ISSN 1068-1620, Russian Journal of Bioorganic Chemistry, 2008, Vol. 34, No. 6, pp. 762–767. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © V.D. Rumyantseva, T.A. Khabarova, D.A. Cheshkov, G.A. Fedorova, A.F. Mironov, 2008, published in Bioorganicheskaya Khimiya, 2008, Vol. 34, No. 6, pp. 847–853.

Synthesis of Tetraphenylsubstituted Porphyrins by Interaction of 5-Aryldipyrromethanes with 4-Substituted Benzaldehydes

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Received February 4, 2008; in final form, April 21, 2008

Abstract—Synthesis of tetraphenyl substituted porphyrins with *tert*-butyl and methoxycarbonyl groups in *meso*-aryl radicals is described. It is shown that, during the condensation of dipyrromethanes with substituted benzaldehydes, a rearrangement occurs with the formation of a mixture of isomeric porphyrins. The character of these rearrangements depends on the position of substituents in the starting compounds.

Key words: platinum complexes, rearrangement, substituted dipyrromethanes, tetraarylporphyrins

DOI: 10.1134/S1068162008060186

INTRODUCTION

One of prospective directions in modern oncology is the fluorescent diagnostics of malignant neoplasms with the help of platinum and some other metal complexes with natural [1] and synthetic porphyrins [2][2]. Among the synthetic porphyrins, an important place occupy substituted TPPs [3]. The interest in them is caused by a relative availability of these compounds and an opportunity of wide variation of substituents both in phenyl radicals, and on the periphery of macrocycle [4]. The amphiphilic porphyrins with a certain ratio of large hydrophobic substituents and carboxylic groups possess the greatest selectivity to tumors [5]. Their sodium salts allow one to avoid the porphyrin dissolution in water in the presence of phospholipids, cremophor EL, and other detergents, while hydrophobic groups can provide the transfer of PSs through the phospholipid cell membrane.

It is known that, among similar compounds, porphyrins containing both hydrophobic and hydrophilic substituents are accumulated in a number of tumors, especially if these substituents are asymmetrically situated. Especially useful are the porphyrins that have a good solubility in water (which allows one to carry biological tests without use of detergents), stability on storage, low toxicity, substantial selectivity to tumors in comparison with surrounding normal tissues, photochemical stability, high extinction coefficients, and high quantum yields of fluorescence. A successful development of this direction depends on the presence of reliable methods of synthesis, isolation, and modification of similar porphyrins.

In this work, we synthesized isomeric porphyrins containing two *tert*-butyl and two ester groups, and then, on their basis, platinum complexes of 5,10-bis(4-*tert*-butylphenyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin and 5,15- bis(4-*tert*-butylphenyl)-10,20-bis(4-methoxycarbonylphenyl)porphyrin; the subsequent saponification of the second compound allowed us to obtain the water-soluble PS.

RESULTS AND DISCUSSION

Synthesis of porphyrins was realized proceeding from 5-aryldipyrromethanes. In the first variant 5-(4-*tert*-butylphenyl)dipyrromethane was condensed with a methyl ether 4-formylbenzoic acid by the Lindsey method [6, 7]. The second variant differed from the first by a return arrangement of *tert*-butyl and ester groups in dipyrromethane and benzaldehyde at preservation of conditions of their condensation.

Both starting 5-aryldipyrromethanes (**I**) and (**VIII**) were obtained by treatment of the corresponding 4-substituted benzaldehydes by pyrrole, which simultaneously played role of solvent [8, 9]. As condensing agents, have been used trifluoroacetic acid [10], indium salts [11], ion-exchange resins [12], and a hydrochloric acid [13]. The best results were reached with trifluoroacetic acid and a ratio pyrrole to substituted benzaldehyde of 40 : 1. There were data in literature on the formation during this condensation of *N*-substituted dipyrromethanes and tripyrrine compounds as by-products [7, 9]. In this connection, a problem arises of purification of starting (**I**) and (**VIII**) from impurities. For the removal of pyrrole excess and also oligomers, authors

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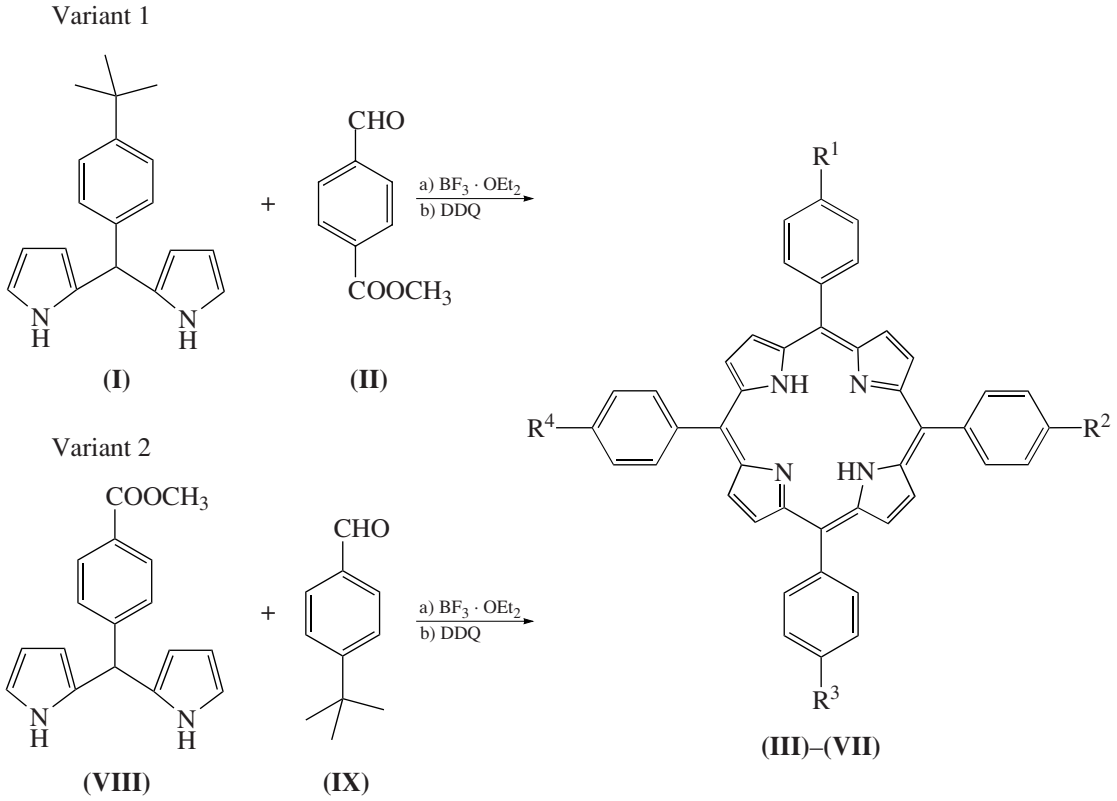
[2] Abbreviations: DDQ, 2,3-dichloro-5,6-dicyanobenzoquinone; EAS, electronic absorption spectrum; PS, photosensitizer; and TPP, tetraphenylporphyrin.

of work [7] used distillation and the subsequent recrystallyzation or a flash chromatography and recrystallyzation. We obtained the best results at the isolation and purification of the substituted dipyrrolmethanes (**I**) and (**VIII**) at the use of reprecipitation from ether and hexane, and then the recrystallyzation from aqueous ethanol. The monitoring of the individuality of dipyrromethanes was carried out by TLC, comparison of melting points with the literature data and ^{1}H NMR spectra.

Condensation of (**I**) and substituted benzaldehyde (**II**) was carried out in chloroform in the presence of trifluoroboron etherate with the subsequent oxidation of the formed porphyrinogen with the help of DDQ (Scheme 1). After the treatment of reaction mixture, the porphyrins obtained were filtered and subjected to flash chromatography on aluminum oxide. The total yield of porphyrins under the first scheme was 20%. The subsequent chromatographic separation on a silica gel column allowed obtaining five individual compounds.

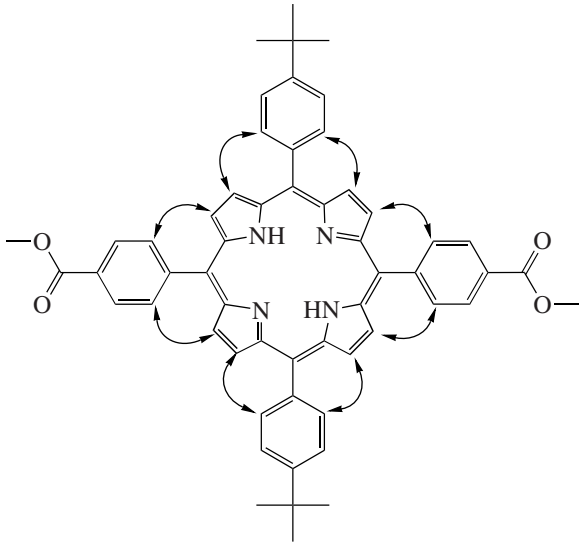


Compound	R^1	R^2	R^3	R^4
(**III**)	$-C(CH_3)_3$	$-C(CH_3)_3$	$-C(CH_3)_3$	$-C(CH_3)_3$
(**IV**)	$-C(CH_3)_3$	$-C(CH_3)_3$	$-C(CH_3)_3$	$-COOCH_3$
(**V**)	$-C(CH_3)_3$	$-COOCH_3$	$-C(CH_3)_3$	$-COOCH_3$
(**VI**)	$-C(CH_3)_3$	$-C(CH_3)_3$	$-COOCH_3$	$-COOCH_3$
(**VII**)	$-C(CH_3)_3$	$-COOCH_3$	$-COOCH_3$	$-COOCH_3$

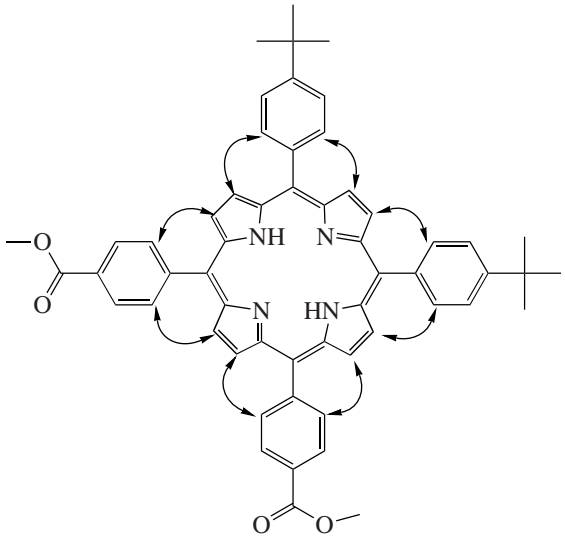
Scheme 1. Two variants of porphyrin synthesis.

The least polar first fraction contained symmetric porphyrin (**III**) (A_4) in which in all four phenyl rings bore *tert*-butyl substituents. The structure of this porphyrin was confirmed by EAS, mass spectrum, and ^{1}H NMR spectrum, and also by the coincidence of chromatographic mobility with the standard sample obtained by the direct synthesis.

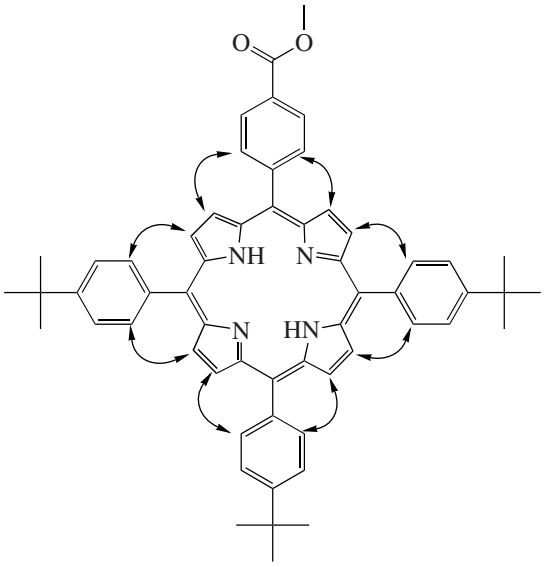
The next (second) fraction contained porphyrin of the A_3B type in which three residues represented 4-*tert*-butylphenyl groups, and the fourth was 4-methoxycarbonylphenyl substituent. The structure of this compound was proved by EAS, IR (C=O band at 1721 cm^{-1}), mass spectrum (*m*/*z* 841.6), ^{1}H NMR spectrum, and the elemental analysis (see below).



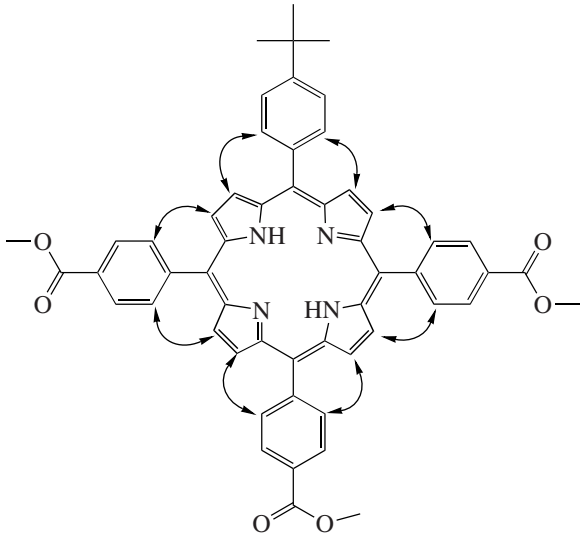
(V)



(VI)



(IV)



(VII)

NOE-contacts in structures (**IV**), (**V**), (**VI**), and (**VII**).

Further, two fractions with close TLC mobilities and identical absorption spectra were eluted. Substances in the third and fourth fractions exhibited the same mass spectra and belonged to the type of A_2B_2 porphyrins. It followed from their IR spectra followed that both compounds contain 4-methoxycarbonyl residues. Individuality of the substances was confirmed by HPLC. The content of the main substance in the third fraction was 98.68%, and the retention time was 10.065 min. For the fourth fraction, the content of the main substance was 98.62% and RT, 10.102 min.

In the spectrum of proton resonance (T 313 K), compounds from the second fraction exhibited signals of β protons as AB-system (δ_A 8.75 and (δ_B 8.88 ppm, J_{AB} 4.75 Hz) with the integral intensity of four protons. A singlet signal at 8.86 ppm was also registered with integral intensity of four protons. In the NOESY spectrum (see the figure), correlations were observed between the signal of β proton at 8.75 ppm and the signal at 8.30 ppm (*o*-H of 4-methoxycarbonylphenyl substituent, integral intensity of two protons) and also between signals at 8.86 and 8.88 ppm and a signal at 8.13 ppm (*o*-H of 4-*tert*-butylphenyl substituent, integral intensity of six protons). The data allow us to ascribe structure (**IV**) to the compound from the second fraction.

The establishment of structures (**V**) and (**VI**) for the compounds from fractions 3 and 4, respectively, was carried out by bidimentional spectroscopy of a ^{1}H NMR: ^{1}H NOESY and ^{1}H–^{13}N HSQC. In the spectrum

of proton resonance (T 318 K) of (**V**), signals of β protons were displayed as an AB-system (δ_A 8.88, δ_B 8.76 ppm, J_{AB} 4.77 Hz), the integral intensity of eight protons. In a NOESY spectrum, correlations between signals were observed at 8.76 and 8.30 ppm (*o*-H of 4-methoxycarbonylphenyl substituent), and also between signals at 8.88 and 8.12 ppm (*o*-H of 4-*tert*-butylphenyl substituent). The data allowed us to ascribe to (**V**) the structure of *trans*-isomer.

The signals of β protons of (**VI**) were exhibited in the spectrum of proton resonance (T 305 K) as an AB system (δ_A 8.76, δ_B 8.90 ppm, J_{AB} 4.69 Hz), with the integral intensity of four protons, and two singlets at 8.88 and 8.78 ppm with integral intensity of two protons each. The β protons displayed as singlet signals are magnetically equivalent, which is possible only when in the neighboring *meso*-positions are occupied by identical substituents. In the NOESY-spectrum, correlations were observed between the signals of β protons at 8.76 and 8.78 ppm and a signal at 8.30 ppm (*o*-H of 4- methoxycarbonylphenyl substituent) and also between signals at 8.88 and 8.90 ppm and at 8.13 ppm (*o*-H of 4-*tert*-butylphenyl substituent). The data allowed us to ascribe for (**VI**) structure of *cis*-isomer.

The fifth fraction (**VII**) was isolated in a small yield. It turned out to be an AB_3 porphyrin. Its structure was proved by mass spectrometry and ^{1}H NMR spectroscopy.

The results show that the considered synthetic scheme leads to a mixture of porphyrins, with the yield of target (**V**) being only 4%.

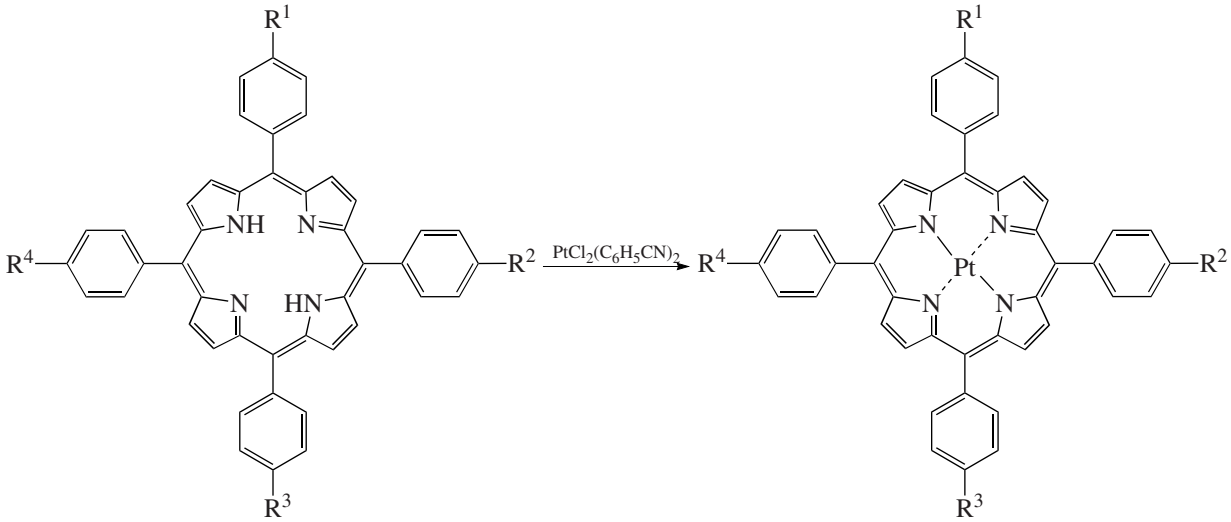
The variant 2 of the syntheses 5-(4-methoxycarbonylphenyl)dipyrromethane (**VIII**) with 4-*tert*-butylbenzaldehyde (**IX**) was carried out with a condensation similar to that in the earlier considered case; the total yield of porphyrins was 17%.

Although in this variant of synthesis, four isomeric porphyrins were formed [the fifth fraction AB_3 (**VII**) was absent], we managed to increase the yield of the target compound (**V**) up to 9%.

At the synthesis of porphyrins by variant 2, we also used an anhydrous indium chloride as an Lewis acid [11]. In this case, the total yield of porphyrins was 12%, the greatest yield was that of porphyrin A_3B (**IV**) (5%), the contents of *trans* and *cis*-isomers were rather close, and porphyrin AB_3 (**VII**) has not been detected at all.

Thus, the executed studies confirmed an opportunity of acid-catalyzed rearrangements at the condensation of dipyrromethanes and substituted benzaldehydes [7]. At the same time, it was shown that the nature of substituents in benzaldehyde and in position 5 of dipyrromethane substantially affect the character of the condensation. More specifically it proceeds in the presence of electron donor substituents in starting benzaldehyde electron acceptor substituents in dipyrromethane compared with their reverse arrangement.

The *cis* and *trans*-isomeric porphyrins (**VI**) and (**V**) were used for obtaining of platinum complexes (Scheme 2). Introduction of Pt(II) was carried out at boiling of porphyrins in benzonitrile with $PtCl_2(C_6H_5CN)_2$ salt [14]. The saponification of dimethyl esters of both isomers was carried out in pyridine in the presence of 2M KOH [15]. It turned out that *cis*-isomer (**VI**) is not saponified under these conditions, which was confirmed by TLC and mass spectrometry. Probably, this is due to stereochemical features of the *cis*-isomer structure (**VI**).



(V), (IV) **(IXа), (IXб), (X)**

(IX) a: $R^1 = R^3 = -C(CH_3)_3$, $R^2 = R^4 = COOCH_3$

b: $R^1 = R^3 = -C(CH_3)_3$, $R^2 = R^4 = COOH$

(X) $R^1 = R^2 = -C(CH_3)_3$, $R^3 = R^4 = COOCH_3$

Scheme 2. Synthesis of porphyrin platinum complexes.

EXPERIMENTAL

Spectra of ^{1}H NMR (δ, ppm) were obtained on a Brucker AVANCE-600 instrument (300 and 600 MHz, Germany) for solutions in $CDCl_3$ with Me_4Si as an internal standard. Bidimentional spectra were recorded and processed with the use of standard Bruker software XWINNMR 3.5". Time of mixing for gNOESY experiment was 0.8 s. EAS (nm) were obtained on a spectrometer Jasco 7800 (Japan) in $CHCl_3$. Mass spectra were measured on a Brucker Ultraflex TOF (Germany) spectrometer. IR spectra (ν, cm^{-1}) were registered on a FT spectrometer Brucker EQUINOX55 (Germany) by a method diffuse reflection with the subsequent mathematical processing by means of the Kubelka–Munk function. The reaction course and purity of compounds were monitored by TLC on Kieselgel 60 F 254 plates (Merck, Germany) in $CHCl_3$–hexane 9 : 1 system. Flash-chromatography was carried out on aluminum oxide (activity II) in $CHCl_3$. Column chromatography was carried out on silica gel Kieselgel 60 (Merck, Germany) in $CHCl_3$. HPLC was carried out on a Waters Breeze chromatograph using a column Nova-Pack 18.4 μm 4.6 × 150 mm. Compounds (**V**) and (**VI**) were eluted by a mixture of 20% A–80% B (eluent A: water; eluent B: acetone–acetonitrile, 6 : 4) for 7 min, further 100% B, flow rate 1 ml/min. Detection at a band of 400 nm. Spectra of excitation and emission of phosphorescence are measured on luminescent spectrometer Perkin-Elmer (United States). The phosphorescent characteristics were obtained for samples, polymerized in a lexan film (a polycarbonate based on biphenyl).

Synthesis of Porphyrins

Variant 1. A solution of 5-(4-*tert*]-butylphenyl)dipyrromethane (85 mg, 0.31 mmol) (**I**) obtained by method [6] (additionally purified by reprecipitation from ether and hexane with the subsequent recrystallization from aqueous ethanol) and methyl 4-formylbenzoate (**II**) (55 mg, 0.37 mmol) in $CHCl_3$ (60 ml) and MeOH (1.5 ml) blew through by argon for 20 min. Then $BF_3 \cdot O(Et)_2$ (5 μl) was added and stirred for 80 min in an argon atmosphere. DDQ (35 mg) was then added and stirred by bubbling air for 60 min. After addition Et_3N, solvent was evaporated in a vacuum and the residue was triturated in isopropanol. After a day, precipitate of violet color was filtered and subjected to flash chromatography on aluminum oxide, and porphyrins were then separated on a silica gel column. As a result, five fractions were obtained in the following quantities: 1, 10 mg (4%); 2, 13 mg (5%), 3, 10 mg (4%); 4, 10 mg (4%); and 5, 8 mg (3 %). Characteristics of the isolated porphyrins are given below in the order of increase in fraction number.

5,10,15,20-Tetrakis(4-*tert*-butylphenyl)porphyrin (III), Rf 0.8; EAS, nm: 419.4, 517.0, 553.0, 591.4, and 647.2; mass spectrum, *m*/*z*: 839.7 $[M]^+$; ^{1}H NMR spectrum: 8.80 (8 H, s, H2, H3, H7, H8, H12, H13, H17, H18), 8.15 (8 H, m, Ph), 7.76 (8 H, m, Ph), 1.62 [36 H, s, (CH3)3C].

5,10,15-TrHs(4-*tert*-butylphenyl)-20-(4-methoxycarbonylphenyl)porphyrin (IV): R_f 0.55, RT 11.106 min, EAS, λ_{max}, nm (ε 10^{-3}, M^{-1} cm^{-1}): 419.4 (276), 517.2 (11.3), 553.0 (7.5), 591.8 (3.9), 647.2; IR spectrum: 1721 (C=O); mass spectrum, *m*/*z*: 841.6 $[M]^+$; ^{1}H NMR spectrum: 8.88 (2 H, m, H3, H7), 8.86 (4 H, s, H12, H13, H17, H18), 8.75 (2 H, m, H2, H8), 8.43 (2H, m, Ph), 8.31 (2 H, m, Ph), 8.13 (6 H, m, Ph), 7.77 (6 H, m, Ph), 4.12 (3 H, c, $COOCH_3$); 1.61 [27 H, s, $(CH_3)_3C$]. Found, %: C 82.47, H 6.35, N 6.47. $C_{58}H_{56}N_4O_2$. Calc., %: C 82.82, H 6.71, N 6.66.

5,15-Bis(4-*tert*-butylphenyl)-10,20-bis(4-methoxycarbonylphenyl)porphyrin (V): R_f 0.3, RT 10.065 min (content 98.68%), EAS, λ_{max}, nm (ε 10^{-3}, M^{-1} cm^{-1}): 419.8 (252), 516.8 (11.1), 552.6 (6.4), 591.2 (3.7), 646.8 (2.8); IR spectrum: 1728 (N=I); mass spectrum, *m*/*z*: 843.5 $[M]^+$; 1H NMR spectrum: 8.88 (4 H, m, H3, H7, H13, H17), 8.76 (4 H, m, H2, H8, H12, H18), 8.45 (4 H, m, Ph), 8.31 (4 H, m, Ph), 8.13 (4 H, m, Ph), 7.77 (4 H, m, Ph), 4.13 (6 H, s, $COOCH_3$), 1.63 [18 H, s, $(CH_3)_3C$]. Found, %: C 79.54, H 5.85, N 6.58. $C_{56}H_{50}N_4O_4$. Calc., %: C 79.78, H 5.98, N 6.65.

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin (VI): R_f 0.2, RT 10.102 min (content 98.62%), EAS, λ_{max}, nm (ε 10^{-3}, M^{-1} cm^{-1}): 420 (222), 517.0 (9.5), 552.2 (5.3), 590.6 (3.2), 646.4 (2.3); IR spectrum: 1727 (C=O); mass spectrum, *m*/*z*: 843.5 $[M]^+$; ^{1}H NMR spectrum: 8.90 (2 H, m, H17, H18), 8.88 (2 H, s, H2, H3), 8.78 (2 H, s, H12, H13), 8.76 (2 H, m, H7, H8), 8.44 (4 H, m, Ph), 8.31 (4 H, m, Ph), 8.13 (4 H, m, Ph), 7.76 (4 H, m, Ph), 4.12 (6 H, s, $COOCH_3$); 1.62 [18 H, s, $(CH_3)_3C$). Found, %: C 79.62, H 5.87, N 6.61. $C_{56}H_{50}N_4O_4$. Calc., %: C 79.78, H 5.98, N 6.65.

5-(4-*tert*-Butylphenyl)-10,15,20-tris(4-methoxycarbonylphenyl)porphyrin (VII): R_f 0.1, EAS, λ_{max}, nm: 417.0, 515.9, 552.7, 590.1, 646.0; mass spectrum, *m*/*z*: 845.19 $[M]^+$; ^{1}H NMR spectrum: 8.89 (2 H, m, H2, H8), 8.78 (4 H, s, H12, H13, H17, H18); 8.76 (2 H, m, H3, H7), 8.44 (6 H, m, Ph), 8.29 (6 H, m, Ph), 8.13 (2 H, m, Ph), 7.77 (2 H, m, Ph), 4.11 (9 H, c, $COOCH_3$), 1.62 [9 H, s, $(CH_3)_3C$].

Variant 2. A solution of 5-(4-methoxycarbonylphenyl)dipyrromethane (**VIII**) (85 mg, 0.3 mmol) obtained by method [8] (it was additionally purified by reprecipitation byhexane from ether and with the subsequent recrystallization from aqueous ethanol), and 4-*tert*-butylbenxaldehyde (**IX**) (55 mg, 0.34 mmol) in 60 ml of $CHCl_3$ and 1.5 ml of MeOH was bubbled by argon for 20 min. Trifluoroboron etherate (5 μl) was added, and the mixture was stirred in argon atmosphere for 80 min. Then DDQ (35 mg) was added, and air was bubbled through the mixture for 60 min. Acid was neutralized by Et_3N addition. Solvent was evaporated in a vacuum, and isopropanol was also added for the removal of DDQ and precipitation. After a day, porphy-

rin of violet color was separated, and the mixture was separated on a silica gel column. Four compounds were revealed by TLC, and their structures similar to thoese in the first variant of synthesis. Yields were: first fraction, 6 mg (2%), second, 8 mg (3%), third, 24 mg (9%), and fourth, 8 mg (3%).

Platinum complex a 5,15-bis(4-*tert*-butylphenyl)-10,20-bis(4-methoxycarbonylphenyl)porphyrin (IXa). *cis*-Bis(benzonitril)dichloroplatium (10 mg, 0.021 mmol) was added to a suspension of (**V**) (11 mg, 0.013 mmol) in 5 ml of benzonitrile, and the mixture was boiled in a current of nitrogen for 1.5 h. Benzonitril was evaporated in a vacuum, the residue was chromatographed on silica gel in chloroform, isolating the mobile orange-red fraction containing a complex (**IXa**) (R_f 0.5). Solvent was removed in a vacuum, and the residue was recrystallized from a $CHCl_3$–MeOH mixture. Complex (**IXa**) was obtained, yield 9 mg (67%); EAS, λ_{max}, nm: 403.8, 510.0, and 538.1. A spectrum of a phosphorescence, λ_{max}, nm:: 662 and 725. Lifetime, τ, μs: 58.4 ± 9.7 ($+O_2$), 84.4 ± 13.6 ($-O_2$).

Platinum complex of 5,10-bis(4-*tert*-butylphenyl)-15,20-bis(4-methoxycarbonylphenyl)porphyrin (X). *cis*-Bis(benzonitril)dichloroplatium (16 mg, 0.034 mmol) was added to a suspension of (**VI**) (18 mg, 0.021 mmol) in 5 ml of benzonitrile, and the mixture was boiled in a current of nitrogen for 2 h. Benzonitril was evaporated in a vacuum, the residue was chromatographed on silica gel in chloroform, isolating the mobile orange-red fraction containing a complex (**X**) (R_f 0.5). Solution was evaporated, the residue was recrystallized from a chloroform–methanol mixture. Yield of complex 14 mg (64%); EAS, λ_{mao}, nm: 403.6, 510.2, and 538.9; mass spectrum, *m/z*: 1035.139 $[M]^+$; spectrum of phosphorescence, λ_{max}, nm: 664, 725; lifetime, τ, μs: 52.5 ± 9.1 ($+O_2$), 79.8 ± 4.0 ($-O_2$).

Platinum complex a 5,15-bis(4-*tert*-butylphenyl)-10,20-bis(4-carboxyphenyl)porphyrin (IXb). 2 M KOH solution (3 ml) was added to a solution of (**IXa**) (5 mg) in 3 ml pyridine, and boiled for 3 h. Pyridin was evaporated in a vacuum, the residue was diluted with water, filtered, acidified with 10% HCl to pH 2.0, and left in a refrigerator. The precipitated solid was separated on a centrifuge (4000 rpm, 15 min), several times washed with water containing a small amount of acid, and dried in vacuum desiccator over P_2O_5; EAS, λ_{max}, nm: 403.8, 511, and 539.6; mass spectrum, *m/z*: 1007.151 $[M]^+$.

The treatment of the platinum complex of 5,10-bis(4–*tert*-butylphenyl)-15,20-bis(4-methoxycarbonylphenyl) porphyrin (**X**) under the conditions similar to those at the obtaining of (**IXb**) did not lead to saponification of ester groups.

ACKNOWLEDGMENTS

This work was supported by ISTC, grant no. 3065.

REFERENCES

1. Bykhovskii, V.Ya., Zaitseva, N.I., Mironov, A.F., Osin, N.S., Pecherskikh, E.V., Rumyantseva, V.D., and Sukhin, G.M., *Prikl. Biokhim. Mikrobiol.,* 2001, vol. 37, pp. 660–668.
2. Gaiduk, M.I., Grigoryants, V.V., Mironov, A.F., Rumyantseva, V.D., Chissov, V.I., and Sukhin, G.M., *J. Phochem. Photobiol. B: Biology,* 1990, vol. 7, pp. 15–20.
3. Schomaecker, K., Gaidouk, M.I., Rumyantseva, V.D., Fischer, T., Loehr, H., and Salditt, S., *Nuklearmedizin*, 1999, vol. 38, pp. 285–291.
4. Berezin, B.D. and Enikolopyan, N.S., in *Porfiriny: Struktura. Svoistva. Sintez* (Porphyrins: Structure, Properties, and Synthesis), Moscow: Nauka, 1985.
5. Bonnet, R., *Chemical Aspects of Photodynamic Therapy,* Amsterdam: Gordon and Breach Science Publishers, 2000.
6. Rao, P.D., Litter, B.J., Geier, IIIG.R., and Lindsey, J.S., *J. Org. Chem.*, 2000, vol. 65, pp. 1084–1092.
7. Rao, P.D., Dhanalekshmi, S., Litter, B.J., and Lindsey, J.S., *J. Org. Chem.,* 2000, vol. 65, pp. 7323–7344.
8. Littler, B.J., Miller, M.A., Hung, C.-H., Wagner, R.W., O'Shea, D.F., Boyle, P.D., and Lindsey, J.S., *J. Org. Chem.*, 1999, vol. 64, pp. 1391–1396.
9. Lee, C.H. and Lindsey, J.S., *Tetrahedron Lett.*, 1999, vol. 50, pp. 11 427–11 440.
10. Ryppa, C., Senge, M.O., Hatscher, S.S., Kleinpeter, E., Wacker, P., Schilde, U., and Wiehe, A., *Chem.-Eur. J.,* 2005, vol. 11, pp. 3427–3442.
11. Lindseu, J.S., US Patent 6849730, class NKI 540-145.
12. Naik, R., Joshi, P., and Deshpande, R.K., *Tetrahedron*, 2003, vol. 59, pp. 2207–2213.
13. Sobral, A.J.F.N., Rebanda, N.G.C.,L., Silva, M., and Lamreia, S.H., Silva, M.R., Beja, A.M., Paixao, J.A., and Gonsales, A.R., *Tetrahedron Lett.*, 2003, vol. 44, pp. 3971–3973.
14. Lee, W.W.-S., Wong K.-Y., Li, X.-M., Leung, Y.-B., Chan, C.-S., Chan, C.-S., *J. Mater. Chem.*, 1993, vol. 3, pp. 1031–1035.
15. Vasil'ev, V.V., Borisov, S.M., Chubarova, Yu.O., and Rumyantseva, V.D., *Zh. Neorg. Khim.,* 2003, vol. 48, pp. 455–461.