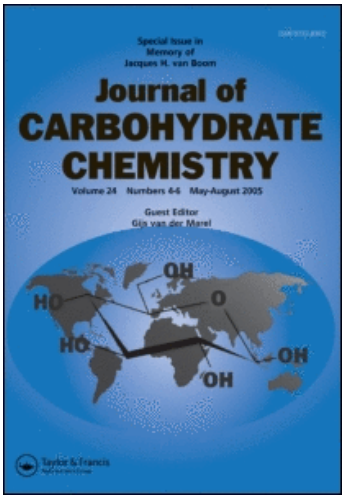

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SYNTHESES OF D-GLUCOSAMINYL BOLAAMPHIPHILES[1]

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ABSTRACT

Twelve *N*-acetyl or NH_2-free D-glucosaminyl bolaamphiphiles have been synthesized by the intermediate of *N*-allyloxycarbonyl-D-glucosaminyl precursors. Thus, glycosylation of α,ω-diols with 1,3,4,6-tetra-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranose (**1**) gave the bis(glycosides) **2a-h** in good yields and without column chromatography. Alkaline treatment of these derivatives followed by acetylation gave the peracetylated *N*-acetyl compounds **3a-h** which were further deprotected by the Zemplén deacetylation procedure to the *N*-acetyl-D-glucosaminyl bolaamphiphiles **4a-h**. The bis(glycosides) **2c,d,g** were also transformed into the *O*-acetylated amino-free derivatives **5c,d,g** by chemospecific deprotection of the *N*-allyloxycarbonyl groups with palladium (0). Further deprotection of the ester functions led to the completely deprotected bolaamphiphiles **7c,d,g** with high yields. Fully deprotected compounds **7a,d,g,h** were also obtained from **2a,d,g,h** by alkaline treatment and purification by column chromatography. Surface tension measurements were realized for aqueous solutions containing the soluble bolaamphiphiles.

INTRODUCTION

Bolaamphiphiles are α,ω-surfactants which consist of a hydrophobic core and hydrophilic groups at both ends.[2,3] There is increasing interest in these compounds, from a fundamental and an applied point of view. Most of them have been studied for their

polymorphic behaviours in water as a function of their structures.[4-10] When dissolved in aqueous medium, upon sonication, these molecules often self-organize into monolayer vesicles (monolayer lipid membranes) which are stable over a long period of time to the variations of temperature or to ionic strength changes and could be used as membrane models.

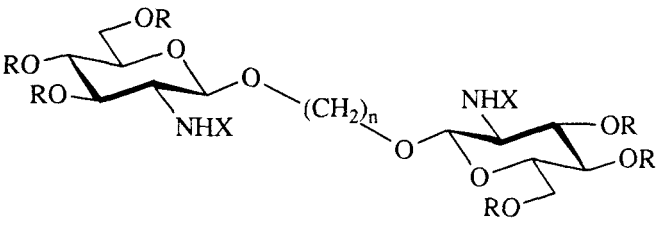
Bolaamphiphile surfactants with sugars at both ends have already been synthesized, because of their ability to form vesicles and supramolecular arrangements, and because of their applications in the biomedical and pharmaceutical fields.[7,11] For example, bolaamphiphiles with carbohydrate head groups (thioglucose, thiogalactose or thiomannose) have been used to entrap polynucleotides or inorganic colloids.[11] More recently a series of bis(lactobionamide) surfactants has been prepared in one step from lactobionic acid and α,ω-diamines.[12] The condensation of dimeric acid with D-glucosamine, by the methods often used in peptide chemistry, also led to bis(amido sugar) bolaamphiphiles.[13]

Very recently, J. Lehmann *et al.* have published the synthesis of a series of homologous spacer-modified disaccharides and they have demonstrated that the pentasaccharide inserted between two *N*-acetyl-D-glucosaminyl residues in an *N*-linked core-heptasaccharide could be replaced by an acyclic flexible spacer of appropriate length for the galactosylation by a galactosyltransferase.[14] Thus, these authors prepared four bis-(*N*-acetyl-D-glucosaminide) molecules with linear alkyl chains of 6, 8, 10 and 12 methylene groups. This prompted us to report our results in the synthesis of D-glucosaminyl bolaamphiphiles derived from α,ω-diols.

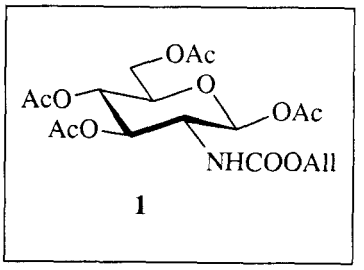
RESULTS AND DISCUSSION

Amongst the various β-glycosylation methods described in the literature in the D-glucosamine series,[15] the allyloxycarbonyl procedure[16] seemed to be the most attractive for the synthesis of bolaamphiphilic structures of α,ω-diols, since good yields were generally obtained[16-18] and since the chemoselective and mild deprotection of the *N*-allyloxycarbonyl groups allowed the preparation of amino-free D-glucosamine derivatives. Furthermore, the Kiso and Anderson glycosylation methods[19] could not be used, since an excess of one reactant (donor or acceptor) is most often required. In this case the donor should be used in excess - in order to avoid the formation of the monoglycosylated compound - and it would result in a very difficult separation of the latter from the reaction product.

Glycosylation of α,ω-diols $HO(CH_2)_nOH$ (n = 6-12,16) with 1,3,4,6-tetra-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranose (**1**) (1.08 equiv per *OH*

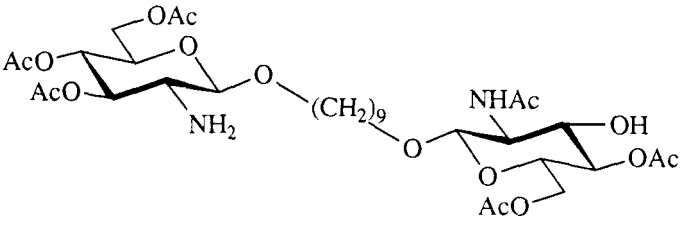


2a-h	R = Ac, X = COOAll
3a-h	R = X = Ac
4a-h	R = H, X = Ac
5c,d,g	R = Ac, X = H
7a,c,d,g,h	R = X= H



1

a n = 6 **e** n = 10
b n = 7 **f** n = 11
c n = 8 **g** n = 12
d n = 9 **h** n = 16



6d

group) promoted by trimethylsilyl trifluoromethanesulfonate afforded the expected bis (glycosides) **2a-h** in good yields (63-83%) and without column chromatography, except in the case of **2h** where two successive chromatographic separations were necessary to give the pure product as an amorphous solid. The β-structures of these compounds were ascertained from ^{1}H and ^{13}C NMR data (Tables 1, 2 and 3). The yields for compounds **2a**, **2c**, **2e** and **2g** were of the same order of magnitude as those reported by Lehmann *et*

Table 1: ^{1}H NMR chemical shifts (ppm) of β-D-glucosaminyl derivatives **2-7**.

Product	Solvent	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	H-a	H-b
2a-h[a]	$CDCl_3$	4.60(d)	3.58(ddd)	5.23(dd)	5.05(dd)	3.69(ddd)	4.28(dd)	4.12(dd)	3.88(ddd)	3.48(ddd)
3a-h[a]	$CDCl_3$	4.71(d)	3.88(ddd)	5.32(dd)	5.07(dd)	3.73(ddd)	4.29(dd)	4.13(dd)	3.88(ddd)	3.46(ddd)
4a-h[a]	$C_5D_5N+D_2O$	5.11(d)	4.62(dd)	4.47(dd)	4.21(dd)	4.01(ddd)	4.59(dd)	4.35(dd)	4.11(ddd)	3.68(ddd)
5c,d,g[a]	$CDCl_3$	4.24(d)	2.93(dd)	4.98(dd)	5.02(dd)	3.69(ddd)	4.30(dd)	4.11(dd)	3.91(ddd)	3.50(ddd)
6d	$CDCl_3$	4.25(d) 4.61(d)	2.93(dd) 3.43(ddd)	4.98(dd) 3.97(dd)	5.02(dd) 4.93(dd)	3.67(m) 3.67(m)	4.30(dd) 4.30(dd)	4.11(dd) 4.11(dd)	3.87(m) 3.87(m)	3.48(m) 3.48(m)
7a	C_5D_5N	4.93(d)	3.37(dd)	4.22(dd)	4.30(dd)	3.97(ddd)	4.54(dd)	4.38(dd)	4.01(ddd)	3.62(ddd)
7c	C_5D_5N	4.76(d)	3.32(dd)	4.11(dd)	4.23(dd)	3.90(ddd)	4.55(dd)	4.40(dd)	3.92(ddd)	3.59(ddd)
7d	C_5D_5N	4.72(d)	3.32(dd)	4.08(dd)	4.23(dd)	3.94(ddd)	4.56(dd)	4.41(dd)	4.07(ddd)	3.61(ddd)
7g	C_5D_5N	4.76(d)	3.34(dd)	4.13(dd)	4.23(dd)	3.94(ddd)	4.56(dd)	4.41(dd)	4.09(ddd)	3.63(ddd)
7g	C_5D_5N	4.82(d)	3.36(dd)	4.15(dd)	4.24(dd)	3.95(ddd)	4.56(dd)	4.42(dd)	4.09(ddd)	3.64(ddd)

a. The chemical shifts for all compounds on the same line are identical (± 0.03 ppm)

Table 2: ^{1}H NMR coupling constants (Hz) of the β-D-glucosaminyl derivatives **2-7**.

Product	Solvent	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
2a-h[a]	$CDCl_3$	8.2	9.7	8.6	9.5	4.7	2.3	12.2
3a-h[a]	$CDCl_3$	8.3	10.2	9.4	9.8	4.7	2.6	12.2
4a-h[a]	$C_5D_5N+D_2O$	8.2	10.0	8.6	9.5	2.0	5.6	11.8
5c,d,g[a]	$CDCl_3$	8.5	9.2	10.0	9.2	4.7	2.3	12.2
6d	CD_3Cl_3	8.3 8.2	9.3 9.7	10.0 8.8	9.2 9.5	4.7 4.7	2.5 2.3	12.2 12.2
7a	C_5D_5N	8.0	9.5	8.5	9.7	2.4	5.2	11.9
7c	C_5D_5N	7.9	9.4	8.6	9.4	2.3	5.1	11.8
7d	C_5D_5N	7.8	9.6	8.8	9.4	2.4	5.2	11.8
7g	C_5D_5N	7.9	9.4	8.8	9.4	2.2	5.2	11.7
7h	C_5D_5N	7.9	9.5	8.7	9.3	2.2	5.1	11.8

a. The coupling constants for all compounds on the same line are identical (± 0.1 Hz)

Table 3: ^{13}C NMR chemical shifts (ppm) of the β-D-glucosaminyl derivatives **2-7**.

Product	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-α	CH_3CON
2a-h[a]	$CDCl_3$	101.01	52.04	72.22	68.83	71.53	62.17	70.05	-
3a-h[a]	$CDCl_3$	100.66	54.67	72.35	68.85	71.20	62.20	69.75	23.20
5c,d,g[a]	$CDCl_3$	103.87	55.74	75.22	68.77	71.60	62.15	70.15	-
6d	$CDCl_3$	103.82 100.25	55.80 57.87	75.22 72.07	68.87 68.87	71.64 71.38	62.26 62.47	70.27 69.81	- 23.33
7a	C_5D_5N	103.47	58.41	78.46	71.62	76.59	62.39	69.62	-
7c	C_5D_5N	104.57	58.59	78.52	71.68	77.53	62.60	69.67	-
7d	C_5D_5N	104.75	58.57	78.50	71.62	77.65	62.59	69.66	-
7g	C_5D_5N	104.71	58.56	78.51	71.62	77.52	62.57	69.70	-
7h	C_5D_5N	104.52	58.64	78.62	71.77	77.48	62.62	69.75	-

a. The chemical shifts for all compounds on the same line are identical (± 0.12 ppm)

al. using the phthalimido procedure.[14,20] However these authors used a more important excess of the donor, relative to the acceptor alcohols (1.50 equiv per *OH* group instead of 1.08 equiv in this work).

Treatment of compounds **2a-h** in refluxing 2.5N sodium hydroxide, followed by neutralization (2.5 N hydrochloric acid), concentration and peracetylation (acetic anhydride, 4-dimethylaminopyridine, pyridine) led to the peracetylated bis-(*N*-acetyl-β-D-glucosaminyl) derivatives **3a-h** as crystalline materials (yields 73-83%). It is of interest to mention that compounds **3a**, **3c** and **3e** previously reported by Lehmann *via* the hydrazinolysis of *N*-phthaloyl precursors were not crystalline.[14,20]

The *O*-deprotected bis-(*N*-acetyl-β-D-glycosides) **4a-h** were easily obtained by the Zemplén deacetylation procedure. Thus, the treatment of insoluble compounds **3a-h** with a catalytic amount of sodium methylate in methanol gave a clear solution after 10 min . The products started to crystallize after a few minutes and were recovered in a pure form by filtration 16 h later.

Treatment of bis-(*O*-acetylated-*N*-allyloxycarbonyl-β-D-glucosaminyl) derivatives **2c**, **2d** and **2g** with tetrakis(triphenylphosphine)palladium and dimethyl malonate as the allyl acceptor afforded the *O*-acetylated amino-free compounds (**5c**, **5d**, and **5g** respectively) in good yields (76-79%). The structures of these compounds were confirmed from ^{1}H and ^{13}C NMR data (Tables 1, 2 and 3). In the case of **5d**, an important amount (15%) of a polar by-product **6d** was isolated after column chromatography: this compound could have resulted from migration of the *O*-3 acetyl group to the neighbouring amino group of the same D-glucosaminyl residue as was ascertained by ^{1}H NMR. The irradiation of *H*-4 (δ = 4.93 ppm) and *H*-5 (δ = 3.67 ppm) evidenced a 3.97 ppm chemical shift for *H*-3 which is characteristic of a OH-3 free position.

The complete deprotections of the amino-free derivatives **5c**, **5d** and **5g** to afford **7c**, **7d** and **7g** (yields 87 to 93%) were realized by the Zemplén procedure. A purification by column chromatography with mixtures of chloroform, ethanol and 25% aqueous ammonium hydroxide as eluent was nevertheless necessary to remove a polar by-product which was formed during the deacetylation (1-3%) and which could be a mono *N*-acetyl derivative. Compounds **7a**, **7d**, **7g** and **7h** were also obtained from **2a**, **2c**, **2d** and **2h** respectively. Deacetylation of the starting materials by the Zemplén procedure afforded the bis-(*O*-deprotected-*N*-allyloxycarbonylamino-β-D-glucosaminyl) derivatives which were then refluxed overnight in 2.5 N sodium hydroxide. It is to be mentioned that the deacetylation step, prior to the treatment with sodium hydroxide, avoided the formation of important amounts of sodium acetate and allowed a rapid solubilization of the intermediate product in alkaline aqueous medium. The crude mixtures obtained after refluxing and concentration were directly applied at the top of a column and eluted with the same eluents

Table 4

Compound	Krafft T (°C)	T[a] (°C)	cac[b] (mmol/L)	a_o (Å^2/molecule)	γ_{cac} (mN/m)
4a	<25	25	-	-	-
7a	<25	25	70	68	30.7
7d	34	37	76	72	35.9
7d	34	65	80	84	33.0
7g	54	65	74	88	32.9

a. Temperature of surface tension measurements. b. Critical aggregation concentration.

as previously mentioned. We observed that neutralization of the alkaline solution with hydrochloric acid prior to purification by column chromatography could result in impure compounds, probably containing ammonium chloride.[21]

Krafft temperatures were measured by slowly heating surfactant-water mixtures of various composition. The temperature of dissolution was the same for all surfactant concentrations and was taken as the Krafft temperature (reported in Table 4). As expected, the longer the alkyl chain, the higher the Krafft temperature.

Surface tensions were measured above the Krafft temperature, and were carried out by the Lecomte du Nouÿ[22] ring method at the intersection of the two linear parts of the $\gamma = f(\log[C])$ curve.[23] The aspects of these curves are looking like those observed for compounds forming micelles. Nevertheless, the nature of the supramolecular assemblies should be confirmed by other physical methods. Conventionally, the observed value at the break of the slope will be called critical aggregation concentration (cac). Above the cac, the surface tension was constant. The area per surfactant molecule at the air-water interface was calculated by the mean of the Gibbs law, from the slope $d\gamma/d(\log[C])$ in the linear domain below the cac. Results are reported in Table 4 and Figure 1. These results were not mistaken by changes of the pH values due to the dilution of the samples. Thus, in the concentration range used for the surface tension measurements, the NH_2-free compounds **7a**,**d**,**g** buffered the aqueous medium at pH 7.3. This is in accordance with the pKa values reported for the β-alkyl glycosides of D-glucosamine.[24]

For the *N*-acetylated compound **4a**, the surface tension lowering is rather weak and a break point cannot be unambiguously observed in the $\gamma = f(\log[C])$ plot. In the high concentration domain, the surface tension remains rather high (56 mN/m), which is much higher than the surface tension values of the conventional surfactants above their cmc. The

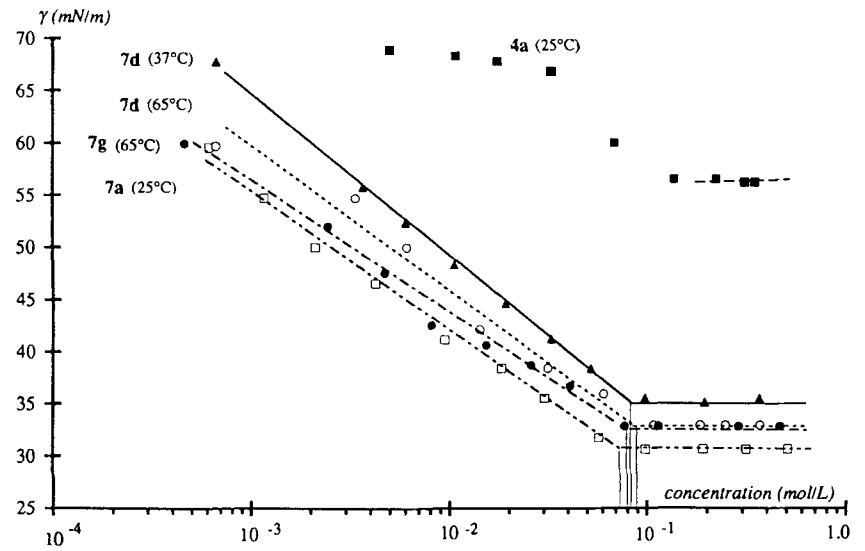


Figure 1

behaviour of this molecule in aqueous medium is rather difficult to display, a limited and progressive aggregation cannot nevertheless be discarded from these experimental data.

For the NH_2-free surfactants with chain lengths from 6 to 12 carbons (**7a**,**d**,**g**), the surface tension data were typical of those of conventional (single polar head) micelle forming surfactants:[23] a clear break of the slope is observed at the cac; the surface tension remains constant for concentration above this value and the surface tension values measured in this high concentration domain (γ = 30 to 36 mN/m) are in the range encountered for dense surfactants monolayers at the air-water interface.

The surface tension of **7d** has been measured at two different temperatures so as to avoid comparisons of values of different surfactants taken at different temperatures.

The cac is rather insensitive to temperature. No measurement could be realized for compound **7h** due to its very low solubility in water.

Surprisingly, these values do not depend on the alkyl chain length. This behaviour contrasts with that of conventional single head surfactants for which the cmc decreases as the alkyl chain is increasing because of the larger hydrophobic character of the surfactant.[25] We have no explanation for this experimental observation but we mention below two reports on the same phenomenon taken from the scarce surface tension data dealing with bolaamphiphiles. Thus, for cationic α,ω-bis(trimethylammonium)alkylene halides, the concentrations above which surfactant aggregations occur were shown not to depend on the alkylene chain lengths, as determined from electrical conductivity data[26] and

partial molar volumes.[27] These data concern short alkyl spacer molecules (from 3 to 10 carbon atoms) like the present work. It seems that a cmc decrease, as the chain is lengthened, occurs for longer chain lengths (above 12 carbon atoms) as reported by R. Zana *et al.*.[28] Our results also show that interfacial areas per molecules (a_o) are of the same order of magnitude for all compounds (Table 4).

EXPERIMENTAL

General Procedures. Pyridine was dried by boiling with calcium hydride prior to distillation. Dichloromethane was washed twice with water, dried with calcium chloride and distilled from phosphorous pentoxide. Tetrahydrofuran was distilled from a sodium-benzophenone mixture under an argon atmosphere. Methanol was refluxed with sodium methylate before distillation. Pyridine, dichloromethane and tetrahydrofuran were stored over 4 Å molecular sieves and methanol over 3 Å molecular sieves. Melting points were determined on a Büchi apparatus and were uncorrected. TLC analyses were performed on aluminium sheets coated with silica gel 60 F 254 Merck. Compounds were visualized by spraying the TLC plates with dilute 15 % aqueous sulfuric acid, followed by charring at 150 °C for a few minutes. Column chromatographies were performed on silica-gel Geduran Si 60 Merck. Optical rotations were recorded on a Perkin Elmer 241 polarimeter in a 1 dm cell at 21 °C. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-200 or AM-300 spectrometers working at 200 or 300 MHz and 50 or 75.5 MHz respectively, with tetramethylsilane as internal standard. Elemental analyses were realized by the "Laboratoire Central d'Analyses du CNRS" (Vernaison, France). The amounts of water present in some of the derivatives were determined by the Karl Fisher method.

General procedure for the glycosylation of 1,n-diols (n = 6-12,16): The 1,3,4,6-tetra-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranose (**1**) (4.0 g, 9.27 mmol) and the diol (4.31 mmol) were added to alcohol-free dichloromethane (50 mL) in a Schlenck tube. The reaction mixture was flushed with argon while cooling to -10 °C. Trimethylsilyl trifluoromethanesulfonate (1.84 mL, 10.2 mmol) was then introduced through a syringe and the argon flush maintained for 0.5 hour. The mixture was stirred overnight at -10 °C, then poured into a saturated sodium bicarbonate solution (50 mL) and the product was extracted with dichloromethane (3x50 mL). After drying (Na_2SO_4), concentration of the solution afforded a solid which was purified by three successive recrystallizations in absolute ethanol. In the case of hexadecan-1,16-diol, the glycosylation was performed starting from the compound **1** (2.85 g, 6.60 mmol) and the alcohol (0.773 g, 3.0 mmol). However, the residue obtained after concentration of the

organic phase did not crystallize and two successive column chromatographies were necessary to afford the pure bis(glycoside) **2h** (eluents : ethyl acetate/hexane 1:1 v/v, then dichloromethane/ acetone 6:1 v/v).

Hexan-1,6-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2a). Prepared according to the above procedure starting from hexan-1,6-diol. Yield: 83%; mp 176 °C (ethanol); R_f 0.61 (ethyl acetate/ hexane 1:1, v/v); $[\alpha]_D$ - 9.5 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{38}H_{56}N_2O_{20}$ (860.84): C, 53.01; H, 6.56; N, 3.25. Found: C, 52.76; H, 6.55; N, 3.26.

Heptan-1,7-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2b). Prepared according to the above procedure starting from heptan-1,7-diol. Yield: 72%; mp 186 °C (ethanol); R_f 0.64 (ethyl acetate/ hexane 2:1, v/v); $[\alpha]_D$ - 7.3 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{39}H_{58}N_2O_{20}$ (874.87): C, 53.54; H, 6.68; N, 3.20. Found: C, 53.64; H, 6.87; N, 3.26.

Octan-1,8-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2c). Prepared according to the above procedure starting from octan-1,8-diol. Yield: 72%; mp 160 °C (ethanol); R_f 0.65 (ethyl acetate/hexane 2:1, v/v); $[\alpha]_D$ - 4.4 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{40}H_{60}N_2O_{20}$ (888.89): C, 54.05; H, 6.80; N, 3.15. Found: C, 54.08; H, 6.81; N, 3.25.

Nonan-1,9-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2d). Prepared according to the above procedure starting from nonan-1,9-diol. Yield: 70%; mp 161 °C (ethanol); R_f 0.68 (ethyl acetate/ hexane 2:1, v/v); $[\alpha]_D$ - 4.2 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1- 3.

Anal. Calcd for $C_{41}H_{62}N_2O_{20}$ (902.92): C, 54.53; H, 6.90; N, 3.10. Found: C, 54.31; H, 6.85; N, 3.04.

Decan-1,10-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (2e). Prepared according to the above procedure starting from decan-1,10-diol. Yield: 70%; mp 162 °C (ethanol); R_f 0.69 (ethyl acetate/ hexane 2:1, v/v); $[\alpha]_D$ - 7.1 (*c* 1.0, dichloromethane): ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{42}H_{64}N_2O_{20}$ (916.95): C, 55.01; H, 7.03; N, 3.06. Found: C, 54.69; H, 7.16; N, 3.05.

Undecan-1,11-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2f). Prepared according to the above procedure starting from undecan-1,11-diol. Yield: 71%; mp 182 °C (ethanol); R_f 0.71 (ethyl acetate/hexane 2:1, v/v); $[\alpha]_D$ - 4.7 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{43}H_{66}N_2O_{20}$ (930.97): C, 55.47; H, 7.14; N, 3.01. Found: C, 55.64; H, 7.03; N, 3.07.

Dodecan-1,12-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2g). Prepared according to the above procedure starting from dodecan-1,12-diol. Yield: 68%; mp 167-168 °C (ethanol); R_f 0.73 (ethyl acetate/hexane 2:1, v/v); $[\alpha]_D$ - 7.5 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{44}H_{68}N_2O_{20}$ (945.00): C, 55.92; H, 7.25; N, 2.96. Found: C, 55.73; H, 7.11; N, 2.90.

Hexadecan-1,16-diyl Bis-(3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside) (2h). Prepared according to the above procedure starting from hexadecan-1,16-diol. Yield: 63%; mp 161-163 °C (chloroform); R_f 0.50 (dichloromethane/acetone 6:1, v/v); $[\alpha]_D$ - 5.0 (*c* 1.0, dichloromethane); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{48}H_{76}N_2O_{20}$ (1001.10): C, 57.58; H, 7.65; N, 2.80. Found: C, 57.24; H, 7.71; N, 2.76.

General procedure for the preparation of peracetylated *N*-acetyl-β-D-glucosaminyl derivatives 3a-h: Compounds **2a-h** (2-3 mmol) were deacetylated overnight by use of a catalytic amount of sodium methylate in methanol (25 mL). After concentration, the residue was refluxed in 2.5 N sodium hydroxide (20-30 mL) for 5 hours. Then, the solution was cooled to room temperature, neutralized with 2.5N hydrochloric acid and concentrated *in vacuo*. The residue was acetylated overnight with a 2:1 v/v mixture of pyridine and acetic anhydride (15 mL) in the presence of a catalytic amount of DMAP and the solution was concentrated again. The crude residue was dissolved in a mixture of dichloromethane (100 mL) and water (30 mL) and the organic phase was washed twice with water (2x30 mL), dried (Na_2SO_4) and concentrated. The product was rapidly purified by chromatography on a short column of silica-gel (ethyl acetate/ dichloromethane/ethanol 4:2:1 v/v/v) to afford a solid which was recrystallized from ethanol.

Hexan-1,6-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3a). Prepared according to the above procedure starting from compound **2a**. Yield: 73%; mp 231 °C (ethanol) [lit.[14] oil]; R_f 0.62 (ethyl acetate/ dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 16.8 (*c* 1.0, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{34}H_{52}N_2O_{18}$ (776.77): C, 52.57; H, 6.75; N, 3.61. Found: C, 52.39; H, 7.13; N, 3.55.

Heptan-1,7-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3b). Prepared according to the above procedure starting from

compound **2b**. Yield: 79%; mp 217 °C (ethanol); R_f 0.65 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 17.9 (*c* 1.0, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{35}H_{54}N_2O_{18}$ (790.80): C, 53.16; H, 6.88; N, 3.54. Found: C, 52.70; H, 6.55; N, 3.88.

Octan-1,8-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3c). Prepared according to the above procedure starting from compound **2c**. Yield: 77%; mp 207-209 °C (ethanol) [lit.[14] oil]; R_f 0.65 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 10.9 (*c* 1.0, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{36}H_{56}N_2O_{18}$ (804.82): C, 53.72; H, 7.01; N, 3.48. Found: C, 53.84; H, 7.11; N, 3.44.

Nonan-1,9-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3d). Prepared according to the above procedure starting from compound **2d**. Yield: 83%; mp 196-197 °C (ethanol); R_f 0.69 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 16.8 (*c* 1.0, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{37}H_{58}N_2O_{18}$ (818.85): C, 54.27; H, 7.14; N, 3.42. Found: C, 54.36; H, 7.27; N, 3.60.

Decan-1,10-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3e). Prepared according to the above procedure starting from compound **2e**. Yield: 77%; mp 215-216 °C (ethanol) [lit.[20] oil]; R_f 0.72 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 14.5 (*c* 1.0, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{38}H_{60}N_2O_{18}$ (832.87): C, 54.80; H, 7.26; N, 3.36. Found: C, 54.87; H, 7.59; N, 3.36.

Undecan-1,11-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3f). Prepared according to the above procedure starting from compound **2f**. Yield: 73%; mp 195-196 °C (ethanol); R_f 0.62 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 16.8 (*c* 1.0, chloroform); ^1H and ^{13}C NMR, Tables 1- 3.

Anal. Calcd for $C_{39}H_{62}N_2O_{18}$ (846.90): C, 55.31; H, 7.38; N, 3.31. Found: C, 55.22; H, 7.27; N, 3.29.

Dodecan-1,12-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3g). Prepared according to the above procedure starting from compound **2g**. Yield: 73%; mp 187-188 °C (ethanol) [lit.[14] mp 168-170 °C (ethanol)]; R_f 0.74 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 14.3 (*c* 1.0, chloroform) [lit.[14] $[\alpha]_D$ - 20.0 (*c* 1.0, chloroform)]; ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{40}H_{64}N_2O_{18}$ (860.93): C, 55.80; H, 7.49; N, 3.25. Found: C, 55.45; H, 7.49; N, 3.25.

Hexadecan-1,16-diyl Bis-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside) (3h). Prepared according to the above procedure starting from compound **2h**. Yield: 81%; mp 175-176 °C (ethanol); R_f 0.73 (ethyl acetate/dichloromethane/ethanol 4:2:1, v/v/v); $[\alpha]_D$ - 11.6 (*c* 1.0, chloroform).; ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{44}H_{72}N_2O_{18}$ (917.03): C, 57.62; H, 7.91; N, 3.05. Found: C, 57.84; H, 7.79; N, 3.08.

General procedure for the preparation *N*-acetyl-β-D-glucosaminyl derivatives 4a-h: To a suspension of **3a-h** (2 mmol) in methanol was added a catalytic amount of sodium. After 10 min, the mixture became clear. After 20 min, crystals appeared. The suspension was stirred overnight, and the product (**4a-h**) was recovered by filtration, washed with methanol and dried *in vacuo*.

Hexan-1,6-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4a). Prepared as described above, starting from **3a**. Yield: 87%; mp 237-238 °C (methanol) [lit.[14] mp 198 °C (methanol/ethyl acetate)]; R_f 0.27 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 32.7 (*c* 1.0, water) [lit.[14] $[\alpha]_D$ - 35 (*c* 1.0, water)]; ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{22}H_{40}N_2O_{12}$ (524.55): C, 50.37; H, 7.69; N, 5.34. Found: C, 50.08; H, 7.56; N, 5.30.

Heptan-1,7-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4b). Prepared as described above, starting from **3b**. Yield: 93%; mp 237-238 °C (methanol); R_f 0.30 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 41.3 (*c* 0.8, dimethylsulfoxide); ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{23}H_{42}N_2O_{12}$, H_2O (556.60): C, 49.62; H, 7.97; N, 5.03. Found: C, 49.75; H, 7.78; N, 4.98.

Octan-1,8-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4c). Prepared as described above, starting from **3c**. Yield: 91%; mp 235-236 °C (methanol) [lit.[14] mp 190-192 °C (ethyl acetate)]; R_f 0.34 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 37.7 (*c* 0.8, dimethylsulfoxide) [lit.[14] $[\alpha]_D$ - 26 (*c* 1.0, water)]; ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{24}H_{44}N_2O_{12}$ (552.61): C, 52.16; H, 8.02; N, 5.07. Found: C, 51.98; H, 7.96; N, 4.97.

Nonan-1,9-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4d). Prepared as described above, starting from **3d**. Yield: 93%; mp 235-236°C (methanol); R_f 0.37 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 37.7 (*c* 0.8, dimethylsulfoxide); ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{25}H_{46}N_2O_{12}$, $2H_2O$ (602.66): C, 49.82; H, 8.36; N, 4.64. Found: C, 49.55; H, 8.22; N, 4.55.

Decan-1,10-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4e). Prepared as described above, starting from **3e**. Yield: 89%; mp 238-239°C (methanol) [lit.[20] mp 234-235°C]; R_f 0.41 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 36.9 (*c* 0.8, dimethylsulfoxide) [lit.[20] $[\alpha]_D$ - 30 (*c* 1.0, dimethylsulfoxide)]; ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{26}H_{48}N_2O_{12}$ (580.66): C, 53.78; H, 8.33; N, 4.82. Found: C, 53.68; H, 8.47; N, 4.79.

Undecan-1,11-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4f). Prepared as described above, starting from **3f**. Yield: 96%; mp 229-230 °C (methanol); R_f 0.45 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 35.9 (*c* 0.8, dimethylsulfoxide); ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{27}H_{50}N_2O_{12}$, H_2O (612.90): C, 52.92; H, 8.56; N, 4.57. Found: C, 52.88; H, 8.40; N, 4.51.

Dodecan-1,12-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4g). Prepared as described above, starting from **3g**. Yield: 91%; mp 228-229 °C (methanol) [lit.[14] mp 202 °C (methanol]; R_f 0.50 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 37.2 (*c* 0.8, dimethylsulfoxide) [lit.[14] $[\alpha]_D$ - 28 (*c* 1.0, dimethylsulfoxide)]; ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{28}H_{52}N_2O_{12}$, H_2O (626.93): C, 53.65; H, 8.68; N, 4.47. Found: C, 53.47; H, 8.58; N, 4.45.

Hexadecan-1,16-diyl Bis-(2-acetamido-2-deoxy-β-D-glucopyranoside) (4h). Prepared as described above, starting from **3h**. Yield: 89%; mp 229-230 °C (methanol); R_f 0.55 (ethyl acetate/methanol/water 7:3:1 v/v/v); $[\alpha]_D$ - 34.0 (*c* 0.8, dimethylsulfoxide); ^1H NMR, Tables 1 and 2.

Anal. Calcd for $C_{32}H_{60}N_2O_{12}$, H_2O (682.83): C, 56.29; H, 9.15; N, 4.10. Found: C, 56.60; H, 9.07; N, 4.10.

General procedure for the preparation of the *O*-acetylated 2-amino-β-D-glucosaminyl derivatives 5c,d,g: Tris(dibenzylideneacetone)dipalladium (16 mg, 17.5 μmol) was reacted with triphenylphosphine (50 mg, 0.19 mmol) in dry oxygen-free oxolane (3.5 mL) at room temperature for 10 min. Then, the yellow solution was added through a syringe to a solution of compound **2c**, **2d** or **2g** (2 mmol) and dimethylmalonate (1.60g, 14 mmol) in oxygen-free oxolane (15 mL). The mixture was stirred overnight, concentrated to 3 mL and the residue was applied at the top of a silica-gel column which was first eluted with ethyl acetate, to remove the triphenylphosphine by-products, and then with ethyl acetate/ethanol (6:1 v/v), to recover the expected amino-free derivative as

hygroscopic solids. In the case of **2d**, a more polar compound **6d** was isolated by further elution.

Octan-1,8-diyl Bis-(3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside) (5c). Prepared according to the above procedure starting from compound **2c**. Yield: 79%; mp 155-156 °C; R_f 0.55 (ethyl acetate/ethanol 5:1 v/v); $[\alpha]_D$ +3.1 (*c* 0.8, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{32}H_{52}N_2O_{16}$ (720.75): C, 53.32; H, 7.27; N, 3.89. Found: C, 53.45; H, 7.23; N, 3.86.

Nonan-1,9-diyl Bis-(3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside) (5d). Prepared according to the above procedure starting from compound **2d**. Yield: 77%; mp 137-138 °C; R_f 0.36 (ethyl acetate/ethanol 6:1 v/v); $[\alpha]_D$ 0 (*c* 0.8, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{33}H_{54}N_2O_{16}$, $2H_2O$ (770.81): C, 51.40; H, 7.52; N, 3.63. Found: C, 51.40; H, 7.22; N, 3.77.

1-(2-Acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyloxy)-non-9-yl 3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (6d). Recovered by further elution of the above mixture as a white solid. Yield 15%; mp 160-162 °C; R_f 0.20 (ethyl acetate/ethanol 6:1 v/v); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{33}H_{54}N_2O_{16}$, H_2O (752.79): C, 52.65; H, 7.50; N, 3.72. Found: C, 52.83; H, 7.33; N, 3.79.

Dodecan-1,12-diyl Bis-(3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside) (5g). Prepared according to the above procedure starting from compound **2g**. Yield: 76%; mp 136-137 °C; R_f 0.54 (ethyl acetate/ethanol 6:1 v/v); $[\alpha]_D$ -11.7 (*c* 0.8, chloroform); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{36}H_{60}N_2O_{16}$ (776.85): C, 55.66; H, 7.79; N, 3.61. Found: C, 55.25; H, 7.79; N, 3.70.

General procedure for the preparation of the fully deprotected β-D-glucosaminyl derivatives 7a, 7c, 7d, 7g and 7h:

Method A: Compounds **5c**, **5d** or **5g** (2-3 mmol) were de-*O*-acetylated overnight with a catalytic amount of sodium methylate in methanol (25 mL). After concentration, the residue was directly applied at the top of a silica-gel column (chloroform/ethanol/ammonium hydroxide 16:16:5 v/v/v) to afford the pure deprotected compounds **7c**, **7d** or **7h** as amorphous hygroscopic solids.

Method B: compounds **2a**, **2d**, **2g** or **2h** (2-3 mmol) were deacetylated overnight with a catalytic amount of sodium methylate in methanol (25 mL). After concentration, the residue was refluxed in 2.5 N sodium hydroxide (20-30 mL) for 5 hours. Then, the solution was cooled to room temperature and concentrated *in vacuo*. The residue was

directly applied at the top of a silica-gel column [(chloroform/ethanol/ammonium hydroxide 16:16:5 v/v/v) or (chloroform/ethanol/ammonium hydroxide 4:5:1 v/v/v for **7h**)] to afford the pure deprotected compounds **7c**, **7d** or **7h** as amorphous hygroscopic solids.

Hexan-1,6-diyl Bis-(2-amino-2-deoxy-β-D-glucopyranoside) (7a). Prepared according to method B, starting from compound **2a**. Yield: 71 %; R_f 0.28 (chloroform/ethanol/ammonium hydroxide 16:16:5 v/v/v); $[\alpha]_D$ - 41.7 (*c* 1.0, water); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{18}H_{36}N_2O_{10}$, $2H_2O$ (476.51): C, 45.36; H, 8.46; N, 5.88. Found: C, 44.82; H, 8.19; N, 5.39.

Octan-1,8-diyl Bis-(2-amino-2-deoxy-β-D-glucopyranoside) (7c). Prepared according to method A, starting from compound **5c**. Yield: 85 %; R_f 0.29 (chloroform/ethanol/ammonium hydroxide 16:16:5 v/v/v); $[\alpha]_D$ - 41.8 (*c* 1.0, water); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{20}H_{40}N_2O_{10}$, $1.5H_2O$ (495.56): C, 48.47; H, 8.74; N, 5.65. Found: C, 48.63; H, 8.95; N, 5.51.

Nonan-1,9-diyl Bis-(2-amino-2-deoxy-β-D-glucopyranoside) (7d). Prepared according to method A, starting from compound **5d** (Yield: 93 %) and according to method B starting from **2d** (yield 75%): R_f 0.30 (chloroform/ethanol /ammonium hydroxide 16:16:5 v/v/v); $[\alpha]_D$ - 45.7 (*c* 1.0, water); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{21}H_{42}N_2O_{10}$, $2H_2O$ (518.59): C, 48.63; H, 8.94; N, 5.40. Found: C, 48.17; H, 8.63; N, 5.23.

Dodecan-1,12-diyl Bis-(2-amino-2-deoxy-β-D-glucopyranoside) (7g). Prepared according to method A, starting from compound **5g** (Yield: 87 %) and according to method B, starting from **2g** (yield 71%): R_f 0.32 (chloroform/ethanol /ammonium hydroxide 16:16:5 v/v/v); $[\alpha]_D$ - 43.2 (*c* 0.8, dimethylsulfoxide); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{24}H_{48}N_2O_{10}$, $1.5H_2O$ (551.66): C, 52.25; H, 9.31; N, 5.08. Found: C, 52.32; H, 9.08; N, 5.06.

Hexadecan-1,16-diyl Bis-(2-amino-2-deoxy-β-D-glucopyranoside) (7h). Prepared according to method B starting from **2h** (yield 76%): R_f 0.32 (chloroform/ethanol/ammonium hydroxide 4:5:1 v/v/v); $[\alpha]_D$ - 33.7 (*c* 0.8, dimethylsulfoxide); ^1H and ^{13}C NMR, Tables 1-3.

Anal. Calcd for $C_{28}H_{56}N_2O_{10}$, $2H_2O$ (616,77): C, 54.52; H, 9.80; N, 4.54. Found: C, 54.76; H, 9.80; N, 4.45.

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