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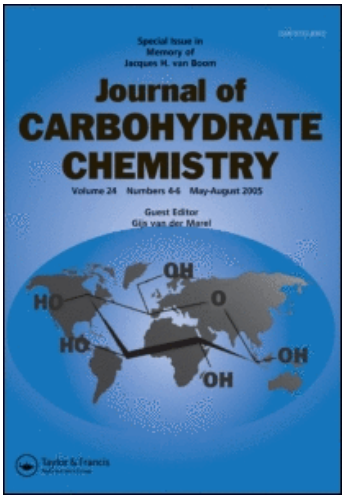

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OXAZOLIDINES FROM SUGARS, III. A NEW METHOD FOR N-ALKYL AND N,N-DIALKYL-D-GLUCOSAMINE DERIVATIVES[1]

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ABSTRACT

Title compounds can be synthesised by an easy two-step method from the readily available benzyl 2-acylamino-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosides (**1-5**), by nucleophilic cleavage of the oxazolidine ring previously formed between the positions 2 and 3 of the aminosugars.

INTRODUCTION

As a part of our work on the synthesis and reactivity of oxazolidines derived from sugars,[2,3] we present herein a new method to prepare *N*-alkyl and *N,N*-dialkyl-D-glucosamine derivatives from the readily available benzyl 2-acylamino-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosides (**1-5**). Previously reported preparations of related D-glucosamine derivatives include direct reduction of the amido function,[4] and the alkylation of an acylamino-D-glucosamine derivative followed by reduction of the amido function.[5]

Our methodology implies the formation of an oxazolidine ring between the positions 2 and 3 of the aminosugar followed by cleavage of the oxazolidine ring by nucleophilic reagents (i.e., hydride or Grignard reagents).

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RESULTS AND DISCUSSION

Methylenation[6] of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**) with dibromomethane under phase-transfer conditions (50% NaOH, tetra-*n*-butylammonium bromide) afforded compound **6**, 3-acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine, in 89% of yield. In the same way, compounds of related structure, **7-9**, were obtained from different *N*-acyl-D-glucosamine derivatives (**2-4**) in good yields (Fig 1). The IR spectra of these products showed no hydroxy-stretching frequencies. The ^{1}H NMR chemical-shift data from these compounds included two doublets at about 5 ppm, indicating the presence of methylene protons. The low values (~3.6 Hz) of the geminal proton coupling constants for the OCH_2N groups indicated that they are part of a five-membered ring.[7] The ^{13}C NMR spectra of these compounds showed the presence of a new methylene carbon at about 80 ppm, and the C-2 and C-3 carbons of the pyranosyl ring were deshielded due to the β-effect of the methylene group between these positions (Table 1).

On the other hand, compound **10**, 3-acetyl-2-methoxycarbonyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-glucopyranosido)[2,3-*d*]oxazolidine, was obtained from **5**, benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside, as described previously,[2] by reaction with dichloroacetic acid in presence of an excess of sodium hydride in refluxing 1,4-dioxane followed by esterification with diazomethane.

Variously substituted *N,N*-dialkyl-D-glucosamine derivatives (**11-15**) were easily prepared by reduction of compounds **6-10** with lithium aluminium hydride (LAH) in THF, the best reaction conditions being three moles of LAH *per* mole of substrate in refluxing THF for 1 h (Table 2).

Under these conditions, simultaneous C-O bond cleavages, at the oxazolidine ring and the amide function, occurred. The amide carbonyl-stretching band around 1650 cm^{-1} was missing in the IR spectra of the reduction products. In their ^{1}H NMR spectra, the two 5 ppm doublets were replaced by a three-proton singlet around 2.4 ppm due to the NMe produced (in compound **15** an ABX_2 system for the NCH_2CH_2OH group was observed).

The *N*-alkyl derivatives (**16-20**) were obtained by reaction with lithium triethylborohydride (Superhydride®) or Grignard reagents. It is known that the reduction of tertiary amides with superhydride proceeds[8] with carbon-nitrogen rather than carbon-oxygen bond fission. Consequently, the reaction of **6** or **10** with superhydride in anhydrous tetrahydrofuran at 0 °C for 30 min gave, after the usual work-up, compounds **16** (92%) and **20** (48%), respectively. In contrast, the reaction of **6** with methyl, ethyl or vinylmagnesium bromide in dry toluene at room temperature overnight yielded

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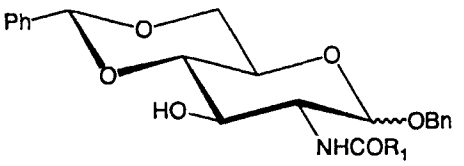
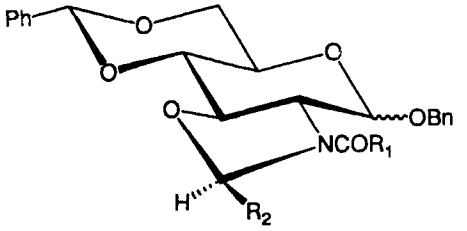
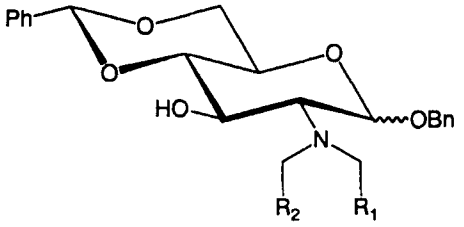


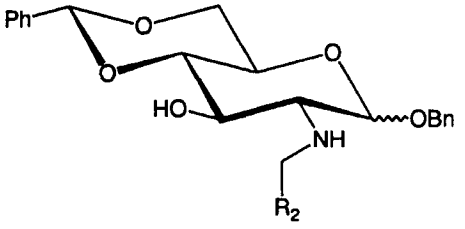
	Anomer	R_1
1	α	Me
2	α	^{n}Hept
3	α	^{t}Bu
4	α	Ph
5	β	Me



	Anomer	R_1	R_2
6	α	Me	H
7	α	^{n}Hept	H
8	α	^{t}Bu	H
9	α	Ph	H
10	β	Me	COOMe



	Anomer	R_1	R_2
11	α	Me	H
12	α	^{n}Hept	H
13	α	^{t}Bu	H
14	α	Ph	H
15	β	Me	CH_2OH



	Anomer	R_2
16	α	H
17	α	Me
18	α	Et
19	α	$CH=CH_2$
20	β	CH_2OH

FIG. 1. Starting compounds **1-5**, oxazolidine products **6-10**, and final reduction products **11-20**.

TABLE 1. ^{13}C NMR Selected Spectral Data[a] for Compounds **6-9**.

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OCH_2N
6	98.5	60.5	76.8	80.8	64.6	68.8	101.5	80.2
7	98.7	60.6	76.6	80.8	64.6	68.8	101.5	79.9
8	98.8	62.1	75.5	80.9	64.6	68.8	101.5	80.2
9	98.2	61.2	76.9	80.8	64.7	68.8	101.5	82.2

a. In $CDCl_3$; chemical shifts are relative to Me_4Si (0 ppm).

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TABLE 2. Reaction conditions for compounds **11-20**.

Starting material	Reagent (molar ratio) mol reagent/ mol compd	Temperature (° C)	Time (h)	Product	Yield (%)
6	LAH (1)	0	0.5	**11**	57
6	LAH (2)	0	0.5	**11**	70
6	LAH (3)	65	1	**11**	90
6	$LiEt_3BH$ (4)	0	0.5	**16**	92
6	MeMgBr (6)	20	12	**17**	87
6	EtMgBr (8)	20	12	**18**	91
6	CH_2=CHMgBr (8)	20	12	**19**	79
7	LAH (3)	65	1	**12**	88
8	LAH (3)	65	1	**13**	83
9	LAH (1)	0	0.5	**14**	0
9	LAH (2)	0	0.5	**14**	0
9	LAH (3)	65	1	**14**	65
10	LAH (2)	0	0.5	**15**	54
10	LAH (3)	65	0.5	**15**	67
10	$LiEt_3BH$ (4)	0	0.5	**20**	48

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compounds **17** (87%), **18** (91%) and **19** (79%), respectively. Their structures were also confirmed by spectroscopic and analytical data, which are recorded in the experimental part.

As seen in Table 2, the methodology reported provides an easy and versatile way to synthesize *N*-alkyl and *N,N*-dialkyl-D-glucosamine derivatives (e.g., compounds **11** and **16-19** were obtained from compound **6** in high yield).

EXPERIMENTAL

General procedures. Melting points were determined with a Gallenkamp apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241-MC polarimeter, and IR spectra (KBr) were recorded with a Bomem Michelson 100

spectrophotometer. ^1H and ^{13}C NMR spectra (200 and 50 MHz, respectively; internal Me_4Si) were recorded on a Bruker AC-200 instrument. Mass spectra (CI with isobutane) were obtained with a Kratos MS-80-RFA spectrometer. Solvent evaporations were conducted *in vacuo*. Column chromatography was performed on silica gel 60 (Merck).

3-Acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido) [2,3-*d*]oxazolidine (6). To a solution of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**1**, 2.05 g, 5 mmol) in dibromomethane (50 mL), were added tetrabutylammonium bromide (0.5 g) and 50% aqueous sodium hydroxide (50 mL) and the mixture was vigorously stirred at 100 °C. After 4 h, the organic phase was separated, and the aqueous phase was extracted three times with chloroform. The combined organic phase was washed with water until pH 7 was reached, dried (sodium sulphate), and the solvent removed under reduced pressure. The ensuing solid was chromatographied on a column of silica gel using dichloromethane as the eluent to give 1.83 g (89%) of compound **6** as a white solid: mp 169-170 °C; $[\alpha]_D$ +153° (*c* 1.1, dichloromethane); IR (KBr) 3064 and 3034 (Ar), and 1664 cm^{-1} (amide); ^1H NMR ($CDCl_3$) δ 1.99 (s, 3H, NAc), 3.33 (dd, 1H, $J_{1,2}$ = 2.9 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.68 (AB q, 2H, ^2J = 11.5 Hz, PhCH_2), 4.93 and 5.04 (2 d, 2H, ^2J = 3.4 Hz, OCH_2N), 5.61 (s, 1H, PhC*H*), and 5.90 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1); mass spectrum (CI) m/z 412 (100%) $[M+H]^+$.

Anal. Calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 66.99; H, 6.41; N, 3.27.

3-Octanoyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (7). Reaction of benzyl 4,6-*O*-benzylidene-2-deoxy-2-octanamido-α-D-glucopyranoside (**2**, 2.4 g, 0.5 mmol) with dibromomethane, as described for the preparation of **6**, yielded crude **7**. Recrystallization from ethanol gave **7** (2.14 g, 87 %) as a white solid: mp 129-130 °C; $[\alpha]_D$ +185° (*c* 1, dichloromethane); IR (KBr) 3066 and 3035 (Ar), and 1662 cm^{-1} (amide); ^1H NMR ($CDCl_3$) δ 0.87 (t, 3H, ^3J = 6.5 Hz, Me), 2.17 (t, 2H, ^3J = 7.1 Hz, NCOCH_2), 3.34 (dd, 1H, $J_{1,2}$ = 2.7 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.67 (AB q, 2H, ^2J = 11.5 Hz, PhCH_2), 4.93 and 5.05 (2 d, 2H, ^2J = 3.4 Hz, OCH_2N), 5.59 (s, 1H, PhC*H*), and 5.92 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1); mass spectrum (CI) m/z 496 (100%) $[M+H]^+$.

Anal. Calcd for $C_{29}H_{37}NO_6$: C, 70.28; H, 7.52; N, 2.83. Found: C, 70.42; H, 7.31; N, 3.09.

3-Pivaloyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (8). Reaction of benzyl 4,6-*O*-benzylidene-2-deoxy-2-pivalamido-α-D-glucopyranoside (**3**, 2.2 g, 0.5 mmol) with dibromomethane, as described for the preparation of **6**, yielded crude **8**, which was purified by column

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chromatography using dichloromethane as the eluent to give 1.7 g (76 %) of **8** as a white solid: mp 77-79 °C; $[\alpha]_D$ +143° (*c* 1, dichloromethane); IR (KBr) 3065 and 3033 (Ar), and 1640 cm^{-1} (amide); ^1H NMR ($CDCl_3$) δ 1.21 (s, 9H, ^{t}Bu), 3.43 (dd, 1H, $J_{1,2}$ = 2.7 Hz, $J_{2,3}$ = 10.3 Hz, H-2), 4.66 (AB q, 2H, ^2J = 12.0 Hz, PhCH_2), 4.96 and 5.27 (2 d, 2H, ^2J = 3.7 Hz, OCH_2N), 5.61 (s, 1H, PhC*H*), and 5.86 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1); mass spectrum (CI) m/z 454 (100%) $[M+H]^+$.

Anal. Calcd for $C_{26}H_{31}NO_6$: C, 68.86; H, 6.89; N, 3.09. Found: C, 68.86; H, 6.89; N, 3.06.

3-Benzoyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (9). Reaction of benzyl 4,6-*O*-benzylidene-2-benzamido-2-deoxy-α-D-glucopyranoside (**4**, 2.3 g, 0.5 mmol) with dibromomethane, as described for the preparation of **6**, yielded crude **9**, which was purified by column chromatography using dichloromethane as the eluent to give 1.9 g (81 %) of **9** as a white solid: mp 139-140 °C; $[\alpha]_D$ +193° (*c* 1.1, dichloromethane); IR (KBr) 3061 and 3029 (Ar), and 1640 cm^{-1} (amide); ^1H NMR (DMSO, 100 °C) δ 3.58 (dd, 1H, $J_{1,2}$ = 2.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.57 (AB q, 2H, ^2J = 12.1 Hz, PhCH_2), 4.97 and 5.08 (2 d, 2H, ^2J = 4.1 Hz, OCH_2N), 5.37 (broad s, H-1), and 5.72 (s, 1H, PhC*H*); mass spectrum (CI) m/z 474 (78%) $[M+H]^+$.

Anal. Calcd for $C_{28}H_{27}NO_6$: C, 71.02; H, 5.75; N, 2.96. Found: C, 71.14; H, 5.78; N, 2.96.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-ethylmethylamino-α-D-glucopyranoside (11). To a solution of 3-acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**6**, 411 mg, 1 mmol) in THF (10 mL) at 65 °C under an atmosphere of argon, was added a 1M solution of lithium aluminium hydride in THF (3 mL). The solution was stirred, and after 1 h, cooled and a saturated solution of sodium sulphate (0.9 mL) was added to it dropwise. The solid was removed by filtration and washed with anhydrous THF. The solution was concentrated to give a white solid (420 mg) which was purified by column chromatography (2:1 ether-hexane). Compound **11** (360 mg, 90%) was obtained as a white solid: mp 96-98 °C; $[\alpha]_D$ +149° (*c* 0.3, dichloromethane); IR (KBr) 3413 (OH),3065, and 3034 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 1.05 (t, 3H, ^3J = 7.1 Hz, NCH_2CH_3), 2.44 (s, 3H, NMe), 2.69 (m, 2H, NCH_2CH_3), 2.81 (dd, 1H, $J_{1,2}$ = 3.2 Hz, $J_{2,3}$ = 10.5 Hz, H-2), 4.61 (AB q, 2H, ^2J = 11.7 Hz, PhCH_2), 5.04 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), and 5.57 (s, 1H, PhC*H*); mass spectrum (CI) m/z 400 (98%) $[M+H]^+$.

Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.50. Found: C, 69.17; H, 7.25; N, 3.46.

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Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-methyloctylamino-α-D-glucopyranoside (12). Reaction of 3-octanoyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**7**, 495 mg, 1 mmol) with LAH as described for the preparation of **11** gave crude **12**, which was purified by column chromatography using 50:1 dichloromethane-methanol as the eluent to give 425 mg (88%) of **12** as a white solid: mp 47-49 °C; $[\alpha]_D$ +83° (*c* 1, dichloromethane); IR (KBr) 3412 (OH), 3067 and 3036 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, ^3J = 5.9 Hz, CH_3), 2.43 (s, 3H, NMe), 2.62 (m, 2H, NCH_2), 2.78 (dd, 1H, $J_{1,2}$ = 2.8 Hz, $J_{2,3}$ = 10.5 Hz, H-2), 4.62 (AB q, 2H, ^2J = 11.7 Hz, $PhCH_2$), 5.06 (d, 1H, $J_{1,2}$ = 2.8 Hz, H-1), and 5.56 (s, 1H, PhC*H*); mass spectrum (CI) m/z 484 (100%) $[M+H]^+$.

Anal. Calcd for $C_{29}H_{41}NO_5$: C, 72.02; H, 8.54; N, 2.89. Found: C, 71.84; H, 8.67; N, 2.92.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-methyl*neo*pentylamino-α-D-glucopyranoside (13). Reaction of 3-pivaloyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**8**, 453 mg, 1 mmol) with LAH as described for the preparation of **11** gave crude **13**, which was purified by column chromatography using 50:1 dichloromethane-methanol as the eluent to give 366 mg (83%) of **13** as a syrup: $[\alpha]_D$ +96° (*c* 0.8, dichloromethane); IR (KBr) 3420 (OH), 3066 and 3030 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 0.86 (s, 9H, ^tBu), 2.41 (AB q, 2H, ^2J = 14.2 Hz, $NCH_2{}^tBu$), 2.51 (s, 3H, NMe), 2.69 (dd, 1H, $J_{1,2}$ = 3.2 Hz, $J_{2,3}$ = 10.5 Hz, H-2), 4.63 (AB q, 2H, ^2J = 12.0 Hz, $PhCH_2$), 5.03 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), and 5.55 (s, 1H, PhC*H*); mass spectrum (CI) m/z 442 (83%) $[M+H]^+$.

Anal. Calcd for $C_{26}H_{35}NO_5$: C, 70.72; H, 7.99; N, 3.17. Found: C, 70.75; H, 8.08; N, 3.23.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-benzylmethylamino-α-D-glucopyranoside (14). Reaction of 3-benzoyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**9**, 473 mg, 1 mmol) with LAH as described for the preparation of **11** gave crude **14**, which was purified by column chromatography using 50:1 dichloromethane-methanol as the eluent to give 300 mg (65%) of **14** as a syrup: $[\alpha]_D$ +94° (*c* 2.8, dichloromethane); IR (KBr) 3416 (OH), 3062 and 3033 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H, NMe), 2.84 (dd, 1H, $J_{1,2}$ = 3.3 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.62 (s, 2H, NCH_2Ph), 4.63 (AB q, 2H, ^2J = 11.8 Hz, $PhCH_2$), 5.03 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), and 5.53 (s, 1H, PhC*H*); mass spectrum (CI) m/z 462 (100%) $[M+H]^+$.

Anal. Calcd for $C_{28}H_{31}NO_5$: C, 72.86; H, 6.77; N, 3.03. Found: C, 72.67; H, 6.82; N, 3.06.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-ethyl(2'-hydroxyethyl)amino-β-D-glucopyranoside (15). Reaction of 3-acetyl-2-methoxycarbonyl-(benzyl 4,6-*O*-

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benzylidene-2,3-dideoxy-β-D-glucopyranosido)[2,3-*d*]oxazolidine (**10**, 469 mg, 1 mmol) with LAH as described for the preparation of **11** gave crude **15**, which was purified by column chromatography using a mixture 3:1:4 of dichloromethane-acetone-hexane as the eluent to give 287 mg (67%) of **15** as a white solid: mp 100-102 °C; $[\alpha]_D$ -52° (*c* 1, dichloromethane); IR (KBr) 3372 (OH), 3063, and 3033 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 1.05 (t, 3H, ^3J = 7.1 Hz, NCH_2CH_3), 2.75 (q, 2H, NCH_2CH_3), 2.80 (t, 1H, $J_{1,2}$ = 8.6 Hz, $J_{2,3}$ = 9.1 Hz, H-2), 4.64 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 4.76 (AB q, 2H, ^2J = 11.6 Hz, $PhCH_2$), and 5.57 (s, 1H, PhCH); mass spectrum (CI) m/z 430 (95%) $[M+H]^+$.

Anal. Calcd for $C_{24}H_{31}NO_6$: C, 67.11; H, 7.27; N, 3.26. Found: C, 67.02; H, 7.39; N, 3.46.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-methylamino-α-D-glucopyranoside (16). To a solution of 3-acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**6**, 205 mg, 0.5 mmol) in THF (5 mL) at 0 °C under an atmosphere of argon, was added a 1M solution of lithium triethylborohydride (Superhydride®) in THF (2 mL) and the solution was stirred for 30 min. Water (2 mL) was added dropwise and the mixture was concentrated to give a liquid residue, which was extracted twice with dichloromethane. The organic phase was washed with water, dried (sodium sulphate), and concentrated to give a white solid (200 mg), which was purified by column chromatography (50:1 dichloromethane-methanol). Compound **16** (175 mg, 92%) was obtained as a white solid: mp 153-155 °C; $[\alpha]_D$ +131° (*c* 1, dichloromethane); IR (KBr) 3452 (OH), 3200 (NH), 3063, and 3032 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3H, NMe), 2.53 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.9 Hz, H-2), 4.63 (AB q, 2H, ^2J = 11.9 Hz, $PhCH_2$), 5.02 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), and 5.55 (s, 1H, PhCH); mass spectrum (CI) m/z 372 (100%) $[M+H]^+$.

Anal. Calcd for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.77. Found: C, 67.99; H, 6.81; N, 3.78.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-ethylamino-α-D-glucopyranoside (17). To a solution of 3-acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**6**, 205 mg, 0.5 mmol) in dry toluene (20 mL) at 0 °C under atmosphere of argon, was added a 3M solution of methylmagnesium bromide in ether (1 mL) and the solution was stirred overnight. The reaction mixture was extracted with water and the aqueous phase washed with toluene. The combined organic phase was washed with water, dried (sodium sulphate) and concentrated to dryness. The residue was chromatographied on a column of silica gel (50:1 dichloromethane-methanol) to give **17** (167 mg, 87%), as a white solid: mp 120-121 °C; $[\alpha]_D$ +118° (*c* 0.6, dichloromethane); IR (KBr) 3468 (OH), 3262 (NH), 3064 and 3032 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 1.10 (t, 3H, ^3J = 7.1 Hz, NCH_2CH_3), 2.61 (dq, 2H, ^2J = 9.2 Hz,

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NCH_2CH_3), 2.76 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 4.65 (AB q, 2H, ^2J = 12.0 Hz, $PhCH_2$), 5.03 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), and 5.57 (s, 1H, PhC*H*); mass spectrum (CI) m/z 386 (100%) $[M+H]^+$.

Anal. Calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.79; H, 6.82; N, 3.56.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-propylamino-α-D-glucopyranoside (18). Reaction of 3-acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**6**, 205 mg, 0.5 mmol) with a 2M solution of ethylmagnesium bromide in ether (2 mL), as described for the preparation of **17** gave crude **18**, which was purified by column chromatography (3:1:4 dichloromethane-acetone-hexane) to give **18** (164 mg, 82%): mp 96-97 °C; $[\alpha]_D$ +126° (*c* 0.8, dichloromethane); IR (KBr) 3485 (OH), 3210 (NH), 3065, and 3037 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 0.82 (t, 3H, ^3J = 7.2 Hz, $NCH_2CH_2CH_3$), 1.39 (m, 2H, $NCH_2CH_2CH_3$), 2.41 (m, 2H, $NCH_2CH_2CH_3$), 2.61 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 4.62 (AB q, 2H, ^2J = 11.9 Hz, $PhCH_2$), 4.99 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), and 5.55 (s, 1H, PhC*H*); mass spectrum (CI) m/z 400 (100%) $[M+H]^+$.

Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.50. Found: C, 69.28; H, 7.51; N, 3.51.

Benzyl 2-Allylamino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (19). Reaction of 3-acetyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-glucopyranosido)[2,3-*d*]oxazolidine (**6**, 205 mg, 0.5 mmol) with a 1M solution of vinylmagnesium bromide in THF (4 mL), as described for the preparation of **17**, gave crude **19**, which was purified by column chromatography (60:1 dichloromethane-methanol) to give **19** (157 mg, 79%): mp 78-79 °C; $[\alpha]_D$ +125° (*c* 1, dichloromethane); IR (KBr) 3450 (OH), 3323 (NH), 3068 and 3033 (Ar), and 1645 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 2.65 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.7 Hz, H-2), 3.12 (m, 2H, NCH_2-CH=CH_2), 4.62 (AB q, 2H, ^2J = 11.9 Hz, $PhCH_2$), 4.97 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.04 (m, 2H, $CH=CH_2$), 5.55 (s, 1H, PhC*H*), and 5.78 (m, 1H, $CH=CH_2$); mass spectrum (CI) m/z 398 (100%) $[M+H]^+$.

Anal. Calcd for $C_{23}H_{27}NO_5$: C, 69.52; H, 6.80; N, 3.52. Found: C, 69.55; H, 6.89; N, 3.50.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-(2'-hydroxyethyl)amino-β-D-glucopyranoside (20). Reaction of 3-acetyl-2-methoxycarbonyl-(benzyl 4,6-*O*-benzylidene-2,3-dideoxy-β-D-glucopyranosido)[2,3-*d*]oxazolidine (**10**, 400 mg, 0.85 mmol) with Superhydride, as described for the preparation of **16**, afforded crude **20**, which was purified by column chromatography (3:2:2 dichloromethane-acetone-hexane). Compound **20** (164 mg, 48%) was obtained as a white solid: mp 146-148 °C; $[\alpha]_D$ -41°

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(*c* 0.5, dichloromethane); IR (KBr) 3410 (OH), 3241 (NH), 3068, and 3037 cm^{-1} (Ar); ^1H NMR ($CDCl_3$) δ 2.62 (t, 1H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 8.5 Hz, H-2), 2.88 and 3.58 (ABX_2 system, ^2J = 13.2 Hz, NCH_2CH_2OH), 4.45 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 4.68 (AB q, 2H, ^2J = 11.6 Hz, $PhCH_2$), and 5.50 (s, 1H, PhCH); mass spectrum (CI) m/z 402 (100%) $[M+H]^+$.

Anal. Calcd for $C_{22}H_{27}NO_6$: C, 65.82; H, 6.78; N, 3.49. Found: C, 65.78; H, 6.87; N, 3.28.

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