SYNTHESIS OF PORPHYRIN RECEPTORS MODIFIED BY GLYCOSYLATED STEROIDS+

Karel ZELENKA[a1], Tomáš TRNKA[a2], Iva TIŠLEROVÁ[a], Vladimír KRÁL[b,c1], Mykhaylo DUKH[b,c] and Pavel DRAŠAR[b,c2,*]

[a] *Department of Organic Chemistry, Charles University, Albertov 8, 128 40 Prague 2, Czech Republic; e-mail:* [1] *zeli1@post.cz,* [2] *trnka@natur.cuni.cz*

[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic*

[c] *Department of Chemistry of Natural Compounds, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail:* [1] *vladimir.kral@vscht.cz,* [2] *pavel.drasar@vscht.cz*

Received January 19, 2004
Accepted February 16, 2004

Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday.

5,10,15,20-Tetrakis-[3α-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-5β-cholan-24-yl]porphyrin and 5,10,15,20-tetrakis-[3α-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-5β-cholan-24-yl]-porphyrin were synthesized by condenzation of the respective steroid aldehydes and pyrrole-1-yl magnesium bromide.

Keywords: Porphyrinoids; Porphyrins; Pyrrols; Steroids; meso-Substitution; Receptor modification; Steroid glycosides; Supramolecular chemistry.

The aim of the work was to prepare compounds containing tailored carbohydrate, steroid and porphyrin moieties. The idea was based on their function as they might show many interesting properties like ion complexation, molecular and chiral recognition, formation of self-assembling systems and ion channels followed by unspecified biological activities. We aimed our work at possible analytical use of this new type of receptor[4,5], which has practically important two levels of its lipophilicity/hydrophilicity control. First, via utilization of different bile acids as linkers (cholic, lithocholic, deoxycholic, etc.)[6,7] and second, via utilization of carbohydrates with dif-

+ Presented in parts as preliminary communication[1–3].

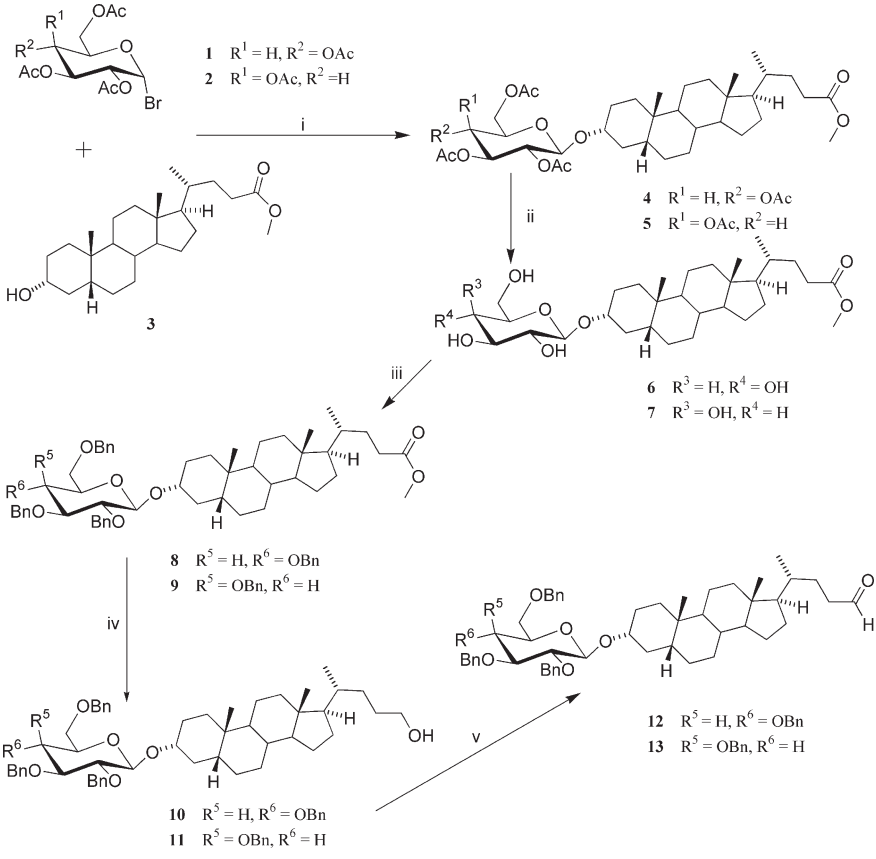
doi:10.1135/cccc20041149

ferent configuration and levels of deoxygenation and OH groups protection. As an additional function, carbohydrate could anchor the lipophilic steroid moiety (and vice versa) to the interphase between immiscible phases or onto a membrane, allowing the porphyrin to complex or transfer the ionic substrates[8,9]. Another role of steroid–saccharide structure could be the utilization of different types of recognition[10,11] and hydrogen bonding during molecular recognition[12–14] and self-assembly. This paper aims to open synthetic pathway to this family of modified receptors. The properties of these compounds are being studied.

The above compounds possess special properties and could play an important role in biological systems. It was shown in a similar study of phenanthroline receptors[15] that this expectation was fulfilled in many aspects. The key structural features responsible for different aspects of the functionality could be controlled even by using cation complexation[15]. Recently, porphyrin and calix[4]pyrrole structures substituted in *meso* positions by steroid units were prepared[16–21]. We present the synthesis of porphyrin ring core substituted with glycosylated steroid linkers. The synthetic target of this study was the development of a multistep synthesis of glycosylated steroid-substituted porphyrin with a protected carbohydrate moiety, as a bulky lipophilic system with good chiral UV chromophores aside from a typical Sorret one.

Strategies for the synthesis of lipophilic type of symmetric tetrasubstituted porphyrin structures were investigated (Scheme 1). Starting compounds **1**, **2** and **3** were prepared according to literature[22,23]. Glycosylation of **3** with **1** or **2** under Königs–Knorr conditions gave compounds **4** and **5** in good yields. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**) in acetonitrile gave with methyl ester of lithocholic acid (**3**) under catalysis with mercuric cyanide β-glucoside **4** in 50% yield; similarly 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**2**) gave 54% of β-galactoside **5**. The acetylated glycoside donors were chosen for the expected higher yields of glycosides.

Deprotection of acetyl groups was achieved under Zemplén conditions with sodium methoxide in methanol to give compounds **6** and **7** in 70–80% yields. The reaction of **6** and **7** with benzyl bromide in toluene provided compounds **8** and **9** in 82 and 43% yields, respectively. These compounds were reduced with $LiAlH_4$ in diethyl ether at room temperature to obtain compounds **10** and **11** in 82 and 89% yields, respectively. Oxidation of **10** and **11** with pyridinium chlorochromate (PCC) in CH_2Cl_2 gave aldehydes **12** and **13** in ca. 80% yields. All the above compounds were fully characterized.



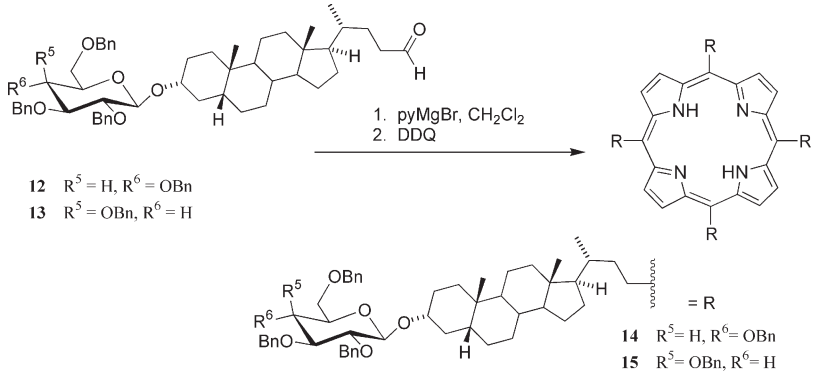
i) MeCN, $Hg(CN)_2$; ii) MeOH, MeONa; iii) toluene, BnBr, KOH, TBAI; iv) Et_2O, $LiAlH_4$; v) CH_2Cl_2, PCC
TBAI = tetrabutylammonium iodide

SCHEME 1

Reaction of pyrrol-1-yl magnesium bromide (for comparison with other chiral aldehydes see[24]) with aldehydes **12** and **13** (Scheme 2) formed porphyrinogen which was oxidized to porphyrin ring with DDQ to give **14** and **15**, respectively which were fully characterized. The reaction sequence used was selected as the most efficient after a comparison with alternative routes.

The final chromatographies on a silica gel column in toluene–diethyl ether and on preparative TLC plates gave two colored fractions each. Only the second fractions were fully characterized and elucidated in both *galacto*- and *gluco*-series as single defined chemical entities **14** and **15** in the yields of 9.5 and 6.3%, respectively. The first fractions were not fully character-

ized due to insufficient amounts of experimental material; so we denote them just as fractions in both cases not to cause possible misinterpretations. Initial analyses show both first fractions are analogous porphyrins as **14** and **15**, however one *meso* position in each had significantly changed.



SCHEME 2

The suitabile synthetic pathway for the new type of *meso*-substituted porphyrins (**14** and **15**) enables the study of this new kind of supramolecules and supramolecular synthons. These are being utilized in electrochemistry[4], membrane, super assembly and biological studies, i.a. We will employ this new synthetic pathway for the synthesis of hexasaccharide and pentasaccharide series of this receptor types with a tailored level of lipophilicity.

This paper shows the possibility of overcoming several methodological problems in the synthesis of a new complex type of conjugates and opens rather vast territory of their possible exploitations. The authors aimed to demonstrate the possibility of combining the known receptor molecules with carbohydrates that can serve as anchors, chiral selectors, or polarity modifiers, depending on their level and kind of protection, as discussed above.

EXPERIMENTAL

Melting points were determined on a Boetius micro-melting point apparatus (Germany). Optical rotations were measured on an Autopol III (Rudolph Research Analytical, Flanders, U.S.A.) polarimeter at 23 °C, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1} and concentrations in 10^{-1} g l^{-1}. IR spectra (wavenumbers in cm^{-1}) were recorded on a Bruker IFS 88 spectrometer in chloroform solutions (23 °C). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity 400 Inova (^{1}H at 400 MHz, ^{13}C at 100 MHz). All NMR spectra were measured at 25 °C in $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. Mass spectra were recorded on a VG Analytical ZAB-EQ spectrometer (FAB) and Bruker Esquire 3000 (ESI). MALDI-TOF analyses were carried out with a Biflex IV

Bruker Daltonic mass spectrometer, equipped with a UV nitrogen laser (337 nm) and a dual microchannel plate detector. Microanalyses were performed on a Perkin–Elmer 2400 Series II CHNS/O elemental analyzer. Thin layer chromatography was carried out on analytical plates Merck (type 5554, with a layer of Kieselgel 60 F254) or silica gel G (ICN Biomedicals), detection by UV lamp or by spraying with concentrated sulfuric acid or 3% anisaldehyde solution in ethanol and sulfuric acid, followed by heating. Preparative thin layer chromatography was performed on 200 × 200 mm plates (layer thickness 0.4 mm) of silica gel G (ICN Biomedicals). For column chromatography, neutral silica gel SiliTech 32-63, 60A (ICN Biomedicals) or Silpearl (Kavalier, Czech Republic) was used. Analytical samples were dried under vacuum over P_2O_5 at room temperature. For neutralization of methanolic solutions after deacetylations, strongly acid cation exchanger Fluka (Dowex 50W×8) in H^+ cycle was used. Freshly distilled solvents were used.

Methyl 3α-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyloxy)-5β-cholan-24-oate (**4**)

To a solution of methyl lithocholate (**3**; 10 g, 25.6 mmol) and D-acetobromoglucose (**1**; 20 g, 48.6 mmol) in dry acetonitrile (300 ml), mercuric cyanide (12.27 g, 48.6 mmol) was added and the reaction mixture was heated to reflux. The reaction course was monitored by TLC (hexane–ethyl acetate, 2.5:1). After 5 h, the reaction mixture was allowed to warm to room temperature, the solvent was evaporated, the residue was dissolved in dichloromethane (200 ml) and washed with water (3 × 100 ml). The organic layer was separated, dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum on a rotary evaporator. The residue was purified by chromatography on a silica gel column (toluene–ethyl acetate, 9:1). Recrystallization from a mixture of ether–petroleum ether gave **4** (9.3 g, 50%). M.p. 132–133 °C, $[\alpha]_D$ +12 (*c* 0.5, $CHCl_3$). ^{1}H NMR: 0.63 s, 3 H (H-18); 0.91 d, 3 H (*J* = 6.4, H-21); 0.91 s, 3 H (H-19); 2.01 s, 3 H; 2.02 s, 3 H; 2.05 s, 3 H; 2.08 s, 3 H (4 × OAc); 0.86–2.40, 28 H (steroid fingerprint); 3.57 tt, 1 H (Σ*J* = 31.6, H-3β); 3.67 s, 3 H ($COOCH_3$); 3.69 ddd, 1 H (J_1 = 9.9, J_2 = 5.0, J_3 = 2.4, H-5′); 4.11 dd, 1 H (J_1 = 12.2, J_2 = 2.4, H-6a′); 4.26 dd, 1 H (J_1 = 12.2, J_2 = 5.2, H-6b′); 4.59 d, 1 H (*J* = 7.9, H-1′); 4.95 dd, 1 H (J_1 = 9.6, J_2 = 7.9, H-2′); 5.07 t, 1 H (*J* = 9.9, H-4′); 5.21 t, 1 H (*J* = 9.5, H-3′). ^{13}C NMR: 11.98, 18.22, 20.59, 20.63, 20.72 (2C); 20.79, 23.34, 24.13, 26.22, 27.15, 27.18, 28.14, 30.95, 31.02, 34.16, 34.61, 35.12, 35.32, 35.77, 40.05, 40.23, 42.16, 42.67, 51.46, 55.84, 56.24, 62.18, 68.56, 71.56 (2C); 72.86, 80.90, 99.87, 169.33, 169.40, 170.36, 170.70, 174.77. MS (FAB, $CHCl_3$), *m/z*: 743 ($M + Na^+$), 720 (M^+). MS (ESI, MeOH): 743.7 ($M + Na^+$), 759.5 ($M + K^+$); MS^2 (743.7) 683.6, 311.2; MS^3 (683.6) 623.4, 581.4, 521.4, 479.3, 427.0, 311.1, 251.1. For $C_{39}H_{60}O_{12}$ (720.9) calculated: 64.98% C, 8.39% H; found: 64.77% C, 8.17% H.

Methyl 3α-(β-D-Glucopyranosyloxy)-5β-cholan-24-oate (**6**)

To a stirred solution of **4** (9.0 g, 12.5 mmol) in dry methanol (250 ml), sodium methoxide in methanol (10 mmol, 10 ml) was added. The reaction mixture was stirred at room temperature and monitored by TLC. After complete deacetylation (approximately 1 h), Dowex 50 in H^+ cycle (2 g) was added to the mixture and the suspension was stirred until the reaction mixture was neutral to pH paper. The resin was filtered off and methanol was evaporated. The residue was crystallized from methanol to give compound **6** (5 g, 72%). M.p. 192–194 °C, $[\alpha]_D$ +18 (*c* 0.45, MeOH). ^{1}H NMR (MeOH-d_4, 45 °C): 0.65 s, 3 H (H-18); 0.91 d, 3 H (*J* = 6.8, H-21); 0.92 s, 3 H (H-19); 0.89–2.40, 28 H (steroid fingerprint); 2.55 bs, 1 H (OH); 3.03 bs,

1 H (OH); 3.32–3.62, 6 H (H-2′, H-3′, H-4′, H-5′, 2 × OH); 3.66 s, 3 H ($COOCH_3$); 3.67 tt, 1 H (ΣJ = 31.8, H-3β); 3.78–3.92, 2 H (H-6a′, H-6b′); 4.42 d, 1 H (J = 7.8, H-1′). ^{13}C NMR (25 °C): 12.03, 18.28, 20.85, 23.38, 24.21, 26.39, 26.95, 27.23, 28.17, 31.00, 31.09, 34.25, 34.72, 35.15, 35.35, 35.83, 40.12, 40.37, 42.22, 42.72, 51.47, 56.00, 56.38, 61.90, 69.86, 73.52, 75.41, 76.39, 79.50, 100.75, 174.74. MS (FAB, MeOH), *m/z*: 553 ($M + H^+$). MS (ESI, MeOH): 575.6 ($M + Na^+$), 591.4 ($M + K^+$); MS^2 (575.6) 557.1, 515.5, 485.4, 455.3, 413.2; MS^3 (413.2) 347.8. For $C_{31}H_{52}O_8$ (552.7) calculated: 67.36% C, 9.48% H; found: 67.28% C, 9.54% H.

Methyl 3α-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyloxy)-5β-cholan-24-oate (**8**)

To a solution of compound **6** (4.8 g, 8.7 mmol) in dry toluene (200 ml), freshly powdered potassium hydroxide (2.5 g, 44.6 mmol), benzyl bromide (5.3 ml, 44.4 mmol) and tetrabutylammonium iodide (3.2 g, 8.7 mmol) were added. The reaction mixture was refluxed under argon and monitored by TLC. After 24 h, the second portion of potassium hydroxide (0.5 g) was added. The reaction went to completion after 2 days, potassium hydroxide was filtered off on a silica gel column, the filtrate was washed with water (2 × 75 ml), dried and then evaporated to dryness. After chromatography on a silica gel column (toluene–ethyl acetate, 29:1), pure compound **8** (3.2 g, 40%) was obtained by crystallization from ethanol. M.p. 102–104 °C, $[\alpha]_D$ +22 (*c* 0.5, $CHCl_3$). ^{1}H NMR: 0.64 s, 3 H (H-18); 0.91 s, 3 H (H-19); 0.92 d, 3 H (J = 6.4, H-21); 0.80–2.45, 28 H (steroid fingerprint); 3.43 dd, 1 H (J_1 = 9.3, J_2 = 7.9, H-2′); 3.46 ddd, 1 H (J_1 = 9.8, J_2 = 5.2, J_3 = 1.7, H-5′); 3.52 dd, 1 H (J_1 = 9.8, J_2 = 8.6, H-4′); 3.63 t, 1 H (J = 8.9, H-3′); 3.63 dd, 1 H (J_1 = 10.6, J_2 = 5.2, H-6a′); 3.68 tt, 1 H (ΣJ = 31.6, H-3β); 3.74 dd, 1 H (J_1 = 10.8, J_2 = 1.8, H-6b′); 4.50 d, 1 H (J = 7.8, H-1′); 4.54 d, 1 H (J = 10.8, H-benzyl); 4.55 d, 1 H (J = 12.4, H-benzyl); 4.60 d, 1 H (J = 12.2, H-benzyl); 4.72 d, 1 H (J = 10.8, H-benzyl); 4.78 d, 1 H (J = 11.0, H-benzyl); 4.82 d, 1 H (J = 11.0, H-benzyl); 4.92 d, 1 H (J = 11.0, H-benzyl); 4.98 d, 1 H (J = 10.8, H-benzyl); 7.16–7.38, 20 H (H-arom.). ^{13}C NMR: 12.00, 18.24, 20.78, 23.37, 24.15, 26.31, 27.14, 27.34, 28.14, 30.95, 30.98, 34.61 (2C); 35.18, 35.30, 35.76, 40.10, 40.33, 42.08, 42.68, 51.42, 55.89, 56.40, 69.19, 73.33, 74.77, 74.83, 74.95, 75.66, 78.00, 80.15, 82.41, 84.77, 102.26, 127.47, 127.55, 127.56 (2C); 127.60, 127.70, 127.86 (2C); 127.95 (2C); 128.17 (2C); 128.25 (2C); 128.31 (4C); 128.33 (2C); 138.06, 138.26, 138.53, 138.58, 174.71. MS (FAB, $CHCl_3$), *m/z*: 936 ($M + Na^+$), 913 (M^+). MS (ESI, MeOH): 935.7 ($M + Na^+$), 951.6 ($M + K^+$); MS^2 (935.7) 905.6, 819.1, 563.3, 455.4; MS^3 (563.3) 456.1, 413.2, 323.2, 231.1, 173.2. For $C_{59}H_{76}O_8$ (913.2) calculated: 77.6% C, 8.39% H; found: 77.52% C, 8.29% H.

3α-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyloxy)-5β-cholan-24-ol (**10**)

To a solution of methyl ester **8** (2.9 mg, 3.2 mmol) in diethyl ether (100 ml, dry), lithium aluminium hydride (245 mg, 6.4 mmol) was added cautiously. The reaction mixture was stirred at room temperature under argon atmosphere and the reaction was monitored by TLC. After 2 h, when no methyl ester was detected by TLC, the excess $LiAlH_4$ was carefully decomposed by addition of a mixture of ethyl acetate (3 ml) and water (1.5 ml). The formed suspension was filtered over Celite and washed with ethyl acetate. The filtrate was dried over anhydrous $MgSO_4$ and evaporated to dryness. The crude product was crystallized from ethanol to obtain alcohol **10** (2.3 g, 82%). M.p. 73–74 °C, $[\alpha]_D$ +22 (*c* 0.5, $CHCl_3$). ^{1}H NMR: 0.65 s, 3 H (H-18); 0.91 s, 3 H (H-19); 0.93 d, 3 H (J = 6.4, H-21); 0.90–2.00, 28 H (steroid fingerprint); 3.44 dd, 1 H (J_1 = 9.2, J_2 = 7.9, H-2′); 3.47 ddd, 1 H (J_1 = 9.8, J_2 = 5.2, J_3 = 1.8,

H-5′); 3.53 dd, 1 H (J_1 = 9.8, J_2 = 8.6, H-4′); 3.58–3.72, 5 H (CH_2OH, H-6a′, H-3′, H-3β); 3.74 dd, 1 H (J_1 = 10.8, J_2 = 1.8, H-6b′); 4.51 d, 1 H (J = 7.9, H-1′); 4.54 d, 1 H (J = 10.8, H-benzyl); 4.56 d, 1 H (J = 12.4, H-benzyl); 4.60 d, 1 H (J = 12.2, H-benzyl); 4.72 d, 1 H (J = 10.8, H-benzyl); 4.78 d, 1 H (J = 11.0, H-benzyl); 4.82 d, 1 H (J = 10.8, H-benzyl); 4.92 d, 1 H (J = 10.8, H-benzyl); 4.99 d, 1 H (J = 10.8, H-benzyl); 7.16–7.37, 20 H (H-arom.). ^{13}C NMR: 12.04, 18.65, 20.84, 23.41, 24.21, 26.38, 27.21, 27.38, 28.30, 29.42, 31.82, 34.67 (2C); 35.25, 35.57, 35.84, 40.19, 40.41, 42.16, 42.71, 56.19, 56.49, 63.62, 69.27, 73.39, 74.82, 74.87, 74.99, 75.69, 78.07, 80.20, 82.47, 84.82, 102.29, 127.50, 127.57, 127.61 (2C); 127.64, 127.74, 127.90 (2C); 127.99 (2C); 128.21 (2C); 128.30 (2C); 128.35 (4C); 128.38 (2C); 138.12, 138.33, 138.60, 138.65. MS (FAB, $CHCl_3$), *m/z*: 907 ($M + Na^+$), 885 ($M + H^+$) 884 (M^+). MS (ESI, MeOH): 907.8 ($M + Na^+$), 923.6 ($M + K^+$); MS^2 (907.8) 875.4, 815.5, 667.6, 563.3, 472.3, 353.2, 323.1; MS^3 (563.3) 455.2, 413.4, 323.1, 231.1, 203. For $C_{58}H_{76}O_7$ (885.2) calculated: 78.70% C, 8.65% H; found: 77.47% C, 8.56% H.

3α-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyloxy)-5β-cholan-24-al (**12**)

Alcohol **10** (2.1 g, 2.4 mmol) was dissolved in dichloromethane (6 ml, dry) and pyridinium chlorochromate (650 mg, 3 mmol) was added. The mixture was stirred under argon and the course of reaction was monitored by TLC. After 4 h, diethyl ether (6 ml) was added. The dark suspension was filtered through a silica gel column (100 g), the column was further washed out with a mixture of dichloromethane–diethyl ether (1:1), and solvents were evaporated. Chromatography on a silica gel column (toluene–ethyl acetate, 29:1) followed by crystallization from diethyl ether gave crystalline aldehyde **12** (1.6 g, 76%) . M.p. 55–57 °C, $[\alpha]_D$ +20.7 (*c* 0.53, $CHCl_3$). IR ($CHCl_3$): ν(C=O): ≈1722 m; ν(C–H) + 2β(HCO): visible bottom band: 2726 w; $\beta_s(CH_2)$: ≈1409 w, sh; –OBn: ν(=C–H): 3089 w (20a), 3066 w (2), 3033 (20b); ν(ring): 1497 w (19a), 1453 m (19b); $\beta_s(CH_2)$: 1362 m; $\gamma_s(CH_2)$: 1332 w; aromatic: 1277 w (13), 1029 m (18a), 913 w (17b), 699 s (4), 613 w (6b), 462 w (6a); ν_{as}(COC) + ν(ring) tetrahydropyran: 1150 w, ≈1117 m, sh; ≈1091 s, sh; 1067 vs, 1004 m. ^{1}H NMR: 0.65 s, 3 H (H-18); 0.91 s, 3 H (H-19); 0.92 d, 3 H (J = 6.4, H-21); 0.80–2.50, 28 H (steroid fingerprint); 3.43 dd, 1 H (J_1 = 9.2, J_2 = 7.9, H-2′); 3.47 ddd, 1 H (J_1 = 9.9, J_2 = 5.2, J_3 = 1.7, H-5′); 3.53 dd, 1 H (J_1 = 9.8, J_2 = 8.5, H-4′); 3.63 t, 1 H (J = 9.0, H-3′); 3.63 dd, 1 H (J_1 = 10.7, J_2 = 5.0, H-6a′); 3.68 m, 1 H (H-3β); 3.74 dd, 1 H (J_1 = 10.8, J_2 = 1.8, H-6b′); 4.51 d, 1 H (J = 7.8, H-1′); 4.54 d, 1 H (J = 10.8, H-benzyl); 4.56 d, 1 H (J = 12.2, H-benzyl); 4.60 d, 1 H (J = 12.2, H-benzyl); 4.72 d, 1 H (J = 11.0, H-benzyl); 4.78 d, 1 H (J = 11.0, H-benzyl); 4.82 d, 1 H (J = 10.8, H-benzyl); 4.92 d, 1 H (J = 11.0, H-benzyl); 4.99 d, 1 H (J = 10.8, H-benzyl); 7.16–7.37, 20 H (H-arom.); 9.77 t, 1 H (J = 2.0, CHO). ^{13}C NMR: 12.05, 18.38, 20.82, 23.40, 24.19, 26.35, 27.18, 27.40, 27.96, 28.24, 34.66 (2C); 35.24, 35.31, 35.82, 40.15, 40.39, 40.92, 42.14, 42.76, 55.99, 56.46, 69.27, 73.39, 74.82, 74.87, 74.99, 75.69, 78.07, 80.21, 82.47, 84.82, 102.32, 127.51, 127.58, 127.61 (2C); 127.64, 127.90 (2C); 127.99 (2C); 128.21 (2C); 128.30 (2C); 128.35 (4C); 128.38 (2C); 138.12, 138.33, 138.61, 138.64, 203.23. MS (FAB, $CHCl_3$), *m/z*: 883 ($M + H^+$). MS (ESI, MeOH): 937.5 ($M + MeOH + Na^+$), 905.5 ($M + MeOH + K^+$), 905.5 ($M + Na^+$), 921.3 ($M + K^+$); MS^2 (935.5) 905.5; MS^3 (905.5) 563.2, 323.2. For $C_{58}H_{74}O_7$ (883.2) calculated: 78.87% C, 8.45% H; found: 78.67% C, 8.37% H.

5,10,15,20-Tetrakis[3α-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyloxy)-5β-cholan-24-yl]-porphyrin (**14**)

Pyrrole (34 mg, 0.5 mmol) and dry diethyl ether (30 ml) were added to a flask with a septum and ethylmagnesium bromide (170 μl, 2.93 mol l^{-1}) was added dropwise under argon. The reaction mixture was stirred for 20 min and then the solvent was evaporated. The residue was dissolved in dichloromethane (50 ml, dry) and aldehyde **12** (440 mg, 0.5 mmol) was added. This solution was stirred under argon and the progress of the reaction was monitored by TLC (ethyl acetate–hexane, 2:1). After 3 days, when the mixture became dark, DDQ (150 mg, 0.65 mmol) was added, the suspension was stirred for 2 h and then acetic acid (2.5 ml) in water (20 ml) was added. The heterogeneous mixture was stirred for 15 min and then the organic layer was separated. It was washed with a saturated solution of sodium hydrogencarbonate (50 ml) and water (2 × 50 ml), then dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was dissolved and chromatographed over a silica gel column (75 g) using a mixture of ethyl acetate–hexane (2:1), the fraction containing porphyrins (after spraying TLC with acid, porphyrin became green) was taken and evaporated. Repeated chromatography on a silica gel column (50 g) in toluene–diethyl ether (90:3, 2×) and on preparative TLC plates gave two colored fractions.

Second fraction contained 45 mg of red-brown amorphous product **14** (9.5%). $[\alpha]_D$ –0.4 (*c* 0.08, $CHCl_3$). UV ($CHCl_3$): λ_{max} 419 nm (log ε = 5.09). IR ($CHCl_3$): ν(N–H): 3323 w; pyrrole: ν(=C–H) 3109 vw; ν(C=C): 1567 w; ν(C=N): 1480 w, sh; ν(C–H rocking): 1004 m, ≈966 m, sh; –OBn: ν(=C–H): 3089 w (20a), 3066 w (2), 3030 m (20b); ν(ring): 1606 w (8a), 1587 w (8b), 1497 m (19a), 1453 s (19b); aromatic + other bands: 1278 w (13), 1029 s (18a), 917 m (17b), 699 s (4), 615 w (6b), 461 w (6a); $\nu_s(CH_2)$: 2867 s; $\beta_s(CH_2)$: 1362 s (+ ν(C–N)pyrrole); $\gamma_s(CH_2)$: 1336 w; ν_{as}(COC) + ν(ring) tetrahydropyran, aromatic 18b: 1150 s, ≈1117 s; ≈1088 s; 1067 vs; $\delta_s(CH_3)$: 1376 m. ^{1}H NMR: –2.61 bs, 2 H (2 × NH-pyrrole); 0.82 s, 12 H (4 × H-18); 0.97 s, 12 H (4 × H-19); 1.59 d, 12 H (*J* = 6.5, 4 × H-21); 0.80–2.75, 112 H (4 × steroid fingerprint); 3.43 dd, 4 H (J_1 = 9.1, J_2 = 7.8, 4 × H-2′); 3.46 ddd, 4 H (J_1 = 9.8, J_2 = 5.2, J_3 = 1.8, 4 × H-5′); 3.51 dd, 4 H (J_1 = 9.8, J_2 = 8.6, 4 × H-4′); 3.62 dd, 4 H (J_1 = 10.8, J_2 = 5.3, 4 × H-6a′); 3.63 t, 4 H (*J* = 8.7, 4 × H-3′); 3.70 tt, 4 H (Σ*J* = 31.6, 4 × H-3β); 3.73 dd, 4 H (J_1 = 10.8, J_2 = 1.9, 4 × H-6b′); 4.52 d, 4 H (*J* = 7.6, 4 × H-1′); 4.52 d, 4 H (*J* = 11.4, 4 × H-benzyl); 4.55 d, 4 H (*J* = 12.2, 4 × H-benzyl); 4.59 d, 4 H (*J* = 12.2, 4 × H-benzyl); 4.71 d, 4 H (*J* = 10.8, 4 × H-benzyl); 4.77 d, 4 H (*J* = 10.9, 4 × H-benzyl); 4.80 d, 4 H (*J* = 11.0, 4 × H-benzyl); 4.91 d, 4 H (*J* = 11.0, 4 × H-benzyl); 4.99 d, 4 H (*J* = 10.9, 4 × H-benzyl); 7.16–7.36, 80 H (H-arom.); 9.44 bs, 8 H (8 × H-pyrrole). For $C_{248}H_{302}N_4O_{24}$ calculated exact mass: 3720.25, m.w.: 3723.06, *m/z*: 3722.26 (100.0%), 3723.26 (90.6%), 3721.26 (72.7%), 3724.27 (60.0%), 3725.27 (36.6%), 3720.25 (26.7%), 3726.27 (16.8%), 3724.26 (6.1%), 3727.28 (5.5%), 3723.27 (3.3%), 3728.28 (2.4%), 3727.27 (1.8%), 3722.25 (1.1%), 3726.28 (1.0%); found MS (MALDI, $CHCl_3$), *m/z*: 3723.

Methyl 3α-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyloxy)-5β-cholan-24-oate (**5**)

Compound **5** was synthesized in the same way as **4** from methyl lithocholate **3** (10 g, 25.6 mmol) and acetobromogalactose **2** (20 g, 48.6 mmol), and mercuric cyanide (12.27 g, 48.6 mmol). The preparation gave the solid product **5** (10 g, 54%). M.p. 74–76 °C, $[\alpha]_D$ +20 (*c* 0.5, $CHCl_3$). ^{1}H NMR: 0.63 s, 3 H (H-18); 0.91 s, 3 H (H-19); 0.91 d, 3 H (*J* = 6.4, H-21); 1.98 s, 3 H; 2.04 s, 3 H; 2.06 s, 3 H; 2.15 s, 3 H (4 × OAc); 0.90–2.40, 28 H (steroid fingerprint); 3.56 tt, 1 H (Σ*J* = 31.7, H-3β); 3.67 s, 3 H ($COOCH_3$); 3.89 td, 1 H (J_1 = 6.8, J_2 = 1.2,

H-5′); 4.11 dd, 1 H (J_1 = 11.1, J_2 = 7.0, H-6a′); 4.20 dd, 1 H (J_1 = 11.3, J_2 = 6.6, H-6b′); 4.54 d, 1 H (J = 7.9, H-1′); 5.01 dd, 1 H (J_1 = 10.5, J_2 = 3.5, H-3′); 5.18 dd, 1 H (J_1 = 10.5, J_2 = 7.9, H-2′); 5.38 dd, 1 H (J_1 = 3.4, J_2 = 1.1, H-4′). ^{13}C NMR: 12.00, 18.24, 20.60, 20.66, 20.68, 20.82 (2C); 23.35, 24.16, 26.25, 27.20, 27.31, 28.15, 30.98, 31.06, 34.34, 34.63, 35.16, 35.35, 35.81, 40.10, 40.25, 42.19, 42.70, 51.46, 55.89, 56.30, 61.35, 67.04, 69.17, 70.48, 71.01, 81.25, 100.66, 169.42, 170.22, 170.33, 170.40, 174.76. MS (FAB, $CHCl_3$), *m/z*: 720 (M^+). MS (ESI, MeOH): 743.7 (M + Na^+), 759.5 (M + K^+); MS^2 (743.7) 683.6, 581.4, 371.2, 311.2; MS^3 (683.6) 641.5, 623.4, 581.1, 521.1, 413.2, 311.1, 251.1, 227.1. For $C_{39}H_{60}O_{12}$ (720.9) calculated: 64.98% C, 8.39% H; found: 64.94% C, 8.53% H.

Methyl 3α-(β-D-Galactopyranosyloxy)-5β-cholan-24-oate (**7**)

Compound **7** was synthesized as **6** from protected galactoside **5** (9.5 g, 13.2 mmol) and sodium methoxide in methanol (10 mmol, 10 ml). The residue was recrystallized from methanol to obtain **7** (5.8 g, 79.5%). M.p. 211–213 °C, $[\alpha]_D$ +22 (*c* 0.5, MeOH). ^{1}H NMR (MeOH-d_4, 45 °C): 0.65 s, 3 H (H-18); 0.91 d, 3 H (J = 6.4, H-21); 0.92 s, 3 H (H-19); 0.90–2.40, 28 H (steroid fingerprint); 2.40 bs, 1 H (OH); 2.70 bs, 1 H (OH); 3.10 bs, 2 H (2 × OH); 3.54 ddd, 1 H (J_1 = 6.1, J_2 = 4.9, J_3 = 1.2, H-5′); 3.58–3.64, 2 H (H-2′, H-3′); 3.66 s, 3 H ($COOCH_3$); 3.69 tt, 1 H (ΣJ = 31.4, H-3β); 3.86 dd, 1 H (J_1 = 11.8, J_2 = 5.0, H-6a′); 3.93 dd, 1 H (J_1 = 11.7, J_2 = 6.0, H-6b′); 4.01 dd, 1 H (J_1 = 2.9, J_2 = 1.2, H-4′); 4.37 d, 1 H (J = 7.5, H-1′). ^{13}C NMR (45 °C): 12.06, 18.32, 20.91, 23.36, 24.23, 26.42, 27.10, 27.25, 28.17, 31.09, 31.16, 34.44, 34.78, 35.23, 35.38, 35.93, 40.23, 40.52, 42.30, 42.82, 51.38, 56.12, 56.54, 62.59, 69.50, 71.97, 73.64, 74.34, 79.37, 101.22, 174.67. MS (FAB, MeOH), *m/z*: 553 (M + H^+). MS (ESI, MeOH): 575.5 (M + Na^+), 591.3 (M + K^+); MS^2 (575.5) 405.8, 355.2, 313.6, 203. For $C_{31}H_{52}O_8$ (552.7) calculated: 67.36% C, 9.48% H; found: 66.65% C, 9.57% H.

Methyl 3α-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyloxy)-5β-cholan-24-oate (**9**)

Compound **9** was synthesized as **8** from **7** (5.5 g, 10 mmol) in toluene (200 ml, dry), freshly powdered potassium hydroxide (2.9 g, 52 mmol), benzyl bromide (6.2 ml, 52 mmol) and tetrabutylammonium iodide (3.7 g, 10 mmol). After chromatography on a silica gel column (toluene–ethyl acetate, 29:1), pure product **9** (4 g, 43%) was obtained as a syrup. $[\alpha]_D$ +11.4 (*c* 0.52, $CHCl_3$). ^{1}H NMR: 0.64 s, 3 H (H-18); 0.89 s, 3 H (H-19); 0.92 d, 3 H (J = 6.4, H-21); 0.85–2.46, 28 H (steroid fingerprint); 3.47–3.69, 5 H (H-3′, H-5′, H-6a′, H-6b′, H-3β); 3.66 s, 3 H ($COOCH_3$); 3.80 dd, 1 H (J_1 = 9.8, J_2 = 7.6, H-2′); 3.86 bd, 1 H (J = 2.4, H-4′); 4.41 d, 1 H (J = 11.8, H-benzyl); 4.45 d, 1 H (J = 11.8, H-benzyl); 4.46 d, 1 H (J = 7.8, H-1′); 4.61 d, 1 H (J = 11.8, H-benzyl); 4.70 d, 1 H (J = 11.8, H-benzyl); 4.75 d, 2 H (J = 11.3, 2 × H-benzyl); 4.93 d, 1 H (J = 11.6, H-benzyl); 4.95 d, 1 H (J = 10.8, H-benzyl); 7.23–7.39, 20 H (H-arom.). ^{13}C NMR: 12.01, 18.26, 20.80, 23.38, 24.17, 26.33, 27.18, 27.27, 28.15, 31.03, 31.27, 34.50, 34.65, 35.28, 35.34, 35.80, 40.15, 40.35, 42.13, 42.71, 51.44, 55.93, 56.43, 69.16, 73.06, 73.40, 73.50, 73.61, 74.38, 75.19, 79.75, 79.92, 82.36, 102.48, 127.43, 127.48 (2C); 127.50 (2C); 127.69, 127.77 (2C); 128.08 (2C); 128.19 (2C); 128.22 (2C); 128.30 (4C); 128.36 (2C); 138.01, 138.61, 138.71, 138.89, 174.76. MS (FAB, $CHCl_3$), *m/z*: 913 (M^+). MS (ESI, MeOH): 935.7 (M + Na^+); MS^2 (935.7) 805.6, 563.4, 471.4, 324.2; MS^3 (563.3) 455.1, 413.1, 323.1. For $C_{59}H_{76}O_8$ (913.2) calculated: 77.6% C, 8.39% H; found: 77.76% C, 8.43% H.

3α-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyloxy)-5β-cholan-24-ol (**11**)

Compound **11** was synthesized as **10** from methyl ester **9** (3.5 g, 3.8 mmol) and lithium aluminum hydride (290 mg, 7.6 mmol). Product **11** (3 g, 89%) was obtained as a syrup. $[\alpha]_D$ +14.5 (*c* 0.55, $CHCl_3$). ^{1}H NMR: 0.64 s, 3 H (H-18); 0.90 s, 3 H (H-19); 0.93 d, 3 H (*J* = 6.4, H-21); 0.85–2.00, 28 H (steroid fingerprint); 3.47–3.69, 7 H (CH_2OH, H-3′, H-5′, H-6a′, H-6b′, H-3β); 3.80 dd, 1 H (J_1 = 9.8, J_2 = 7.7, H-2′); 3.86 bd, 1 H (*J* = 2.5, H-4′); 4.41 d, 1 H (*J* = 11.8, H-benzyl); 4.45 d, 1 H (*J* = 11.7, H-benzyl); 4.46 d, 1 H (*J* = 7.7, H-1′); 4.61 d, 1 H (*J* = 11.8, H-benzyl); 4.70 d, 1 H (*J* = 11.8, H-benzyl); 4.75 d, 2 H (*J* = 10.6, 2 × H-benzyl); 4.93 d, 1 H (*J* = 11.7, H-benzyl); 4.95 d, 1 H (*J* = 10.8, H-benzyl); 7.24–7.39, 20 H (H-arom.). ^{13}C NMR: 12.03, 18.65, 20.82, 23.39, 24.20, 26.36, 27.20, 27.27, 28.30, 29.43, 31.81, 34.52, 34.67, 35.27, 35.57, 35.82, 40.19, 40.38, 42.15, 42.69, 56.18, 56.48, 63.62, 69.17, 73.07, 73.41, 73.51, 73.62, 74.40, 75.21, 79.76, 79.94, 82.37, 102.48, 127.45, 127.50 (4C); 127.71, 127.79 (2C); 128.10 (2C); 128.22 (2C); 128.25 (2C); 128.32 (4C); 128.38 (2C); 138.02, 138.61, 138.71, 138.89. MS (FAB, $CHCl_3$), *m/z*: 907 ($M + Na^+$), 885 ($M + H^+$). MS (ESI, MeOH): 907.8 ($M + Na^+$), 923.6 ($M + K^+$); MS^2 (907.8) 815.6, 563.5; MS^3 (563.3) 455.2, 413.2, 365.1, 323.1, 203. For $C_{58}H_{76}O_7$ (885.2) calculated: 78.69% C, 8.65% H; found: 78.65% C, 8.57% H.

3α-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyloxy)-5β-cholan-24-al (**13**)

Compound **13** was synthesized as given for **12** from alcohol **11** (2.8 g, 3.1 mmol) and pyridinium chlorochromate (870 mg, 4 mmol). Chromatography on a silica gel column (toluene–ethyl acetate, 29:1) gave syrup aldehyde **13** (2.2 g, 80%). $[\alpha]_D$ +11.2 (*c* 0.49, $CHCl_3$). IR ($CHCl_3$): ν(C=O): 1722 m; ν(C–H) + 2β(HCO): visible only bottom band of doublet: 2726 w; $\beta_s(CH_2)$: ≈1410 w, sh; –OBn: ν(=C–H): 3089 w (20a), 3066 w (2), 3033 m (20b); ν(ring): 1606 vw (8a), 1586 vw (8b), 1497 m (19a), 1454 s (19b); $\beta_s(CH_2)$: 1363 s; aromatic: 1288 w (13), 1028 s (18a), 912 w (17b), 699 s (4), 612 w (6b), 465 w (6a); ν_{as}(COC) + ν(ring) tetrahydropyran: 1158 m, 1134 m, 1093 vs, 1073 vvs , 1043 s, 1004 m. ^{1}H NMR: 0.64 s, 3 H (H-18); 0.90 s, 3 H (H-19); 0.92 d, 3 H (*J* = 6.4, H-21); 0.80–2.50, 28 H (steroid fingerprint); 3.45–3.62, 4 H (H-3′, H-5′, H-6a′, H-6b′); 3.64 tt, 1 H (Σ*J* = 32.0, H-3β); 3.80 dd, 1 H (J_1 = 9.8, J_2 = 7.6, H-2′); 3.86 bd, 1 H (*J* = 2.6, H-4′); 4.41 d, 1 H (*J* = 11.8, H-benzyl); 4.45 d, 1 H (*J* = 11.7, H-benzyl); 4.45 d, 1 H (*J* = 7.8, H-1′); 4.61 d, 1 H (*J* = 11.6, H-benzyl); 4.70 d, 1 H (*J* = 11.8, H-benzyl); 4.75 d, 2 H (*J* = 11.6, 2 × H-benzyl); 4.93 d, 1 H (*J* = 11.8, H-benzyl); 4.95 d, 1 H (*J* = 10.8, H-benzyl); 7.20–7.40, 20 H (H-arom.); 9.76 t, 1 H (*J* = 1.8, CHO). ^{13}C NMR: 12.03, 18.37, 20.79, 23.37, 24.17, 26.33, 27.16, 27.28, 27.94, 28.23, 34.50, 34.65, 35.25, 35.29, 35.80, 40.14, 40.35, 40.89, 42.12, 42.73, 55.95, 56.43, 69.17, 73.06, 73.40, 73.50, 73.61, 74.39, 75.19, 79.75, 79.95, 82.36, 102.51, 127.44, 127.50 (4C); 127.70, 127.78 (2C); 128.10 (2C); 128.20 (2C); 128.23 (2C); 128.31 (4C); 128.37 (2C); 138.01, 138.60, 138.71, 138.90, 203.21. MS (FAB, $CHCl_3$), *m/z*: 883 ($M + H^+$). MS (ESI, MeCN): 905.6 ($M + Na^+$), 921.4 ($M + K^+$); MS^2 (905.6) 813.2, 563.3. For $C_{58}H_{74}O_7$ (883.2) calculated: 78.87% C, 8.45% H; found: 78.92% C, 8.67% H.

15,10,15,20-Tetrakis-[3α-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyloxy)-5-cholan-24-yl]-porphyrin (**15**)

The porphyrin **15** was synthesize as **14** from pyrrole (34 mg, 0.5 mmol), ethylmagnesium bromide (170 μl, 2.93 mol l^{-1}), aldehyde **13** (440 mg, 0.5 mmol) and DDQ (150 mg, 0.65 mmol). The residue was dissolved and chromatographed over a silica gel (75 g) with a mix-

ture of ethyl acetate–hexane (2:1), the fraction containing porphyrin (after spraying TLC with acid, porphyrin became green) was taken and evaporated. Next purification by chromatography on a silica gel column (50 g) in toluene–diethyl ether (90:3, 2×) and on preparative TLC plates gave two colored fractions.

Second fraction contained 30 mg of red-brown amorphous product **15** (6.3%). $[\alpha]_D$ –3 (*c* 0.05, $CHCl_3$). UV ($CHCl_3$): λ_{max} 419 nm (log ε = 5.47). IR ($CHCl_3$): ν(N–H): 3323 w; pyrrole: ν(=C–H) 3109 vw; ν(C=C): 1567 w; ν(C=N): ≈1480 m, sh; ν(C–H rocking): 1004 m, ≈966 w; –OBn: ν(=C–H): 3089 w (20a), 3066 m (2); ν(ring): 1606 w (8a), 1585 w (8b), 1497 m (19a), 1454 s (19b); aromatic + other bands: 1028 s (18b), 917 m (17b), 699 s (4), 613 w (6b), 464 w (6a); $\nu_s(CH_2)$: 2866 s; $\beta_s(CH_2)$: 1363 s (+ ν(C–N)pyrrole); $\nu_{as}(COC)$ + ν(ring) tetrahydropyran, aromatic 18b: 1163 s, 1135 s; 1093 vs; 1074 vs, 1043 vs; $\delta_s(CH_3)$: 1376 m. ^{1}H NMR: –2.61 bs, 2 H (2 × NH-pyrrole); 0.82 s, 12 H (4 × H-18); 0.95 s, 12 H (4 × H-19); 1.60 d, 12 H (*J* = 6.5, 4 × H-21); 0.80–2.70, 112 H (4 × steroid fingerprint); 3.48–3.60, 16 H (4 × (H-3′, H-5′, H-6a′, H-6b′)); 3.67 tt, 4 H (Σ*J* = 32.0, 4 × H-3β); 3.79 dd, 4 H (J_1 = 9.7, J_2 = 7.7, 4 × H-2′); 3.85 dd, 4 H (J_1 = 3.0, J_2 = 0.9, 4 × H-4′); 4.40 d, 4 H (*J* = 11.8, 4 × H-benzyl); 4.44 d, 4 H (*J* = 11.7, 4 × H-benzyl); 4.47 d, 4 H (*J* = 7.7, 4 × H-1′); 4.59 d, 4 H (*J* = 11.8, 4 × H-benzyl); 4.67 d, 4 H (*J* = 11.9, 4 × H-benzyl); 4.74 d, 8 H (*J* = 11.6, 8 × H-benzyl); 4.91 d, 4 H (*J* = 11.7, 4 × H-benzyl); 4.96 d, 4 H (*J* = 10.7, 4 × H-benzyl); 7.18–7.38, 80 H (H-arom.); 9.45 bs, 8 H (8 × H-pyrrole). For $C_{248}H_{302}N_4O_{24}$ calculated exact mass: 3720.25, m.w.: 3723.06, *m/z*: 3722.26 (100.0%), 3723.26 (90.6%), 3721.26 (72.7%), 3724.27 (60.0%), 3725.27 (36.6%), 3720.25 (26,7%), 3726.27 (16.8%), 3724.26 (6.1%), 3727.28 (5.5%), 3723.27 (3.3%), 3728.28 (2.4%), 3727.27 (1,8%), 3722.25 (1.1%), 3726.28 (1.0%); found MS (MALDI, $CHCl_3$), *m/z*: 3723.

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, projects No. 1131 00001 (T. Trnka), No. 2233 00006 (P. Drašar), OCD 31 (M. Dukh), grant No. FRVS 2796 (K. Zelenka), and it was a part of project Z4 055 905 (V. Král).

REFERENCES

1. Zelenka K., Trnka T., Drašar P., Dukh M.: *Cukrblik 03; Current Chemistry and Biochemistry of Saccharides*. Book of Abstracts (T. Trnka and J. Moravcová, Eds), p. 36. Czech Chemical Society, Prague 2003.
2. Zelenka K., Trnka T., Drašar P., Dukh M.: *36th Conference on Advances in Organic, Bioorganic and Pharmaceutical Chemistry, Nymburk, November 19–21, 2001*; Abstract published in: *Chem. Listy* **2001**, *95*, 777.
3. Zelenka K., Trnka T., Drašar P., Dukh M.: *38th Conference on Advances in Organic, Bioorganic and Pharmaceutical Chemistry, Nymburk, November 28–30, 2003*; Abstract published in: *Chem. Listy* **2003**, *97*, 1139.
4. Dukh M., Černý I., Pouzar V., Král V., Barek J., Drašar P.: *US–CZ Workshop on Electrochemical Sensors*. Book of Abstracts, p. 5. Czech Chemical Society, Prague 2001.
5. Drašar P.: *Crit. Rev. Anal. Chem.* **1999**, *29*, 71.
6. Tamminen J., Kolehmainen E.: *Molecules* **2001**, *6*, 21.
7. Davis A. P., Bonar-Law R. P., Sanders K. M. in: *Comprehensive Supramolecular Chemistry* (J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Eds), Vol. 4, p. 257. Pergamon, Oxford 1996.

8. Mishima K., Satoh K., Suzuki K.: *Colloids Surf., B* **1997**, *9*, 9.
9. Ikezawa H.: *Tanpakushitsu Kakusan Koso* **1991**, *36*, 596; *Chem. Abstr.* **1991**, *114*, 180414.
10. Davis A. P., Perry J. J., Williams R. P.: *J. Am. Chem. Soc.* **1997**, *119*, 1793.
11. Ayling A. J., Nieves Pérez-Payán M., Davis A. P.: *J. Am. Chem. Soc.* **2001**, *123*, 12716.
12. Wallimann P., Marti T., Furer A., Diedrich F.: *Chem. Rev.* **1997**, *97*, 1567.
13. Kim Y. H., Hong J. I.: *Angew. Chem., Int. Ed.* **2002**, *41*, 2947.
14. Davis A. P., Joos J. B.: *Coord. Chem. Rev.* **2003**, *240*, 143.
15. Dukh M., Šaman D., Kroulík J., Černý I., Pouzar V., Král V., Drašar P.: *Tetrahedron* **2003**, *59*, 4069.
16. Dukh M., Černý I., Urbanský M., Pouzar V., Král V., Drašar P.: Czech 290491; Czech Appl. 1999, 3098.
17. Dukh M., Šaman D., Lang K., Pouzar V., Černý I., Drašar P., Král V.: *Org. Biomol. Chem.* **2003**, *19*, 3458.
18. Dukh M., Pouzar V., Černý I., Urbanský M., Král V., Drašar P.: *52nd Congress of Czech and Slovak Chemical Societies, České Budějovice, August 30–September 20, 2000*; Abstract published in: *Chem. Listy* **2000**, *94*, 797.
19. Drašar P., Dukh M., Urbanský M., Černý I., Pouzar V., Král V. M.: *34th Conference on Advances in Organic, Bioorganic and Pharmaceutical Chemistry, Nymburk, November 15–17, 1999*; Abstract published in: *Chem. Listy* **1999**, *93*, 747.
20. Dukh M., Pouzar V., Černý I., Urbanský M., Král V. M., Drašar P.: *35th Conference on Advances in Organic, Bioorganic and Pharmaceutical Chemistry, Nymburk, November 13–15, 2000*; Abstract published in: *Chem. Listy* **2000**, *94*, 1039.
21. Dukh M., Drašar P., Černý I., Pouzar V., Shriver J. A., Král V., Sessler J. L.: *Supramol. Chem.* **2002**, *14*, 237.
22. Latham H. G., May E. L., Mosettig E.: *J. Org. Chem.* **1950**, *15*, 884.
23. Reindel F.: *Chem. Ber.* **1935**, *68B*, 1969.
24. Cornia M., Capacchi S., Porcari S., Tarasconi P.: *Tetrahedron: Asymmetry* **1997**, *8*, 2885.