Glycoconjugated Porphyrins. 2. Synthesis of Sterically Constrained Polyglycosylated Compounds Derived from Tetraphenylporphyrins

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Received November 16, 1992

A variety of glycoconjugated porphyrins has been synthesized by Lindsey's method from pyrrole and *o*-acetylglycosylated benzaldehyde precursors. Deprotection of glucose and maltose moieties allows the production of derivatives which had a good solubility in neutral aqueous solution and covered a range of amphiphilic character. The structure in solution of these new compounds was studied by ^{1}H NMR analysis. A study of the complexation characteristics of their zinc derivatives shows low values of affinity constants which are dependent on the steric hindrance of both faces of the porphyrin macrocycle. The present strategy should prove applicable to the synthesis of other glycoconjugated tetrapyrrolic compounds.

Introduction

A great variety of superstructured metalloporphyrins have been designed in order to know how the immediate environment of the macrocycle controls oxygen affinity or activation in hemoproteins,[1] electron-transfer function,[2] or molecular recognition.[3] In these modeling systems, the superstructures, which differ by their chemical nature, are linked at the ortho positions of the phenyl rings of a tetraphenylporphyrin by means of secondary amide or ether linkages. However, the limit of these compounds as metalloenzyme models was their insolubility in aqueous media. Thus, it was of great interest to synthesize new water-soluble molecules. Some groups have recently described tetrapyrrolic complexes with such properties in order to obtain efficient catalysis in water[4] as well as compounds able to go through the membrane of cells or interact with it and destroy the cells after light irradiation.[5] That has been achieved by introducing cationic, anionic, or amphoteric substituents on the tetrapyrrolic macrocycle itself or on the superstructures.

In a preliminary paper, we have recently reported[6] the synthesis of a new class of pure neutral water-soluble tetrapyrrolic macrocycles bearing sugar groups which induce some attractive properties. Other tetrapyrrolic macrocycles having such a functionality have been described in the literature.[7] More recently, one natural tolyporphyrin containing C-glycosyl substituents has been isolated from the blue-green alga "tolypothrix nodosa".[8]

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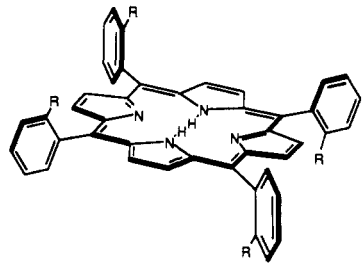
Chart I



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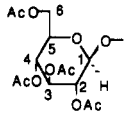

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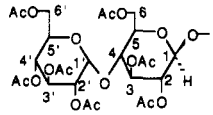

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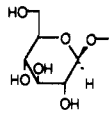

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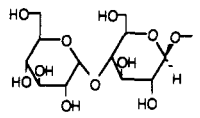

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In our case these properties can been achieved by fixation of glycosylated substituents on ortho positions of the phenyl groups of *meso*-tetraarylporphyrins (Chart I). Furthermore, such substituents in ortho positions induce strong steric hindrance on both faces of the porphyrin macrocycle against unwanted secondary reactions with their metallic derivatives.[9]

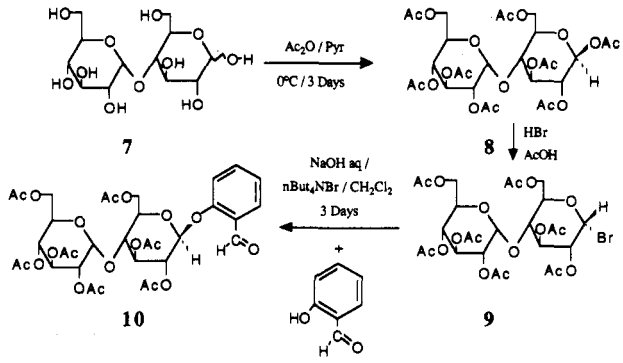
In this paper, we report full experimental data concerning the synthesis and characterization of porphyrins with glucosyl and maltosyl substituents. In addition, we relate the synthesis and the conformation of new compounds in which the four *meso*-phenyl groups are partially substituted by glycosylated moieties.

Results and Discussion

Tetraglycosylated Porphyrins 1–4. Such molecules (Chart I) could be synthesized following two different strategies, either starting from a *meso*-tetrakis(*o*-hydroxyphenyl)porphyrin on which glycosylated groups are linked or starting from glycosylated precursors. The second route involves the reaction of an ortho-substituted benzaldehyde bearing the protected sugar with pyrrole (Scheme II). The latter procedure gave directly glycosylated porphyrins with β-D-glucopyranose and β-D-maltose moieties linked at the ortho position of *meso*-phenyl groups. 2-(2,3,4,6-Tetraacetyl-β-D-glucosyl)benzaldehyde (helicin tetraacetate) (**6**) was used to prepare compound **1** (Scheme II). In contrast, the 2-(2,3,6,2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)-benzaldehyde (**10**) must be first prepared to obtain the porphyrin **3**; this was achieved following the method of Halazy et al.[10] (Scheme I).

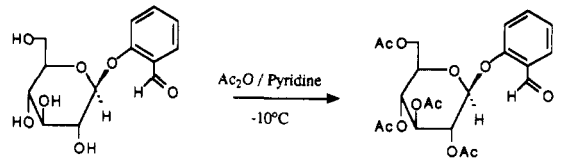
Treatment of maltose **7** in a mixture of acetic anhydride and pyridine at 0 °C for 3 days gave the acetyl derivative **8** which was transformed to α-bromoacetylmaltose **9** by reaction with HBr/Acetic acid. The 2-(2,3,6,2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)benzaldehyde (**10**) was obtained by a coupling reaction of *o*-hydroxybenzaldehyde with compound **9** in a heterogeneous phase[10] (mixture of aqueous sodium hydroxide, methylene chloride, and nBu_4NBr) in 36% yield (Scheme I).

Scheme I



7 8 9 10

Scheme II



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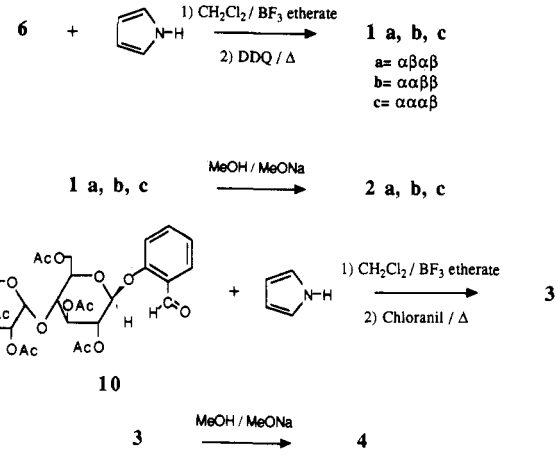

meso-5,10,15,20-Tetrakis(*o*-glycosylphenyl)porphyrins **1** and **3** were obtained following Lindsey's method[11] (Scheme II). This consisted of a high-dilution condensation of glycosylated aldehydes **6** and **10** and pyrrole in the presence of a Lewis acid catalyst (BF_3·Et_2O) in methylene chloride at room temperature to afford the corresponding porphyrinogens. These were oxidized in situ by treatment of the reaction mixtures with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or tetrachloro-1,4-benzoquinone (*p*-chloranil) to give porphyrins **1** and **3** in 25 and 10% yield, respectively.

Thin-layer chromatographic analysis on silica gel showed that the tetraglucosylated derivative **1** contained three atropoisomers. They were separated by two successive preparative chromatographies on a silica gel column using

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a mixture of CH_2Cl_2–acetone (10/1–5/1, v/v) as eluent. The three compounds **1a–c** were identified by their ^1H NMR spectra as the $\alpha\beta\alpha\beta$, $\alpha\alpha\beta\beta$, and $\alpha\alpha\alpha\beta$ atropoisomers. The formation of the $\alpha\alpha\alpha\alpha$ atropoisomer was not observed. This absence could be attributed to the very strong steric hindrance of the glycosylated substituents. The relative ratios of the three isolated compounds are in the same order of those observed for other tetrakis ortho-substituted phenylporphyrins.[12] In contrast, thin-layer chromatographic analysis of the tetramaltosylated compound **3** obtained after usual workup gave a single spot. After warming in boiling xylene overnight, no change was observed in the thin-layer chromatographic pattern indicating a priori only one atropoisomer. Such a behavior is in constrast to that shown by one of the three compounds **1** which gave three atropoisomers after such a treatment.

The unprotected saccharide compounds **2** and **4** were obtained after reaction of porphyrins **1** and **3** with a catalytic amount of sodium methanolate in dry methanol,[13] followed by purification by gel filtration on Sephadex LH20 with methanol as eluent. Neutral free-base porphyrins bearing tetraacetyl glucose **1** are soluble in nonpolar solvents, and free glucose compounds **2** are soluble in alcohol and weakly soluble in neutral water. The solubility of the different atropoisomers **2** in water was largely dependent on the geometry of the molecules. The solubility increases with the protection of the faces of the macrocycle (concd max **2c** = 0.9×10^{-5} mol/L, concd max **2b** = 1.6×10^{-5} mol/L, concd max **2a** > 3.5×10^{-5} mol/L). This variation of solubility might be partly due to the difference of solvation of the isomers. In contrast, tetramaltosyl derivative **4** is very soluble in aqueous solution even at high concentration.

Zinc complexes **Zn–1a–c** and **Zn–3** were prepared and purified as previously described[14] but here metalation was much more difficult indicating a strong steric hindrance of both faces of the macrocycles.

Polyglucosylated Porphyrins. In order to obtain mono-, bis-, and tris[(*o*-tetraacetylglucosyl)phenyl]tri-, di-, and monophenyl porphyrins, pyrrole was condensed with a mixture of benzaldehyde and 2-(2,3,4,6-tetraacetyl-β-D-glucosyl)benzaldehyde (**6**) with a relative proportion of 4/2/2 under the same conditions used for the synthesis of the tetraglucosyl derivatives **1** and **3**. These reaction conditions minimize the formation of tetraphenylporphyrin and tetraglucosylated compound **1**. The thin-layer chromatography of the reaction mixture showed the presence of eight of the 10 possible porphyrins. This statistical distribution of 10 compounds corresponds to the formation of different *meso*-phenyl derivatives and the different conformers having substituents "up" or "down" with respect to the macrocycle when two different ortho-substituted benzaldehydes are used. The structures of these eight compounds, isolated by preparative chromatography, are reported in Chart II. The order in increasing polarity was: TPP > **11** > $\mathbf{12}_{5,15}$ > $\mathbf{12}_{5,10}$ > $\mathbf{12}_{5,10,15}$. Except for compounds $\mathbf{12}_{5,10,15,\alpha,\alpha,\alpha}$ and $\mathbf{12}_{5,10,15\alpha,\alpha,\beta}$ which have polarities too close for a good TLC separation, all these compounds were separated and then identified by ^1H NMR spectroscopy.

Deprotected mono-, di-, and triglucoconjugated porphyrins were obtained following the method described above. Among the triglucosylated porphyrins, only compound $\mathbf{13}_{5,10,15,\alpha,\beta,\alpha}$ has been prepared and characterized.

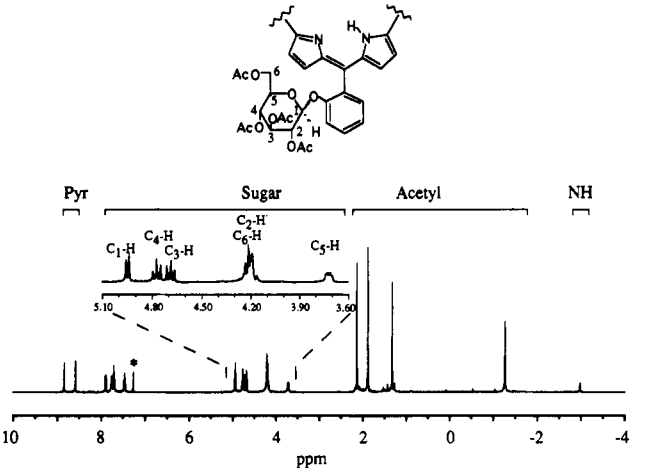
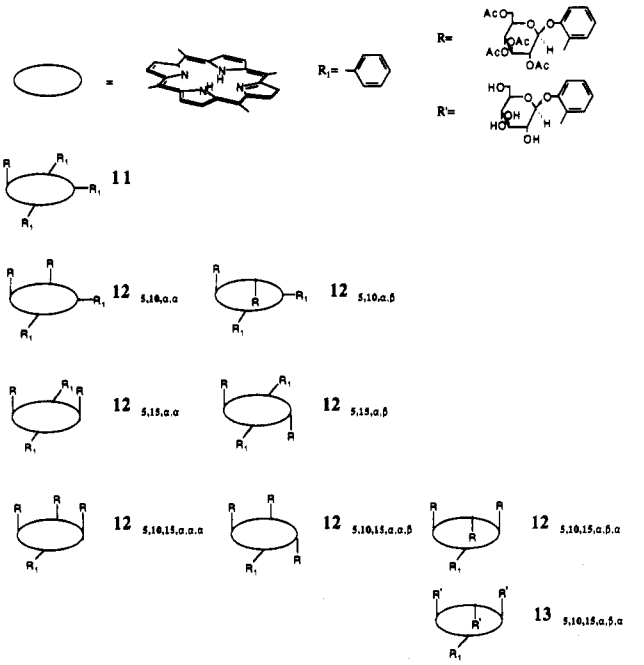


Figure 1. ^1H NMR spectra of compound **1a** in $CDCl_3$ at room temperature: *, $CHCl_3$.

Chart II



^1H NMR Characterization. ^1H NMR spectra recorded at 400 MHz were used for the characterization of all compounds **1–13**. The general aspects of these spectra are similar to those of the both-faces hindered porphyrins previously studied[15] and are shown in Figures 1–3.

Assignments of the resonances to individual protons are based on integration and selective homonuclear decoupling experiments.

The spectra of these compounds are governed by the symmetry properties of the products. For example, the isomers **1a, b, c**, which have, respectively, D_2, C_2, and C_1 symmetries, should be differentiated from each other. The spectra of **1a** (Figure 1) and **2a** are relatively simple, each resonance system corresponding to four equivalent protons while for compounds **1b** (Figure 2) and **2b** they appear as two distinct resonances of two chemically equivalent protons; each proton of **1c** (Figure 3) and **2c** has its own

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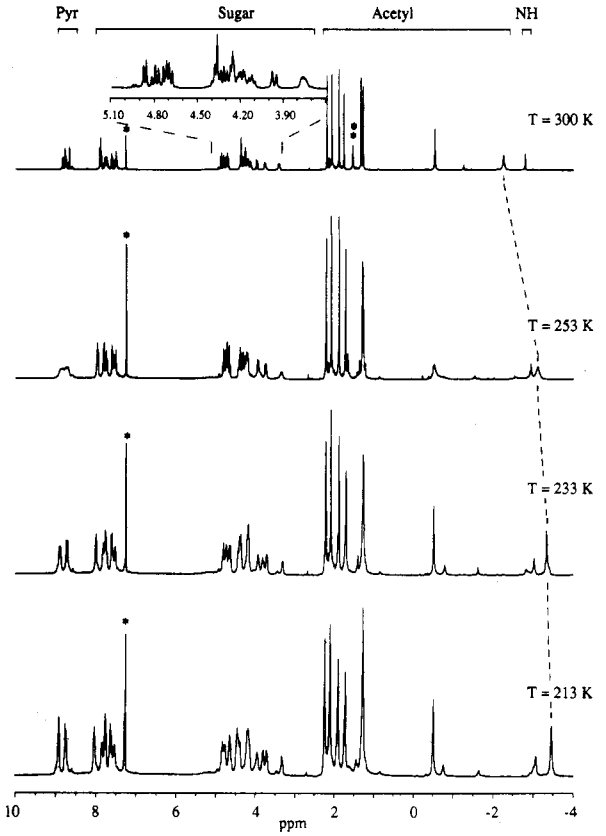

Figure 2. ^{1}H NMR spectra of compound **1b** in $CDCl_3$ at different temperatures: *, $CHCl_3$; **, HOD.

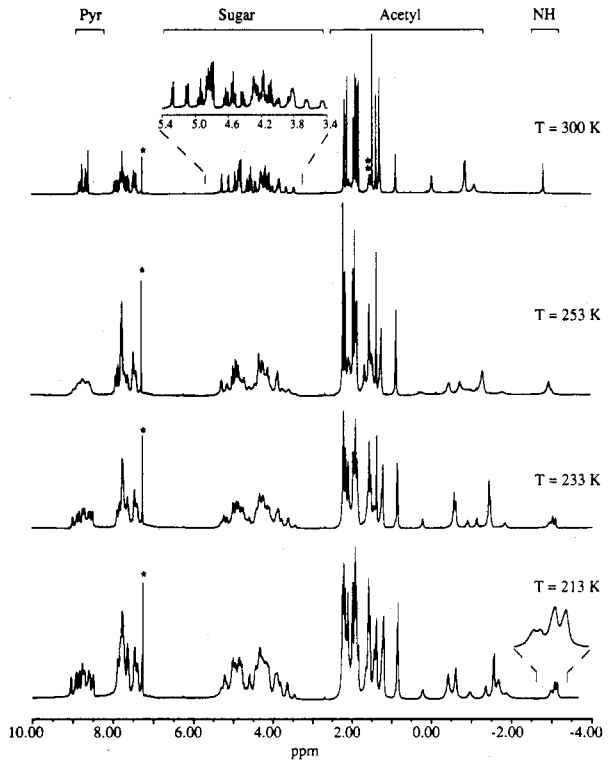

Figure 3. ^{1}H NMR spectra of compound **1c** in $CDCl_3$ at different temperatures: *, $CHCl_3$; **, HOD.

resonance. In the case of porphyrins **1–4**, **11**, and **12**, steric considerations suggest that the "ose" groups should all be oriented in the same direction with C-2 and C-3 protons towards the center of the porphyrin. Furthermore, the resonance of the C-1 proton of the glycosyl substituents

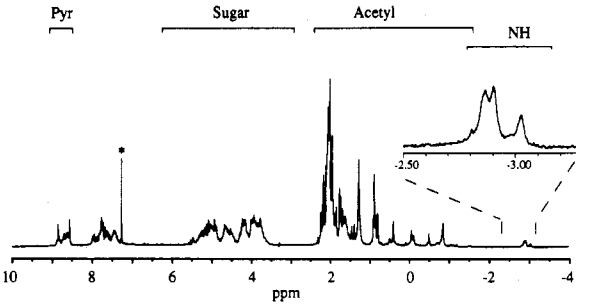

Figure 4. ^{1}H NMR spectra of compound **3** in $CDCl_3$ at room temperature: *, $CHCl_3$.

in all protected and unprotected porphyrins **1–2**, **11**, and **12** appears as a well-defined doublet (J = 8 Hz) between 4.80 and 5.30 ppm in $CDCl_3$ and 5.60 and 5.80 pmm in deuterated pyridine, respectively. This indicates a pure β-configuration of the anomeric carbon of the sugars.[16]

For compounds **1a, b, c**, resonances of the "ose" protons are shifted upfield between 0.1 and 1.3 ppm with respect to the resonance of the same protons in the protected helicin **5** taken as reference. At the same time the methyl protons of the acetyl groups are shifted up to 4.3 ppm. That suggests the meso substituents of these compounds bend over the porphyrin ring in spite of the spatial congestion. The same observation can be made for the compound **2a**.

The effect of temperature on the number of NH resonances in the ^{1}H NMR spectra of compounds **1a–c** is shown in Figures 2 and 3 for products **1b** and **1c**. This intense tautomerism effect observed near room temperature could be explained by the motional restriction resulting from a very high steric hindrance due to acetylglucosyl groups. Such an effect has been described by others with similar molecules.[17]

The ^{1}H NMR spectrum of the maltosyl compound **3** is similar to those of the porphyrins bearing four glucose groups in the ortho position of the *meso*-phenyl substituents (Figure 4). Relative to the resonances of the acetyl groups of aldehyde **10**, resonances of protons of the same protecting groups in compound **3** are shifted upfield to −2.80 ppm, suggesting that the sugars associated with the *meso*-phenyls bend over the porphyrin ring. NH pyrrolic protons appear as three distinct resonances, while anomeric protons of the sugar appear as a multiplet suggesting that this product, which seems pure by chromatography, could be in fact a mixture of three different atropoisomers. Furthermore, an increase in temperature, limited to 50 °C by the solvent ($CDCl_3$), has no effect on the NMR spectrum. This seems to indicate that we do not have a mixture of tautomers at room temperature.

Electronic Spectra. The electronic spectra of all compounds are very similar to those of known free base tetraphenylporphyrins with a Soret band at 419 nm and four less intense Q bands near 514, 541–551, 588, and 650 nm (Table I). The spectra of protected polyglycosylated porphyrins are etio type for monoglucosyl porphyrin **11** and evolve progressively toward phyllo type when the number and the position of ortho substituents for the polysubstituted compounds **1–4** and **12** vary (Table I).

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Table I. UV–Visible Spectra of Glycosylated Porphyrins and Zinc Complexes in (a) $CHCl_3$, (b) MeOH, and (c) H_2O

compd (solvent)	λ nm, (ε mmol·L^{-1})	ratio $\epsilon_{548}/\epsilon_{590}$
1a (a)	418 (370.5), 515 (17), 544 (6), 588 (7), 654.5 (5.5)	0.857
1b (a)	419.5 (421.5), 514.5 (18.5), 551 (8.5), 589 (7.5), 655.5 (5.5)	1.133
1c (a)	418.5 (418.5), 513.5 (19), 546 (7.5), 588 (8), 653 (5.5)	0.957
2a (b)	415.5 (340), 513.5 (15), 546.5 (5.5), 586 (6), 633 (3.3)	0.917
2a (c)	413.5 (353), 515 (13.4), 542 (4.2), 578.5 (5.7), 643.5 (3.2)	0.737
2b (b)	415 (358.3), 513 (14.9), 546.5 (5.2), 586 (5.7), 641.5 (3.3)	0.912
2b (c)	414, 515, 549, 580, 630	
2c (b)	415 (305.6), 513 (12.6), 546.5 (4.5), 586 (4.8), 642 (2.9)	0.937
2c (c)	413, 516.5, 551, 586, 639	
3 (a)	418 (452.8), 513 (22.1), 546 (7.6), 588 (8.5), 643 (4.7)	0.894
4 (c)	414 (230), 515 (10.3), 552.5 (4.8), 579 (5.6), 632 (3.4)	0.857
11 (a)	418.5 (418.7), 515 (18.6), 549.5 (7.5), 590 (6.5), 645.5 (4.2)	1.154
$\mathbf{12}_{5,10,15\text{-}\alpha,\beta,\alpha}$ (a)	418.5 (474.5), 514 (22.6), 547 (7.8), 588.5 (8.1), 644 (4.7)	0.963
$\mathbf{12}_{5,10\text{-}\alpha,\alpha}$ (a)	418.5 (464.8), 514.5 (20.6), 548.5 (7.4), 589.5 (7.0), 645 (3.9)	1.057
$\mathbf{12}_{5,10\text{-}\alpha,\beta}$ (a)	418.5 (455.1), 514.5 (20.4), 548 (7.2), 589.5 (7.0), 644.5 (4.2)	1.028
$\mathbf{12}_{5,15\text{-}\alpha,\alpha}$ (a)	418.5 (400.3), 515 (18.8), 548 (7.2), 589 (7.1), 644 (4.5)	1.014
$\mathbf{12}_{5,15\text{-}\alpha,\beta}$ (a)	418.5 (398.9), 514.5 (18.3), 548 (6.7), 590 (6.3), 645.5 (3.7)	1.060
$\mathbf{13}_{5,10,15\text{-}\alpha,\beta,\alpha}$ (b)	415 (225.8), 513.5 (10.5), 547.5 (4), 587 (5), 642 (3.6)	0.800
Zn–1a (a)	404 (40), 425 (517.5), 557 (17.2), 593 (5.5)	
Zn–1b (a)	405 (49.5), 426 (632), 558 (23.2), 595 (5.9)	
Zn–1c (a)	404 (53.2), 425 (720.2), 557 (25), 594 (5.8)	
Zn–3 (a)	403 (shoulder), 425 (638.8), 557 (26.8), 594 (shoulder)	

This effect was shown by the evolution of the ratio $\epsilon_{548}/\epsilon_{590}$. Such an observation could result from a decrease of the solvation between the macrocycle and the solvent molecules due to the large steric hindrance of the glycosylated substituents. The intensity of Soret band in the electronic spectra[14] of zinc complexes of glycosylated porphyrins **1** and **3** in chloroform is much more intense than that of zinc tetraphenylporphyrin. This behavior could be interpreted by a modification of the planarity of the macrocycle induced by repulsive interactions between adjacent and opposite sugars on the same side. The structural phenomena are confirmed by the difficulty of obtaining the five coordinated species of complexes **Zn–1** and **Zn–3** in the presence of pyridine. The formation of such species requires a high concentration of ligands. Affinity constants [binding constants of pyridine at 25 °C in methylene chloride (K in L·mol^{-1}) **Zn–TPP**, (5900); **Zn–1a**, (15); **Zn–1b**, (39); **Zn–1c**, (14); **Zn–3**, (39)] are decreased by a factor of 150–300 compared to those measured with flat **Zn–TPP**. This last point underlines the very large hindrance in compounds **1** and **3**.

Conclusion

In this paper, we describe the synthesis and the characterization of a new class of tetrapyrrolic macrocycles on which one, two, three, or four glucopyranosyl or four maltosyl groups were linked in order to increase the solubility of the macrocycle in aqueous solution. The present strategy may be easily used for the preparation of other neutral glycoconjugated tetrapyrrolic compounds. The structure of these new porphyrins determined in solution, by ^{1}H NMR spectroscopy, shows a great hindrance to both faces of the porphyrin macrocycle created by the presence of glycosylated groups in the ortho position of the *meso*-phenyl groups. This is confirmed by the difficulty in the preparation of zinc complexes and the low values of affinity constants for ligand binding. In the case of the free glucosyl $\alpha\beta\alpha\beta$ atropoisomer **1a**, this protection permits a good solubility of this compound in neutral water. Furthermore, the presence of four disaccharide groups in the vicinity of the macrocycle of the tetramaltosyl derivative **3** confers on this compound a very high solubility in water.

Experimental Section

General. All chemicals used were of reagent grade and were purchased from Aldrich. Methylene chloride and chloroform were distilled from K_2CO_3. Merck silica gel 60 (0.040–0.060 mm) was used for column chromatography. Pure porphyrins were obtained by preparative high-pressure liquid chromatography (HPLC) with a Jobin-Yvon apparatus. Merck precoated plates (silica gel 60, 2 mm) were used for TLC.

Elemental analysis were carried out by the Service Central de Microanalyse du CNRS. ^{1}H spectra were obtained in the indicated deuteriated solvents with Brucker AM-200 and AM-400 instruments. Optical spectra in the Soret and visible regions were recorded using a Varian DMS 200 spectrometer.

2-(2,3,4,6-Tetraacetyl-β-D-glucosyl)benzaldehyde (Helicin Tetraacetate) (6). Helicin **5** (10 g, 3.5×10^{-2} mol), in a mixture of acetic anhydride (100 mL) and pyridine (130 mL), was stirred at −15 °C for 4 h. The resulting solution was then kept at 0 °C for 3 days. The reaction mixture was poured into 1.5 L of water and ice. The precipitate was filtered and washed with cooled water. The crude product was crystallized from ethanol to give white needles (13.97 g; 88%), mp 140 °C (lit.[18] mp 142 °C).

5,10,15,20-Tetrakis[2-(2,3,4,6-tetraacetyl-β-D-glucosyl)-phenyl]porphyrin (1). Pyrrole (0.167 g, 2.5×10^{-3} mol) in methylene chloride (25 mL) and helicin tetraacetate (**6**) (1.130 g, 2.5×10^{-3} mol) in the same solvent (25 mL) were added separately to methylene chloride (200 mL) purged by argon for 30 min. The mixture was stirred and purged by argon for 10 min after which a BF_3·etherate solution (100 μL, 0.5 M) in methylene chloride was added. This mixture was stirred for 20 h at room temperature. Dichlorodicyanobenzoquinone (DDQ) (0.420 g, 1.85×10^{-3} mol) was then added. After reflux for 1 h, 10 g of silica gel was added to the dark solution and all solvent was evaporated to dryness. The porphyrins absorbed on silica gel were placed on the top of a silica gel column. The crude products were eluted with a mixture of methylene chloride and acetone (10/1–5/1, v/v). The three red bands were separately collected (0.316 g, total yield 25.5%) and were purified by thin-layer chromatography eluted twice with methylene chloride and acetone (10/1, v/v): **1a**, 20 mg (1.6%); **1b**, 81 mg (6.5%); **1c**, 216 mg (17.3%). Anal. Calcd for the mixture of the three isomers of free base $C_{100}H_{102}N_4O_{40}$: C, 60.1; H, 5.1; N, 2.8. Found: C, 59.6; H, 5.5; N, 2.6. **1a**: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.86 (s, 4 H, pyr) and 8.60 (s, 4 H, pyr), 7.90 (d, 4 H, H_6 phenyl), 7.76 (t, 4 H, H_4 phenyl), 7.70 (d, 4 H, H_3 phenyl) and 7.47 (t, 4 H, H_5 phenyl), 4.95 (d, 4 H, H_1 ose, J = 8 Hz), 4.76 (t, 4 H, H_4), 4.68 (t, 4 H, H_3), 4.20 (m, 12 H, H_2 and H_{6a}, H_{6b} ose), and 3.72 (m, 4 H, H_5 ose), 2.14 (s, 12 H, acetyl), 1.88 (s, 12 H, acetyl), 1.32 (s, 12 H, acetyl) and −1.27

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(s, 12 H, acetyl), −2.99 (s, 2 H, NH). **1b**: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.84 (d, 2 H, pyr), 8.78 (d, 2 H, pyr), 8.75 (d, 2 H, pyr) and 8.67 (s, 2 H, pyr), 7.90 (m), 7.77 (dt), 7.61 (d), and 7.51 (m) (16 H, phenyl), 4.86 (d, 2 H, H′$_1$ ose, J = 8 Hz), 4.79 (d), 4.77 (d) (2 H, H′$_1$ ose, J = 8 Hz), 4.70 (m), 4.36 (m), 4.25 (m), 4.18 (m), 4.11 (m), 3.96 (dd), 3.76 (m), and 3.40 (m) (24 H, H_2, H_3, H_4, H_{6a}, H_{6b}, H_5 ose), 2.19 (s, 6 H, acetyl), 2.06 (s, 6 H, acetyl), 1.88 (s, 6 H, acetyl), 1.75 (s, 6 H, acetyl)s, 1.32 (s, 6 H, acetyl), 1.26 (s, 12 H, acetyl), −0.54 (s, 3 H, acetyl), and −2.25 (broad, 3 H, acetyl), −2.79 (s, 2 H, NH). **1c**: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.83 (d, 2 H, pyr), 8.77 (m, 2 H, pyr), 8.67 (d, 2 H, pyr) and 8.61 (s, 2 H, pyr), 7.95 (dd), 7.77 (m), 7.62 (d), and 7.45 (m) (16 H, phenyl), 5.29 (d, 1 H, H_1 ose, J = 8 Hz), 5.11 (d, 1 H, H_1 ose, J = 8 Hz), 4.95 (d, 1 H, H_1 ose, J = 8 Hz), 4.93 (d, 1 H, H_1 ose, J = 8 Hz), 4.84 (m), 4.64 (t), 4.56 (t), 4.43 (t), 4.29 (m), 4.19 (m), 4.10 (t), 4.02, 3.82 (m), 3.65 (m), and 3.45 (m) (24 H, H_2, H_3, H_4, H_{6a}, H_{6b}, H_5 ose), 2.17 (s, 3 H, acetyl), 2.15 (s, 3 H, acetyl), 2.10 (s, 3 H, acetyl), 1.92 (s, 3 H, acetyl), 1.89 (s, 3 H, acetyl)s, 1.88 (s, 3 H, acetyl), 1.83 (s, 3 H, acetyl), 1.79 (s, 3 H, acetyl), 1.53 (s, 3 H, acetyl), 1.47 (s, 3 H, acetyl), 1.36 (s, 3 H, acetyl), 1.29 (s, 3 H, acetyl), 0.01 (s, 3 H, acetyl), −0.85 (d, 6 H, acetyl), and −1.08 (broad, 3 H, acetyl), −2.81 (s, 2 H, NH).

5,10,15,20-Tetrakis(2-β-D-glucosylphenyl)porphyrin (2). To a solution of compound 1 (**a**, **b**, or **c**) (15 mg, 7.5 × 10^{-6} mol) in dry methanol (10 mL) was added sodium methanolate in dry methanol (100 μL, 0.1 N). The mixture was stirred for 15 min at room temperature. The crude solution was submitted to gel filtration on a LH20 column eluted by methanol to give the pure products which were crystallized from methanol/methylene chloride: **2a**, 9 mg (90%); **2b**, 8 mg (80%); **2c**, 10 mg (100%). Anal. Calcd for the mixture of the three isomers $C_{68}H_{68}N_4O_{24}$, $15CH_2Cl_2$: C, 38.35; H, 3.8; N, 2.62. Found: C, 38.6; H, 4.0; N, 2.25. **2a**: ^{1}H NMR (pyridine-d_5) δ (ppm) 9.15 (s, 4 H, pyr), 8.90 (s, 4 H, pyr), 8.09 (dd, 4 H, H_6 phenyl), 7.95 (d, 4 H, H_3 phenyl), 7.73 (td, 4 H, H_4 phenyl), 7.32 (t, 4 H, H_5 phenyl), 6.95 (broad, 4 H, OH ose), 6.65 (broad, 4 H, OH ose), 6.42 (broad, 4 H, OH ose), 6.11 (broad, 4 H, OH ose), 5.60 (d, 4 H, H_1 ose, J = 7.9 Hz), 4.45 (d), 4.25 broad (8 H, H_6 ose), 4.0 (t, 4 H, H_5 ose), 3.92 (t, 4 H, H_3 ose), 3.73 (d, 4 H, H_4 ose), 2.85 (t, 4 H, H_2 ose), −2.59, (2 H, NH). **2b**: ^{1}H NMR (pyridine-d_5) δ (ppm) 9.21 (d), 9.00 (d), 9.10 (s), 8.96 (s) (8 H, pyr), 8.30 (dd, 2 H, H_6, phenyl), 8.15 (dd, 2 H, H_6, phenyl), 8.02 (dd, 2 H, H_3, phenyl), 7.98 (dd, 2 H, H_3, phenyl), 7.75 (tt, 2 H, H_5, phenyl), 7.43 (t, 2 H, H_5, phenyl), 7.73 (t, 2 H, H_4, phenyl), 7.35 (t, 2 H, H_4, phenyl), 7.02 (broad, 4 H, OH ose), 6.44 (broad, 4 H, OH ose), 6.09 (broad, 4 H, OH ose), 5.62 (broad, 4 H, OH ose), 5.76 (d, 2 H, H_1 ose, J = 7.80 Hz), 5.59 (d, 2 H, H_1 ose, J = 8 Hz), 4.57 (t, 2 H, H_6 ose), 4.45 (t, 2 H, H_6 ose), 4.31 (m, 2 H, H_6 ose), 4.22 (m, 2 H, H_6 ose), 4.08 (t, 2 H, H_5 ose), 3.97 (t, 2 H, H_5 ose), 4.0 (broad, 2 H, H_4 ose), 3.68 (broad, 2 H, H_4 ose), 4.03-4.0 (broad, 4 H, H_3 ose), 3.61 (d, 2 H, H_2 ose), 2.95 (d, 2 H, H_2 ose), −3.21 (s, 2 H, NH). **2c**: ^{1}H NMR (pyridine-d_5) δ (ppm) 9.37 (d), 9.11 (m) (8 H, pyr), 8.05 (m, 4 H, phenyl), 7.74 (m 4 H, phenyl), 7.55 (broad 4 H, phenyl), 7.36 (m, 4 H, phenyl), 7.06 (broad, 4 H, OH ose), 6.68 (broad, 4 H, OH ose), 6.47 (broad, 4 H, OH ose), 6.14 (broad, 4 H, OH ose), 5.82 (d, 1 H, H_1 ose, J = 7.3 Hz), 5.71 (d, 1 H, H_1 ose, J = 11 Hz), 5.66 (d, 1 H, H_1 ose, J = 8.7 Hz), 5.62 (d, 1 H, H_1 ose J = 8.5 Hz) 4.47 (m, 4 H, ose), 4.34 (m, 4 H, ose), 4.05 (m, 8 H, ose), 3.73 (m, 4 H, ose), 3.38 (t, 2 H, H_2 ose), 3.01 (m, 2 H, H_2 ose), −3.04 (s, 2 H, NH).

D-(+)-Octaacetylmaltose (8). A solution of D-(+)-maltose (7) (36 g, 0.1 mol) in a mixture of acetic anhydride (360 mL) and pyridine (470 mL) was stirred at −15 °C for 4 h. The resulting solution was kept at 0 °C for 3 days with occasional stirring. The solution was poured into 5 L of water and ice. The precipitate was filtered and washed with cooled water. The crude product was crystallized from ethanol (48.7 g, 72%).

α-1-Bromo-2,3,6,2′,3′,4′,6′-heptaacetylmaltose (9). Hydrogen bromide in acetic acid (30%, 24 mL) was added to octaacetylmaltose (8) (11.75 g, 17.3 mmol) at 0 °C and the mixture then stirred at room temperature for 3 h. The solution was concentrated under vacuum at 40 °C and then 60 °C. The crude oil was dissolved in dry toluene and evaporated under vacuum. The residue was dissolved in methylene chloride and quickly washed with cold saturated aqueous sodium bicarbonate solution and then with cold water. The solution was dried over sodium sulfate and evaporated under vacuum. The crude bromo derivative was used without other purification (12.1 g, 100%).

2-(2,3,6,2′,3′,4′,6′-Heptaacetyl-β-D-maltosyl)benzaldehyde (10). A solution of 2-hydroxybenzaldehyde (3.4 g, 26 mmol) in methylene chloride (31 mL) was vigorously stirred at room temperature with an aqueous solution of sodium hydroxide (5%, 43 mL) and tetrabutylammonium bromide (1.384 g, 4.3 mmol). To this mixture was added a solution of crude compound **9** (12.1 g, 17.3 mmol) in methylene chloride (12 mL) and stirring continued for 3 days at room temperature. After separation, the organic layer was washed with aqueous sodium hydroxide aqueous solution (5%, 2 × 40 mL) and with water. The organic layer was dried over sodium sulfate, filtered, and evaporated under vacuum. The yellow oil was chromatographed on a silica gel column using a mixture of ethyl acetate/hexane (1/1, v/v) affording pure product **10** (4.70 g, 36%). Anal. Calcd for $C_{33}H_{40}O_{18}\cdot 2H_2O$: C, 52.11; H, 5.83. Found: C, 52.36; H, 5.55. ^{1}H NMR ($CDCl_3$) δ (ppm) 10.30 (1 H, CHO), 7.84 (dd, 1 H, *o*-phenyl), 7.56 (dd, 1 H, *o*-phenyl), 7.15 (dd, 2 H, *m*-phenyl), 6.60 (s, 1 H, ose), 5.33–4.20 (13 H, ose), 2.10 (s, 3 H, acetyl), 2.08 (s, 3 H, acetyl), 2.07 (s, 3 H, acetyl), 2.06 (s, 3 H, acetyl), 2.04 (s, 3 H, acetyl), 2.03 (s, 3 H, acetyl), 2.01 (s, 3 H, acetyl).

5,10,15,20-Tetrakis[2-(2,3,6,2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)phenyl]porphyrin (3). Pyrrole (330 μL, 5 × 10^{-3} mol) in methylene chloride (53 mL) and the aldehyde **10** (3.8 g, 5 × 10^{-3} mol) in the same solvent (53 mL) were added separately to methylene chloride (600 mL) purged by argon for 30 min. The mixture was stirred and purged by argon for 10 min more after which a BF_3·etherate solution (213 μL, 0.5 M) in methylene chloride was added (twice during 2 h). This mixture was stirred for 20 h at room temperature. Chloranil (0.315 g, 1.28 × 10^{-3} mol) was then added. After reflux for 1 h, 10 g of silica gel was added to the dark solution and solvent was evaporated. The absorbed products on silica gel were placed on the top of a silica gel column and were eluted with a mixture of methylene chloride and acetone (5/1, v/v). Only one red band was collected and was purified by thin-layer chromatography eluted twice with methylene chloride and acetone (5/1, v/v). The pure product crystallized from methylene chloride/hexane (0.420 g, 10%). Anal. Calcd for $C_{148}H_{166}N_4O_{72}$: C, 56.38; H, 5.31 N, 1.78. Found C, 55.95; H, 5.32; N, 1.61. ^{1}H NMR ($CDCl_3$) δ (ppm) 8.82 (s, 2 H, pyr), 8.62 (m, 4 H, pyr), 8.54 (s, 2 H, pyr), 7.69 (m, 16 H, phenyl), 5.03 (m, 16 H, ose), 4.62 (m, 10 H, ose), 4.15 (m, 10 H, ose), 3.84 (m, 20 H, ose), 2.23 (s), 2.22 (s), 2.18 (s), 2.15 (s), 2.08 (s), 2.07 (s), 2.04 (s), 2.02 (s), 2.00 (s), 1.99 (s), 1.96 (s), 1.93 (s), 1.91 (s), 1.84 (s), 1.83 (s), 1.74 (s), 1.71 (s), 1.67 (s), 1.55 (s), 1.43 (s), 1.37 (s), 1.25 (s), 0.90 (s), 0.87 (s), 0.84 (s), 0.78 (s), 0.47 (s), 0.39 (s), −0.05 (s), −0.10 (s), −0.49 (s), −0.83 (s) (84 H, acetyl), −2.87, −2.91, −3.03 (s, 2 H, NH).

5,10,15,20-Tetrakis(2-β-D-maltosylphenyl)porphyrin (4). This compound was prepared according to the procedure described above for the preparation of compound **2**. The crude product was purified by gel filtration on a LH20 column eluted by methanol. The pure product (90%) was crystallized from methanol/1,2-dichloroethane. Anal. Calcd for $C_{92}H_{108}N_4O_{44}$, $7CH_2ClCH_2Cl$: C, 47.75; H, 5.14; N, 2.10. Found: C, 45.85; H, 4.73; N, 2.14. ^{1}H NMR (pyridine-d_5) δ (ppm) 9.34 (s, 2 H, pyrrole), 9.25 (m, 2 H, pyrrole), 9.16 (m, 2 H, pyrrole), 9.06 (s 2 H, pyrrole), 8.50 (m), 8.27 (m), 7.95 (m) (16 H, phenyl + 24 H, OH ose), 6.58 (m, 4 H, OH ose), 5.79 m (4 H, H_1 ose), 4.67 (m), 4.48 (m), 4.28 (m), 4.06 (m) (52 H, ose), −2.54 (s), −3.07 (s), −3.26 (s) (2 H, NH).

5,10,15,20-Mono-, Bis-, or Tris[2-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]tri-, di-, or monophenylporphyrins 11 and 12. These compounds were prepared in a manner similar to compound **1**. In this case, pyrrole (0.430 g, 6.4 × 10^{-3} mol) in chloroform (65 mL) and aldehyde **6** (1.412, 3.2 × 10^{-3} mol) and benzaldehyde (0.330 g, 3.2 × 10^{-3} mol) in the same solvent (65 mL) were added to chloroform (500 mL). The resulting mixture was treated with a BF_3·etherate solution (250 μL, 0.5 M) in chloroform. Chloranil (1.140 g, 4.63 mmol) was then added. After reflux for 1 h, 10 g of silica gel was added to the dark solution and solvent was evaporated. The crude products were eluted with pure methylene chloride to give monoglucosyl compound **11** (65 mg, 4.4%) in the first red band. Elution with a mixture of methylene chloride and ether (10/1, v/v) gave di "ose" products $\mathbf{12}_{5,10,\alpha,\beta}$ (40 mg, 2%) and $\mathbf{12}_{5,15,\alpha,\beta}$ (60 mg, 3.2%). Elution was

continued with a mixture of methylene chloride/acetone (10/1, v/v) to give three other bands which corresponded to $12_{5,10,\alpha,\alpha}$ (34 mg, 1.3%), $12_{5,15,\alpha,\alpha}$ (traces), and the three "oses" compounds $12_{5,10,15}$ (310 mg, 12%), respectively. This last band was collected and submitted to a thin-layer chromatography [methylene chloride and acetone (10/1, v/v)] to give compound $12_{5,10,15,\alpha,\beta,\alpha}$ (172 mg, 6.7%) and a mixture of compounds $12_{5,10,15,\alpha,\alpha,\beta}$ and $12_{5,10,15,\alpha,\alpha,\alpha}$ (87 mg, 3.4%). All products were crystallized from methylene chloride/hexane. 11: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.85 (m, 8 H, pyr), 8.70 (d 1 H, phenyl-ose), 8.02 (t, 1 H, phenyl-ose), 7.57 (d, 1 H, phenyl-ose) and 7.50 (t, 1 H, phenyl-ose), 8.30 (m, 4 H, phenyl), 8.22 (t, 4 H, phenyl) and 7.78 (d, 4 H, phenyl), 4.87 (d, 1 H, H_1 ose, J = 8 Hz), 4.74 (t, 1 H, H_2 or H_3 ose), 4.58 (t, 1 H, H_3 or H_2 ose), 4.25 (t, 1 H, H_4 ose), 4.13 (m, 1 H, H_{6a} ose), 4.02 (m, 1 H, H_{6b} ose), 3.56 (m, 1 H, H_5 ose), 2.04 (s, 3 H, acetyl), 1.85 (s, 3 H, acetyl), 1.32 (s, 3 H, acetyl) and −1.06 (s, 3 H, acetyl), −2.76 (s, 2 H, NH). Anal. Calcd for $C_{58}H_{48}N_4O_{10}\cdot H_2O$: C, 71.09; H, 5.11; N, 6.12. Found: C, 71.23; H, 4.96; N, 5.79. $12_{5,15,\alpha,\beta}$: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.80 (m, 8 H, pyr), 8.69 (d, 2 H, phenyl-ose), 8.02 (d, 2 H, phenyl-ose), 7.66 (d, 2 H, phenyl-ose) and 7.50 (t, 2 H, phenyl-ose), 8.24 (d, 2 H, phenyl), 8.20 (d, 2 H, phenyl), 7.76 (m, 6 H, phenyl), 4.80 (d, 2 H, H_1 ose, J = 8 Hz), 4.70 (t, 2 H, H_2 or H_3 ose), 4.52 (t, 2 H, H_3 or H_2 ose), 4.22 (t, 2 H, H_4 ose), 4.07 (m, 2 H, H_{6a} ose), 3.96 (m, 2 H, H_{6b} ose), 3.48 (m, 2 H, H_5 ose), 2.01 (s, 6 H, acetyl), 1.83 (s, 6 H, acetyl), 1.30 (s, 6 H, acetyl) and −1.02 (s, 6 H, acetyl), −2.78 (s, 2 H, NH). Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 3H_2O$: C, 63.58; H, 5.33; N, 4.12. Found: C, 62.68; H, 4.87; N, 3.68. $12_{5,15,\alpha,\alpha}$: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.83 (m), 8.77 (m), 8.63 (m) (8 H, pyr), 8.17 (d), 7.91 (d), 7.74 (d) and 7.44 (m) (8 H, H_6, H_4, H_5, H_3 phenyl and phenyl-ose), 8.22 (d), 7.74 (m) (8 H, phenyl), 4.92 (d, 2 H, H_1 ose, J = 8 Hz), 4.78 (t, 2 H, H_2 or H_3 ose), 4.63 (t, 2 H, H_3 or H_2 ose), 4.22 (m, 2 H, H_4 ose), 4.22 (m, 2 H, H_{6a} ose), 4.22 (m, 2 H, H_{6b} ose), 3.68 (m, 2 H, H_5 ose), 2.14 (s, 6 H, acetyl), 1.87 (s, 6 H, acetyl), 1.31 (s, 6 H, acetyl) and −1.22 (s, 6 H, acetyl), −2.83 (s, 2 H, NH). Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 2H_2O$: C, 64.38; H, 5.25; N, 4.17. Found: C, 64.75; H, 4.88; N, 4.15. $12_{5,10,\alpha,\beta}$: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.85 (m), 8.80 (m, 4 H, pyr), 8.67 (m, 4 H, pyr), 8.07 (d), 7.98 (d), 7.67 (dd) and 7.50 (t) (8 H, H_6, H_4, H_5, H_3 phenyl and phenyl-ose), 8.30 (d), 8.20 (d), 7.76 (t) (8 H, phenyl), 4.86 (d, 1 H, H_1 ose, J = 8 Hz), 4.82 (d, 1 H, H_1 ose, J = 8 Hz), 4.70 (dt, 2 H, H_2 or H_3 ose), 4.57 (dt, 2 H, H_3 or H_2 ose), 4.20 (dt, 2 H, H_4 ose), 4.09 (m, 2 H, H_{6a} ose), 3.98 (m, 2 H, H_{6b} ose), 3.54 (m, 2 H, H'_5 ose), 2.02 (d, 6 H, acetyl), 1.83 (d, 6 H, acetyl), 1.31 (d, 6 H, acetyl), −1.01 (s, 3 H, acetyl) and −1.07 (s, 3 H, acetyl), −2.78 (s, 2 H, NH). Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 2H_2O$: C, 64.38; H, 5.25; N, 4.17. Found C, 63.91; H, 4.76; N, 4.04. $12_{5,10,\alpha,\alpha}$: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.81 (m), 8.73 (d), 8.66 (d) (8 H, pyr), 7.91 (d), 7.83 (t), 7.65 (d) and 7.46 (t) (8 H, H_6, H_4, H_5, H_3 phenyl and phenyl-ose), 8.20 (m), 8.04 (d), 7.74 (m) (8 H, phenyl), 4.90 (d, 1 H, H_1 ose, J = 8 Hz) and 4.81 (d, 1 H, H_1 ose, J = 8 Hz), 4.74 (dt, 2 H, H_2 or H_3 ose), 4.43 (t, 2 H, H_3 or H_2 ose), 4.26 (m, 2 H, H_4 ose), 4.26 (m, 2 H, H_{6a} ose), 4.02 (m, 2 H, H_{6b} ose), 3.74 and 3.50 (m, 2 H, H_5 ose), 2.17 (s, 3 H, acetyl), 2.07 (s, 3 H, acetyl), 1.86 (s, 3 H, acetyl), 1.78 (s, 3 H, acetyl), 1.34 (s, 3 H, acetyl), 1.30 (s, 3 H, acetyl), −0.67 (s, 3 H, acetyl) and −1.92 (s, 3 H, acetyl), −2.78 (s, 2 H, NH). Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 2H_2O$: C, 64.38; H, 5.25; N, 4.17. C, 64.79; H, 4.95; N, 4.20. $12_{5,10,15,\alpha,\beta,\alpha}$: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.80 (m), 8.70 (m), 8.65 (m) (8 H, pyr), 7.80 (m), 7.60 (m), 7.61 (d) and 7.42 (m) (12 H, H_6, H_4, H_5, H_3 phenyl and phenyl-ose), 8.18 (m), 8.04 (m), 7.83 (m) (4 H, phenyl), 5.28 (d, 2 H, H_1 ose, J = 8 Hz), 5.11 (d, 1 H, H_1 ose, J = 8 Hz), 4.95 t and 4.85 m (3 H, H_2 or H_3 ose), 4.95 and 4.85 (t, 3 H, H_3 or H_2 ose), 4.55 and 4.50 (m, 4 H, H_4 ose), 4.31 (m, 3 H, H_{6a} ose), 4.20 (m, 3 H, H_{6b} ose), 3.83 and 3.67 (m, 3 H, H_5 ose), 2.20 (s, 3 H, acetyl), 2.18 (s, 3 H, acetyl), 2.14 (s, 3 H, acetyl), 1.93 (s, 3 H, acetyl), 1.91 (s, 3 H, acetyl), 1.87 (s, 3 H, acetyl), 1.50 (s, 3 H, acetyl), 1.49 (s, 3 H, acetyl), 1.40 (s, 3 H, acetyl), 0.02 (s, 3 H, acetyl), −0.78 (s, 3 H, acetyl) and −1.17 (s, 3 H, acetyl), −2.78 (s, 2 H, NH). Anal. Calcd for $C_{88}H_{84}N_4O_{30}\cdot 2H_2O$: C, 61.68; H, 5.18; N, 3.27. Found: C, 62.35; H, 5.08; N, 3.50. $12_{5,10,15,\alpha,\alpha,\alpha}$ and $12_{5,10,15,\alpha,\alpha,\beta}$. Anal. Calcd for the mixture of two isomers for $C_{88}H_{84}N_4O_{30}\cdot 2H_2O$: C, 61.68; H, 5.18; N, 3.27. Found: C, 61.10; H, 5.04; N, 3.30.

α,β,α-5,10,15-Tris(2-β-D-glucosylphenyl)-20-phenylporphyrin, ($13_{5,10,15,\alpha,\beta,\alpha}$). To a solution of compound $12_{5,10,15,\alpha,\beta,\alpha}$ (40 mg, 3.5×10^{-6} mol) in dry methanol (10 mL) was added sodium methanolate in dry methanol (100 μL, 0.1 N). The mixture was stirred for 60 minutes at room temperature and submitted to a gel filtration on a LH20 column. Elution with a mixture of methanol/water (5.1, v/v) gave a pure oily product which crystallized slowly from methanol/water (28 mg, 100%): ^{1}H NMR (pyridine-d_5) δ (ppm) 9.07 (m, 8 H, pyr and 4 H, phenyl), 8.40 (m, 3 H, OH ose), 8.15 (m, 6 H, phenyl), 8.00 (t, 3 H, OH ose), 7.73 (m, 7 H, phenyl), 7.40 (m, 6 H, OH ose), 5.81 (d, 1 H, H_1 ose, J = 7.1 Hz), 5.75 (d, 1 H, H_1 ose, J = 7.6 Hz), 5.65 (d, 1 H, H_1 ose, J = 7.6 Hz), 4.43 (m, 3 H, ose), 4.10 (m, 3 H, ose), 3.69 (m, 3 H, ose), 3.38 (t, 3 H, ose), 3.04 (t, 3 H, ose), −2.91 (s, 2 H, NH). Anal. Calcd for $C_{62}H_{59}N_4O_{18}\cdot 3H_2O$: C, 62.78; H, 5.52; N, 4.72. Found: C, 62.23; H, 5.10; N, 4.47.

Zinc-5,10,15,20-Tetrakis[2-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]porphyrins (Zn-1a, Zn-1b, and Zn-1c). Zinc complexes **Zn-1** were prepared and purified as previously described[14] in $CHCl_3$ under reflux in the presence of zinc chloride in methanol. Anal. Calcd for the mixture of the three isomers of zinc complexes $C_{100}H_{98}N_4O_{40}Zn$: C, 58.2; H, 4.8; N, 2.7. Found: C, 58.0; H, 5.0; N, 2.3. **Zn-1a**: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.74 (s, 4 H, pyr), 8.60 (s, 4 H, pyr), 7.83 (d, 4 H), 7.72 (t, 4 H), 7.38 (t, 4 H), 7.56 (d, 4 H) (H_6, H_4, H_5, H_3 phenyl), 5.00 (d, 4 H, H_1 ose, J = 8 Hz), 4.27 (4 H, H_2 ose), 4.77 (m, 4 H, H_3 ose), 4.78 (m, 4 H, H_4 ose), 3.76 (m, 4 H, H_5 ose), 4.24 (d, 4 H, H_{6a} ose), 4.17 (d, 4 H, H_{6b} oses), 2.14 (s, 12 H, acetyl), 1.89 (s, 12 H, acetyl), 1.43 (s, 12 H, acetyl), −0.56 (s, 12 H, acetyl). **Zn-1b**: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.80 (s, 2 H, pyr), 8.72 (d, 2 H, pyr), 8.68 (d, 2 H, pyr), 8.60 (s 2 H, pyr), 7.87 (m, 4 H, H_6 phenyl), 7.73 (d, 2 H, H_4 phenyl), 7.72 (d, 2 H, H_4 phenyl), 7.60 (d, 2 H, H_3 phenyl), 7.53 (d, 2 H, H_3 phenyl), 7.40 (t, 4 H, H_5 phenyl), 5.06 (d, 2 H, H_1 ose, J = 8 Hz), 4.84–3.69 (26 H, H_1, H_2, H_3, H_4, H_{6a}, H_{6b}, H_5 ose), 2.15 (s, 6 H, acetyl), 2.13 (s, 6 H, acetyl), 1.91 (s, 6 H, acetyl), 1.87 (s, 6 H, H), 1.45 (s, 6 H, acetyl), 1.44 (s, 6 H, acetyl), −0.15 (broad, 6 H, acetyl), −0.68 (s, 6 H, acetyl). **Zn-1c**: ^{1}H NMR ($CDCl_3$) δ (ppm) 8.71 (d), 8.64 (d), 8.58 (m), 8.52 (m) (8 H, pyr), 7.94 (d), 7.69 (m), 7.58 (m), 7.40 (d), 7.28 (m) (16 H, H_6, H_4, H_5, H_3 phenyl), 5.35 (d, 1 H, H_1 ose, J = 8 Hz), 5.31 (d, 1 H, H_1 ose, J = 8 Hz), 5.18 (d, 1 H, H_1 ose, J = 8 Hz), 5.12 (d, 1 H, H_1 ose, J = 8 Hz), 5.10 (m), 4.81 (m), 4.62 (m), 4.50 (m), 4.39 (m), 4.28 (m), 3.98 (m), 3.31 (m) (24 H, H_2, H_3, H_4, H_5, H_{6a}, H_{6b} oses), 2.21 (s, 3 H, acetyl), 2.17 (s, 3 H, acetyl), 2.15 (s, 3 H, acetyl), 2.00 (s, 3 H, acetyl), 1.99 (s, 3 H, acetyl), 1.97 (s, 3 H, acetyl), 1.93 (s, 3 H, acetyl), 1.80 (s, 3 H, acetyl), 1.71 (s, 3 H, acetyl), 1.68 (s, 3 H, acetyl), 1.62 (s, 3 H, acetyl), 1.31 (s, 3 H, acetyl), 0.86 (broad s, 3 H, acetyl), 0.47 (s, 3 H, acetyl), 0.22 (s, 3 H, acetyl), −0.97 (s, 3 H, acetyl).

Zinc-5,10,15,20-Tetrakis[2-(2,3,6,2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)phenyl]porphyrin (Zn-3). Zinc complex **Zn-3** was prepared and purified as previously described[14] in $CHCl_3$ under reflux in the presence of zinc chloride in methanol. ^{1}H NMR ($CDCl_3$) δ (ppm) 8.78 (m, 1 H, pyr), 8.70 (m, 2 H, pyr), 8.61 (d 1 H, pyr), 8.58 (d, 1 H, pyr), 8.53 (m 2 H, pyr), 8.41 (m, 1 H, pyr), 7.86 (dt, 2 H), 7.16 (m, 6 H), 7.50 (t, 4 H), 7.35 (m, 4 H) (H phenyl), 5.34–3.63 (m) (56 H, H_1, H_2, H_3, H_4, H_5, H_{6a}, H_{6b} oses), 2.27 to 1.77 (57 H, acetyl), 1.66 to −0.59 (27 H, acetyl). Anal. Calcd for $C_{148}H_{164}N_4O_{72}Zn\cdot 5H_2O$: C, 53.76; H, 5.30; N, 1.69. Found: C, 53.72; H, 5.14; N, 1.89.

Acknowledgment. This work was supported by the Centre de la Recherche Scientifique and Institut National de la Santé et de la Recherche Médicale.