Synthesis of *N*-chloroacetyl-β-glycopyranosylamines, derivatives of monosaccharides and lactose

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N-Chloroacetyl-β-glycopyranosylamines were synthesized from various monosaccharides (hexoses, pentoses, deoxysugars, uronic acids, and sugar phosphates) and a disaccharide (lactose) by *N*-acylation of the corresponding β-glycosylamines with chloroacetic anhydride in DMF. In some cases, treatment of monosaccharides with NH_3 in the presence of $(NH_4)_2CO_3$ in MeOH or aqueous MeOH was more efficient than the methods previously described, as it gave β-glycosylamines in higher yields.

Key words: β-glycopyranosylamines, monosaccharides, lactose, *N*-chloroacetylation, glycoconjugates.

Studies of many biological processes connected with sugar—protein interactions (including those with enzymes, receptors, or lectins) require the conversion of mono- and oligosaccharides to conjugates that are easily detectable by various physicochemical techniques. Glycosylamines have proved to be convenient sugar derivatives that can be used as intermediates to obtain various glycoconjugates.

The classic method for obtaining glycosylamines includes the condensation of monosaccharides with NH_3 in MeOH.[1] However, this method is not stereospecific and is unsuitable for amino sugars and complex oligosaccharides. We have worked out a simple stereospecific method for the synthesis of β-glycopyranosylamines, which are derivatives of *N*-acetylamino sugars, based on treatment of mono- and oligosaccharides with NH_4HCO_3 in H_2O.[2—4] This method has also been shown to be highly convenient for obtaining β-glycopyranosylamines of other mono- and oligosaccharides.[5,6] Modifications of this method using $(NH_4)_2CO_3$ in H_2O [7] or aqueous NH_3 in the presence of NH_4HCO_3 [8] as reagents have been suggested.

The main route for the synthesis of glycoconjugates from glycosylamines includes N-acylation of the glycosylamines, which results in stable products that are the target compounds *per se* or contain the functional groups (NH_2—, —COOR, or —CH=CH_2) in the acyl moiety that afford further conjugation.[2,3,5,6,9] Recently *N*-chloroacetylglycosylamines have been shown to be convenient intermediates for the synthesis of glycoconjugates starting from *N*-acetylglucosamine and oligosaccharides with *N*-acetylglucosamine at the reducing end.[9]

This work deals with the synthesis of *N*-chloroacetyl-β-glycopyranosylamines, which are derivatives of lactose and monosaccharides of various classes (hexoses, pentoses, deoxy sugars, uronic acids, and sugar phosphates).

The initial β-glycopyranosylamines **1a**, **2a**, **3a**, and **1c** (the derivatives of D-Glc, D-Gal, D-Man, and D-Gal-(β1-4)-D-Glc, respectively) were smoothly obtained in 70—90 % yields by treating a reducing sugar with aqueous NH_4HCO_3, as described previously.[6] Glycosylamines **4a**, **5a**, and **6a** (derivatives of D-Xyl, 2-deoxy-D-*arabino*-hexose (2dGlc), and L-Fuc, respectively) were also generated in high yields (~80 %) according to paper electrophoresis data. However, our attempts to isolate glycosylamines **4a** and **5a** from the reaction mixtures resulted in their hydrolysis, which was especially substantial (~50 %) in the case of **4a**. Moreover, ^1H NMR data showed that the more stable bis(β-glycosyl)amine **5c**, rather than β-glycosylamine **5a**, was the main product arising from 2dGlc. Glycosylamines **7a** and **8a** were obtained from D-glucose 6-phosphate (Glc6P) and D-glucuronic acid (GlcA) in ~80 and ~20 % yields, respectively, according to electrophoresis data. D-Glucuronolactone interacted with NH_4HCO_3 more actively than GlcA, but the relation gave two products. The major product was β-glycosylamine **8c**, a derivative of GlcA amide. This fact was proved by elemental analysis and ^1H and ^{13}C NMR data for *N*-acetyl derivative **8d** obtained in 30 % yield. The minor product was probably GlcA glycosylamine **8a**. The low yield of **8a**, substantial hydrolysis of **4a**, and the formation of bis(β-glycosyl)amine **5c** stimulated the search for more convenient routes for glycosylamine synthesis.

The condensation of D-Xyl, 2dGlc, L-Fuc, Glc6P, and D-GlcA with NH_3 + $(NH_4)_2CO_3$ in MeOH (or in aqueous MeOH for the two latter sugars) made it possible to obtain β-glycosylamines in higher yields and to inhibit the side processes, such as hydrolysis and the

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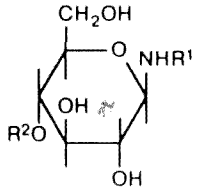
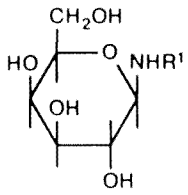


1a—d



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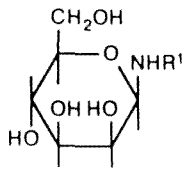
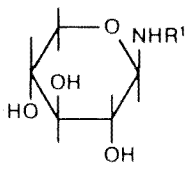
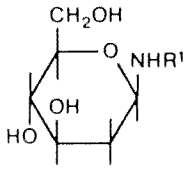


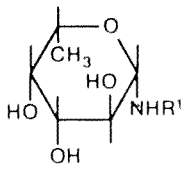
3a,b



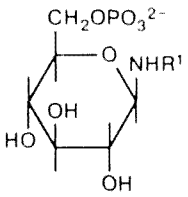
4a,b



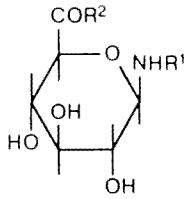
5a—c



6a,b



7a—c



8a—e

Compound	R	a	b	c	d	e
1	R^1	H	$COCH_2Cl$	H	$COCH_2Cl$	—
	R^2	H	H	Galβ1	Galβ1	—
8	R^1	H	$COCH_2Cl$	H	Ac	$COCH_2Cl$
	R^2	ONH_4	OH	NH_2	NH_2	NH_2
2—7	R^1	H	$COCH_2Cl$	2dGlc (**5**), $COONH_4$ (**7**)	—	—

formation of bis(glycosyl)amines. According to ^{1}H NMR data, the presence of $(NH_4)_2CO_3$ markedly increased the yields of the target compounds (to 90 % after 3 days) in the case of D-Xyl and Glc6P. Treatment with NH_3 in MeOH in the absence of $(NH_4)_2CO_3$ [1] resulted in β-glycosylamines **4a** and **7a** in maximum yields of 65 and 45 %, respectively, after 8 days, accompanied by a marked increase in the bis(glycosyl)amine content and the appearance of other by-products. Particulary in the reaction with D-Xyl small quantity (2.5 %) of α-glycosylamine (δ 4.73, d, H(1), J = 2 Hz) was formed and an unidentified product (~20 %) was found in the reaction with Glc6P.

It should be mentioned that in spite of the extraordinary tendency of β-glycosylamines **5a** and **8a** to form bis(glycosyl)amines, we succeeded in obtaining products containing 40 and 65 %, respectively, of these β-glycosylamines by the reaction with NH_3 + $(NH_4)_2CO_3$. At the same time, another deoxysugar, L-Fuc, was smoothly converted to glycosylamine **6a** under these conditions (the yield of crystalline product was 81 %).

Crude β-glycosylamines containing the initial sugar and bis(glycosyl)amine impurities were used for *N*-acylation in parallel with practically pure crystalline β-glycosylamines **6a** and **4a**. A solution of $(ClCH_2CO)_2O$ in DMF was used as the acylating agent. This is a more convenient method for preparative synthesis than that described previously for the *N*-acylation of small amounts of β-glycosylamines, amino sugar derivatives.[9] The excess of anhydride was increased from 1.3 to 1.8 mol per 1 mol of glycosylamine if CO_2 was evolved during the reaction due to the presence of ammonium carbonates or *N*-glycosylcarbamates (the latter are also capable of *N*-acylation) in the initial compound. Besides *N*-acylation, we also observed (chromatography) the formation of minor products of the *O*-acylation of sugar hydroxyl groups under the used conditions. For *O*-deacylation, the reaction products were treated with Et_3N in aqueous MeOH and then crystallized and/or chromatographed to give *N*-chloroacetyl-β-glycosylamines in 50—80 % yields for **1b,d**, **2b—4b**, and **6b**, and ~25 % yield for **5b** and **8b,e**.

The low yields of *N*-chloroacetyl derivatives in the latter cases are likely caused by the lability of glycosylamines **5a** and **8a,d** under the acidic conditions of acylation. The acylation of phosphates **7a,c** under the optimum conditions selected was impossible because of their low solubility in DMF and their lability in the acidic medium. In this case, acylation was performed in aqueous DMF in the presence of diisopropylethylamine, and the reaction product was isolated in 15 % yield.

The structures of *N*-chloroacetyl-β-glycopyranosylamines were confirmed by elemental analysis and ^{1}H and ^{13}C NMR spectral data. ^{1}H NMR spectra included the singlets of $ClCH_2CO$ groups at δ 4.2 ppm and the signals of sugar H(1) at ~5 ppm with the coupling constants ~9 Hz (except for mannose derivative **3b**), characteristic for β-anomers. The β-configuration of mannose derivative **3b** was unambiguously evident from the ^{13}C NMR spectrum with characteristic signals of C(3) and C(5) atoms at δ 74.4 and 79.1 ppm, respectively.[10]

Thus, we suggested a new modification of the method for obtaining β-glycosylamines and synthesized a series of their *N*-chloroacetyl derivatives as potential agents for obtaining various glycoconjugates.

Experimental

^{1}H and ^{13}C NMR spectra were recorded in D_2O on a Bruker WM-250 spectrometer at 300 K with acetone as the internal standard. Ascending chromatography was performed on Filtrak FN no. 15 paper in the *n*-BuOH—AcOH—H_2O (4 : 1.4 : 2.5) solvent system. Electrophoresis was carried out on Filtrak FN no. 1 paper in 6 % HCOOH. The spots were visualized with ninhydrin, $AgNO_3$—KOH, and KIO_4—$AgNO_3$—KOH. Glycosylamine solutions were evaporated *in vacuo* at a bath temperature ≤30 °C.

β-D-Glucopyranosylamine (1a), β-D-galactopyranosylamine (2a), β-D-mannopyranosylamine (3a), and 4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosylamine (1c) were obtained by the condensation of the corresponding 0.25 *M* aqueous sugar solu-

tions with NH_4HCO_3 [6] and isolated as powders containing 70—90 % of the glycosylamines and 10—30 % of the initial sugars.

β-D-Xylopyranosylamine (4a), 2-deoxy-β-D-*arabino*-hexopyranosylamine (5a), and β-D-fucopyranosylamine (6a). Powdered $(NH_4)_2CO_3$ (0.25 g) was added to a solution of a monosaccharide (0.5 g) in MeOH (20 mL) containing NH_3 (17 %). The mixture was stirred for 1 h and kept for 3 days at 20 °C. Then the mixture was evaporated with MeOH (4×20 mL, 2×20 mL for **5a**) to 5 mL (last time to dryness).

Compound 4a: The residue was dissolved in a small volume of MeOH containing NH_3 (17 %) and $(NH_4)_2CO_3$ (1 %). The crystals precipitated after 16 h were filtered off, washed with cold MeOH and ether, and dried to give **4a** (0.38 g, 75 %), m.p. 126—127 °C, $[\alpha]_D^{20}$ −17.0° (*c* 1.0, H_2O) (*cf.* ref. 11). ^1H NMR (δ): 4.02 (d, 1 H, H(1), J = 9 Hz). ^{13}C NMR (δ): 67.5 (C-5), 70.7 (C-4), 75.4 (C-2), 77.8 (C-3), 87.1 (C-1).

Compound 5a: The residue contained glycosylamine **5a** (42 %), bis(β-glycosyl)amine **5c** (52 %), and the initial monosaccharide (6 %). ^1H NMR (δ): 4.33 (dd, H(1), J = 2.5 and 10.5 Hz) for **5a**; 4.54 (dd, H(1) and H(1′), J = 2.5 and 10.5 Hz) for **5c**.

Compound 6a: The residue was treated as described for obtaining **4a**. Yield: 0.4 g (81 %), m.p. 131—133 °C, $[\alpha]_D^{20}$ −47.9° (*c* 1.0, H_2O). Found (%): C, 44.16; H, 7.75; N, 8.57. $C_6H_{13}NO_4$. Calculated (%): C, 44.16; H, 8.03; N, 8.58. ^1H NMR (δ): 1.23 (d, 3 H, CH_3), 4.02 (d, 1 H, H(1), J = 8.6 Hz).

6-Phospho-β-D-glucopyranosylamine, disodium salt (7a). A solution of NH_3 (17 %) in MeOH (6.6 mL) and $(NH_4)_2CO_3$ (2 g) were added to a solution of D-glucose 6-phosphate disodium salt (0.2 g) in H_2O (4.4 mL), and the mixture was kept for 3 days at 20 °C. The excess of $(NH_4)_2CO_3$ was filtered off, and the filtrate was diluted with H_2O and evaporated with H_2O (4×20 mL) *in vacuo* to 5—10 mL. The residue was freeze-dried and then dried for 3 h at 50 °C *in vacuo* to yield 0.18 g of a product containing glycosylamine **7a** (48 %), carbamate **7c** (40 %), bis(β-glycosyl)amine (2 %), and the initial phosphate (10 %). ^1H NMR (δ): 4.05 (d, H(1), J = 9 Hz) for **7a**; 4.66 (d, H(1), J = 9 Hz) for **7c**; and 4.24 (d, H(1) and H(1′), J = 9 Hz) for bis(β-glycosyl)amine.

Ammonium (β-D-glucopyranosylamine)uronate (8a). A solution of NH_3 (17 %) in MeOH (6.6 mL) was added to a solution of D-glucuronic acid (0.3 g) in strong NH_4OH (2 mL) containing powdered $(NH_4)_2CO_3$ (0.1 g), and the mixture was kept for 2 days at 15 °C. The mixture was diluted with MeOH (150 mL) and evaporated to ~7 mL. The precipitated amorphous compound was filtered off, washed with MeOH and ether, and dried *in vacuo* to yield 0.2 g of a product containing glycosylamine **8a** (65 %), bis(β-glycosyl)amine (27 %), and the initial monosaccharide (8 %). ^1H NMR (δ): 4.09 (d, H(1), J = 8.9 Hz) for **8a**; and 4.3 (d, H(1) and H(1′), J = 8.9 Hz) for bis(β-glycosyl)amine.

(*N*-Acetyl-β-D-glucopyranosylamine)uronamide (8d). A solution of D-glucurono-γ-lactone (0.4 g) in H_2O (6 mL) was condensed with NH_4HCO_3 as described above. The resulting powder was dissolved in H_2O (5 mL), MeOH (1 mL) and Ac_2O (2 mL) were added, and the mixture was kept for 16 h at 20 °C. Then the reaction mixture was diluted with MeOH and evaporated with toluene *in vacuo* to dryness. The residue was dissolved in H_2O (5 mL) and stirred with Dowex 1×8 (OH^-) ion-exchange resin (3 mL) for 30 min. The resin was filtered off and washed with H_2O. The filtrate was evaporated to dryness, and the residue was chromatographed on SiO_2 in EtOAc—MeOH—H_2O (3 : 2 : 0.5) to give the amorphous compound (0.14 g, 29 %), $[\alpha]_D^{20}$ −22.5° (*c* 1.0, H_2O). Found (%): N, 12.30. $C_8H_{14}N_2O_6$. Calculated (%): N, 11.96. ^1H NMR (δ): 2.11 (s, 3 H, CH_3), 5.06 (d, 1 H, H(1), J = 8.5 Hz). ^{13}C NMR (δ): 23.3 (CH_3), 72.3 (C-4), 72.5 (C-2), 77.1 (C-3), 77.4 (C-5), 80.4 (C-1), 176.6 (C=O).

***N*-Chloroacetyl-β-glycosylamines (the general procedure).** A powdered product containing ~2 mmol of a glycosylamine was added to a solution of $(ClCH_2CO)_2O$ (2.6 mmol) in DMF (3 mL for **1c** and **3a**, 5 mL for **8a**, and 2 mL in other cases) at 0 °C with stirring. If CO_2 was evolved, another 1 mmol of $(ClCH_2CO)_2O$ was added. The mixture was kept at 0 °C for 3—5 h (the absence of the glycosylamine was monitored by electrophoresis). DMF was removed *in vacuo* with H_2O and *n*-BuOH. The residue was triturated several times with ether until the absence of acidic reaction and diluted with H_2O (1 mL). MeOH (1 mL) containing Et_3N (20 %) was added, and the solution was kept for 3 h at 20 °C and evaporated. The residue was triturated with ether (3×10 mL) and then crystallized and/or chromatographed on silica gel.

***N*-Chloroacetyl-β-D-glucopyranosylamine (1b)** was obtained by crystallization from MeOH. Yield: 0.31 g (61 %), m.p. 205—206 °C (decomp.), $[\alpha]_D^{20}$ −15.2° (*c* 1.0, H_2O). Found (%): C, 37.75; H, 5.55; Cl, 13.96; N, 5.34. $C_8H_{14}ClNO_6$. Calculated (%): C, 37.58; H, 5.52; Cl, 13.87; N, 5.48. ^1H NMR (δ): 4.22 (s, 2 H, CH_2), 5.02 (d, 1 H, H(1), J = 9 Hz).

***N*-Chloroacetyl-β-D-galactopyranosylamine (2b)** was obtained by crystallization from MeOH—H_2O (1 : 1) and chromatography of the mother liquid in acetone. Yield: 0.26 g (51 %), m.p. 217—219 °C (from acetone, decomp.), $[\alpha]_D^{20}$ +13.3° (*c* 1.0, H_2O). Found (%): C, 37.74; H, 5.71; Cl, 13.60; N, 5.42. $C_8H_{14}ClNO_6$. Calculated (%): C, 37.58; H, 5.52; Cl, 13.87; N, 5.48. ^1H NMR (δ): 4.22 (s, 2 H, CH_2), 4.96 (d, 1 H, H(1), J = 9 Hz).

***N*-Chloroacetyl-β-D-mannopyranosylamine (3b)** was obtained by crystallization from acetone and chromatography of the mother liquid in acetone. Yield: 0.32 g (63 %), m.p. 176—177 °C, $[\alpha]_D^{20}$ −37.5° (*c* 1.0, H_2O). Found (%): C, 37.87; H, 5.59; Cl, 13.55; N, 5.34. $C_8H_{14}ClNO_6$. Calculated (%): C, 37.58; H, 5.52; Cl, 13.87; N, 5.48. ^1H NMR (δ): 4.22 (s, 2 H, CH_2), 5.26 (d, 1 H, H(1), J = 1.2 Hz). ^{13}C NMR (δ): 43.5 (CH_2), 62.1 (C-6), 67.6 (C-4), 71.2 (C-2), 74.4 (C-3), 79.1 (C-1, C-5), 171.0 (C=O).

***N*-Chloroacetyl-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosylamine (1d)** was obtained by crystallization from aqueous MeOH. Yield: 0.63 g (70 %), m.p. 185—187 °C (decomp.), $[\alpha]_D^{20}$ +2.2° (*c* 1.0, H_2O). Found (%): C, 37.35; H, 6.31; Cl, 7.79; N, 2.97; H_2O, 8.21. $C_{14}H_{24}ClNO_{11} \cdot H_2O$. Calculated (%): C, 37.05; H, 6.21; Cl, 7.81; N, 3.09; H_2O, 7.94. ^1H NMR (δ): 4.23 (s, 2 H, CH_2), 4.47 (d, 1 H, H(1′), J = 7.6 Hz), 5.05 (d, 1 H, H(1), J = 9.2 Hz).

***N*-Chloroacetyl-β-D-xylopyranosylamine (4b)** was obtained by crystallization from propanol-2. Yield: 0.34 g (75 %), m.p. 167—169 °C, $[\alpha]_D^{20}$ +2.1° (*c* 1.0, H_2O). Found (%): C, 37.13; H, 5.34; Cl, 15.34; N, 5.88. $C_7H_{12}ClNO_5$. Calculated (%): C, 37.26; H, 5.36; Cl, 15.71; N, 6.21. ^1H NMR (δ): 4.2 (s, 2 H, CH_2), 4.93 (d, 1 H, H(1), J = 9 Hz). ^{13}C NMR (δ): 43.3 (CH_2), 68.1 (C-5), 70.1 (C-4), 72.7 (C-2), 77.7 (C-3), 81.5 (C-1), 171.9 (C=O).

***N*-Chloroacetyl-2-deoxy-β-D-*arabino*-hexopyranosylamine (5b)** was obtained by chromatography on SiO_2 in acetone. Yield: 0.11 g (23 %), m.p. 162—164 °C (from acetone), $[\alpha]_D^{20}$ −18.2° (*c* 1.0, H_2O). Found (%): C, 40.29; H, 6.16; Cl, 14.64; N, 5.60. $C_8H_{14}ClNO_5$. Calculated (%): C, 40.09; H, 5.89; Cl, 14.79; N, 5.84. ^1H NMR (δ): 4.19 (s, 2 H, CH_2Cl), 5.24

(dd, 1 H, H(1), J = 2.1 and 11.0 Hz). ^{13}C NMR (δ): 38.0 (C-2), 43.3 (CH_2Cl), 62.0 (C-6), 71.7 and 72.0 (C-3, C-4), 77.5 (C-5), 78.9 (C-1), 171.0 (C=O).

***N*-Chloroacetyl-β-L-fucopyranosylamine (6b)** was obtained by crystallization from MeOH. Yield: 0.38 g (80 %), m.p. 159—160 °C, $[\alpha]_D^{20}$ −1.1° (*c* 1.0, H_2O). Found (%): C, 39.02; H, 6.40; Cl, 14.18; N, 5.34; H_2O, 4.17. $C_8H_{14}ClNO_5 \cdot 1/2\ H_2O$. Calculated (%): C, 38.64; H, 6.08; Cl, 14.26; N, 5.63; H_2O, 3.62. ^1H NMR (δ): 1.23 (d, 3 H, CH_3), 4.21 (s, 2 H, CH_2), 4.93 (d, 1 H, H(1), J = 8.6 Hz).

(*N*-Chloroacetyl-β-D-glucopyranosylamine)uronic acid (8b) was obtained after dilution in H_2O (3 mL), treatment with cation-exchange resin KU-2 (H^+, 3 mL, 20 min), elution with H_2O, and chromatography in $CHCl_3$—MeOH—H_2O (5 : 4 : 0.8). Yield: 0.2 g (25 %), m.p. 195—196 °C, $[\alpha]_D^{20}$ −35.4° (*c* 0.5, H_2O). Found (%): C, 35.79; H, 4.65; Cl, 12.74; N, 4.97. $C_8H_{12}ClNO_7$. Calculated (%): C, 35.64; H, 4.49; Cl, 13.15; N, 5.19. ^1H NMR (δ): 4.22 (s, 2 H, CH_2), 5.09 (d, 1 H, H(1), J = 8.8 Hz).

(*N*-Chloroacetyl-β-D-glucopyranosylamine)uronamide (8e) was obtained by chromatography in EtOAc→EtOAc—MeOH (9 : 1) and subsequent crystallization from EtOH. Yield: 0.14 g (26 %), m.p. 197—198 °C, $[\alpha]_D^{20}$ −30.4° (*c* 1, MeOH). Found (%): N, 10.16. $C_8H_{13}ClN_2O_6$. Calculated (%): N, 10.43. ^1H NMR (δ): 4.22 (s, 2 H, CH_2), 5.09 (d, 1 H, H(1), J = 8.5 Hz).

***N*-Chloroacetyl-6-phospho-β-D-glucopyranosylamine diammonium salt (7b)**. Diisopropylethylamine (0.25 mL, 1.5 mmol) and $(ClCH_2CO)_2O$ (0.35 g, 2 mmol) in DMF (2.5 mL) cooled to 0 °C were added to a solution of the product containing glycosylamine **7a** (1 mmol) and carbamate **7c** (~1 : 1) in H_2O (1.7 mL) at 0 °C, and the mixture was kept for 4 h. Then the reaction mixture was treated according to the general procedure described above. The resulting product was chromatographed on silica gel in $CHCl_3$—MeOH (1 : 1)→$CHCl_3$—MeOH—H_2O (3 : 3 : 1). Fractions containing the chloroacetyl derivative were evaporated to dryness. The residue was dissolved in H_2O (1.5 mL), mixed with Dowex 50×8 (H^+, 0.7 mL), and stirred for 30 min. Then the resin was filtered off and washed with H_2O. The filtrate was treated with strong NH_4OH to pH ~11, concentrated, and freeze-dried. Yield: 0.055 g (15 %), $[\alpha]_D^{20}$ −23° (*c* 1, H_2O). Found (%): P, 8.46. $C_8H_{21}ClN_3O_9P$. Calculated (%): P, 8.38. ^1H NMR (δ): 4.22 (s, 2 H, CH_2), 5.03 (d, 1 H, H(1), J = 8.7 Hz).

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