of methanol was hydrogenated at room temperature in a Parr apparatus at 3 atm for 15 h. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure. Sublimation of the residue at 60 °C (0.5 mm) afforded crystalline **24**: mp 130–131 °C; $[\alpha]^{25}_D$ −144.96° (*c* 0.502, CH_3OH) [lit.[23] mp 132–133 °C, $[\alpha]^{26}_D$ −145.1° (*c* 0.61, CH_3OH)]; IR (KBr) 3335, 3290 cm^{-1} (NH_2); NMR ($CDCl_3$) δ 1.28 (d, J = 7 Hz, CH_3-6), 1.50, 1.98 (2 ddd, 2 H, J_{gem} = 13, $J_{1,2ax}$ = 3.5, $J_{1,2eq} \simeq 1$, $J_{2ax,3}$ = 11.5, $J_{2eq,3}$ = 4.5 Hz, CH_2-2), 1.94 (s, 3 H, OH and NH_2), 2.84 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, CH-4), 2.97 (m, 1 H, CH-3), 3.32 (s, 3 H, OCH_3), 3.61 (dq, 1 H, $J_{4,5}$ = 9, $J_{5,6}$ = 7 Hz, CH-5), 4.67 (d, 1 H, $J_{1,2ax}$ = 3.5 Hz, CH-1).

Anal. Calcd for $C_7H_{15}NO_3$ (161.21): C, 52.16; H, 9.38; N, 8.69. Found: C, 52.24; H, 9.60; N, 8.81.

Methyl 3-Azido-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside (25). To a stirred solution of 277 mg (1.48 mmol) of **23** in 6 mL of anhydrous pyridine was added at 0 °C 0.55 mL (71 mmol) of methanesulfonyl chloride. The reaction mixture was allowed to stir at 0 °C for 6 h and subsequently poured onto 15 mL of crushed ice. The mixture was stirred until all the ice had melted and then extracted three times with 20 mL of ethyl acetate. The combined extract was washed successively with 1 N HCl, saturated $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and evaporated to dryness under reduced pressure to afford 330 mg of crystalline methyl 3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside 4-methanesulfonate. A solution of this material and 540 mg of sodium benzoate in 25 mL of anhydrous dimethylformamide was heated at 135 °C under a blanket of nitrogen for 28 h. The solvent was removed at 45 °C (0.1 mm) and the residue was extracted six times with chloroform. The combined extract was concentrated and the residue was chromatographed on 33 g of silica gel (benzene–ethyl acetate, 9:1) to give 170 mg of methyl 3-azido-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside 4-benzoate. The benzoate was dissolved in 10 mL of a 0.1 N sodium hydroxide solution in methanol–water (4:1) and the solution was stirred at room temperature under a stream of nitrogen for 6.5 h. After removal of the solvent under reduced pressure, the residue was extracted four times with acetone. The combined organic solution was filtered; concentration of the filtrate under reduced pressure gave 127 mg (46%) of liquid **25** after distillation in a short-path distillation apparatus: bp 55–60 °C (bath temperature), 0.05 mm; $[\alpha]^{25}_D$ −145.29° (*c* 0.9099, $CHCl_3$); IR ($CHCl_3$) 3580 (OH) 2105 cm^{-1} (N_3); NMR ($CDCl_3$) δ 1.27 (d, 3 H, J = 7 Hz, CH_3-6), 1.80–2.20 (m, 3 H, CH_2-2 and OH), 3.33 (s, 3 H, OCH_3), 3.60–3.80 (m, 2 H, CH-3 and CH-4), 3.87 (q, 1 H, J = 7 Hz, CH-5), 4.80 (d, 1 H, J = 3.5 Hz, CH-1); mass spectrum, m/e (relative intensity) 187 (1), 156 (17), 145 (2), 129 (20), 113 (6), 150 (9), 86 (40), 72 (31), 69 (46), 58 (100), 45 (60), 43 (45).

Anal. Calcd for $C_7H_{13}N_3O_3$ (187.2): C, 44.91; H, 7.00; N, 22.45. Found: C, 44.84; H, 7.18; N, 22.67.

Methyl 3-Amino-2,3,6-trideoxy-α-L-*lyxo*-hexopyranoside (Methyl Daunosaminide, 26). To a solution of 185 mg (1 mmol) of **25** in 5 mL of methanol was added 300 mg of platinum oxide. The mixture was hydrogenated at room temperature and atmospheric pressure until the hydrogen uptake ceased. The catalyst was removed by filtration through Celite filter aid and the filtrate was evaporated to dryness under reduced pressure. Sublimation of the white solid residue at 50–60 °C (0.05 mg) afforded 146 mg (92%) of **26**. Recrystallization from ether gave analytically pure **26**: mp 110–112 °C; $[\alpha]^{25}_D$ −161.01° (*c* 1.0024, H_2O), $[\alpha]^{25}_D$ −173.79° (*c* 0.8274, $CHCl_3$) [lit.[7] mp 109–110 °C, $[\alpha]^{25}_D$ −210 ($CHCl_3$)]; IR ($CHCl_3$) 3580 (OH), 1122, 1050, 978 cm^{-1} (OCH_3); NMR ($CDCl_3$) δ 1.27 (d, 3 H, J = 7 Hz, CH_3-6), 1.68 (m, 5 H, CH_2-2, NH_2 and OH), 3.23, 3.38 (2 m, 2 H, CH-4 and CH-3), 3.32 (s, 3 H, OCH_3), 3.84 (q, 1 H, $J_{5,6}$ = 7 Hz, CH-5), 4.71 (t, 1 H, J_{vic} = 2.5 Hz, CH-1); mass spectrum, m/e (relative intensity) 143 (4), 104 (17), 86 (47), 72 (60), 59 (100), 44 (95).

Anal. Calcd for $C_7H_{15}NO_3$ (161.20): C, 52.16; H, 9.38; N, 8.69. Found: C, 52.15; H, 9.43; N, 8.60.

3-Amino-2,3,6-trideoxy-L-*lyxo*-hexose Hydrochloride (Daunosamine Hydrochloride, 1·HCl). A solution of 7 mg of **26** in 1 mL of 0.5 N hydrochloric acid was kept at room temperature for 18 h and subsequently heated at 80 °C for 2.5 h. Removal of the solvent under reduced pressure yielded 6 mg (75%) of daunosamine hydrochloride. Recrystallization from acetone afforded analytically pure **1**·HCl: mp 173 °C; $[\alpha]^{25}_D$ −59.94° (*c* 1.0510, H_2O) [lit.[8] 168–170 °C; $[\alpha]^{25}_D$ −65.4° (*c* 1.3, H_2O)]; IR (KBr) 3360 (OH), 2920, 2005 cm^{-1} (N^+H_3); NMR (Me_2SO-d_6) δ 1.08 (d, 3 H, J = 7 Hz, CH_3-6), 1.70 (m, 2 H, CH_2-2), 3.50, 3.56 (m, 2 H, CH-3 and CH-4), 3.96 (q, 1 H, J = 7 Hz, CH-5), 5.14 (br s, 1 H, CH-1), 5.27, 6.27 (b, 2 H, 2 OH), 8.08 (b, 3 H, N^+H_3); mass spectrum, m/e (relative intensity) 148 (1), 103 (2), 90 (45), 72 (90), 59 (60), 44 (100).

Anal. Calcd for $C_6H_{13}NO_3$·HCl (183.64): C, 39.24; H, 7.68; N, 7.63. Found: C, 39.09; H, 7.74; N, 7.40.

Acknowledgment. We thank the staff of our Physical Chemistry Department for spectra and analyses.

Registry No. 1·HCl, 19196-51-1; **4**, 87858-16-0; *gluco*-**5**, 69257-51-8; *manno*-**5**, 6027-42-5; *gluco*-**6**, 87859-93-6; *manno*-**6**, 87858-13-7; **7**, 87858-14-8; **8**, 87858-15-9; **10**, 87782-50-1; **11**, 87782-51-2; **12**, 87782-52-3; **13**, 19131-10-3; **14**, 87782-54-5; **15**, 19131-11-4; **16**, 18981-61-8; **17**, 67758-44-5; **18**, 67758-43-4; **19**, 85439-70-9; **20**, 87782-55-6; **21**, 87782-57-8; **22**, 87782-56-7; **23**, 54623-22-2; **23** 4-methanesulfonate, 18981-62-9; **24**, 54623-23-3; **25**, 18981-64-1; **25** 4-benzoate, 19129-68-1; **26**, 18977-92-9; L-arabinose, 5328-37-0; nitromethane, 75-52-5; methyl 2-deoxy-β-L-*arabino*-hexopyranoside 6-*p*-toluenesulfonate, 87782-53-4.

Asymmetric Synthesis of Daunosamine[1]

Guenter Grethe,* John Sereno, Thomas H. Williams, and Milan R. Uskokovič

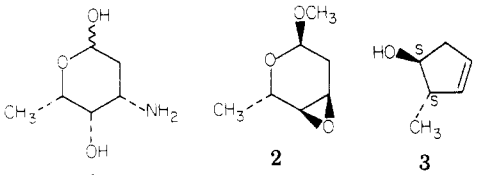
Chemical Research Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110

Received January 26, 1983

An asymmetric approach to L-daunosamine (**1**) from cyclopentadiene is described. Chiral centers and functional groups of the well-established intermediate in the synthesis of **1**, methyl 3,4-anhydro-2,6-dideoxy-α-L-*ribo*-hexopyranoside (**2**),[2,3] were derived from the asymmetrically formed 2(*S*)-methyl-3-cyclopenten-1(*S*)-ol (**3**)[4] by stereospecific epoxidation of **3** → **6** and Baeyer–Villiger ring enlargement of **7** → **8** and stereoselective reduction–glycosidation of **8** → **9** → **2**.

In the preceding paper,[2] we have outlined the objectives in the synthesis of the amino sugar L-daunosamine (**1**). Our strategy was to elaborate a practical preparation of methyl 3,4-anhydro-2,6-dideoxy-α-L-*ribo*-hexopyranoside

0022-3263/83/1948-5315$01.50/0



1 2 3

(2), the key intermediate in Goodman's synthesis,[3] which has been converted to 1 in a straightforward manner. Our first paper[2] dealt with the synthesis of 2 from naturally occurring L-arabinose. In this paper, we report on an approach to 2 from a noncarbohydrate precursor, the asymmetrically synthesized 2(*S*)-methyl-3-cyclopenten-1-(*S*)-ol (3).[4]

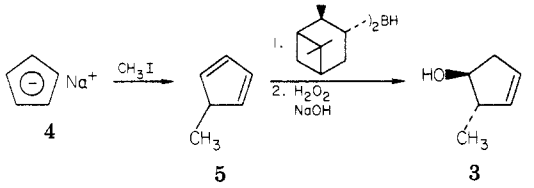
While this work was in progress, three syntheses of L-daunosamine (1) from noncarbohydrate precursors were reported. In the first case,[5] a chiral intermediate was obtained from cinnamaldehyde and fermenting baker's yeast. In the second case,[6] the chirality was introduced by addition of a chiral diol to the double bond of *trans*-4-hexenol acetal. In the most recent synthesis,[7] originating from these laboratories, three chiral centers were simultaneously formed by an enantioselective intramolecular addition involving a chiral nitrone.

In the following synthesis, we utilized an asymmetric hydroboration and a stereoselective epoxidation to introduce the required three chiral centers. Based on a process worked out previously in these laboratories,[4] hydroboration of 5 with (−)-di-3-pinanylborane on a 1-mol scale produced 2(*S*)-methyl-3-cyclopenten-1(*S*)-ol (3) in 50% yield with an optical purity higher than 95% ee (Scheme I). The directing effect of the homoallylic hydroxy group[8] was then employed to introduce the remaining two chiral centers of our target 2. As expected, epoxidation of 3 with *m*-chloroperbenzoic acid occurred cis to the hydroxy group to give the epoxide 6 in 69% yield.[9]

To complete construction of the carbohydrate skeleton, our plan called for Baeyer–Villiger ring enlargement. Jones oxidation of 6 gave the cyclopentanone 7 in 64.5% yield (Scheme II). Compound 7 could also be obtained directly from the starting 3 by oxidation with *m*-chloroperbenzoic acid in the presence of 2,2,6,6-tetramethylpiperidine hydrochloride[10] albeit in modest yield. The ring enlargement was carried out by treatment with *m*-chloroperbenzoic acid in the presence of sodium bicarbonate. The nicely crystalline lactone 8 was obtained stereospecifically (vide NMR) in almost quantitative yield.

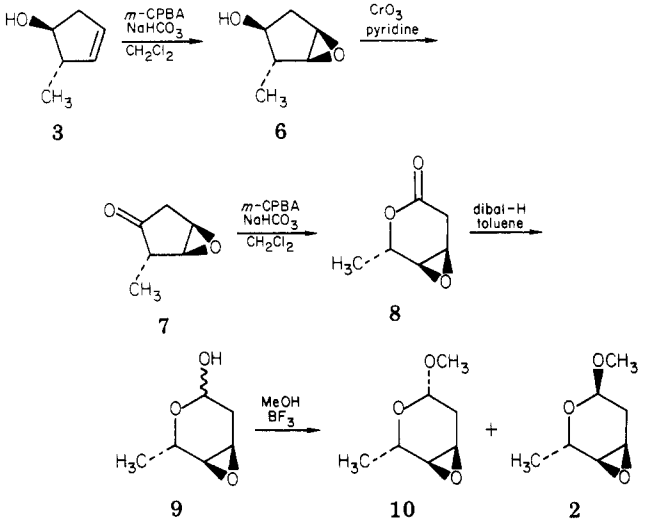
Reduction of the epoxy lactone 8 with diisobutylaluminum hydride in toluene at −70 °C gave in 77% yield

Scheme I



4 5 3

Scheme II



3 6 7 8 9 10 2

a mixture of the desired 3,4-anhydro-2,6-dideoxy-L-*ribo*-hexopyranose (9) and its anomer in a 1:3 ratio which on standing equilibrated to a 4:5 mixture. The ratio of anomers was readily determined by integration of characteristic signals in the NMR spectrum. The crucial step in the synthesis was the glycosidation of 9 without opening of the epoxide ring. This was achieved by dissolving the crude lactol in anhydrous methanol and treating the solution at 35 °C with carefully purified boron trifluoride.[11] For the success of this reaction it was essential that the progress of the reaction was closely monitored by thin-layer chromatography and that the boron trifluoride was completely devoid of any traces of hydrogen fluoride. The 2:1 product mixture of anomeric methyl glycosides 2 and 10 was obtained in 85% yield. Using rapid chromatography[12] on silica gel we were able to separate the two anomers. The spectrum of compound 2 was in complete agreement with the α-anomer described in the preceding paper.[2]

In summary, an asymmetric seven-step synthesis of methyl 3,4-anhydro-2,6-dideoxy-α-L-*ribo*-hexopyranoside (2) from cyclopentadiene was achieved. The epoxide 2 is the key intermediate in the Goodman synthesis[3] of L-daunosamine (1).

Experimental Section

General. Most details are given in the preceding paper.[2] Additionally, medium-pressure chromatography[12] was carried out on silica gel (Silica Gel Merck G-60, 230–400 mesh) at a flow rate of 40 mL/min. Toluene and acetone were distilled from and stored over molecular sieves (4 Å); 3-Å molecular sieves were used for methanol. Tetrahydrofuran was distilled from lithium aluminum hydride. Dichloromethane was passed through a column of neutral alumina (Woelm, activity I).

(1*S*,2*S*)-2-Methyl-3-cyclopenten-1-ol (3). When the procedure of Partridge, et al.[4] was followed, 3 was obtained in 49%

(1) Presented in part at the 178th National Meeting of the American Chemical Society, Washington, DC; Sept 9–14, 1979; American Chemical Society: Washington, DC, 1979; ORGN 126.

(2) Grethe, G.; Mitt, T.; Uskoković, M. R. *J. Org. Chem.*, preceding paper in this issue.

(3) Marsh, J. P.; Mosher, C. W.; Acton, E. M.; Goodman, L. *Chem. Commun.* **1967**, 973.

(4) Partridge, J. J.; Chadha, N. K.; Uskoković, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 532.

(5) Fronza, G.; Fuganti, C.; Grasselli, P. *J. Chem. Soc., Chem. Commun.* **1980**, 442.

(6) Dyong, I.; Wiemann, R. *Chem. Ber.* **113**, 2666.

(7) Wovkulich. P. M.; Uskoković, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 3956.

(8) Henbest, H. H. *Proc. Chem. Soc., London* **1963**, 159. Berti, G. In "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1973; Vol. 7, pp 93–251.

(9) After completion of our work the preparation of this compound from 3 by epoxidation with $VO(acac)_2$ and *tert*-butyl hydroperoxide in benzene was reported by Stork et al. (Stork, G.; Parkson, I.; Lee, F. K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4686).

(10) Cella, J. A.; McGrath, J. P.; Kelley, J. A.; Elsoukkary, O.; Hilper, L. *J. Org. Chem.* **1977**, *42*, 2077.

(11) Kuhn, M.; v.Wartburg, A. *Helv. Chim. Acta* **1968**, *51*, 1631.

(12) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(13) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99.

yield after distillation: bp 44 °C (7 mm); $[\alpha]^{25}_D$ +151° (*c* 1.15, CH_3OH) [lit.[4] bp 53–54 °C (10 mm); $[\alpha]^{25}_D$ +170° (*c* 1.23, CH_3OH)].

(1*S*,2*S*,3*S*,5*R*)-2-Methyl-6-oxabicyclo[3.1.0]hexan-3-ol (6). To a stirred mixture of 27.2 g (0.28 mol) of **3** and 50 g of sodium bicarbonate in 400 mL of anhydrous dichloromethane was added at 0 °C over a period of 2 h a solution of 58.3 g (0.29 mol) of 85% *m*-chloroperbenzoic acid in 1 L of anhydrous dichloromethane. After complete addition, stirring was continued for an additional 2 h at 0 °C followed by the addition of 38 g of potassium carbonate and 60 mL of a saturated aqueous solution of potassium carbonate. The solids were collected by filtration and thoroughly washed with dichloromethane. Concentration of the filtrate under reduced pressure and distillation of the residue afforded 21.8 g (69%) of **6**: bp 72–75 °C (20 mm); $[\alpha]^{25}_D$ +43.35° (*c* 1.169, CH_3OH) [lit.[9] bp 32–35 °C (0.2 mm); $[\alpha]^{25}_D$ +45.6° (*c* 1.02, CH_3OH)]; IR ($CHCl_3$) 3570 (OH), 1008 cm^{-1} (epoxide); NMR ($CDCl_3$) δ 0.86 (d, 3 H, J = 7 Hz, CH-CH_3), 2.02 (d, 2 H, $J_{3,4}$ = 3 Hz, CH_2-4), 2.30 (q, 1 H, J = 7 Hz, CH-2), 2.30 (d, 1 H, J = 9.5 Hz, OH), 3.43 and 3.61 (2 m, 2 H, CH-5 and CH-1), 3.65 (d, 1 H, J = 9.5 Hz, CH-3); mass spectrum, *m/e* (relative intensity) 114 (28), 113 (26), 99 (13), 97 (22), 96 (40), 95 (20), 85 (26), 81 (33), 73 (34), 72 (30), 71 (70), 69 (32), 68 (40), 67 (28), 61 (22), 59 (20), 58 (50), 57 (92), 55 (25), 45 (62), 44 (36), 43 (100), 41 (60).

(1*S*,2*S*,5*R*)-2-Methyl-6-oxabicyclo[3.1.0]hexan-3-one (7). A. To a solution of 40.6 g (0.37 mol) of **6** in 1 L of acetone was added at 0 °C with vigorous stirring 180 mL of 1 N Jones reagent within a period of 10 min. The heavy suspension was stirred for an additional 10 min and subsequently poured into 2 L of ice water. The mixture was extracted with dichloromethane (5×), and the combined extract was washed successively with a saturated aqueous solution of sodium bicarbonate and brine, dried over magnesium sulfate, and evaporated to dryness to afford 30.8 of crude **7**. The crude material obtained in several runs from 145 g of starting material **6** was distilled through a Vigreaux column to afford 91.9 g (64.5%) of **7**: 80.1 g boiling between 74–84 °C (20 mm), $[\alpha]^{25}_D$ +76° (*c* 1.045, CH_3OH), and 11.8 g boiling between 84–86 °C (20 mm): $[\alpha]^{25}_D$ +78° (*c* 1.115, CH_3OH); IR ($CHCl_3$) 1743 (C=O); 1040 cm^{-1} (epoxide); NMR ($CDCl_3$) δ 1.20 (d, 3 H, J = 7 Hz, CH-CH_3), 2.53 (s, 2 H, CH_2-4), 3.53 (d, 1 H, $J_{1,5}$ = 4 Hz, CH-5), 3.77 (m, 1 H, CH-1); mass spectrum, *m/e* (relative intensity) 112 (55), 97 (15), 84 (60), 69 (85), 55 (80), 41 (100), 21 (55).

B. To a stirred solution of 1.96 g (20 mmol) of **3** in 20 mL of anhydrous dichloromethane was added over a period of 20 min at 0 °C under a blanket of argon a solution of 4.44 g (21.5 mmol) of 85% *m*-chloroperbenzoic acid. After complete addition, the mixture was stirred for an additional 2 h at 0 °C. The precipitate was removed by filtration and the filter cake was washed with dichloromethane. To the filtrate was added at 0 °C 4.5 g (22 mmol) of 85% *m*-chloroperbenzoic acid and 1 mL (0.2 mol) of a 0.2 M solution of 2,2,6,6-tetramethylpiperidine hydrochloride in a 1% mixture of ethanol in dichloromethane. The reaction mixture was stirred at 0 °C for 30 min and subsequently for 2 h at 35 °C. The precipitate was removed by filtration and the filtrate was washed twice with a saturated aqueous solution of sodium bicarbonate and brine. The organic layer was dried over magnesium sulfate and evaporated to dryness under reduced pressure. Distillation of the residue in a Büchi-Kugelrohr distillation apparatus at 80 °C (20 mm) afforded 0.553 g (25%) of **7**.

(1*S*,2*S*,6*R*)-2-Methyl-3,7-dioxabicyclo[4.1.0]heptan-4-one (8). To a solution of 5.6 g (50 mmol) of **7** in 400 mL of anhydrous dichloromethane was added 15 g of sodium bicarbonate and 12.9 g (64 mmol) of 85% *m*-chloroperbenzoic acid. The suspension was stirred at room temperature for 72 h and then filtered through Celite filter aid. The filtrate was evaporated to dryness under reduced pressure, the residue was triturated with dichloromethane, and insolubles were removed by filtration. The filtrate was washed twice with a saturated aqueous solution of sodium bicarbonate, dried over magnesium sulfate, and evaporated to dryness under reduced pressure. After removing volatile material by distillation at 70 °C (0.1 mm), the residue slowly crystallized on standing to give 6.25 g (98%) of **8**, mp 51–52 °C. Recrystallization from ether afforded analytically pure **8**: mp 52.5–53.5 °C; $[\alpha]^{25}_D$ +147.26° (*c* 0.995, CH_3OH); IR ($CHCl_3$) 1740 (CO), 1188 cm^{-1} (epoxide); NMR ($CDCl_3$) δ 1.48 (d, 3 H, J = 7 Hz, $CHCH_3$), 2.83, 3.15 (*AB*X, 2 H, J_{gem} = 18.5, J_{vic} = 1.5 and 2 Hz, CH_2-5), 3.29 and 3.45 (m, 1 H each, $J_{1,6}$ = 4.5 Hz, CH-1 and CH-6), 4.85 (m, 1 H, J_{CHCH_3} = 7 Hz, $J_{1,2}$ = 1 Hz, CH-2); mass spectrum, *m/e* (relative intensity) 128 (20), 113 (10), 84 (50), 69 (50), 55 (100).

Anal. Calcd for $C_6H_8O_3$ (128.12): C, 56.25; H, 6.29. Found: C, 56.04; H, 6.43.

3,4-Anhydro-2,6-dideoxy-L-*ribo*-hexose (9). To a solution of 2.58 g (20 mmol) of **8** in 300 mL of anhydrous toluene cooled to −75 °C was added under a blanket of argon 14 mL (24.5 mmol) of a 1.75 M solution of Dibal–H in toluene. The reaction mixture was stirred at −75 °C for 2 h and then quickly poured in an argon atmosphere into a Buchner funnel containing a slurry of 260 g of silica gel in toluene. The slurry was washed with dichloromethane–methanol (9:1). Care has to be taken that the slurry does not dry out during the filtration procedure. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residual oil (2.66 g) was distilled in a Büchi-Kugelrohr distillation apparatus to afford 2.03 g (77%) of **9** as a 1:3 mixture of α and β anomers: bp 90 °C (bath temperature) (0.1 mm). NMR ($CDCl_3$) for α-anomer: δ 1.39 (d, 3 H, $J_{5,6}$ = 7 Hz, CH-CH_3), 2.18 (t, 2 H, $J_{1,2}$ = 2.5 Hz, CH_2-2), 3.13 (d, 1 H, $J_{3,4}$ = 4.5 Hz, CH-4), 3.44 (m, 1 H, CH-3), 4.34 (d, 1 H, $J_{1,OH}$ = 11 Hz, OH), 4.42 (q, 1 H, $J_{5,6}$ = 7 Hz, CH-5), 5.03 (dt, 1 H, $J_{1,OH}$ = 11 Hz, $J_{1,2}$ = 2.5 Hz, CH-1). NMR for the β-anomer: δ 1.41 (d, 3 H, $J_{5,6}$ = 7 Hz, CH-CH_3), 1.76 (ddd, 1 H, J_{gem} = 14.5 Hz, $J_{1,2ax}$ = 9 Hz, $J_{2ax,3}$ = 2 Hz, CH_2-2, axial H), 2.33 (dt, 1 H, J_{gem} = 14.5, $J_{1,2eq}$ = $J_{2eq,3}$ = 2 Hz, CH_2-2, equatorial H), 2.97 (d, 1 H, $J_{3,4}$ = 4.5 Hz, CH-4), 3.40 (m, 1 H, CH-3), 3.94 (d, 1 H, $J_{1ax,OH}$ = 5 Hz, OH), 4.07 (q, 1 H, $J_{5,6}$ = 7 Hz, CH-5), 4.82 (ddd, 1 H, $J_{1,OH}$ = 5, $J_{1,2ax}$ = 9, $J_{1,2eq}$ = 3 Hz, CH-1).

Anal. Calcd for $C_6H_{10}O_3$ (130.14): C, 55.37; H, 7.75. Found: C, 54.70; H, 7.67.

Methyl 3,4-Anhydro-2,6-dideoxy-α-L-*ribo*-hexopyranoside (2) and Methyl 3,4-Anhydro-2,6-dideoxy-β-L-*ribo*-hexopyranoside (10). A stock solution of 8.8% (w/v) of boron trifluoride in methanol was prepared by passing boron trifluoride successively through concentrated sulfuric acid, sodium fluoride, and boric acid anhydride into anhydrous methanol. At 35 °C, 0.45 mL of this reagent was added under a blanket of argon to a stirred solution of 8.8 g (68 mmol) of **9** in 150 mL of anhydrous methanol. Stirring was continued at 35 °C until TLC (benzene–ethyl acetate, 1:1) indicated complete consumption of the starting material (2 h). The reaction mixture was quenched by the addition of 2.5 g of sodium bicarbonate and stirred at room temperature for an additional 0.25 h. The solids were removed by filtration, the filter cake was washed with methylene chloride, and the combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was triturated with dichloromethane, the solids were removed by filtration, and the filtrate was concentrated under reduced pressure. Distillation of the residue in a Büchi-Kugelrohr distillation apparatus at 90 °C (bath temperature) (0.1 mm) yielded 8.3 g (85%) of a crude mixture of anomers **2** and **10** as a pale yellow liquid.

For separation of the anomers, a small amount (ca. 1 g) was chromatographed on a 20-mm × 150-mm column of silica gel (toluene–ethyl acetate, 1:1) using medium pressure. From fractions 11–15 (10-mL fractions) was obtained 100 mg of the oily β-anomer **10**: NMR ($CDCl_3$) δ 1.41 (d, 3 H, $J_{5,6}$ = 7 Hz, CH-CH_3), 1.75 (ddd, 1 H, J_{gem} = 14.5, $J_{1,2ax}$ = 9, $J_{2ax,3}$ = 2Hz, CH_2-2, axial H), 2.26 (m, 1 H, J_{gem} = 14.5, $J_{1,2eq}$ = $J_{2eq,3}$ = 2 Hz, CH_2-2, equatorial H), 2.97 (d, 1 H, $J_{3,4}$ = 4.5 Hz, CH-4), 3.37 (m, 1 H, H-3), 3.40 (s, 3 H, OCH_3), 4.04 (q, 1 H, $J_{5,6}$ = 7 Hz, CH-5), 4.38 (dd, 1 H, $J_{1,2ax}$ = 9, $J_{1,2eq}$ = 3 Hz, CH-1).

Fractions 17–22 yielded 200 mg of the oily α-anomer **9**:[1] NMR ($CDCl_3$) δ 1.39 (d, 3 H, $J_{5,6}$ = 7 Hz, CH-CH_3), 2.12 (m, 2 H, $J_{1,2}$ = 3.5 Hz, CH_2-2), 2.99 (d, 1 H, $J_{3,4}$ = 4.5 Hz, CH-4), 3.28 (m, 1 H, CH-3), 3.36 (s, 3 H, OCH_3), 4.17 (q, 1 H, $J_{5,6}$ = 7 Hz, CH-5), 4.65 (t, 1 H, $J_{1,2}$ = 3.5 Hz, CH-1).

Registry No. **2**, 67909-18-6; **3**, 39947-42-7; **5**, 96-38-8; **6**, 82335-24-8; **7**, 87858-17-1; **8**, 87858-18-2; **9** (α-isomer), 87782-58-9; **9** (β-isomer), 87782-59-0; **10**, 85439-72-1; L-daunosamine, 26548-47-0.