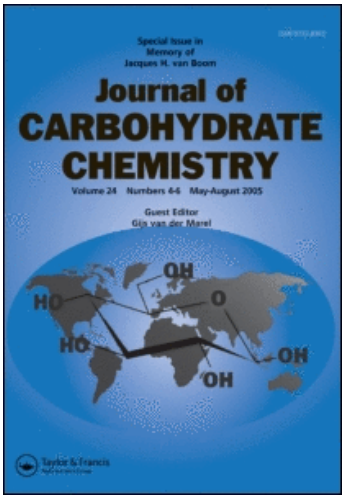

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AN ALTERNATIVE SYNTHESIS OF ACOSAMINE AND RISTOSAMINE

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ABSTRACT

The Henry reaction of (2S)-2-benzyloxypropanal with (2S)-1,2-O-isopropylidene-4-nitro-1,2-butanediol, leading to naturally occurring 3-amino-2,3,6-trideoxy-L-hexoses, acosamine and ristosamine, is described.

INTRODUCTION

Recently, much interest has been focused on the synthesis of important carbohydrates from non-carbohydrate precursors.[1] 3-Amino-2,3,6-trideoxy-L-hexoses have been chosen as targets of the present study, since a number of such compounds are components of important antibiotics; doxorubicin (daunosamine), actinoidin (acosamine) and ristomycin (ristosamine).[2] Several synthetic routes toward 3-amino-2,3,6-trideoxy-L-hexoses have been described starting from L-rhamnose[3] or D-mannose.[4] Now, we wish to report an alternative synthesis of acosamine and ristosamine from (2S)-2-benzyloxypropanal (8) and (2S)-1,2-O-isopropylidene-4-nitro-1,2-butanediol (12).

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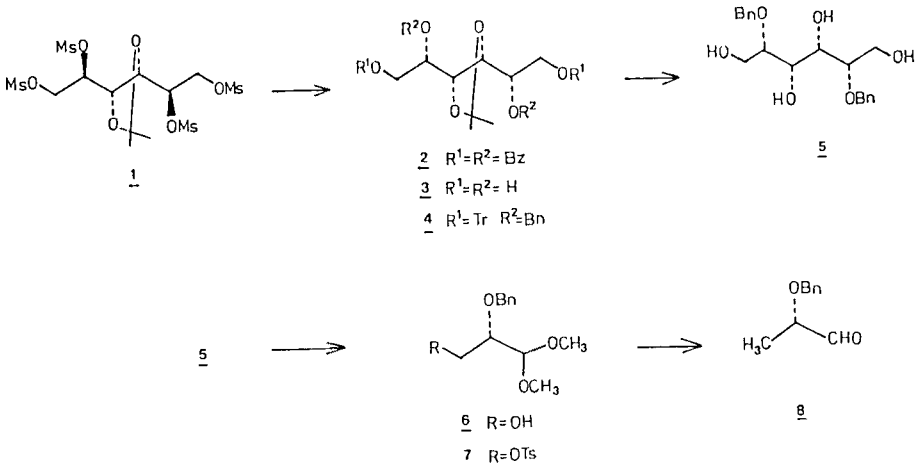
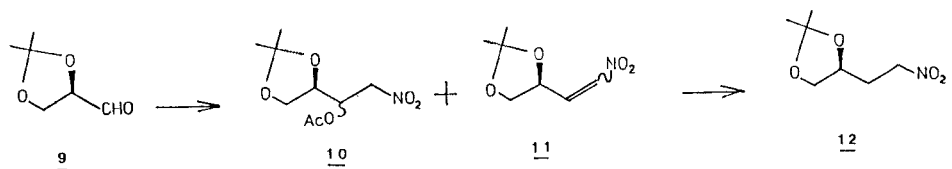


Scheme 1



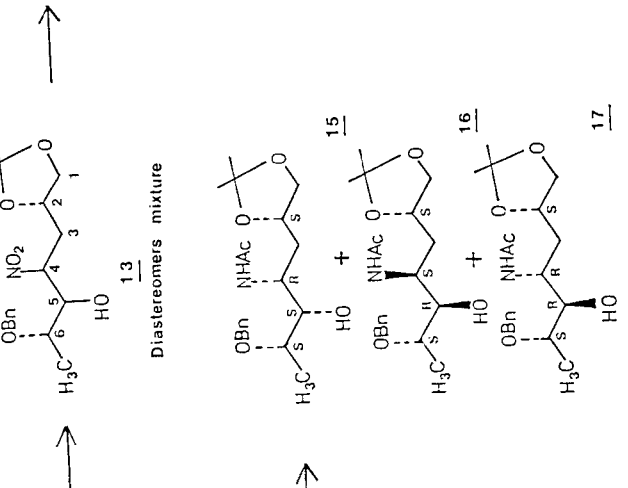
Scheme 2

RESULTS AND DISCUSSION

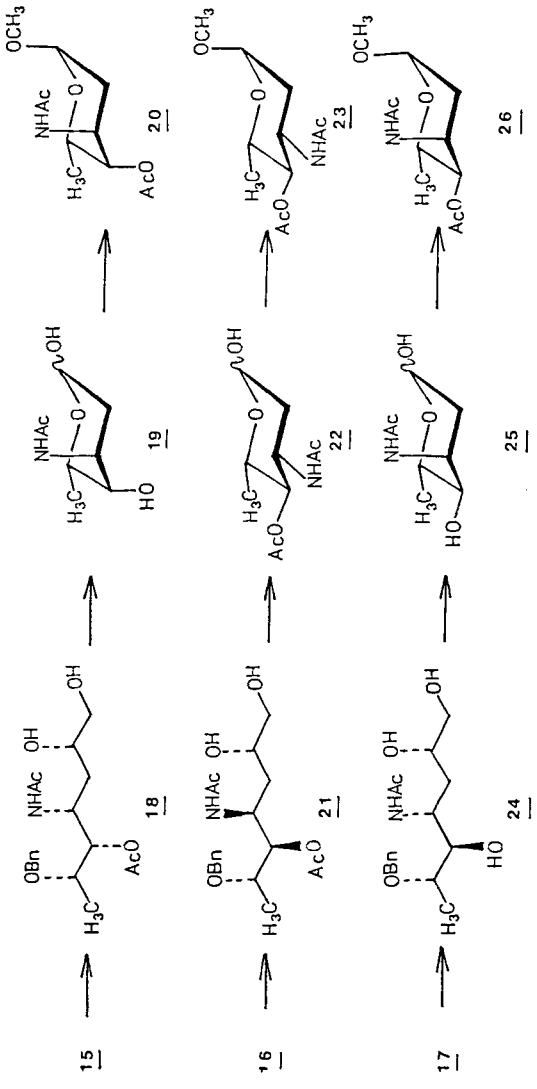
Recently, a derivative of (2S)-hydroxypropanal was simply prepared from (S)-ethyl lactate[5] in a synthesis of rhodinose, a trideoxyhexose moiety of the antibiotic streptolydigin.[6] The synthesis of 8 was initiated from a D-mannitol derivative, 3,4-O-isopropylidene-1,2,5,6-tetra-O-mesyl-D-mannitol[7] (1), furnishing 8 in an overall yield of 16% (Scheme 1). Another synthon, (2S)-1,2-O-isopropylidene-4-nitro-1,2-butanediol 12 has been prepared from 2,3-O-isopropylidene-D-glyceraldehyde[8] (9) in an overall yield of 52% (Scheme 2).

The Henry reaction of 8 and 12 in the presence of sodium methoxide gave a diastereomeric mixture of the nitro alcohol derivative (13), which was converted to the amino alcohols (14) (Scheme 3). N-Acetylation of 14 afforded the three 4-acetamido-6-O-benzyl-1,2-O-isopropylidene-1,2,5,6-heptanetetrols: (2S,4R,5S,6S)- (15), (2S,4S,5R,6S)- (16), and (2S,4R,5R,6S)- (17), in 15, 14, and 15% yields respectively from 8. Acetylation of 15, successive de-O-isopropylidenation, catalytic de-O-benzylation, periodate oxidation of the resultant diol, and de-O-acetylation gave 3-acetamido-2,3,5-trideoxy-L-hexopyranose (19) in 78% yield (Scheme 4). Glycosidation of 19 and subsequent acetylation afforded methyl 3-acetamido-4-O-acetyl-2,3,6-trideoxy-α-L-hexopyranoside (20) in 38% yield. Analogous reactions of 16 and 17 gave the corresponding methyl 3-acetamido-4-O-acetyl-2,3,6-trideoxy-L-hexopyranoside (23) and (26) in 36 (from 16) and 18 (from 17)% yields, respectively.

There are four theoretically possible stereoisomers from the Henry reaction of 8 and 12. Of the three methyl glycosides ultimately derived from this reaction, compounds 23 and 26 have been identified as methyl N,O-diacetyl-α-acosaminide[9] and methyl N,O-diacetyl-α-ristosaminide,[10] by comparison of observed and reported physical data (mp, $[\alpha]_D$ and ^1H NMR). Compound 20 is not identical with a daunosamine derivative,[11] but has been identified as methyl 3-acetamido-4-O-acetyl-2,3,6-trideoxy-α-L-xylo-hexopyranoside. The ^1H NMR spectrum of 20 contains two three proton



Scheme 3



Scheme 4

singlets at δ 1.98 and 2.13 which are attributed to axial acetamido methyl protons and to axial acetoxy methyl protons, respectively. The anomeric configuration of 20 was established as α after observing its large negative specific rotation. Such large negative specific rotations were also observed for 23 and 26, each being an α-L-pyranoside. Therefore, the designated structures of 15, 16 and 17 have been reasonably deduced from the structures of 20, 23 and 26.

When potassium fluoride was used as a catalyst in the Henry reaction between 8 and 12, the reaction proceeded to give 15, 16 and 17 in 16, 22 and 16% yields, respectively.

EXPERIMENTAL

General Procedures. Melting points were determined with a Mitamura Riken micro apparatus and are uncorrected. Solutions were evaporated under diminished pressure at a bath temperature below 40° C. Specific rotations were measured in a 1-dm tube with a JEOL DIP-4 polarimeter. Column chromatography was performed using Wakogel C-300, and TLC carried out on glass plates coated with Merck Kieselgel 60 F_{254}, compounds being detected under UV light and by spraying with a H_2SO_4 followed by heating. Preparative TLC (PTLC) was performed on glass plates (20x20 cm) coated with Merck Kieselgel 60 PF_{254}. IR spectra were recorded with Hitachi Model-255 (KBr) and JEOL Model A-202 ($CHCl_3$) spectrometers. ^1H NMR spectra were recorded with a Varian EM 390 spectrometer. Chemical shifts for $CDCl_3$ solution were reported from internal tetramethylsilane. Exact mass spectra were taken on a Hitachi M-80 mass spectrometer. Elemental analyses were performed by Mr. Saburo Nakada of the University, to whom our thanks are due.

(2S)-2-Benzyloxypropanal (8). Starting from 3,4-O-isopropylidene-1,2,5,6-tetra-O-mesyl-D-mannitol[7] (1) (25.2 g, 47.2 mmol), 21.8 g (72%) of 1,2,5,6-tetra-O-benzoyl-3,4-O-isopropylidene-L-iditol (2), mp 100-101 °C; $[\alpha]_D^{24}$+1.4° (c 0.97, $CHCl_3$) was obtained

by refluxing with sodium benzoate (33.6 g, 236 mmol) in DMF (240 mL) for 3 h and then purified by SiO_2 column chromatography. A 21.8 g (34 mmol) portion of 2 was hydrolyzed in 0.4 M methanolic sodium methoxide (340 mL) overnight giving 4.5 g (59%) of 3,4-O-isopropylidene-L-iditol (3) as a syrup. The compound 3 (17.1 g, 76.9 mmol) was tritylated with trityl chlorde (53.6 g, 193 mmol) in pyridine (150 mL) containing 4-dimethylaminopyridine (1.9 g, 15.4 mmol) and subsequently benzylated with benzyl bromide (23.1 mL, 194 mmol) in the usual manner to give 52.6 g (77%) of 2,5-di-O-benzyl-3,4-O-isopropylidene-1,6-di-O-trityl-L-iditol (4) as a syrup $[\alpha]_D^{20}$+23.1° (c 1.05, $CHCl_3$). A 58.0 g (65.4 mmol) portion of 4 was hydrolyzed in 4 M HCl (240 mL) and dioxane (400 mL) at 50 °C for 5 h yielding 16.4 g (70%) of 2,5-di-O-benzyl-L-iditol (5), mp 79-79.5 °C; $[\alpha]_D^{23}$+28.8° (c 1.01, $CHCl_3$). Oxidative cleavage of 5 (73.9 mg, 0.2 mmol) with sodium periodate (48.0 mg, 0.22 mmol) in aqueous MeOH (2:5, 1.4 mL) for 5 h, followed by refluxing in MeOH (1.5 mL) in the presence of Amberlite IR 120 (H^+) resin (16 mg) afforded 86.9 mg (94%) of (2S)-2-benzyloxy-3-hydroxy-1,1-dimethoxypropane (6) as a syrup, $[\alpha]_D^{23}$+22.8° (c 0.98, $CHCl_3$). A 106 mg (0.47 mmol) portion of 6 was tosylated with p-toluenesulfonyl chloride (134 mg, 0.70 mmol) in pyridine (1.5 mL) giving 167.0 mg (94%) of the 3-O-tosylate (7), $[\alpha]_D^{19}$-1.9° (c 1.19, $CHCl_3$). Deoxygenation of 7 (143 mg. 0.38 mmol) with lithium aluminum hydride (21.3 mg, 0.56 mmol) in THF (2 mL) under reflux, followed by hydrolysis in 80% aqueous trifluoroacetic acid (1 mL) gave 49 mg (78)% of the title compound 8 as a syrup, $[\alpha]_D^{16}$-28.8 (c 3.79, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.30 (3H, d, J=7 Hz, CH_3), 3.87 (1H, dq, J=7 Hz, J=2 Hz, H-2), 4.61 (2H, s, $OCH_2C_6H_5$), 7.33 (5H, s, $OCH_2C_6H_5$), 9.66 (1H, d, J=2 Hz, CHO).

Anal. Calcd for $C_{10}H_{12}O_2$: m/z 164.0836. Found: M, 164.0828.

(2S)-1,2-O-Isopropylidene-4-nitro-1,2-butanediol (12). To a solution of 2,3-O-isopropylidene-D-glyceraldehyde[8] (9) (5.01 g, 38.2 mmol) in MeOH (33 mL) were added nitromethane (21 mL, 382 mmol) and 1 M sodium methoxide in MeOH (57 mL). The mixture was

stirred at 0°C for 1.5 h. After acidification with acetic acid (pH 5), the reaction mixture was evaporated and the residue was acetylated with acetic anhydride (10.8 mL) and pyridine (6.2 mL) in dichloromethane (55 mL). The mixture was worked up, giving 7.3 g of a mixture of the nitro acetate (10) and the nitro olefin (11); IR ($CHCl_3$) 2980, 1750 and 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08 (s, $OCOCH_3$) and 5.20-5.42 (m, CH=CH). The mixture was hydrogenated with sodium borohydride (4.3 g, 115 mmol) in EtOH (70 mL) to afford 3.5 g (52%) of the title compound 12 as a syrup: R_f 0.74 on TLC (1:10 v/v EtOH:$PhCH_3$); $[\alpha]_D^{23}$-15.4° (c 1.19, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.30 and 1.38 (each 3H, each s, $C(CH_3)_2$), 1.91-2.55 (2H, m, H-3), 3.44-3.74 (1H, m, H-2), 3.99-4.34 (2H, m, H-1), 4.51 (2H, t, J=7 Hz, H-4).

Anal. Calcd for $C_7H_{13}NO_4$ m/z 175.0843. Found: M, 175.0826.

Henry reaction of 8 and 12. 1) The sodium methoxide-catalyzed reaction. To a stirred solution of 12 (2.65 g, 15.2 mmol) in MeOH (30 mL) were added 1 M sodium methoxide in MeOH (16 mL) and a solution of 8 (1.97 g, 12.6 mmol) in MeOH (20 mL) under ice cooling. After 15 h at 5 °C, the solution was acidified with acetic acid to pH 4 and hydrogenated in the presence of Raney nickel T-4 (ca. 10 g) under hydrogen atmosphere (3.4 kg/cm^2) for 2.5 h. The catalyst was removed by filtration, and the filtrate was concentrated. The residue was acetylated with acetic anhydride (50 mL) in MeOH (50 mL), giving 3.7 g of a crude product. The product was fractionated on a SiO_2 column (300 g) using 1:20 (v/v) EtOH:$PhCH_3$ as the eluent. Fractions corresponding to R_f 0.41 on TLC (1:5 EtOH:$PhCH_3$) were evaporated to afford 623 mg (15%) of (15) as a syrup: $[\alpha]_D^{23}$+64.3° (c 1.01, $CHCl_3$); IR ($CHCl_3$) 3340, 2990, 1645, 1530, 1210, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (3H, d, J=5 Hz, CH_3-7), 1.31 and 1.39 (each 3H, each s, $C(CH_3)_2$), 1.71-2.11 (2H, m, H-3), 1.91 (3H, s, $NCOCH_3$), 3.13-4.30 (7H, m, H-1,1',2,4,5,6 and OH), 4.54 (2H, ABq, $OCH_2C_6H_5$), 5.91 (1H, d, J=10 Hz, NH), 7.34 (5H, s, $OCH_2C_6H_5$).

Anal. Calcd for $C_{19}H_{30}NO_5$: m/z 352.2122. Found: M+H, 352.2114.

Fractions corresponding to R_f 0.38 on TLC (1:5 EtOH:$PhCH_3$) were evaporated to afford 589 mg (14%) of (16) as a syrup: $[\alpha]_D^{23}$+28.8° (c 1.08, $CHCl_3$); IR ($CHCl_3$) 3350, 2980, 1640, 1520, 1370, 1210, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (3H, d, J=5 Hz, CH_3-7), 1.32 and 1.38 (each 3H, each s, $C(CH_3)_2$), 1.65-2.04 (2H, m, H-3), 1.82 (3H, s, $NCOCH_3$), 3.27-4.27 (7H, m, H-1,1',2,4,5,6 and OH), 4.50 (2H, ABq, $OCH_2C_6H_5$), 6.09 (1H, d, J=8 Hz, NH), 7.36 (5H, s, $OCH_2C_6H_5$).

Anal. Calcd for $C_{19}H_{29}NO_5$: C, 64.93; H, 8.32; N, 3.99. Found: C, 64.62; H, 8.28; N, 3.82.

Fractions corresponding to R_f 0.35 on TLC (1:5 EtOH:$PhCH_3$) were evaporated to afford 643 mg (15%) of (17) as a syrup: $[\alpha]_D^{24}$+24.7° (c 1.38, $CHCl_3$); IR ($CHCl_3$) 3300, 2990, 1645, 1545, 1370, 1215, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) 1.32 (9H, s, CH_3-7 and $C(CH_3)_2$), 1.62-2.05 (2H, m, H-3), 1.90 (3H, s, $NCOCH_3$), 3.33-4.27 (7H, m, H-1,1',2,4,5,6 and OH), 4.51 (2H, ABq, $OCH_2C_6H_5$ 6.16 (1H, d, J=9 Hz, NH), 7.36 (5H, s, $OCH_2C_6H_5$).

Anal. Calcd for $C_{19}H_{29}NO_5$: m/z 351.2043. Found: M, 351.2006.

2) The potassium fluoride-catalyzed reaction. A solution of 12 (673 mg, 3.84 mmol) and 8 (505 mg, 3.20 mmol) in acetonitrile (4 mL) was stirred in the presence of potassium fluoride (201 mg, 3.46 mmol). After 10 h, the mixture was worked up as described for the methoxide catalyzed reaction to give 167 mg (16%) of 15, 233 mg (22%) of 16 and 170 mg (16%) of 17.

(2S,4R,5S,6S)-4-Acetamido-5-O-acetyl-6-O-benzyl-1,2,5,6-heptanetetrol (18). The compound 15 (30 mg, 0.08 mmol) was acetylated with acetic anhydride (3 mL) in pyridine (3 mL) for 3 h. The product was hydrolyzed in 80% aqueous acetic acid (0.5 mL) for 4 h. A crude product was purified on a SiO_2 column using 1:5 (v/v) EtOH:$PhCH_3$. Fractions corresponding to R_f 0.11 on TLC (1:5 EtOH:$PhCH_3$) were evaporated to afford 25 mg (93%) of 18 as a syrup: $[\alpha]_D^{22}$+66.0° (c 1.25, MeOH); ^1H NMR (CD_3OD) δ 1.23 (3H, d, J=6 Hz, CH_3-7), 1.42-1.72 (2H, m, H-3), 1.92 (3H, s, $NCOCH_3$), 2.01 (3H, s, $OCOCH_3$), 3.38-4.54 (5H, m, H-1,1',2,4 and 6), 4.51 (2H, ABq,

$OCH_2C_6H_5$), 5.02 (1H, dd, J=3 Hz, J=7 Hz, H-5), 7.32 (5H, s, $OCH_2C_6H_5$).

Anal. Calcd for $C_{18}H_{28}NO_6$: m/z 354.1915. Found: M+H, 354.1942.

3-Acetamido-2,3,6-trideoxy-L-xylo-hexopyranose (19). A solution of 18 (87 mg, 0.25 mmol) was hydrogenolyzed in the presence of 20% $Pd(OH)_2/C$ (22 mg) and cyclohexene (0.9 mL)[12] under reflux for 2.5 h. After the catalyst was removed by filtration, the filtrate was evaporated. To a stirred solution of the residue in MeOH (1 mL) was added an aqueous solution (0.5 mL) of sodium periodate (52 mg, 0.25 mmol). After 2 h, the mixture was filtered and the filtrate was concentrated. The residue was dissolved in 0.1 M methanolic sodium methoxide (4 mL). After 3 h stirring, the solution was neutralized with acetic acid and evaporated. The residue was purified on a SiO_2 column using 10:1 (v/v) $CHCl_3$:EtOH as the eluent. Fractions corresponding to R_f 0.35 on TLC (10:1 $CHCl_3$:EtOH) were concentrated to dryness to give 39 mg (84%) of 19, mp 105-106 °C; $[\alpha]_D^{24}$-11.0° (c 0.99, MeOH); ^1H NMR (CD_3OD) 1.15 and 1.20 (total 3H, each d, J=7 Hz, H-6), 1.34-2.31 (2H, m, H-2), 1.95 (3H, s, $NCOCH_3$), 3.51-4.37 (3H, m, H-3,4 and 5), 4.81-5.28 (total 1H, dd and m, J=3 Hz, J=10 Hz, H-1).

Anal. Calcd for $C_8H_{16}NO_4$: m/z 190.1078. Found: M+H, 190.1080.

Methyl 3-Acetamido-4-O-acetyl-2,3,6-trideoxy-α-L-xylo-hexopyranoside (20). Compound 19 (35.0 mg. 0.19 mmol) was acetylated with acetic anhydride (1 mL) in pyridine (1 mL) for 3 h, the reaction mixture was concentrated, the residue was dissolved in 1.4 wt% HCl in MeOH (1.5 mL), and the mixture refluxed for 5.5 h. After neutralization with basic lead carbonate, insoluble material was removed. Concentration of the filtrate gave a residue which was acetylated with acetic anhydride (1 mL) in pyridine (1 mL) for 13 h. Extractive work up of the reaction mixture was followed by purification of the crude product on a SiO_2 column using EtOH:$PhCH_3$ (v/v) 1:20 as the eluent. Fractions corresponding to R_f 0.33 on TLC (EtOH:$PhCH_3$ 1:5) were concentrated to dryness affording 20 (17 mg, 38%), mp 69-70 °C; $[\alpha]_D^{24}$-109.2° (c 0.54, MeOH);

IR ($CHCl_3$) 3430, 2950, 1740, 1670, 1515, 1370, 1235, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (3H, d, J=6 Hz, H-6), 1.46-1.76 (1H, m, H-2 eq), 1.94-2.37 (1H, m, H-2 ax), 1.98 (3H, s, $NCOCH_3$), 2.13 (3H, s, $OCOCH_3$), 3.42 (3H, s, OCH_3), 3.97-4.29 (2H, m, H-3 and 5), 4.73-4.90 (2H, m, H-1 and 4), 6.84 (1H, d, J=8 Hz, NH).

Anal. Calcd for $C_{11}H_{19}NO_5$: m/z 245.1262. Found: M, 245.1263.

(2S,4S,5F,6S)-4-Acetamido-5-O-acetyl-6-benzyl-1,2,5,6-heptanetetrol (21). The compound 16 was converted to 21 as described in the case of 15 to 18 in 85% yield: 21, as a syrup R_f 0.12 on TLC (1:5 EtOH:$PhCH_3$); $[\alpha]_D^{28}$-46.3 (c 1.67, MeOH); ^1H NMR (CD_3OD) δ 1.16 (3H, d, J=6 Hz, CH_3-7), 1.33-1.63 (2H, m, H-3), 1.96 (3H, s, $NCOCH_3$), 2.10 (3H, s, $OCOCH_3$), 3.36-4.61 (5H, m, H-1,1',2,4 and 6), 4.52 (2H, s, $OCH_2C_6H_5$), 4.94 (1H, dd, J=4 Hz, J=7 Hz, H-5), 7.34 (5H, s, $OCH_2C_6H_5$).

Anal. Calcd for $C_{18}H_{28}NO_6$: m/z 354.1914. Found: M+H, 354.1905.

3-Acetamido-4-O-acetyl-2,3,6-trideoxy-L-arabino-hexopyranose (22). Hydrogenolysis and successive periodate oxidation of 21 as described in the case of 18 to 19 afforded 22 in 86% yield after purification on a SiO_2 column using 10:1 $CHCl_3$:EtOH as the eluent: 22, R_f 0.16 on TLC (1:5 EtOH:$PhCH_3$); mp 182.5-183 °C; $[\alpha]_D^{25}$-92.0° (c 1.34, MeOH); IR (KBr) 3480, 3290, 1735, 1650, 1545, 1375, 1240, 1045 cm-1; ^1H NMR (CD_3OD) δ 1.10 and 1.16 (total 3H, each s, J=6.5 Hz, H-6), 1.43-2.18 (2H, m, H-2), 1.87 (3H, s, $NCOCH_3$), 2.01 (3H, s, $OCOCH_3$), 3.46-4.60 (3H, m, H-3,4 and 5), 4.85-5.32 (1H, m, H-1).

Anal. Calcd for $C_{10}H_{17}NO_5$: C, 51.94; H, 7.41; N, 6.06. Found: C, 51.86; H, 7.24; N, 5.86.

Methyl 3-Acetamido-4-O-acetyl-2,3,6-54ideoxy-α-L-arabino-hexopyranoside (methyl N,O-diacetylacosaminide) (23). The acosaminide 23 was obtained starting from 22 as described in the case of 19 to 20 in 49% yield: R_f 0.33 on TLC (1:5 EtOH;$PhCH_3$); mp 160.5-161 °C (lit.[9] mp 163-164 °C); $[\alpha]_D^{25}$-192.3° (c 0.63, MeOH), lit.[9] $[\alpha]_D^{22}$-191 (c 0.52, MeOH) ; IR ($CHCl_3$) 3280, 1730, 1640, 1540, 1365, 1235, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (3H, d, J=6 Hz, H-6), 1.41-2.57 (2H, m, H-2), 1.91 (3H, s, $NCOCH_3$), 2.07 (3H, s, $OCOCH_3$),

3.34 (3H, s, OCH_3), 3.71-4.08 (1H, m, H-5), 4.21-4.58 (2H, m, H-3 and 4), 4.63-4.80 (1H, m, H-1), 5.80 (1H, br d, J=9 Hz, NH).

Anal. Calcd for $C_{11}H_{19}NO_9$: m/z 245.1261. Found: M, 245.1235.

(2S,4R,5R,6S)-4-Acetamido-6-O-benzyl-1,2,5,6-heptanetetrol (24). Hydrolysis of 17 with 80% aqueous acetic acid afforded 24 in 90% yield as a syrup, R_f 0.09 on TLC (1:5 EtOH:$PhCH_3$); $[\alpha]_D^{25}$+6.3° (c 1.15, MeOH); ^1H NMR (CD_3OD) δ 1.23 (3H, d, J=6 Hz, CH_3-7), 1.38-2.01 (2H, m, H-3), 1.91 (3H, s, $NCOCH_3$), 3.11-5.15 (8H, m, H-1,1',2,4,5,6 and $OCH_2C_6H_5$), 7.33 (5H, s, $OCH_2C_6H_5$).

Anal. Calcd for $C_{16}H_{26}NO_5$ m/z 312.1810. Found: M+H, 312.1814.

3-Acetamido-2,3,6-trideoxy-L-ribo-hexopyranose (25). Periodate oxidation of 24, followed by hydrogenolysis with cyclohexene-$Pd(OH)_2$/C as described in the case of 18 to 19 gave 25 in 36% yield: R_f 0.13 on TLC (1:5 EtOH:$PhCH_3$); mp 129-130 °C; $[\alpha]_D^{25}$-20.8 (c 2.10, MeOH); ^1H NMR (CD_3OD) δ 1.16 and 1.24 (total 3H, each d, J=6 Hz, H-6), 1.46-2.10 (2H, m, H-2), 1.95 (3H, s, $NCOCH_3$), 3.32-4.56 (3H, m, H-3,4 and 5), 5.13-5.64 (total 1H, m, H-1).

Anal. Calcd for $C_8H_{15}NO_4$: m/z 189.1002. Found: M, 189.1001.

Methyl 3-Acetamido-4-O-acetyl-2,3,6-trideoxy-α-L-ribo-hexopyranoside (methyl) N,O-diacetylristosaminide) (26). By the reaction sequence used to convert 19 to 20, the compound 25 was converted to 26 in 56% yield: R_f 0.31 on TLC (1:5 EtOH:$PhCH_3$); mp 53-54 °C (lit.[10] mp 51-52 °C); $[\alpha]_D^{23}$-130.4 (c 0.49, $CHCl_3$) lit.[10] $[\alpha]_D^{21}$-134 (c 0.5, $CHCl_3$) ; IR ($CHCl_3$) 3420, 2930, 1730, 1680, 1515, 1235, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (3H, d, J=6 Hz, H-6), 1.68-2.38 (2H, m, H-2), 1.99 (6H, s, $NCOCH_3$ and $OCOCH_3$), 3.41 (3H, s, OCH_3), 3.75-4.11 (1H, m, H-5), 4.44-4.81 (3H, m, H-1,3 and 4), 6.79 (1H, br d, J=8 Hz, NH).

Anal. Calcd for $C_{11}H_{18}NO_5$ m/z 244.1183. Found: M-H, 244.1178.

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