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Peculiarities of the Diimide Reduction of Tetrakis(3-pyridyl)porphyrin

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Dedicated to the memory of Academician of Russian Academy of Sciences Oskar I. Koifman

Diimide reduction processes of 5,10,15,20-tetrakis(3-pyridyl)porphine (T3PyP), in pyridine and solvent-free, were studied in detail. Both methods yielded the mixture of 5,10,15,20-tetrakis(3-pyridyl)chlorin (T3PyCh) and 5,10,15,20-tetrakis(3-pyridyl)bacteriochlorin (T3PyBCh) as a major product. UV-Vis and ^{1}H NMR methods for monitoring of diimide reduction of T3PyP were used. The behavior of hydrogenated products on aluminum oxide and silica gel during their chromatographic purification has been studied, and a method of isolation of individual T3PyCh and T3PyBCh with minimal contact with sorbents has been proposed.

Keywords: Diimide reduction, tetrapyridylporphine, chlorin, bacteriochlorin, spectroscopy, chromatography.

Особенности диимидного восстановления тетра(3-пиридил)порфирина

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В работе детально изучено диимидное восстановление 5,10,15,20-тетра(3-пиридил)порфина (T3PyP) в пиридине и в плаве. Показано, что в результате реакции образуется смесь 5,10,15,20-тетра(3-пиридил)-хлорина (T3PyCh) и 5,10,15,20-тетра(3-пиридил)бактериохлорина (T3PyBCh) с преобладанием последнего. Методами электронной и ^{1}H ЯМР спектроскопии определены оптимальные условия процесса диимидного восстановления T3PyP для получения T3PyCh или T3PyBCh. Изучено поведение гидрированных продуктов на окиси алюминия и силикагеле при их хроматографической очистке и предложен метод выделения индивидуальных T3PyCh и T3PyBCh с минимальным контактом с сорбентами.

Ключевые слова: Диимидное восстановление, тетрапиридилпорфин, хлорин, бактериохлорин, электронная спектроскопия, хроматография.

Introduction

Chlorins and bacteriochlorins (hydroporphyrins) are modified porphyrin-type compounds with distinct structural, physical, and chemical attributes. These unique characteristics position chlorins and bacteriochlorins as essential components in various fields of application, particularly in medicine, where they serve as crucial agents for the diagnosis and treatment of neoplastic conditions through photodynamic therapy (PDT) as photosensitizers (PS).[1,2] Both natural chlorin e6 derivatives (such as Photoditazin (Deco, Russia), Photoran e_6 (Ranfarma, Russia), Photolon (Medfarmkhim, Republic of Belarus), and others) and synthetic photosensitizers (such as Photosens (FGUP SSC NIOPIK, Russia) and Foscan (Biolitec AG, Germany)) are currently used as PSs for PDT.

Numerous scientific groups suggest novel synthetic photosensitizers derived from hydroporphyrins for application in PDT.[3-14] The synthetic strategy for obtaining the vast majority of these synthetic chlorins is based on the diimide reduction of porphyrins proposed by Whitlock in 1969.[15] The classic Whitlock procedure involves heating

porphyrin in pyridine at 100-105°C with *p*-toluenesulfonylhydrazide (p-TSH) in the presence of potassium carbonate. In all cases p-TSH is added portionwise throughout the entire process. The reaction time is 6.5 h and 12 h to obtain chlorin or bacteriochlorin, respectively.[15] Several modifications of the diimide reduction method have been proposed by now, differing in the nature of the solvent, reaction time, amount of reducing agent, as well as techniques for isolating the final products.[13] One of the modifications of the Whitlock procedure is solvent-free diimide reduction of porphyrins.[16] This solvent-free synthesis was based on the heating of a thoroughly ground mixture of two solids, p-TSH and the porphyrin, at 140 °C in vacuum tube. However, despite the popularity of the diimide reduction method, there is a lack of detailed information on the process.

Our interests revolve around the synthesis of chlorins and bacteriochlorins based on *meso*-tetraarylsubstituted porphyrins, particularly cationic derivatives of tetra(3-pyridyl)hydroporphyrins. Previously, the 5,10,15,20-tetrakis(3-N-methylpyridyl)bacteriochlorin (T3NMePyBCh) or the tetrahydroporphyrin tetratosylate (THPT) was investigated as a photosensitizer for photodynamic therapy of glioblastoma, colon carcinoma, bile duct cancer, and human choroidal melanoma cells. It is also exhibited significant antimicrobial activity against both gram-positive and gram-negative bacteria, with a high degree of photodynamic inactivation.[17-19] Furthermore, the tetra- and octacationic derivatives of 5,10,15,20-tetrakis(pyridin-3-yl)bacteriochlorin (T3PyBCh) with different alkyl chain lengths were proposed as effective PSs for PDT.[20-27] Recently,[7] we have proposed a method for obtaining a photosensitive controlled composition containing 5,10,15,20-tetrakis(3-N-methylpyridyl)chlorin (T3NMePyCh) and T3NMePyBCh, which showed positive results in photodynamic therapy of spontaneous fibrosarcomas and spontaneous mammary gland cancer sarcomas in domestic animals.[28,29] This study provides a detailed investigation of diimide reduction of 5,10,15,20-tetrakis(3-pyridyl)porphine and the peculiarities of purification of T3PyCh and T3PyBCh.

Experimental

All reagents and solvents were commercially available. UV-Vis electronic absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer, ^{1}H NMR spectra were recorded on a Bruker Advance 500 MHz radiospectrometer, and mass spectra (MALDI-TOF) were recorded on a Shimadzu Axima Confidence time-of-flight mass spectrometer.

Diimide reduction of 5,10,15,20-tetrakis(3-pyridyl)porphine (T3PyP) in pyridine was carried out according to [7]. Every 1.5 h, 1 mL aliquot was taken, and UV-Vis and ^{1}H NMR spectra were recorded.

Diimide reduction of T3PyP in a melt. The thoroughly ground mixture of T3PyP (0.32 mmol) and *p*-toluenesulfonylhydrazide (p-TSH) (6.4 mmol) was heated at 115 °C during 1.5 h. In all experiments 0.32 mmol of K_2CO_3 was added. In the first experiment, before melting of porphyrin and p-TSH, potassium carbonate was added to the initial mixture. In second and the third experiments, K_2CO_3 was added to the melted mixture after 30 min and after 60 min, respectively. After cooling the residue was dissolved in methanol and UV-Vis spectra were recorded.

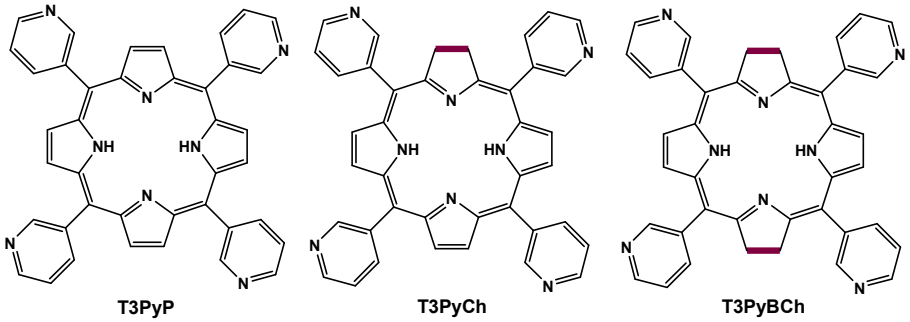
Interaction of mixture of T3PyCh and T3PyBCh with sorbents. Two identical column was prepared with aluminum oxide and silica gel. The solution of mixture of T3PyCh and T3PyBCh was allowed to penetrate each column to maximize the surface area of adsorption. The mixture was allowed to stand for 2 h, whereupon all products were eluted off the column with a CH_2Cl_2-MeOH (1:1) mixture. As a result, four chromatographic portions were obtained. Each sample was analyzed by UV-Vis spectroscopy and mass spectrometry.

Purification of T3PyCh and T3PyBCh. *o*-Chloranil was added in portions to the stirred CH_2Cl_2 solution of T3PyCh and T3PyBCh mixture at room temperature until the bacteriochlorin absorption peak at 746 nm disappeared. The chromatography on silica gel with CH_2Cl_2-MeOH (up to 5% MeOH) gave the T3PyCh in 56% yield.

The solution of $Zn(OAc)_2$ in methanol was added to boiling solution of T3PyCh and T3PyBCh mixture in CH_2Cl_2 in portions every 15 min. The reaction was complete when the absorption peak of chlorin at 653 nm disappeared. The resulting solution was separated on the aluminum oxide with CH_2Cl_2 and CH_2Cl_2-MeOH (up to 5% MeOH) mixture as eluent, giving T3PyBCh as a first zone in 52% yield. ZnT3PyCh was collected as a second zone. For ZnT3PyCh: MS (MALDI TOF) *m/z*: found 682 $[M]^+$; calc. for $C_{40}H_{26}N_8Zn$: 682.16. UV-Vis ($CHCl_3$) λ_{max} nm: 405 (sh), 423 (1.00), 529 (0.02), 598 (0.05), 628 (0.18). ^{1}H NMR (DMSO-d_6) δ ppm: 9.06 bs (2H), 8.94 bs (2H), 8.83 d (2H, *J* = 4.7 Hz), 8.76 d (2H, *J* = 4.7Hz), 8.38 d (2H, *J* = 5.8 Hz), 8.27 d (2H, *J* = 4.6 Hz), 8.25 d (2H, *J* = 5.8 Hz), 8.13 s (2H), 7.87 d (2H, *J* = 4.6Hz), 7.74 t (2H, *J* = 6.2Hz), 7.70 t (2H, *J* = 6.2Hz), 4.06 s (4H).

Results and Discussion

In our previous work,[7] we have demonstrated that the reduction of T3PyP under Whitlock's reaction conditions and in the melt resulted in a mixture of 5,10,15,20-tetrakis(3-pyridyl)chlorin and 5,10,15,20-tetrakis(3-pyridyl)bacteriochlorin. Both hydrogenated products T3PyCh and T3PyBCh as well as initial 5,10,15,20-tetrakis(3-pyridyl)porphine have characteristic UV-Vis and ^{1}H NMR spectra (Figure 1).



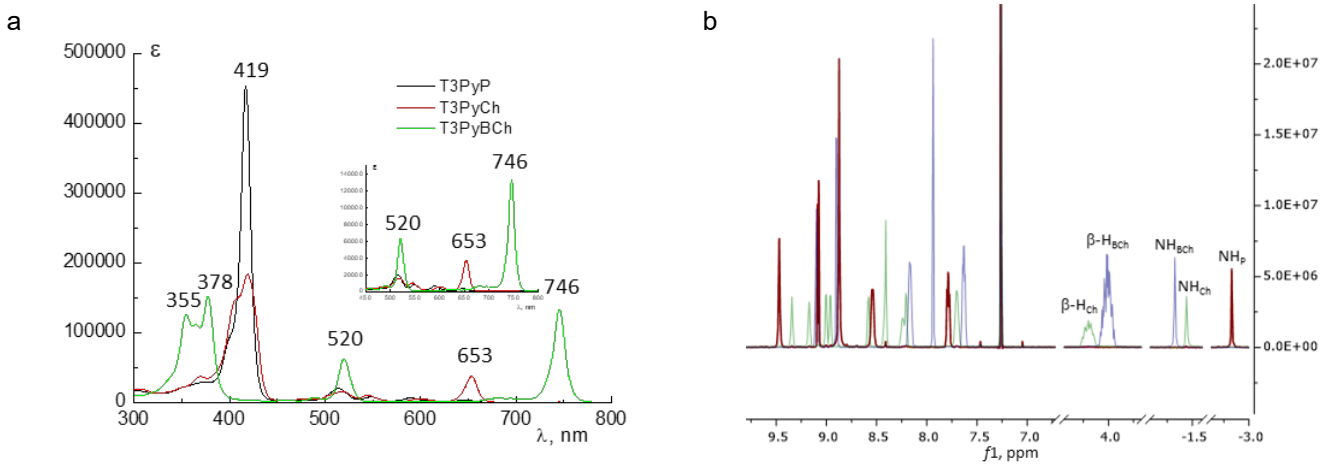


Figure 1. UV-Vis spectra (dichloromethane) (a) and superimpose ^{1}H NMR spectra ($CDCl_3$) of T3PyP (P), T3PyCh (Ch) and T3PyBCh (BCh) (the data is represented from [7]).

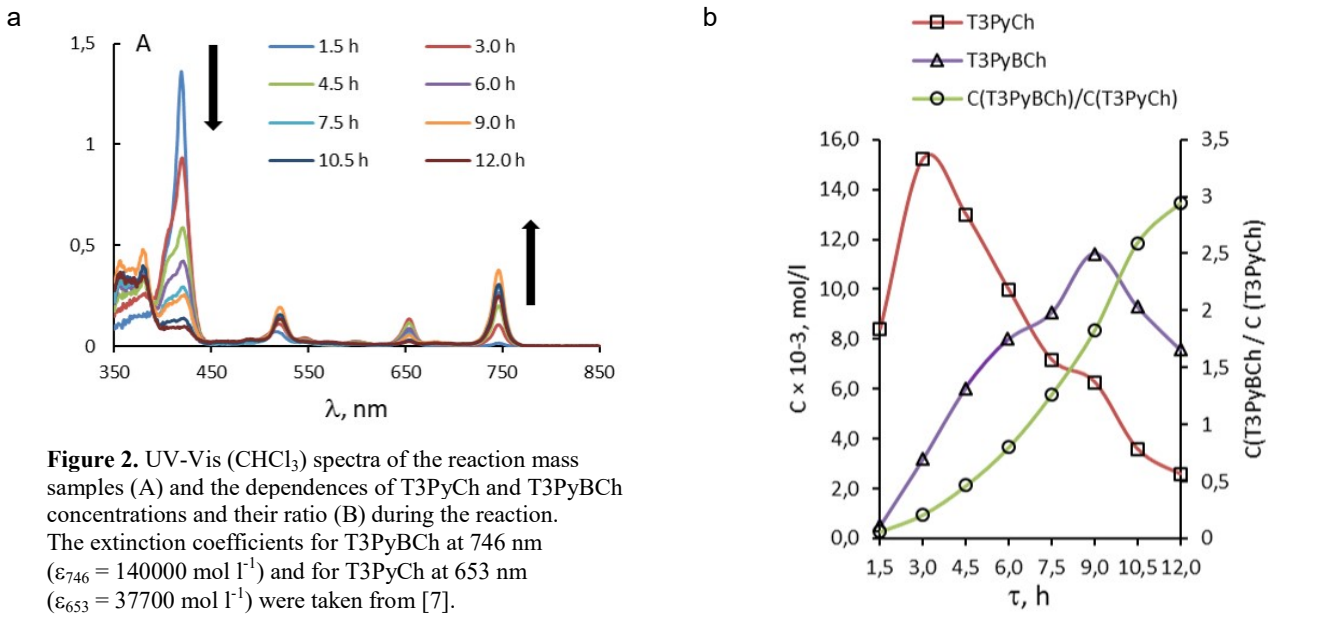


Figure 2. UV-Vis ($CHCl_3$) spectra of the reaction mass samples (A) and the dependences of T3PyCh and T3PyBCh concentrations and their ratio (B) during the reaction. The extinction coefficients for T3PyBCh at 746 nm (ε_{746} = 140000 mol l^{-1}) and for T3PyCh at 653 nm (ε_{653} = 37700 mol l^{-1}) were taken from [7].

Unlike T3PyP, the absorption spectrum of T3PyCh exhibits lower absorption of the Soret band (around 420 nm) and more intense absorption in the 650 nm region. T3PyBCh is characterized by the presence of two intense absorption bands in the short wavelength region at 355 nm and 378 nm and an intense band in the red region (746 nm) (Figure 1a). It should be noted that the overlap of the bands of porphyrin and chlorin does not allow us to clearly determine the presence or absence of porphyrin in the reaction mixture during the process.

This problem can be eliminated when considering the ^{1}H NMR spectra of these compounds (Figure 1b). The signals of aromatic protons and unsaturated β-protons of all three macrocycles are weak and most of them overlap, making it impossible to use their characteristics to control the progression of the process. However, the signals of saturated β-protons of chlorin and bacteriochlorin as well as those of protons of intracyclic imino groups turn out to be more isolated. So the analysis of ^{1}H NMR spectra only in a strong magnetic field, containing the signals of NH protons of porphyrin, chlorin and bacteriochlorin, will assess the relative content of each component in the reaction mixture. Therefore, the use of ^{1}H NMR method in addition to UV-Vis measurements will allow us to correctly determine the course of reaction.

At the beginning, we investigated the diimide reduction of T3PyP under the Whitlock procedure conditions. For this T3PyP was heated at 105 °C with 2 equiv. of *p*-toluensulfonylhydrazide in dry pyridine in the presence of 9 equiv. of anhydrous potassium carbonate. Every 1.5 h 2 equiv. of p-TSH were being added during 12 h. UV-Vis and ^{1}H NMR measurements were conducted before each addition of the reducing agent for monitoring the progress of the reaction. The formation of T3PyCh and T3PyBCh was detected by the changes of the absorption bands at 653 nm and 746 nm, respectively (Figure 2a,b). Additionally, the relative content of each component in the reaction mixture was determined by integrating the NH proton signals in the ^{1}H NMR spectra (Figure 3a,b).

As shown in Figure 2b, the concentration of chlorin reaches its maximum value within 3.5 h and then decreases to its final concentration in the resulting mixture. Detectable amounts of T3PyBCh were recorded just after 1.5 h of the reaction by the peaks, indicating an increase in

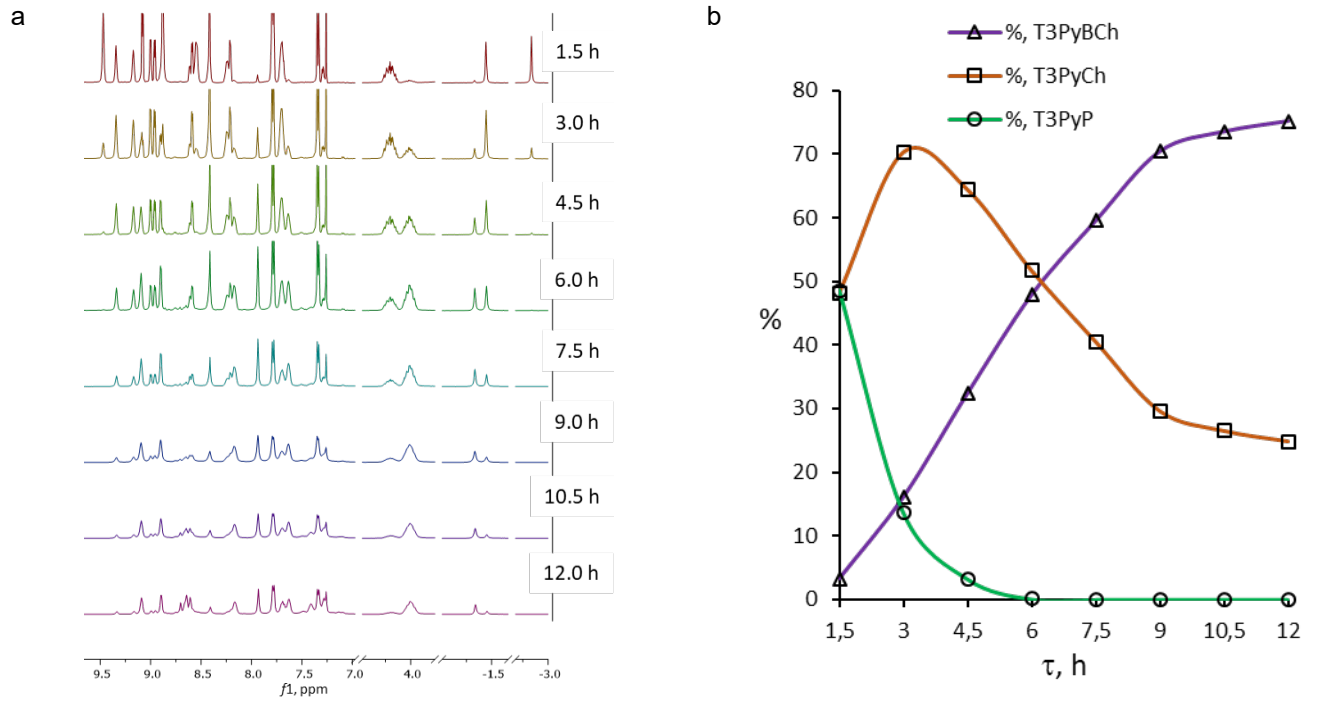


Figure 3. [1]H NMR spectra of the reaction mass samples (a) and the relative content (%) of T3PyP, T3PyCh and T3PyBCh in the reaction mixture (b) during the reaction.

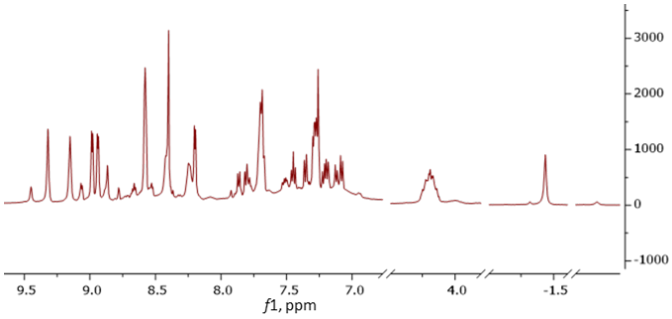


Figure 4. [1]H NMR spectra of the reaction mass (see text)

absorption at 746 nm (Figure 2 a,b). An increase in the concentration of bacteriochlorin was observed within 9 h. Furthermore, the concentration of T3PyBCh decreased. Moreover, throughout the entire process, the ratio of T3PyBCh concentration to T3PyCh concentration constantly increases.

[1]H NMR spectroscopy data provided additional information about the process (Figure 3). These data confirmed the results of changes in the concentrations of chlorin and bacteriochlorin and their ratios during the reaction, which were obtained by absorption spectroscopy method. In addition, the time of complete conversion of porphyrin into reaction products was determined by [1]H NMR spectra. Time of porphyrin conversion was 6 h.

The Whitlock procedure involved the gradual addition of a reducing agent to the reaction mass. We managed to show that single dosing of the whole amount of a reducing agent at the beginning of the process led to obtaining of T3PyCh with an insignificant content of T3PyBCh and T3PyP after 12 h (Figure 4).

Earlier, we have applied solvent-free synthesis method for reduction of T3PyP.[7] It was shown that complete conversion of porphyrin to the reaction products was achieved at 115 °C after 1.5 h and the ratio of porphyrin/p-TSH was 1:20. In the resulting mixture the content of bacteriochlorin was higher when reduction was carried out in pyridine.

Further, a series of experiments on the reduction of T3PyP in the melt in the presence of K_2CO_3 was carried out. In the first case, potassium carbonate was added to the initial mixture of porphyrin and p-TSH before melting began. In two subsequent experiments, K_2CO_3 was added to the melted mixture after 30 min and after 60 min, respectively. In all experiments, the total duration of the process was 1.5 h. The compositions of the reaction masses were analyzed by UV-Vis spectroscopy.

When the potassium carbonate was added before melting began, the reduction was incomplete; absorption bands of all three macrocycles were detected by electronic spectroscopy (Figure 5, line A). In the second experiment

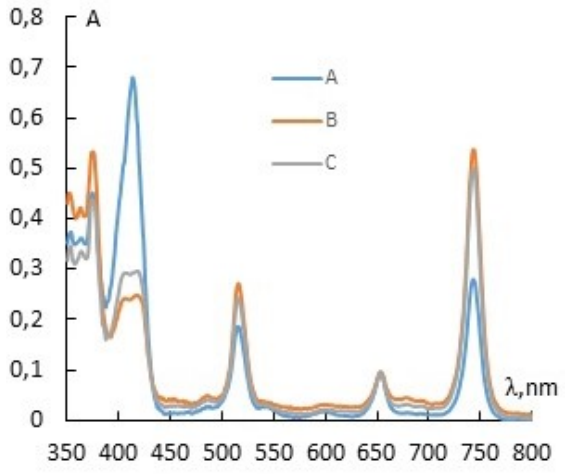


Figure 5. UV-Vis spectra (methanol) of the reaction masses. Addition of K_2CO_3: A – 0 min; B – 30 min, C – 60 min.

(Figure 5, line B) and the third one (Figure 5, line C), the content of the reduced products in the final mixture was approximately the same. Therefore, initial addition of K_2CO_3 resulted in incomplete conversion of porphyrin into reaction products. Adding potassium carbonate during the reduction process did not affect the outcome of the diimide reduction.

The Whitlock diimide reaction has extensive use as it is demonstrated by multiple examples.[13] In some cases, the reports indicated difficulties in separating hydrogenated porphyrins.[30] The mixture of T3PyCh and T3PyBCh can not undergo treatment with acids due to protonation of both intracyclic and peripheral nitrogen atoms. Therefore, the only method for their isolation was column chromatography. The authors[31] reported the separation of this mixture using aluminum oxide, resulting bacteriochlorin in 40% yield. However, we showed[7] that the reduction of T3PyP and subsequent quaternization of the reduction products without chromatographic purification led to a mixture of methylated derivatives of chlorin and bacteriochlorin with a yield of about 90%, based on the starting porphyrin. This indicates significant losses of T3PyCh and T3PyBCh specifically during chromatography.

We found out that chromatographic separation of the mixture of T3PyCh and T3PyBCh on sorbents (silica gel or aluminum oxide) depend on the contact time of the solution of the given mixture with the sorbent and was applicable only for the separation of small quantities of substances. The results of chromatography showed that except chlorin and bacteriochlorin on the column, there are several less mobile zones of chlorin nature.

To study the interaction of chlorin and bacteriochlorin with sorbents, the solution of the mixture of T3PyCh and T3PyBCh was allowed to interact with the sorbents directly on a chromatographic column during 2 h. Then the products were completely eluted with a CH_2Cl_2/MeOH (1:1) mixture, and 4 portions from each of the columns (aluminum oxide and silica gel) were collected. All portions were characterized by UV-Vis spectroscopy and mass spectrometry (Figures 6-8).

Absorption bands at 727 and 709 nm are present in the UV-Vis spectra of chromatographic portions, and signals at *m/z* values at approximately 636, 654 and 669 are recorded in the mass spectra of these portions. Based on the comparison of these results with the spectral characteristics of β-hydroxytetraphenylchlorin and β-hydroxytetraphenylbacteriochlorin[32] one can suggest that the chromatographic portions contain additional products with from one to three hydroxy groups at the reduced C-C bonds of T3PyCh and T3PyBCh.

Basing on the obtained data, it is recommended to minimize the chromatography time such as using flash chromategraphy for purification of a mixture of T3PyCh and T3PyBCh.

To obtain T3PyCh from its mixture with T3PyBCh, oxidation with both *o*-chloranil or DDQ can be applied. After the disappearance of the absorption peak of bacteriochlorin at 746 nm, chromatography on silica gel yields pure chlorin with an yield of over 50%.

For the purification of T3PyBCh the treatment of the T3PyCh and T3PyBCh mixture with zinc acetate was used. As a result, a mixture of the zinc complex of T3PyCh and the metal-free T3PyBCh was obtained. The mixture could be rapidly separated by flash chromatography on aluminum oxide. The yield of bacteriochlorin was 52%. But, the yield of T3PyCh and T3PyBCh still remained at the 50% level, despite the proposed approach to purification.

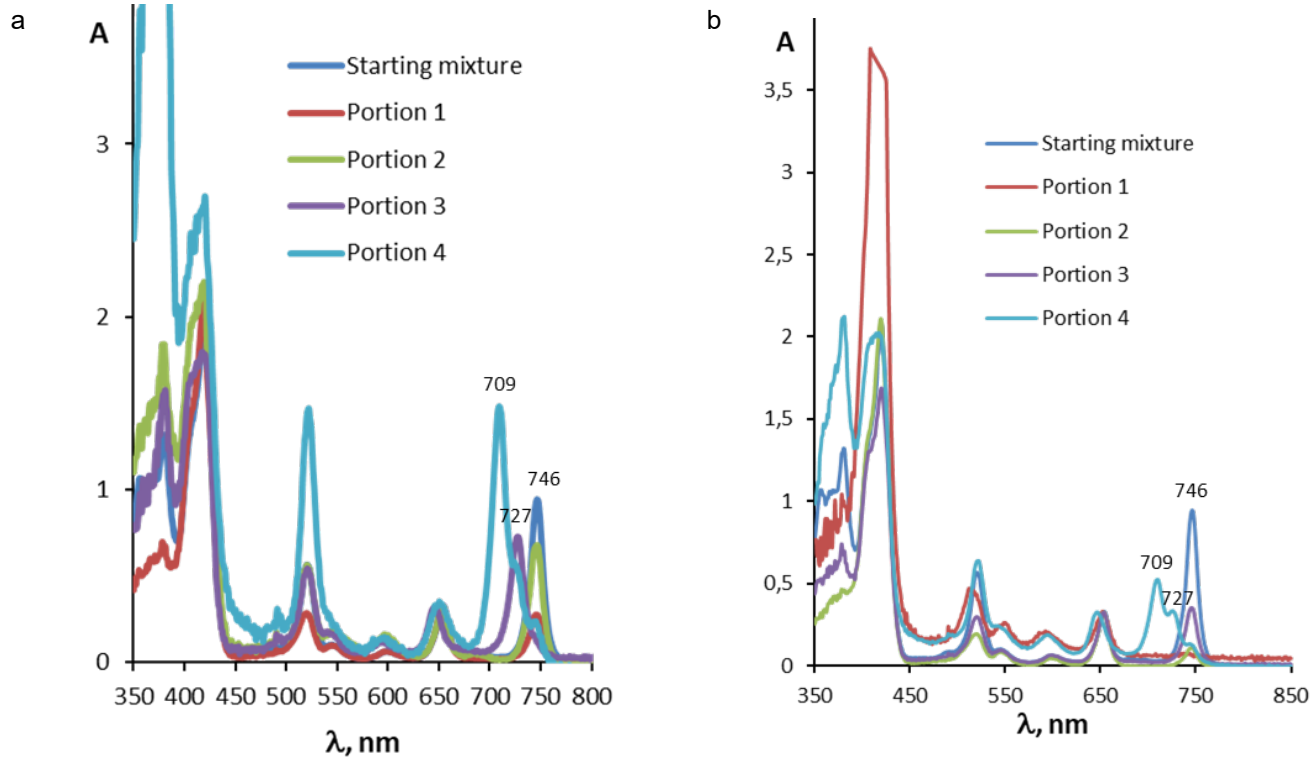


Figure 6. UV-Vis spectra (CH_2Cl_2) of the chromatographic bands: (a) on aluminum oxide column; (b) on silica gel column.

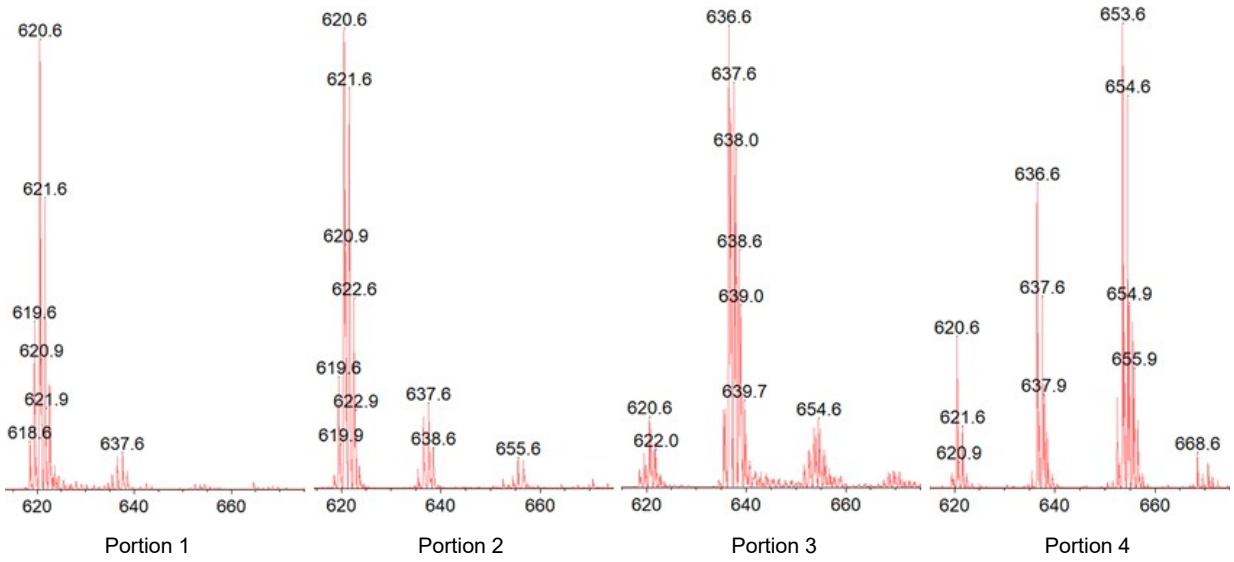


Figure 7. MALDI TOF spectra of chromatographic bands (aluminum oxide).

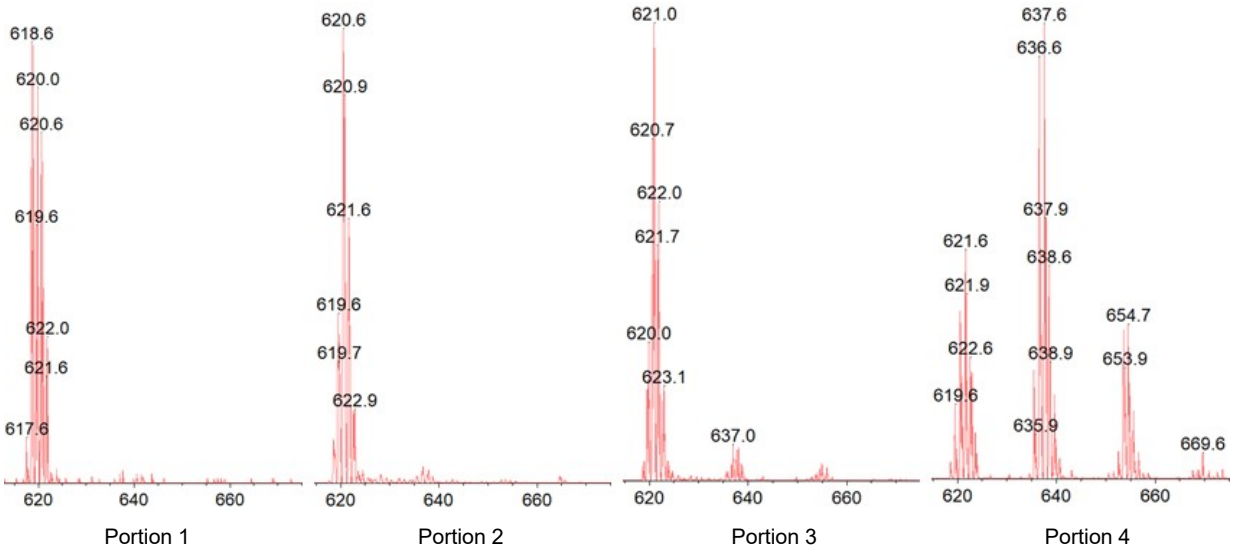


Figure 8. MALDI TOF spectra of chromatographic bands (silica gel).

Conclusion

Diimide reduction processes of 5,10,15,20-tetrakis(3-pyridyl)porphine (T3PyP) in pyridine and in a melt were studied. It was shown that complete conversion of porphyrin into reaction products in pyridine occurs after 6 hours. The maximum yield of reduction products is achieved just after 9 hours. If it is necessary to isolate T3PyCh and T3PyBCh by chromatography, contact of these compounds with sorbents should be minimized.

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Conflict of interests. The authors declare no conflict of interest.

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