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SYNTHESIS AND MODIFICATION OF SPACERED GLYCOSIDES OF N-ACETYLGLUCOSAMINE

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From glucosaminyl chloride peracetate, in the presence of HgI_2, we have obtained β-p-nitrobenzyl-, β-ω-chloro- and β-ω-azido-spacered glycosides of N-acetylglucosamine (NAG) with spacers of different lengths and chemical natures. The corresponding amino derivatives have been synthesized from them. The possibility has been shown of modifying the ω-chloro- and ω-azido-spacered glycosides of NAG.

Spacered derivatives of carbohydrates, especially N-acetylglucosamine, are being used throughout the world in the synthesis of glucoconjugates, glycolipids, and immunosorbents. Spacered glycosides are the most convenient both to prepare and to use. Spacers with active functions of the type of amino groups are usually obtained at the end of the synthesis from stable "prespacers." Such precursors that have been described include: *p*-nitrophenyl [1], *p*-acetamidobenzyl [2], and *p*-nitrophenylethyl [3] glycosides; ω-aminoalkyl glycosides with phthaloyl [4], trifluoroacetamido, [5] or Z [6] or Boc [7] protection; and also ω-azidoalkyl glycosides [8]. In recent years, great interest has been aroused by ω-halogenoalkyl glycosides, which are easily modified to form ω-carboxy and ω-amino derivatives or glycolipids [9].

As catalyst in the synthesis of glycosides of N-acetylglucosamine (NAG)glycosides, we propose HgI_2, which permits the use of a readily obtainable and stable glycosyl donor — the α-chloride (**1**) [10]. Our aim was to develop a convenient method of synthesizing ω-chloro- and ω-amino-spacered glycosides of NAG with spacers of different chemical natures, and their modification.

The glycosylation of *p*-nitrobenzyl alcohol with the α-chloride (**1**) was carried out at room temperature in dichloroethane in the presence of mercury(II) iodide and molecular sieves 3. The β-*p*-nitrobenzyl glycoside (**2**) was obtained by crystallization with a yield of 52%. Its structure was confirmed by its PMR spectrum, in which we identified signals from the protons of the carbohydrate residue (see the Experimental part) and the aglycon: two doublets of an *AB*-system of methylene protons with CSs of 4.70 and 5.02 ppm and two doublets of aromatic protons with CSs of 7.48 and 8.20 ppm. The β-configuration of the glycosidic bond followed from the presence in the spectrum of the doublet of the anomeric proton with a CS of 4.76 ppm and the SSCC 8.5 Hz. The nitro group in compound (**2**) was subjected to hydrogenation over a platinum catalyst, and the amine (**3**) obtained was converted by the action of 2-dodecyltetradecanoic acid into the lipophilic derivative (**4**). As compared with that of compound (**2**), its PMR spectrum contained an additional triplet with a CS of 0.88 ppm from two terminal methyl groups and an intense multiplet of methylene protons with a CS of 1.24 ppm, which confirmed the introduction of the lipophilic component.

Analogously, the interaction of 4-chlorobutyl and 6-chlorohexyl alcohols with the α-chloride (**1**) gave the ω-chloroglycosides (**5a, b**), which we had obtained previously by an oxazoline synthesis [8]. The treatment of chlorine derivatives (**5a, b**) with sodium azide in the presence of tetraethylammonium bromide led to the ω-azidoalkyl glycosides (**6a, b**). The PMR spectrum of compound (**6a**) included a triplet with the CS 3.23 ppm of a ω-methylene group, two multiplets with CSs of 3.49 and 3.81 ppm of nonequivalent protons of an α-methylene group, and two multiplets with CSs of 1.18 and 1.59 ppm for the other CH_2 groups (see the Experimental part). The Zemplen deacetylation of glycoside (**6a**), followed by reduction of the azido function, led to the amine (**8a**), from which, by the method of [11], we obtained a conjugate of β-N-acetylglucosamine with polyacrylamide. Such conjugates can be used for typing lectins or antibodies [12].

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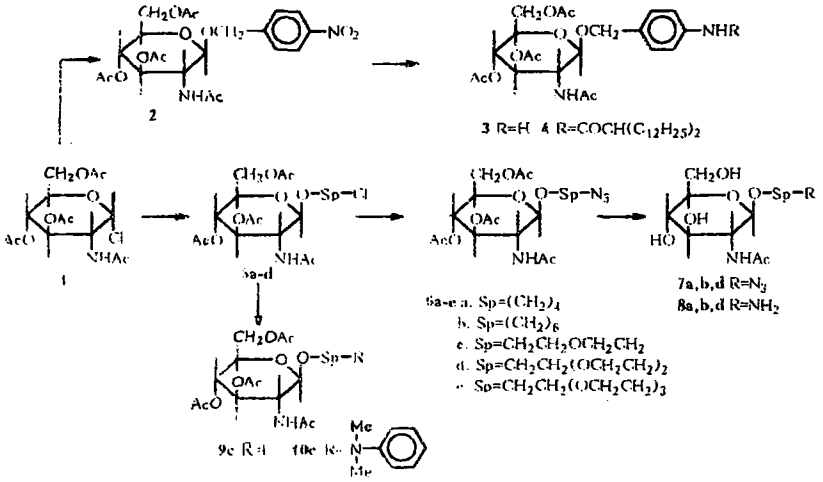

A point of view exists according to which not only aromatic but also aliphatic aglycons are fairly rigid and do not ensure adequate conformational tuning of the carbohydrate ligands of glycoconjugates in biological recognition. Oligoethyleneglycol "bridges" have been proposed as alternatives to such spacers [13]. We have performed the synthesis of ω-azido-spacered glycosides with spacers of ethylene glycolic nature having various lengths. By glycosylating di- and triethylenechlorohydrins in the presence of HgI_2 we obtained glycosides (**5c, d**). Their structures were confirmed by their PMR spectra, which contained, in particular, the signal of the protons of a glycosidic center (doublets with CSs of 4.78 and 4.77 ppm and SSCCs of 8.5 Hz). The protons of the methylene groups of the aglycons appeared in the form of a broad multiplet in the 3.60-3.80 ppm region. The chlorine atom in each of these compounds was replaced by an azido group, as described above. The IR spectra of the azides (**6c, d**) contained the intense absorption band at 2100 cm^{-1} that is characteristic for the azido group. Elimination of the acetyl protections and hydrogenation of the azide functions over PdO in the triols (**7c, d**) enabled the desired ω-amino-spacered glycosides of NAG (**8c, d**) to be obtained.

In order to obtain an even longer spacer, as the starting compound we used tetraethyleneglycol. It was monomesylated in THF at 0°C. The monomesylate was isolated with a yield of 77% by column chromatography. The mesyloxy group was replaced by an azido group by treatment with sodium azide. The azidoalcohol was glycosylated with the α-chloride (**1**), giving the prespacer glycoside (**6e**).

As examples of the transfunctionalization of the spacer glycosides we may give the reactions of the ω-chloroglycoside (**5c**). Thus, its treatment with sodium iodide in acetone gave the more reactive iodide (**9c**), and its interaction with N,N-dimethylaniline led to the quaternary ammonium salt (**10c**), modeling a new type of carbohydrate-containing ionogenic SAAs.

EXPERIMENTAL

Melting points were determined on a PTP instrument, and optical rotations at 20-22°C on a Polamat-A polarimeter. PMR spectra were obtained on Bruker WP-200 (200 MHz), Varian VXR-300 (300 MHz), and Bruker WM-500 (500 MHz) instruments, with tetramethylsilane as internal standard and C^2HCl_3 the solvent; chemical shifts are given on the δ-scale. TLC was conducted on Kieselgel 60 F254 plates (Merck). The substances were revealed with a 2% solution of sulfuric acid in ethanol followed by heating at 150°C. The following systems were used: benzene–ethanol (10:1) (1) and (5:1) (2); chloroform–ethanol (15:1) (3); and ethanol–butanol-1–pyridine–water–acetic acid (100:10:10:10:3) (4). Column chromatography was performed on Aldrich 70-230 mesh silica gel. The elementary analyses of the compounds synthesized corresponded to the calculated values.

p-Nitrobenzyl alcohol was obtained by reducing *p*-nitrobenzaldehyde with $NaBH_4$. In the syntheses we employed mesyl chloride and thionyl chloride from Aldrich.

A number of general procedures were used in the work.

Glycosylation. A solution of 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-*D*-glucopyranosyl chloride [14] in dry dichloroethane (25 ml/g) was treated with 1.16 equiv. of mercury(II) iodide and 1 equiv. of alcohol. The reaction mixture was stirred in the presence of molecular sieves 3 until the glycosyl donor had disappeared (monitoring by TLC in systems 1 and 2). The molecular sieves and the undissolved catalyst were filtered off, and the filtrate was diluted with chloroform and washed

with potassium iodide solution and with water. The organic layer was separated off, dried with anhydrous Na_2SO_4, and evaporated.

Zemplen Deacetylation. A solution of the acetate in dry methanol or in a 1:1 mixture of methanol and dichloromethane (10 ml/g) was treated with 0.01-0.05 equiv. of a 0.1 N solution of sodium methanolate in methanol, and the mixture was kept for 12-24 h. It was then neutralized with KU-2 cation-exchange resin (H^+), the resin was washed with methanol, and the filtrate was evaporated.

Azidation. A solution of an ω-spacered derivative in dry DMFA (10 ml/g) was treated with 3 equiv. of sodium azide and 1 equiv. of tetraethylammonium bromide. The reaction mixture was kept in an oil bath at 80-90°C for 24 h. Salts were filtered off and washed with chloroform. The organic layer was washed with water, and the extract was dried with anhydrous Na_2SO_4 and evaporated.

***p*-Nitrobenzyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (2).** The glycosylation of 420 mg (2.74 mmole) of *p*-nitrobenzyl alcohol with chloride (**1**) (1.0 g, 2.74 mmole) gave, after recrystallization from ethanol, 665 mg (52%) of glycoside (**2**); mp 172-173°C, $[\alpha]_{546}$ −48° (*c* 1.0 chloroform). PMR spectrum (200 MHz): 1.97, 2.04, 2.05, 2.10 (12H, NAc and 3 OAc, s), 3.72 (1H, H-5; $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 4.5 Hz, ddd), 4.02 (1H, 11-2, $J_{2,3}$ 10 Hz, ddd), 4.17 and 4.28 (2H, H-6a, H-6b; $J_{6a,6b}$ 12 Hz, dd). 1.70 and 5.02 (2H, OCH_2; J_{gem} 13 Hz, d), 4.76 (1H, H-1; $J_{1,2}$ 8.8 Hz, d), 5.12 (1H, H-4; $J_{4,5}$ 9.5 Hz, dd). 5.27 (1H, H-3; $J_{3,4}$ 9.5 Hz, dd), 5.60 (1H, NH; $J_{2,NH}$ 8.5 Hz, d), 7.48 and 8.20 (4H, CH_{arom}, d).

***p*-Aminobenzyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (3).** In solution in 5 ml of THF at room temperature, 90 mg (0.19 mmole) of compound (**2**) was subjected to catalytic hydrogenation over 10% Pt/C (90 mg). After 4 h (monitoring by TLC in system 2) the catalyst was filtered off and washed with THF; the filtrate was evaporated, and the addition of ether led to the crystallization of 53 mg (63%) of the amine (**3**); mp 99-101°C, $[\alpha]_{546}$ −60°C (*c* 1.0; chloroform).

***p*-(2-Dodecyltetradecanoylamino)benzyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (4).** A solution of 88 mg (0.22 mmole) of 2-dodecyltetradecanoic acid in 2 ml of dry toluene was treated with 20 ml of thionyl chloride. The mixture was boiled for 30 min and cooled, and 100 mg (0.22 mmole) of the amine (**3**) and 50 μl of triethylamine were added. After 24 h (monitoring by TLC in system 2), the mixture was evaporated and subjected to column chromatography (eluent: CCl_4 → CCl_4−propan-2-ol (25:1)), which gave 114 mg (62%) of compound (**4**); mp 146-148°C, $[\alpha]_{546}$ −33° (*c* 1.0; chloroform).

4-Chlorobutyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (5a). The glycosylation of 130 mg (1.4 mmole) of 4-chlorobutan-1-ol with chloride (**1**) (500 mg, 1.4 mmole) gave, after purification by column chromatography (eluent: CCl_4 → CCl_4−propan-2-ol (20:1)), 380 mg (64%) of glycoside (**5a**): mp 102-103°C, $[\alpha]_{546}$ −18° (*c* 1.0; chloroform).

6-Chlorohexyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (5b). Similarly, the glycosylation of 187 mg (1.4 mmole) of 6-chlorohexan-1-ol with chloride (**1**) (500 mg, 1.4 mmole) followed by column chromatographic purification (eluent: CCl_4 → CCl_4−propan-2-ol (10:1)) gave 326 mg (51%) of glycoside (**5b**), mp 112-114°C, $[\alpha]_{546}$ −21° (*c* 1.0; chloroform).

5-Chloro-3-oxapentyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (5c). The glycosylation of 170 mg (1.36 mmole) of 5-chloro-3-oxapentan-1-ol with chloride (**1**) (500 mg, 1.4 mmole) gave, after column chromatography (eluent: CCl_4→CCl_4−propan-2-ol (25:1)), 392 mg (62%) of glycoside (**5c**): mp 129-130°C, $[\alpha]_{546}$ −23° (*c* 1.0; chloroform). PMR spectrum (500 MHz): 1.95, 2.02, 2.03, 2.09 (12H, NAc and 3 OAc, s), 3.65-3.75 (−OCH_2CH_2−, m), 3.79 (1H, H-5; $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5 Hz, ddd), 3.95 (1H, H-2; $J_{2,3}$ 10 Hz, ddd), 4.14 and 4.25 (2H, H-6a, H-6b; $J_{6a,6b}$ 12.5 Hz, dd), 4.76 (1H, H-1, $J_{1,2}$ 8.5 Hz, d), 5.08 (1H, H-4; $J_{4,5}$ 9.5 Hz, dd), 5.21 (1H, H-3; $J_{3,4}$ 9.5 Hz, dd), 5.60 (1H, NH; $J_{2,NH}$ 8.5 Hz, d).

8-Chloro-3,6-dioxaoctyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (5d). The glycosylation of 233 mg (1.4 mmole) of 8-chloro-3,6-dioxaoctan-1-ol with chloride (**1**) (500 mg; 1.4 mmole) and column chromatography (eluent: CCl_4 → CCl_4−propan-2-ol (25:1)) led to 513 mg (74%) of glycoside (**5d**): mp 80°C, $[\alpha]_{546}$ −23° (*c* 1.0; chloroform). PMR spectrum (200 MHz): 1.96, 1.99 (6H), 2.06 (12H, NAc and 3 OAc, s), 3.60-3.80 (−OCH_2CH_2−, H-5, m), 3.85 (1H, H-2, m), 4.07 and 4.23 (2H, H-6a, H-6b; $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 4.5 Hz, $J_{6a,6b}$ 12 Hz, dd), 4.78 (1H, H-1; $J_{1,2}$ 8.5 Hz, d), 5.04 (1H, H-4; $J_{4,5}$ 9.5 Hz, dd), 5.10 (1H, H-3; $J_{3,4}$ 9.5 Hz, dd), 5.45 (1H, NH; $J_{2,NH}$ 8.5 Hz, d).

4-Azidobutyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (6a). The azidation of 200 mg (0.46 mmole) of the chlorine derivative (**5a**) yielded 180 mg (88%) of glycoside (**6a**): mp 95-96°C, $[\alpha]_{546}$ −17° (*c* 1.0; chloroform). PMR spectrum: (200 MHz): 1.18, 1.59 (CH_2, m), 1.89, 1.96, 1.97, 2.02 (12H, NAc and 3 OAc, s), 3.23 (2H, CH_2N_3, t), 3.49 and 3.81 (2H, OCH_2, m), 3.62 (1H, H-5; $J_{5,6a}$ 2.5 Hz, $J_{5,6b}$ 5 Hz, ddd), 3.81 (1H, H-2, m), 4.06 and 4.20 (2H, H-6a,

H-6b; $J_{6a,6b}$ 12.5 Hz, dd), 4.60 (1H, H-1; $J_{1,2}$ 8.5 Hz, d), 5.00 (1H, H-4; $J_{4,5}$ 9.5 Hz, dd), 5.22 (1H, H-3; $J_{3,4}$ 9.5 Hz, dd), 5.52 (1H, NH; $J_{2,NH}$ 8.5 Hz, d).

6-Azidohexyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (6b). The azidation of 100 mg (0.21 mmole) of chlorine derivative (**5b**) gave 69 mg (68%) of glycoside (**6b**); mp 107-108°C, $[\alpha]_{546}$ −17° (*c* 1.0; chloroform).

5-Azido-3-oxapentyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (6c). By analogy with compound (**6a**), the azidation of 100 mg (0.22 mmole) of the chlorine derivative (**5c**) led to 70 mg (69%) of azide (**6c**); mp 71-73°C, $[\alpha]_{546}$ −23° (*c* 1.0; chloroform)

8-Azido-3,6-dioxaoctyl) 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (6d). The azidation of 100 mg (0.2 mmole) of the chlorine derivative (**5d**) yielded 64 mg (64%) of glycoside (**6d**); mp 54-56°C, $[\alpha]_{546}$ −25° (*c* 1.0; chloroform).

11-Azido-3,6,9-trioxaundecan-1-ol. With cooling to 0°C and stirring, a solution of 2.0 g (17 mmole) of mesyl chloride in 10 ml of THF was added in portions over 1 h to a solution of 3.38 g (17 mmole) of tetraethyleneglycol (3,6,9-trioxaundecane-1,11-diol) and 1.93 g (19 mmole) of triethylamine in 20 ml of THF, after which the mixture was kept, with cooling, for 30 min (monitoring by TLC in system 3). The precipitate that had deposited was filtered off, the filtrate was evaporated, and column chromatography (eluent: CCl_4 → CCl_4−propan-2-ol (25:1)) led to the isolation of 3.65 g (77%) of 11-mesyloxy-3,6,9-trioxaundecan-1-ol.

A solution of 300 mg (1.1 mmole) of the monomesylate in 5 ml of acetonitrile and 3 ml of DMFA was treated with 215 mg (3.3 mmole) of sodium azide, and the mixture was boiled for 5 h (monitoring by TLC in system 3). The precipitate was filtered off and washed with acetonitrile, and the filtrate was evaporated. This gave 194 mg (75%) of the azidoalcohol.

11-Azido-3,6,9-trioxaundecyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (6e). The glycosylation of 321 mg (1.4 mmole) of 11-azido-3,6,9-trioxaundecan-1-ol with chloride (**1**) (500 mg, 1.4 mmole) gave, after column chromatographic purification (eluent: CCl_4 → CCl_4−propan-2-ol (15:1)), 390 mg (50%) of glycoside (**6e**); mp 147-149°C, $[\alpha]_{546}$ −29° (*c* 1.0; chloroform).

4-Azidobutyl 2-Acetamido-β-*D*-glucopyranoside (7a). The deacetylation of 195 mg (0.44 mmole) of the peracetate (**6a**) gave 128 mg (92%) of the triol (**7a**): mp 140-142°C, $[\alpha]_{546}$ −27° (*c* 1.0; ethanol).

6-Azidohexyl 2-Acetamido-β-*D*-glucopyranoside (7b). The deacetylation of 200 mg (0.42 mmole) of the peracetate (**6b**) gave 138 mg (94%) of the triol (**7b**): mp 140-142°C, $[\alpha]_{546}$ −26° (*c* 1.0; ethanol).

8-Azido-3,6-dioxaoctyl 2-Acetamido-β-*D*-glucopyranoside (7d). The deacetylation of 100 mg (0.2 mmole) of the peracetate (**6d**) led to 74 mg (99%) of the amorphous triol (**7d**); $[\alpha]_{546}$ −28° (*c* 1.0; chloroform).

8-Amino-3,6-dioxaoctyl 2-Acetamido-β-*D*-glucopyranoside (8d). At room temperature, the azide (**7d**) (74 mg (0.15 mmole) dissolved in 3 ml of methanol) was subjected to catalytic hydrogenation over 55 mg of PdO for 48 h (monitoring by TLC in system 4). The catalyst was filtered off and the filtrate was evaporated, after which the addition of ether led to the crystallization of 70 mg (100%) of the amine (**8d**)

Conjugate of N-Acetylglucosamine with Polyacrylamide. As described above, 30 mg (0.068 mmole) of the azide (**7a**) in 3 ml of methanol was subjected to catalytic hydrogenation at room temperature over 20 mg of PdO for 48 h, giving 27 mg (96%) of 4-aminobutyl 2-Acetamido-β-*D*-glucopyranoside (**8a**).

A solution of 65 mg (0.323 meq.) of polyacrylamide in 4 ml of DMSO was treated with a solution of 27 mg (0.065 mmole) of the amine (**8a**) in 1 ml of DMSO and 50 μl of triethylamine. The reaction mixture was kept for 24 h, and, before the final disappearance of the amine (monitoring by TLC in system 4), 100 ml of conc. ammonia solution was added, and the mixture was stirred for 2 h. Gel filtration on Sephadex G-15 led to the isolation of 44 mg (90%) of polymeric conjugate.

5-Iodo-3-oxapentyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside (9c). To a solution of 100 mg (0.22 mmole) of the chlorine derivative (**5c**) in 5 ml of acetone was added 82 mg (0.55 mmole) of sodium iodide, and the mixture was boiled for 50 min (monitoring by TLC in system 3). Then it was evaporated and diluted with chloroform, and the precipitate of salts was filtered off. The filtrate was washed with water, and the organic layer was dried with anhydrous $CaCl_2$ and evaporated. This gave 90 mg (75%) of the iodide (**9c**); mp 124-126°C, $[\alpha]_{546}$ −21° (*c* 1.0; chloroform).

(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranosyl)dimethyl(3-oxapentyl-5-yl)phenylammonium Chloride (10c). A solution of 100 mg (0.22 mmole) of the chlorine derivative (**5c**) in 2 ml of acetone was treated with 27 mg (0.22 mmole) of N,N-dimethylaniline, and the mixture was boiled for 20 min (monitoring by TLC in system 3). Then it was evaporated, and crystallization from ether yielded 58 mg (46%) of the ammonium salt (**10c**); mp 128-129°C, $[\alpha]_{546}$ −4° (*c* 1.0; chloroform).

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