(3.45 mmol) of acetone, and 1 mL of $POCl_3$ in 20 mL of benzene was allowed to stand at room temperature under N_2 for 15 h. The solution was poured into ice–water and neutralized with $NaHCO_3$. The organic layer was separated, washed with water, dried, and evaporated to yield 380 mg (90%) of a colorless solid: mp 115.5–116.5 °C; ^1H NMR ($CDCl_3$) δ 1.92 (s, 6 H), 7.20–7.65 (AA'BB', 4 H), 7.60 (s, 2 H, 4-, 9-H); CIMS, m/e 232 (M^+). Anal. Calcd for $C_{13}H_{12}S_2$: C, 67.18; H, 5.21; S, 27.60. Found: C, 67.34; H, 5.25; S, 27.58.

Spiro[1,3-benzodioxole-2,2'-naphtho[2,3-*d*][1,3]dioxole] (9). To a quickly stirred suspension of 8.0 g (50 mmol) of naphthalene-2,3-diol in 100 mL of dry CH_2Cl_2 was added dropwise over a period of 30 min a solution of 9.5 g (50 mmol) of 2,2-dichloro-1,3-benzodioxole[16] in 50 mL of dry CH_2Cl_2. During the addition the mixture was cooled by a water bath. After being stirred an additional hour, the mixture was filtered, the filtrate washed two times with water and dried, and the solvent removed. The dark residue was stirred with 100 mL of MeOH and filtered. The dark solid was dissolved in CCl_4 and chromatographed on silica gel. The first fractions were collected and recrystallized twice from isopropyl alcohol to yield 2.6 g (19%) of a colorless solid: mp 156–157 °C; ^1H NMR (CCl_4) δ 6.95 (m, 4 H), 7.24 (s, 2 H, 4'-, 9'-H), 7.25–7.75 (AA'BB', 4 H). Anal. Calcd for $C_{17}H_{10}O_4$: C, 73.38; H, 3.62. Found: C, 73.18; H, 3.82.

1,1',3,3'-Tetramethylspiro[2,3-dihydrobenzimidazole-2,2'-[2,3]dihydro[1*H*]perimidine] (7). 7 was prepared analogously to 1 from 1.5 g (15.60 mmol) of 2-chloro-1,3-dimethylbenzimidazolium tetrafluoroborate,[8] 1.04 g (5.60 mmol) of *N,N'*-dimethylnaphthalene-1,8-diamine (**21**),[11] and 1.2 g (12 mmol) of triethylamine in 25 mL of acetonitrile: yield, 1.35 g (73%) of a colorless solid, mp 325 °C dec; ^1H NMR ($CDCl_3$) δ 2.62 (s, 6 H), 2.68 (s, 6 H), 6.24–6.68 (AA'BB', 4 H), 6.27–6.37 (dd, 2 H, 4'-, 9'-H), 7.03–7.38 (m, 4 H, 5'-, 6'-, 7'-, 8'-H); mass spectrum EIMS, (M^+) calcd 330.1844, obsd 330.1866. Anal. Calcd for $C_{21}H_{22}N_4$: C, 76.33; H, 6.71; N, 16.96. Found: C, 76.48; H, 6.81; N, 16.92.

1',3'-Dimethylspiro[1,3-benzodithiole-2,2'-[2,3]dihydro-[1*H*]perimidine] (8). 8 was analogously prepared to 1 from 1.00 g (3.14 mmol) of 2-chloro-1,3-dimethylperimidinium tetrafluoroborate (**20**), 0.446 g (3.14 mmol) of benzene-1,2-dithiol,[19] and 0.7 g (6.9 mmol) of triethylamine in 40 mL of acetonitrile. The crude product was recrystallized from petroleum ether and charcoal to yield 350 mg (33%) of colorless needles: mp 187–188 °C; ^1H NMR ($CDCl_3$) δ 3.25 (s, 6 H), 6.25 (dd, J = 6.9, 2.3 Hz, 2 H, 4'-, 9'-H), 6.88–7.3 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 138.8 (C-3a'), 135.7 (C-3a), 133.7 (C-6a), 127.3 (C-5' or C-5), 124.7 (C-5 or C-5'), 121.2 (C-4), 118.5 (C-6'), 113.2 (C-9b'), 104.5 (C-4'), 37.6 (NCH_3); EIMS, (M^+) calcd 336.0755, obsd 336.0746. Anal. Calcd for $C_{19}H_{16}N_2S_2$: C, 67.82; H, 4.79; N, 8.33; S, 19.06. Found: C, 67.79; H, 4.94; N, 8.09; S, 19.07.

Calculations. The PPP calculations were carried out with the parameters suggested by Zahradnik et al.[26] The core energy, I_C, for the lone pairs of the methylamino groups in **1**, **5**, and **23–25** was set equal to −26.3 eV. For **22** we reduced the value to −25.3 eV to take care of the inductive effect of the cyclopentane ring. In **1** and **22**, I_c for the carbon atoms bearing methyl groups was reduced by 1 eV (I_c = −10.40 eV) in order to account for the inductive effect of methyl groups in aromatic systems.[39]

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Registry No. **1**, 99643-38-6; **2**, 837-01-4; **3**, 99643-39-7; **4**, 99643-40-0; **5**, 99643-41-1; **6**, 99643-42-2; **7**, 99643-43-3; **8**, 99643-44-4; **9**, 82823-46-9; **15**, 75751-21-2; **16**, 99643-47-7; **18**, 30837-50-4; **19**, 30837-60-6; **20**, 99643-49-9; **21**, 20734-56-9; **23**, 37471-00-4; **24**, 64482-94-6; **25**, 99643-50-2; **26**, 67177-41-7; **27**, 92-44-4; **32**, 6156-25-8; **33**, 17534-15-5; **35**, 99643-52-4; **36**, 13214-70-5; **38**, 99643-51-3; **39**, 87473-92-5; **40**, 99643-54-6; **41**, 99643-53-5; 2,5,6-trimethylbenzimidazole, 3363-56-2; 1,2,3,5,6-pentamethylbenzimidazolium iodide, 99643-45-5; 2-chloro-1,5,6-trimethylbenzimidazole, 39791-97-4; trimethyloxonium tetrafluoroborate, 420-37-1; formaldehyde, 50-00-0; acetone, 67-64-1; cyclopentanone, 120-92-3; thiophosgene, 463-71-8; benzyl mercaptan, 100-53-8; naphthalene-1,8-dithiol, 25079-77-0; 2,2-dichloro-1,3-benzodioxole, 2032-75-9; 2-chloro-1,3-dimethylbenzimidazolium tetrafluoroborate, 18116-10-4.

(39) Klessinger, M. *Angew. Chem.* **1972**, *84*, 544; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 525.

Synthesis of (−)-Methyl Ravidosaminide

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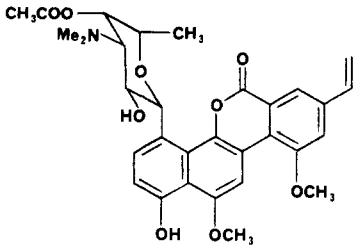
The title compound (**9b**) was prepared in five steps (48% overall yield) from ethyl 2,3,6-trideoxy-α-D-*erythro*-hex-2-enopyranoside (**4b**) as a 1:2.3 mixture of α- and β-anomers. The key step was the iodocyclization reaction of unsaturated carbonimidothioate derivative **5**. An improved procedure for the synthesis of **4b** is also described.

Ravidomycin (**1**), isolated[1,2] at Ayerst Laboratories by culturing a streptomycete found in a Guatemala soil sample, is an aromatic C-glycoside with antitumor and antibiotic properties.[1,3] It may be considered a derivative of the aminosugar 3,6-dideoxy-3-(*N,N*-dimethylamino)altropyranose (**9a**), herein referred to as ravidosamine[1] (the absolute configuration of this portion of **1** has not been determined). We became interested in the synthesis of **1** because of the cis, vicinal *N,N*-dimethylamino alcohol



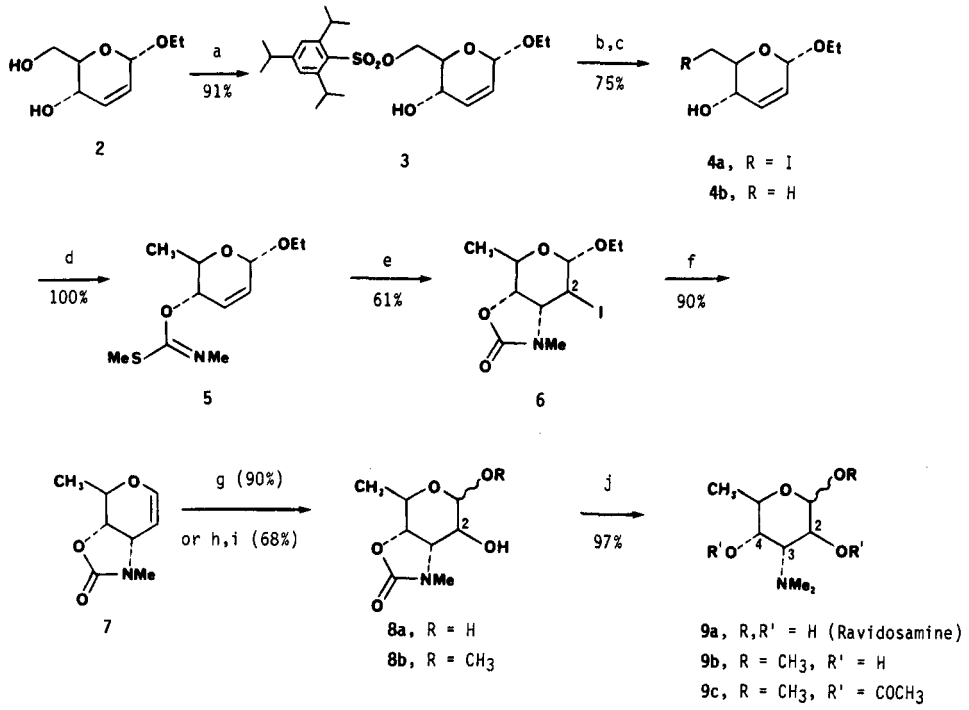
1

grouping at C-3,4 of **9a**. Based on our earlier work on aminocyclitol synthesis,[4,5] we believed this functionality

(1) Sehgal, S. N.; Czerkawski, H.; Kudelski, A.; Pandev, K.; Saucier, R.; Vézina, C. *J. Antibiot.* **1983**, *36*, 355.
(2) Findlay, J. A.; Liu, J-S.; Radics, L.; Rakhit, S. *Can. J. Chem.* **1981**, *59*, 3018.
(3) Singh, K. *J. Antibiot.* **1984**, *37*, 71.

0022-3263/86/1951-0380$01.50/0

Scheme I[a]



[a] (a) Tp-Cl, pyr; (b) NaI; (c) $LiEt_3BH$; (d) NaH, MeNCS, MeI; (e) I_2, THF, aqueous Na_2CO_3; (f) Zn, EtOH; (g) *m*-CPBA, MeOH; (h) OsO_4, NMO; (i) MeOH, TsOH; (j) $LiAlH_4$, THF.

could be introduced by a hydroxyl-directed halo–amination reaction (**5** → **6**) using an unsaturated sugar as the substrate. We have reported one example of such a process in the carbohydrate series,[5] and both Fraser-Reid[6] and Cardillo[7] have applied related transformations[8] to the synthesis of amino sugars. Also crucial to the success of this approach would be the ability to replace halogen with hydroxyl with retention of configuation (**6** → **8**). Our recent model studies[4] using cyclohexane substrates appeared promising in this regard. Finally, the preparation of the appropriate unsaturated substrate **4b** from α-D-glucose via the diol **2** had been reported.[9,10] We therefore set out to prepare a quantity of **4b** and study its conversion to methyl ravidosaminide (**9b**) by the steps indicated in Scheme I.

Results

The synthesis of **2**[9] from commercially available tri-*O*-acetyl-D-glucal proceeded on a multigram scale without difficulty. Reaction of **2** with *p*-toluenesulfonyl chloride,[10] however, did not give good yields or selectivity in our hands, so we turned to the more hindered reagent 2,4,6-triisopropylbenzenesulfonyl chloride.[11] Thus **2** was selectively converted to its mono-"tripsylate" derivative **3** with total consumption of starting material and no overreaction. Conversion of **3** to the iodide **4a** necessarily preceded reduction because **3** was very susceptible to rearrangement to a furan, as had been reported for the corresponding tosylate.[10] The iodide **4a** was treated with 3 equiv of lithium triethylborohydride[12] to give the unsaturated alcohol **4b**, a procedure which was found superior to the use of Raney nickel.[10] The overall yield for **2** → **4b** was thus 68% and several grams of **4b** could be conveniently prepared in less than a week.

The unsaturated alcohol **4b** was converted to its *N*-methylcarbonimidothioate derivative **5**, which in turn was iodocyclized according to our usual protocol,[4] giving the iodide **6** in 61% overall yield. All of the carbons destined for **9a** are in place in **6**, inasmuch as the *N*-methyloxazolidine group can be transformed to a cis, vicinal *N,N*-dimethylamino alcohol by lithium aluminum hydride reduction[13] at an appropriate point in the sequence. The altropyranose stereochemistry is also present, although an iodide-to-hydroxyl transformation at C-2 is required for completion of the synthesis. Our intent was to accomplish the latter using silver(I)-promoted solvolysis, since model studies showed that the oxazolidinone nitrogen participates in this reaction, and the new hydroxyl group replaces iodide with retention of configuration.[4]

To our dismay, treatment of **6** with silver(I) trifluoroacetate in nitromethane containing 1 equiv of water gave no reaction whatsoever at 0 °C, or at 23 °C. Upon heating at 90–100 °C, slow consumption of starting material was observed, but many new products were formed, and we were unable to isolate a pure alcohol corresponding to **8b**. We attribute the difference in reactivity between **6** and our

(4) Knapp, S.; Patel, D. V. *J. Org. Chem.* **1984**, *49*, 5072.
(5) Knapp, S.; Patel, D. V. *J. Am. Chem. Soc.* **1983**, *105*, 6985.
(6) (a) Pauls, H. W.; Fraser-Reid, B. *J. Chem. Soc. Chem. Commun.* **1983**, 1031. (b) Pauls, H. W.; Fraser-Reid, B. *J. Org. Chem.* **1983**, *48*, 1392.
(7) (a) Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *J. Org. Chem.* **1984**, *49*, 3951. (b) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Chem. Soc. Chem. Commun.* **1982**, 1308. (c) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *Ibid*, **1982**, *1309*. (d) Bongini, A.; Cardillo, G.; Orena, M.; Sandri, S.; Tomasini, C. *Tetrahedron* **1983**, *39*, 3801.
(8) Recent related cyclizations: (a) Harding, K. E.; Stephens, R.; Hollingsworth, D. R. *Tetrahedron Lett.* **1984**, *25*, 4631. (b) Hirama, N.; Iwashita, M.; Yamazaki, Y.; Itô, S. *Ibid.* **1984**, 4963. (c) Hirama, N.; Shigemoto, T.; Yamazaki, Y.; Itô, S. *J. Am. Chem. Soc.* **1985**, *107*, 1797.
(9) Ferrier, R. J.; Prasad, N. *J. Chem. Soc. C* **1969**, 570.
(10) Yunker, N. B.; Tam, S. Y-K.; Hicks, D. R.; Fraser-Reid, B. *Can. J. Chem.* **1976**, *54*, 2411.
(11) (a) Lohrmann, R.; Khorana, H. G. *J. Am. Chem. Soc.* **1966**, *88*, 829. (b) Creasey, S. E.; Guthrie, R. D. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1373.
(12) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1983**, *48*, 3085.
(13) For a recent application of this reaction see: Heathcock, C. H.; Montgomery, S. H. *Tetrahedron Lett.* **1983**, *24*, 4637.

cyclohexane model system to the presence of two electron-withdrawing C–O bonds β to the developing positive charge at C-2 of **6**.[14]

Fortunately, a more successful, and with regard to an eventual synthesis of **1**, more flexible approach to the conversion of **6** to **8b** was found. Reduction of **6** with zinc powder gave not the *N*-methylcarbamoyl derivative of **4b** (C–N cleavage), but rather the glycal **7** (C–O cleavage). Whereas either reductive cleavage process seems feasible based on a trans-anti-parallel bond arrangement, the observed alkene formation at C-1 might reflect stabilizing π overlap with the ring oxygen lone pair electrons in the transition state. Whatever the cause of the regioselectivity of this reductive elimination, glycal **7** offers two routes to ravidosamine derivatives. Reaction of **7** with *m*-chloroperoxybenzoic acid in methanol[15] gave a 2.3:1 mixture of anomeric methyl glycosides **8b**. The α-anomer structure was assigned to the minor product based on the similarity of its ^{1}H NMR coupling constants with those shown by **6**.[16] Since fused oxazolidines normally add reagents from the less hindered exo face,[4,17] the assumption was made that the C-2 hydroxyl of **8b** had the β-configuration in both anomers. This was substantiated by an independent synthesis of **8b**. Treatment of **7** with osmium tetraoxide and *N*-methylmorpholine *N*-oxide[18] gave diol **8a** as a mixture of anomers, which in turn was converted in acidic methanol to its methyl glycoside **8b**. The same 2.3:1 mixture of **8b** anomers was obtained in this way as with the *m*-chloroperoxybenzoic acid reaction; that is, both sequences gave the thermodynamic anomeric mixture in methanol.

As expected, lithium aluminum hydride reduction of **8b** gave (–)-methyl ravidosamine **9b** as a 2.3:1 mixture of anomers. The anomers were inseparable but could be converted to a pair of diacetate derivatives **9c**, which were separated and characterized independently by 400-MHz ^{1}H NMR, optical rotation, and elemental analysis.

Discussion

The synthesis of (–)-methyl ravidosaminide (**9b**) requires five steps from **4b** and proceeds in 48% overall yield with stereochemical control at C-2 and C-3. In the process two compounds, **7** and **8a**, are generated which might be transformed into glycosylation substrates for eventual linkage to an aromatic portion for the synthesis of **1**. Particularly useful in this regard is the fact that in **7** and **8a** the cis, vicinal *N*,*N*-dimethylamino alcohol functionality is protected within the *N*-methyloxazolidinone ring. The synthesis of **9b** also demonstrates the applicability of our unsaturated carbonimidothioate halocyclization reaction[4,5] to amino sugar targets, particularly *N*-methyl-substituted ones.[19] Thus the trichloroacetimidate iodocyclization reaction developed by Fraser-Reid[6] and Cardillo[7] and the present method are nicely complementary: the former allows introduction of an amino group in a "lightly protected" form, whereas the latter is more suited to situations where the cis, vicinal amino alcohol unit must survive several intervening steps before the amino group is liberated. Finally, the reductive elimination reaction **6** → **7** adds new scope to the chemistry of iodooxazolidinones, which also encompasses reductive deiodination, dehydroiodination, and for some substrates silver-assisted solvolysis.[4]

Experimental Section

Apparatus and Reagents. Melting points were determined on an Electrothermal apparatus and are uncorrected. Optical rotations [α] were taken by using a Perkin-Elmer Model 141 polarimeter at 25 °C, sodium D line, and 1-dm path length. Infrared (IR) spectra were recorded by using a Perkin-Elmer Model 727 B spectrophotometer (selected absorption maxima are reported in cm^{-1}). Proton nuclear magnetic resonance (NMR) spectra were obtained on deuteriochloroform solutions with a Varian Associates T-60 or XL-400 instrument. Proton-decoupled ^{13}C NMR spectra were obtained on trideuterioacetonitrile solutions with a Varian Associates CFT-20 instrument. Chemical shifts are reported in parts per million downfield from tetramethylsilane, and coupling constants are in hertz. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, TN).

Precoated silica gel plates (Baker Si250F) were used for analytical thin-layer chromatography (TLC). E. Merck silica gel 60 (230–400 mesh) was employed for column chromatography. Tetrahydrofuran (THF) was distilled from benzophenone ketyl. Pyridine was distilled from calcium hydride. Other reagents were obtained commercially and used as received. Organic solutions were dried over anhydrous magnesium sulfate, and all reactions were run under argon atmosphere.

Ethyl 2,3-Dideoxy-6-*O*-(2,4,6-triisopropylphenylsulfonyl)-α-D-*erythro*-hex-2-enopyranoside (3). A solution of 5 g (28.74 mmol) of diol **2** in 40 mL of pyridine was treated with 8.71 g (28.74 mmol) of 2,4,6-triisopropylbenzenesulfonyl chloride and stirred at 23 °C for 16 h, by which time TLC indicated the absence of **2**. The reaction mixture was concentrated using a vacuum pump and the residue was dissolved in 100 mL of dichloromethane. The organic solution was washed with 50 mL of saturated aqueous sodium bicarbonate and 50 mL of water, dried, and concentrated. Chromatography using 1:1 ethyl acetate/petroleum ether as eluant gave 11.53 g (91%) of **3** as a clear syrup: NMR (60 MHz) 7.09 (s, 2 H), 5.46–5.98 (m, 2 H), 4.85 (br s, 1 H), 2.60–4.40 (m, 10 H), 1.17 (t, 3 H, J = 7), 1.13 (app d, 18 H, J = 6).

Ethyl 6-Iodo-2,3,6-trideoxy-α-D-*erythro*-hex-2-enopyranoside (4a). A solution of 6 g (13.64 mmol) of sulfonate ester **3** in 60 mL of butanone was heated at reflux with 10.23 g (68.2 mmol) of sodium iodide and 3.3 mL (40.92 mmol) of pyridine. After 3 h TLC indicated the absence of **3**. The reaction mixture was concentrated and the residue was partitioned between 100 mL of ether and 50 mL of water. The organic solution was washed with 50 mL of 5% aqueous sodium thiosulfate, dried, and concentrated. Chromatography using 1:1 ethyl acetate/petroleum ether as eluant gave 3.29 g (85%) of **4a** as an oil whose NMR and TLC characteristics matched those reported previously.[10]

Ethyl 2,3,6-Trideoxy-α-D-*erythro*-hex-2-enopyranoside (4b). A solution of iodide **4a** (3 g, 10.56 mmol) in 15 mL of THF was treated with 31.68 mL of a 1 M solution of lithium triethylborohydride in THF. After 16 h at 23°, TLC indicated that no **4a** remained. The reaction was quenched with 10 mL of saturated aqueous potassium carbonate and extracted with ether (3 × 50 mL). The combined organic extracts were dried, concentrated, and chromatographed using 1:1 ethyl acetate/petroleum ether as the eluant to give 1.47 g (88%) of **4b**, identical by TLC and NMR with the reported[10] compound.

Ethyl 2-Iodo-3-(methylamino)-2,3,6-trideoxy-α-D-altropyranoside 3,4-(*N*,*O*)-Cyclic Carbamate (6). A solution of 232 mg (1.47 mmol) of **4b** in 2 mL of THF was added to a stirred suspension of oil-free sodium hydride (46 mg, 1.93 mmol) in 1 mL of THF at 0 °C. After 30 min a solution of 0.1 mL (1.47 mmol) of methylisothiocyanate in 1 mL of THF was added, and the reaction mixture was warmed to 23 °C and stirred for 3 h. Iodomethane (0.4 mL) was added, stirring was continued for an additional 1 h at 23 °C, and then the reaction mixture was concentrated, diluted with 50 mL of ether, and filtered through Celite. Evaporation of the solvent gave 366 mg (101% crude yield) of

(14) (a) March, J. "Advanced Organic Chemistry", 3rd ed.; Wiley: New York, 1985, p 303. (b) Steric repulsion by the C-1 methoxy substituent might also deter nitrogen participation at C-2 during the solvolysis reaction. We are grateful to a referee for this suggestion.
(15) Sweet, F.; Brown, R. K. *Can. J. Chem.* **1966**, *44*, 1571.
(16) Compare, for instance, the C-4 methine of **6** (dd, J = 7, 9) with that of the major (dd, J = 2, 7) and minor (dd, J = 8, 9) anomers of **8b**.
(17) Knapp, S.; Sebastian, M. J.; Ramanathan, H. *J. Org. Chem.* **1983**, *48*, 4786.
(18) Van Rheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *17*, 1973.
(19) Knapp, S.; Patel, D. V. *Tetrahedron Lett.* **1982**, *23*, 3539.

the carbonimidothioate derivative **5**: NMR (60 MHz) 5.60–6.20 (m, 2 H), 5.00–5.40 (m, 1 H), 3.18–4.29 (m, 4 H), 3.00 (s, 3 H), 2.35 (s, 3 H), 1.22 (d, 3 H, J = 6), 1.20 (t, 3 H, J = 7).

Crude **5**, as obtained above, was treated with a solution of 411 mg (1.62 mmol) of iodine in 5 mL of THF and the solution was left at 23 °C for 16 h. The reaction was quenched with 2 mL of saturated aqueous sodium sulfite, then 2 mL of saturated aqueous sodium carbonate was added, and the mixture was stirred at 23 °C for 2 h to hydrolyze the iminium salt intermediate. The mixture was concentrated and extracted with dichloromethane (3 × 50 mL), and the combined extracts were washed with 25 mL of brine, dried, and concentrated. The residue was chromatographed by using 3:7 ethyl acetate/petroleum ether as the eluant to give 306 mg (61% overall yield from **4b**) of white crystals. A sample recrystallized from ether/petroleum ether had mp 98–99 °C: NMR (400 MHz), 5.09 (d, 1 H, J = 4), 4.25 (dd, 1 H, J = 7, 9), 4.17 (dd, 1 H, J = 7, 4), 4.12 (dd, 1 H, J = 8, 7), 3.92 (qd, 1 H, J = 9, 6), 3.45 (app qd, 2 H, J = 7, 2), 3.04 (s, 3 H), 1.35 (d, 3 H, J = 6), 1.20 (t, 3 H, J = 7); IR (carbon tetrachloride) 1775; [α] +53° (c 0.017, methanol). Anal. Calcd for $C_{10}H_{16}NO_4I$: C, 35.20; H, 4.73; N, 4.10: I, 37.19. Found: C, 34.82; H, 4.45; N, 4.02; I, 36.80.

1,5-Anhydro-3-(methylamino)-2,3,6-trideoxy-D-*ribo*-hex-1-enitol 3,4-(*N,O*)-Cyclic Carbamate (7). A solution of 75 mg (0.22 mmol) of the iodide **6** in 2 mL of ethanol and 0.2 mL of water was treated with unactivated zinc powder (120 mg, 1.8 mmol) and heated at 70 °C for 1 h. The reacted mixture was cooled, filtered, diluted with 10 mL of water, and extracted with ether (3 × 25 mL). The combined organic extracts were dried and concentrated, and the resulting white solid was crystallized from ether/pentane, giving 34 mg (90%) of **7**, mp 120 °C: NMR (400 MHz) 6.60 (d, 1 H, J = 6), 4.91 (dd, 1 H, J = 6, 4), 4.16 (dd, 1 H, J = 9, 3), 3.99 (dd, 1 H, J = 4, 3), 3.63 (dq, 1 H, J = 9, 6), 2.81 (s, 3 H), 1.42 (d, 3 H, J = 6); IR (carbon tetrachloride) 1750, 1640; [α] +116° (c 0.066, methanol). Anal. Calcd for $C_8H_{11}O_3N$: C, 56.80; H, 6.55; N, 8.28. Found C, 57.02; H, 6.40; N, 8.24.

Methyl 3,6-Dideoxy-3-(methylamino)-α- and -β-D-altropyranoside 3,4-(*N,O*)-Cyclic Carbamate (8b). A solution of 34 mg (0.20 mmol) of glycal **7** in 1 mL of methanol was stirred at 23 °C. A solution of m-chloroperoxybenzoic acid (87 mg, 0.60 mmol) in 1 mL of methanol was added dropwise. After 3 h the reaction mixture was concentrated, diluted with 75 mL of dichloromethane, and washed with 5% aqueous sodium sulfite (25 mL) and saturated aqueous sodium bicarbonate (25 mL). The organic layer was dried, concentrated, and chromatographed using 3:1 ether/petroleum ether as the eluant to give 39 mg (90%) of **8b** as a 1:2.3 mixture of α- and β-anomers. **Major anomer**: NMR (400 MHz) 4.55 (d, 1 H, J = 7), 4.12 (dd, 1 H, J = 7, 2), 4.05 (dd, 1 H, J = 7, 4), 3.74–3.82 (m, 2 H), 3.53 (s, 3 H), 2.9 (s, 3 H), 1.37 (d, 3 H, J = 6); ^{13}C NMR 160.0, 102.3, 75.7, 69.7, 67.9, 58.0, 56.4, 31.5, 19.7.

Minor anomer: NMR (400 MHz) 4.46 (d, 1 H, J = 6), 4.25 (dd, 1 H, J = 9, 8), 3.86 (dd, 1 H, J = 9, 8), 3.67–3.74 (m, 2 H), 3.44 (s, 3 H), 3.02 (s, 3 H), 1.33 (d, 3 H, J = 6); ^{13}C NMR 160.0, 130.4, 75.9, 71.7, 65.8, 59.9, 55.8, 31.08, 18.71. Mixture of α- and β-anomers of **8b**: IR (film) 3550, 3500–3200 (br), 1770; [α] + 45° (c 0.035, methanol).

An independent preparation of **8b** was carried out as follows: A solution of 25 mg (0.15 mmol) of glycal **7** in 8 mL of acetone was mixed with 0.13 mL of water, 0.64 mg of osmium tetraoxide and 28 mg (0.16 mmol) of N-methylmorpholine N-oxide. The reaction was stirred at 23 °C for 16 h, then treated with 250 mg of sodium thiosulfate, 250 mg of Celite, and 2.5 mL of water and stirred for an additional 3 h. The mixture was filtered, concentrated, and extracted with ethyl acetate (3 × 25 mL). The combined extracts were dried and concentrated to give the (presumed) vicinal diol **8a**, which was not characterized. Rather, the crude product was heated at reflux in 5 mL of methanol containing 0.1 mg of p-toluenesulfonic acid for 24 h. The reaction was cooled, concentrated, and partitioned between 50 mL of dichloromethane and 25 mL of saturated aqueous sodium bicarbonate. The organic layer was dried and concentrated and the residue chromatographed as before to give 22 mg (68% overall yield from **7**) of **8b** as a 2.3:1 mixture of anomers, identical in its TLC, IR, and ^{1}H NMR characteristics with **8b** from the m-chloroperoxybenzoic acid reaction.

Methyl 3,6-Dideoxy-3-(dimethylamino)-α- and -β-D-altropyranoside (Methyl Ravidosaminide, 9b). A solution of 22 mg (0.1 mmol) of **8b** in 2 mL of THF was added to a suspension of 8 mg (0.2 mmol) of lithium aluminum hydride in 0.5 mL of THF and the mixture was heated at reflux for 2 h. The reaction was cooled, quenched by dropwise addition of 1 mL of water and 2 mL of 15% aqueous sodium hydroxide, and extracted with ethyl acetate (3 × 25 mL). The combined extracts were dried and conentrated to give 20 mg (97% crude yield) of the amino diol **9b** as a 2.3:1 mixture of anomers. NMR (major anomer, 400 MHz) 4.42–4.62 (m, 2 H), 3.80–4.00 (m, 2 H), 3.40 (s, 3 H), 3.00–3.20 (m, 1 H), 2.54 (s, 6 H), 2.10 (m, 2 H), 1.26 (d, 3 H, J = 6); (minor anomer) 4.70–4.90 (m, 2 H), 4.0–4.40 (m, 2 H), 3.50 (s, 3 H), 2.70–3.00 (m, 1 H), 2.64 (s, 6 H), 1.8–2.00 (m, 2 H), 1.40 (d, 3 H, J = 6). ^{13}C NMR (major anomer) 104.32, 76.06, 70.82, 68.57, 59.33, 55.74, 42.72, 20.16; (minor anomer) 103.71, 74.05, 70.21, 64.70, 61.00, 56.11, 42.92, 17.72. [α] −38° (c 0.067, methanol). The amino sugar **9b** was more conveniently characterized as its diacetate **9c**, which was prepared as follows. A mixture of 20 mg of **9b**, 0.5 mL of pyridine, 0.04 mL of acetic anhydride, and 25 mg of 4-dimethylaminopyridine was kept at 23 °C for 16 h. The crude product was chromatographed using ether as the eluant to give the major anomer (14.m mg, 50% yield, R_f 0.14, mp 57–59 °C) and the minor anomer 6.3 mg, 21% yield, R_f 0.38, oil) of **9c**. **Major anomer**: NMR (400 MHz) 5.21 (dd, 1 H, J = 2, 1), 5.13 (dd, 1 H, J = 2, 1), 4.70 (d, 1 H, J = 2), 4.13 (dq, 1 H, J = 7, 2), 3.43 (s, 3 H), 2.61 (dd, 1 H, J = 1), 2.31 (s, 6 H), 2.20 (s, 3 H), 2.19(s, 3 H), 1.46 (d, 3 H, J = 7), IR (carbon tetrachloride) 1730. [α] −59° (c 0.032, methanol). Anal. Calcd for $C_{13}H_{23}NO_6$: C, 53.97; H, 8.01; N, 4.84. Found: C, 54.05; H, 7.83; N, 4.62. ^{13}C NMR 171.26, 101.59, 74.30, 71.06, 68.64, 5.46, 56.01, 43.43, 21.50, 21.39, 20.35.

Minor anomer: NMR 5.26 (dd, 1 H, J = 11,5), 5.03 (app t, 1 H, J = 2), 4.55 (d, 1 H, J = 5), 4.01 (qd, 1 H, J = 7, 2), 3.40 (s, 3 H), 3.00 (dd, 1 H, J = 11, 2), 2.37 (s, 6 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 1.31 (d, 3 H, J = 7); IR (film) 1735; [α] −51° (c 0.066, methanol). Anal. Calcd for $C_{13}H_{23}NO_6$: C, 53.97; H, 8.01; N, 4.84. Found: C, 54.13; H, 8.02; N, 4.64.

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