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# Spin-labelled glycolipid analogues: D-glucose series

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**Abstract**

Neoglycolipids bearing a paramagnetic probe in their lipophilic aglycon have been prepared. All belong to the D-glucose series, both anomers for the glucoside representatives, respectively $\beta$ and $\alpha$ anomers in the *S*- and *C*-glucosyl series. Two different types of radical sites have been used, a relatively short-lived imino *N*-oxyl group for glucosides and a more stable *N*-acylamino *N*-oxyl moiety in the other cases. EPR spectra of these radical species afforded information on the conformation of the lipophilic chain in the vicinity of the paramagnetic probe.

*Keywords:* EPR spectroscopy; Neoglycolipids; Spin labels; Glycosides

## 1. Introduction

Artificial glycolipids exhibit a large spectrum of useful properties: liquid crystals [1], specific detergents [2,3], immunomodulators [4], recognition markers for targeting drug delivery systems [5], or antiviral agents [6,7]. In most of these applications, the usefulness of neoglycolipids should be further increased by spin-labelling which would allow the monitoring of the interaction of these compounds with neighbouring molecules. We have described a number of close analogues of carbohydrate derivatives in which an oxygen atom is replaced with an NOH group. These compounds are spontaneously oxidized into the corresponding aminoxyl free radicals (for a review, see ref. [8]). These free radicals, the structurally closest possible paramagnetic analogues of natural sugars, have a half-life sufficient to allow good EPR spectra to be obtained but a little too short to afford comfortable monitoring of these compounds in biological media. For this reason, we also prepared sugar *N*-acylaminoxyls, markedly more stable than simple

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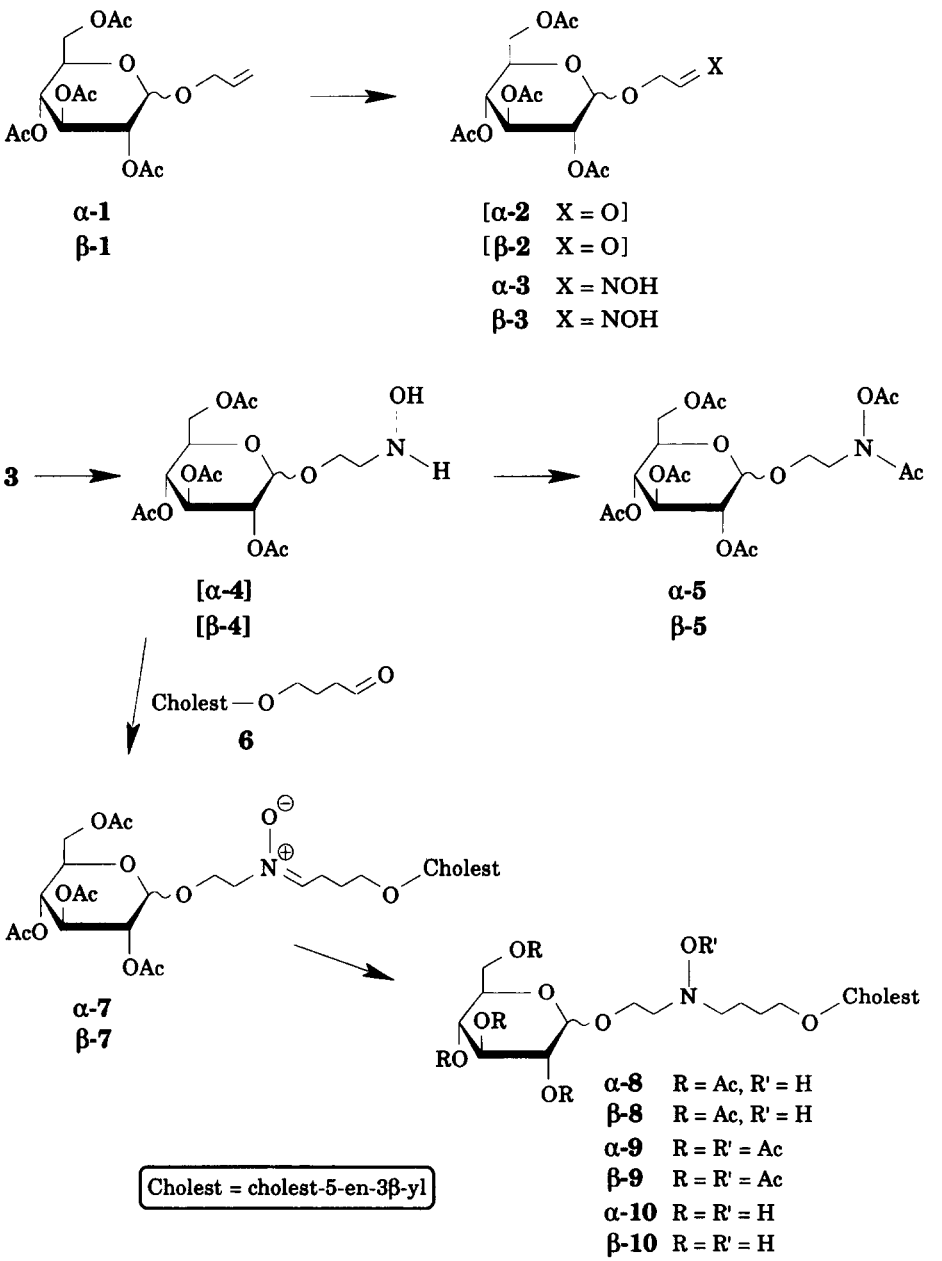
aminoxyls. We describe here *O*-, *S*-, and *C*-glucosyl compounds bearing a mono- or bi-antennary lipophilic chain, the monoantennary ones being spin-labelled. Part of this work has been reported at a Carbohydrate symposium [9].




Scheme 1.

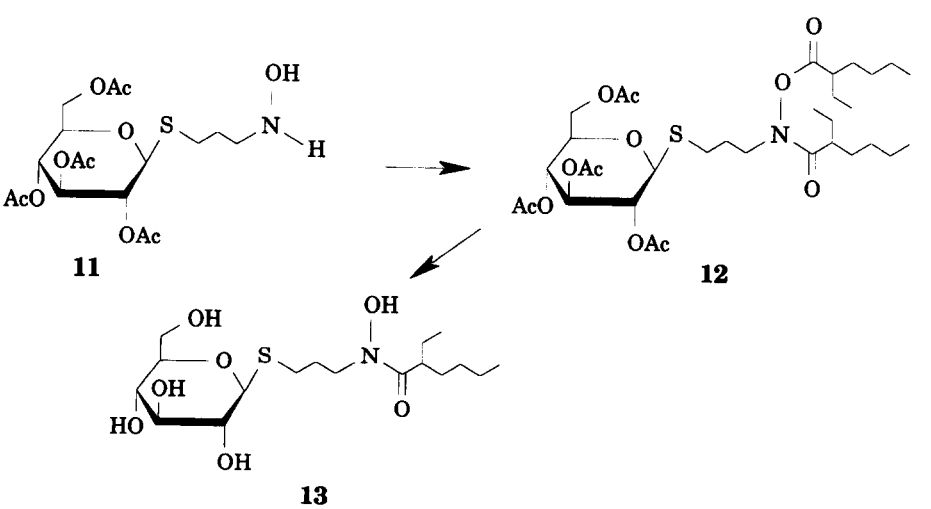
## 2. Results and discussion

Glycosidation of D-glucose with allyl alcohol in the presence of boron trifluoride etherate followed by peracetylation gave a resolvable 8:1 mixture (64%) of α-**1** [10] and β-**1** [10,11]. Each separated anomer was converted into the aldehyde **2**, which was not isolated in an analytically pure form but characterized by IR [$\nu_{C=O}$ 1757 (α-**2**), 1751 $cm^{-1}$ (β-**2**)] and $^1H$ NMR [HC=O at δ 9.73 (α-**2**) and 9.65 (β-**2**), respectively, as badly resolved triplets]. Oximes α-**3** and β-**3** were obtained in good yield as 4:5 and 11:7 *E:Z* mixtures respectively (Scheme 1).

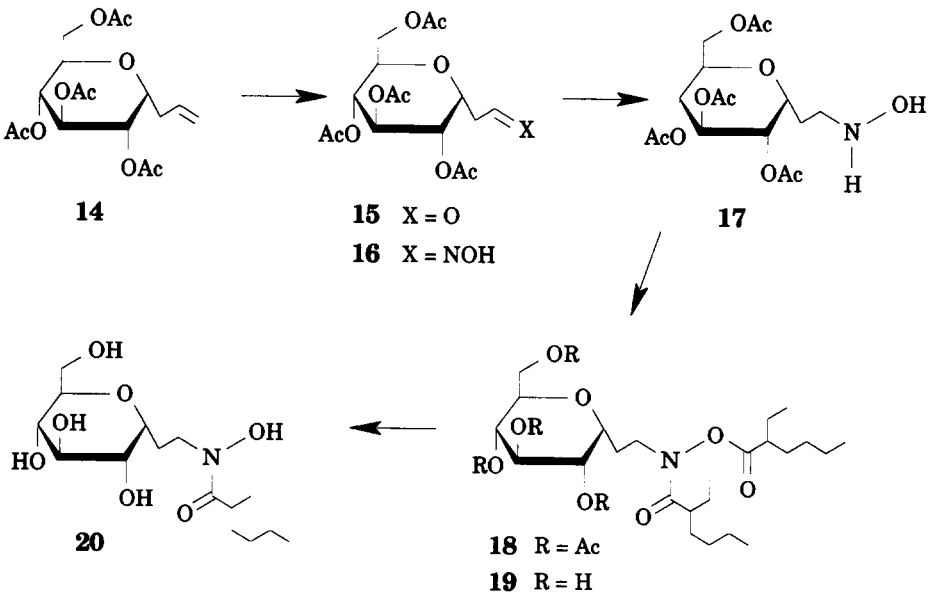
Upon sodium borohydride reduction in acidic medium [12,13], α-**3** and β-**3** afforded the corresponding hydroxylamines α-**4** and β-**4** in 63 and 69% yields, respectively. These compounds were converted in high yield into their *N,O*-diacetyl derivatives α-**5** and β-**5**, thus confirming the structures of the parent compounds, particularly that of β-**4** which was not obtained in a state of analytical purity.

The hydroxyamino group of compounds **4** was used as an anchor to fix a lipophilic chain onto the sugar moiety. Treated with the aldehyde **6** [14], each anomer of **4** yielded the expected nitrones α-**7** (68%) and β-**7** (64%) each as the *Z* diastereoisomer. These nitrones were characterized in particular by the appearance, in their NMR spectra, of a triplet (δ ca. 6.75, *J* 6 Hz) corresponding to the nitronic methine proton, thus establishing their *Z* configuration [15]. A high-yielding reduction (sodium borohydride) of α-**7** and β-**7** afforded α-**8** and β-**8**, which were almost quantitatively *O*-acetylated to α-**9** and β-**9** or *O*-deacetylated to α-**10** and β-**10**. The assignment of an α or β configuration to compounds **1**–**10** was straightforward. All these molecules adopted essentially the $^4C_1$ conformation, thus allowing an easy distinction between the β ($J_{1,2}$ 7–8 Hz) and the α anomers ($J_{1,2}$ 3.5–4 Hz).

Compounds such as **8** and **10**, in which a *N*-hydroxyimino group is included in an alkylidene chain, are spontaneously oxidized in the air to give the corresponding




Scheme 2.




Scheme 3.

aminoxyl, which is sufficiently long-lived to provide good EPR spectra, thus affording structural information concerning the isolated radical species in solution. Longer-lived radicals, necessary to study interactions between glycolipid analogues and macromolecules, were generated from hydroxamic acids. Such compounds have been prepared in the *S*- and *C*-glucosyl series.

The β-thioglucoside **11** [14], when treated with an excess of racemic 2-ethylhexanoyl chloride, underwent a di-*N,O*-acylation to the biantennary glycolipid analogue **12** in 77% yield (Scheme 2). Selective *O*-deacylation of **12** afforded **13** in 80% yield. Compounds **12** and **13** adopted an essentially pure $^4C_1$ conformation and their β configuration was confirmed by a large (9.5 Hz) $J_{1,2}$ coupling. The peracetylated *C*-glucosylpropene **14** [16] was oxidized (osmium tetraoxide then sodium periodate) in 75% yield to give crystalline **15**, which was converted into its crystalline *E*-oxime **16** (80%) (Scheme 3). Upon reduction, compound **16** gave the hydroxylamine **17** (67%), which was di-*O*-acylated to **18** (91%). *O*-Deacylation of **18** afforded a resolvable mixture of **19** (31%) and **20** (60%). The *C*-glucosyl compounds **15–20** also adopt principally a $^4C_1$ conformation and the $J_{1,2}$ couplings (4–5.5 Hz) of these α anomers are, as expected, a little larger than those of α-glucosides owing to the reduced electronegativity of their anomeric substituent. As a consequence of the presence of one or two (*RS*)-2-ethylhexanoyl groups on compounds **12**, **13**, and **18–20**, these molecules are diastereoisomeric mixtures. However, due to the distance between the sugar moiety and the chiral center on the acyl group and the flexibility of the chain linking these two parts of the molecule, no difference between such diastereoisomers was revealed, either by chromatography or by NMR spectroscopy.

Diglyme solutions of hydroxylamines α-**8** and β-**8** and of hydroxamic acids **13** and

Table 1
EPR data (diglyme, $a$ in G) of free radicals formed from selected sugar hydroxylamines and hydroxamic acids

| Compound | Temp (°C) | $g$ | $a_N$ | $a_H^\beta$ | | $a_H^\gamma$ | |
|---|---|---|---|---|---|---|---|
| **α-8** | 110 | 2.0059 | 14.6 | 10.2 | 9.8 | 0.5 | 0.5 |
| | | | | 10.2 | 9.8 | 0.5 | 0.5 |
| **β-8** | 110 | 2.0062 | 14.5 | 10.5 | 10.5 | 0.5 | 0.5 |
| | | | | 10.5 | 8.2 | 0.5 | 0.5 |
| **13** | 70 | 2.0056 | 7.43 | 6.37 | 6.37 | | |
| **20** | 70 | 2.0067 | 7.45 | 6.90 | 5.60 | | |

**20** were spontaneously oxidized to give the corresponding free radicals, EPR data of which are collected in Table 1. The spectra corresponding to **α-8** and **β-8** are very similar. The $a_N$ hyperfine coupling constants correspond to the value expected from this type of compound [17]. The values of $a_H^\beta$ of **α-8** speak in favour of a local symmetry of the $CH_2N(O^\cdot)CH_2$ group and one can assign to each methylene group a pair of different values (10.2 and 9.8 G). Their sum corresponds to a situation often encountered [8,18], in which a fast exchange takes place between conformers where one C–H bond lies in the plane of the aminoxyl group. The situation is approximatively the same for **β-8**. In both cases, the number of long-range hyperfine couplings ($a_H^\gamma$) confirm the existence of a $(CH_2)_2N(O^\cdot)(CH_2)_2$ moiety.

Owing to the spin delocalization over the carbonyl group, free radicals derived from **13** and **20** exhibit hyperfine couplings approximatively halved relative to those from **8**. Taking this fact into account, the EPR data are close to those expected from a conformational equilibrium between forms in which one C–H bond of the methylene group would reside in the amidoxyl plane [8].

The biological usefulness of these compounds is being investigated.

## 3. Experimental

*General.*—The 2-ethylhexanoyl chloride was prepared from the corresponding carboxylic acid by the thionyl chloride method [19]. Solutions were concentrated under diminished pressure at < 40°C. Melting points are uncorrected and were obtained with a Mettler FP52 melting-point microscope. TLC was performed on Silica Gel $HF_{254}$ (Merck) with detection by UV light or with phosphomolybdic acid–$H_2SO_4$ [20]. Column chromatography was conducted on Silica Gel 60 (0.063–0.2 mm, Merck). Silica Gel 60 (0.04–0.2 mm, Merck) was used for flash column chromatography [21]. IR spectra were recorded with a Perkin–Elmer FT-1600 or 1310 spectrometer and UV spectra with a Unicam SP 800 spectrophotometer. NMR spectra were recorded at 20°C for solutions in $CDCl_3$ (internal $Me_4Si$) with a Bruker WP 200 SY spectrometer ($^1H$, 200 MHz; $^{13}C$, 50.4 MHz; chemical shifts in ppm from $Me_4Si$, $\delta$ units). Optical rotations were measured on solutions in $CHCl_3$ with a Schmidt–Haensch polarimeter. Mass spectra (EIMS, 70 eV) were recorded on a VG-70-70E spectrometer. EPR spectra were recorded on a Varian E-9 spectrometer (X band, 100 kHz modulation) equipped

with a variable temperature device and a UV irradiation facility. The $g$ values were measured by using a DPPH sample and the magnetic field was calibrated with an NMR marker. All hyperfine coupling constants were checked by simulating the corresponding EPR spectra using a PC program developed in this laboratory [22].

*Allyl 2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranoside* (α-**1**).—To a suspension of D-glucose (2 g, 11 mmol) in anhydrous allyl alcohol (40 mL) was added $BF_3$ etherate (0.2 mL, 1.63 mmol), and the mixture was heated under reflux for 2 h. The clear solution was cooled, concentrated to a syrup, then, to remove some minor impurities, submitted to column chromatography (9:1 $CH_2Cl_2$–MeOH) which yielded 1.7 g (69.5%) of an 8:1 α/β syrupy mixture. This mixture was peracetylated with $Ac_2O$ (20 mL) in pyridine (50 mL). After the usual work-up, the anomers were separated by column chromatography (1:1 hexane–ether) to give α-**1** (2.5 g, 83%) and β-**1** (0.3 g, 10%). Compound α-**1** had mp 56–58°C; $R_f$ 0.13 (1:1 hexane–ether); $[\alpha]_D^{27}$ +136° ($c$ 1.9, $CHCl_3$); $\nu_{max}^{KBr}$ 2938 (CH), 1740 (C=O), and 1652 $cm^{-1}$ (C=C). $^1H$ NMR ($CDCl_3$): δ 5.89 (dddd, 1 H, $J_{2',3'a}$ 17.5, $J_{2',3'b}$ 10.5, $J_{2',1'a}$ 6, $J_{2',1'b}$ 5 Hz, H-2′), 5.52 (t, 1 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3), 5.32 (dq, 1 H, $J_{3'a,3'b}$ 1.5 Hz, H-3′a), 5.23 (dq, 1 H, H-3′b), 5.11 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.09 (t 1 H, $J_{4,5}$ 10 Hz, H-4), 4.90 (dd, 1 H, H-2), 4.28 (dd, 1 H, $J_{5,6b}$ 5 Hz, H-6b), 4.20 (ddt, 1 H, $J_{3'b,1'b}$ 1.5 Hz, H-1′b), 4.10 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 13 Hz, H-6a), 4.08 (m, 1 H, H-5), 4.02 (ddt, 1 H, $J_{1'a,1'b}$ 13, $J_{1'a,3'a}$ 1.5 Hz, H-1′a), 2.11, 2.07, 2.02, and 2.00 (4 s, each 3 H, 4 OAc). EIMS: $m/z$ (%) 388 (0.1, $M^{\cdot+}$), 347 (0.2, $M^{\cdot+} - CH_2{-}CH{=}CH_2$), 331 (1.5, $M^{\cdot+} - OAc$), 200 (17.8), 169 (28.3), 157 (58), 115 (70.4), 98 (68.4), 81 (100), 69 (52), 55 (18.7), and 45 (9.5). Anal. Calcd for $C_{17}H_{24}O_{10}$ (388.37): C, 52.58; H, 6.23. Found: C, 52.39; H, 6.12.

*Allyl 2,3,4,6-tetra*-O-*acetyl*-β-D-*glucopyranoside* (β-**1**).—Obtained as described for α-**1**; mp 89–90°C (from ether); lit. mp 88°C [11], 86°C [10]; $R_f$ 0.11 (1:1 hexane–ether); $[\alpha]_D^{25}$ −11.7° ($c$ 1.0, $CHCl_3$); $\nu_{max}^{KBr}$ 2950 (CH), 1754 (C=O), and 1650 $cm^{-1}$ (C=C). $^1H$ NMR ($CDCl_3$): δ 5.84 (dddd, 1 H, $J_{2',3'a}$ 17.5, $J_{2',1'b}$ 4.5, $J_{2',1'a}$ 6.5, $J_{2',3'b}$ 10.5 Hz, H-2′), 5.26 (dq, 1 H, $J_{3'a,3'b} = J_{3'a,1'a} = J_{3'a,1'b} = 1.5$ Hz, H-3′a), 5.20 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.18 (dq, 1 H, H-3′b), 5.06 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.00 (dd, 1 H, $J_{2,1}$ 8 Hz, H-2), 4.54 (d, 1 H, H-1), 4.32 (ddt, 1 H, $J_{1'a,1'b}$ 13.2 Hz, H-1′b), 4.26 (dd, 1 H, $J_{6b,5}$ 5, $J_{6a,6b}$ 11.7 Hz, H-6b), 4.11 (dd, 1 H, $J_{6a,5}$ 2.5 Hz, H-6a), 4.08 (ddt, 1 H, H-1′a), 3.66 (ddd, 1 H, H-5), 2.07, 2.02, 2.00, and 1.99 (4 s, each 3 H, 4 OAc). EIMS: $m/z$ (%) 347 (0.2, $M^{\cdot+} - CH_2{-}CH = CH_2$), 331 (0.9, $M^{\cdot+} - OAc$), 243 (8.6), 200 (15.3), 169 (17.2), 157 (38), 115 (55), 98 (62), 81 (100), 69 (51), 55 (13.6), and 45 (7.7). Anal. Calcd for $C_{17}H_{24}O_{10}$ (388.37): C, 52.58; H, 6.23. Found: C, 52.33; H, 6.38.

*2-Oxoethyl 1,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranoside* (α-**2**).—To a solution of α-**1** (1.2 g, 3.09 mmol) in a mixture of 1,4-dioxane (20 mL) and water (2 mL) was added $OsO_4$ (15 mg, 0.059 mmol); after 40 min stirring, saturated aq $NaIO_4$ (1.5 g, 7.01 mmol) was slowly added to the mixture, which was further stirred for 1.5 h, filtered, and concentrated to a syrup. Column chromatography (1:1 hexane–EtOAc) yielded α-**2** (0.82 g, 67.6%) as a somewhat unstable syrupy material which was not obtained in analytically pure form but used for the preparation of α-**3**; $R_f$ 0.13 (1:1 hexane–EtOAc); $\nu_{max}^{NaCl}$ 2963 (CH) and 1757 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): δ 9.73 (t, 1 H, H-2′), 5.53 (t, 1 H, H-3), 5.13 (d, 1 H, H-1), 5.10 (t, 1 H, H-4), 4.92 (dd, 1 H, H-2), 4.30 (d, 2 H, H-1′a,1′b), 4.35–4.05 (m, 3 H, H-6a,b + H-5), 2.12, 2.10, 2.06, and 2.05 (4 s, each 3 H,

4 OAc). EIMS: $m/z$ (%) 349 (0.9, $M^{\cdot+}-Ac$), 331 (7.9, $M^{\cdot+}-OAc$), 243 (4.7), 169 (76.5), 157 (50.7), 115 (100), 109 (83.7), 98 (66), 21 (76), 69 (62), and 57 (18).

*2-Oxoethyl 1,3,4,6-tetra*-O-*acetyl-β*-D-*glucopyranoside* (**β-2**).—Obtained as described under **α-2**, yield 63%; $R_f$ 0.14 (2:3 hexane–EtOAc) $\nu_{max}^{NaCl}$ 2960 (CH), and 1751 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): δ 9.65 (t, 1 H, H-2'), 5.20 (t, 1 H, H-2), 5.10 (dt, 1 H, H-4), 4.60 (d, 1 H, H-1), 4.35–4.02 (m, 4 H, H-1'a,1'b + H-6a,b), 3.20 (ddd, 1 H, H-5), 2.10, 2.02, 2.00 (each s, 4 × 3 H, 4 OAc). EIMS: $m/z$ (%) 389 (0.7, $M^{\cdot+}-1$), 331 (23, $M^{\cdot+}-OAc$), 243 (17), 200 (22), 169 (93), 145 (62), 115 (100), 81 (83), 69 (61), and 61 (17).

(E)- *and* (Z)-*2-(Hydroxyimino)ethyl 2,3,4,6-tetra*-O-*acetyl-α*-D-*glucopyranoside* (**α-3**).—To a solution of **α-2** (5.5 g, 14 mmol) in EtOH (50 mL) and pyridine (5 mL) was added hydroxylamine hydrochloride (2.1 g, 30 mmol). After 14 h stirring at 20°C the mixture was concentrated, diluted with $CH_2Cl_2$ (200 mL), washed (water), dried ($Na_2SO_4$), and submitted to column chromatography (2:3 hexane–EtOAc) to yield **α-3** (5.28 g, 92.5%) as a 4:5 $E/Z$ mixture, mp 138–139°C (from ether); $R_f$ 0.28 (1:1 hexane–EtOAc); $[\alpha]_D^{27}$ +128.1° (*c* 1.6, $CHCl_3$); $\nu_{max}^{KBr}$ 3470 (OH), 2979 (CH), 1745 (C=O), and 1705 $cm^{-1}$ (C=N). $^1H$ NMR ($CDCl_3$): δ 8.20 (bs, =N–OH *Z*), 8.05 (bs, =N–OH *E*), 7.50 (t, $J_{2',1'}$ 6 Hz, H-2' *E*), 6.95 (t, $J_{2',1'}$ 3.5 Hz, H-2' *Z*), 5.50 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.12 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.10 (t, 1 H, H-4), 4.90 (dd, 1 H, H-2), 4.12–3.98 (m, 5 H, H-1'a,1'b, H-6a,b, H-5), and 2.12–1.98 (each s, 4 × 3 H, 4 OAc). EIMS: $m/z$ (%) 345 (4), 331 (11, $M^{\cdot+}-OCH_2CH{=}N\sim OH$), 243 (15), 200 (23), 157 (100), 115 (87), 92 (78), 81 (57), 74 (32), and 58 (10). Anal. Calcd for $C_{16}H_{23}NO_{11}$ (405.36): C, 47.41; H, 5.72; N, 3.46. Found: C, 47.39; H, 5.60; N, 3.40.

(E)- *and* (Z)-*2-(Hydroxyimino)ethyl 2,3,4,6-tetra*-O-*acetyl-β*-D-*glucopyranoside* (**β-3**).—Applied to **β-2** the procedure described for the preparation of **α-3** yielded **β-3** (89%) as an 11:7 mixture of $E/Z$ isomers; $R_f$ 0.24 (2:3 hexane–EtOAc); mp 107–108°C (from ether); $[\alpha]_D^{19}$ −14.44° (*c* 1.4, $CHCl_3$); $\nu_{max}^{KBr}$ 3485 (N–OH), 2968 (CH), 1760 (C=O), and 1720 $cm^{-1}$ (C=N). $^1H$ NMR ($CDCl_3$): δ 7.75 (bs, =N ~ OH *Z*), 7.58 (bs, =N ~ OH*E*), 7.49 (t, $J_{2',1'}$ 5 Hz, H-2' *E*), 6.92 (t, $J_{2',1'}$ 3 Hz, H-2' *Z*), 5.30–5.00 (m, 3 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-2, H-3, H-4), 4.70–4.53 (m, ~ 2 H, H-1, H-1'a,1'b *Z*), 4.44–4.10 (m, ~ 3 H, H-1'a,1'b *E*, H-6a,b), 3.75 (m, 1 H, H-5), and 2.13–2.00 (each s, 4 × 3 H, 4 × OAc). EIMS: $m/z$ (%) 375 (0.5), 345 (5, $M^{\cdot+}$ – AcOH), 331 (7, $M^{\cdot+}-OCH_2{-}CH{=}N\sim OH$), 286 (4), 243 (13), 200 (22), 157 (68), 115 (90), 98 (100), 81 (93), and 73 (59). Anal. Calcd for $C_{16}H_{23}NO_{11}$ (405.36): C, 47.41; H, 5.72; N, 3.46. Found: C, 47.37, H, 5.65; N, 3.47.

*2-(Hydroxyamino)ethyl 2,3,4,6-tetra*-O-*acetyl-α*-D-*glucopyranoside* (**α-4**).—To a solution of **α-3** (1.0 g, 2.47 mmol) in MeOH (10 mL) was added $NaBH_4$ (1.7 g, 27 mmol), and the pH was kept at 2–3 by dropwise addition of 6 M methanolic HCl. After the pH had stabilized to 3 without further addition of acid, the mixture was stirred for another 2 h, then concentrated, and the residue dissolved in citrate/HCl Titrisol pH 3 buffer (20 mL). The aqueous phase was washed ($CH_2Cl_2$, 5 mL), brought to pH 8–8.5 (aq 10% NaOH saturated with NaCl), and extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phase was dried ($Na_2SO_4$) and subjected to column chromatography (19:1 $CH_2Cl_2$–MeOH) to give syrupy **α-4** (0.63 g, 63%); $R_f$ 0.20 (19:1 $CH_2Cl$–MeOH); $\nu_{max}^{NaCl}$ 3425 (NH), 3390 (OH), 2957 (CH), and 1747 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): δ

6.20–5.50 (bs, 2 H, NH, N-OH), 5.45 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.12 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.10 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.88 (dd, 1 H, H-2), 4.00–4.35 (m, 3 H, H-6a,b + H-5), 3.90 and 3.65 (2 m, each 1 H, H-1'a,1'b), 3.12 (t, 2 H, H-2'a,b), 2.10, 2.08, 2.05, and 2.02 (4 s, each 3 H, 4 OAc). EIMS: *m/z* (%) 408 (1.3, $M^{\cdot+}+1$), 390 (0.2, $M^{\cdot+}-OH$), 366 (0.8, $M^{\cdot+}-Ac$), 350 (0.25), 331 (1.8), 289 (1.1), 169 (62.6), 139 (11.3), 127 (32), 109 (100), 102 (67.5), and 60 (79.5), Anal. Calcd for $C_{16}H_{25}NO_{11}$ (407.38): C, 47.17; H, 6.19; N, 3.44. Found: C, 46.79; H, 6.28; N, 3.57.

*2-(Hydroxyamino)ethyl 2,3,4,6-tetra*-O-*acetyl-β-*D-*glucopyranoside* (*β*-**4**).—Treatment of *β*-**3** as described for the preparation of *α*-**4** yielded syrupy *β*-**4** (69%) which was not obtained in an analytically pure form but characterized as its diacetyl derivative *β*-**5**; $R_f$ 0.28 (19:1 $CH_2Cl_2$–MeOH); $\nu_{max}^{NaCl}$ 3470 (NH), 3280 (OH), and 1754 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): *δ* 5.30–4.90 (bs, 2 H, NH, N-OH), 5.22 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.08 (t, 1 H, H-4), 5.00 (dd, 1 H, $J_{2,1}$ 8 Hz, H-2), 4.55 (d, 1 H, H-1), 4.22 (m, 2 H, $J_{5,6b}$ 5, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 12 Hz, H-6a,b), 3.98 and 3.85 (2 m, each 1 H, H-1'a,1'b), 3.72 (ddd, 1 H, H-5), 3.08 (t, 2 H, H-2'a,b), 2.10, 2.08, 2.02, and 2.00 (4 s, each 3 H, 4-OAc). EIMS: *m/z* (%) 408 (0.06, $M^{\cdot+}+1$), 392 (10.17, $M^{\cdot+}-OH$), 331 (0.7), 229 (1.9), 187 (2), 169 (38), 157 (6.7), 109 (43), 86 (100), 72 (16), and 60 (14.5).

*2-(*N-*Acetoxyacetamido)ethyl 2,3,4,6-tetra*-O-*acetyl-α-*D-*glucopyranoside* (*α*-**5**).—A solution of *α*-**4** (0.2 g, 0.49 mmol) in a mixture of pyridine (5 mL) and $Ac_2O$ (1 mL) was kept 14 h at room temperature. After the usual work-up, the residue was subjected to column chromatography (3:2 hexane–acetone) to give *α*-**5** (0.19 g, 79%) as a syrup; $R_f$ 0.11 (3:2 hexane–acetone); $[\alpha]_D^{23}$ +45.2° (*c* 1.0, $CHCl_3$); $\nu_{max}^{NaCl}$ 2956 (CH), 1795, 1743 (C=O, acetyl), and 1680 $cm^{-1}$ (C=O, NAc). $^1H$ NMR ($CDCl_3$): *δ* 5.45 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.05 (m, 2 H, $J_{1,2}$ 3.5 Hz, H-1 + H-4), 4.35 (dd, 1 H, H-2), 4.18 (m, 2 H, $J_{5,6b}$ 5, $J_{5,6a}$ 3, $J_{6a,6b}$ 13 Hz, H-6a,b), 4.10–3.50 (m, 5 H, H-1'a,b + H-2'a,b + H-5), 2.25 (s, 3 H, NAc), 2.12, 2.10, 2.05, and 2.02 (each s, 5 × 3 H, 5 × OAc). EIMS: *m/z* (%) 491 (0.1, $M^{\cdot+}$), 432 (0.2, $M^{\cdot+}-OAc$), 331 (4), 169 (64), 144 (55), 127 (16.5), 102 (100), 81 (29), 73 (11.6), and 60 (18.9). Anal. Calcd for $C_{20}H_{29}NO_{13}$ (491.45): C, 48.88; H, 5.95; N, 2.85. Found: C, 48.65; H, 6.01; N, 2.95.

*2-(*N-*Acetoxyacetamido)ethyl 2,3,4,6-tetra*-O-*acetyl-β-*D-*glucopyranoside* (*β*-**5**).—Treated as described for the preparation of *α*-**5**, *β*-**4** gave *β*-**5** (82%) as a white crystalline powder, mp 110–111°C (from ether); $R_f$ 0.23 (3:2 hexane–acetone); $[\alpha]_D^{21}$ −12.36° (*c* 0.9, $CHCl_3$); $\nu_{max}^{KBr}$ 2880 (CH), 1789, 1759, 1744 (C=O, OAc), and 1688 $cm^{-1}$ (C=O, NAc). $^1H$ NMR ($CDCl_3$): *δ* 5.15 (t, 1 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3), 5.08 (t, 1 H, H-4), 5.00 (dd, 1 H, $J_{2,1}$ 7.5 Hz, H-2), 4.52 (d, 1 H, H-1), 4.18 (m, 2 H, H-6a,b), 4.05–3.60 (m, 5 H, H-1'a,b + H-2'a,b + H-5), 2.18 (s, 3 H, NAc), 2.10, 2.08, 2.05, 2.02, and 1.98 (5 s, each 3 H, 5 OAc). EIMS: *m/z* (%) 492 (1.1, $M^{\cdot+}+1$), 389 (0.3, $M^{\cdot+}-AcOH-CH_3CO$), 331 (10.7), 169 (65), 144 (83.5), 127 (14.7), 109 (65.9), 102 (100), 81 (23.5), and 60 (10.8). Anal. Calcd for $C_{20}H_{29}NO_{13}$ (491.45): C, 48.88; H, 5.95; N, 2.85. Found: C, 48.90; H, 5.85; N, 2.90.

*3-Aza-7-(cholest-5-en-3β-yloxy)hept-3-enyl 2,3,4,6-tetra*-O-*acetyl-α-*D-*glucopyranoside* N-*oxide* (*α*-**7**).—To a solution of *α*-**5** (0.6 g, 1.47 mmol) in $CH_2Cl_2$ (20 mL) was added **6** (0.8 g, 1.75 mmol), and the mixture was stirred 2 h at room temperature. The concentrated mixture was then subjected to column chromatography (19:1 ether–MeOH)

to give α-**7** (0.85 g, 68%); $R_f$ 0.13 (19:1 ether–MeOH); $[\alpha]_D^{20}$ +42.3° (*c* 1.0, $CHCl_3$); $\lambda_{max}^{EtOH}$ 202 (ε 5160) and 234 nm (8998); $\nu_{max}^{KBr}$ 2937 (CH), 2868 (CH), and 1758 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): δ 6.87 (t, 1 H, $J_{4',5'a,b}$ 6 Hz, H-4′), 5.39 (t, 1 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3), 5.32 (m, 1 H, =CH chol), 5.08 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.06 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.90 (dd, 1 H, H-2), 4.33–3.68 (ms, 7 H, H-6a,b, H-5, H-1′a,b, H-7′a,b), 3.50 (dt, 2 H, H-2′a,b), 3.13 (tt, 1 H, $J_{Chol2a,3} = J_{Chol4a,3} = 11$ Hz, $J_{Chol2b,3} = J_{Chol4b,3} = 4.5$ Hz, H-3 chol), 2.66–0.54 (m, chol skeleton), 2.57 (q, 2 H, H-5′a,b), 2.08, 2.06, 2.03, and 2.00 (4 s, each 3 H, 4 OAc). EIMS: *m/z* (%) 829 (1, $M^{\cdot+}$), 770 (2.5), 531 (4.5), 462 (20, $M^{\cdot+}$ – Ochol), 386 (40, Ochol), 368 (90), 353 (38), 247 (40), 213 (38), 169 (82), 145 (76), 115 (80), 95 (78), and 55 (72). Anal. Calcd for $C_{47}H_{75}NO_{12}$ (846.12): C, 66.72; H, 8.93; N, 1.66. Found: C, 66.44; H, 8.88; N, 1.66.

*3-Aza-7-(cholest-5-en-3β-yloxy)hept-3-enyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside* N*-oxide* (β-**7**).—Treatment of β-**5** and **6** as described for the preparation of α-**7** gave β-**7** (64%) as a white foam; $R_f$ 0.09 (19:1 ether–MeOH); $[\alpha]_D^{25}$ −26.1° (*c* 0.77, $CHCl_3$); $\lambda_{max}^{EtOH}$ 233 nm (ε 8472); $\nu_{max}^{KBr}$ 2936 (CH), 2867 (CH), and 1757 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): δ 6.75 (t, 1 H, $J_{4',5'a,b}$ 6 Hz, H-4′), 5.33 (m, 1 H, =CH chol), 5.20 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.12 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.98 (dd, 1 H, $J_{2,1}$ 7.5 Hz, H-2), 4.53 (d, 1 H, H-1), 4.35–3.80 (ms, 6 H, H-6a,b + H-1′a,b + H-7′a,b), 3.72 (m, 1 H, H-5), 3.50 (t, 2 H, H-2′a,b), 3.15 (tt, 1 H, H-3 chol), 2.70–0.60 (m, chol skeleton), 2.60 (m, 2 H, H-5′a,b), 2.10, 2.05, and 2.03 (each s, 4 × 3 H, 4 × OAc). EIMS: *m/z* (%) 846 (0.5, $M^{\cdot+}$), 829 (4, $M^{\cdot+}$ – $OH^{\cdot}$), 770 (10), 462 (100, $M^{\cdot+}$ – Ochol), 386 (28, Ochol), 368 (70), 247 (22), 169 (100), 109 (65), 72 (67), and 55 (43). Anal. Calcd for $C_{47}H_{75}NO_{12}$ (846.12): C, 66.72; H, 8.93; N, 1.66. Found: C, 66.50; H, 8.93; N, 1.80.

*3-Aza-7-(cholest-5-en-3β-yloxy)-3-hydroxyheptyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranoside* (α-**8**).—To a solution of α-**7** (0.7 g, 0.83 mmol) in MeOH (20 mL) was added $NaBH_3CN$ (0.2 g, 0.2 mmol), and the pH was kept at 3 as described for the preparation of α-**4**. After completion of the reaction (TLC), the mixture was neutralized (pH 7–8), concentrated, and extracted with $CH_2Cl_2$ (50 mL). The organic phase was washed (water, 10 mL), dried ($Na_2SO_4$), concentrated, and subjected to column chromatography (4:1 ether–petroleum ether) to give α-**8** (0.59 g, 84%) as a white foam; $R_f$ 0.16 (4:1 ether–petroleum ether); $[\alpha]_D^{21}$ +48.2° (*c* 0.9, $CHCl_3$); $\nu_{max}^{KBr}$ 3472 (OH), 2935 (CH), 2866 (CH), and 1753 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$); δ 5.50 (t, 2 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3 + N-OH), 5.33 (m, 1 H, =CH chol), 5.11 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.02 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.86 (dd, 1 H, H-2), 4.28 (m, 2 H, H-5 + H-6b), 4.10 (m, 1 H, H-6a), 3.90 (m, 1 H, H-1′b), 3.73 (m, 1 H, H-1′a), 3.48 (m, 2 H, H-7′a,b), 3.14 (tt, 1 H, H-3 chol), 2.85 (m, 2 H, H-2′a,b), 2.70 (m, 2 H, H-4′a,b), 2.45–0.60 (m, chol skeleton), 2.10, 2.08, 2.03, and 2.00 (4 s, each 3 H, 4 OAc). EIMS: *m/z* (%) 531 (0.1), 512 (0.4), 462 (12, $M^{\cdot+}$ – Ochol), 368 (100, Ochol), 247 (50), 145 (68), 81 (80), and 60 (68). Anal. Calcd for $C_{47}H_{77}NO_{12}$ (848.14): C, 66.56; H, 9.15; N, 1.65. Found: C, 66.48; H, 9.23; N, 1.74.

*3-Aza-7-(cholest-5-en-3β-yloxy)-3-hydroxyheptyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside* (β-**8**).—Treatment of β-**7** as described for the preparation of α-**8** gave β-**8** (76%) as a white foam; $R_f$ 0.11 (4:1 ether–petroleum ether); $[\alpha]_D^{27}$ −26° (*c* 0.67,

$CHCl_3$); $\nu_{max}^{KBr}$ 3490 (OH), 2956 (CH), 2869 (CH), and 1757 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 5.62 (bs, 1 H, NOH), 5.33 (m, 1 H, =CH chol), 5.20 (t, 1 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3), 5.12 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.05 (dd, 1 H, $J_{2,1}$ 7.5 Hz, H-2), 4.62 (d, 1 H, H-1), 4.20 (m, 2 H, H-6a,b), 3.97 (m, 1 H, H-1'a), 3.85 (m, 1 H, H-1'b), 3.73 (m, 1 H, H-5), 3.48 (m, 2 H, H-7'a,b), 3.13 (tt, 1 H, H-3 chol), 2.83 (m, 2 H, H-2'a,b), 2.65 (m, 2 H, H-4'a,b), 2.50–0.60 (m, chol skeleton), 2.10, 2.02, 2.00, and 1.98 (4 s, each 3 H, 4 OAc). EIMS: *m/z* (%) 831 (1.5, $M^{\cdot+}$ – OH), 772 (1.5), 713 (2), 512 (10), 462 (100, $M^{\cdot+}$ – Ochol), 368 (48, Ochol), 353 (20), 347 (30), 169 (92), 109 (80), 72 (100), and 55 (55). Anal. Calcd for $C_{47}H_{77}NO_{12}$ (848.14): C, 66.56; H, 9.15; N, 1.65. Found: C, 66.46; H, 9.17; N, 1.73.

*3-Acetoxy-3-aza-7-(cholest-5-en-3β-yloxy)heptyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranoside* (**α-9**).—A solution of **α-8** (0.2 g, 0.24 mmol) in pyridine (2 mL) and $Ac_2O$ (0.5 mL) was kept at 20°C for 16 h. Usual work-up followed by column chromatography (4:1 ether–petroleum ether) afforded **α-9** (0.2 g, 95%) as a white foam; $R_f$ 0.15 (4:1 ether–petroleum ether); $[\alpha]_D^{23}$ +45.2° (*c* 1.5, $CHCl_3$); $\nu_{max}^{KBr}$ 2935 (CH), 2902 (CH), and 1754 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 5.48 (t, 1 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3), 5.35 (m, 1 H, =CH chol), 5.10 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.05 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.85 (dd, 1 H, H-2), 4.30 (m, 1 H, $J_{5,6b}$ 4, $J_{6a,6b}$ 12.5 Hz H-6b), 4.15–4.00 (m, 2 H, $J_{5,6a}$ 2 Hz, H-6a, H-5), 3.85 (m, 1 H, H-1'b), 3.65 (m, 1 H, H-1'a), 3.48 (m, 2 H, H-7'a,b), 3.12 (m, 2 H, H-2'a,b), 2.90 (m, 2 H, H-4'a,b), 2.50–0.60 (m, chol skeleton), 2.12, 2.10, 2.08, 2.03, and 2.01 (5 s each 3 H, 5 OAc). EIMS: *m/z* (%) 674 (1), 448 (2), 404 (10), 389 (12), 322 (100), 309 (32), 216 (43), 148 (35), 127 (55), 83 (80), 74 (98), and 60 (50). Anal. Calcd for $C_{49}H_{79}NO_{13}$ (890.17): C, 66.12; H, 8.95; N, 1.57. Found: C, 66.02; H, 8.90; N, 1.74.

*3-Acetoxy-3-aza-7-(cholest-5-en-3β-yloxy)heptyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside* (**β-9**).—Obtained from **β-8**, as described for the preparation of **α-9**, in 91% yield as a white foam; $R_f$ 0.12 (4:1 ether–petroleum ether); $[\alpha]_D^{20}$ −21.4° (*c* 1.1, $CHCl_3$); $\nu_{max}^{KBr}$ 2934 (CH) and 1756 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 5.35 (m, 1 H, =CH chol), 5.20 (t, 1 H, $J_{3,2} = J_{3,4} = 10$ Hz, H-3), 5.12 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.00 (dd, 1 H, $J_{2,1}$ 7 Hz, H-2), 4.63 (d, 1 H, H-1), 4.28 (m, 1 H, H-6b), 4.12 (m, 1 H, H-6a), 3.92 (m, 1 H, H-1'b), 3.72 (m, 2 H, H-1'a + H-5), 3.45 (m, 2 H, H-7'a,b), 3.10 (m, 3 H, H-3 chol + H-2'a,b), 2.85 (m, 2 H, H-4'a,b), 2.50–0.60 (m, chol skeleton), 2.10, 2.08, 2.06, 2.02, and 2.00 (5 s, each 3 H, 5 OAc). EIMS: *m/z* (%) 531 (1), 441 (3), 386 (33, Ochol), 368 (18), 301 (20), 275 (22), 157 (80), 140 (25), 98 (95), 86 (95), and 60 (100). Anal. Calcd for $C_{49}H_{79}NO_{13}$ (890.17): C, 66.12; H, 8.95; N, 1.57. Found: C, 66.38; H, 8.66; N, 1.57.

*3-Aza-7-(cholest-5-en-3β-yloxy)-3-hydroxyheptyl α-*D*-glucopyranoside* (**α-10**).—A solution of **α-8** (0.33 g, 0.39 mmol) in 0.02 M methanolic NaOMe was kept at 20°C for 14 h, neutralized (0.1 M aq AcOH), concentrated, then subjected to flash column chromatography (15:2:3 $CHCl_3$–acetone–MeOH) to give **α-10** (0.24 g, 90.3%) as a white foam; $R_f$ 0.20 (15:2:3 $CHCl_3$–acetone–MeOH); $[\alpha]_D^{24}$ +12.4° (*c* 0.74, $CHCl_3$); $\nu_{max}^{KBr}$ 3355 (OH), 2935 (CH), and 2848 $cm^{-1}$ (CH). $^1H$ NMR (pyridine-$d_5$, 60°C): $\delta$ 7.80 (s, 1 H, N-OH), 5.40 (m, 1 H, =CH chol), 5.25 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.65–4.40 (m, 3 H, H-2,3,4), 4.30 (m, 2 H, H-1'a,b), 4.20–3.90 (m, 3 H, H-5 + H-6a,b), 3.45 (t, 2 H, H-7'a,b), 3.20 (m, 1 H, CH chol), 3.10 (t, 2 H, H-2'a,b), 2.83 (t, 2 H,

H-4′a,b), and 2.50–0.50 (m, cholesterol + 2 $CH_2$). EIMS: *m/z* (%) 633 (0.5), 470 (17), 386 (32, Ochol), 308 (100), 353 (28), 294 (43, $M^{\cdot+}$ − Ochol), 247 (32), 145 (70), 95 (85), 81 (90), 73 (98), and 55 (100). Anal. Calcd for $C_{39}H_{69}NO_8$ (679.99): C, 68.89; H, 10.23; N, 2.06. Found: C, 68.60; H, 10.31; N, 2.15.

*3-Aza-7-(cholest-5-en-3β-yloxy)-3-hydroxyheptyl β-*D*-glucopyranoside* (*β*-**10**).—Obtained from *β*-**8**, as described for the preparation of *α*-**10**, in 88% yield as a white foam; $R_f$ 0.22 (15:2:3 $CHCl_3$–acetone–MeOH); $[\alpha]_D^{20}$ −24.3° (*c* 1.2, $CHCl_3$); $\nu_{max}^{KBr}$ 3355 (OH), 2945 (CH), and 2836 $cm^{-1}$ (CH). $^1H$ NMR (pyridine-$d_5$): *δ* 7.80 (bs, 1 H, N-OH), 5.38 (m, 1 H, =CH chol), 4.75 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.60–3.95 (m, 7 H, $J_{5,6b}$ 2.5, $J_{6a,6b}$ 12, $J_{5,6a}$ 5.5 Hz, H-6a,b + H-1′a,b + H-2,3,4), 3.87 (m, 1 H, $J_{4,5}$ 9 Hz, H-5), 3.48 (t, 2 H, H-7′a,b), 3.15 (m, 3 H, H-2′a,b + CH chol), 2.83 (t, 2 H, H-4′a,b), 2.60–0.60 (m, cholesterol + 2 $CH_2$). EIMS: *m/z* (%) 663 (0.5, $M^{\cdot+}$ − OH), 648 (10.6), 470 (5), 386 (20, Ochol), 368 (100), 353 (20), 294 (12, $M^{\cdot+}$ − Ochol), 213 (20), 159 (32), 145 (42), and 90 (72). Anal. Calcd for $C_{39}H_{69}NO_8$ (679.99): C, 68.89; H, 10.23; N, 2.06. Found: C, 68.68; H, 10.24; N, 2.12.

*4-Aza-6-ethyl-4-(2-ethylhexanoyloxy)-5-oxodecyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucopyranoside* (**12**).—To a solution of **11** (1.15 g, 2.63 mmol) in a mixture of $CHCl_3$ (50 mL) and pyridine (5 mL) was added dropwise 2-ethylhexanoyl chloride (1.7 mL, 10.5 mmol). After 2 h at 20°C, water (2 mL) was added and the concentrated mixture subjected to column chromatography (4:1 → 3:2 hexane–EtOAc) to give **12** (1.4 g, 77%) as a syrup; $R_f$ 0.37 (3:2 hexane–EtOAc); $[\alpha]_D^{20}$ −25.2° (*c* 1.2, $CHCl_3$); $\lambda_{max}^{EtOH}$ 205 nm (*ε* 5894); $\nu_{max}^{NaCl}$ 2961 (CH), 1780 (C=O), 1757 (C=O), and 1670 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): *δ* 5.10 (t, 1 H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.07 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.00 (t, 1 H, $J_{2,1}$ 9.5 Hz, H-2), 4.50 (d, 1 H, H-1), 4.23 (m, 1 H, $J_{5,6b}$ 5, $J_{6a,6b}$ 12.5 Hz, H-6b), 4.10 (m, 1 H, $J_{5,6a}$ 3 Hz, H-6a), 3.90–3.60 (m, 3 H, H-5 + 2 CH), 2.90–1.10 (m, alkyl chains), 2.10, 2.08, 2.02, and 1.98 (4 s, each 3 H, 4 OAc), and 1.10–0.70 (4 t, each 3 H, 4 Me). EIMS: *m/z* (%) 629 (0.6, $M^{\cdot+}$ − AcOH), 531 (1), 509 (0.6), 331 (20), 215 (12), 169 (38), 127 [22, $COCHEt(CH_2)_3Me$], 109 (18), 99 (28), 88 (67), and 57 (100). Anal. Calcd for $C_{33}H_{55}NO_{12}S$ (689.87): C, 57.40; H, 8.04; N, 2.03; S, 4.65. Found: C, 57.60; H, 8.11; N, 2.06; S, 4.87.

*4-Aza-6-ethyl-4-hydroxy-5-oxodecyl 1-thio-β-*D*-glucopyranoside* (**13**).—A solution of **12** (0.5 g, 0.72 mmol) in 0.02 M methanolic NaOMe (50 mL) was kept 16 h at 24°C, then neutralized (0.1 M aq AcOH). The mixture was concentrated and subjected to column chromatography (9:1 EtOAc–MeOH) to give **13** (0.23 g, 80%); mp 59.1–59.8°C; $R_f$ 0.14 (9:1 EtOAc–MeOH); $[\alpha]_D^{23}$ −36° (*c* 1.0, $CHCl_3$); $\lambda_{max}^{EtOH}$ 204 nm (*ε* 281); $\nu_{max}^{KBr}$ 3374 (OH), 2930 (CH), and 1606 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): *δ* 9.55 (bs, 1 H, N-OH), 5.10 (d, 1 H, OH), 5.00 (d, 1 H, OH), 4.92 (d, 1 H, OH), 4.47 (t, 1 H, $J_{6a,b,OH}$ 6 Hz, $CH_2OH$), 4.12 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 3.70–1.00 (m, 19 H, H-2,3,4,5,6a,b, CH, and 6 $CH_2$), and 1.00–0.70 (2 t, each 3 H, 2 Me). EIMS: *m/z* (%) 396 (0.2, $M^{\cdot+}$ + 1), 359 (0.9), 312 (0.4), 275 (0.2), 233 (0.8), 145 (5), 127 [17, $COCHEt(CH_2)_3Me$], 99 (11), 88 (36), 73 (58), and 57 (100). Anal. Calcd for $C_{17}H_{33}NO_7S \cdot 0.5\ H_2O$ (404.52): C, 50.47; H, 8.47; N, 3.46; S, 7.93. Found: C, 50.53; H, 8.35; N, 3.50; S, 7.87.

*2-(2,3,4,6-Tetra-*O*-acetyl-α-*D*-glucopyranosyl)ethanal* (**15**).—Compound **14** (1 g, 2.7 mmol) was treated with $OsO_4$ and $NaIO_4$ as described for the preparation of *α*-**2**. Column chromatography (7:3 hexane–acetone) yielded **15** (0.75 g, 75%) as white

crystals; mp 71.5–72.5°C; $R_f$ 0.14 (7:3 hexane–acetone); $\nu_{max}^{KBr}$ 2952 (CH), 2825 (CH), 2727 (CH), and 1742 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 9.72 (t, 1 H, $J_{2',1'a,b}$ 2 Hz, H-2'), 5.26 (t, 1 H, $J_{3,2} = J_{3,4} = 8$ Hz, H-3), 5.15 (dd, 1 H, $J_{2,1}$ 5.5 Hz, H-2), 5.00 (t, 1 H, $J_{4,5}$ 8 Hz, H-4), 4.88 (dt, 1 H, $J_{1,1'a,b}$ 7.5 Hz, H-1), 4.25 (m, 1 H, $J_{5,6b}$ 5.5, $J_{6a,6b}$ 12.5 Hz, H-6b), 4.07 (m, 1 H, $J_{5,6a}$ 3 Hz, H-6a), 3.88 (m, 1 H, H-5), 2.80 (m, 2 H, H-1'a,b), and 2.25–2.90 (4 s, each 3 H, 4 OAc). EIMS: *m/z* (%) 331 (0.4, $M^{\cdot+} - Ac$), 315 (1, $M^{\cdot+} - OAc$), 301 (1), 212 (22), 169 (52), 139 (100), 115 (21), 97 (40), and 69 (13). Anal. Calcd for $C_{16}H_{22}O_{10}$ (374.35): C, 51.34; H, 5.92. Found: C, 50.77; H, 5.90.

(E)- *and* (Z)-*1-(Hydroxyimino)-2-(2,3,4,6-tetra*-O-*acetyl-α*-D-*glucopyranosyl)ethane* (**16**).—Compound **15** (1.4 g, 3.74 mmol) treated as described for the preparation of *α*-**3** yielded, after column chromatography (7:3 hexane–acetone), **16** (1.2 g, 82%) as white crystals; mp 149–149.5°C; $R_f$ 0.11 (7:3 hexane–acetone); $[\alpha]_D^{22}$ +63° (*c* 1.8, $CHCl_3$); $\nu_{max}^{KBr}$ 3250 (OH), 3045 (CH), 2950 (CH), and 1743 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 7.78 (bs, 1 H, N-OH), 6.78 (dd, 1 H, $J_{2',1'a}$ 4.5, $J_{2',1'b}$ 6 Hz, H-2'), 5.35 (t, 1 H, $J_{3,4} = J_{3,2} = 9$ Hz, H-3), 5.12 (dd, 1 H, $J_{2,1}$ 5.5 Hz, H-2), 5.00 (t, 1 H, $J_{4,5}$ 9 Hz, H-4), 4.46 (dt, 1 H, $J_{1,1'a,b}$ 6.5 Hz, H-1), 4.25 (m, 1 H, $J_{5,6b}$ 5, $J_{6a,6b}$ 13 Hz, H-6b), 4.10 (m, 1 H, $J_{5,6a}$ 3 Hz, H-6a), 3.93 (m, 1 H, H-4), 3.10 (ddd, 1 H, $J_{1'a,1'b}$ 16 Hz, H-1'b), 2.50 (dt, 1 H, H-1'a), and 2.12–1.98 (4 s, each 3 H, 4 OAc). EIMS: *m/z* (%) 390 (2, $M^{\cdot+} + 1$), 331 (1.5, $M^{\cdot+} - OAc$), 312 (0.5), 270 (2), 227 (2), 211 (4), 169 (74), 154 (29), 127 (32), 109 (100), 97 (38), 81 (41), 70 (39), 61 (20), and 55 (19). Anal. Calcd for $C_{46}H_{23}NO_{10}$ (389.36): C, 49.36; H, 5.95; N, 3.60. Found: C, 48.96; H, 5.79; N, 3.71.

N-*Hydroxy-2-(2,3,4,6-tetra*-O-*acetyl-α*-D-*glucopyranosyl)ethylamine* (**17**).—Compound **16** (1 g, 2.57 mmol) was treated with $NaBH_4$ as described for the preparation of *α*-**4**, to yield **17** (0.67 g, 67%) as white crystals; mp 116.5–118.0°C; $R_f$ 0.39 (19:1 $CHCl_3$–MeOH); $[\alpha]_D^{25}$ +63.6° (*c* 0.9, $CHCl_3$); $\nu_{max}^{KBr}$ 3477 (NH), 3230 (OH), 2938 (CH), 1739 (C=O), and 1720 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 6.30–5.70 (bs, 2 H, NHOH), 5.31 (t, 1 H, $J_{3,2} = J_{3,4} = 9$ Hz, H-3), 5.07 (dd, 1 H, $J_{2,1}$ 4 Hz, H-2), 4.97 (t, 1 H, $J_{4,5}$ 9 Hz, H-4), 4.30 (m, 1 H, H-1), 4.25 (m, 1 H, $J_{5,6b}$ 5.5, $J_{6a,6b}$ 12 Hz, H-6b), 4.10 (m, 1 H, $J_{5,6a}$ 3 Hz, H-6a), 3.95 (m, 1 H, H-5), 3.05 (t, 2 H, H-2'a,b), 2.40–1.90 (4 s, each 3 H, 4 OAc), ~ 2.20 (m, 1 H, H-1'b), and 1.70 (m, 1 H, H-1'a). EIMS: *m/z* (%) 392 (4.6, $M^{\cdot+} + 1$), 350 (0.6), 331 (0.9), 289 (1), 272 (1.2), 212 (4.6), 169 (24), 137 (33), 124 (78), 97 (26), 81 (40), and 46 (100). Anal. Calcd for $C_{16}H_{25}NO_{10}$ (391.38): C, 49.10; H, 6.44; N, 3.58. Found: C, 49.10; H, 6.45; N, 3.66.

*2-Ethyl*-N-*(2-ethylhexanoyloxy)*-N-*[2-(2,3,4,6-tetra*-O-*acetyl-α*-D-*glucopyranosyl)ethyl]hexanamide* (**18**).—To a solution of **17** (0.3 g, 0.77 mmol) in a mixture of $CH_2Cl_2$ (20 mL) and pyridine (1 mL) was added dropwise 2-ethylhexanoyl chloride (0.28 mL, 1.72 mmol). After 2 h at 20°C, water (2 mL) was added and the concentrated mixture subjected to column chromatography (7:3 hexane–EtOAc) to give **18** (0.57 g, 91%) as a syrup; $R_f$ 0.22 (7:3 hexane–EtOAc); $[\alpha]_D^{20}$ +47° (*c* 0.9, $CHCl_3$); $\nu_{max}^{NaCl}$ 2961 (CH), 2874 (CH), 1781 (C=O), 1752 (C=O), and 1670 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$): $\delta$ 5.30 (t, 1 H, $J_{2,3} = J_{3,4} = 9$ Hz, H-3), 5.10 (dd, 1 H, $J_{2,1}$ 5.5 Hz, H-2), 4.98 (t, 1 H, $J_{4,5}$ 9 Hz, H-4), 4.23 (m, 2 H, $J_{5,6b}$ 5, $J_{6a,6b}$ 12.5 Hz, H-6b + H-1), 4.10 (m, 1 H, $J_{5,6a}$ 3 Hz, H-6a), 3.90 (m, 2 H, H-5 + H-2'b), 3.60 (m, 1 H, H-2'a), 2.40 (m, 2 H, 2 CH), 2.20–1.10 (m, alkyl chain), 2.12, 2.10, 2.08, and 1.98 (4 s, each 3 H, 4 OAc), and 1.10–0.75 (4 t, each 3 H, 4 Me). EIMS: *m/z* (%) 644 (0.5, $M^{\cdot+}$), 531 (0.4),

442 (10), 397 (2), 264 (10), 127 [60, $COCHEt(CH_2)_3Me$], 99 (48), and 57 (100). Anal. Calcd for $C_{32}H_{53}NO_{12}$ (643.78): C, 59.70; H, 8.30; N, 2.18. Found: C, 59.53; H, 8.28; N, 2.22.

*2-Ethyl*-N-*(2-ethylhexanoyloxy)*-N-*[2-(α-D-glucopyranosyl)ethyl]hexanamide* (**19**). —A solution of **18** (0.5 g, 0.78 mmol) in 0.02 M methanolic NaOMe (50 mL) was kept 4 h at 20°C, then neutralized (0.1 M aq AcOH). The mixture was concentrated and subjected to column chromatography (15:2:3 $CHCl_3$–acetone–MeOH) to give **19** (0.12 g, 31%) and **20** (0.17 g, 60%) as syrups; $R_f$ 0.55 (15:2:3 $CHCl_3$–acetone–MeOH); $[\alpha]_D^{22}$ +41.3° (*c* 0.6, $CHCl_3$); $\nu_{max}^{KBr}$ 3390 (OH), 2960 (CH), 1765 (C=O), and 1644 $cm^{-1}$ (C=O). $^1H$ NMR ($CDCl_3$, 55°C): δ 4.08 (dt, 1 H, $J_{1,2}$ 5, $J_{1,1'a,b}$ 9.5 Hz, H-1), 3.90–3.60 (m, 10 H, H-2,3,4,5,6a,b + 4 OH), 2.40 (m, 2 H, 2 CH), 2.15–1.10 (m, alkyl chain), and 1.10–0.75 (4 t, each 3 H, 4 Me). EIMS: *m/z* (%) 476 (1, $M^{\cdot+}$), 458 (2, $M^{\cdot+} - OH$), 440 (1.2), 423 (1.5), 404 (1.8), 349 [1.5, $M^{\cdot+} - COCH(Et)(CH_2)_3Me$], 331 (1.8), 127 [23, $COCH(Et)(CH_2)_3Me$], 99 [32, $Me(CH_2)_3CHEt$], and 57 [100, $Me(CH_2)_3$]. Anal. Calcd for $C_{24}H_{45}NO_8 \cdot 0.5\ H_2O$ (484.63): C, 59.48; H, 9.56; N, 2.89. Found: C, 59.76; H, 9.63; N, 2.92.

*2-Ethyl*-N-*[2-(α-D-glucopyranosyl)ethyl]*-N-*hydroxyhexanamide* (**20**).—Obtained as described for the preparation of **19**; $R_f$ 0.33 (15:2:3 $CHCl_3$–acetone–MeOH); $[\alpha]_D^{21}$ +120° (*c* 0.4, $CHCl_3$); $\nu_{max}^{KBr}$ 3353 (OH), 2960 (CH), 2867 (CH), and 1605 $cm^{-1}$ (C=O).$^1H$ NMR ($CD_3COCD_3$): δ 8.80 (bs, 1 H, N-OH), 4.40–4.10 (m, 3 H, 3 × OH), 3.95 (dt, 1 H, H-1), 3.85–3.10 (m, 7 H, H-2,3,4,5,6a,6b,$CH_2OH$), 3.02 (m, 1 H, CH), 1.98 (m, 2 H, H-2'a,b), 1.70–1.10 (m, alkyl chain), and 1.00–0.80 (2 t, each 3 H, 2 Me). EIMS: *m/z* (%) 348 (0.5, $M^{\cdot+} - 1$), 331 (1, $M^{\cdot+} - H_2O$), 296 (2.5), 277 (5), 262 (2), 144 (10), 127 [15, $COCH(Et)(CH_2)_3Me$], 99 [22, $CH(Et)(CH_2)_3Me$], 88 (12), and 57 [100, $Me(CH_2)_3$]. Anal. Calcd for $C_{16}H_{31}NO_7 \cdot 0.5\ H_2O$ (358.43): C, 53.61; H, 9.00; N, 3.91. Found: C, 53.81; H, 8.94; N, 3.94.

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