compound **10** (5.9 g, 0.02 mol), abs. pyridine (30 ml), and chlorotriphenylmethane (6 g) were heated for 3 h at 110°. The reaction mixture was poured on ice, and the precipitate was filtered off and recrystallized from ether–hexane to give 7.2 g (70%) of **12**, m.p. 139–40°, $[\alpha]_D^{30}$ +8.5° (*c* 1, pyridine).

Anal. Calc. for $C_{33}H_{31}NO_6$: C, 73.72; H, 5.81; N, 2.61; O, 17.86. Found: C, 73.75; H, 6.00; N, 2.90; O, 17.09.

Benzyl 2-deoxy-4-O-methyl-6-O-triphenylmethyl-α-D-gulopyranosido[2,3:4′,5′]-3′-methyl-2′-oxazolidinone (**13**). — A solution of **12** (5.4 g, 0.01 mol), in abs. *N,N*-dimethylformamide (20 ml) was stirred at room temperature with barium oxide (15 g), barium hydroxide octahydrate (0.1 g), and methyl iodide (2 ml). After 90 h, the mixture was filtered, and the solids were washed with a small amount of *N,N*-dimethylformamide. The combined filtrates were poured into ice–water. The crystalline precipitate was filtered off and recrystallized from 2-propanol and from ether–heptane to give 4.5 g (80%) of **13**, m.p. 65–70°, $[\alpha]_D^{28}$ +75° (*c* 1, pyridine).

Anal. Calc. for $C_{35}H_{35}NO_6$: C, 74.31; H, 6.22; N, 2.48; OMe, 5.48. Found: C, 75.04; H, 6.82; N, 2.48; OMe, 4.87.

Benzyl 3,6-di-O-acetyl-4-O-methyl-2-(N-methylacetamido)-α-D-gulopyranoside (**17**). — Water (50 ml) was added dropwise for 3 h at 80° to a solution of **13** (5.6 g, 0.01 mole) in glacial acetic acid (50 ml). After being kept for 5 h at 0°, the mixture was filtered to remove the triphenylmethanol, and the filtrate and washings (50% acetic acid) were evaporated *in vacuo* at 40°. The resulting syrup was found to be homogeneous by t.l.c. Methanol (25 ml) and potassium hydroxide (3 g) were added, and the solution was heated for 4 h under reflux and then extracted with chloroform (10 × 20 ml), each time the chloroform layer being washed with water. Benzene (50 ml) was added to the combined chloroform extracts, and the solution was evaporated *in vacuo* to give a syrup that was found to be homogeneous by t.l.c. It was dissolved in abs. pyridine (8 ml) and treated with acetic anhydride (5 ml) for 36 h at room temperature. Addition of ice–water produced a precipitate, that was crystallized from 2-propanol–heptane to give 3.8 g (90%) of **17**, m.p. 88–90°, $[\alpha]_D^{27}$ +72.2° (*c* 1, chloroform).

Anal. Calc. for $C_{21}H_{29}NO_8$: C, 59.52; H, 6.91; N, 3.31; O, 30.32; OMe, 7.32. Found: C, 59.65; H, 7.05; N, 3.49; O, 30.03; OMe, 7.67.

2-Deoxy-4-O-methyl-2-methylamino-D-gulose hydrochloride (**21**). — Compound

17 (0.42 g, 1 mmol) was hydrolyzed with 2M hydrochloric acid (30 ml) for 3 h at 50° and for 2 h under reflux. The solution was treated with charcoal and evaporated *in vacuo*. The remaining syrup was dried by addition and distillation *in vacuo* of ethanol and crystallized from 2-propanol. The crystals were deliquescent and could not be collected in solid form. When the solution was evaporated *in vacuo*, the dry residue weighed 0.12 g (55%), $[\alpha]_D^{30}$ −20° (after 12 h, *c* 1.6, water); descending chromatography on Whatman No. 1 paper in 5:6:3 pyridine–acetic acid–water: R_F 0.75, $R_{GN\cdot HCl}$ 1.24, and $R_{2\text{-amino-2-deoxy-D-gulose.HCl}}$ 1.21.

*Benzyl 2-deoxy-4,6-di-*O*-methyl-α-*D*-gulopyranosido(2,3:4′,5′)-3′-methyl-2′-oxazolidinone* (**14**). — Compound **10** (5 9 g, 0.02 mol) was stirred with *N*,*N*-dimethylformamide (45 ml), barium oxide (18 g), barium hydroxide octahydrate (0.15 g), and methyl iodide (6 ml) for 72 h at room temperature. The mixture was filtered, and the solids were washed with *N*,*N*-dimethylformamide (10 ml). The filtrate was poured into water (150 ml), and the mixture was extracted with chloroform. The extracts were washed with a small quantity of water, benzene was added, and the solvent was evaporated *in vacuo*. The sirupy residue was dissolved in methanol, and the solution treated twice with charcoal. The filtrate gave at −10° rocky crystals (3.7 g, 57%), m.p. 90–1°, $[\alpha]_D^{30}$ +78.5° (*c* 1, pyridine).

Anal. Calc. for $C_{17}H_{23}NO_6$: C, 60.53; H, 6.87; N, 4.15; OMe, 18.40; *N*-Me, 4.50; O, 28.45. Found: C, 60.29; H, 7.01; N, 4.11; OMe, 18.91; *N*-Me, 4.69; O, 28.55.

*Benzyl 2-deoxy-4,6-di-*O*-methyl-2-methylamino-α-*D*-gulopyranoside hydrochloride* (**18**). — Compound **14** (3.2 g, 0.01 mol) was heated with ethanolic potassium hydroxide (8%, 50 ml) for 4 h under reflux. Then the mixture was partitioned between chloroform and water, and the chloroform extracts were evaporated *in vacuo*. The residue was recrystallized from 2-propanol to give 2.8 g (90%), m.p. 83–4°, $[\alpha]_D^{27}$ +94.5° (*c* 1, pyridine). For analysis, this free base was transformed into the hydrochloride by addition of a slight excess of 2M methanolic hydrogen chloride. Crystallization from 2-propanol–ether gave 2.8 g (90%) of **18**, m.p. 176–7°, $[\alpha]_D^{30}$ +87.5° (*c* 1, pyridine).

Anal. Calc. for $C_{16}H_{26}ClNO_5$: C, 55.24; H, 7.53; Cl, 10.19; N, 4.03; OMe, 17.85; *N*-Me, 4.31; O, 23.00. Found: C, 55.27; H, 7.36; Cl, 10.06; N, 4.15; OMe, 17.80; *N*-Me, 4.28; O, 23.21.

*Benzyl 3-*O*-acetyl-2-deoxy-4,6-di-*O*-methyl-2-(*N*-methylacetamido)-α-*D*-gulopyranoside* (**19**). — Compound **18** (1.7 g, 5 mmol) was treated with absolute pyridine (10 ml) and acetic anhydride (2 ml) for 36 h at room temperature. Addition of ice–water produced a precipitate which was recrystallized from 2-propanol to give 2 g (91%) of **19**, m.p. 104–5°, $[\alpha]_D^{30}$ +87.5° (*c* 1, pyridine).

Anal. Calc. for $C_{20}H_{29}NO_7$: C, 60.84; H, 7.34; N, 3.55; OMe, 15.70; *N*-Me, 4.00; O, 28.32. Found: C, 60.62; H, 7.26; N, 3.71; OMe, 15.72; *N*-Me, 4.06; O, 28.39.

*2-Deoxy-4,6-di-*O*-methyl-2-methylamino-*D*-gulose hydrochloride* (**22**). — Compound **19** (0.8 g, 2 mmol) was heated with 2M hydrochloric acid (100 ml) for 2 h at 50°, and for 2 h at reflux. The solution was treated with charcoal and evaporated at

50° *in vacuo*. The residue was dried by addition and distillation *in vacuo* of abs. ethanol to give a glass (0.27 g, 60%), $[\alpha]_D^{30}$ −13° (after 24 h; *c* 1.84, water), descending chromatography on Whatman No. 1 paper in 5:6:3 pyridine–acetic acid–water: R_F 0.81, $R_{GN\cdot HCl}$ 1.31, and $R_{2\text{-amino-2-deoxy-D-gulose. HCl}}$ 1.30.

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