Glycoconjugated Porphyrins. 3. Synthesis of Flat Amphiphilic Mixed *meso*-(Glycosylated aryl)arylporphyrins and Mixed *meso*-(Glycosylated aryl)alkylporphyrins Bearing Some Mono- and Disaccharide Groups

Dalila Oulmi,[†] Philippe Maillard,[†] Jean-Luc Guerquin-Kern,[‡] Christiane Huel,[‡] and Michel Momenteau*,[†]

Institut Curie, Section de Biologie, URA 1387 CNRS, Bât 112, Centre Universitaire, 91405 Orsay, France, and Institut Curie, Section de Biologie, U 350 INSERM, Bât 112, Centre Universitaire, 91405 Orsay, France

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p-Acetylglycosylated benzaldehydes react with pyrrole by Lindsey's method to produce a variety of flat glycosylated porphyrins. By the same method a large series of amphiphilic mixed glycosylated arylaryl- and mixed glycosylated arylalkylporphyrins have been synthesized, using pyrrole, *p*-acetylglycosylated benzaldehyde and aryl aldehyde or alkyl aldehyde as starting materials. Under optimized conditions, the di- or triglycosylated derivatives were principally obtained whereas the formation of *meso* tetrasubstituted porphyrins is minimized. Deprotection of acetyl glycoside moieties allows us to obtain products with good solubility in neutral aqueous solution and a wide range of amphiphilic character. The structure of these new protected and unprotected compounds in solution was confirmed by ^{1}H NMR studies.

Introduction

The construction of water soluble superstructured porphyrins with predictable, well defined structures is essential to the preparation of new, designed compounds to serve as models of hemoprotein active sites, as well as photoactive molecules. Rapid progress has been made in the quest for glycosylated porphyrins during the last 5 years, owing to the development of catalysts for dioxygen activation[1] and of new photosensitizers[2] for cancer photochemotherapy. Recently, we became interested in the synthesis of neutral glycosylated porphyrins derived from 5,10,15,20-*meso*-tetraphenylporphyrin in which mono- or disaccharide moieties are linked at the *ortho* positions of the phenyl groups.[3] Metallic complexes of their acetylated derivatives are proven active catalysts for alkene epoxidation with asymmetric induction, due to the presence of chiral sugar substituents in the vicinity of the metal center.[1] Their deprotected, neutral derivatives exhibit neither toxicity nor phototoxicity against tumoral cells.[4] A possible explanation could be that the globular structure of the molecules prevents suitable cell penetration. Thus, we turned our attention to the preparation of flat *meso*-tetrakis(glycosylated aryl)porphyrins, mixed *meso*-tetrakis[(glycosylated aryl)aryl]porphyrins, and mixed *meso*-tetrakis[(glycosylated aryl)alkyl]porphyrins in which mono- or disaccharide moieties are linked at the *para* positions of the *meso*-phenyl groups. In such compounds, electron density, hydrophilicity, and lipophilicity, which are pertinent physical properties to the use of dyes as potential agents in photodynamic therapy,[5] can be easily modulated by changing the nature and the number of saccharide substituents. Furthermore, the presence of lipophilic *meso*-phenyl or *meso*-pentafluorophenyl groups or *meso*-alkyl substituents could increase the interactions of dyes with the lipid parts of cell membranes whereas the glycosyl moieties could be functional components involved in cell recognition.[6] This paper describes the synthesis and characterization of such flat glycosylated porphyrins.

Results and Discussion

The synthesis of all porphyrins requires the condensation of pyrrole and *para*-glycosylated benzaldehyde in which hydroxyl functions of sugars are protected by suitable groups. The latter may be easily cleaved to afford the water soluble compounds without even partial destruction of the sugar moieties. This was achieved by using acetyl as a protecting group, which can be removed

[†] Institut Curie, URA 1387 CNRS.

[‡] Institut Curie, U 350 INSERM.

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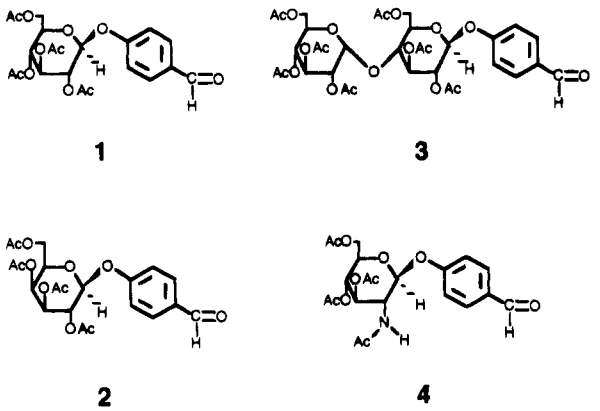
Chart 1



by treating the products with sodium methanolate in dry methanol.[7] Such a treatment does not change the β configuration of the anomeric carbon of sugars.[8] Water-soluble unprotected glycosylated porphyrins were purified by gel chromatography on Sephadex LH 20 or by anion exchange on amberlite resin MB-3. *p*-Glycosylbenzaldehydes (Chart 1) were prepared according to the classical Halazy procedure.[9] 4-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucosyl)benzaldehyde (**4**) was obtained by condensation, in the presence of potassium *tert*-butoxide in dry dimethylformamide (DMF),[10] of *p*-hydroxybenzaldehyde and α-chlorotetraacetylglucosamine,[11] previously prepared by treatment of *N*-acetylglucosamine with acetyl chloride. The pure β anomer of compound **4** was obtained by simple crystallization from chloroform/heptane.

Tetrakis(glycosylated aryl)porphyrins 5–12. The condensation of benzaldehyde substituted by peracetylglucose, -galactose, -maltose, and -glucosamine (**1–4**) with pyrrole under Lindsey's conditions[12] gave *meso*-tetrakis(*p*-tetraglycosylated aryl)porphyrins **5–8** (Chart 2). They were then purified by chromatography on a silica gel column and individually identified by ^{1}H NMR spectroscopy. The porphyrins were obtained in 28, 20, 12, and 15% yields, respectively. Whereas porphyrins **5**, **6**, and **8** bearing peracetyl monosaccharides are very soluble in nonpolar solvents exclusively, porphyrin **7** is poorly soluble in these solvents. The unprotected tetramonosaccharide compounds **9**, **10**, and **12** obtained from **5–8** by treatment with sodium methanolate in dry methanol[7] are soluble in alcohol and weakly soluble in neutral water. In contrast, the tetramaltosyl derivative **11** is very soluble in aqueous solution, even at high concentration.

Poly(glycosylated aryl)phenylporphyrins 13–16 (Chart 3). In order to obtain mono-, bis-, and tris[*p*-(2,3,4,6-tetraacetyl-β-D-glucosyloxy)phenyl]tri-, di-, and monophenylporphyrins **13**, pyrrole was condensed with a mixture of benzaldehyde and *p*-(2,3,4,6-tetraacetyl-β-D-glucosyloxy)benzaldehyde (**1**) in relative proportions of 4/2/2 under the same conditions as those used for the synthesis of the tetraacetylglycosyl derivatives **5–8**. The overall yield of porphyrins was 31%. These reaction conditions minimized the formation of the tetraphenylporphyrin (2.8%) and the tetraglucosylated compound **5** (5%). The other porphyrins were obtained in 3.7% yield for $\mathbf{13}_5$, 4.3 and 5.6% yields for $\mathbf{13}_{5,10}$ and $\mathbf{13}_{5,15}$, respectively (or *vice versa*), and 9.7% yield for $\mathbf{13}_{5,10,15}$ after separation by preparative thin layer chromatography. The galactosylated porphyrins **14** were prepared by the same method. However, several attempts were made to preferentially produce the partially substituted tetraphenylporphyrins, which appeared to have the most potential as photosensitizers because of their amphiphilic properties. Thus, when the reaction was performed using pyrrole, benzaldehyde, and suitable glycosylated benzaldehyde in the relative proportions 4/1/3, analytical thin layer chromatography of the reaction mixture on silica gel plates indicated essentially four porphyrins. For example, under such conditions, simple TPP and a monosugar derivative were detected as traces whereas the di-, tri-, and tetragalactosyled porphyrins were obtained in 11.4 ($\mathbf{14}_{5,10}$ and $\mathbf{14}_{5,15}$), 13.4 ($\mathbf{14}_{5,10,15}$), and 8% (**6**) yields, respectively.

Poly(glycosylated aryl)alkylporphyrins (Chart 4). It has been shown for a number of tetrapyrrolic derivatives that the presence of alkyl side chains tends to increase the efficacy of dyes used for PDT.[13] This prompted us to investigate the preparation of mixed (glycosylated aryl)alkylporphyrins in which at least one of the four *meso* carbons of the macrocycle bears an alkyl side chain. We have selected two substituents of different lengths in order to modify the hydrophilicity of compounds: an *n*-undecyl chain and a butyl chain.

Since the first low yield preparation of *meso*-tetraalkylporphyrins reported by Treibs,[14] few examples have been described in the literature. Direct condensation of pyrrole and alkyl aldehyde under Lindsey's conditions[12b] gave tetraalkylporphyrins in lower yields than those of tetraarylporphyrins, but comparable to those obtained by a more elaborate procedure reported by Rocha Gonsalves.[15] More recently, Onaka *et al.* developed a much more efficient and reliable synthetic method for *meso*-tetraalkylporphyrins by using mineral clays as strong acid and reaction media.[16] In order to test the possibility of preparing mixed *meso*-arylalkylporphyrins, we have first synthesized the *meso*-tetrabutylporphyrin (**17**) and the *meso*-tetra-*n*-undecylporphyrin (**18**) (Chart 5) by condensation of pyrrole and *n*-pentanal or *n*-dodecanal in methylene chloride in the presence of BF_3/ether. Oxidation of porphyrinogens by chloranil afforded porphyrins **17** and **18** in satisfactory results (25% and 16.5%, respectively). For the preparation of mixed mono-, bis-, and tris(*meso*-glycosylated aryl)alkylporphyrins, pyrrole was condensed with a mixture of alkyl aldehyde and glycosylated benzaldehyde **1** or **3**. So, the condensation of pyrrole, pentanal, or *n*-dodecanal and *p*-(2,3,4,6-tetra-

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Chart 2

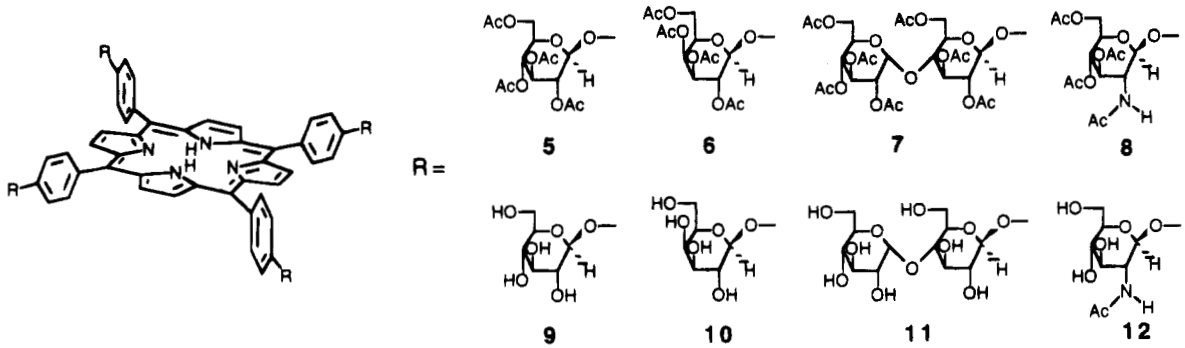


Chart 3

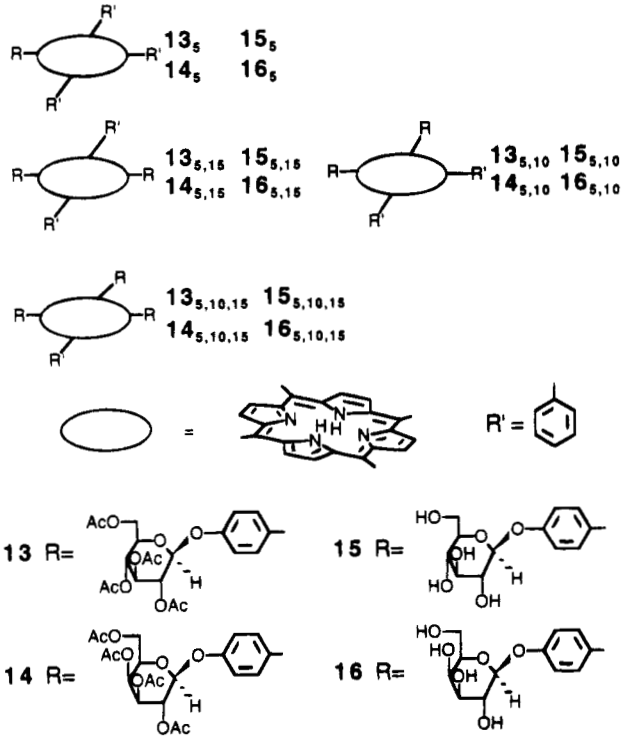
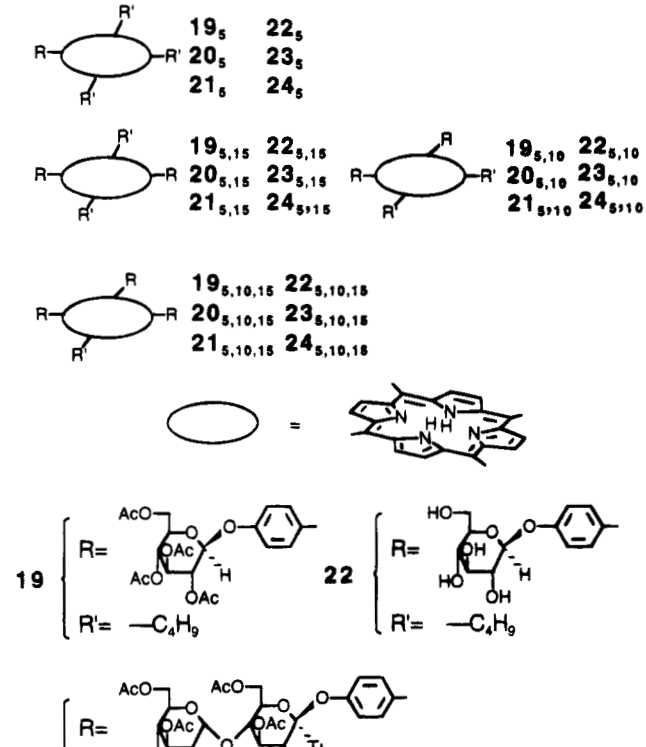


Chart 4



acetyl-β-D-glucosyl)benzaldehyde (**1**) or *p*-(2,3,6,2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)benzaldehyde (**3**) in methylene chloride in the presence of BF_3/ether gave a mixture of six porphyrins of which four were the *meso*-(glycosylated phenyl)alkylporphyrins **19**–**21**. The effects of addition order and timing of reagents and their relative proportion have been studied in order to increase the formation yields of the di- and triglycosylated compounds. Three experimental conditions were tested for the synthesis of compound **21**. In all cases, the reagents were added to methylene chloride as solvent under argon at 20 °C. After usual workup the products were separated on silica gel and individually characterized by ^1H NMR analysis. The yields are shown in Table 1. (i) In the first case, the reagents (pyrrole/*para*-glycosylated benzaldehyde/*n*-dodecanal) in relative proportions of 4/2/2 were simultaneously added to the solvent. (ii) The relative proportions of reagents were modified (4/3/1), and their addition was identical with procedure i. (iii) The third method entailed the addition of the *para*-glycosylated aldehyde 10 min before the *n*-dodecanal. The first method (i) led mainly to the formation of the *meso*-tetraalkyl and *meso*-trialkyl derivatives **18** and $\mathbf{21}_5$. The second (ii) and third (iii) procedures appear to give the triglycoconjugated compound $\mathbf{2}_{15,10,15}$ in better yields, 1.7 and 2.3%, respectively. Thus, the choice of reaction conditions allowed us to minimize the formation of the *meso*-tetrakis(*n*-undecyl)porphyrin **18** while the *meso*-tetrakis(glucosylphenyl)porphyrin **5** was always obtained in very small amounts. In the case of porphyrins bearing *n*-butyl

Chart 5

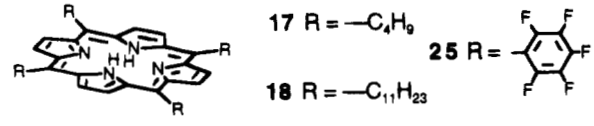
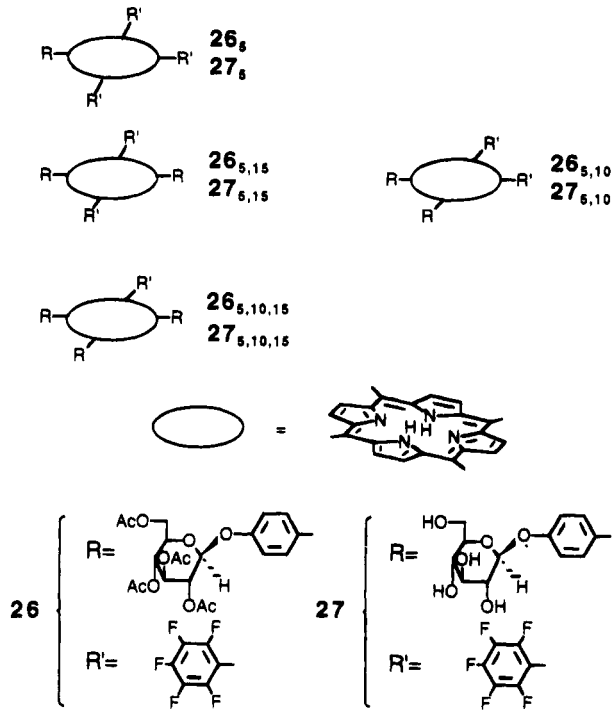


Table 1. Effects of Addition Order and Timing of Reagents on the Synthesis of Polyglucosylated Arylalkylporphyrins.

compd	method i,[a] yield (%)	method ii,[b] yield (%)	method iii,[c] yield (%)
18	4.6	1.9	1.4
21$_5$	4.8	2.1	1.7
21$_{5,10}$	1.8	1.3	1.8
21$_{5,15}$	1.2	1.1	1.7
21$_{5,10,15}$	traces	1.7	2.3
5	traces	traces	traces
total yield	12.4	8	9

[a] All reagents are simultaneously added. [b] Glucosylated aldehyde is added 10 min before *n*-dodecanal. [c] Ratio of reagents: glucosylaldehyde 1/*n*-dodecanal/pyrrole 3/1/4.

Chart 6



chains, the reaction conditions for macrocycle formation were those that gave the better yield of the triglycosylated porphyrin **19$_{5,10,15}$**, i.e., iii. The same method was used for the preparation of maltosyl compounds **20**. In this case, only **20$_5$**, **20$_{5,10}$** and **20$_{5,10,15}$** compounds were obtained in 7.2, 1.5, and 0.6% yields, respectively. The order of polarity of compounds determined by thin layer chromatography was the same in all families of compounds and increased with the number of glycosyl residues. For example, in the case of mixed *meso*-(glycosylatedphenyl)butylporphyrins, this order was **17** > **19$_5$** > **19$_{5,15}$** > **19$_{5,10}$** > **19$_{5,10,15}$** > **5**.

The unprotected saccharide compounds **22**–**24** were obtained by the same treatment used above for the preparation of tetraglycosylphenyl porphyrins **9**–**12**. The solubility of the different compounds in methanol or in water was largely dependent on the number of glycosyl groups and *meso*-alkyl substituents.

Poly(glycosylated aryl)(perfluorophenyl)porphyrins (Chart 6). The synthesis of mixed *meso*-(glucosylphenyl)(pentafluorophenyl) compound **26** was carried out using the condensation of *para*-glycosylated benzaldehyde **1** and pentafluorobenzaldehyde under the conditions of iii. This reaction gave the *meso*-tetrakis(pentafluorophenyl)porphyrin **25**, the triglucosylated derivative **26$_{5,10,15}$**, and the tetraglucosylated compound **5** in 0.5%, 2.5%, and 9.5% yields, respectively. The other theoretical products **26$_5$**, **26$_{5,10}$**, and **26$_{5,15}$** were obtained only as traces. Deprotection of compound **26$_{5,10,15}$** with sodium methanolate in dry ethanol gave **27$_{5,10,15}$** in 87% yield.

^{1}H NMR Characterization. ^{1}H-NMR spectroscopy (200 and 400 MHz) was used for the characterization of protected and unprotected compounds in $CDCl_3$ and pyridine-d_5 solution, respectively. Assignments of the resonances to individual protons are based on integration and selective homonuclear decoupling experiments. The general aspect of these spectra is similar to that of the *ortho*-glycosylated porphyrins previously studied[3b] except for the acetyl resonances of saccharide moieties which are not shifted downfield. This shows that the glycosylated substituents are not affected by the ring current of the macrocycle. The absence of the deshielding effects is consistent with a conformation of compounds in which the glycosylated substituents are located in the same plane of the porphyrin ring.

The NMR spectral properties are governed by the symmetry properties of the products allowing us to differentiate molecules from each other. Because of the D_{2h} symmetry of *meso*-tetralkylporphyrins and *meso*-tetraarylporphyrins, the resonances of the eight equivalent pyrrolic protons appear as single peaks at 9.45 ppm and 8.80 ppm, respectively.

In contrast, the pyrrolic proton resonances of mixed aryl alkyl compounds are more complicated. They depend on the number and the linking position of *meso* substituents (Figure 1). The comparison of the integrals of peaks of phenyl and β pyrrolic protons permits us to distinguish three classes of compounds bearing one (**19$_5$**–**24$_5$**), two (**19$_{5,10}$**–**24$_{5,10}$**, **19$_{5,15}$**–**24$_{5,15}$**), or three (**19$_{5,10,15}$**–**24$_{5,10,15}$**) phenyl groups. The symmetry of compounds **19$_{5,10}$** and **19$_{5,15}$** permits us to assign spectrum 1 (Figure 1) to the most symmetrical compound **19$_{5,15}$**. Thus, for this derivative, β pyrrolic protons give an AX spectrum, each resonance corresponding to four equivalent protons. The upfield shift of resonance for proton A at 8.7 ppm, near the phenyl group, was induced by important electronic contribution of this aromatic group. By analogy, the upfield resonances (near 9 ppm) of compound **19$_{5,10}$** are assigned to protons A and D. In this case the doublet or singlet forms of these resonances result from the symmetry of **19$_{5,10}$** which has a symmetry plane directed along the nitrogen atoms of the pyrroles bearing protons C and D. Such a difference between the chemical shifts of the pyrrolic protons C and D is a good argument to identify without ambiguity the isomers (**5**, **10**) and (**5**, **15**) in the glycosylated aryl alkyl series. In contrast to the spectra of mixed glycosylated aryl alkyl compounds, those of compounds **13$_{5,10}$** and **13$_{5,15}$** or **4$_{5,10}$** and **4$_{5,15}$** in mixed glycosylated aryl aryl series were identical. The eight pyrrolic protons appeared as a singlet near 8.85 ppm. This indicates that the glycosylated substituents do not appear to induce important electronic and/or steric contributions to modify the chemical shifts of the adjacent β pyrrolic protons. Thus, no differentiation between the two protons borne by the same pyrrole ring was observed. So the differentiation of the two isomers can been made only by comparison of their polarity as revealed by thin layer chromatography on silica gel plates with those of the two isomers of *meso*-(glycosyl aryl)alkyl compounds. We can postulate that the most polar compounds are the porphyrins **13$_{5,10}$** and **14$_{5,10}$** in which the glycosylated phenyls are adjacent.

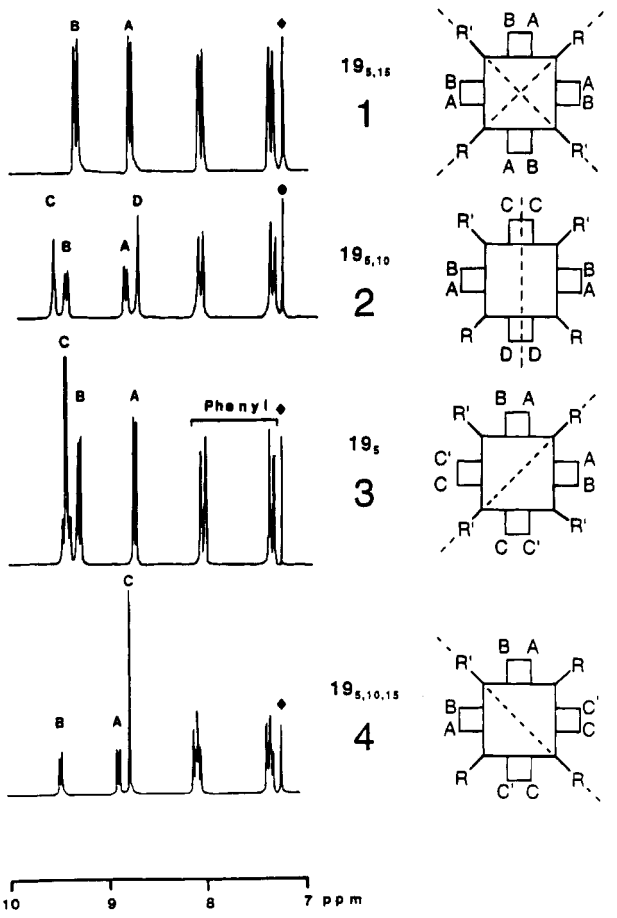


Figure 1. Low field part of the 200 MHz ^{1}H NMR spectra of compounds $\mathbf{19}_{5,15}$, $\mathbf{19}_{5,10}$, $\mathbf{19}_5$, and $\mathbf{19}_{5,10,15}$ in $CDCl_3$ at room temperature, ◆ $CHCl_3$. The diagrams indicate the molecular symmetry: R, 4-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl group; R′, *n*-butyl group; A–D, β pyrrolic protons.

Compounds $\mathbf{19}_5$ and $\mathbf{19}_{5,10,15}$ possess a symmetry plane defined by the differently substituted *meso*-positions. Thus, the pyrrolic proton resonances appear as two systems AX. In the case of monoglycosylated compounds, only A protons are shifted upfield by the electronic effect of the phenyl group. In contrast, the three phenyl substituents of triglycosylated derivatives induced an upfield shift for protons A, C, and C′. In spectrum 4 (Figure 1), protons C and C′, possessing a quasi-equivalent electronic environment, are accidentally equivalent.

Furthermore, the resonance of the C_1 proton of glycosyl substituents in all protected and unprotected porphyrins appears as well-defined doublets (J = 8 Hz) near 5.50 ppm in $CDCl_3$ and between 5.30 and 6 ppm in pyridine-d_5, respectively. This coupling constant indicates a pure β-configuration of the anomeric carbon of the sugars.[8]

Electronic Spectra. The electronic spectra of all compounds are very similar to those of known free base *meso*-5,10,15,20-tetraphenylporphyrins or *meso*-tetraalkylporphyrin, with a Soret band near 420 nm and four less intense Q bands near 520, 550, 595, and 655 nm (Table 2). But the introduction of *meso*-alkyl substituents instead of *meso*-aryl substituents markedly influences the absorption intensities of the Q bands I and II. The ratio $\epsilon I/\epsilon II$ of about 0.6 for compounds in the aryl series is weaker than in the alkyl series, between 1.7 and 2.7 depending on the nature of the alkyl groups. The ratio of the intensities of the Q bands I and II of mixed *meso*-5,10,15,20-tetraarylalkylporphyrins is intermediate between those of *meso*-tetraarylporphyrins and those of *meso*-tetraalkylporphyrins varying between 0.800 and 1.535. It is interesting to note that increasing the absorption maximum of the longest wavelength is an important property for an eventual application of compounds with alkyl groups in photodynamic therapy.

Conclusion

In this paper, we have described the synthesis and the characterization of mixed flat *meso*-(glycosylaryl)arylporphyrins or *meso*-(glycosylaryl)alkylporphyrins obtained by condensation of *para*-glycosylated benzaldehyde, benzaldehyde, or alkyl aldehyde with pyrrole using Lindsey's conditions. After the acetyl protecting groups were removed the porphyrins bearing one, two, and three glucopyranosyl, galactopyranosyl, maltosyl, or glucosaminosyl groups linked at the *para* position of the phenyl groups have relatively good solubility in aqueous solutions. Furthermore, the presence of *meso*-phenyl groups, *meso*-alkyl chains, or one *meso*-pentafluorophenyl substituent increases the lipophilicity of these compounds. An intensive study is now being carried out to correlate their *in vitro* photosensitizing efficacy with their chemical structure. The first results indicate that the degree of glycosylated substitution and the nature of lipophilic moieties strongly affect cell survival after photoactivation.[4] Among these new compounds, *meso*-butyl and *meso*-pentafluorophenyl derivatives showed the best antitumoral activities. Amphiphilic compounds $\mathbf{15}_{5,10,15}$, $\mathbf{22}_{5,10}$, $\mathbf{27}_{5,10,15}$ are better than HpD, taken as reference. These results are parallel to the previous observations with sulfonated derivatives of tetraphenylporphyrins[17] or phthalocyanines,[18] for which the most efficient photosensitizers for cell killing were those having a strong amphiphilic character.

Experimental Section

General. Methylene chloride and chloroform were distilled on potassium carbonate. All chemicals used were of reagent grade and were purchased from Aldrich or Fluka. Amberlite MB-3 ion exchange resin was purchased from Prolabo and was washed with methanol before use. Merck silica gel 60 (0.040–0.060 mm) was used for column chromatography. Merck precoated plates (silica gel 60, 2 mm) were used for preparative thin layer chromatography. Sephadex LH 20 was purchased from Pharmacia LKB. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. ^{1}H NMR spectra were obtained in the indicated deuteriated solvents with Brucker AM-200 and AM-400 instruments. Chemical shift values were given in ppm relative to TMS. Coupling constants were given in Hz. Optical spectra were recorded using a Varian DMS 200 spectrometer.

General Procedure for Synthesis of β-D-Glycosylbenzaldehydes. A solution of 4-hydroxybenzaldehyde (5.12 g, 42

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Table 2. UV–Vis Spectra of Glycosylated Porphyrins in Various Solvents

compd (solvent[a])	λ nm (ϵ mmol·L^{-1})	ratio ϵI/ϵII
5 (a)	421 (499.5), 517 (19.9), 553 (11.2), 592 (7), 648 (6)	0.857
9 (c)	417 (462.8), 516 (17.3), 552 (11.5), 590.5 (6.4), 646.5 (6.1)	0.953
6 (a)	421 (454.6), 517.5 (19.3), 554 (11.4), 592 (7.4), 648 (6.4)	0.865
10 (b)	417 (477), 515 (19.7), 551.5 (13.8), 592 (8.5), 648 (8.3)	0.976
7 (a)	421 (358.1), 517.5 (16.6), 553.5 (10.4), 592 (7), 648 (5.6)	0.800
11 (d)	417 (445), 517 (17.5), 554 (12.5), 590 (8.3), 645.5 (7.8)	0.939
11 (b)	413 (162), 523.5 (13.6), 561.5 (10.1), 594 (6.5), 650.5 (6.4)	0.984
8 (g)	421 (440.6), 517.5 (18.4), 554 (11.8), 592 (8.4), 649 (7.1)	0.845
12 (h)	429 (390.3), 517 (16.2), 553.5 (12), 596 (7.1), 651 (6.7)	0.943
13$_5$ (a)	419 (401.5), 515.5 (18.1), 551 (8.7), 590.5 (6.4), 646 (4.8)	0.750
13$_{5,10}$ (a)	419.5 (382), 516 (18.1), 551 (9.9), 590.5 (7.2), 647 (5.7)	0.791
13$_{5,15}$ (a)	419.5 (413.5), 516.5 (17.0), 552 (8.9), 591 (6.4), 646.5 (5.3)	0.828
13$_{5,10,15}$ (a)	420.5 (383.1), 516.5 (19.2), 552 (11.0), 591 (7.4), 647 (5.7)	0.770
14$_{5,10}$ (a)	419 (441), 516 (17.5), 552 (9), 592 (6), 646.5 (5)	0.833
14$_{5,15}$ (a)	419 (589), 516 (24.4), 551.5 (12.2), 591.5 (7.9), 646.5 (6.6)	0.835
14$_{5,10,15}$ (a)	420 (468.8), 516 (18.6), 552.5 (10), 592 (6.3), 648 (5.5)	0.873
15$_{5,10}$ (c)	417 (462.8), 516 (17.3), 552 (11.5), 590.5 (6.4), 646.5 (6.1)	0.953
15$_{5,15}$ (b)	415 (415.6), 513.5 (17.5), 549 (8), 590 (4.5), 646 (3.6)	0.800
15$_{5,10,15}$ (b)	416 (440.4), 514 (17.4), 550 (10.6), 591 (6.1), 647 (5.6)	0.918
16$_{5,10,15}$ (b)	416.5 (411.5), 515 (16.7), 551 (10), 591 (5.7), 647.5 (5.2)	0.912
17 (a)	418 (376), 520 (13.3), 555 (8.9), 601 (3.8), 659 (6.6)	1.737
18 (a)	419 (350), 521 (10.6), 555 (6.9), 602 (1.8), 659 (4.8)	2.667
19$_5$ (a)	419 (418), 519 (15.7), 554 (9.7), 597 (4.3), 655 (6.6)	1.535
19$_{5,10}$ (a)	419 (429), 519 (15.7), 554 (9.2), 596 (4.5), 650 (5.5)	1.222
19$_{5,15}$ (a)	419 (437), 518 (18.4), 554 (10.6), 596 (5.2), 652 (6.9)	1.327
19$_{5,10,15}$ (a)	429 (419), 518 (16.7), 553 (9.4), 594 (5), 650 (5.2)	1.040
20$_5$ (a)	420 (446), 520 (17.2), 555 (10.8), 598 (4.8), 655 (7.2)	1.500
20$_{5,10}$ (a)	419 (388), 518 (15.8), 553 (9.3), 596 (4.5), 652 (5.8)	1.289
20$_{5,10,15}$ (a)	419 (405), 518 (16.1), 553 (9.2), 595 (4.6), 649 (5)	1.087
21$_5$ (a)	419 (392), 517 (17.8), 553 (10.5), 596 (5.3), 652 (7.2)	1.358
21$_{5,10}$ (a)	419 (427), 519 (16.1), 554 (9.9), 596 (5.1), 653 (6.2)	1.216
21$_{5,15}$ (a)	419 (376), 518 (17.2), 554 (10.1), 596 (5.1), 652 (6.9)	1.353
21$_{5,10}$ (a)	419 (419), 517 (16.7), 553 (9.7), 594 (5.5), 645 (6.1)	1.109
26$_{5,10,15}$ (a)	419 (410), 514 (27.4), 549 (12.5), 589 (9.8), 645 (6.3)	0.642
22$_{5,10}$ (i)	418 (346), 518 (13.7), 553 (8.8), 598 (3.9), 655 (4.9)	1.256
22$_{5,10,15}$ (f)	416 (399), 516 (15.2), 552 (9.4), 592 (4.6), 649 (4.8)	1.043
23$_{5,10}$ (i)	418 (351), 518 (14.1), 552 (9), 598 (3.9), 655 (5.1)	1.308
24$_{5,10}$ (i)	418 (346), 518 (13.7), 553 (8.8), 598 (3.9), 655 (5)	1.282
24$_{5,10,15}$ (e)	416 (222), 516 (10.4), 552 (7.2), 591 (4.7), 645 (5.3)	1.228
27$_{5,10,15}$ (b)	416 (364), 513 (16.2), 549 (7.2), 589 (5.1), 645 (3)	0.559

[a] The solvents used are as follows: (a) $CHCl_3$, (b) MeOH, (c) MeOH/H_2O (1/4, v/v); (d) MeOH/H_2O (1/1, v/v); (e) MeOH/H_2O (24/1, v/v); (f) MeOH/H_2O (2/1, v/v), (g) $CHCl_3$, 1% pyridine; (h) THF/H_2O (1/1, v/v); (i) THF/H_2O (23/2, v/v).

$\times 10^{-3}$ mol) in methylene chloride (50 mL) was vigorously stirred at room temperature with an aqueous solution of sodium hydroxide (5%, 70 mL) and tetrabutylammonium bromide (2.26 g, 7×10^{-3} mol). To this stirred mixture was added a solution of protected α-D-glycosyl bromide (28×10^{-3} mol) in methylene chloride (20 mL) at room temperature. Stirring was continued for 3 days. After separation, the organic phase was washed with aqueous sodium hydroxide solution (5%, 2 × 20 mL) and water and then dried over sodium sulfate, filtered, and evaporated in vacuum.

4-(2,3,4,6-Tetraacetyl-β-D-glucopyranosyl)benzaldehyde (1). The crude yellow oil was chromatographed on a silica gel column using a mixture of ethyl acetate/hexane (4/1, v/v) affording the pure product after crystallization from methylene chloride/hexane (5.53 g, 49%). Anal. Calcd for $C_{21}H_{24}O_{11}$: C, 55.75; H, 5.35. Found: C, 55.90; H, 5.31. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.93 (s, 1H, CHO), 7.84 (d, 2H, *o*-phenyl, J = 8 Hz), 7.10 (d, 2H, *m*-phenyl, J = 8 Hz), 5.26 (m, 5H, "ose"), 4.21 (m, 2H, "ose"), 2.05 (s, 12H, acetyl).

4-(2,3,4,6-Tetraacetyl-β-D-galactopyranosyl)benzaldehyde (2). Yield: 3.80 g, 60%. Anal. Calcd for $C_{21}H_{24}O_{11}$: C, 55.75; H, 5.35. Found: C, 56.02; H, 5.41. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.89 (s, 1H, CHO), 7.82 (d, 2H, *o*-phenyl, J = 8.6 Hz), 7.10 (d, 2H, *m*-phenyl, J = 8.6 Hz), 5.47 (m, 2H, C_2, C_4, "ose"), 5.17 (d, 1H, C_1 "ose", J = 8 Hz), 5.13 (m, 1H, C_3, "ose"), 4.14 (m, 3H, C_5, C_6, "ose"), 2.15 (s, 3H, acetyl), 2.03 (s, 6H, acetyl), 2.00 (s, 3H, acetyl).

4-(2,3,6-2′,3′,4′,6′-Heptaacetyl-β-D-maltosyl)benzaldehyde (3). The pure product (7.590 g) was obtained by chromatography (ethyl acetate/hexane, 1/1, v/v) in 36% yield. Anal. Calcd for $C_{33}H_{40}O_{18}$·$2H_2O$: C, 52.11; H, 5.83. Found: C, 51.73; H, 5.50. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.92 (s, 1H, CHO), 7.84 (dd, 2H, *o*-phenyl, J = 8 Hz), 7.15 (dd, 2H, *m*-phenyl, J = 8 Hz), 5.42–5.0 (m, 7H, "ose"), 4.60–3.90 (m, 7H, "ose"), 2.10 (s, 3H, acetyl), 2.08 (s, 3H, acetyl), 2.07 (s, 3H, acetyl), 2.06 (s, 3H, acetyl), 2.04 (s, 3H, acetyl), 2.03 (s, 3H, acetyl), 2.01 (s, 3H, acetyl).

4-(2-Acetamido-3,4,6-triacetyl-2-deoxy-β-D-glucosyl)benzaldehyde (4). 4-Hydroxybenzaldehyde (3.120 g, 25.6×10^{-3} mol) was added to a suspension of potassium *tert*-butoxide (3.40 g, 30×10^{-3} mol) in dry dimethylformamide (160 mL). After the mixture was stirred for 30 min, α-chlorotetraacetylglucosamine (12 g, 33×10^{-3} mol) was added, and the mixture was stirred overnight at room temperature under argon. The red solution was filtered and then concentrated under vacuum. The residue was dissolved in methylene chloride and washed twice with NaOH aqueous solution (5%) and water. The organic phase was dried on sodium sulfate and filtered, and the solvent was evaporated. The crude product was crystallized from a mixture of chloroform/heptane (2.300 g, 20%), mp 131 °C. Anal. Calcd from $C_{21}H_{25}NO_{10}$: C, 55.87; H, 5.58; N, 3.10. Found: C, 55.43; H, 5.40; N, 3.06. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.89 (s, 1H, CHO), 9.43 (d, 1H, NH, J = 8.3 Hz), 7.89 (dd, 2H, *o*-phenyl, Jo = 9.4 Hz, Jm = 2 Hz), 7.34 (dd, 2H, *m*-phenyl, Jo = 9.4 Hz, Jm = 2 Hz), 6.14 (d, 1H, C_1 "ose", J = 8.5 Hz), 6.08 (d, 1H, C_3 "ose", J = 9 Hz), 5.56 (t, 1H, C_4 "ose", J = 9.5 Hz), 4.67 (q, 1H, C_2 "ose", J = 8.4 Hz), 4.58–4.43 (m, 2H, C_6 "ose"), 4.37 (m, 1H, C_5 "ose"), 2.27 (s, 3H, acetyl), 2.25 (s, 3H, acetyl), 2.22 (s, 3H, acetyl), 2.20 (s, 3H, *N*-acetyl).

General Procedure for Synthesis of 5,10,15,20-Tetrakis[(acetyl-β-D-glycosyl)phenyl]porphyrins. Pyrrole (0.148 g, 2.2×10^{-3} mol) in methylene chloride solution (22 mL) and protected β-D-glycosyl aldehyde (2.2×10^{-3} mol) in methylene chloride (22 mL) were added to methylene chloride containing

ethanol (0.75%) (200 mL) purged by argon for 30 min. The mixture was purged by argon for 10 min more after which a BF_3–etherate solution (100 μL, 0.5M) in methylene chloride was added. The mixture was stirred overnight at room temperature. Chloranil (0.4 g, 1.63×10^{-3} mol) was added. After reflux for 1 h, silica gel (10 g) was added to the dark solution and all solvent was evaporated. The absorbed products were placed on the top of a silica gel column.

5,10,15,20-Tetrakis[4-(2,3,4,6-tetracetyl-β-D-glucosyl)phenyl]porphyrin (5). The crude products were eluted with a mixture of methylene chloride/ether (1/1, v/v). The red band was collected and purified by thin layer chromatography eluted twice with chloroform/acetone (10/1, v/v). The porphyrin **5** was crystallized from methylene chloride/hexane (0.240 g, 28%). Anal. Calcd for $C_{100}H_{102}N_4O_{40}$: C, 60.06; H, 5.14; N, 2.80. Found: C, 60.06; H, 5.00; N, 2.75. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.86 (s, 8H, pyr), 8.14 (d, 8H, *o*-phenyl, J = 8 Hz), 7.40 (d, 8H, *m*-phenyl, J = 8 Hz), 5.47 (m, 12H, C_1, C_2, C_3 "ose"), 5.33 (m, 4H, C_4 "ose"), 4.43–4.32 (m, 8H, C_6 "ose"), 4.07 (m, 4H, C_5 "ose"), 2.23 (s, 12H, acetyl), 2.14 (s, 12H, acetyl), 2.13 (s, 12H, acetyl), 2.12 (s, 12H, acetyl), −2.79 (s, 2H, NH).

5,10,15,20-Tetrakis[4-(2,3,4,6-tetraacetyl-β-D-galactosyl)phenyl]porphyrin (6). The absorbed products were eluted with a mixture of methylene chloride/acetone (5/1, v/v). The red band was collected and purified on a silica gel column using a mixture of methylene chloride/acetone (10/1, v/v) affording the title product (0.220 g, 20%) after crystallization from methylene chloride/hexane. Anal. Calcd for $C_{100}H_{102}N_4O_{40}$: C, 60.06; H, 5.14; N, 2.80. Found: C, 59.75; H, 5.37; N, 2.76. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 8H, pyr), 8.13 (d, 8H, *o*-phenyl, J = 8 Hz), 7.39 (d, 8H, *m*-phenyl, J = 8 Hz), 5.70 (dd, 4H, C_2 "ose", J_{1-2} = 8 Hz, J_{2-3} = 10 Hz), 5.57 (dd, 4H, C_4 "ose", J_{4-3} = 3.4 Hz), 5.42 (d, 4H, C_1 "ose", J_{1-2} = 8 Hz), 5.24 (dd, 4H, C_3 "ose, J_{3-2} = 10 Hz, J_{3-4} = 3.4 Hz), 4.35 (m, 8H, C_6 "ose"), 4.25 (m, 4H, C_5 "ose"), 2.26 (s, 12H, acetyl), 2.23 (s, 12H, acetyl), 2.08 (s, 12H, acetyl), 2.07 (s, 12H, acetyl), −2.81 (s, 2H, NH).

5,10,15,20-Tetrakis[4-(2,3,6-2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)phenyl]porphyrin (7). The absorbed products were eluted with a mixture of methylene chloride/acetone (5/1, v/v). The red band was collected and was purified by preparative thin layer chromatography eluted twice with methylene chloride/acetone (5/1, v/v). The pure product was crystallized from methylene chloride/hexane (0.187 g, 10%). Anal. Calcd for $C_{148}H_{166}N_4O_{72}$: C, 56.38; H, 5.31; N, 1.78. Found: C, 55.54; H, 5.41; N, 1.54. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.86 (s, 8H, pyr), 8.15 (d, 8H, *o*-phenyl, J = 8 Hz), 7.39 (d, 8H, *m*-phenyl, J = 8 Hz), 5.46–4.10 (m, 56H, "ose"), 2.20, 2.17, 2.15, 2.12, 2.11, 2.09, 2.05, 2.03 (s, 84H, acetyl), −2.79 (s, 2H, NH).

5,10,15,20-Tetrakis[4-(2-acetamido-3,4,6-triacetyl-2-deoxy-β-D-glucosyl)phenyl]porphyrin (8). The crude products were eluted with a mixture of acetone/methylene chloride (2/1, v/v). The pure product was crystallized from pyridine/chloroform/heptane (0.164g, 15%). Anal. Calcd for $C_{100}H_{106}N_8O_{36}$: C, 60.18; H, 5.35; N, 5.61. Found: C, 58.22; H, 5.43; N, 6.34. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.64 (d, 4H, NHAc "ose", J = 8.4 Hz), 9.02 (s, 8H, pyr), 8.29 (d, 8H, *o*-phenyl, J = 8.4 Hz), 7.77 (d, 8H, *m*-phenyl, J = 8.4 Hz), 6.40 (d, 4H, C_1 "ose", J = 8.4 Hz), 6.24 (t, 4H, C_3 "ose", J = 9.7 Hz), 5.70 (t, 4H, C_4 "ose", J = 9.7 Hz), 4.95 (m, 4H, C_2 "ose"), 4.71 (dd, 4H, C_6 "ose"), 4.53 (m, 8H, C_5, C_6 "ose"), 2.22 (s, 12H, acetyl), 2.14 (s, 12H, acetyl), 2.08 (s, 12H, acetyl), 2.07 (s, 12H, acetyl), −2.37 (s, 2H, NH).

General Procedure for Synthesis of 5,10,15,20-Tetrakis(4-β-D-glycosylphenyl)porphyrins 9–12. Sodium methanolate in dry methanol (100 μL, 0.1 N) was added to a solution of protected glycosylated porphyrin (4.5×10^{-5} mol) in dry methanol (10 mL). The mixture was stirred for 60 min at room temperature.

5,10,15,20-Tetrakis(4-β-D-glucosylphenyl)porphyrin (9). After solvent reduction under vacuum, the crude product was purified by gel filtration on a Sephadex LH20 column eluted with a mixture of methanol/water (5/1, v/v). The pure product was crystallized from methanol/water (53 mg, 88%). Anal. Calcd for $C_{68}H_{68}N_4O_{24}\cdot 3H_2O$: C, 59.16; H, 5.36; N, 4.05. Found: C, 58.97; H, 5.46; N, 4.05. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.04 (s, 8H, pyr), 8.27 (d, 8H, *o*-phenyl, J = 8 Hz), 7.81 (d, 8H, *m*-phenyl, J = 8 Hz), 7.98 broad (4H, OH "ose"), 7.50 broad (4H, OH "ose"), 6.90 broad (4H, OH "ose"), 6.01 (d, 4H, C_1 "ose", J = 8 Hz), 4.74–4.54 (m, 8H, C_6 "ose"), 4.50 (m, 4H, C_2 "ose", 4H, C_3 "ose", 4H, C_4 "ose"), 4.35 (m, 4H, C_5 "ose"), −2.37 (s, 2H, NH).

5,10,15,20-Tetrakis(4-β-D-galactosylphenyl)porphyrin (10). After solvent reduction under vacuum, the crude solution was purified by gel filtration on a Sephadex LH20 column eluted with methanol. The desired product was crystallized from methanol/methylene chloride (53 mg, 88%). Anal. Calcd for $C_{68}H_{68}N_4O_{24}\cdot 6H_2O$: C, 56.98; H, 5.63; N, 3.91. Found: C, 57.07; H, 5.56; N, 3.89. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.00 (s, 8H, pyr), 8.23 (d, 8H, *o*-phenyl, J = 8 Hz), 7.79 (d, 8H, *m*-phenyl, J = 8 Hz), 7.80 (s, 4H, OH, C_2 "ose"), 7.12 (d, 4H, OH, C_3 "ose", J = 6 Hz), 6.92 (t, 4H, OH, C_6 "ose", J = 6 Hz), 6.74 (d, 4H, OH, C_4 "ose", J = 4 Hz), 5.92 (d, 4H, C_1 "ose", J = 8 Hz), 4.99 (m, 4H, C_2 "ose"), 4.74 (m, 4H, C_4 "ose"), 4.64 (m, 8H, C_3, C_5 "ose"), 4.60 (m, 8H, C_6 "ose"), −2.40 (s, 2H, NH).

5,10,15,20-Tetrakis(4-β-D-maltosylphenyl)porphyrin (11). After solvent reduction under vacuum, the crude product was purified by gel filtration on a Sephadex LH20 column eluted by methanol. The title product was crystallized from methanol/1,2-dichloroethane (85 mg, 96%). Anal. Calcd for $C_{92}H_{108}N_4O_{44}\cdot 7CH_2ClCH_2Cl$: 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) 9.03 (s, 8H, pyr), 8.26 (d, 8H, *o*-phenyl, J = 8 Hz), 7.76 (d, 8H, *m*-phenyl, J = 8 Hz), 6 (m, 4H, C_1 "ose"), 4.59–4.25 (m, 52H, "ose"), −2.39 (s, 2H, NH).

5,10,15,20-Tetrakis[4-(2-acetamido-2-deoxy-β-D-glucosyl)phenyl]porphyrin (12). This compound was prepared according the general procedure described above from porphyrin **8**. Amberlite MB-3 ion exchange resin (2 g) was added to the red solution. The mixture was stirred for 15 min and filtered. Resin was washed with methanol and then a mixture of THF/water (1/1, v/v). After solvent evaporation under vacuum, the crude product was crystallized from pyridine/1,2-dichloroethane (35 mg, 97%). Anal. Calcd for $C_{76}H_{82}N_8O_{24}$: C, 61.12; H, 5.67; N, 7.50. Found: C, 54.90; H, 5.61; N, 7.70. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.29 (d, 4H, NHAc "ose", J = 8.5 Hz), 8.93 (s, 8H, pyr), 8.22 (d, 8H, *o*-phenyl, J = 8.4 Hz), 7.80 (d, 8H, *m*-phenyl, J = 8.4 Hz), 6.19 (d, 4H, C_1 "ose", J = 8.4 Hz), 5.03 (q, 4H, C_3 "ose", J = 9.5 Hz), 4.70 (t, 8 H, "ose", J = 8.7 Hz), 4.44 (m, 8H, "ose"), 4.32 (m, 4H, "ose"), 2.22 (s, 12H, *N*-acetyl), −2.40 (s, 2H, NH).

5,10,15,20-Mono-, Bis- or Tris[4-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]tri, -di- or -monophenylporphyrins (13). Pyrrole (0.430 g, 6.4×10^{-3} mol), 4-(2,3,4,6-tetraacetyl-β-D-glucopyranosyl)benzaldehyde (**1**) (1.412 g, 3.12×10^{-3} mol), and benzaldehyde (0.330 g, 3.12×10^{-3} mol) each in chloroform solution (65 mL), were added to chloroform (500 mL) purged by argon for 30 min. The mixture was stirred and purged by argon for a further 10 min after which a BF_3·etherate solution (250 μL, 0.5 M) in chloroform was added. This reaction mixture was stirred overnight at room temperature. Chloranil (1.140 g, 4.63×10^{-3} mol) was then added. After reflux for 1 h, silica gel (10 g) was added to the dark solution and the solvent was evaporated. The absorbed products were placed on the top of a silica gel column. The porphyrin mixture was eluted successively with pure methylene chloride to give TPP as the first red band (30 mg, 2.8%), with a mixture of methylene chloride/ether (10/1, v/v) to give monoglucosylated compound $\mathbf{13}_5$, with a mixture of methylene chloride and ether (5/1, v/v) to give di "ose" products $\mathbf{13}_{5,10}$ and $\mathbf{13}_{5,15}$, and with methylene chloride/ether (2/1, v/v) to give tri "ose" product $\mathbf{13}_{5,10,15}$. Finally, the tetraglucosylated porphyrin **5** was eluted with a mixture of methylene chloride/acetone (3/1, v/v). All products were separately purified by preparative thin layer chromatography, eluted with methylene chloride/ether (15/1, v/v) for $\mathbf{13}_5$, with methylene chloride/ether (15/1, v/v, three elutions) for $\mathbf{13}_{5,10}$, with methylene chloride/ether (2/1, v/v, two elutions) for $\mathbf{13}_{5,15}$ and $\mathbf{13}_{5,10,15}$, and then with a mixture of methylene chloride/acetone (5/1, v/v, two elutions) for **5**. All porphyrins were crystallized from methylene chloride/heptane

and washed with pure heptane in order to remove the traces of chloranil: $\mathbf{13_5}$ (55 mg, 3.7%), $\mathbf{13_{5,15}}$ (89 mg, 4.3%), $\mathbf{13_{5,10}}$ (116 mg, 5.6%), $\mathbf{13_{5,10,15}}$ (255 mg, 9.7%), and **5** (165 mg, 5%). $\mathbf{13_5}$. Anal. Calcd for $C_{58}H_{48}N_4O_{10}\cdot 0.5H_2O$: C, 71.75; H, 5.05; N, 3.94. Found: C, 71.40; H, 4.99; N, 5.71. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 8H, pyr), 8.59 (m, 3H, *p*-phenyl), 8.22 (d, 6H, *o*-phenyl, J = 8 Hz), 8.15 (d, 2H, *o*-phenyl "ose", J = 8 Hz), 7.78 (m, 6H, *m*-phenyl), 7.41 (d, 2H, *m*-phenyl "ose", J = 8 Hz), 5.48–5.33 (m, 4H, C_1, C_2, C_3, C_4 "ose"), 4.39 (m, 2H, C_6 "ose"), 4.07 (m, 1H, C_5 "ose"), 2.25 (s, 3H, acetyl), 2.11, 2.10 (s, 9H, acetyl), −2.75 (s, 2H, NH). $\mathbf{13_{5,15}}$. Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot H_2O$: C, 65.25; H, 5.17; N, 4.23. Found: C, 65.54; H, 5.17; N, 3.87. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 8H, pyr), 8.6 (m, 4H, *o*-phenyl), 8.15 (d, 4H, *o*-phenyl "ose", J = 8 Hz), 7.39 (d, 4H, *m*-phenyl "ose", J = 8 Hz), 8.22 (d, 2H, *p*-phenyl, J = 8 Hz), 7.78 (m, 4H, *m*-phenyl), 5.48 (m, 6H, C_1, C_2, C_3 "ose"), 5.33 (m, 2H, C_4 "ose"), 4.35 (m, 4H, C_6 "ose"), 4.07 (m, 2H, C_5 "ose") 2.23, 2.14, 2.13 (s, 24H, acetyl), −2.75 (s, 2H, NH). $\mathbf{13_{5,10}}$. Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 7H_2O$: C, 60.78; H, 5.63; N, 3.94. Found: C, 60.15; H, 4.93; N, 2.72. ^{1}H NMR ($CDCl_3$): δ(ppm) 8.86 (d, 8H, pyr), 8.59 (m, 4H, *o*-phenyl), 8.22 (d, 2H, *p*-phenyl, J = 8 Hz), 8.12 (d, 4H, *o*-phenyl, J = 8 Hz), 7.78 (m, 4H, *m*-phenyl), 7.39 (d, 4H, *m*-phenyl, J = 8 Hz), 5.48 (m, 6H, C_1, C_2, C_3 "ose"), 5.33 (m, 2H, C_4 "ose"), 4.37 (m, 4H, C_6 "ose"), 4.07 (m, 2H, C_5 "ose"), 2.23, 2.07, 2.06 (s, 24H, acetyl), −2.78 (s, 2H, NH). $\mathbf{13_{5,10,15}}$. Anal. Calcd for $C_{88}H_{84}N_4O_{30}$: C, 63.00; H, 5.05; N, 3.34. Found: C, 65.32; H, 5.13; N, 3.92. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.87 (s, 8H, pyr), 8.15 (d, 6H, *o*-phenyl "ose", J = 8 Hz), 7.40 (d, 6H, *m*-phenyl "ose", J = 8 Hz), 8.53 (m, 1H, *p*-phenyl), 8.22 (d, 2H, *o*-phenyl, J = 8 Hz), 7.78 (m, 2H, *m*-phenyl), 5.48 (m, 9H, C_1, C_2, C_3 "ose"), 5.33 (d, 3H, C_4 "ose"), 4.39 (m, 6H, C_6 "ose"), 4.07 (m, 3H, C_5 "ose"), 2.23 (s, 9H, acetyl), 2.13 (s, 9H, acetyl), 2.11 (s, 18H, acetyl), −2.78 (s, 2H, NH).

5,15-Bis(4-β-D-glucosylphenyl)-15,20-diphenylporphyrin ($\mathbf{15_{5,15}}$). This compound was prepared according to the procedure described above for the preparation of compounds **9**–**12** from $\mathbf{13_{5,15}}$ (40 mg, 3×10^{-5} mol). It was purified by gel filtration on a Sephadex LH20 column eluted with a mixture of methanol/water (5/1, v/v). The pure product was crystallized from methanol/water (21 mg, 72%). Anal. Calcd for $C_{56}H_{50}N_4O_{12}\cdot 13H_2O$: C, 55.76; H, 6.3; N, 4.64. Found: C, 55.76; H, 5.16; N, 3.84. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.05 (s, 2H, pyr), 9.04 (s, 2H, pyr), 9.00 (s, 2H, pyr), 8.98 (s, 2H, pyr), 8.34, 8.26 (m, 8H, *o*-phenyl), 7.80 (m, 2H, *p*-phenyl), 7.77 (m, 8H, *m*-phenyl), 7.97 (broad, 2H, OH, C_3 "ose"), 7.48 (broad, 2H, OH, C_2 "ose"), 6.87 (t, 2H, OH, C_6 "ose"), 6.01 (d, 2H, C_1 "ose", J = 8 Hz), 4.67 (m, 2H, C_6 "ose"), 4.50 (m, 8H, C_2, C_3, C_4, C_6 "ose"), 4.34 (m, 2H, C_5, "ose"), −2.40 (s, 2H, NH).

5,10-Bis[4-(β-D-glucosyloxy)phenyl]-10,20-diphenylporphyrin ($\mathbf{15_{5,10}}$). This compound was prepared according to the procedure described above for the preparation of compounds **9**–**12** from $\mathbf{13_{5,10}}$ (60 mg, 4.5×10^{-5} mol) and then purified by gel filtration on a Sephadex LH20 column eluted with a mixture of methanol/water (5/1, v/v). The pure porphyrin was crystallized from methanol/1,2-dichloroethane (35 mg, 67%). Anal. Calcd for $C_{56}H_{50}N_4O_{12}\cdot 4H_2O$: C, 64.44; H, 5.56; N, 5.37. Found: C, 64.93; H, 5.0; N, 5.32. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.07 (s, 2H, pyr), 9.04 (s, 2H, pyr), 9.02 (s, 2H, pyr), 9.01 (s, 2H, pyr), 8.34 (m, 8H, *o*-phenyl), 8.27 (m, 2H, *p*-phenyl), 7.99 (broad, 2H, OH, C_3 "ose"), 7.82 (m, 8H, *m*-phenyl), 7.58 (broad, 2H, OH, C_4 "ose"), 6.91 (t, 2H, OH, C_6 "ose"), 6.02 (d, 2H, C_1 "ose", J = 8 Hz), 4.70 (m, 2H, C_6 "ose"), 4.52 (m, 8H, C_2, C_3, C_4, C_6 "ose"), 4.36 (m, 2H, C_5 "ose"), −2.38 (s, 2H, NH).

5,10,15-Tris(4-β-D-glucosylphenyl)-20-phenylporphyrin ($\mathbf{15_{5,10,15}}$). This compound was prepared according to the procedure described above for the preparation of compounds **9**–**12** from $\mathbf{13_{5,10,15}}$ (65 mg, 3.9×10^{-5} mol) and then purified by gel filtration on a Sephadex LH20 column eluted with methanol. The title compound was crystallized from methanol/water (37 mg, 83%). Anal. Calcd for $C_{62}H_{59}N_4O_{18}\cdot 2H_2O$: C, 49.37; H, 6.62; N, 3.71. Found: C, 49.89; H, 4.55; N, 3.43. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.05 (s, 2H, pyr), 9.02 (s, 2H, pyr), 9.01 (s, 2H, pyr), 8.99 (s, 2H, pyr), 8.35 (m, 8H, *o*-phenyl), 7.95 broad (3H, OH, C_3 "ose"), 7.81 (m, 8H, *m*-phenyl), 7.54 (broad, 3H, OH, C_2 "ose"), 7.47 (broad, 3H, OH, C_3 "ose"), 6.87 (t, 3H, OH, C_6 "ose"), 6.01 (d, 3H, C_1 "ose", J = 8 Hz), 4.68–4.49 (m, 6H, C_6 "ose"), 4.53 (m, 3H, C_2, C_3, C_4 "ose"), 4.36 (m, 3H, C_5 "ose"), −2.37 (s, 2H, NH).

5,10,15,20-Mono, Bis-, or Tris[4-(2,3,4,6-tetraacetyl-β-D-galactosyl)phenyl]tri-, -di-, or monophenylporphyrins (14). Pyrrole (0.650 g, 9.7×10^{-3} mol), 4-(2,3,4,6-tetraacetyl-β-D-galactopyranosyl)benzaldehyde **2** (3.290 g, 7.28×10^{-3} mol) and benzaldehyde (0.254 g, 2.4×10^{-3} mol) each one in methylene chloride solution (90 mL) were added to methylene chloride (1 L) containing ethanol (0.75%) purged by argon for 30 min. The resulting mixture was stirred and purged by argon for a further 10 min, after which a BF_3·etherate solution (400 μL, 0.5 M) in methylene chloride was added. This mixture was stirred overnight at room temperature. Chloranil (1 g, 4.06×10^{-3} mol) was added. After reflux for 1 h, silica gel (10 g) was added to the dark solution and all solvent was evaporated. The absorbed products were placed on the top of a silica gel column. The crude porphyrins were eluted with a mixture of methylene chloride/ether (10/1, v/v) to give monogalactosylated compound $\mathbf{14_5}$ (traces), with a mixture of methylene chloride/ether (5/1, v/v) to give di "ose" products $\mathbf{14_{5,10}}$ and $\mathbf{14_{5,15}}$, and with methylene chloride/ether (2/1, v/v) to give tri "ose" product $\mathbf{14_{5,10,15}}$. The tetragalactosylated porphyrin **2** was eluted by a mixture of methylene chloride/acetone (5/1, v/v). $\mathbf{14_{5,10}}$ and $\mathbf{14_{5,15}}$ were separated and purified by preparative thin layer chromatography by three elutions with methylene chloride/ether (15/1, v/v). $\mathbf{14_{5,10,15}}$ was purified by thin layer chromatography by two elutions with methylene chloride/ether (2/1, v/v). The most polar porphyrin **6** was obtained by two elutions with a mixture of methylene chloride/acetone (5/1, v/v). All porphyrins was crystallized from methylene chloride/hexane and washed with pure hexane: $\mathbf{14_{5,15}}$ (180 mg, 5.7%), $\mathbf{14_{5,10}}$ (180 mg, 5.7%) and $\mathbf{14_{5,10,15}}$ (545 mg, 13.4%), **6** (400 mg, 8%). $\mathbf{14_{5,15}}$. Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 2H_2O$: C, 64.38; H, 5.25; N, 4.17. Found: C, 64.11; H, 5.41; N, 3.65. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.86 (s, 8H, pyr), 8.19 (t, 4H, *o*-phenyl), 8.17 (d, 4H, *o*-phenyl "ose", J = 8 Hz), 7.75 (m, 6H, *m*- + *p*-phenyl), 7.40 (d, 4H, *m*-phenyl "ose", J = 8 Hz), 5.72 (m, 2H, C_2 "ose"), 5.57 (d, 2H, C_4 "ose"), 5.42 (d, 2H, C_1 "ose", J = 8 Hz), 5.28 (m, 2H, C_3 "ose"), 4.31 (m, 4H, C_6 "ose", 2H, C_5 "ose"), 2.27 (s, 6H, acetyl), 2.24 (s, 6H, acetyl), 2.09 (s, 6H, acetyl), 2.08 (s, 6H, acetyl), −2.78 (s. 2H, NH). $\mathbf{14_{5,10}}$. Anal. Calcd for $C_{72}H_{66}N_4O_{20}\cdot 2H_2O$: C, 64.38; H, 5.25; N, 4.17. Found: C, 64.83; H, 5.18; N, 3.97. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.84 (s, 8H, pyr), 8.21 (t, 4H, *o*-phenyl), 8.14 (d, 4H, *o*-phenyl "ose", J = 8 Hz), 7.77 (m, 6H, *m*- + *p*-phenyl), 7.37 (d, 4H, *m*-phenyl "ose", J = 8 Hz), 5.70 (m, 2H, C_2 "ose"), 5.61 (d, 2H, C_4 "ose"), 5.41 (d, 2H, C_1 "ose", J = 8 Hz), 5.27 (m, 2H, C_3 "ose"), 4.33 (m, 4H, C_6 "ose", 2H, C_5 "ose"), 2.26 (s, 6H, acetyl), 2.23 (s, 6H, acetyl), 2.08 (s, 6H, acetyl), 2.07 (s, 6H, acetyl), −2.79 (s, 2H, NH). $\mathbf{14_{5,10,15}}$. Anal. Calcd for $C_{88}H_{84}N_4O_{30}\cdot 3H_2O$: C, 61.04; H, 5.24; N, 3.24. Found: C, 60.87; H, 5.18; N, 3.19. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 4H, pyr), 8.84 (s, 4H, pyr), 8.22 (m, 2H, *o*-phenyl), 8.20 (d, 6H, *o*-phenyl "ose", J = 8 Hz), 7.78 (m, 3H, *m*- + *p*-phenyl), 7.43 (d, 6H, *m*-phenyl "ose", J = 8 Hz), 5.72 (m, 3H, C_2 "ose"), 5.58 (d, 3H, C_4 "ose"), 5.44 (d, 3H, C_1 "ose", J = 8 Hz), 5.29 (m, 3H, C_3 "ose"), 4.33 (m, 6H, C_6 "ose", 3H, C_5 "ose"), 2.29, 2.28, 2.25, 2.24, 2.19, 2.14, 2.13, 2.12, 2.11 (s, 36H acetyl), −2.77 (s, 2H, NH).

5,10,15-Tris(4-β-D-galactophenyl)-20-phenylporphyrin ($\mathbf{16_{5,10,15}}$). This compound was prepared according to the procedure described above for the preparation of compounds **9**–**12** from $\mathbf{14_{5,10,15}}$ (65 mg, 3.9×10^{-5} mol). The crude solution was purified by gel filtration on a Sephadex LH20 column eluted with methanol. The pure product was crystallized from methanol/water (37 mg, 83%). Anal. Calcd for $C_{62}H_{59}N_4O_{18}\cdot 7H_2O$: C, 58.44; H, 5.77; N, 4.40. Found: C, 58.35; H, 5.39; N, 4.49. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.00 (m, 8H, pyr), 8.34 (m, 2H, *o*-phenyl), 8.24 (dd, 6H, *o*-phenyl "ose"), 7.78 (dd, 6H, *m*-phenyl "ose", J = 8 Hz), 7.76 (m, 3H, *m*- + *p*-phenyl), 7.16 (broad, 3H, OH, C_5 "ose"), 6.91 (broad, 3H, OH, C_6 "ose"), 6.74 (broad, 3H, OH, C_4 "ose"), 5.96 (d, 3H, C_1 "ose", J = 8 Hz), 4.75 (m, 3H, C_2 "ose"), 4.59 (m, 3H, C_4 "ose"), 4.47 (m, 9H, C_6, C_5, C_3 "ose"), −2.40 (s, 2H, NH).

5,10,15,20-Tetrabutylporphyrin (17). The title compound was prepared according to the Lindsey's method using pyrrole (0.27 g, 4×10^{-3} mol), pentanal (0.35 g, 4×10^{-3} mol), and 200 μL of a BF_3·etherate solution (0.5 M) in 400 mL of methylene chloride containing 0.75% of EtOH. **17** was purified by chromatography on a silica gel column with methylene chloride as eluent and crystallized from methylene chloride/methanol (0.135 g, 25%). Anal. Calcd for $C_{36}H_{46}N_4$: C, 80.84; H, 8.68; N, 10.48. Found: C, 81.07; H, 8.37; N, 10.56. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.46 (s, 8H, pyr), 4.93 (t, 8H, α CH_2), 2.50 (m, 8H, β CH_2), 1.83 (m, 8H, γ CH_2), 1.13 (t, 12H, CH_3), −2.64 (s, 2H, NH).

5,10,15,10-Tetra-*n*-undecylporphyrin (18). This compound was prepared according to Lindsey's method using pyrrole (0.3 g, 4.5×10^{-3} mol), *n*-dodecanal (0.83 g, 4.5×10^{-3} mol), and 200 μL of a BF_3·etherate solution (0.5 M) in 250 mL of methylene chloride (ethanol 0.75%). **18** was purified by chromatography on a silica gel column with methylene chloride/hexane (3/1, v/v) as eluent and then crystallized from methylene chloride/methanol (160 mg, 16.5%). Anal. Calcd for $C_{64}H_{102}N_4$: C, 82.86; H, 11.09; N, 6.04. Found: C, 80.49; H, 11.54; N, 6.25. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.45 (s, 8H, pyr), 4.92 (m, 8H, α CH_2), 2.51 (m, 8H, β CH_2), 1.53 (m, 8H, γ CH_2), 1.25 (broad, 56H, CH_2), 0.87 (t, 12H, CH_3), −2.58 (s, 2H, NH).

5,10,15,20-Mono-, Bis-, or Tris[4-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]tri-, -di-, or monobutylporphyrin (19). Pyrrole (0.59 g, 8.8×10^{-3} mol) and 4-(2,3,4,6-tetraacetyl-β-D-glucopyranosyl)benzaldehyde **(1)** (1.98 g, 4.4×10^{-3} mol) in methylene chloride (132 mL) were added to methylene chloride containing ethanol (0.75%) (1 L) purged by argon for 30 min. The mixture was stirred for 10 min after which 200 μL of a BF_3-etherate solution (0.5 M) in dry methylene chloride was added. After 10 min, pentanal (0.38 g, 4.4×10^{-3} mol) in methylene chloride (44 mL) was added. After 1 h, 200 μL of a BF_3·etherate solution in dry methylene chloride was added again. This mixture was stirred at room temperature overnight. Then chloranil (1 g, 4.06×10^{-3} mol) was added and the solution was refluxed for 1 h. Silica gel (20 g) was added to the resulting dark solution, and all solvent was evaporated. The absorbed porphyrins on silica gel were placed on the top of a silica gel column. The crude products were eluted with pure methylene chloride to give *meso*-5,10,15,20-tetrabutylporphyrin (**17**) as the first red band which was purified by thin layer chromatography on preparative silica gel plates eluted with a mixture of methylene chloride/hexane (2/3, v/v) (7 mg, 0.6%). A mixture of methylene chloride and ether (10/1, v/v) gave a second red band corresponding to monoglucosylated compound $\mathbf{19_5}$. A third red band which contains three products (the di "ose" products $\mathbf{19_{5,10}}$, $\mathbf{19_{5,15}}$, and tri "ose" $\mathbf{19_{5,10,15}}$) was eluted with a mixture of methylene chloride and acetone (10/1, v/v). All glucosylated products were purified by preparative thin layer chromatography on silica gel. $\mathbf{19_5}$ was eluted with methylene chloride/ether (10/1, v/v). $\mathbf{19_{5,15}}$, $\mathbf{19_{5,10}}$, and $\mathbf{19_{5,10,15}}$ were eluted with methylene chloride/acetone (15/1, v/v). They were crystallized from methylene chloride/methanol for $\mathbf{19_5}$ (185 mg, 9.5%) and $\mathbf{19_{5,15}}$ (65 mg, 2.3%), and from methylene chloride/hexane for $\mathbf{19_{5,10}}$ (94 mg, 3.4%) and $\mathbf{19_{5,10,15}}$ (50 mg, 1.4%). $\mathbf{19_5}$. Anal. Calcd for $C_{52}H_{60}N_4O_{10}$·CH_2Cl_2: C, 64.31; H, 6.35; N, 5.69. Found: C, 62.75; H, 5.70; N, 5.23. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.53 (d, 2H, pyr, J = 6 Hz), 9.50 (d, 2H, pyr, J = 6 Hz), 9.38 (d, 2H, pyr, J = 6 Hz), 8.79 (d, 2H, pyr, J = 6 Hz), 8.06 (dd, 2H, *o*-phenyl, Jo = 8 Hz, Jm = 2 Hz), 7.36 (dd, 2H, *m*-phenyl, Jo = 8 Hz, Jm = 2 Hz), 5.45 (m, 3H, C_1, J = 8 Hz, C_2, C_3 "ose"), 5.33 (m, 1H, C_4 "ose"), 4.96 (q, 6H, α CH_2), 4.43 (dd, 1H, C_6 "ose"), 4.35 (dd, 1H, C_6 "ose"), 4.05 (m, 1H, C_5 "ose"), 2.49 (m, 6H, β CH_2), 2.23, 2.13, 2.11, 2.06 (s, 12H, acetyl), 1.82 (m, 6H, γ CH_2), 1.14 (t, 9H, CH_3), −2.50 (broad, s, 2H, NH). $\mathbf{19_{5,10}}$. Anal. Calcd for $C_{68}H_{74}N_4O_{20}$: C, 64.45; H, 5.89: N, 4.42. Found: C, 63.56; H, 5.65; N, 4.39. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.57 (s, 2H, pyr), 9.44 (d, 2H, pyr, J = 4 Hz), 8.84 (d, 2H, pyr, J = 4 Hz), 8.72 (s, 2H, pyr), 8.08 (d, 4H, *o*-phenyl, J = 8 Hz), 7.35 (d, 4H, *m*-phenyl, J = 8 Hz), 5.47 (d, 2H, C_1 "ose", J = 8 Hz), 5.47 (m, 4H, C_2, C_3 "ose"), 5.32 (m, 2H, C_4 "ose"), 4.99 (t, 4H, α CH_2), 4.37 (dd, 2H, C_6 "ose"), 4.35 (dd, 2H, C_6 "ose"), 4.05 (m, 2H, C_5 "ose"), 2.54 (m, 4H, β CH_2), 2.21, 2.11, 2.10, 2.09 (s, 24H, acetyl), 1.83 (m, 4H, γ CH_2), 1.14 (t, 6H, CH_3), −2.72 (s, 2H, NH). $\mathbf{19_{5,15}}$. Anal. Calcd for $C_{68}H_{74}N_4O_{20}$: C, 64.45; H, 5.89; N, 4.42. Found: C, 64.03; H, 5.39; N, 4.35. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.42 (d, 4H, pyr, J = 6 Hz), 8.84 (d, 4H, pyr, J = 6 Hz), 8.10 (d, 4H, *o*-phenyl, J = 8 Hz), 7.37 (d, 4H, *m*-phenyl, J = 8 Hz), 5.48 (d, 2H, C_1 "ose", J = 8 Hz), 5.47 (m, 4H, C_2, C_3 "ose"), 5.30 (m, 2H, C_4 "ose"), 5.30 (m, 2H, C_4 "ose"), 4.96 (broad, t, 4H, α CH_2), 4.45 (dd, 2H, C_6 "ose"), 4.28 (dd, 2H, C_6 "ose"), 4.06 (m, 2H, C_5 "ose"), 2.49 (m, 4H, β CH_2), 2.23, 2.13, 2.11, 2.10 (s, 24H, acetyl), 1.78 (m, 4H, $\gamma$$CH_2$), 1.10 (t, 6H, CH_3), −2.72 (s, 2H, NH). $\mathbf{19_{5,10,15}}$. Anal. Calcd for $C_{84}H_{88}N_4O_{30}$: C, 61.76; H, 5.43; N, 3.43. Found: C, 60.9; H, 5.36; N, 3.35. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.49 (d, 2H, pyr, J = 6 Hz), 8.90 (d, 2H, pyr, J = 6 Hz), 8.78 (s, 4H, pyr), 8.12 (d, 4H, phenyl, J = 8 Hz), 8.08 (d, 2H, phenyl, J = 8 Hz), 7.37 (d, 4H, phenyl), 7.35 (d, 2H, phenyl), 5.46 (m, 6H, C_1, C_2, C_3 "ose"), 5.32 (m, 2H, C_4 "ose"), 5.02 (t, 2H, α CH_2), 4.39 (dd, 3H, C_6 "ose"), 4.30 (dd, 3H, C_6 "ose"), 4.04 (m, 3H, C_5 "ose"), 2.53 (m, 2H, β CH_2), 2.22, 2.21, 2.16, 2.12, 2.11, 2.10, 2.09 (s, 36H, acetyl), 1.83 (m, 2H, γCH2), 1.1 (t, 3H, CH_3), −2.77 s (2H, NH).

5,10-Bis(4-β-D-glucosylphenyl)-15,20-dibutylporphyrin ($\mathbf{22_{5,10}}$). The protecting acetyl groups of compound $\mathbf{19_{5,10}}$ (25 mg, 3×10^{-5} mol) were removed following the same method used for the preparation of compounds **9**−**12**. The crude product was purified by gel filtration on a Sephadex LH20 column eluted with tetrahydrofuran (THF)/water (1/1, v/v) (15 mg, 82%) and used without other purification. Anal. Calcd for $C_{44}H_{40}N_4O_{12}$: C, 64.7; H, 4.94; N, 6.86. Found: C, 64.34; H, 5.20; N, 6.53. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.83 (s, 2H, pyr), 9.71 (d, 2H, pyr, J = 4 Hz), 9.01 (d, 2H, pyr, J = 4 Hz), 8.94 (s, 2H, pyr), 8.18 (d, 4H, *o*-phenyl, J = 8 Hz), 7.78 (d, 4H, *m*-phenyl, J = 8 Hz), 5.98 (d, 2H, C_1 "ose", J = 8 Hz), 5.08 (m, 6H, C_2, C_3, C_4 "ose"), 4.94 (t, 4H, α CH_2), 4.52 (m, 6H, C_6, C_5 "ose"), 2.54 (m, 4H, β CH_2), 1.74 (m, 4H, γ CH_2), 1.02 (t, 6H, CH_3), −2.23 (s, 2H, NH).

5,10,15-Tris(4-β-D-glucosylphenyl)-20-butylporphyrin ($\mathbf{22_{5,10,15}}$). This compound was prepared from $\mathbf{19_{5,10,15}}$ (40 mg, 2.4×10^{-5} mol) according to the procedure described above for the preparation of compounds **9**−**12**. The title compound was purified by gel filtration on a Sephadex LH20 column eluting with methanol/water (4/1, v/v) (22 mg, 78%) and used without other purification. Anal. Calcd for $C_{60}H_{64}N_4O_{18}$: C, 63.82; H, 5.71; N, 4.96. Found: C, 63.43; H, 5.98; N, 5.28. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.76 (d, 2H, pyr, J = 4 Hz), 9.05 (d, 2H, pyr, J = 4 Hz), 8.99 (s, 4H, pyr), 8.23 (d, 6H, *o*-phenyl, J = 8 Hz), 7.95 (m, 3H, OH "ose"), 7.81 (d, 4H, *m*-phenyl, J = 8 Hz, 3H, OH "ose"), 7.77 (d, 2H, *m*-phenyl, J = 8 Hz), 7.48 (m, 3H, OH "ose"), 6.85 (m, 3H, OH "ose"), 6.0 (m, 3H, C_1 "ose"), 5.07 (m, 3H, C_4 "ose", 2H, α CH_2), 4.70, 4.53, 4.33 (m, 15H, "ose"), 2.55 (m, 2H, β CH_2), 1.71 (m, 2H, γ CH_2), 1.01 (t, 3H, CH_3), −2.30 (s, 2H, NH).

5,10,15,20-Mono-, Bis-, or Tris[4-(2,3,6,2′,3′,4′,6′-heptaacetyl-β-D-maltosyl)phenyl]tri, -di-, or mono-*n*-undecylporphyrin (20). Pyrrole (0.590 g, 8.8×10^{-3} mol) and aldehyde **10** (3.25 g, 4.4×10^{-3} mol) in methylene chloride (132 mL) were added to methylene chloride containing ethanol (0.75%) (1 L) purged by argon for 30 min. The mixture was stirred for 10 min after which 200 μL of a BF_3·etherate solution (0.5 M) in dry methylene chloride was added. After 10 min, *n*-dodecanal (0.810 g, 4.4×10^{-3} mol) in methylene chloride (44 mL) was added. After 1 h, 200 μL of a BF_3·etherate solution was added again. This mixture was stirred at room temperature overnight. Chloranil (1 g, 4.06×10^{-3} mol) was added. After reflux for 1 h, silica gel (20 g) was added to the dark solution and all solvent was evaporated. The absorbed porphyrins on silica gel were placed on the top of a silica gel column. The crude products were eluted successively with pure methylene chloride to give *meso*-5,10,15,20-tetra-*n*-undecylporphyrin **18** (7 mg, 0.6%) with a mixture of methylene chloride/ether (10/1, v/v) to give monoglycosylated compound $\mathbf{20_5}$ and with a mixture of methylene chloride/acetone (10/1, v/v) to give the mixture of di "ose" products $\mathbf{20_{5,10}}$ and $\mathbf{20_{5,15}}$ and tri "ose" product $\mathbf{20_{5,10,15}}$. Compound **7** was finally eluted by a mixture of methylene chloride/acetone (5/1, v/v) (traces). All products were purified by preparative thin layer chromatography on silica gel. $\mathbf{20_5}$ was obtained with methylene

chloride/ether (15/1, v/v) as eluent. **$20_{5,10}$** was recovered after three elutions with methylene chloride/ether (15/1, v/v). Compound **20_5** was crystallized from methylene chloride/methanol (87 mg, 7.2%). Other porphyrins (**$20_{5,10}$** (45 mg, 1.5%), **$20_{5,15}$** (traces), and **$20_{5,10,15}$** (24 mg, 0.6%)) were crystallized from methylene chloride/hexane and washed with pure hexane until the color disappeared. **20_5**. Anal. Calcd for $C_{85}H_{118}N_4O_{18}$: C, 68.8; H, 8.02; N, 3.78. Found: C, 68.65; H, 7.96; N, 3.84. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.51 (broad, 4H, pyr), 9.38 (d, 2H, pyr, J = 6 Hz), 8.79 (d, 2H, pyr, J = 6 Hz), 8.08 (d, 2H, *o*-phenyl, J = 8 Hz), 7.34 (d, 2H, *m*-phenyl, J = 8 Hz), 5.43 (m, 5H, C_1, C_3, C'_1, C'_2, C'_3 "ose"), 4.96 (m, 2H, C'_4 "ose" + 6H, α CH_2), 4.62 (1H, C_6 "ose"), 4.42 (m, 6H, C_5, C_6, C_4, C'_5, 2H, C'_6 "ose"), 2.50 (m, 6H, β CH_2), 2.20, 2.17, 2.14, 2.12, 2.11, 2.04, 2.02 (s, 21H, acetyl), 1.79 (q, 6H, γ CH_2), 1.27 (broad, 42H, CH_2), 0.86 (m, 9H, CH_3), −2.67 (s, 2H, NH). **$20_{5,10}$**. Anal. Calcd for $C_{106}H_{134}N_4O_{36}\cdot 3H_2O$: C, 60.79; H, 6.74; N, 2.68. Found: C, 60.92; H, 6.47; N, 2.54. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.57 (s, 2H, pyr), 9.44 (d, 2H, pyr, J = 4 Hz), 8.84 (d, 2H, pyr, J = 4 Hz), 8.72 (s, 2H, pyr), 8.08 (d, 4H, *o*-phenyl, J = 8 Hz), 7.34 (d, 4H, *m*-phenyl, J = 8 Hz), 5.47 (m, 10H, C_1, C_3, C'_1, C'_2, C'_3 "ose"), 5.33 (m, 4H, "ose"), 4.99 (m, 4H, "ose" + 4H, α CH_2), 4.60 (dd, 2H, C_6 "ose"), 4.25 (m, 8H, C'_4, C_6, C_5, C'_5, 2H, C'_6 "ose"), 2.55 (4m, H, β CH_2), 2.19, 2.16, 2.13, 2.11, 2.10, 2.03, 2.02 (s, 42H, acetyl), 1.81 (m, 4H, γ CH_2), 1.25 (broad, 28H, CH_2), 0.86 (m, 6H, CH_3), −2.72 (s, 2H, NH). **$20_{5,10,15}$**. Anal. Calcd for $C_{127}H_{150}N_4O_{54}$: C, 58.75; H, 5.82; N, 2.16. Found: C, 59.02; H, 6.01; N, 2.05. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.47 (d, 2H, pyr, J = 4 Hz), 8.90 (d, 2H, pyr, J = 4 Hz), 8.78 (s, 4H, pyr), 8.12 (d, 4H, *o*-phenyl, J = 4 Hz), 8.09 (d, 2H, *o*-phenyl, J = 8 Hz), 7.37 (d, 4H, *m*-phenyl, J = 8 Hz), 7.35 (d, 2H, *m*-phenyl, J = 8 Hz), 5.47 (m, 15H, C_1, C_3, C'_1, C'_3, C_2 or C'_2 "ose"), 5.33 (m, 4H, "ose" + 2H, α CH_2), 4.64 (m, 3H, C_6 "ose"), 4.33 (m, 18H, C_6, C'_6, C_5, C'_5, C'_4 "ose"), 2.54 (m, 2H, β CH_2), 2.20, 2.18, 2.16, 2.15, 2.14, 2.13, 2.11, 2.10, 2.04, 2.02 (s, 63H, acetyl), 1.80 (q, 2H, γ CH_2), 1.24 (broad, 14H, CH_2), 0.86 (m, 3H, CH_3), −2.76 (s, 2H, NH).

5,10-Bis(4-β-D-maltosylphenyl)-15,20-di-*n*-undecylporphyrin ($23_{5,10}$). Compound **$20_{5,10}$** (20 mg, 0.77 × 10^{-5} mol) was treated according to the procedure described above for the preparation of compounds **9**−**12**. The title compound was purified by gel filtration on a Sephadex LH20 column using THF/water (23/2 v/v) as eluent then was crystallized from THF/water/methanol (10 mg, 80%). Anal. Calcd for $C_{78}H_{106}N_4O_{22}\cdot H_2O$: C, 64.74; H, 7.41; N, 3.81. Found: C, 64.43; H, 7.30; N, 3.53. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.90 (s, 2H, pyr), 9.75 (d, 2H, pyr, J = 6 Hz), 9.03 (d, 2H, pyr, J = 6 Hz), 8.90 (s, 2H, pyr), 8.15 (d, 4H, *o*-phenyl, J = 8 Hz), 7.75 (m, 4H, *m*-phenyl), 5.90 (m, 2H, C_1 "ose"), 4.60−4.30 (m, 26H, H "ose"), 2.65 (m, 4H, β CH_2), 1.8 (m, 4H, γ CH_2), 1.20 (broad, 28H, CH_2), 0.90 (m, 6H, CH_3), −2.15 (s, 2H, NH).

5,10,15,20-Mono-, Bis-, or Tris[4-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]tri, -di-, or mono-*n*-undecylporphyrin (21). For simplicity, only method i is described (Table 1). Pyrrole (0.590 g, 8.8 × 10^{-3} mol), glucosylaldehyde **1** (1.98 g, 4.4 × 10^{-3} mol), and *n*-dodecanal (0.180 g, 4.4 × 10^{-3} mol) in methylene chloride (176 mL) were added to methylene chloride containing ethanol (0.75%) (1 L) purged by argon for 30 min. The mixture was stirred for 10 min after which time 200 μL of a BF_3 etherate solution (0.5 M) in dry methylene chloride was added. After 1 h, 200 μL of a BF_3·etherate solution was added again. This mixture was stirred at room temperature for 20 h. Chloranil (1 g, 4.06 × 10^{-3} mol) was added, and the resulting solution was refluxed for 1 h. Silica gel (20 g) was added to the dark solution, and all solvent was evaporated. The absorbed porphyrins on silica gel were placed on the top of a silica gel column. The crude products were eluted with methylene chloride/hexane (5/1, v/v) to give *meso*-5,10,15,20-tetrakis-*n*-undecylporphyrin (**18**), with a mixture of methylene chloride/ether (10/1, v/v) to give monoglycosylated compound **21_5** and diglycosylated compound **$21_{5,15}$**, with a mixture of methylene chloride/ether (5/1, v/v) to give the product **$21_{5,10}$**, and finally with methylene chloride/ether (2/1, v/v) to give tri "ose" product **$21_{5,10,15}$** and porphyrin **5**. All products were purified by preparative thin layer chromatography on silica gel using methylene chloride/ether (10/1, v/v) for compounds **21_5** and **$21_{5,15}$** and methylene chloride/acetone (5/1, v/v) for **$21_{5,10}$** and **$21_{5,10,15}$**. The pure products were obtained by crystallization from methylene chloride/methanol for **21_5** and **$21_{5,15}$** and methylene chloride/hexane and then washed with pure hexane until the hexane was colorless for **$21_{5,10}$** and **$21_{5,10,15}$**. The yields of glucosylated derivatives are shown in Table 1. **21_5**. Anal. Calcd for $C_{73}H_{102}N_4O_{10}$: C, 73.33; H, 8.6; N, 4.6. Found: C, 70.81; H, 8.31; N, 4.3. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.52 (m, 4H, pyr), 9.38 (d, 2H, pyr, J = 4 Hz), 8.78 (d, 2H, pyr, J = 4 Hz), 8.08 (d, 2H, *o*-phenyl, J = 8 Hz), 7.37 (d, 2H, *m*-phenyl, J = 8 Hz), 5.47 (m, 3H, C_1, J = 6 Hz, C_2, C_3 "ose"), 5.31 (m, 1H, C_4 "ose"), 4.96 (m, 6H, α CH_2), 4.36 (m, 2H, C_6 "ose"), 4.06 (m, 1H, C_5 "ose"), 2.55 (m, 6H, β CH_2), 2.22, 2.12, 2.11, 2.10 (s, 12H, acetyl), 1.80 (m, 6H, γ CH_2), 1.26 (broad, 42H, CH_2), 0.86 (m, 9H, CH_3), −2.67 (s, 2H, NH). **$21_{5,10}$**. Anal. Calcd for $C_{82}H_{102}N_4O_{20}$: C, 67.29; H, 7.02; N, 3.83. Found: C, 66.98; H, 6.87; N, 4.03. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.54 (s, 2H, pyr), 9.41 (d, 2H, pyr, J = 4 Hz), 8.81 (d, 2H, pyr, J = 4 Hz), 8.70 (s, 2H, pyr), 8.05 (d, 4H, *o*-phenyl, J = 8 Hz), 7.33 (d, 4H, *m*-phenyl, J = 8 Hz), 5.43 (d, 6H, C_1, C_2, C_3 "ose"), 5.27 (m, 2H, C_4 "ose"), 4.98 (t, 4H, α CH_2), 4.38 (dd, 2H, C_6 "ose"), 4.29 (dd, 2H, C_6 "ose"), 4.03 (m, 2H, C_5 "ose"), 2.52 (m, 4H, β CH_2), 2.19, 2.09, 2.07, 2.03 (s, 24H, acetyl), 1.77 (q, 4H, γ CH_2), 1.23 (broad, 28H, CH_2), 0.83 (t, 6H, CH_3), −2.74 (s, 2H, NH). **$21_{5,15}$**. Anal. Calcd for $C_{82}H_{102}N_4O_{20}$: C, 67.29; H, 7.02; N, 3.83. Found: C, 66.23; H, 6.93; N, 4.04. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.41 (d, 4H, pyr, J = 4 Hz), 8.85 (d, 4H, pyr, J = 4 Hz), 8.10 (d, 4H, *o*-phenyl, J = 8 Hz), 7.37 (d, 4H, *m*-phenyl, J = 8 Hz), 5.47 (m, 6H, C_1, J = 8 Hz, C_2, C_3 "ose"), 5.21 (m, 2H, C_4 "ose"), 4.95 (t, 4H, α CH_2), 4.38 (m, 2H, C_6 "ose"), 4.36 (m, 2H, C_6 "ose"), 4.06 (m, 2H, C_5 "ose"), 2.50 (m, 4H, β CH_2), 2.23, 2.13, 2.11, 2.10, 2.03 (s, 24H, acetyl), 1.77 (q, 4H, γ CH_2), 1.24 (broad, 28H, CH_2), 0.85 (t, 6H, CH_3), −2.72 (s, 2H, NH). **$21_{5,10,15}$**. Anal. Calcd for $C_{91}H_{102}N_4O_{30}$: C, 63.11; H, 5.94; N, 3.2. Found: C, 62.25; H, 5.72; N, 3.21. ^{1}H NMR ($CDCl_3$): δ (ppm) 9.48 (d, 2H, pyr, J = 4 Hz), 8.90 (d, 2H, pyr, J = 4 Hz), 8.78 (s, 4H, pyr), 8.10 (d, 4H, *o*-phenyl, J = 14 Hz), 8.06 (d, 2H, *o*-phenyl, J = 12 Hz), 7.37 (d, 4H, *m*-phenyl, J = 8 Hz), 7.35 (d, 2H, *m*-phenyl, J = 8 Hz), 5.47 (m, 9H, C_1, C_2, C_3 "ose"), 5.32 (q, 3H, C_4 "ose"), 4.95 (t, 2H, α CH_2), 4.37 (m, 6H, C_6 "ose"), 4.06 (m, 3H, C_5 "ose"), 2.54 (m, 2H, β CH_2), 2.23, 2.20, 2.12, 2.10, (s, 36H, acetyl), 1.80 (q, 6H, γ CH_2), 1.24 (broad, 14H, CH_2), 0.85 (t, 3H, CH_3), −2.72 (s, 2H, NH).

5,10-Bis(4-β-D-glucosylphenyl)-15,20-di-*n*-undecylporphyrin ($24_{5,10}$). This compound was prepared from **$21_{5,10}$** (50 mg, 3.4 × 10^{-5} mol) according to the procedure described above for the preparation of compounds **9**−**12**. It was purified by gel filtration on a Sephadex LH20 column eluted by methanol/THF (4/1, v/v). The pure product was crystallized from methanol/methylene chloride (27 mg, 70%). Anal. Calcd for $C_{66}H_{78}N_4O_{18}\cdot H_2O$: C, 64.27; H, 6.54; N, 4.54. Found: C, 63.98; H, 6.78; N, 4.86. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.91 (s, 2H, pyr), 9.80 (d, 2H, pyr, J = 4 Hz), 9.01 (d, 2H, pyr, J = 4 Hz), 8.93 (s, 2H, pyr), 8.20 (d, 4H, *o*-phenyl, J = 8 Hz), 7.77 (d, 4H, *m*-phenyl, J = 8 Hz), 5.99 (m, 2H, "ose"), 2.60 (m, 4H, β CH_2), 1.77 (m, 4H, γ CH_2), 1.22 (m, 28H, CH_2), 0.83 (m, 6H, CH_3), −2.22 (s, 2H, NH).

5,10,15-Tris(4-β-D-glucosylphenyl)-20-*n*-undecylporphyrin ($24_{5,10,15}$). The title compound was prepared from **$21_{5,10,15}$** (40 mg, 2.3 × 10^{-5} mol) according to the procedure described above for the preparation of compounds **9**−**12**. It was purified by gel filtration on a Sephadex LH20 column eluted by methanol/water (2/1, v/v) and was crystallized from methanol/methylene chloride (25 mg, 86%). Anal. Calcd for $C_{67}H_{78}N_4O_{18}$: C, 65.57; H, 6.41; N, 4.56. Found: C, 65.21; H, 6.28; N, 4.21. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.84 (d, 2H, pyr, J = 4 Hz), 9.07 (d, 2H, pyr, J = 4 Hz), 8.98 (s, 4H, pyr), 8.22 (d, 6H, *o*-phenyl, J = 8 Hz), 7.95 (broad, 3H, OH "ose"), 7.7 (m, 9H, 6H *m*-phenyl + 3H, OH "ose"), 7.54 (broad, 3H, OH "ose"), 6.85 (3H, OH "ose"), 5.99 (m, 3H, H "ose"), 4.96 (broad, 2H, α CH_2), 4.67 (m, 3H, H "ose"), 4.53 (broad, 12H, H "ose"), 4.40 (m, 3H, H "ose"), 2.65 (m, 2H, β CH_2), 1.8 (m, 2H, γ CH_2), 1.16 (broad, 14H, CH_2), 0.79 (t, 3H, CH_3), −2.29 (s, 2H, NH).

5,10,15-Tris[4-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]-20-mono(2,3,4,5,6-pentafluorophenyl)porphyrin ($26_{5,10,15}$).

Pyrrole (0.59 g, 8.8×10^{-3} mol) and glucosylaldehyde **1** (1.98, 4.4×10^{-3} mol) in methylene chloride (132 mL) were added to methylene chloride containing ethanol (0.75%) (1 L) purged by argon for 30 min. The mixture was stirred for 10 min after which 200 μL of a BF_3·etherate solution (0.5 M) in dry methylene chloride was added. After 10 min 2,3,4,5,6-pentafluorobenzaldehyde (0.862 g, 4.4×10^{-3} mol) in methylene chloride (44 mL) was added. After 1 h 200 μL of a BF_3·etherate solution was added again. This mixture was stirred at room temperature overnight. Chloranil (1 g, 4.06×10^{-3} mol) was added, and the solution was refluxed for 1 h. Silica gel (20 g) was added to the dark solution and all solvent was evaporated. The absorbed porphyrins on silica gel were placed on the top of a silica gel column. The crude products were eluted with methylene chloride to give porphyrin **25** in the first red band (10 mg, 0.5%) and then with a mixture of methylene chloride/ether (10/1, v/v) to give tri "ose" product $\mathbf{26}_{5,10,15}$. The 5,10,15,20-tetrakis[4-(2,3,4,6-tetraacetyl-β-D-glucosyl)phenyl]porphyrin **5** was eluted finally with a mixture of methylene chloride/acetone (15/1, v/v) (427 mg, 9.5%). Compound $\mathbf{26}_{5,10,15}$ was purified by preparative thin layer chromatography on silica gel using a mixture of methylene chloride/acetone (7/1, v/v) as eluent. It was crystallized from methylene chloride/heptane (189 mg, 2.5%). $\mathbf{26}_{5,10,15}$. Anal. Calcd for $C_{86}H_{79}N_4O_{30}F_5$: C, 59.23; H, 4.57; N, 3.21. Found: C, 58.67; H, 4.51; N, 3.27. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.89 (d, 2H, pyr, J = 4 Hz), 8.82 (broad, 4H, pyr), 8.75 (d, 2H, pyr, J = 4 Hz), 8.10 (d, 6H, o-phenyl, J = 8 Hz), 7.37 (d, 6H, m-phenyl, J = 8 Hz), 5.45 (m, 9H, C_1, C_2, C_3 "ose"), 5.29 (q, 3H, C_4 "ose"), 4.36 (m, 6H, C_6 "ose"), 4.07 (m, 3H, C_5 "ose"), 2.19, 2.14, 2.08, 2.03 (s, 36H, acetyl), −2.72 (s, 2H, NH).

5,10,15-Tris(4-β-D-glucosylphenyl)-20-(2,3,4,5,6-pentafluorophenyl)porphyrin ($\mathbf{27}_{5,10,15}$). Removal of the acetyl protecting groups of $\mathbf{26}_{5,10,15}$ (65 mg, 3.7×10^{-5} mol) was made according to the procedure described above for the preparation of compounds **9**−**12**. The crude solution was submitted to gel filtration on a Sephadex LH20 column. Elution with methanol gave the title compound which was crystallized from methanol/water (40 mg, 87%). Anal. Calcd for $C_{62}H_{55}N_4O_{18}F_5$: C, 60.1; H, 4.47; N, 4.25. Found: C, 60.69; H, 5.32; N, 4.52. ^{1}H NMR (pyridine-d_5): δ (ppm) 9.33 (d, 2H, pyr, J = 4 Hz), 9.12 (d, 2H, pyr, J = 4 Hz), 9.03 (s, 4H, pyr), 8.24 (d, 6H, o-phenyl, J = 8 Hz), 7.95 (broad, 3H, OH "ose), 7.78 (d, 6H, m-phenyl, J = 8 Hz), 7.54 (broad, 3H, OH "ose"), 7.17 (broad, 3H, OH "ose"), 6.85 (broad, 3H, OH "ose"), 5.99 (m, 3H, "ose"), 4.68 (m, 3H, "ose"), 4.52 (broad, 12H, "ose"), 4.25 (m, 3H, "ose"), −2.41 (s, 2H, NH).

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