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Novel Porphyrin Ribose Derivatives; Synthesis and Physicochemical Characterization

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Four new mono-ribosyl derivatives (**5**, **6**, **9**, and **11**) and one four-ribosyl derivative (**12)** were synthesized. Complexes of a few of these compounds with metals were also synthesized. All compounds were characterized by spectroscopic methods.

Key words: porphyrins, metalloporphyrins, glycoconjugated porphyrins, ribose

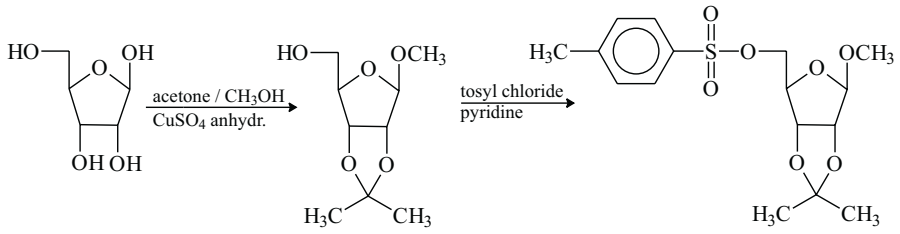
One of the most serious obstacles in using tetraphenylporphyrins (TPP) in biological systems is their low solubility in water. Various strategies for the synthesis of water-soluble porphyrin have been developed. Thus, porphyrins with hydrophilic moieties *e.g*. amines [1–3], guanidine [4], pyridine [5], sulphate [6], polyglycols [7], dextrose [8,9], viologen [10], phosphoniumyl [11,12] are known to have a good solubility in water. Sugar units linked to tetraphenylporphyrin also enhance water solubility, owing to the presence of hydrophilic carbohydrate moiety. Such modified porphyrins have been used in numerous model studies. A number of carbohydrate-substituted porphyrins have been synthesized recently [13–15].

The mono-hydroxyphenyl derivatives of tetraphenylporphyrin are available in large quantities. Their hydroxy moieties are readily functionalized in the course of various transformations. Simple modification of phenyl substituents in tetraphenylporphyrins has little effect on the photophysical properties of parent compounds. Preparation of such derivatives gained importance when it was realized that modified porphyrins, due to their specific properties (as a result of transformation), might be able to perform functions that simple tetraphenylporphyrins cannot, primarily in some biochemical applications. Glycoconjugated compounds, imitating natural ones, can be useful in photodynamic therapy (PDT), as well as other medical or material science applications (*e.g*. amphiphilic porphyrinic sensitizers may be incorporated more efficiently into cell membranes [16,17]).

In this paper, we present a number of ribosyl derivatives of tetraphenylporphyrin and some of their physicochemical properties. Although recently several ribosyl-substituted tetraphenylporphyrins were synthesized, their ribosyl units were linked to phenyl unit(s) by ribosyl C1 carbon atom [18–20] or formed a fragment of nucleobases [21–23]. Phenyl-modified compounds were often synthesized by reacting carbohydrate-substituted benzaldehyde and another benzaldehyde derivative with pyrrole under Lindsay conditions [24]. The reaction leads to a mixture of different carbohydrate-substituted porphyrins, bearing also two to four carbohydrate moieties.

The best way to avoid multistep chromatographic purification-separation procedure in the synthesis of mono-ribosyl substituted porphyrins is to proceed with modification of simple hydroxyphenylporphyrins. On the other hand, the tetra-ribosyl-substituted porphyrin is more easily synthesized by reacting ribosyl-substituted benzaldehyde with pyrrole under Adler-Longo conditions [25]. We synthesized our compounds according to Schemes 1 and 2.

Scheme 1



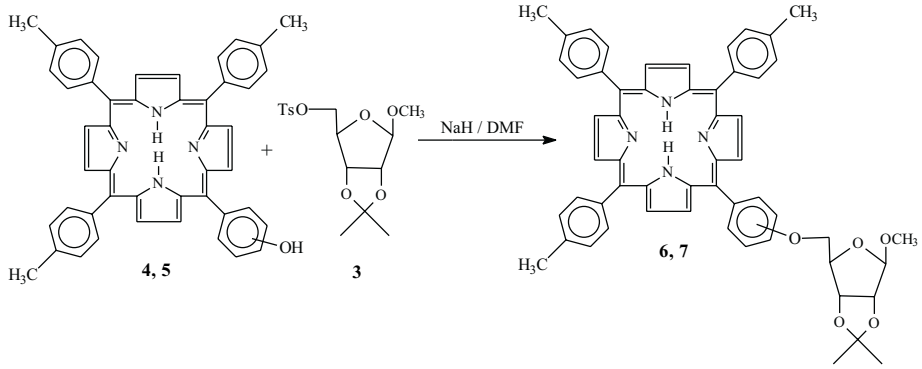
1 2 3

RESULTS AND DISCUSSION

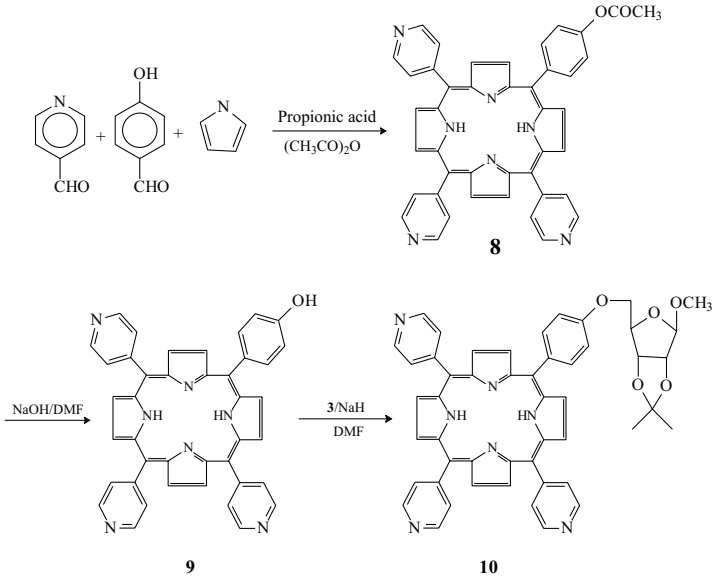
Coupling of tosylate **3** with hydroxyphenyl porphyrins **4** (*para*) and **5** (*meta*) in the presence of NaH in DMF produces the protected compounds: methyl 5-[5′-para-phenylene-10′,15′,20′-tritolylporphyrin]-2,3-O-isopropylidene-β-D-ribofuranoside **6** and methyl 5-[5′-meta-phenylene-10′,15′,20′-tritolylporphyrin]-2,3-O-isopropylidene-β-D-ribofuranoside **7** – in good yields (Scheme 2). The obtained ribosyl-substituted tetraphenylporphyrins were purified by chromatography on alumina with hexane-chloroform mixture (**6**) or silica with chloroform (**7**) as eluent. The Zn(II) derivatives of **6** and **7** were obtained by refluxing the chloroform/methanol solutions of porphyrins **6** or **7**, respectively, with fivefold excess of $Zn(CH_3COO)_2$ for 1 hour, followed by evaporation of the resulting mixture. The crude products were precipitated from methanol solutions of metalloporphyrins with water and finally chromatographed on silica gel with chloroform as eluent. The Co(II) and In(III) derivatives of **6** were obtained in a similar way.

Tripyridylporphyrin derivative **10** was synthesized starting from 5-(para-hydroxyphenyl)-10,15,20-tripyridylporphyrin **9** [26] and methyl ribosyl tosylate **3** in a similar way to compound **6** (Scheme 3). The yield was lower than for tolyl porphyrin derivative.

Scheme 2

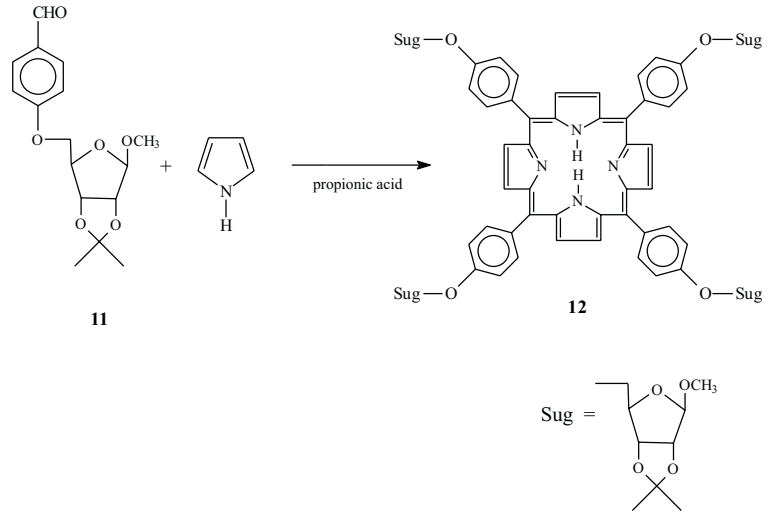


Scheme 3



Another problem was to obtain the four-substituted compound **12**. As is well known, the tetrahydroxy derivative of tetraphenylporphyrin is practically insoluble in all commonly used solvents so it was not possible to obtain compound **12** by simply coupling tosyl derivative of ribose and tetrahydroxy derivative of tetraphenyl-porphyrin. Tetra-ribosyl-TPP was synthesized according to Scheme 4. Protected ribosyl tosylate was coupled with 4-hydroxybenzaldehyde in DMF in the presence of NaH. The obtained ribosyl-benzaldehyde **11** was condensed with pyrrole in propionic acid to give the desired four-ribosyl-substituted tetraphenylporphyrin **12,** but in very low yield. The crude compound requires several purification procedures on silica gel columns. The yield of compound **12** was lower than 1%. Deprotection of this compound was not attempted.

Scheme 4



Removal of the 2,3-O-isopropylidene group from **6** by hydrolysis with trifluoroacetic acid/water mixture yields the free methyl ribosoporphyrine **13**. During purification procedure, small amount of methyl ryboside of **6** was converted to pure riboside **14** and was detected by LSIMS spectroscopy [m/z: 805 $(M+1)^+$]. The relative abundance of fragment ions for all compounds is very low. The base peaks are low-molecular fragmentary ions instead of molecular ions. Accurate high-resolution mass data for ions **6-Zn(II)**, **6-Co(II)**, and **6-In(III)** indicate m/z values corresponding to elemental composition of $C_{56}H_{48}O_5N_4Zn$, $C_{56}H_{49}O_5N_4Co$ and $C_{56}H_{48}O_5N_4In$, respectively. Vis-spectra for all obtained porphyrins were similar to parent tetratolylporphyrin and show the Soret band at 420 nm and four Q-bands at 517, 553, 590 and 648 nm. Vis-spectra for Zn, Co and In-derivatives of **6** and Zn – derivative of **7** show the typical peak pattern for metal derivatives of tetraphenylporphyrins.

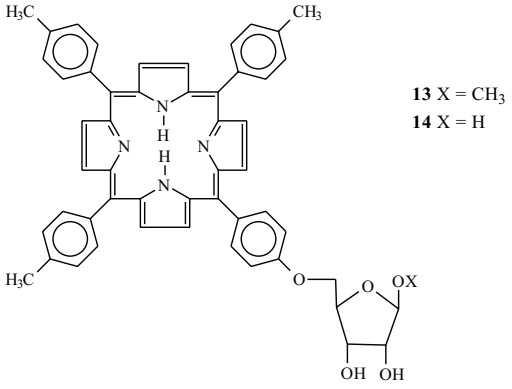


Figure 1.

The IR spectra were recorded as thin films prepared by evaporating solvent from appropriate solutions placed on KBr plate surface. The N–H (imino) group vibrations are observed at 3314–3318 cm^{-1}. In thin film of porphyrins there appear bands in the region of about 3120 cm^{-1} (such band was reported earlier for thin films of porphyrins [27]). The bands of deformational vibrations of phenyl rings are observed at 1594–1609 cm^{-1} and 1547–1575 cm^{-1} for all compounds and its metal complexes. The bands at 2921–2925 cm^{-1} and 2853–2855 cm^{-1} for cobalt and zinc derivatives of **6** and **7**, respectively, and at 2869–2881 cm^{-1} for both types of compounds (parent porphyrins and they metal complexes), are associated with vibrations of C–H groups in the porphyrin core. The bands at 1472–1475 and 1449–1457 cm^{-1} for compounds **6**, **7**, **10**, **12**, and **13** are associated with the C=N and C–C vibrations of the porphyrin macrocycle. Similarly, the bands at 1507–1510 or 1455–1462 cm^{-1} are associated with these same vibrations of metal complexes. The absorption band near 1000 cm^{-1} (996–1009 cm^{-1}) is characteristic for the tetraphenylporphyrin chelates [28]. It has been noticed that the occurrence of such band depends on the nature of the particular metal ion. The γ vibration of the C–H and N–H groups of the porphyrin core appears at 796–805 and 731–735 cm^{-1}, respectively. No vibrations originating directly from metal-N fragments could be recorded since they occur outside of the recording capacity of the equipment used.

EXPERIMENTAL

Ribose was purchased from Aldrich Chemical Co. and used as received. The proton NMR spectra were recorded with Varian Unity INOVA-300 spectrometer operating at 300 MHz; chemical shifts are in ppm ($CDCl_3$/TMS). Electronic spectra were recorded on a JASCO V-530 spectrophotometer in chloroform solutions. The IR spectra were recorded with the Perkin Elmer Spectrum One FT-IR spectrometer in KBr pellets or as thin films on KBr plate surface. Mass spectrometry was performed on a LSIMS(+) model AMD 604 (AMD Intectra) spectrometer (NBA matrix).

Methyl 2,3-O-isopropylidene-β-D-ribofuranoside 2 (pale yellow oil) was obtained following described procedure [29] from D-ribose in 70% yield. ^{1}H NMR ($CDCl_3$), δ = 4.97 s (1H), 4.83, 4.58 dd (2H, J = 5.9 Hz), 4.42 t (1H, J = 7 Hz), 3.6–3.75 m (2H), 3.43 s (3H), 3.3–3.4 m (1H), 1.48 s (3H), 1.32 s (3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 25.1, 26.8, 55.9, 64.0, 64.4, 81.9, 86.2, 88.7, 110.3, 112.5. IR (KBr, cm^{-1}): 3452, 2987, 2940, 2836, 1457, 1382, 1374, 1272, 1259, 1241, 1211, 1161, 1093, 1062, 1043, 1010, 962, 869, 827, 772, 648, 579, 515.

Methyl 2,3-O-isopropylidene-5-O-p-tolylsulfonyl-β-D-ribofuranoside 3 was obtained from **1** according to procedure described in [30]. The white, solid compound was obtained in 50–60% yield. M.p. = 82–83°C. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.81, 7.36 dd (4H, J = 8.8 Hz), 4.93 s (1H), 4.60, 4.53 dd (2H, J = 5.9 Hz), 4.31 t (1H, J = 7 Hz), 4.00, 4.02 dd (2H, J = 7 Hz, J = 1.8 Hz), 3.23 s (3H), 2.46 s (3H), 1.45 s (3H), 1.28 s (3H); ^{13}C NMR ($CDCl_3$), δ (ppm): 21.6, 24.8, 26.3, 55.0, 69.2, 81.3, 83.5, 84.8, 109.4, 112.7, 127.9, 129.9, 132.6, 145.1. IR (KBr, cm^{-1}): 3040, 3005, 2990, 2948, 2929, 2845, 1597, 1496, 1453, 1385, 1359, 1273, 1247, 1211, 1191, 1180, 1092, 1043, 975, 959, 902, 866, 854, 833, 825, 813, 682, 663, 565, 556, 523.

5-(p-Hydroxyphenyl)-10,15,20-tritolylporphyrin (**4**) and **5-(m-hydroxyphenyl)-10,15,20-tritolylporphyrin** (**5**) were synthesized according procedure described in [31]. **Methyl 2,3-O-isopropylidene-5-O-(5′-para-phenylene-10′,15′,20′-tri-p-tolylporphyrin)-β-D-ribofuranoside 6.** A suspension containing sodium hydride (0.02 g, 0.5 mmol, 60% in mineral oil), 0.218 g (0.32 mmol) of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin **4**, and 0.20 g (0.5 mmol) of **3** in 30 ml of DMF was

stirred at 60–70°C for 7 h. Then 100 ml of water was added to the reaction flask and the mixture was extracted with chloroform. The organic layer was separated, washed with water (several times), then saturated sodium bicarbonate and dried over anh. $MgSO_4$. The product was purified by chromatography (twice) on alumina using hexane-chloroform mixture as eluent (first elutes the fraction product; unreacted **4** comes second). Yield 0.2 g (46.6%). LSIMS (m/z): 859 $(M+1)^+$; ^{1}H NMR ($CDCl_3$), δ = 8.85 (bs, 8H, β-H), 8.13, 8.11 (d, 2H, ArH), 8.10, 8.08 (d, 6H, ArH), 7.56, 7.54 (d, 6H, ArH), 7.30, 7.28 (d, 2H, ArH), 5.12 (s, 1H, H1), 5.02, 5.00 (d, 1H, J = 5.7 Hz, H2 or H3), 4.77, 4.75 (d, 1H, J = 5.7 Hz, H2 or H3), 4.77–4.73 (m, 1H, H4), 4.35–4.2 (m, 2H, H5), 3.47 (s, 3H, OCH_3), 2.70 (s, 9H, $ArCH_3$), 1,59, 1.43 (2s, 6H, $C(CH_3)_2$), –2.78 (bs, 2H, NH); IR (cm^{-1}): 3318s, 3120w, 3080w, 3023m, 2988m, 2921s, 2871w, 2833w, 1606m, 1559w, 1509s, 1472s, 1456sh, 1401w, 1384vs, 1350m, 1221m, 1181m, 1159w, 1108s, 1095s, 1051w, 1036w, 1025w, 992w, 982w, 966vs, 870w, 837w, 799vs, 735m, 709w, 645w, 523w; UV (nm, logε): 420(5.58), 517(4.15), 553(3.91), 591(3.64), 647(3.59).

Methyl 2,3-O-isopropylidene-5-O-(5′-meta-phenylene-10′,15′,20′-tri-p-tolylporphyrin)-β-D-ribofuranoside 7. This compound was obtained in the same way as **6**; the substrates were 5-(3-hydroxyphenyl)-10,15,20-tritolylporphyrin (**5**) and **3**. The crude product was purified by chromatography on a silica gel column with chloroform as eluent. Yield: 55%. LSIMS (m/z): 859 $(M+1)^+$. ^{1}H NMR ($CDCl_3$), δ = 8.78 (s, 8H, β-H), 8.03, 8.00 (d, 6H, ArH), 7.77, 7.74 (d, 1H, ArH), 7.69 (s, 1H, ArH), 7.55 (t, 1H, ArH), 7.49, 7.46 (d, 6H, ArH), 7.25, 7.28 (d, 1H, ArH), 4.93 (s, 1H, H1), 4.82, 4.80 (d, 1H, J = 6 Hz, H2 or H3), 4.57, 4.55 (d, 1H, J = 6 Hz, H2 or H3), 4.12–4.01 (m, 1H, H4), 4.05–4.00 (m, 2H, H5), 3.19 (s, 3H, OCH_3), 2.63 (s, 9H, $ArCH_3$), 1.43, 1.26 (2 × s, 6H, $C(CH_3)_2$), –2.86 (bs, 2H, NH); IR (cm^{-1}): 3315s, 3122w, 3081w, 3022w, 2989m, 2919s, 2879m, 2835w, 1597s, 1559w, 1506w, 1471vs, 1426w, 1401w, 1382w, 1372m, 1348s, 1315w, 1288w, 1261m, 1247w, 1219m, 1211m, 1195m, 1182s, 1161w, 1112s, 1090s, 1043s, 1022w, 995w, 982w, 970s, 947w, 921w, 870m, 837w, 797vs, 731s, 709w, 645w, 518w; UV (nm, logε): 420(5.73), 516(4.24), 552(3.92), 590(3.70), 646(3.61).

Methyl 2,3-O-isopropylidene-5-O-[5′-para-phenylene-10,15,20-tri(4-pyridyl)porphyrin]-β-D-ribofuranoside 10. A suspension containing sodium hydride (0.01 g, 0.25 mmol, 60% in mineral oil), 0.08 g (0.12 mmol) of 5-(4-hydroxyphenyl)-10,15,20-tripyridylporphyrin **9**, and 0.08 g (0.22 mmol) of **3** in 10 ml of DMF was stirred at room temperature for 10 h. Water (20 ml) and 1 ml of H_2SO_4 (1 mol solution) was added to the reaction flask. Then, 1 ml of ammonium hydroxide (25%) was added to the green mixture. The precipitated brown solid was collected, washed with water and dried. The product was purified by chromatography on silica gel with ethyl acetate – methanol as eluent. Yield: 0.034 g (35%). LSIMS (m/z):820 $(M+1)^+$. ^{1}H NMR ($CDCl_3$), δ = 8.88 (d, 2H, β-H), 8.78 (bs, 4H, β-H), 8.74 (d, 2H, β-H), 8.11, 8.08, (dd, 12H, ArH), 8.06, 8.03 (d, 2H, ArH), 7.27, 7.24 (d, 2H, ArH), 5.07 (s, 1H, H1), 4.95, 4.93 (d, 1H, J = 6 Hz, H2 or H3), 4.71, 4.69, (d, 1H, H2 or H3), 4.69 (t, 1H, H4), 4.15 (t, 1H, H5), 4.27 (m, 1H, H5), 3.41 (s, 3H, OCH_3), 1.53, 1.36 (2 × s, 6H, $C(CH_3)_2$), –2.95 (bs, 2H, NH); IR (cm^{-1}): 3314w, 3013w, 2962s, 2920m, 2851w, 1594w, 1506w, 1492w, 1471w, 1447w, 1402w, 1384w, 1259s, 1210sh, 1175w, 1154w, 1089vs, 1017vs, 967sh, 865m, 796vs, 703w, 660w, 508w; UV (nm, logε): 419(5.44), 514(4.12), 549(3.70), 589(3.60), 645(3.25).

Methyl 2,3-isopropylidene-5-O-p-formylphenyl-β-D-ribofuranoside 11. NaH (0.1 g, 2.5 mmol, 60% in mineral oil) was added to a solution of p-hydroxybenzaldehyde (0.3 g, 2.45 mmol) in DMF (30 ml). The mixture was stirred for 1 h at room temperature. Tosyl derivative **3** (0.9 g, 2.5 mmol) was added and the mixture was stirred for 20 h at 60°C. After that the mixture was cooled and evaporated. The residue was treated with water and dichloromethane. Organic layer was separated, washed with water, dried with anh. $MgSO_4$. The crude product was purified by chromatography (silica gel, chloroform as eluent) to provide **11** as an oil, which was used directly in the next reaction. Yield: 0.66 g (86%); ^{1}H NMR ($CDCl_3$), δ = 9.76 s (1H), 7.69, 7.72 d (2H, J = 8.7 Hz), 6.91, 6.88 d (2H, J = 8.7 Hz), 4.7 s (1H), 3.7 m (2H), 3.8–4.5 m (3H), 3.25 s (3H), 2.36 s (3H), 2.29 s (3H). IR (film on KBr plate): ν_{CO} = 1692 cm^{-1}.

5,10,15,20-Tetra[4-(1′-O-methyl-2′,3′-isopropylidene-β-D-ribofuranos-5′-yl)phenyl]-porphyrin 12. A solution of 0.62 g (*ca*. 2 mmol) of **11** in 50 ml of propionic acid was brough to reflux and 0.135 g (*ca*. 2 mmol) of pyrrole was then added. Reflux was continued for 2 h. The reaction mixture was allowed to cool and was kept at room temperature overnight. Water and then solid sodium carbonate were added to neutralize propionic acid. The mixture was extracted with chloroform several times. The combined organics were washed with water, sat. $NaHCO_3$ and dried over $MgSO_4$. The crude product was chromatographed several times on silica gel column with chloroform as eluent. Further purification by

preparative TLC (silica gel/chloroform) afforded **12** as purple solid (0.006 g, 0.84%). LSIMS (m/z): 1423,5 $(M+1)^+$. ^{1}H NMR ($CDCl_3$), δ = 8.78 (s, 8H, β-H), 8.06, 8.04 (d, 8H, ArH), 7.24, 7.22 (d, 8H, ArH), 5.06 (s, 4H, H1), 4.95, 4.93 (d, 4H, J = 6 Hz, H2 or H3), 4.70, 4.68 (d, 4H, J = 6 Hz, H2 or H3), 4.17 (t, 4H, H4), 4.24 (d, 8H, H5), 3.41 (s, 12H, OCH_3), 1.52, 1.37 (2 × s, 24H, $C(CH_3)_2$), –2.84 (bs, 2H, NH); IR (cm^{-1}): 3320w, 3066w, 3033w, 2977s, 2936s, 2881m, 2835w, 1605s, 1575w, 1509s, 1472s, 1457sh, 1417w, 1383s, 1373s, 1292sh, 1246s, 1211m, 1190m, 1178s, 1162m, 1109s, 1095vs, 1050w, 1034w, 1019w, 983m, 965m, 869m, 805m, 760m, 665w, 554w; UV (nm, logε): 422(5.09), 518(3.74), 555(3.60), 592(3.39), 650(3.36).

Methyl 5-O-(5′-para-phenylene-10′,15′20′-tri-p-tolylporphyrin)-β-D-ribofuranoside 13. 0.05 g of **5** was dissolved in the trifluoroacetic acid – dichloromethane mixture (10 ml, 1:4), and stirred at room temperature for 0.5 h. Then, water (20 ml) and dichloromethane (20 ml) were added to the mixture. Organic layer was separated and washed with water, sat. sodium bicarbonate and dried with anh. $MgSO_4$. The crude product was chromatographed on silica gel with chloroform as eluent afforded **13** as a purple solid (0.032 g, 57%). LSIMS (m/z): 819.3 $(M+1)^+$. ^{1}H NMR ($CDCl_3$), δ = 8.78 (bs, 8H, β-H), 8.06, 8.04 (d, 2H, ArH), 8.04, 8.01 (d, 6H, ArH), 7.49, 7.47 (d, 6H, ArH), 7.24, 7.21 (d, 2H, ArH), 4.91 (s, 1H, H1), 4.45–4.27 (m, 4H), 4.1–4.04 (m, 1H), 3.41 (s, 3H, OCH_3), 2.63 (s, 9H, $ArCH_3$), –2.85 (bs, 2H, NH); IR (cm^{-1}): 3434, 3317m, 3023w, 2962m, 2921s, 2871w, 2853m, 1606m, 1558w, 1507m, 1472m, 1449w, 1400w, 1384m, 1349w, 1260m, 1246sh, 1219m, 1180m, 1097s, 1056m, 1022s, 993w, 982w, 966w, 878w, 835w, 799vs, 754m, 734m, 708w, 665w, 524w; UV (nm, logε): 420(5.62), 517(4.13), 553(3.91), 592(3.61), 648(3.52).

Second very small fraction was pure ryboside derivative **14** [LSIMS $(M+1)^+$ = 805].

The Zn(II), Co(II) and In(III) complexes of selected compounds were prepared from the free-base compounds and purified according to standard methods [32].

6-Zn(II): LSIMS(+) HR: calc. for $C_{56}H_{48}O_5N_4Zn$ – 920.29162; found – 920.29241; ^{1}H NMR ($CDCl_3$), δ = 8.88 (m, 8H, β-H), 8.04, 8.02 (d, 8H, ArH), 7.49, 7.47 (d, 6H, ArH), 7.15, 7.13 (d, 2H, ArH), 4.63 (s, 1H, H1), 4.73, 4.71 (d, 1H, J = 6 Hz, H2 or H3), 4.46, 4.44 (d, 1H, J = 6 Hz, H2 or H3), 3.91 (t, 1H, H4), 3.91, 3.88 (d, 2H, H5), 3.13 (s, 3H, OCH_3), 2.63 (s, 9H, $ArCH_3$), 1.39, 1.23 (2 × s, 6H, $C(CH_3)_2$); IR (cm^{-1}): 3122w, 3022w, 2956s, 2924vs, 2854s, 1607m, 1575w, 1526m, 1510m, 1493m, 1462s, 1402w, 1383s, 1339s, 1300w, 1261s, 1247m, 1208m, 1179m, 1162w, 1107s, 1069s, 1016m, 998vs, 963w, 919w, 869m, 847w, 798vs, 737w, 722m, 525w; UV (nm, logε): 425.5(5.30), 552(3.92), 597(3.44).

6-In(III): LSIMS(+) HR: calc. for $C_{56}H_{48}O_5N_4In$ – 971.26635; found – 971.26493; ^{1}H NMR ($CDCl_3$), δ = 9.00 (m., 8H, β-H), 8.19, 8.16 (d, 4H, ArH), 7.93, 7.91 (d, 4H, ArH), 7.55, 7.53 (d, 3H, ArH), 7.49, 7.47 (d, 3H, ArH), 7.3–7.18 (m., 2H,ArH), 5.01 (s, 1H, H1), 4.96, 4.94 (d, 1H, J = 6 Hz, H2 or H3), 4.71, 4.69 (d, 1H, J = 6 Hz, H2 or H3), 4.73–4.7 (m, 1H, H4), 4.3–4.15 (m, 2H, 5H), 3.41 (s, 3H, OCH_3), 2.65 (s, 9H, $ArCH_3$), 1.53, 1.47 (2 × s, 6H, $C(CH_3)_2$); IR (cm^{-1}): 3125w, 3023m, 2963s, 2924vs, 2873w, 2853w, 1606m, 1574w, 1518m, 1507m, 1475m, 1455w, 1403w, 1384m, 1338m, 1299w, 1260m, 1249m, 1210m, 1181m, 1161w, 1108s, 1095s, 1071m, 1047w, 1009vs, 964w,869m, 848w, 799vs, 736w, 723m, 523w; UV (nm, logε): 417(5.35), 540(3.93).

6-Co(II): LSIMS(+) HR: calc. for $C_{56}H_{49}O_5N_4Co$ – 916.30349; found – 916.30470; IR (cm^{-1}): 3024w, 2959s, 2925vs, 2869sh, 2855s, 1609w, 1547w, 1508m, 1455m, 1383vs, 1352s, 1261m, 1248w, 1209w, 1180w, 1161w, 1107m, 1094m, 1077m, 1051w, 1002m, 963w, 871w, 799s, 718w; UV (nm): 433, 548, 585 (A_{433}/A_{548} = 14.6).

7-Zn(II): LSIMS(+) HR: calc. for $C_{56}H_{48}O_5N_4Zn$ – 920.29162; found – 920.2917; ^{1}H NMR ($CDCl_3$), δ = 8.96 (m, 8H, β-H), 8.11, 8.09 (d, 6H, ArH), 7.84, 7.81 (d, 1H, ArH), 7.73 (bs, 1H, ArH), 7.60 (m, 1H, ArH), 7.56, 7.53 (d, 6H, ArH), 7.36 (m, 1H, ArH), 4.68 (s, 1H, H1), 4.75, 4.73 (d, 1H, J = 6 Hz, H2 or H3), 4.50, 4.48 (d, 1H, J = 6 Hz, H2 or H3), 4.29 (t, 1H, H4), 3.93, 3.91 (d, 2H, H5), 3.08 (s, 3H, OCH_3), 2.71 (s, 9H, $ArCH_3$), 1.41, 1.25 (2 × s, 6H, $C(CH_3)_2$); IR (cm^{-1}): 3119w, 3022w, 2957sh, 2924s, 2855s, 1597m, 1577m, 1525w, 1510w, 1493w, 1455m, 1402w, 1373m, 1338m, 1283w, 1261m, 1240w, 1209m, 1190m, 1179m, 1161w, 1109s, 1095s, 1067m, 1051m, 998s, 983sh, 961w, 869m, 797s, 721m, 663w, 526w; UV (nm, logε): 424(5.53), 552(4.00), 594(3.52).

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