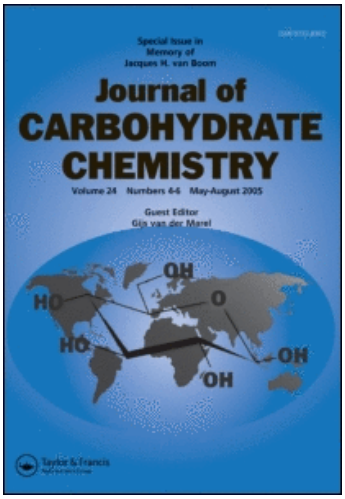

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Synthesis of 2-Amino-3-C-(Carboxymethyl)-2,3-Dideoxy-Allopyranose Derivatives

Ana Calvo-mateo[a]; María José Camarasa[a]; Federico G. de las Heras[a]
[a] Institute de Química Médica, Madrid, Spain

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SYNTHESIS OF 2-AMINO-3-C-(CARBOXYMETHYL) -2,3-DIDEOXY-ALLOPYRANOSE DERIVATIVES

Ana Calvo-Mateo, María José Camarasa
and Federico G. de las Heras*

Instituto de Química Médica, Juan de la Cierva 3
Madrid-6, Spain

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ABSTRACT

The Wittig reaction of methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-ribo-hexopyranosid-3-ulose with ethoxycarbonylmethylenetriphenylphosphorane afforded the corresponding 3-C-(E)-ethoxycarbonylmethylene-3-deoxy glycoside 3. Catalytic hydrogenation of 3 (Pd/C) gave stereoselectively, after removal of benzylidene and ethyl ester protecting groups, methyl 2-acetamido-3-C-carboxymethyl-2,3-dideoxy-α-D-allo-hexopyranoside (11).

INTRODUCTION

For a project underway in our laboratory it became necessary to prepare 2-amino-3-C-alkyl-2,3-dideoxyallo-pyranose derivatives. A common procedure for the introduction of a branched chain onto a carbohydrate[1] involves the reaction of a sugar derivative having a free carbonyl group with a variety of nucleophilic reagents; diazomethane,[2] an organometallic derivative,[3] a Wittig reagent,[4] cyanide ion,[5] compounds having active methylene groups,[6] etc. These reactions are usually aimed at the

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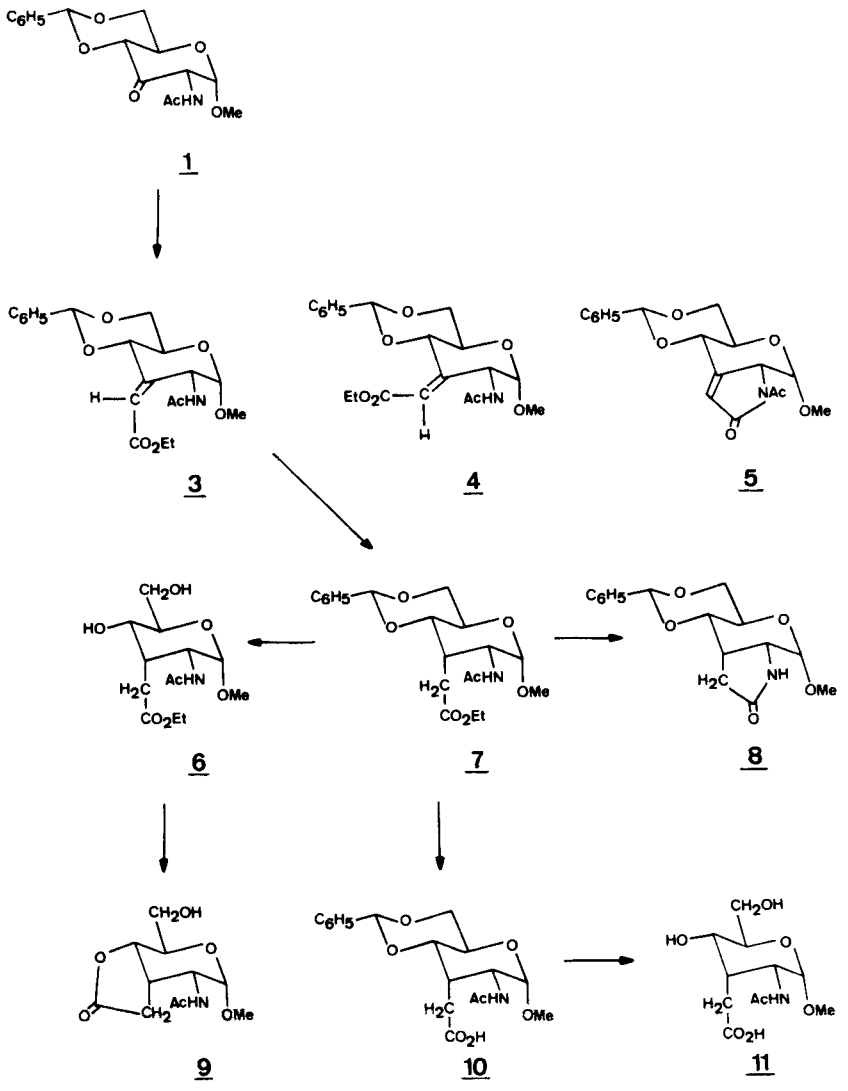
synthesis of naturally occurring branched chain sugars,[1] many of which are found in antibiotic glycosides. Less attention has been focused on the synthesis of branched-chain amino sugars,[7,8] exception being the synthesis of naturally occurring vancosamine,[9] related C-3 branched derivatives having the amino group at the branching point,[9,10,11] and sibirosamine[12,13]. In this paper we report the stereoselective synthesis of some branched chain amino sugar derivatives of 2-amino-3-C-carboxymethyl-2,3-dideoxy-D-allopyranose.

RESULTS AND DISCUSSION

Reaction of methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-*ribo*-hexopyranosid-3-ulose 1,[14] prepared in 98% yield by a modification of the described procedure,[14] with ethoxycarbonylmethylenetriphenylphosphorane 2 in acetonitrile at room temperature, stereoselectively afforded the 3-C-(E)-ethoxycarbonylmethylene-3-deoxy glycoside 3 in 57% yield. When the condensation was carried out at reflux temperature, a mixture of compounds was obtained, from which the 3-C-(E)-ethoxycarbonylmethylene derivative 3, its 3-C-(Z)-ethoxycarbonylmethylene isomer 4 and the N-acetyl-3-C-pyrrolinone derivative 5, were obtained in 22, 13 and 8% yields, respectively.

The ^{1}H NMR spectra of 3, 4 and 5 showed pseudotriplets in the olefinic zone, with allylic $J_{2,2'}$ and $J_{2',4}$ coupling constant values of 1.5-2.0 Hz, which suggested the proposed structures. The presence in the ^{1}H NMR spectra of 3 and 4 of signals corresponding to ethyl groups and the absence of them in the spectrum of 5 further confirmed these assignments. The stereochemistry of the olefinic branch of compounds 3 and 4 was de-

termined after acetonitrile solutions of 3 and 4 were heated at reflux temperature. After 20 h compound 3 gave 50% conversion to 5, while no traces of this pyrrolinone were obtained by a similar treatment of 4. From this, it was concluded the assignment of the (E) confi-



guration to 3 and the (Z) to 4.

Catalytic hydrogenation of 3 over Pd/C occurred stereoselectively to give 2-acetamido-4,6-O-benzylidene-3-C-ethoxycarbonylmethyl-α-D-allo-pyranoside 7 in 70% yield. The use of higher temperatures and hydrogen pressures resulted in additional hydrogenolysis of the 4,6-O-benzylidene group to give 6, which on standing in methanolic solution spontaneously cyclized to afford the 2-acetamido-3-C-allo-pyranose-γ-lactone derivative 9. The formation of 9 was suggested by the disappearance of the bands corresponding to the ethoxy group and the presence of signals corresponding to the AcNH group in the ^{1}H NMR spectrum. The band at 1776 cm^{-1} in the IR spectrum of 9 was assigned to a γ-lactone. The configuration of the new asymmetric center at C-3 of the allo derivatives 6, 7 and 9 was determined by ^{1}H NMR. The observed $J_{2,3}$=4.0 Hz and $J_{3,4}$=3.9 Hz in the 360 MHz spectrum of 7 and the $J_{2,3}$=4.0 and $J_{3,4}$=3.5 Hz in that of 9 indicated the equatorial disposition of H-3. These values and the observed $J_{4,5}$=10.4 Hz for 7, which indicated the $^4C_1$ conformation, determined its D-allo-hexopyranoside structure. The small $J_{4,5}$=6.2 Hz value observed for 9, which reflected the conformational distortion introduced by the 4,2'-δ-lactone, was also consistent with a allo-pyranoside configuration. In both cases, the stereoselective formation of allo compounds is in agreement with the hydrogenation from the less hindered upper side of the molecule, opposite to the axially oriented 1-O-methyl group.

Hydrolysis of 3-C-ethoxycarbonylmethyl-allo-pyranoside 7 with aqueous NaOH followed by treatment of the resulting sodium carboxylate with IRC-50 cation exchange resin afforded acetic acid derivative 10 in 74% yield, along with a small amount of the γ-lactam 8. The

structure of this compound, which precipitated from the reaction mixture during the basic hydrolysis, was demonstrated by the absence in its ^{1}H NMR spectrum of bands corresponding to ethyl and acetyl groups, and the presence of a doublet at δ 7.63 assigned to the 2-NH group. Acidic hydrolysis of the 4,6-O-benzylidene group of 10 with aqueous acetic acid afforded 11 in 87% yield.

EXPERIMENTAL

Melting points were measured with a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Varian EM-390 (90 MHz) and a Bruker WM 360 (360 MHz) using Me_4Si as internal standard. UV absorption spectra were taken with a Perkin-Elmer 402 spectrophotometer. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Optical rotations were determined with a Perkin-Elmer 141 polarimeter. Mass spectra were measured with a Hitachi-Perkin-Elmer RMV-GMG spectrophotometer. Analytical TLC was performed on aluminium sheets coated with a 0.2 mm layer of silica gel 60 F_{254} (Merck) and PLC on glass plates coated with a 2 mm layer of silica gel PF_{254} (Merck). Compounds were detected with UV light (254 nm) or by spraying the plate with ethanol-sulphuric acid (3:1) and heating.

Methyl 2-acetamido-4,6-O-benzylidene-2 deoxy-α-D-ribo-hexopyranosid-3-ulose (1). To a stirred mixture of methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside, (3.85 g, 0.01 mol) 3Å molecular sieves (2 g) and anhydrous dimethyl sulfoxide (100 mL), dicyclohexylcarbodiimide (9.04 g, 0.044 mol) was added. Anhydrous orthophosphoric acid (2.51 mL, 0.048 mol) was then added portionwise with cooling (ice bath) so that the temperature was kept at 25-30°. The reaction mixture was stirr-

ed at room temperature for 21 h and then centrifuged for twenty minutes. The solution was decanted, the precipitated dicyclohexylurea was washed with dimethyl sulfoxide and acetone and the mixture centrifuged. The combined centrifugation liquids were diluted with 4 volumes of chloroform, water was added, and then a potassium carbonate solution (2.4 M) was added to bring the aqueous phase to about pH 8. The aqueous layer was extracted with chloroform and the combined extracts were washed with water until neutral. The organic phase was dried over Na_2SO_4 and evaporated to dryness to give 1 (3.15 g, 98%): mp 224-226 °C (from N,N-dimethylformamide-water), $[\alpha]_D$ + 115° (c 0.5, N,N-dimethylformamide); lit.[14] mp 227-228 °C (dec.), $[\alpha]_D$ + 110 ± 4°; ^{1}H NMR [$(CD_3)_2SO$]: δ 1.96 (s, 3H, NAc), 3.38 (s, 3H, OMe), 3.95 (m, 2H, H-6), 4.36 (m, 1H, H-5), 4.70-5.05 (m, 2H, H-2, H-4), 5.15 (d, 1H, H-1, $J_{1,2}$= 4 Hz), 5.72 (s, 1H, C_6H_5-CH), 8.12 (d, 1H, NH, $J_{NH,2}$= 8 Hz).

Methyl 2-acetamido-4,6-O-benzylidene-2,3-dideoxy-3-C-[(E)-ethoxycarbonylmethylene-α-D-ribo-hexopyranoside (3). To a solution of 1 (1.22 g, 3.8 mmol) in hot acetonitrile (75 mL), ethoxycarbonylmethylenetriphenylphosphorane 2 (2 g, 5.7 mmol) was added and the reaction mixture was stirred at room temperature for five days. The solids were removed by filtration and the filtrate evaporated to dryness to give a solid which was purified by preparative TLC using EtOAc: hexane (1:2) as the eluent, to give 3 (0.66 g, 57%): mp 112 °C (from EtOAc-hexane); $[\alpha]_D$ + 204° (c 1, chloroform); UV λ_{max} (EtOH) 229 nm (ε 5700); IR (KBr) 1736 cm^{-1} (CO_2Et conj.); ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 3H, CH_3CH_2), 2.01 (s, 3H, NAc), 3.41 (s, 3H, OMe), 3.70-3.90 (m, 2H, H-6), 4.03-4.32 (m, 4H, H-4, H-5, CH_3-CH_2), 4.75 (d, 1H, H-1, $J_{1,2}$= 3.7 Hz), 4.95 (ddd, 1H, H-2, $J_{2,NH}$= 8.7 Hz, $J_{2,2'}$= 1.5 Hz), 5.60

(s, 1H, C_6H_5-CH), 6.15 (t, 1H, H-2', $J_{2',4}$= 1.5 Hz), 8.56 (d, 1H, NH).

Anal. Calcd for $C_{20}H_{25}NO_7$: C, 61.36; H, 6.43; N, 3.57. Found: C, 61.12; H, 6.60; N, 3.51.

Reaction of 1 with ethoxycarbonylmethylenetriphenilphosphorane 2 in refluxing acetonitrile. A mixture of 1 (4.8 g, 0.0152 mol), dry acetonitrile (320 mL), and ethoxycarbonylmethylenetriphenylphosphorane (8 g, 0.0228 mol) was refluxed for 24 h. The solids were removed by filtration, the filtrate evaporated in vacuo and the residue purified by preparative TLC with EtOAc-hexane (1:2). Three major bands, visualized under UV light, were removed and the compounds extracted with chloroform EtOH (1:1). The fastest moving band gave methyl 2-acetamido-4,6-O-benzylidene-2,3-dideoxy-3-C-carboxymethylene-α-D-ribo-hexopyranoside-2,2'-lactam, (5) (0.44 g. 8.2%): mp 191-193 °C (from MeOH-water); $[\alpha]_D$ + 270° (c 1, chloroform); ^{1}H NMR [$(CD_3)_2SO$]: δ 2.40 (s, 3H, NAc), 3.28 (s, 3H, OMe), 3.62 (dt, 1H, H-5, $J_{4,5}$= 9 Hz, $J_{5,6a}$= 9.8 Hz, $J_{5,6b}$ = 4.7 Hz), 3.95 (t, 1H, H6a, $J_{6a,6b}$ = 9.8 Hz), 4.32 (dd, 1H, H6b), 4.73 (dd, 1H, H-4, $J_{2',4}$ = 1.8 Hz), 4.88 (dd, 1H, H-2, $J_{1,2}$ = 4.5 Hz, $J_{2,2'}$ = 1.5 Hz), 5.40 (d, 1H, H-1), 5.87 (s, 1H, C_6H_5-CH), 5.96 (pt, 1H, H-2').

Anal. Calcd for $C_{18}H_{19}NO_6$: C, 62.61; H, 5.50; N, 4.06. Found: C, 62.88; H, 5.22; N, 4.17.

The second band gave 1.31 g (22%) of a solid which was identified as 3.

From the slowest running band 0.71 g (13%) of methyl 2-acetamido-4,6-O-benzylidene-2,3-dideoxy-3-C-[(Z)-ethoxycarbonylmethylene]-α-D-ribo-hexopyranoside, (4) were obtained: mp 195-198 °C (from EtOAc-hexane); $[\alpha]_D$ + 32° (c 1, chloroform); IR (KBr) 1734 cm^{-1} (CO_2Et conj.); ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, CH_3CH_2), 2.05 (s, 3H, NAc),

3.38 (s, 3H, OMe), 3.53-4.05 (m, 4H, $\underline{CH_2}$-CH_3, H-6), 4.13-4.40 (m, 2H, H-4, H-5), 4.67 (d, 1H, H-1, $J_{1,2}$= 4.2 Hz), 4.90 (ddd, 1H, H-2, $J_{2,2'}$= 2.0 Hz), 5.55 (s, 1H, $C_6H_5\underline{CH}$), 5.72 (t, 1H, H-2', $J_{2,2'}$= $J_{3,2'}$= 2 Hz), 5.93 (d, 1H, NH, $J_{NH,2}$= 9.3 Hz).

Anal. Calcd for $C_{20}H_{25}NO_7$: C, 61.36; H, 6.43; N, 3.57. Found: C, 61.61; H, 6.56; N, 3.50.

Methyl 2-acetamido-4,6-O-benzylidene-2,3-dideoxy--3-C-ethoxycarbonylmethyl-α-D-allo-hexopyranoside (7). To a solution of 3 (2.059 g, 5.2 mmol) in EtOAc (140 mL), 10% Pd/C (2 g) was added, and the mixture was hydrogenated at 30 psi and 20 °C for 24 h. The catalyst was removed by filtration and the filtrate evaporated to dryness to give a syrup which was purified by preparative TLC (EtOAc) to give 7 (1.448 g, 70%): mp 108-110 °C (from MeOH-water); $[\alpha]_D$ + 24° (c 1, chloroform); IR (KBr) 1732 cm^{-1} (CO_2Et); ^1H NMR ($CDCl_3$, 360 MHz): δ 1.17 (t, 3H, $\underline{CH_3}CH_2$), 1.99 (s, 3H, NAc), 2.73 (dd, 1H, H-2'a, $J_{3,2'a}$ = 7.6 Hz, $J_{2'a,2'b}$ = 15.8 Hz), 2.83 (dd, 1H, H-2'b, $J_{3,2'b}$ = 5.7 Hz), 3.07 (m, 1H, H-3), 3.41 (s, 3H, OMe), 3.69-3.86 (m, 3H, H-5, H-6), 3.98 and 4.06 (AB system, 2H, $\underline{CH_2}CH_3$, J_{gem} = 10.8), 4.29 (dd, 1H, H-4, $J_{3,4}$= 3.9 Hz, $J_{4,5}$ = 10.4 Hz), 4.38 (m, 1H, H-2, $J_{1,2}$ = 4.0 Hz, $J_{2,NH}$ = 8.9 Hz, $J_{2,3}$ = 5.1 Hz), 4.61 (d, 1H, H-1), 5.55 (s, 1H, $C_6H_5\underline{CH}$), 6.14 (d, 1H, NH).

Anal. Calcd for $C_{20}H_{27}NO_7$: C, 61.07; H, 6.87; N, 3.56. Found: C, 61.39; H, 6.80; N, 3.54.

Methyl 2-acetamido-2,3-dideoxy-3-C-ethoxycarbonylmethyl-α-D-allo-hexopyranoside (6). A mixture of 3 (0.36 g, 0.92 mmol), EtOAc (30 mL) and 10% Pd/C (0.4 g) was hydrogenated at 45 psi and 35 °C for 10 h. The catalyst was removed by filtration and the filtrate evaporated to dryness to give a syrup which was purified by preparative TLC EtOAc-MeOH (5:1) to give 6 as a syrup

(0.208 g, 74%):$[\alpha]_D$ + 36° (c 1, chloroform); ^{1}H NMR [$(CD_3)_2SO$]:δ 1.16 (t, 3H, $\underline{CH_3}CH_2$), 1.83 (s, 3H, NAc), 2.40-2.82 (m, 2H, H-2'), 3.28 (s, 3H, OMe), 3.10-3.73 (m, 5H, H-3, H-4, H-5, H-6), 4.00 (m, 3H, H-2, $\underline{CH_2}CH_3$), 4.43 (d, 1H, H-1, $J_{1,2}$ = 3.8 Hz), 4.47 (t, 1H, 6-OH, J = 5 Hz), 5.05 (d, 1H, 4-OH, J = 5 Hz), 7.59 (d, 1H, NH, $J_{NH,2}$ = 8.7 Hz).

Anal. Calcd for $C_{13}H_{23}NO_7$: C, 51.14, H, 7.14; N, 4.59. Found: C, 50.98; H, 6.82; N, 4.60.

Methyl 2-acetamido-3-C-carboxymethyl-2,3-dideoxy-α-D-allo-hexopyranoside-2',4-lactone (9). On standing in ethanolic solution, compound 6 spontaneously cyclized to afford quantitatively 9: mp 263-264 °C (from MeOH-water);$[\alpha]_D$ + 31° (c 1, DMSO); IR (KBr) 1776 cm^{-1} (γ-lactone); ^{1}H NMR [$(CD_3)_2SO$]:δ 1.86 (s, 3H, NAc), 2.83-3.08 (m, 2H, H-2'), 3.30 (s, 3H, OMe), 3.53 (m, 4H, H-3, H-5, H-6), 4.12 (dt, 1H, H-2, $J_{2,3}$ = 4 Hz), 4.43 (dd, 1H, H-4, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 6.2 Hz) 4.61 (d, 1H, H-1, $J_{1,2}$ = 3.5 Hz), 7.75 (d, 1H, NH, $J_{NH,2}$ = 8.6 Hz); m/e: 259 (M^+, 1%), 228 (M^+- 31, 6%).

Anal. Calcd for $C_{11}H_{17}NO_6$: C, 50.96; H, 6.56; N, 5.40. Found: C, 49.56; H, 6.81; N, 5.18.

Methyl 2-acetamido-4,6-O-benzylidene-3-C-carboxymethyl-2,3-dideoxy-α-D-allo-hexopyranoside (10) and Methyl 2-amino-4,6-O-benzylidene-3-C-carboxymethyl-2,3-dideoxy-α-D-allo-hexopyranoside-2',2-lactam (8). A mixture of 7 (0.9 g, 2.3 mmol) and 1.25 M aqueous sodium hydroxide (10 mL) was stirred at room temperature overnight. The precipitate which appeared was removed by filtration and washed with water to give 8 (0.140 g, 17%): mp 247-248 °C (from MeOH-water);$[\alpha]_D$ + 216° (c 1, chloroform); IR (KBr) 1704, 1670 cm^{-1} (γ-lactam); ^{1}H NMR [$(CD_3)_2SO$]:δ 1.85 (dd, 1H, H-2'a, $J_{2'a,3}$ = 8.5 Hz, $J_{2'a,2'b}$ = 15.5 Hz), 2.29 (dd, 1H, H-2'b, $J_{2'b,3}$= 11 Hz),

2.90 (m, 1H, H-3), 3.63-3.99 (m, 4H, H-4, H-5, H-6), 4.26 (d, 1H, H-2, $J_{1,2}$ = 4.5 Hz), 4.65 (d, 1H, H-1), 5.66 (s, 1H, $C_6H_5\underline{CH}$), 7.63 (bs, 1H, NH); m/e:366 (M^++ 1, 2%), 323 (M^+- 42, 1%), 304 (M^+- 61, 3%), 274 (M^+- 91, 4%).

Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.95; H, 6.22; N, 4.59. Found: C, 63.24; H, 6.19; N, 4.50.

The filtrate was passed through an Amberlite IRC-50 (10 g) column and the eluate was concentrated at reduced pressure to give 10 (0.62 g, 74%) as a solid: mp 130-131 °C (from MeOH-water); $[\alpha]_D$ + 17° (c 1, ethanol); ^{1}H NMR data $[(CD_3)_2SO]$: δ 1.87 (s, 3H, NAc), 2.35-2.60 (m, 2H, H-2'), 2.83 (m, 1H, H-3), 3.32 (s, 3H, OMe), 3.53-3.90 (m, 3H, H-5, H-6), 4.03-4.30 (m, 2H, H-2, H-4), 4.49 (d, 1H, H-1, $J_{1,2}$= 3.5 Hz), 5.59 (s, 1H, $C_6H_5\underline{CH}$), 7.72 (d, 1H, NH, $J_{NH,2}$ = 9 Hz), m/e: 365 (M^+, 1%), 347 (M^+- 18, 1%), 334 (M^+- 31, 1%), 306 (M^+- 59, 8%).

Anal. Calcd for $C_{18}H_{23}NO_7$: C, 59.17; H, 6.30; N, 3.83. Found: C, 58.90; H, 6.08; N, 3.80.

Methyl 2-acetamido-3-C-(carboxymethyl)-2,3-dideoxy-α-D-allo-hexopyranoside (11). A mixture of 10 (0.58 g, 1.6 mmol) in 70% aqueous acetic acid (90 mL) was heated to 100 °C for 3 min. The solution was evaporated to dryness and co-evaporated several times with water and then with toluene to give a solid which was crystallyzed to afford 11 (0.376 g, 87%): mp 263.5-264.5 °C (from MeOH-water); $[\alpha]_D$ + 33° (c 1. DMSO); ^{1}H NMR $[(CD_3)_2SO]$: δ 1.85 (s, 3H, NAc), 2.35-2.75 (m, 2H, H-2'), 3.00 (m, 1H, H-3), 3.28 (s, 3H, OMe), 3.36-3.90 (m, 5H, H-5, H-6, 2 OH), 4.13 (dt, 1H, H-2, $J_{2,3}$ = 4.5 Hz), 4.45 (dd, 1H, H-4, $J_{3,4}$ = 3 Hz, $J_{4,5}$ = 7 Hz), 4.62 (d, 1H, $J_{1,2}$ = 4.2 Hz), 7.80 (d, 1H, NH, $J_{NH,2}$ = 8.8 Hz); m/e 279 (M^+ + 2, 3%), 278 (M^++ 1, 9%), 277 (M^+, 15%), 262 (M^+- 15, 2%), 235 (M^+- 42, 3%).

Anal. Calcd for $C_{11}H_{19}NO_7$: C, 47.65; H, 6.86; N, 5.05. Found: C, 47.96; H, 6.77; N, 5.44.

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