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SYNTHESIS OF A MODEL PHOTOSYNTHETIC SYSTEM OF THE "COVERED" TYPE BASED ON MESOPORPHYRIN II

V. V. Borovkov, R. P. Evstigneeva, E. V. Mirakova, and B. V. Rozynov

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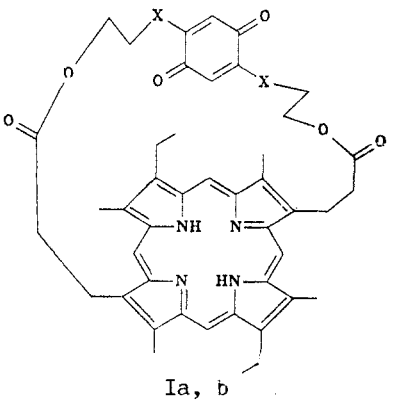
The synthesis of a porphyrinquinone compound of the "covered" type based on mesoporphyrin II was accomplished. Spectral investigations of the compound obtained were carried out.

In connection with the search for alternative sources of energy, much attention is given to the investigation of the primary stages of the absorption of light in photosynthesis. Porphyrinquinone compounds of varying structural organization are widely utilized for the simulation of these processes [1, 2]. Among the models of this class, interest is presented by the "covered" porphyrinquinones in which the acceptor of electrons (the quinone) is oriented exactly over the center of the photosensitizer (the porphyrin [1, 2]) due to two or four covalent bonds between them. The advantages of such systems consist of the possible control of the relative oxidation—reduction potentials of the fragments in the synthesis, the distance between them, and their mutual orientation, and therefore the unambiguous interpretation of the experimental results for the phototransfer of electrons.

Porphyrins of a symmetrical structure are utilized for the synthesis of the "covered" porphyrinquinones. We synthesized the porphyrinquinone (Ia) on the basis of the symmetrical mesoporphyrin II. The substance (Ia) differs from known compounds of a similar type [1] [e.g., (Ib)] by the presence of the sulfur atom directly connected to the quinone structure. It was previously shown [3] for the porphyrinquinone compounds with a flexible covalent bridge that the heteroatom directly connected with the quinone exerts significant influence on the effectiveness of the process of the photoinduced transfer of the electron. The sulfur-containing quinones thereby exhibit the greatest acceptor



Ia, b

Ia X=S; b X=CH_2

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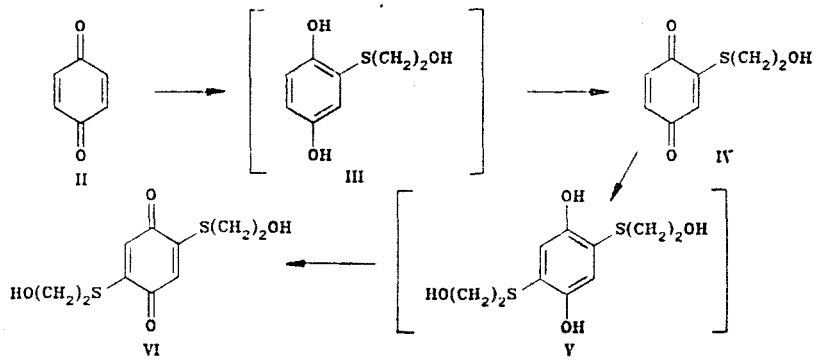
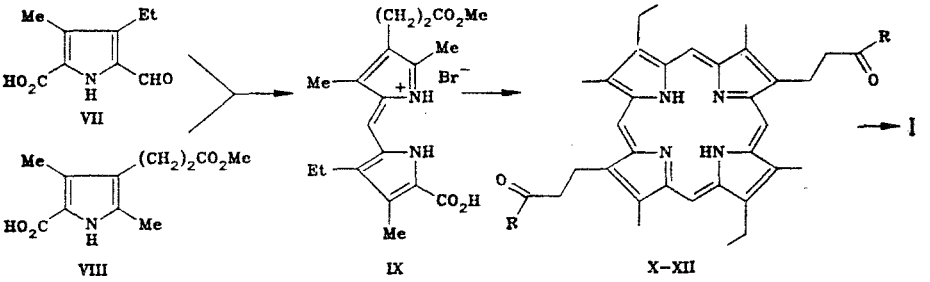
capacity. In the case of the "covered" porphyrinquinones, there is also interest in establishing the influence of the heteroatom on the effectiveness of the process of charge separation and the subsequent selection of the optimal acceptor fragment.

We have developed a method for the synthesis of the acceptor component allowing the directed isolation of the sulfur-containing quinone (VI) with two hydroxyl groups at the positions 2 and 5.



Attempts to obtain the product (VI) in one stage by the addition of 2-mercaptoethanol to 1,4-benzoquinone (II) were unsuccessful. A complex mixture of products of the quinone and hydroquinone structure, the isolation and identification of which were difficult, was formed. The variation of the ratio of the reagents and the sequence of their addition did not lead to the desired result. The separation of the reaction into two stages increased the selectivity of the process. In the reaction of the initial quinone (II) with 2-mercaptoethanol (in the molar ratio of 1:5 or 1:10) in an alcoholic medium, the substituted hydroquinone (III) was obtained; (III) underwent oxidation, without isolation, to the quinone (IV). The addition of a second molecule of 2-mercaptoethanol to the quinone (IV) under analogous conditions led to the formation of the disubstituted hydroquinone (V), which also underwent oxidation, without isolation, by oxygen of the air to the quinone (VI). The low yield (~ 10%) of the products (IV) and (VI) is probably associated with the inadequate effectiveness of the oxidation of the hydroquinones (III) and (V).

The directed 2,5-addition to the quinone (II) was shown by ^{13}C NMR spectroscopy (cf. Fig. 1). The symmetry of the molecule (VI) determines the presence of five signals (one each from the corresponding pair of equivalent carbon atoms) in the ^{13}C NMR spectrum. The structure of the compounds (IV) and (VI) was confirmed by the data of IR and PMR spectroscopy (cf. Fig. 2) and the elemental analysis.



X R=OMe, XI R=OH, XII R=Cl

The carboxyl component [mesoporphyrin II (XI)] was obtained by the acid hydrolysis of its dimethyl ester (X) synthesized from the pyrroles (VII) and (VIII) by the method of Fischer [4] with the yield of 29% via the stage of the formation of the dipyrrolylmethane (IX).

The acid chloride (XII) was obtained by the treatment of the mesoporphyrin II (XI) with oxalyl chloride, and it was introduced, without isolation, into the reaction with the quinone component (VI). The condensation was accomplished in dichloromethane under conditions of high dilution which are characteristic of the reactions of such a type [5, 6]. Both components were added, simultaneously and at the same rate, to the solution of triethylamine. The product (Ia) (the yield of 6.4%) was separated by preparative TLC. For the confirmation of the structure of the "covered" porphyrinquinone (Ia), UV, IR, and PMR spectroscopy and mass spectrometry (the method of fast atom bombardment) were utilized.

The mass spectrum of the compound (Ia) contains the peaks of the ions with the m/z 789-793. The peak of the $[M + H]^+$ ion with the m/z 791 possesses the maximal intensity in this group of signals. The presence of a large amount of ion peaks in this spectral region is explained both by the presence of heavy natural isotopes of elements

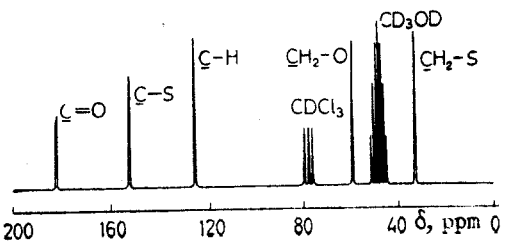


Fig. 1

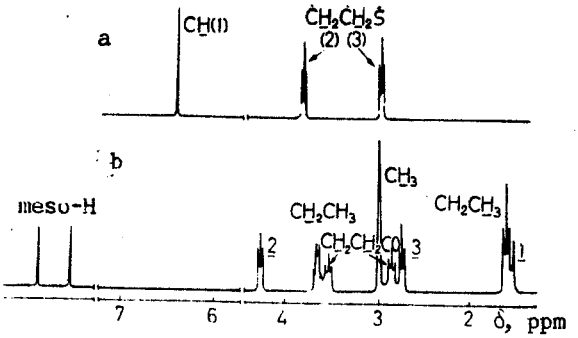


Fig. 2

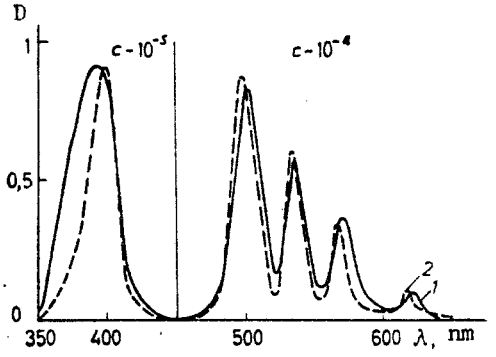


Fig. 3

Fig. 1. ^{13}C NMR spectrum of the quinone (VI) in the 1:1 mixture of $CDCl_3$—CD_3-OD.

Fig. 2. PMR spectra in $CDCl_3$: a) the quinone (VI); b) the "covered" porphyrin-quinone (Ia).

Fig. 3. Electronic spectra in chloroform: 1) the "covered" porphyrinquinone (Ia); 2) the compound (X).

contained in the molecule, and by the course of the processes of protonation and dehydrogenation of the initial molecule in the glycerol matrix or on its surface during the bombardment with fast xenon atoms [7].

The PMR spectrum of the porphyrinquinone (Ia) shows the shifts of the signals ($\Delta\delta$) of the protons of the quinone residue to the region of high field by comparison with the initial quinone (VI) (Fig. 2); this is characteristic of all known porphyrinquinones with the "covered" structure [1]. These effects are caused by the action of the magnetic anisotropy of the porphyrin ring and indicate the proximity of the donor and acceptor parts of the molecule. The steric organization of the molecule can be judged from the $\Delta\delta$ values. In the case of the "covered" compound, the values of $\Delta\delta$ are maximal due to the absence of significant conformational lability of the linear structure characteristic of the porphyrins. The $\Delta\delta$ of the protons of the quinone ring (4.89 ppm) is significantly higher for the compound (Ia) than for the compound (Ib) (4.06 ppm [8]). This indicates the closer disposition of the chromophores in the porphyrin (Ia), which is a result of the steric changes introduced by the atoms of sulfur directly bound to the quinone structure. The triplet of the protons of the SCH_2 group is shifted by 0.26 ppm to the high field region. Such an insignificant change is caused by the separation of this methylene group from the plane of the porphyrin.

The proximity of the chromophores appears in the UV spectrum of the compound (Ia) (cf. Fig. 3). For the previously synthesized "covered" porphyrinquinones, also including the compound (Ib), the UV spectrum represents

the superposition of the spectra of the porphyrin and the quinone without changes in the form or position of the absorption bands [5, 6, 8, 9]. This indicates the absence of significant interactions between the chromophores in the ground state. The UV spectrum of the compound (Ia) shows marked changes by comparison with the spectrum of the initial porphyrin (X) (Fig. 3). The significant broadening and the hypsochromic shift of the Soret band by 8 nm, as well as the small bathochromic shifts of the absorption bands in the visible region by 3-5 nm, indicate the interaction of the π-electron systems of the fragments in the unexcited state, which is characteristic of the dimers of the "surface-to-surface" type [10, 11].

The fluorescence spectrum of the compound (Ia) does not differ from the spectrum of the initial porphyrin (X). However, the compound (Ia) shows strong quenching of the fluorescence of the porphyrin, which is characteristic of covalently bound porphyrinquinones [1] and is a consequence of the photoinduced transfer of the electron from the porphyrin to the quinone.

EXPERIMENTAL

The condensation of the porphyrin and quinone fragments was accomplished in dry solvents. The discreteness of the compounds obtained and the course of the reactions were monitored by the method of TLC on Silufol UV-254 using the 15:1 mixture of chloroform—methanol (the system A), and on Kieselgel 60 F_{254} (Merck) using the 2:1 mixture of chloroform—hexane (the system B). The IR spectra were taken on a Shimadzu IR-435 spectrophotometer. The UV spectra were taken on the Shimadzu UV-240 and Beckman DU-8B spectrophotometers. The ^1H and ^{13}C NMR spectra were obtained on the Bruker WM-250 instrument (250 MHz). The internal standard was HMDS. The fluorescence spectra were taken on the Shimadzu RF-540 spectrofluorimeter. The mass spectrum was obtained on a Krator MS-50 spectrometer by the bombardment with fast atoms of xenon with the energy of 6-8 keV. Glycerol was utilized as the matrix.

2-(2-Hydroxyethylthio)-1,4-benzoquinone (IV, $C_8H_8O_3S$). The solution of 1 g (9.25 mmoles) of 1,4-benzoquinone (II) in 55 ml of the 1:2:4 mixture of water—isopropanol—methanol is added gradually to the solution of 3 ml (43.1 mmoles) of 2-mercaptoethanol in 50 ml of the 1:2:4 mixture of water—isopropanol—methanol with stirring in the course of 3 h. The reaction mass is poured into 250 ml of a saturated solution of copper sulfate; the mixture is maintained for 56 h and filtered prior to the extraction with chloroform (4 × 200 ml). The extract is dried with sodium sulfate. The solvent is removed, and the residue is chromatographed on a column 3.5 × 20 cm with silica gel L 100 × 160; elution is performed with chloroform. The fraction with the R_f 0.23 (A) is collected. The solvent is removed and the residue is crystallized from heptane and dried in a vacuum over paraffin and phosphorus pentoxide. The yield is 173 mg (10.2%). The R_f is 0.23 (A). The mp is 86-88°C. The IR spectrum (mineral oil, KBr) is as follows: 3470 cm^{-1} (OH), 1635 cm^{-1} (CO, quin.), and 1541 cm^{-1} (C=C). The PMR spectrum ($CDCl_3$) is as follows: 6.86-6.71 ppm (2H, m, CH, quin.), 6.50-6.42 ppm (1H, m, CH, quin.), 3.95 ppm (2H, t, J = 6.0 Hz, CH_2CH_2O), and 3.04 ppm (2H, t, J = 6.0 Hz, CH_2CH_2O).

2,5-Bis(2-hydroxyethylthio)-1,4-benzoquinone (VI, $C_{10}H_{12}O_4S_2$). The solution of 298 mg (1.62 mmoles) of the quinone (IV) in 30 ml of the 1:2:4 mixture of water—isopropanol—methanol is added gradually to the solution of 0.56 ml (8.05 mmoles) of 2-mercaptoethanol in 30 ml of the 1:2:4 mixture of water—isopropanol—methanol with stirring in the course of 1 h 30 min. The reaction mass is poured into 250 ml of a saturated solution of copper sulfate, and the mixture is held for 56 h prior to filtration, the extraction with chloroform (4 × 200 ml), and the drying of the extract with sodium sulfate. The solvent is removed, and the residue is chromatographed on a column 3.5 × 29 cm with silica gel L 100 × 160; the elution is performed with the 15:1 system of chloroform—methanol. The fraction with the R_f 0.15 (A) is collected. The solvent is removed, and the residue is crystallized from heptane; it is dried in a vacuum over paraffin and phosphorus pentoxide. The yield is 43 mg (10.2%). The R_f is 0.15 (A), and the mp is 109-111°C. The IR spectrum (mineral oil, KBr) is as follows: 3250 cm^{-1} (OH), 1610 cm^{-1} (CO, quin.), and 1540 cm^{-1} (C=C). The PMR spectrum ($CDCl_3$) is as follows: 6.44 ppm (2H, s, CH, quin.), 3.86 ppm (4H, t, J = 6.5 Hz, CH_2CH_2O), and 3.00 ppm (4H, t, J = 6.5 Hz, CH_2CH_2O). The ^{13}C NMR spectrum (the 1:1 mixture of $CDCl_3$—CD_3OD) is as follows: 182.49 ppm (C=O), 152.72 ppm (C—S, quin.), 126.26 ppm (C—H, quin.), 59.76 ppm (CH_2O), and 33.77 ppm (CH_2S).

2,4,6,8-Tetramethyl-5,9-diethyl-3,7-[2,5-dioxo-1,1-phenylenebis(thioethyloxycarbonylethyl]porphyrin (Ia). To the suspension of 100 mg (0.19 mmole) of the compound (XI) in 10 ml of dichloroemthane is added 1 ml (19 mmoles) of oxalyl chloride, and the mixture is stirred for 2 h. The solvent is removed, and the acid chloride obtained (XII) is dried in a vacuum. To the solution of 0.1 ml of triethylamine in 10 ml of dichloromethane are added, with stirring and simultaneously at the same rate, the solution of the acid chloride (XII) in 40 ml of

dichloromethane and the solution of 50 mg (0.2 mmole) of the quinone (VI) in 40 ml of dichloromethane in the course of 1 h. The reaction mass is stirred for 20 h at 20°C and for 30 min with boiling; the mixture is washed with water (3 × 100 ml) and dried with sodium sulfate. The solvent is removed, and the residue is separated by preparative TLC on plates 20 × 20 cm with Kieselgel; the elution is performed with the 100:1 system of chloroform—methanol. The upper-moving band with the R_f 0.51 (B) is collected; elution is performed with chloroform, and the solvent is removed. Th residue is smoothed out in pentane and dried in a vacuum over paraffin and phosphorus pentoxide. The yield is 9 mg (6.4%). The R_f is 0.51 (B). The electronic spectrum in chloroform, expressed as λ_{max} (log ε), is as follows: 625.7 nm (3.61), 572.7 nm (3.90), 537.9 nm (4.00), 503.5 nm (4.13), and 391.7 nm (5.17) (Soret). The IR spectrum (mineral oil, KBr) is as follows: 3288 cm^{-1} (NH), 1730 cm^{-1} (CO in ester), 1665 cm^{-1} (CO, quin.), and 1595 cm^{-1} (C=C, quin.). The PMR spectrum ($CDCl_3$) is as follows: 9.23 ppm (2H), 8.88 ppm (2H, all s, meso-H), 4.26 ppm (4H, t, J = 6.5 Hz, CH_2CH_2O), 3.66 ppm (4H, q, J = 7.5 Hz, CH_2CH_3), 3.55 ppm (4H, t, J = 8.0 Hz, CH_2CH_2CO), 3.00 ppm (6H), 2.99 ppm (6H, all s, CH_3), 2.86 ppm (4H, t, J = 8.0 Hz, CH_2CH_2CO), and 1.55 ppm (2H, s, CH, quin.). The mass spectrum (m/z; I_{rel}, %) is as follows: 793 (70), 792 (60), 791 (100) $[M + H]^+$, 790 (50), $[M]^+$, 789 (40) $[M - H]^+$, and 788 (45) $[M - 2H]^+$.

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