An improved procedure for the synthesis of *N*-bromoacetyl-β-glycopyranosylamines, derivatives of mono- and disaccharides

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An improved procedure for the synthesis of *N*-bromoacetyl-β-glycopyranosylamines from the corresponding β-glycosylamines was developed. The procedure is applicable to a wide range of derivatives of monosaccharides (hexoses, 2-acetamido-2-deoxyhexoses, hexuronamides, and 6-deoxyhexoses) and some disaccharides. For the derivatives of pentoses and 2-deoxyhexoses, the use of the corresponding β-glycosylammonium carbamates was found to be more convenient. *N*-Bromoacetyl-β-glycopyranosylamines derived from D-mannose, L-rhamnose, D-glucuronamide, 2-deoxy-D-*arabino*-hexose, 2-deoxy-D-*lyxo*-hexose, and melibiose were obtained for the first time.

Key words: *N*-bromoacetyl-β-glycopyranosylamines, β-glycopyranosylamines, β-glycopyranosylammonium carbamates, *N*-bromoacetylation.

In recent years, glycosylamines have found increasingly wide application for the preparation of natural glycopeptides, their analogs, and glycoconjugates for various biological investigations. Within the scope of our program aimed at obtaining glycoconjugates of physiologically active substances, we previously developed the convenient routes to glycopyranosylamines starting from different classes of monosaccharides (hexoses, 2-acetamido-2-deoxyhexoses, pentoses, and 6- and 2-deoxyhexoses) and some disaccharides[1—5] and converted them into the corresponding chloroacetamide derivatives,[3] which were then used to synthesize glycoconjugates of some biologically active amines[6] and amino acids,[7] as well as to prepare *N*-glycylglycopyranosylamines for use in the synthesis of glycoconjugates of carboxylic acids.[8] The goal of the present study was to develop a convenient procedure for the preparation of *N*-bromoacetyl-β-glycopyranosylamines, which can open up new opportunities for the synthesis of glycoconjugates of new types of physiologically active substances.

Earlier, syntheses of several *N*-bromoacetylglycopyranosylamines have been described. Derivatives of β-D-glucose,[9—12] β-D-galactose,[9,10,13] *N*-acetyl-β-D-glucosamine,[12—15] and β-D-xylose[16,17] were synthesized for the introduction of an affinity label into active sites of glycosidases,[10,11,16—19] the preparation of glycopeptide analogs,[12,13] and the study of their cytotoxicity.[14,20] The syntheses of analogous derivatives of L-glucose,[10] L-fucose,[9,10] and some disaccharides[9—12] were also reported. The synthesis usually involves acylation of glycosylamines with $(BrCH_2CO)_2O$ in various solvents; the yields of the same compounds obtained by different authors often differ noticeably.

This prompted us to investigate in more detail the conditions of the synthesis of *N*-bromoacetylglycosylamines from glycosylamines with special emphasis on the glycosylamines differing in stability.

Based on the results of our previous studies on the synthesis of *N*-chloroacetylglycosylamines[3] and the available literature data, we investigated reactions of various glycosylamines **1** with $(BrCH_2CO)_2O$ in DMF leading to *N*-bromoacetylglycosylamines **2** (Scheme 1).

Because this anhydride is commercially inaccessible, we describe a convenient procedure for its preparation, which is based on the general method for the synthesis of carboxylic acid anhydrides,[21] which, to our knowledge, has not been applied for the preparation of this compound.

The starting β-glycopyranosylamines, namely, monosaccharide and disaccharide derivatives (**1a**—**f** and **1h**,**i**), were prepared from the corresponding sugars by the recently developed method[4,5] using ammonium carbamate as the aminating reagent. We used the same method to synthesize an analogous D-glucuronamide derivative **1g** starting from D-glucurono-γ-lactone **3** *via* glycosylammonium carbamate **4g** in 55% total yield (Scheme 2).

Optimization of the conditions for *N*-bromoacetylation of hexose-derived glycosylamines (reaction mixtures

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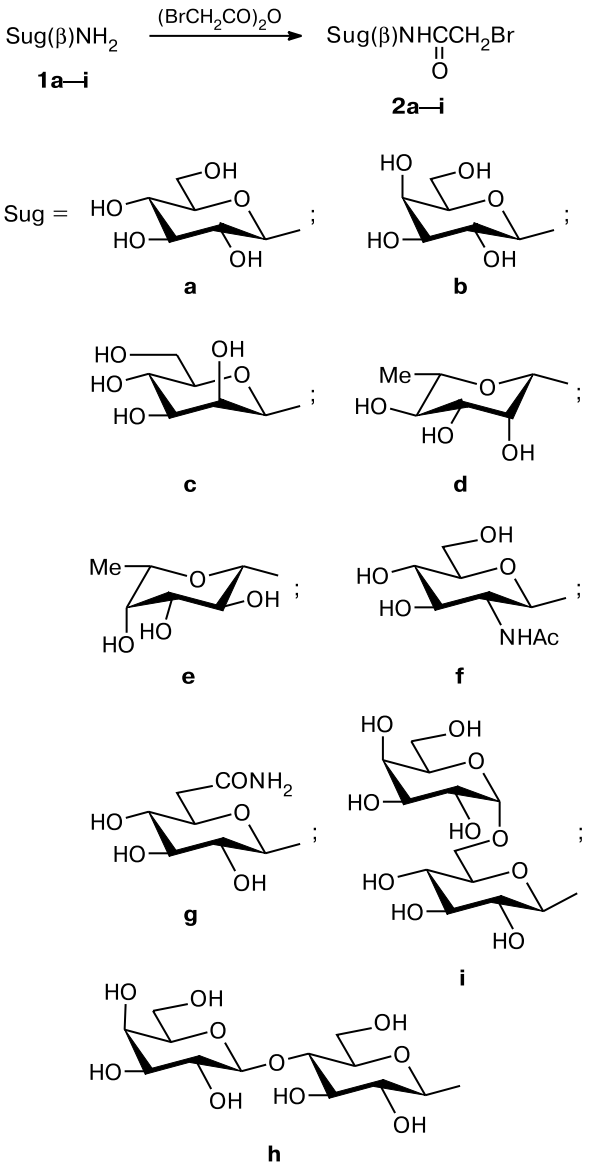
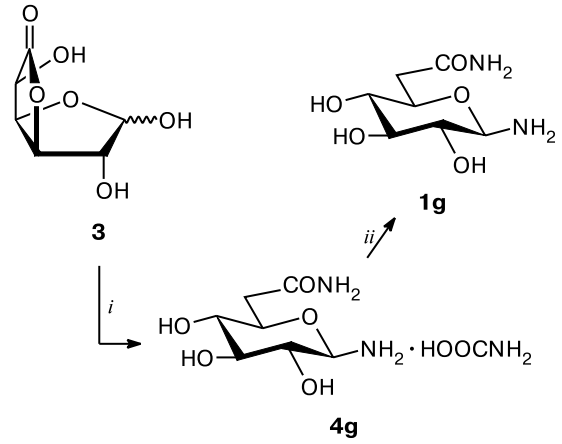
Scheme 1



were analyzed by paper chromatography) showed that the main reaction is accompanied by several side processes such as *O*-acylation, the formation of ninhydrin-positive products (probably, as a result of *N*-alkylation of the unconsumed glycosylamine with a bromoacetamido derivative), and the decomposition of glycosylamine into the free sugar. To suppress these side processes, a slight excess of the acylating reagent (the anhydride : substrate molar ratio is 1.1 to 1.2) and reduced reaction temperature are substantial.

Under these conditions, *N*-bromoacetyl-β-glycopyranosylamines **2a**,**c**,**f**,**g** were obtained in DMF (Table 1). The reaction products can easily be isolated by crystallization (except for **2g**, which was purified by chromatography on SiO_2). *N*-Acylation of D-galactose and 6-deoxy-

Scheme 2



i. NH_2COONH_4/MeOH. *ii*. $EtNPr^i_2$/MeOH—H_2O.

hexose derivatives (**1b** and **1d,e**) occurred more efficiently in tetramethylurea (TMU). Products **2d** and **2e** crystallized directly from the reaction mixture; bromoacetamide **2b** was crystallized upon the addition of MeOH. Apart from the aforementioned hexose and 6-deoxyhexose derivatives (D-mannose, L-rhamnose, and D-glucuronamide derivatives have not been described earlier), lactose and melibiose bromoacetamide derivatives (**2h** and **2i**) were smoothly obtained under similar conditions (in DMF and DMF—TMU, respectively).

Preparation of analogous derivatives of pentoses and 2-deoxyhexoses was more efficient if fairly stable glycosylammonium carbamates rather than glycosylamines themselves, which are difficult to prepare in the pure state

Table 1. Synthesis of *N*-bromoacetyl-β-glycosylamines from glycosylamines (−8 °C, $[(BrCH_2CO)_2O]$/[glycosylamine] = 1.1—1.2)

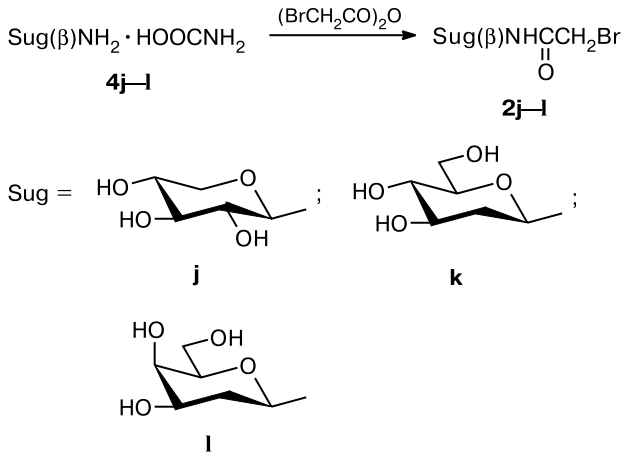
Glycosylamine	$C_0{}^a/M$	Solvent	τ^b/h	Reaction product	Yield (%)
1a	0.7	DMF	3.5	**2a**	41
1b	0.4	TMU	5	**2b**	54
1c	0.9	DMF	3.5	**2c**	39
1d	0.6	TMU	3.5	**2d**	57
1e	0.6	TMU	3.5	**2e**	51
1f	0.9	DMF	3.5	**2f**	52
1g	0.5	DMF	3	**2g**	57
1h	0.3	DMF	5	**2h**	66
1i	0.15	DMF—TMU, 1 : 1	5	**2i**	39

[a] The initial concentration is the amount of the starting compound (mmol) per milliliter of the solvent. This value is approximate since the substrate is dissolved incompletely at the initial reaction moment.

[b] Reaction time.

because of their lability, were subjected to *N*-bromoacetylation. These salts have been described by us earlier.[4,5] This version of the reaction was applied for the preparation of D-xylose, 2-deoxy-D-*arabino*-hexose, and 2-deoxy-D-*lyxo*-hexose derivatives (**4j**, **4k**, and **4l**) (Scheme 3).

Scheme 3



In this case, the use of a greater excess of the acylating reagent is required (the anhydride : substrate molar ratio is 1.7 to 2.0), which noticeably increases the yields of *O*-acylated by-products. Nevertheless, satisfactory yields of bromoacetamide derivatives **2j—l** were attained upon chromatographic separation of the reaction mixtures on SiO_2 (Table 2).

Additional amounts of the target products were obtained by *O*-deacylation of compounds with higher chromatographic mobilities. The *O*-deacylation procedure used by us earlier in the synthesis of *N*-chloroacetylglycosylamines[3] (Et_3N in aqueous MeOH) proved to be unsatisfactory in the case of bromoacetamido derivatives because of substantial substitution of bromine under these conditions. An efficient procedure for *O*-deacylation of this type of compounds which was developed as a result of a series of experiments involved the use of a sterically hindered tertiary amine ($EtNPr^i_2$) in aqueous methanol. Using this procedure, we obtained additional amounts of bromoacetamides **2j** and **2k** (see Note to Table 2). *N*-Bromoacetylglycosylamines of 2-deoxyhexoses (**2k** and **2l**) have not hitherto been described; the yield of D-xylose derivative **2j** from glycosylammonium carbamate **4j** is noticeably higher than that from the corresponding glycosylamine.[16,17]

Table 2. Synthesis of *N*-bromoacetyl-β-glycosylamines from glycosylammonium carbamates[a]

Glycosylamine	$C_0{}^b/M$	Solvent	τ^b/h	Reaction product	Yield (%)
4j	0.8	DMF	5	**2j**	41 [c]
4k	0.4	TMU	5 [d]	**2k**	47 [c]
4l	0.4	DMF	1	**2l**	33

[a] Reaction conditions: −8 °C, $[(BrCH_2CO)_2O]$/[carbamate] = 1.7 (**4j**), 2.0 (**4k**,**l**).
[b] See Notes to Table 1.
[c] The additional amount of the product (12—14%) was obtained upon *O*-deacylation.
[d] At 0 °C.

The structures of the *N*-bromoacetyl-β-glycopyranosylamines obtained were confirmed by elemental analysis data and NMR spectra. The ^1H NMR spectra contain characteristic signals for the protons of the $BrCH_2CO$ group (δ 3.95—4.00) and the H(1) atom of the sugar residue (δ 4.90—5.05 (d, J = 8.5—9.5 Hz) for compounds with the *gluco*- and *galacto*-configurations and δ ~5.2 for 2-deoxyhexoses (dd, J = 2.5 and 10.5 Hz) and compounds with the *manno*-configuration). For D-mannose and L-rhamnose derivatives, the chemical shifts of the signal for C(3) (δ_C ~74.0) unambiguously suggest the β-configuration of the products.

Thus, we have improved the procedure for the synthesis of *N*-bromoacetyl-β-glycopyranosylamines from β-glycopyranosylamines, which is applicable to a wide range of this class of compounds (derivatives of hexoses, 2-acetamido-2-deoxyhexoses, hexuronamides, 6-deoxyhexoses, and disaccharides). It was demonstrated that *N*-bromoacetyl derivatives of pentoses and 2-deoxyhexoses are more conveniently obtained from the corresponding β-glycosylammonium carbamates.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer (250 (^1H) and 62.7 MHz (^{13}C)) in $CDCl_3$ and D_2O at 24 °C with residual solvent protons as the internal standard or acetone as the external standard. Optical rotations were determined on a PU-5 polarimeter (Russia). Electrophoresis was performed on Filtrak FN1 paper in 6% HCOOH (12 V cm^{-1}, 1 h). For ascending chromatography, Filtrak FN15 paper and Bu^nOH—AcOH—H_2O (4 : 1.4 : 2.5) as the solvent system were used. The substances were detected with ninhydrin and KIO_4—$AgNO_3$—KOH in succession. Water of crystallization was determined by the Fischer method.

Bromoacetic anhydride. From a solution of bromoacetic acid (20.8 g, 0.15 mol) in 50 mL of Ac_2O (0.45 mol) and 120 mL of toluene, the solvent (20 mL) was distilled off *in vacuo* to remove residual AcOH and water. The residue was kept at 80 °C for 3 h. The solvent was removed at 70 Torr, and the residue was distilled *in vacuo* with protection against moisture. The last high-boiling fraction (b.p. 117—119 °C, 10 Torr) was collected. The yield of the anhydride was 12.5 g (64%) (*cf.* Ref. 22: b.p. 121—125 °C (11 Torr)). ^1H NMR ($CDCl_3$), δ: 3.98 (s, CH_2); for bromoacetic acid: 3.89 (s, 2 H, CH_2); 9.80 (br.s, 1 H, OH).

Glycosylamines 1a—f,h,i and **glycosylammonium carbamates 4j—l** were synthesized as described earlier.[4,5]

(β-D-Glucopyranosylamine)uronamide (1g). Powdered D-glycofuranurono(6→3)lactone **3** (0.53 g, 3 mmol) (Fluka) was dissolved at 55 °C in MeOH (15 mL) and cooled. Powdered ammonium carbamate (0.94 g, 12 mmol) was added, and the reaction mixture was stirred to homogeneity and left at 20 °C for 16 h. The reaction mixture with the resulting precipitate was kept at 0 °C for 5 h. The precipitate was filtered off, washed with MeOH—Pr^{i}OH (2 : 1) and ether, and dried to give (β-D-glucopyranosylammonium)uronamide carbamate **4g** (0.68 g, 89.5%), m.p. 140—143 °C, $[\alpha]_D^{20}$ −12.5→−9.0 (*c* 1, H_2O, after 5 and 15 min). Found (%): C, 33.26; H, 6.06; N, 16.48. $C_6H_{12}N_2O_5 \cdot NH_2COOH$. Calculated (%): C, 33.20; H, 5.97; N, 16.59.

Ethyl(diisopropyl)amine (0.4 mL, 2.36 mmol) and MeOH (60 mL) were added to a stirred solution of carbamate **4g** (0.5 g, 2 mmol) in 3 mL of water. The solution was concentrated at 70 Torr to 10 mL, diluted with MeOH to 40 mL, and concentrated again analogously. A MeOH—Pr^{i}OH mixture (5 : 1) (18 mL) was added, and the solution was concentrated to 2 mL. The precipitate that formed was filtered off, washed with MeOH—Pr^{i}OH (2 : 1) and ether, and dried to give glycosylamine **1g** (0.23 g, 60.7%), m.p. 144—146 °C, $[\alpha]_D^{20}$ −9.0 (*c* 1, H_2O, after 10 min). Found (%): C, 37.87; H, 6.40; N, 14.67. $C_6H_{12}N_2O_5$. Calculated (%): C, 37.50; H, 6.29; N, 14.58. ^{1}H NMR, δ: 3.17 (m, 1 H, H(2)); 3.47 (m, 2 H, H(3), H(4)); 3.82 (m, 1 H, H(5)); 4.11 (d, 1 H, H(1), J = 8.8 Hz).

***N*-Acylation of glycosylamines 1a—i or glycosylammonium carbamates 4j—l (general procedure).** A suspension of a powdered glycosylamine or carbamate in dry DMF or TMU was cooled to −8 or 0 °C and bromoacetic anhydride was added. The reaction mixture was stirred to homogeneity and kept at this temperature for 1 to 5 h (see Tables 1, 2). The isolation procedure and characteristics of *N*-bromoacetyl derivatives **2a—l** are described below.

***N*-Bromoacetyl-β-D-glucopyranosylamine (2a).** The reaction mixture was poured into 10 volumes of ether with stirring and kept at −10 °C for 16 h. The precipitate was separated by decantation, repeatedly (five times) triturated with ether, and dried. The residue was dissolved at 20 °C in a minimum amount of DMF, and Pr^{i}OH (2.5 vol.) was added. The mixture was kept at −10 °C for 16 h. The precipitate that formed was filtered off, washed with Pr^{i}OH and ether, and dried to give compound **2a**, m.p. 187—188 °C, $[\alpha]_D^{20}$ −13.1 (*c* 1, H_2O); *cf.* Ref. 10: m.p. 187—190 °C, $[\alpha]_D^{20}$ −13.5 (*c* 1, H_2O).

***N*-Bromoacetyl-β-D-galactopyranosylamine (2b).** The reaction mixture was filtered, diluted with MeOH (1.5 vol.), and kept at −18 °C for 16 h. The precipitate that formed was filtered off, washed with MeOH—anhydrous EtOH (1 : 1), acetone, and ether, and dried to give compound **2b**, m.p. 175—177 °C, $[\alpha]_D^{20}$ −11.2 (*c* 1, H_2O); *cf.* Ref. 10: m.p. 192 °C, $[\alpha]_D^{20}$ −13.0° (*c* 1, H_2O). ^{1}H NMR, δ: 3.58—3.83 (m, 5 H); 3.97 (br.s, 3 H, CH_2, H(4)); 4.93 (d, 1 H, H(1), J = 9.0 Hz).

***N*-Bromoacetyl-β-D-mannopyranosylamine (2c).** The reaction mixture was worked up as described for **2a**. The resulting precipitate was triturated with acetone. After the acetone was concentrated, a small amount of product **2c** precipitated. The residue insoluble in acetone was dried and dissolved in MeOH at 20 °C. The solution was concentrated to a small volume, the precipitate that formed was filtered off and dissolved in hot MeOH, and the solution was concentrated. The precipitate that formed was filtered off, washed with acetone and ether, and dried to give compound **2c**, m.p. 191—192 °C, $[\alpha]_D^{20}$ −29.0 (*c* 1, H_2O). Found (%): C, 32.41; H, 4.83; Br, 26.69; N, 4.89. $C_8H_{14}BrNO_6$. Calculated (%): C, 32.02; H, 4.70; Br, 26.62; N, 4.67. ^{1}H NMR, δ: 3.43 (m, 1 H, H(5)); 3.56 (t, 1 H, H(4), $J_{3,4} = J_{4,5}$ = 10.0 Hz); 3.68—3.77 (m, 2 H, H(3), H(6a)); 3.84 (m, 1 H, H(6b)); 3.93 (m, 1 H, H(2)); 3.97 (br.s, 2 H, CH_2); 5.18 (br.s, 1 H, H(1)). ^{13}C NMR, δ: 28.7 (CH_2); 61.6 (C(6)); 67.2 (C(4)); 70.7 (C(2)); 74.0 (C(3)); 78.7 (C(5)); 78.9 (C(1)); 170.1 (CO).

***N*-Bromoacetyl-β-L-rhamnopyranosylamine (2d).** The stirred reaction mixture with a gel-like precipitate was diluted with acetone (3 vol.). The precipitate was filtered off, washed with acetone and ether, and dried to give compound **2d**, m.p. 142—144 °C, $[\alpha]_D^{20}$ +38.3 (*c* 1, H_2O). Found (%): C, 32.13; H, 5.43; Br, 26.89; N, 4.40; H_2O, 5.44. $C_8H_{14}BrNO_5 \cdot H_2O$. Calculated (%): C, 31.80; H, 5.34; Br, 26.45; N, 4.64; H_2O, 5.96. ^{1}H NMR, δ: 1.29 (d, 3 H, CH_3, J = 5.9 Hz); 3.33—3.53 (m, 2 H, H(4), H(5)); 3.67 (dd, 1 H, H(3), $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 9.4 Hz); 3.96 (br.d, 1 H, H(2), J = 3.4 Hz); 4.00 (s, 2 H, CH_2); 5.20 (br.s, 1 H, H(1)). ^{13}C NMR, δ: 17.6 (CH_3); 28.7 (CH_2); 70.8 (C(2)); 72.5 (C(4)); 73.8 (C(3)); 74.8 (C(5)); 78.8 (C(1)); 171.0 (CO).

***N*-Bromoacetyl-β-L-fucopyranosylamine (2e).** The stirred reaction mixture with a precipitate was diluted with acetone—ether (1 : 1, 3 vol.). The precipitate was filtered off, washed with this mixture and ether, and dried to give compound **2e**, m.p. 169—171 °C (from MeOH—Et_2O), $[\alpha]_D^{20}$ −0.7 (*c* 3, H_2O); *cf.* Refs. 9 and 10: m.p. 175 °C, $[\alpha]_D^{20}$ +2.8 (*c* 1, H_2O). ^{1}H NMR, δ: 1.24 (d, 3 H, Me, J = 6.5 Hz); 3.63 (m, 1 H, H(2)); 3.72 (m, 1 H, H(3)); 3.81 (m, 1 H, H(4)); 3.88 (m, 1 H, H(5)); 3.96 (s, 2 H, CH_2); 4.91 (d, 1 H, H(1), J = 8.5 Hz).

2-Acetamido-*N*-bromoacetyl-2-deoxy-β-D-glucopyranosylamine (2f). Ether (1 vol.) was added to a stirred reaction mixture, which was then kept at −10 °C for 16 h. The precipitate that formed was filtered off, washed with acetone and ether, and dried to give compound **2f**, m.p. 201—202 °C (from EtOH—EtOAc), $[\alpha]_D^{20}$ +30.5 (*c* 1, H_2O); *cf.* Ref. 14: m.p. 203—204 °C, $[\alpha]_D$ +31.5. ^{1}H NMR, δ: 1.99 (s, 3 H, Me); 3.42—3.52 (m, 2 H, H(4), H(5)); 3.60 (t, 1 H, H(3), $J_{2,3} = J_{3,4}$ = 9.0 Hz); 3.73 (dd, 1 H, H(6a), $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.5 Hz); 3.79—3.95 (m, 4 H); 5.05 (d, 1 H, H(1), J = 9.5 Hz).

(*N*-Bromoacetyl-β-D-glucopyranosylamine)uronamide (2g). The reaction mixture was worked up as described for **2a**. The resulting precipitate was chromatographed on silica gel in acetone. Fractions containing product **2g** were combined and concentrated. The precipitate that formed was filtered off, washed with acetone and ether, and dried to give compound **2g**, m.p. 197—198 °C, $[\alpha]_D^{20}$ −27.2 (*c* 1, H_2O). Found (%): C, 31.02; H, 4.25; Br, 25.15; N, 8.55. $C_8H_{13}BrN_2O_6$. Calculated (%): C, 30.69; H, 4.18; Br, 25.52; N, 8.94. ^{1}H NMR, δ: 3.48 (m, 1 H, H(2)); 3.60 (m, 2 H, H(3), H(4)); 3.99 (m, 3 H, CH_2, H(5)); 5.05 (d, 1 H, H(1), J = 9.0 Hz).

***N*-Bromoacetyl-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosylamine (2h).** The reaction mixture was filtered, diluted with MeOH (1.3 vol.), and kept at −10 °C for 16 h. The precipitate that formed was filtered off, washed with cold MeOH and ether, and dried to give compound **2h**, m.p. 157—158 °C. After recrystallization from DMF—MeOH, m.p. 174—176 °C, $[\alpha]_D^{20}$ +2.5 (*c* 1, H_2O). Found (%): C, 36.04; H, 5.30; Br, 16.90; N, 3.18. $C_{14}H_{24}BrNO_{11}$. Calculated (%): C, 36.38; H, 5.23; Br, 17.29; N, 3.03. ^{1}H NMR, δ: 3.42—3.55 (m, 2 H); 3.56—3.88 (m, 8 H); 3.89—3.98 (m, 2 H); 3.99 (s, 2 H, CH_2); 4.48 (d, 1 H, H(1) Gal, J = 7.5 Hz); 5.02 (d, 1 H, H(1) Glc, J = 9.5 Hz).

***N*-Bromoacetyl-6-*O*-(α-D-galactopyranosyl)-β-D-glucopyranosylamine (2i).** The reaction mixture was worked up as described for **2a**. The resulting precipitate was chromatographed on silica gel in acetone → acetone—MeOH (2 : 1). Fractions containing product **2i** were combined, concentrated to dryness, and dried to give amorphous compound **2i**, $[\alpha]_D^{20}$ +56.7 (*c* 1, H_2O). Found (%): C, 36.02; H, 5.53; N, 2.87. $C_{14}H_{24}BrNO_{11}$. Calculated (%): C, 36.38; H, 5.23; N, 3.03. ^{1}H NMR, δ: 3.43—3.96 (m, 12 H); 3.97 (s, 2 H, CH_2); 4.97 (m, 2 H, H(1) Gal, H(1) Glc).

***N*-Bromoacetyl-β-D-xylopyranosylamine (2j).** The reaction mixture was worked up as described for **2a**. The resulting precipitate was chromatographed on silica gel in acetone. Fractions containing product **2j** were combined and concentrated. The precipitate that formed was filtered off, washed with acetone—ether (1 : 2) and ether, and dried to give compound **2j**. The mother liquor and the fractions containing chromatographically more mobile substances than **2j** were combined and concentrated to dryness. The residue was dissolved in MeOH—H_2O—$EtNPr^i_2$ (5.5 : 3.5 : 1, 15 vol. per gram of the substance). The solution was kept at 20 °C for 1.5 h and then diluted with MeOH—Pr^iOH (1 : 1, 5 vol.). The solvent was evaporated to dryness. The residue was chromatographed on silica gel in acetone to give an additional amount of compound **2j** (see Table 2), m.p. 155—156 °C (from acetone), $[\alpha]_D^{20}$ +4.8 (*c* 1, H_2O); *cf.* m.p. 150—151 °C (from MeOH),[17] $[\alpha]_D$ +6.4 (*c* 0.3, MeOH).[16] ^{1}H NMR, δ: 3.36—3.53 (m, 3 H, H(2), H(3), H(5a)); 3.63 (m, 1 H, H(4)); 3.93 (m, 1 H, H(5b)); 3.96 (s, 2 H, CH_2); 4.89 (d, 1 H, H(1), J = 9.0 Hz).

***N*-Bromoacetyl-2-deoxy-β-D-*arabino*-hexopyranosylamine (2k).** The reaction mixture was filtered and worked up as described for **2a** (except that ether—light petroleum (1 : 1) was used for precipitation). The resulting precipitate was chromatographed on silica gel in acetone. Fractions containing product **2k** were combined and concentrated to dryness. The residue was dissolved in a minimum amount of MeOH and diluted with ether (10 vol.). The precipitate that formed was filtered off, washed with ether, and dried to give compound **2k**. An additional amount of amorphous compound **2k** was isolated from the mother liquor and other fractions upon *O*-deacylation as described for **2j** (see Table 2), $[\alpha]_D^{20}$ −6.4 (*c* 1, H_2O). Found (%): C, 34.23; H, 5.22; N, 4.66. $C_8H_{14}BrNO_5$. Calculated (%): C, 33.82; H, 4.97; N, 4.93. ^{1}H NMR, δ: 1.70 (m, 1 H, H(2a)); 2.27 (m, 1 H, H(2e)); 3.36 (m, 1 H, H(4)); 3.51 (m, 1 H, H(5)); 3.81 (m, 2 H, H(3), H(6a)); 3.94 (m, 1 H, H(6b)); 3.99 (s, 2 H, CH_2); 5.23 (dd, 1 H, H(1), $J_{1,2e}$ = 2.5 Hz, $J_{1,2a}$ = 10.5 Hz).

***N*-Bromoacetyl-2-deoxy-β-D-*lyxo*-hexopyranosylamine (2l)** was obtained as described above for **2k**. After column chromatography, the fractions containing product **2l** were combined and concentrated. The precipitate that formed was filtered off, washed with cold acetone and ether, and dried to give compound **2l**, m.p. 159—161 °C, $[\alpha]_D^{20}$ −16.2 (*c* 1, H_2O). Found (%): C, 33.98; H, 5.08; N, 4.56. $C_8H_{14}BrNO_5$. Calculated (%): C, 33.82; H, 4.97; N, 4.93. ^{1}H NMR, δ: 1.84 (m, 1 H, H(2a)); 1.99 (m, 1 H, H(2e)); 3.71 (m, 1 H, H(4)); 3.78 (m, 2 H); 3.87 (br.s, 1 H); 3.98 (m, 3 H); 5.16 (dd, 1 H, H(1), $J_{1,2e}$ = 2.5 Hz, $J_{1,2a}$ = 10.5 Hz).

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