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A Synthesis of Heteroaromatic *S*- and *N*-β-Glycosides of *N*-Acetylglucosamine under Phase-Transfer Conditions

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Abstract—The use of crown ethers for a phase transfer-catalyzed synthesis of heteroaromatic glycosides of *N*-acetylglucosamine was studied. The solid–liquid system and catalysis by 15-crown-5 were found to provide for both the 100% conversion of α-*D*-glucosaminyl chloride peracetate and a high reaction rate. The interaction of α-*D*-glucosaminyl chloride peracetate and oxadiazole and triazole mercapto derivatives capable of thiol–thione tautomerism carried out at room temperature in acetonitrile in the presence of anhydrous potassium carbonate and crown ethers was shown to lead to both *S*- and *N*-glucosides. The structures of the compounds synthesized were confirmed by X-ray analysis and ^{13}C and ^{1}H NMR spectroscopy.

Key words: crown ethers, glycosylation, heteroaromatic glycosides, phase transfer catalysis, X-ray analysis

INTRODUCTION

A high efficiency of phase transfer catalysis in the presence of quaternary ammonium salts and crown ethers exemplified by numerous examples of *O*-, *S*-, and *N*-alkylation of alcohols, phenols, thiols, and nitrogen-containing heterocyclic systems [1, 2] was confirmed by a considerable number of examples in carbohydrate chemistry [3–9].[2] The reactions at the anomeric carbon atoms of glycosyl halogenides of both neutral and amino sugars are of a particular interest, because modifications of the monosaccharide glycoside centers provide not only the introduction of protective groups at the carbohydrate C1 atom, but also the preparation of biologically diverse *O*-, *S*-, and *N*-glycosides, including the derivatives of physiologically important natural compounds [10–21]. However, the use of PTC for glycoside synthesis is restricted to classical examples of the preparation of alkyl *O*-β-*D*-glucopyranosides in the presence of silver nitrate and various CEs as catalysts [6, 9]. The synthesis of aryl *O*-β-*D*-gluco- and galactopyranosides and aryl *O*-β-*D*-glucosaminides from the corresponding acetobromosugars and 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-glucopyranosyl chloride in a biphasic liquid–liquid system with alkali as a base and quaternary ammonium salts as catalysts [4, 5, 7, 8] is limited to the glycosylation of aromatic alkali-stable compounds. As to the synthesis of *N*-glycosides under the PTC conditions, only few examples have been known (cf., e.g., [17–21].

The goal of this work is the search for new effective synthetic approaches to the formation of *S*- or *N*-glycoside bonds using CE as phase transfer catalysts, which would result in the synthesis of new glucosaminides with a potential biological activity.

RESULTS AND DISCUSSION

We had earlier shown [22, 23] that the use of 20 mol % (per substrate) of catalysts (15K5 or aromatic CEs) in the presence of K_2CO_3 suspension in dry acetonitrile ensures a smooth phase transfer glycosylation of phenols, synthetic coumarine analogues, and chromones with 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-glucopyranosyl chloride (**I**) (the yields of *O*-glycosides achieve 43–86% with 100% substrate conversion). We discuss here the fundamental possibility of glycosylation and the specific features of interaction of chloride (**I**) with heteroaromatic compounds (**II**)–(**V**) under PTC conditions. A distinguishing feature of the heterocyclic systems under consideration is their ability to tautomeric transformations due to which the glycosylation direction may differ in dependence on the reaction conditions. Proper examples are well known (cf. [15]).

The consideration of equilibrium inherent for compounds (**II**)–(**V**) suggests that the reaction could proceed at one of two nucleophilic centers to give either *S*- or *N*-glycoside or a mixture of both.

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[2] Abbreviations: 15C5, 15-crown-5; 18C6, 18-crown-6; CE, crown ether; and PTC, phase transfer catalysis.

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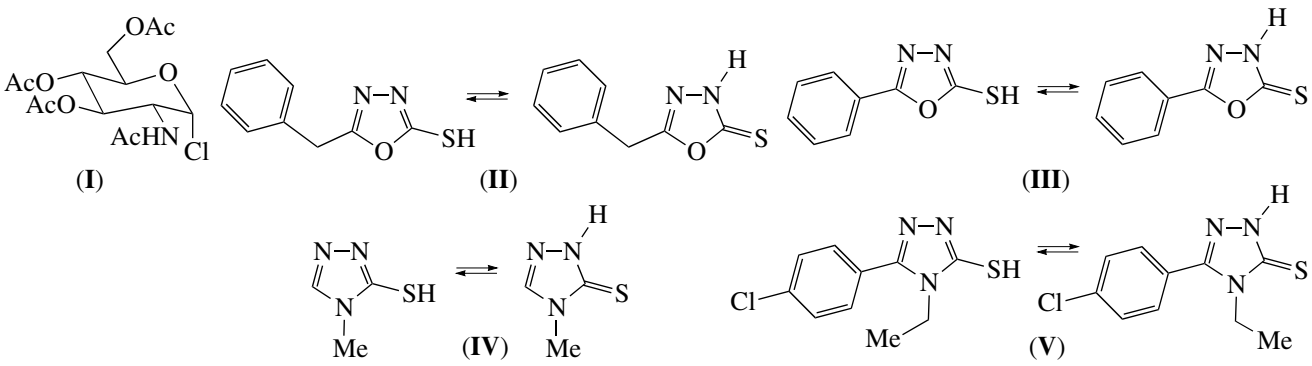


A preliminary experiment carried out in the absence of phase transfer catalysts demonstrated that the major product in acetonitrile–anhydrous potassium carbonate was oxazoline (**XIV**) (TLC monitoring). The total conversion of the substrate was not achieved, and the target glycosides were formed in trace amounts.

The attempts to glycosylate thiols (**II**)–(**V**) in the presence of triethylamine (as described in [24]) also failed. No complete conversion of substrate (**I**) was observed in any of the cases; along with the target products (TLC monitoring), oxazoline (**XIV**) was formed.

The reactions of α-chloride (**I**) with thiol–thione tautomers, namely, 5-benzyl-1,3,4-oxadiazole-2-thiol (**II**), 5-phenyl-1,3,4-oxadiazole-2-thiol (**III**), 4-methyl-1,2,4-triazole-3-thiol (**IV**), and 5-(4-chlorophenyl)-4-ethyl-1,2,4-triazole-3-thiol (**V**), at stoichiometric ratios described in [22, 23] yielded two products in each case: (**VI**) and (**VII**), (**VIII**) and (**IX**), (**X**) and (**XI**), and (**XII**) and (**XIII**), respectively. Note that, in all the cases, chloride (**I**) was completely converted.

We made a number of syntheses in which 18C6 was substituted for 15C5 in order to reveal the effect of the macrocycle size and dentation on the glycosylation time and product yields. As follows from the data in Figs. 1 and 2, this substitution offers no advantages neither in the process time nor in total yields of target glycosides.

^{1}H NMR (Table 1 and Fig. 3) and ^{13}C NMR spectroscopy (see the Experimental section), X-ray analysis (Fig. 4), and the *S*-β- to *N*-β glycoside rearrangement catalyzed by mercury(II) bromide [15] were used for the elucidation of the glycoside bond structure and nature in (**VI**)–(**XIII**), which supposed to be pairs of *S*-β- and *N*-β-glucosaminides. The ^{1}H NMR spectral patterns of the glycoside pairs (**VI**)–(**XIII**) studied (Table 1) showed a significant downfield shift of the anomeric proton resonances of *N*-β-glycosides (**VII**), (**IX**), ((**XI**), and (**XIII**) in comparison with the H1 doublets of *S*-β-*D*-glucosaminides (**VI**), (**VIII**), (**X**), and (**XII**). The coupling constants of *N*-β- and *S*-β-glycosides were 9.6–9.9 and 10.5–10.8 Hz, respectively (Table 1), which corresponds to the published data [4, 24–27]. The chemical shifts of skeletal protons of glycoside residues of *S*- and *N*-glycosides significantly differed from one another and could therefore serve as their characteristic feature (Fig. 3).

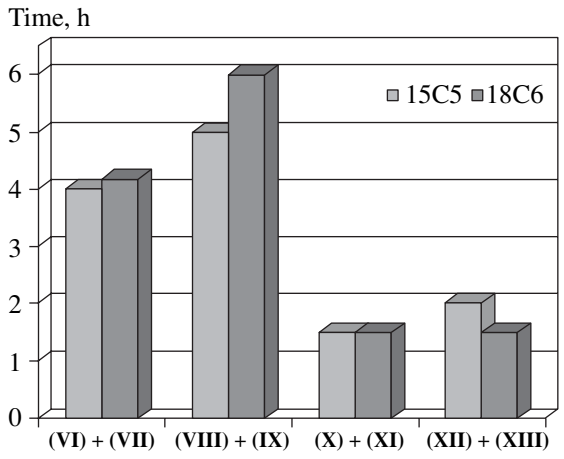


Fig. 1. The formation time of glycoside in the presence of 15C5 and 18C6 crown ethers at 100% conversion of substrate (**I**).

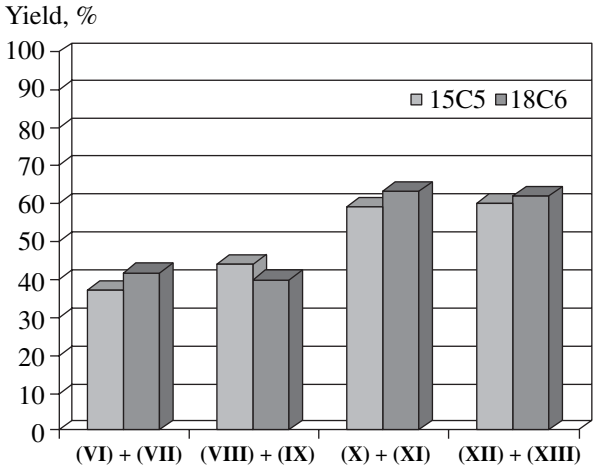
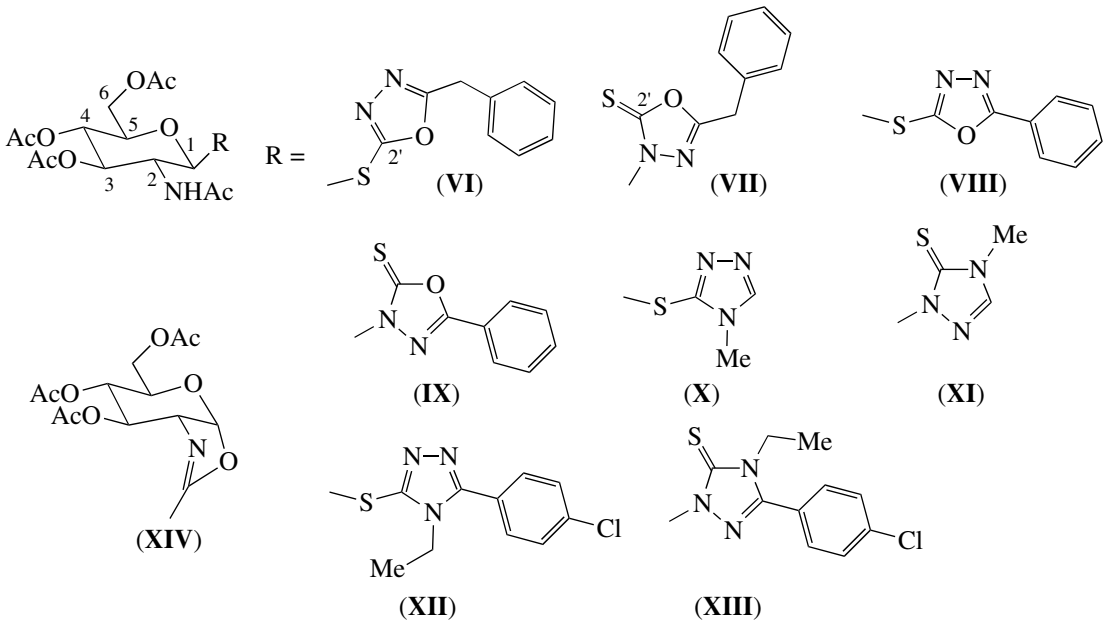


Fig. 2. Total yield of *S*- and *N*-β-glycosides in the presence of 15C5 and 18C6 crown ethers at 100% conversion of substrate (**I**).



Thioglycosides (**VI**), (**VIII**), (**X**), and (**XII**) were isomerized in the presence of mercury(II) bromide [15] into the compounds whose chromatographic mobility, physicochemical characteristics, and ^{1}H NMR data agreed with those of *N*-β-glycosides (**VII**), (**IX**), (**XI**), and (**XIII**). For a more accurate assignment of (**VI**) and (**VII**) to *S*- or *N*-glycosides, ^{13}C NMR spectra were registered (see the Experimental section). A downfield shift of the resonance of the anomeric carbon atom was observed in the ^{13}C NMP spectrum of *N*-glycoside

Table 1. ^{1}H NMR spectra of (**VI**)–(**XIII**)*

Group or atom	(**VI**)	(**VII**)	(**VIII**)	(**IX**)	(**X**)	(**XI**)	(**XII**)	(**XIII**)
H1 ($J_{1,2}$)	5.44 d (10.8)	5.95 d (9.6)	5.57 d (10.5)	6.08 d (9.6)	5.11 d (10.5)	6.15 d (9.9)	5.27 d (10.8)	6.22 d (9.6)
H2 ($J_{2,3}$)	4.07 m (9.6)	4.33 ddd (9.6)	4.11 m	4.36 ddd (9.6)	3.92 ddd (10)	4.45 ddd (9.6)	4.08 m	4.50 ddd (10)
H3 ($J_{3,4}$)	5.19 dd (9.6)	5.38 dd (10)	5.23 dd (9.3)	5.48 dd (9.7)	5.13 dd (9.6)	5.39 dd (9.9)	5.17 dd (9.9)	5.43 dd (9.9)
H4 ($J_{4,5}$)	4.88 dd (9.6)	4.94 dd (10)	4.92 dd (9.6)	4.99 dd (9.6)	4.83 dd (9.9)	4.93 dd (9.9)	4.87 dd (9.9)	4.95 dd (9.9)
H5 ($J_{5,6a}$, $J_{5,6b}$)	3.91 m	4.14 m	4.11 m (2.1, 5.1)	4.20 ddd (2.1, 5.1)	3.81 ddd (2.4, 5.4)	4.01 m (2.1, 5.1)	3.85 ddd (2.1, 5.4)	4.07 m (2.1, 5.1)
H6 (J_{gem})	3.91 m, 4.07 m	4.21 m	4.00 dd, 4.16 dd (12.0)	4.07 dd, 4.26 dd (12.0)	3.96 dd, 4.09 dd (12.5)	4.05 dd, 4.46 dd (12.6)	4.08 m	4.10 dd, 4.25 dd (12.5)
NHAc	1.78 s	1.67 s	1.83 s	1.67 s	1.83 s	1.62 s	1.84 s	1.64 s
OAc	1.94 s, 1.95 s, 1.98 s	1.94 s, 2.00 s	1.95 s, 1.99 s	1.96 s, 2.01 s	1.93 s, 1.96 s, 1.97 s	1.93 s, 1.98 s, 1.99 s	1.90 s, 1.94 s, 1.97 s	1.94 s, 1.99 s, 2.00 s
NH ($J_{NH,2}$)	8.18 d (9.3)	8.03 d (8.7)	8.27 d (9.3)	8.05d (8.4)	8.23 d (9.0)	7.95 d (9.0)	8.28 d (9.3)	7.99 d (8.7)
Alk	4.14 s, 4.29 s	4.17 s, 4.20 s	–	–	3.62 s	3.47 s	1.62 t, 4.08 m	1.14 t, 4.07 m
CH_{arom}	7.33 m	7.33 m	7.65 m	7.65 m, 7.91 d	8.67 s	8.52 s	7.65 d, 7.72 d	7.69 d, 7.76 d

* Working frequency of 300 MHz; DMSO-d_6 as a solvent.

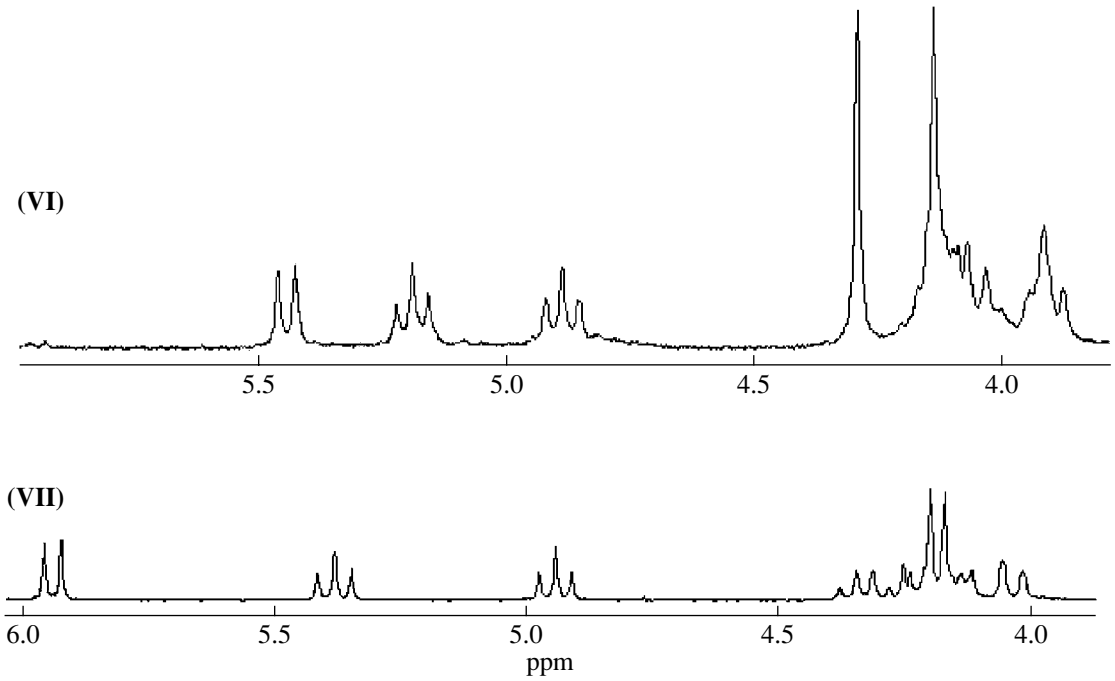


Fig. 3. The resonance region of skeletal protons in ^{1}H NMR spectra of (**VI**) and (**VII**).

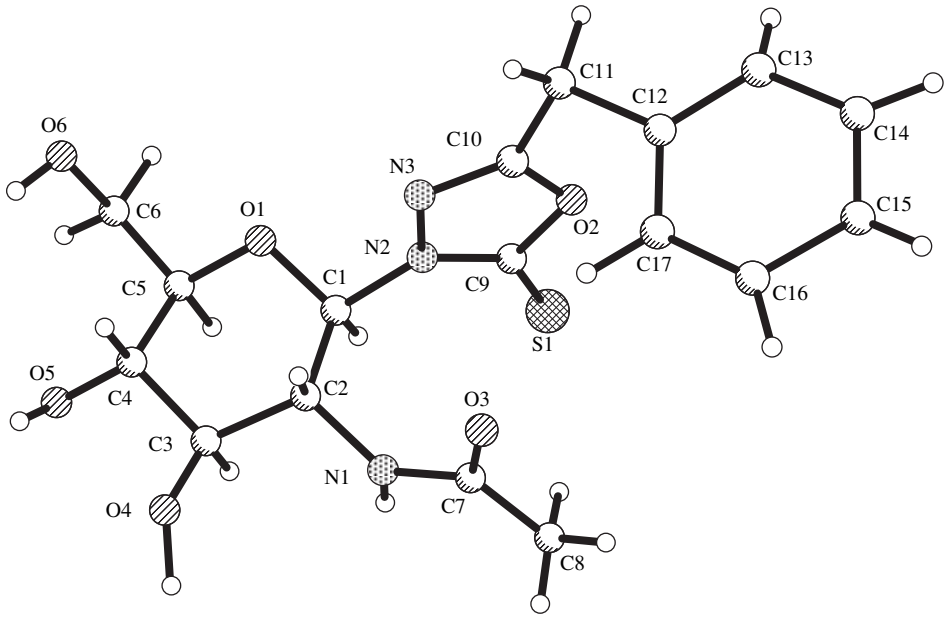


Fig. 4. Molecular structure of *N*-β-glycoside (**XV**).

(**VII**) (δ 85.03 ppm; compare with δ 84.09 ppm for *S*-glycoside) whose C1 is linked to a more electronegative nitrogen atom. Chemical shifts of the C2' aglycone atoms more substantially differ. The resonance of this carbon atom in *N*-glycoside (**VII**) undergo a diamagnetic shift in comparison with that of *S*-glycoside (**VI**) (167.44 ppm versus 178.70 ppm), which correlates to a lower value of the partial negative charge on this atom calculated using the standard programs, e.g., those in ChemOffice Ultra 8.0.

The final proof of the correctness of assigned structures was obtained by the X-ray analysis of deacetylated derivative (**XV**) (Fig. 4). Atomic coordinates, bond lengths, and values of torsion angles in triol (**XV**)

Table 2. The coordinates ($\times 10^4$) and equivalent isotropic temperature parameters ($\times 10^3$, Å^2) of atoms in (**XV**).

Atom	*x*	*y*	*z*	U_{eq}
S1	8621(1)	1690(1)	–18(1)	27(1)
N1	9275(3)	1889(2)	–1798(1)	17(1)
N2	6536(3)	1124(2)	–974(1)	15(1)
N3	5623(3)	102(2)	–1189(1)	16(1)
O1	4912(3)	2686(2)	–1400(1)	15(1)
O2	6954(3)	–386(2)	–328(1)	21(1)
O3	9260(3)	–246(2)	–1861(1)	21(1)
O4	7893(3)	3051(2)	–2932(1)	22(1)
O5	5531(3)	5080(2)	–2564(1)	25(1)
O6	1914(3)	3787(2)	–1989(1)	25(1)
C1	6590(4)	2302(3)	–1312(1)	14(1)
C2	7518(4)	2131(3)	–1929(1)	13(1)
C3	7364(4)	3329(3)	–2320(1)	15(1)
C4	5563(4)	3831(3)	–2326(1)	17(1)
C5	4883(4)	3925(3)	–1672(1)	14(1)
C6	3119(4)	4446(3)	–1628(1)	21(1)
C7	9959(4)	747(3)	–1707(1)	17(1)
C8	11637(4)	787(3)	–1387(2)	25(1)
C9	7374(4)	852(3)	–452(1)	17(1)
C10	5901(4)	–761(3)	–790(1)	19(1)
C11	5213(4)	–2067(3)	–777(2)	25(1)
C12	6582(4)	–3046(3)	–771(2)	22(1)
C13	6585(4)	–3989(3)	–327(2)	23(1)
C14	7812(5)	–4902(3)	–327(2)	28(1)
C15	9094(5)	–4878(3)	–763(2)	29(1)
C16	9100(5)	–3933(3)	–1203(2)	36(1)
C17	7860(5)	–3016(3)	–1207(2)	34(1)

Table 3. Bond lengths (Å) in (**XV**).

S1–C9	1.630(3)	N1–C7	1.342(4)
N1–C2	1.447(4)	N2–C9	1.348(4)
N2–N3	1.385(3)	N2–C1	1.449(3)
N3–C10	1.279(4)	O1–C1	1.406(4)
O1–C5	1.442(3)	O2–C10	1.365(4)
O2–C9	1.380(3)	O3–C7	1.237(4)
O4–C3	1.426(3)	O5–C4	1.422(4)
O6–C6	1.421(4)	C1–C2	1.539(4)
C2–C3	1.533(4)	C3–C4	1.526(4)
C4–C5	1.523(4)	C5–C6	1.509(4)
C7–C8	1.504(4)	C10–C11	1.489(4)
C11–C12	1.504(5)	C12–C13	1.389(4)
C12–C17	1.389(5)	C13–C14	1.373(5)
C14–C15	1.391(5)	C15–C16	1.385(5)
C16–C17	1.383(5)		

are shown in Tables 2–4. The six-membered pyranose cycle has the $^4C_1$ conformation in the crystal (chair, folding parameters: $S = 1.18$, $\Theta = 7.4°$, $\Psi = 16.7°$ [28]). All the substituents are equatorial in the cycle. The bond lengths in the aglycone agree with the published data [29]. Noteworthy is the difference between the C_{sp3}–O bonds in the carbohydrate residue (O1–C5 1.441(3) and O1–C1 1.406(4) Å), which has been described for relative compounds (e.g., see [30]) and is a consequence of anomeric effect.

Thus, the whole information obtained unequivocally proves the chemical structures of *S*-β- and *N*-β-glycosides (**VI**)–(**XIII**). To conclude, the method we have suggested for the crown ether-catalyzed glycosylation of phenols in the phase transfer solid–liquid system turned out to be also effective for β-glucosamidation of aromatic heterocycles both at the exocyclic sulfur atom and endocyclic nitrogen atom; it helps obtain heteroaromatic *S*- and *N*-β-glycosides of *N*-acetylglucosamine.

EXPERIMENTAL

Melting points were measured on a PTP device. Optical rotations were registered at 20–22°C on a Polamat-A polarimeter (at the wavelength λ 546 nm). ^{1}H NMR spectra were obtained in DMSO-d_6 on a Varian VXR-300 spectrometer (300 MHz) with Me_4Si as an internal standard. ^{13}C NMR spectra were registered in $CDCl_3$ on a Varian Mercury-400 spectrometer (100 MHz). The assignment of ^{1}H NMR resonances was achieved using the method of double homonuclear resonance.

X-ray analysis. The rhombic-shaped crystals of compound (**XV**), $C_{17}H_{21}N_3O_6S$, have at −109°C the following parameters: $a = 7.942(2)$, $b = 10.603(3)$, $c = 21.721(5)$ Å, $V = 1829.1(8)$ Å^3, $M_r = 395.43$, $Z = 4$, the spatial group $P2_12_12_1$, $d_{calc} = 1.436$ g/cm^3, $\mu(MoK_\alpha) = 0.217$ mm^{-1}, and $F(000) = 832$. The parameters of the elementary cell and the intensity of 2399 independent images were measured on an automatic four-round Siemens P3/PC diffractometer (MoK_α, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 55°$). The structure was calculated by the direct method using the SHELXTL program complex [31]. The positions of hydrogen atoms were obtained by the differential calculations of electron density and adjusted using the "raider" model with a free U_{iso}. The structure was refined according to the squares of structural amplitudes using a full-matrix method of root least squares and anisotropic approximation for nonhydrogen atoms to $wR_2 = 0.108$ for 2354 reflects ($R_1 = 0.042$ for 2082 reflects with $F > 4\sigma(F)$, $S = 1.076$).

TLC was carried out on Sorbfil-AFB-UV plates ("Sorbpolymer", Russia). Column chromatography was performed on Kieselgel 60 (0.063–0.200 mm, Merck). The substance spots were detected by carbon-

ization or in iodine vapor. For the plate development, the following elution systems were used: (A) 15 : 1 : 1 ethyl acetate–chloroform–ethanol, (B) 10 : 1 benzene–ethanol, (C) 3 : 1 : 1 *n*-butanol–acetic acid–water. The data of elemental analyses of the compounds synthesized agree with the calculated values.

General glycosylation procedure. Equimolar amounts of the corresponding heteroaromatic compound, finely ground anhydrous K_2CO_3, and 15C5 (20 mol % per substrate, 98% according to GLC, Bogatskii Physicochemical Institute, Odessa) were added to a solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-glucopyranosyl chloride (**I**) [32] in acetonitrile (30 ml/g), and the mixture was stirred at room temperature until the complete conversion of the glycosyl donor (TLC monitoring in systems A and B). The solid phase was filtered off, and acetonitrile was evaporated at a reduced pressure. The residue was crystallized from isopropyl alcohol, the precipitate was filtered, and the mother liquor after was evaporated and chromatographed on a silica gel column.

3-*N*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-5-benzyl-1,3,4-oxadiazole-2(3*H*)-thione (VII) and 2-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosylthio)-5-benzyl-1,3,4-oxadiazole (VI). The interaction of oxadiazole (**II**) (0.625 g, 3.26 mmol) and chloride (**I**) (1.19 g, 3.26 mmol) followed by crystallization resulted in glycoside (**VII**); yield 0.287 g (17%); mp 162–165°C (degr.); $[\alpha]_{546}$ +31° (*c* 0.67; chloroform); ^{13}C NMR: 20.95, 21.04, 21.08, 23.40 (4 $\underline{C}H_3CO$), 32.18 ($\underline{C}H_2Ph$), 53.22 (C2), 62.00 (C6), 68.17 (C4), 73.66 (C3), 76.62 (C5), 85.03 (C1), 128.13, 129.22, 129.35, and 133.52 (C_6H_5), 163.00 (C5'), 167.44 (C2'), 169.61, 170.89, 171.04, and 171.38 ($\underline{C}OCH_3$). Glycoside (**VI**) was obtained after chromatography on a column eluted with a gradient benzene to 25 : 1 benzene–propan-2-ol; yield 0.338 g (20%); mp 94–98°C (degr.), $[\alpha]_{546}$ –13° (*c* 0.67 1.0; chloroform); ^{13}C NMR: 21.02, 21.13, and 23.51 (4 $\underline{C}H_3CO$); 32.49 ($\underline{C}H_2Ph$), 52.62 (C2), 62.19 (C6), 68.04 (C4), 73.10 (C3), 75.20 (C5), 84.09 (C1), 128.30, 129.38, 129.43, 129.49, and 132.32 (C_6H_5), 161.75 (C5'), 169.62, 170.39, 171.02, and 171.55 ($\underline{C}OCH_3$), 178.70 (C2').

3-*N*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-5-phenyl-1,3,4-oxadiazole-2(3*H*)-thione (IX) and 2-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosylthio)-5-phenyl-1,3,4-oxadiazole (VIII). The interaction of oxadiazole (**III**) (0.317 g, 1.78 mmol) and chloride (**I**) (0.65 g, 1.78 mmol) followed by crystallization resulted in glycoside (**IX**); yield 0.198 g (22%); mp 257–260°C (degr.); $[\alpha]_{546}$ –39° (*c* 1.0; chloroform). Glycoside (**VIII**), was obtained after chromatography on a column eluted with a benzene to 25 : 1 benzene–isopropanol gradient; yield 0.338 g (20%); mp 244–245°C (degr.), $[\alpha]_{546}$ –18° (*c* 1.0; chloroform).

Table 4. Valence angles (degrees) in (**XV**)

C7–N1–C2	125.3(3)	C9–N2–N3	112.0(2)
C9–N2–C1	126.6(2)	N3–N2–C1	121.3(2)
C10–N3–N2	103.9(2)	C1–O1–C5	109.5(2)
C10–O2–C9	106.4(2)	O1–C1–N2	106.8(2)
O1–C1–C2	111.7(2)	N2–C1–C2	110.7(2)
N1–C2–C3	109.4(2)	N1–C2–C1	108.1(2)
C3–C2–C1	110.2(2)	O4–C3–C4	109.9(2)
O4–C3–C2	108.8(2)	C4–C3–C2	111.6(2)
O5–C4–C5	105.7(2)	O5–C4–C3	110.2(3)
C5–C4–C3	110.3(2)	O1–C5–C6	108.8(2)
O1–C5–C4	108.5(2)	C6–C5–C4	114.4(2)
O6–C6–C5	114.3(2)	O3–C7–N1	123.2(3)
O3–C7–C8	123.1(3)	N1–C7–C8	113.6(3)
N2–C9–O2	104.3(3)	N2–C9–S1	132.1(2)
O2–C9–S1	123.6(2)	N3–C10–O2	113.3(3)
N3–C10–C11	127.9(3)	O2–C10–C11	118.8(3)
C10–C11–C12	112.1(3)	C13–C12–C17	119.2(3)
C13–C12–C11	120.3(3)	C17–C12–C11	120.5(3)
C14–C13–C12	120.6(3)	C13–C14–C15	120.4(3)
C16–C15–C14	119.1(3)	C17–C16–C15	120.7(3)
C16–C17–C12	120.0(3)		

1-*N*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-2,4-dihydro-4-methyl-1,2,4-triazole-3-thione (XI) and 3-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosylthio)-4-methyl-1,2,4-triazole (X). The interaction of triazole (**IV**) (0.221 g, 1.91 mmol) and chloride (**I**) (0.7 g, 1.91 mmol) followed by crystallization resulted in glycoside (**XI**); yield 0.25 g (29%); mp 247–250°C (degr.); $[\alpha]_{546}$ +50° (*c* 1.0; chloroform). Glycoside (**X**); yield 0.26 g (30%) was obtained after chromatography on a column eluted with a benzene to 15 : 1 benzene–isopropanol; mp 144–148°C, $[\alpha]_{546}$ –12° (*c* 1.0; chloroform).

1-*N*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-2,4-dihydro-5-(4-chlorophenyl)-4-ethyl-1,2,4-triazole-3-thione (XIII) and 3-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosylthio)-5-(4-chlorophenyl)-4-ethyl-1,2,4-triazole (XII). The interaction of triazole (**V**) (0.522 g, 2.60 mmol) and chloride (**I**) (0.95 g, 2.60 mmol) followed by crystallization resulted in glycoside (**XIII**); yield 0.50 g (34%); mp 238–242°C (degr.); $[\alpha]_{546}$ –27° (*c* 0.67; chloroform). Glycoside (**XII**) was obtained after a chromatography on a column eluted with a benzene to 20 : 1 benzene–isopropanol; an amorphous compound; yield 0.385 g (26%); $[\alpha]_{546}$ +25° (*c* 1.0; chloroform).

3-*N*-(2-Acetamido-2-deoxy-β-*D*-glucopyranosyl)-5-benzyl-1,3,4-oxadiazole-2(3*H*)-thione (XV). A

solution of 0.1 N sodium methylate in methanol (0.05 ml) was added to a solution of peracetate (**VI**) (150 mg) in absolute methanol (5 ml). After the reaction was completed (TLC monitoring, systems A and B), it was treated with a cation exchange resin KU-2 (H^+ form). The resin was filtered off, the filtrate was evaporated to dryness, and the residue of triol was crystallized from water to give glycoside (**XV**); yield 103 mg (90%); mp 159–161°C (degr.); $[\alpha]_{546}$ +42° (*c* 1.0; DMSO).

General procedure for the *S*-β to *N*-β glycoside rearrangement [15]. Mercury(II) bromide was suspended in a calculated amount of xylene (100 ml per 1.25 mmol of bromide), one quarter of xylene volume was evaporated at a reduced pressure, the corresponding *S*-β glucosaminide (the molar ratio of *S*-β-glucoside to bromide 1 : 5) was added, and the mixture was refluxed until a complete conversion to *N*-β-glycosides (TLC monitoring). Xylene was evaporated, the residue was dissolved in chloroform, and the organic layer was successively washed with 30% potassium iodide, 5% sodium carbonate, and water. The organic layer was separated, dried with anhydrous sodium sulfate, and evaporated. The target compounds were isolated by crystallization from isopropanol.

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