Synthesis of 2-Amino-2,3-dideoxy-L-ribohexose

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2-Amino-2,3-dideoxy-L-glucose (**1**) was synthesized from 2-amino-2-deoxy-L-glucose (**2**). The synthesis was achieved without protection of the anomeric hydroxyl group throughout the reaction sequence. The masked derivative (**9**) of **1** was prepared from **2** by sequential *N*-methoxycarbonylation, benzylidene acetal formation, mesylation, displacement with iodide, and hydrogenolysis. Alkaline hydrolysis of the debenzylidenated product (**10**) led to ring contraction and yielded the 1,2-oxazolidinone derivative (**11**) of a furanose. Acidic hydrolysis of **11** underwent ring expansion and successfully gave **1**.

2-Amino-2,3-dideoxy-L-ribohexose (**1**), an amino L-sugar, is the 3-deoxy derivative of a component of streptomycin. Since the mechanism of resistance of resistant bacteria to streptomycin has been revealed,[1,2,3] and it has been found that the C-3 hydroxyl group of the 2-deoxy-2-methylamino-L-glucose moiety of streptomycin was adenylylated or phosphorylated by ATP and streptomycin adenylyl transferase or streptomycin phosphate transferase, we intended to prepare the unnatural 2-amino-3-deoxy L-sugar (**1**) as an approach to the synthesis of a deoxy variant of streptomycin which does not contain the hydroxyl group masked by the resistant bacteria.

As for the corresponding D-sugar, namely, 2-amino-2,3-dideoxy-D-glucose, Meyer zu Reckendorf and Bonner[4] have reported its synthesis from methyl 2-benzamide-4,6-*O*-benzylidene-2-deoxy-3-*O*-mesyl-β-D-glucopyranoside through 3-thioacetylation followed by catalytic desulfuration, and, subsequently, the amino D-sugar was found in nature as a component of lividomycin.[5] Matsushima and coworkers[6] also prepared 2-acetamido-2,3-dideoxy-D-glucose from benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside through 3-chlorination with sulfuryl chloride followed by reduction with tri-*n*-butyltin hydride and α,α'-azobisisobutyronitrile.

In the present paper, we wish to report a novel method for the preparation of the aminodeoxy L-sugar (**1**) from 2-amino-2-deoxy-L-glucose (**2**) that was achieved without protection of the anomeric hydroxyl group throughout the reaction sequence.

The starting L-sugar (**2**) was prepared from L-arabinose by the method of Kuhn and Kirschenlohr.[7] The 4,6-*O*-benzylidene-*N*-methoxycarbonyl derivative (**4**) was prepared through (**3**) similarly to the preparation of *N*-benzyloxycarbonyl-4,6-*O*-benzylidene derivative of 2-amino-2-deoxy-D-glucose by Wesemann and Zilliken.[8] The position of the acetal group (at 4,6-*O*, not at 5,6-*O* of furanose structure) was confirmed by the PMR spectral studies of the mesyl derivatives (**5**,**5'**), the next compounds. Treatment of **4** with mesyl chloride in pyridine containing triethylamine followed by column chromatography gave two crystalline 3-*O*-mesyl derivatives of α-L- (**5**, 47%) and β-L-glucopyranose form (**5'**, 17%). PMR studies of **5** and **5'** showed the coupling constants, $J_{2,3}$ and $J_{3,4}$=9.5—10 Hz in each of the anomers and $J_{1,2}$=3.5 Hz (in **5**) and 8 Hz (in **5'**). The anomeric proton of **5** or **5'** also coupled with the anomeric hydroxyl proton, respectively, and, on deuteration, the anomeric proton collapsed to a clear doublet, respectively. These results indicated that the anomeric hydroxyl groups of the both compounds were free and that the both compounds have the glucopyranose structure. It can therefore be assumed that, in the mesylation reaction, an unstable 1-chloride or 1-*O*-mesyl derivative would be formed and hydrolyzed during the subsequent isolation procedure.

The structures of **5** and **5'** were further confirmed by the PMR spectral studies of their acetyl derivatives. Treatment of the α-anomer (**5**) with acetic anhydride and pyridine followed by chromatographic separation gave 1-*O*-acetyl-α (**6**) and β-derivative (**6'**) in a yield of 72 and 12%, respectively. Acetylation of the β-anomer (**5'**) gave **6** and **6'** in a yield of 25 and 56%, respectively.

Hydrolysis of **5** or **5'** with 70% acetic acid readily gave the debenzylidenated compound (**7**).

Next, displacement of the 3-*O*-mesyl group of **5** or **5'** with iodine was achieved by treatment with sodium iodide in DMF. In general, displacement reaction of 3-sulfonyloxy group by a nucleophile readily proceeds in the case of β-D-glucopyranosides, whereas α-D-glucopyranosides resistant to the displacement owing to 1,3-diaxial type interaction[9,10] in the transition state. We[11] experienced, however, that iodination of 3-sulfonyloxy group in a 2-benzyloxycarbonylamino-α-D-glucoside structure smoothly proceeded in the synthseis of tobramycin from kanamycin B, although the displacement was carried out in high concentration of sodium iodide in DMF. Possibly, the iodination was facilitated by the neighboring group participation of the 2-acylamino group.[12] Also, in the present case, the displacement was carried out with a high concentration of sodium iodide to give almost equal amounts of two iodination products, **8** (35%) and **8'** (35%), from both of **5** and **5'**. When the concentration of sodium iodide was reduced, the yields of iodinated products became lower. Further details of the structures of **8** and **8'** were not studied, however, since both of **8** and **8'** showed $J_{1,2}$=3—3.5 Hz in their PMR spectra, one of them was assumed to have α-L-glucopyranose structure and the other α-L-allopyranose structure.

Catalytic hydrogenation of **8** or **8'** with Raney nickel gave the 3-deoxy-α-L-pyranose derivative (**9**) in high yield, giving no β-anomer.

Hydrolysis of **9** with 70% acetic acid removed its

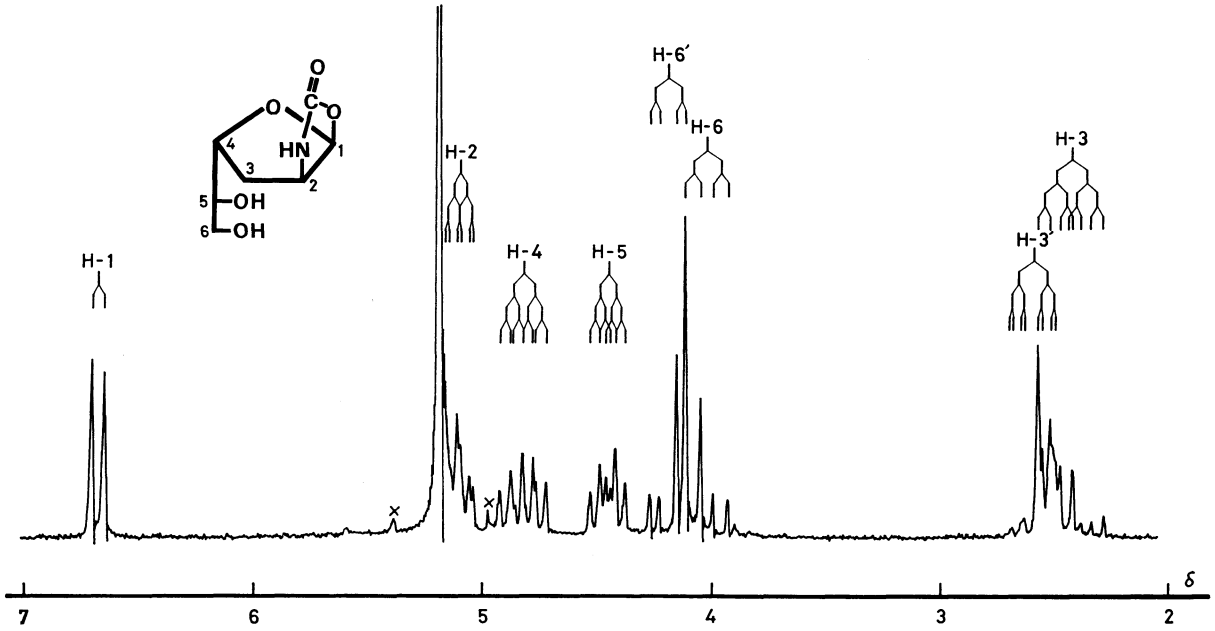
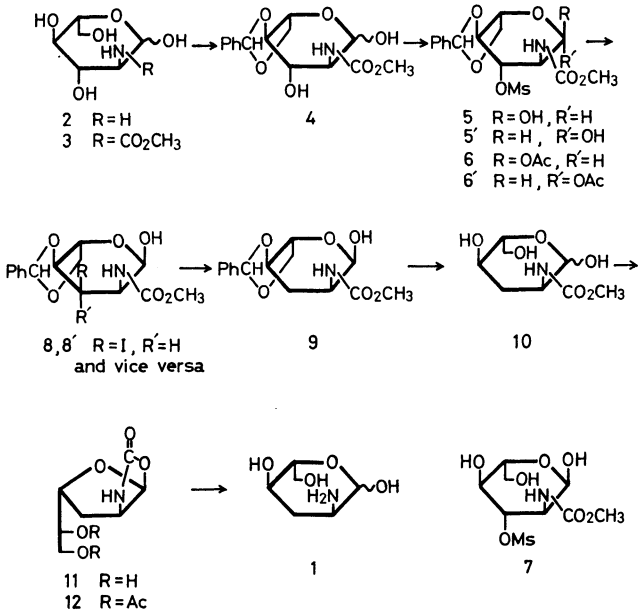


Fig. 1. PMR spectrum of **11**.

benzylidene group to give 2,3-dideoxy-2-methoxycarbonylamino-L-ribohexose (**10**). The compounds **9** and **10** are useful intermediates for the synthesis of related glycosyl halides and glycosides.

Alkaline hydrolysis of **10** with barium hydroxide to remove its methoxycarbonyl group led exclusively to ring contraction, giving an oxazolidinone derivative of α-L-ribohexofuranose (**11**) in 94% yield. Reactions of **11** with ninhydrin and triphenyltetrazolium chloride (TTC) were negative and, in the IR spectrum, **11** showed an absorption at 1730 cm^{-1}. These facts suggested that **11** was a 1,2-oxazolidinone derivative. The PMR spectrum of **11** (Fig. 1) showed the coupling constants, $J_{1,2}=5.5$, $J_{2,3}=5.5$, $J_{2,3'}=-1.5$, $J_{3,4}=10$, $J_{3',4}=5.5$ Hz and these values indicated that **11** has a furanoside structure and that the oxazolidinone is formed in a *cis* configuration at C-1 and C-2.



For further confirmation of the structure of **11**, it was acetylated to give the di-*O*-acetyl derivative (**12**). The PMR spectrum of **12** showed that only the shift values of H-5, 6, and 6' moved to downfield in comparison with those of the corresponding protons of **11**. This indicated that the hydroxyl groups at C-5 and C-6 of **11** were acetylated.

Naturally, it became of interest to investigate the alkaline hydrolysis of **3**. However, similar treatment of **3** with barium hydroxide failed to give a definite product. It seems therefore that the absence of 3-hydroxyl group in **10** facilitates the formation of oxazolidinone.

Acidic hydrolysis of **11** was found to undergo ring expansion of the furanose to a pyranose. Treatment of **11** with 1 M hydrochloric acid under warming successfully gave, in 78% yield, 2-amino-2,3-dideoxy-L-ribohexose (**1**) which showed a specific rotation numerically compatible with that of D-isomer[5] but opposite in direction.

Experimental

Tlc was carried out on 7.5×2.5 cm slides coated with silica gel (Wakogel B-5, Wako Pure Chemicals Co., Ltd., Osaka) and silica gel column chromatography was performed with Wakogel C-200.

2-Deoxy-2-methoxycarbonylamino-L-glucose (**3**). To an ice-cold suspension of 2-amino-2-deoxy-L-glucose hydrochloride[7] (26.3 g) and anhydrous sodium carbonate (16.9 g) in aqueous acetone (1: 1, 440 ml), methyl chloroformate (19.7 ml) was added and the mixture was stirred for 1.5 hr in the cold and then for 1.5 hr at room temperature. Evaporation of the reaction mixture gave a residue, which was washed with methanol. The colorless residue was extracted with DMF (200 ml×5) to remove inorganic matter. Evaporation of the extract gave a solid, which was washed with methanol, 21.7 g (75%). Recrystallization from methanol gave crystals of **3**, mp 195—197 °C (decomp.) (*cf.* 2-deoxy-2-methoxycarbonylamino-D-glucose: mp 196—197 °C[13]); $[\alpha]_D^{26}$ −14.4°→−33.4°

(c 1, H_2O) (D-isomer: +34°,[13] +27°[14]).

Found: C, 40.49; H, 6.63; N, 5.72%. Calcd for $C_8H_{15}NO_7$: C, 40.50; H, 6.37; N, 5.91%.

4,6-O-Benzylidene-2-deoxy-2-methoxycarbonylamino-L-glucopyranose (4). A mixture of **3** (33.2 g), fuse-dried zinc chloride (33.5 g) and benzaldehyde (96 ml) was stirred at room temperature for 20 hr. The resulting viscous solution was poured into water. The oily precipitate was separated and washed with petroleum ether. The solidified mass was washed further with water and petroleum ether. Recrystallization from methanol gave needles of **4**, 32.5 g (71%), mp 238 °C (decomp.); $[\alpha]_D^{26}$ +55 °→+16.2 ° (c 0.5, dioxane); PMR (in $(CD_3)_2SO$) δ: 3.28 (3H s, CO_2CH_3), 5.57 (1H s, PhCH), 7.37 (5H s, Ph).

Found: C, 55.05; H, 5.70; N, 4.09%. Calcd for $C_{15}H_{19}NO_7$: C, 55.38; H, 5.89; N, 4.31%.

4,6-O-Benzylidene-2-deoxy-3-O-mesyl-2-methoxycarbonylamino-α- and β-L-glucopyranose (5 and 5′). To an ice-cold solution of **4** (10.0 g, 30.7 mmols) in pyridine (250 ml), triethylamine (8.6 ml) and mesyl chloride (8.6 ml, 111 mmol) were added and the solution was allowed to stand for 2 hr in the cold. The solution was poured, with stirring, into a mixture of chloroform-1% aqueous sodium carbonate solution. The chloroform layer was washed with water, dried over sodium sulfate and evaporated to give a red-colored solid. The solid was shaken with a mixture of benzene–ethyl acetate (2: 1) and the suspension was filtered to remove the insoluble matter. The filtrate was chromatographed on a column of silica gel with the same solvent system described above. From the eluate, **5** was obtained as a colorless solid, 5.76 g (47%). It was recrystallized from ethanol to give needles, mp 161—161.5 °C (decomp.); $[\alpha]_D^{15}$ −3.3 °→0 ° (c 1.5, acetone); R_f 0.25 (benzene–ethyl acetate 2: 1); positive to TTC; PMR (in $(CD_3)_2CO$) δ: 3.04 (3H s, SO_2CH_3), 3.64 (3H s, CO_2CH_3), 4.05—4.3 (2H m), 4.85 (1H q, H-3; $J_{2,3}$=9.5 or 10 Hz, $J_{3,4}$=9.5 or 10 Hz), 5.28 (1H incomplete t, which collapsed to a doublet ($J_{1,2}$=3.5 Hz) on deuteration, H-1), 5.73 (1H, s, PhCH), 6.13 (1H d with small couplings (<0.5 Hz), OH; J=~4 Hz; disappeared on deuteration). Irradiation of the deuterated sample at δ 3.99 collapsed the doublet of H-1 into a singlet and the quartet of H-3 into a broad singlet. Irradiation at δ 3.89 collapsed the quartet of H-3 into a doublet (J=~8 Hz).

Found: C, 47.59; H, 5.21; N, 3.25; S, 7.96%. Calcd for $C_{16}H_{21}NO_9S$: C, 47.64; H, 5.25; N, 3.47; S, 7.95%.

The insoluble matter described above was recrystallized from ethanol to give colorless needles of **5′**, 2.09 g (17%), mp 153.5—154.5 °C (decomp.); $[\alpha]_D^{15}$ +29 °→−3 ° (c 1.5, acetone); R_f 0.25 (benzene–ethyl acetate 2: 1); active for TTC; PMR (in $(CD_3)_2CO$) δ: 3.00 (3H s, SO_2CH_3), 3.62 (3H s, CO_2CH_3), 4.32 (1H q, H-6?$_{eq}$; J=4.5 and 10.5 Hz), 4.92 (1H t, H-3; J=9.5 Hz), 5.06 (1H t, H-1; J=~7.5 Hz; collapsed to a doublet ($J_{1,2}$=8 Hz) on deuteration), 5.74 (1H s, PhCH), 6.17 (1H d, OH; J=7.5 Hz;disappeared on deuteration), 7.3—7.6 (5H m, Ph).

Irradiation at δ 6.17 (OH) collapsed the triplet of H-1 to a doublet (J=8 Hz). Irradiation of the deuterated sample at δ 3.70 (H-2 resonated here) collapsed the doublet of H-1 to a singlet and the triplet of H-3 to a doublet (J=~8 Hz).

Found: C, 47.51; H, 5.18; N, 3.22; S, 7.66%.

2-Deoxy-3-O-mesyl-2-methoxycarbonylamino-α-L-glucopyranose (7). A suspension of **5** or **5′** in 70% aqueous acetic acid was heated at 95 °C for 5 min. The resulting clear solution was evaporated to give a solid, which was thoroughly washed with ether and recrystallized from ethanol to give needles of **7**, mp 151.5—153 °C (decomp.); $[\alpha]_D^{22}$ −86 °→−36 ° (c 1, methanol); R_f 0.33 (chloroform–methanol 7: 1); PMR (in $CDCl_3$) δ: 3.13 (3H s, SO_2CH_3), 3.67 (3H s, CO_2CH_3), 5.13 (1H d, H-1; $J_{1,2}$=3.5 Hz).

Found: C, 34.45; H, 5.32; N, 4.24; S, 10.10%. Calcd for $C_9H_{17}NO_9S$: C, 34.28; H, 5.44; N, 4.44; S, 10.17%.

1-O-Acetyl-4,6-O-benzylidene-2-deoxy-3-O-mesyl-2-methoxycarbonylamino-α- and β-L-glucopyranose (6 and 6′). *From 5*: A solution of **5** (200 mg) in pyridine (4.6 ml), acetic anhydride (0.05 ml) was added and the solution was allowed to stand at room temperature overnight. After addition of a drop of water, the solution was poured into ice-water. The precipitate was dissolved in chloroform and the solution was washed with water, dried over sodium sulfate and evaporated to give a solid. The solid was shaken with benzene–ethyl acetate (5: 1, 3 ml) and the insoluble product was filtered, washed with the same solvent mixture to give **6**, 60 mg (27%). The filtrate was evaporated and the residue was chromatographed on a column of silica gel with the above solvent mixture. From the earlier fraction, **6′** was obtained, 27 mg (12%), mp 158—159.5 °C (decomp.); $[\alpha]_D^{23}$ −65 ° (c 1, $CHCl_3$); R_f 0.48 (benzene–ethyl acetate 2: 1); PMR (in $CDCl_3$) δ: 2.20 (3H s, Ac), 2.98 (3H s, CO_2CH_3), 3.72 (3H s, SO_2CH_3), 3.75—4.0 (3H m, H-4,6_{ax},6_{eq} (or 5)), 4.1—4.45 (2H m, H-2 and 5 (or 6_{eq})), 4.83 (1H t, H-3; J=~10 Hz), 5.19 (1H d, NH; $J_{2,NH}$=9 Hz; disappeared on addition of D_2O and NaOD), 5.59 (1H s, PhCH), 6.24 (1H d, H-1; $J_{1,2}$=3.5 Hz).

Irradiation of H-1 slightly changed the signal bush near 4.3 but not other signals. Irradiation at δ 4.33 (at which H-2 resonated) collapsed the triplet of H-3 (δ 4.83) into a doublet ($J_{2,3}$=~10 Hz), the doublet of NH (δ 5.19) into a singlet and the doublet of H-1 (δ 6.24) into a singlet. Irradiation at δ 3.87 (H-4) collapsed the triplet of H-3 into a doublet (11 Hz=$J_{3,4}$). Irradiation at 5.19 caused the signals at δ 4.1—4.45 to change.

Found: C, 48.64; H, 5.22; N, 2.85; S, 7.39%. Calcd for $C_{18}H_{23}NO_{10}S$: C, 48.54; H, 5.20; N, 3.14; S, 7.20%.

From the later fraction, **6** was obtained, 100 mg (45%). Thus the total yield of **6** is 72%, mp 156.5—158 °C (decomp.); $[\alpha]_D^{23}$ +9 ° (c 1, $CHCl_3$); R_f 0.50 (benzene–ethyl acetate 2: 1); PMR (in $CDCl_3$) δ: 2.15 (3H s, Ac), 2.93 (3H s, CO_2CH_3), 3.72 (3H s, SO_2CH_3), 3.6—4.0 (4H m, H-2,4,6_{ax},5(or 6_{eq})), 4.3—4.5 (1H m, H-6_{eq} or 5), 4.98 (1H t, H-3; J=10 Hz), 5.32 (1H d, NH; $J_{2,NH}$=9 Hz; disappeared on addition of D_2O and DCl), 5.55 (1H s, PhCH), 5.95 (1H d, H-1; $J_{1,2}$=8.5 Hz).

Irradiation of H-1 changed the signals at δ 3.75—4.0. Irradiation at δ 3.84 (H-2,4,6_{ax}(or 6_{eq})) caused the signals at δ 4.4 (H-6_{eq} or 5), 4.98 (H-3), 5.32 (NH) and 5.95 (H-1) to a singlet, respectively.

Found: C, 48.77; H, 5.22; N, 3.08; S, 7.07%.

From 5′. Prepared in the same way as described above from **5′** (100 mg) giving **6**, 28 mg (25%) and **6′**, 62 mg (56%).

4,6-O-Benzylidene-2-deoxy-3-iodo-2-methoxycarbonylamino-α-L-gluco and α-L-allo(?)-hexopyranose (8 and 8′). A solution of **5** or **5′** (2.5 g) and sodium iodide (25 g) in DMF (30 ml) was heated at 100 °C for 1.5 hr. After addition of chloroform (350 ml), the organic layer was washed with 10% sodium thiosulfate solution (400 ml) and water (400 ml). The solution was dried over sodium sulfate and evaporated to leave a residue, which was shaken with benzene–ethyl acetate (3: 1, 20 ml). The insoluble product was recrystallized from methanol to give needles of **8**, 878 mg (35%), mp 219—221 °C (decomp.); $[\alpha]_D^{22}$ +93.5 °→+29.5 ° (c 1, pyridine); R_f 0.36 (benzene–ethyl acetate 2: 1); PMR (in $CDCl_3$+D_2O) δ: 3.69 (1H s, CO_2CH_3), 5.28 (1H d, H-1; $J_{1,2}$=3 Hz), 5.72 (1H s, PhCH).

Found: C, 40.81; H, 4. 08; N, 2.90; I, 28.70%. Calcd for $C_{15}H_{18}NO_6I$: C, 41.40; H, 4.17; N, 3.22; I, 29.16%.

The benzene–ethyl acetate soluble product was purified by

column chromatography with benzene–ethyl acetate (3: 1) to give **8′**, 945 mg (35%), mp 190—192 °C (decomp.); $[\alpha]_D^{23}$ +59.4 ° (*c* 1, $CHCl_3$) (the value kept constant for 20 hr), $[\alpha]_D^{23}$ +59.1 °→+20.1 ° (*c* 0.7, pyridine); R_f 0.36 (benzene–ethyl acetate 2: 1); PMR (in $CDCl_3+D_2O$) δ: 3.73 (3H s, CO_2CH_3), 5.15 (1H d, H-1; $J_{1,2}$=3.5 Hz), 5.70 (1H s, PhCH). Due to its unstable nature, the compound could not be successfully analyzed.

*4,6-O-Benzylidene-2,3-dideoxy-2-methoxycarbonylamino-α-*L*-ribo-hexopyranose (9).* To a solution of **8** (641 mg) in dioxane (25 ml), triethylamine (0.08 ml) and Raney nickel were added and the mixture was shaken under hydrogen (50 lb. in^{-2}) at room temperature. After 5 hr, Raney nickel was replaced with the fresh one and the reaction was continued for further 6 hr. The solution was evaporated and the residue was extracted with ethyl acetate. The solution was washed successively with saturated sodium hydrogen sulfate solution, sodium hydrogen carbonate solution, and water, dried over sodium sulfate and evaporated to give a solid of **9**, 443 mg (97%).

A similar preparation from **8′** (616 mg) gave **9**, 413 mg (94%), mp 201—203 °C; $[\alpha]_D^{22}$ −11.7 ° (*c* 1, dioxane; the value kept constant for 20 hr); R_f 0.32 (benzene–ethyl acetate 2: 1); positive to TTC; PMR (in $CDCl_3$ $+D_2O$) δ: 1.75—2.35 (2H m, H-3,3′), 3.74 (3H s, CO_2CH_3), 5.19 (1H d, H-1; $J_{1,2}$=3.5 Hz), 5.66 (1H s, PhCH).

Found: C, 58.04; H, 6.13; N, 4.50%. Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53%.

*2,3-Dideoxy-2-methoxycarbonylamino-*L*-ribo-hexose (10).* A suspension of **9** (594 mg) in 70% aqueous acetic acid (21 ml) was heated at 95 °C for 5 min. Evaporation *in vacuo* and coevaporation with water gave a syrup. An aqueous solution (40 ml) of the syrup was washed with ether (40 ml ×2) and evaporated to give a solid, 405 mg (95%); $[\alpha]_D^{23}$ −56 °→−38 ° (*c* 1, methanol).

Found: C, 43.21; H, 6.74; N, 6.10%. Calcd for $C_8H_{15}NO_6$: C, 43.43; H, 6.84; N, 6.33%.

*3-Deoxy-α-*L*-ribo-hexofurano[2,1-d]-2-oxazolidinone (11).* An aqueous solution (4.7 ml) of **10** (238 mg) and barium hydroxide octahydrate (470 mg) was heated at 70 °C for 5 min. After cooling, carbon dioxide was introduced and the reaction mixture was centrifuged. The aqueous layer separated was evaporated to give a residue, which was chromatographed on a column of silica gel with chloroform–ethanol–17% aqueous ammonia (10: 4: 0.6). Evaporation of the fraction containing the main product gave a glassy solid. Recrystallization from methanol–ether gave needles of **11**, 184 mg (94%), mp 127—128 °C; $[\alpha]_D^{23}$ +43 ° (*c* 1, methanol); IR (KBr): 1730, 1750 (sh) cm^{-1}; PMR (in D_2O) δ: 1.96 (1H octet, H-3; J=5.5, 10, 13 Hz), 2.07 (1H octet, H-3′; J=1.5, 5.5, 13 Hz), 3.56 (1H q, H-6; J=6.5, 11.5 Hz), 3.67 (1H q, H-6′; J=4, 11.5 Hz), 3.95 (1H d, H-5; J=~4.5, ~4.5, 6.5 Hz), 4.33 (1H m, H-4), 4.60 (1H d, H-2; J=~1.5, ~5.5, ~5.5 Hz), 6.18 (1H d, H-1; J=5.5 Hz); $J_{1,2}$=5.5 Hz, $J_{2,3}$=5.5 Hz, $J_{2,3'}$=—1.5 Hz, $J_{3,3'}$=13 Hz, $J_{3,4}$=10 Hz, $J_{3',4}$=5.5 Hz, $J_{4,5}$=4.5 Hz, $J_{5,6}$=6.5 Hz, $J_{5,6'}$=4 Hz, $J_{6,6'}$=11.5 Hz; mass spectrum: *m/e* 190 (M^+ +1).

Found: C, 44.69; H, 5.75; N, 7.22%. Calcd for $C_7H_{11}NO_5$: C, 44.44; H, 5.86; N, 7.41%.

*5,6-Di-O-acetyl-3-deoxy-α-*L*-ribo-hexofurano[2,1-d]-2-oxazolidinone (12).* To a solution of **11** (35 mg) in pyridine (1 ml), acetic anhydride (0.09 ml) was added and the solution was allowed to stand at room temperature overnight. After a drop of water was added, the solution was evaporated and the residue was extracted with chloroform. The solution was washed with water, dried over sodium sulfate and evaporated to give a syrup, 37 mg (74%), which was crystallized from ether to give needles of **12**, mp 89—91 °C; $[\alpha]_D^{23}$ −6 ° (*c* 0.7, methanol); IR (KBr): 1740 cm^{-1}; PMR (in $CDCl_3$–D_2O) δ: 1.75—2.3 (2H m, H-3,3′), 2.07 and 2.09 (each 3H s, Ac), 4.11 (1H q, H-6; J=6, 12 Hz), 4.41 (1H q, H-6′; J=3.5, 12 Hz), 4.3—4.55 (3H m, H-2,4,6), 5.23 (1H d, H-5; J=3.5, 5.5, 5.5 Hz), 6.08 (1H d, H-1; J=5.5 Hz); mass spectrum: *m/e* 274 (M^+ +1).

Found: C, 48.15; H, 5.41; N, 4.83%. Calcd for $C_{11}H_{15}NO_7$: C, 48.35; H, 5.53; N, 5.13%.

*2-Amino-2,3-dideoxy-*L*-ribo-hexopyranose Hydrochloride (1).* A solution of **11** (28 mg) in 1M hydrochloric acid (0.9 ml) was kept at 40 °C for 17 hr. Evaporation *in vacuo* gave a syrup, which was precipitated from methanol–acetone to give a solid of **1**, 23 mg (78%); $[\alpha]_D^{23}$ −48.6 ° (*c* 1.4, water; final value) (D-isomer[5]), $[\alpha]_D^{25}$ +43.9 ° (water)); $R_{f\,2\text{-amino-2-deoxy-L-glucose}}$ 1.26 (ppc with 1-butanol–pyridine–water–acetic acid 6: 4:3: 1 and Toyo-Roshi No. 51 of Toyo-Roshi Co.).

Found: C, 36.45; H, 6.78; N, 6.82; Cl, 17.99%. Calcd for $C_6H_{13}NO_4\cdot HCl$: C, 36.10; H, 7.07; N, 7.02; Cl, 17.76%.

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