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# Synthesis of Pyropheophytin-Anthraquinone Linked Molecules as Models for the Study of Photoinduced Electron Transfer

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**Abstract:** The first synthesis of pyropheophytin-anthraquinone compounds with the quinone covalently linked to the P4 allylic position of the phytyl chain is described. The results of preliminary conformational studies are reported for the two P4 stereoisomers obtained. These results suggest differences in the orientation of the anthraquinonyl-phytyl moiety relative to the phorbin macrocycle in the isomers.

Over the past decade, there has been growing activity in the design of model systems or so-called "synthetic reaction centres" to mimic the primary processes of natural photosynthesis[1,2]. A major part of the efforts has been devoted to investigations of photoinduced charge separation for the implementation of efficient capturing and storing of solar energy. A variety of electron donor-acceptor systems has been designed and prepared to study the dependence of the electron transfer rate on the distance and orientation between the donor and the acceptor. However, only a few pheophorbide-quinone molecules have been synthesized[2-4] and there have been no reports on structures consisting of a quinone attached to the phytyl chain of a chlorophyll derivative. We became interested in the latter type of compounds, because the presence of the quinone-phytyl group allows one to construct Langmuir-Blodgett films with a defined distance and orientation between the electron donor and the electron acceptor[5]. Here we would like to present the synthesis and structural characterization of the first pyropheophytin-anthraquinone molecules with the quinone moiety covalently linked to the P4 allylic position of the phytyl chain.

## RESULTS AND DISCUSSION

Our synthetic pathway beginning from chlorophyll *a* (Chl *a*) is shown in Figure 1. In the first step, Chl *a* (**1**)[6] was quantitatively converted into $13^2$-demethoxycarbonyl-Chl *a* (pyroChl *a*, **2**) by heating its degassed pyridine solution at 100 °C in a sealed tube[7]. The $^1$H and $^{13}$C NMR spectra of the product obtained were virtually identical with those previously reported for pyroChl *a*[8,9]. It was then necessary to modify the phytyl chain of **2** in order to create a suitable binding site for coupling with a quinone molecule. To achieve this goal,

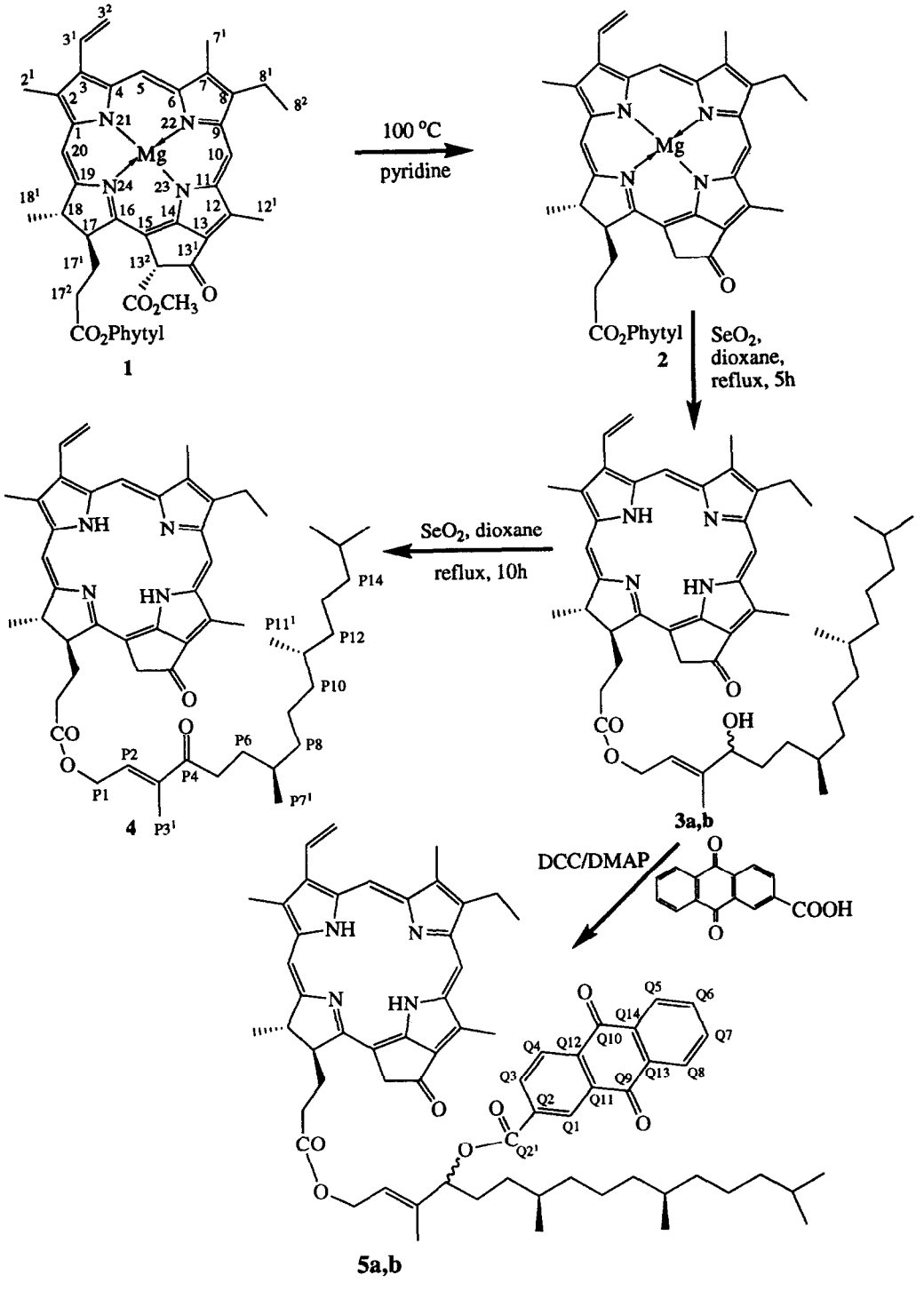


**Figure 1.** Synthesis of pyropheophytin - anthraquinone derivatives

we considered the P4-hydroxy-pyropheophytin *a* (**3a,b**) to be a suitable derivative for binding a quinone carboxylic acid using esterification as the coupling reaction. As reported by us briefly earlier[10], the P4 (*R,S*)-hydroxy-pyropheophytin *a* (**3a,b**) can be obtained in an overall yield of 32% from **2** after 5 hours of refluxing in dioxane under argon, using 4 equivalents of $SeO_2$. Only small amounts of the P4-oxo derivative (**4**) and unreacted pyropheophytin *a* are observed under those conditions. Prolonging the reaction time up to 10 hours in the same solvent, converts the P4-hydroxy derivative (**3a,b**) completely into P4-oxo-pyropheophytin *a* (**4**) with an overall yield of 21 %[10]. In pyridine, the oxidation appears to be less selective. Both products **3** and **4** are formed already in 1 hour despite the variation of the $SeO_2$ amount[10].

The first step of the oxidation process in dioxane is demetalation[10] which can be attributed to the formation of selenious acid ($H_2SeO_3$) as an intermediate in the reaction sequence[11]. Because no demetalation was observed in pyridine, this organic base is a preferable solvent despite its lower selectivity, if it is desirable to retain the central magnesium atom through the oxidation process.

For esterification between the P4-hydroxy derivative (**3a,b**) and 9,10-anthraquinone-2-carboxylic acid, we used *N,N'*-dicyclohexylcarbodiimide with a catalytic amount of 4-(dimethylamino)pyridine[12]. Earlier, this esterification method has been successfully applied by Wasielewski and Svec for the preparation of bis(pheophorbides)[13]. The synthesis of **5** was performed in dry $CH_2Cl_2$ at room temperature. After purification by column chromatography, the yield of the pyropheophytin-anthraquinone was 62%. When the phorbin-quinone was subjected to TLC on silica, it was found to consist of two components **5a** and **5b** (ratio *ca* 1:1). The components could be completely resolved and isolated by chromatography on a silica gel column. The structural analysis including electronic absorption spectra, FAB mass spectra as well as $^1H$ and $^{13}C$ NMR spectra for the components (see Experimental part), verifies the conclusion that **5a** and **5b** represent two diastereomers, differing in the configuration of the P4 carbon atom of the phytyl chain.

The electronic absorption spectra of **5a** and **5b** at the concentration of $2 \cdot 10^{-3}$ mol·litre$^{-1}$ in diethyl ether and at room temperature, were a superposition of the spectra of their phorbin and quinone components with bathochromic shifts of 4 nm and 3 nm for the Soret band and the $Q_{y,0\text{-}0}$ band, respectively, compared to the P4-hydroxy derivative (**3a,b**). This observation indicates that there is noticeable exiton coupling between the two aromatic systems under the conditions used[14].

The FAB mass spectra of **5a** and **5b**, with 1-thioglycerol as a matrix, exhibited a principal protonated molecule ion at m/z 1063 and its thioglycerol adduct at m/z 1172. These m/z values and those of the main fragments indicate that the expected molecules were formed in the synthesis. The fragment ion observed at m/z 812 in the spectra of both components is formed by the loss of anthraquinone-2-carboxylic acid to give pyropheophytin *a*. Both isomers also exhibited an ion at m/z 535 which represents protonated pyropheophorbide *a* formed by replacement of the phytyl chain with a proton.

The $^1H$ and $^{13}C$ NMR spectra of the compounds have been assigned using 2D correlated COSY and HETCOR techniques. The assignment of the $^{13}C$ high-field resonances of the phytyl chain was accomplished relying on the data previously reported for pyropheophytin *a*[9]. Comparison of the $^1H$ δ-values of compounds **5a** and **5b** with the δ-values of the corresponding protons in P4-hydroxy-pyropheophytin *a* (**3a,b**) and with the methyl ester of anthraquinone-2-carboxylic acid, afforded the Δδ-values assembled in Table 1. Inspection of the data in Table 1 shows marked differences in the Δδ-values for different protons of the same derivative both in respect to sign and magnitude, and also differences in the Δδ-values for the same protons of diastereomers **5a** and **5b**. We consider the $|\Delta\delta|$ values exceeding 0.08 ppm significant, because those values are safely above the

experimental error limits of ± 0.05 ppm. Examining first the negative Δδ-values implying upfield shifts and increased shielding, one can clearly see significant upfield shifts for the following protons of both isomers: 5-CH, 10-CH, $13^2$-$CH_2$, 17-CH (significant only for **5a**), 21-NH, 23-NH, and all CH protons of the anthraquinonyl group. Only relatively few protons experience significant downfield shifts, *i.e.* deshielding: $2^1$-$CH_3$ (significant only for **5a**), $8^2$-$CH_3$, $17^1$-$CH_2$, $17^2$-$CH_2$ and $18^1$-$CH_3$.

Table 1. $^1$H NMR Δδ[a] values for **5a** and **5b** in $CDCl_3$ solution.

| Proton | Δδ values, ppm | | Proton | Δδ values, ppm | |
|---|---|---|---|---|---|
| | **5a** | **5b** | | **5a** | **5b** |
| $2^1$-$CH_3$ | + 0.10 | - 0.03 | 17-CH | - 0.10 | - 0.01 |
| $3^1$-CH | + 0.01 | - 0.03 | 18-CH | 0.00 | + 0.03 |
| $3^2$-$CH_2$, H *trans* | - 0.01 | - 0.02 | $18^1$-$CH_3$ | + 0.18 | + 0.16 |
| $3^2$-$CH_2$, H *cis* | + 0.03 | + 0.01 | 20-CH | + 0.04 | - 0.03 |
| 5-CH | - 0.15 | - 0.15 | 21-NH | - 0.52 | - 0.62 |
| $7^1$-$CH_3$ | - 0.07 | - 0.03 | 23-NH | - 0.30 | - 0.49 |
| $8^1$-$CH_2$ | - 0.02 | 0.00 | Q1-CH | - 1.21 | - 0.78 |
| $8^2$-$CH_3$ | + 0.16 | + 0.20 | Q3-CH | - 0.50 | - 0.64 |
| 10-CH | - 0.27 | - 0.08 | Q4-CH | - 0.85 | - 1.13 |
| $12^1$-$CH_3$ | - 0.08 | - 0.01 | Q5-CH | - 1.54 | - 1.28 |
| $13^2$-$CH_2$, $H_A$ | - 0.19 | - 0.11 | Q6-CH | - 0.64 | - 0.79 |
| $13^2$-$CH_2$, $H_B$ | - 0.39 | - 0.22 | Q7-CH | - 0.40 | - 0.56 |
| $17^1$-$CH_2$ | + 0.12 | + 0.17 | Q8-CH | - 0.60 | - 0.82 |
| $17^2$-$CH_2$ | + 0.24 | + 0.24 | | | |

[a] Δδ = δ (protons of compound **5a** or **5b**) - δ (corresponding protons of compound **3a,b**); 9, 10-anthraquinone-2-carboxylic acid methyl ester was taken as a reference compound (the corresponding free carboxylic acid is insoluble in $CDCl_3$ ) for calculating the Δδ values of the quinone part of the molecule. For numbering of the protons see Figure 1.

The upfield shifts can be explained assuming that, in $CDCl_3$ solutions, compounds **5a** and **5b** occur to a significant extent in folded conformations in which the anthraquinonyl moiety is on the top of the phorbin ring (Figure 2). In this context, it should be noted that the chemical shifts of compound **5a** or **5b** do not represent a single folded conformation but are the result of time averaging processes between several conformations in equilibrium. Nevertheless, it seems reasonable to assume that a high percentage of folded conformations is present in solution, as the upfield shifts for some protons of the anthraquinonyl group are of the same order of magnitude as those found for other porphyrin-quinone and pheophorbide-quinone compounds with a flexible spacer, assumed to be in folded conformations[3,15]. The assumption concerning the folded conformations for compounds **5a** and **5b** is further supported by the observation that also all $^{13}$C resonances of the anthraquinonyl group are shifted upfield by *ca* 2 ppm (see Experimental). The factors causing the preference for folded conformations are not well understood[3,15]. In our compounds, intramolecular π–π interactions between the tetrapyrrolic and anthraquinonic π-systems seem to be responsible for the proposed folded conformations.

Comparison of the upfield shifts for the corresponding protons in stereoisomers **5a** and **5b**, leads us to the

conclusion that for **5a**, the right side of the phorbin macrocycle (rings B, C and E) is shielded more effectively than the left side, whereas for isomer **5b**, the shielding is more or less symmetrical. This conclusion is supported by the fact that the Δδ-values for the **5b** NH protons (-0.62 and -0.49 ppm) are higher than those for the **5a** NH protons (-0.52 and -0.30 ppm), which indicates more effective and symmetrical shielding of the internal NH protons in case of isomer **5b**. Further evidence for the conclusion is provided by the Δδ-values for the 10-CH proton: -0.27 ppm for **5a** and -0.08 ppm for **5b**. The higher value for **5a** indicates a more proximal position of the 10-CH proton relative to the shielding region of the quinone carbonyl group. Based on the NMR data and on the inspection of molecular models (HGS Molecular Structure Models, B set for organic chemistry, Maruzen Co. Ltd, Japan), two folded conformations are likely: conformation **I** for **5a** with the anthraquinonyl ring displaced to the right side of the phorbin macrocycle, resulting in increased shielding of pyrrole rings B, C and E, and conformation **II** for **5b** with the anthraquinonyl ring superimposed over the centre of the phorbin system. It is clear that the presence of the two different conformations arises from the two different configurations of the P4 chiral centre in stereoisomers **5a** and **5b**. Relying upon the molecular models and the $^1$H NMR data, we propose that compounds **5a** and **5b** represent the P4(*S*) and P4(*R*) diastereomers, respectively. The probable reason for the upfield shifts of the $13^2$-$CH_2$ resonances was also inferred from the molecular models which indicated that these protons are located in the shielding region, *i.e.* outside the deshielding anisotropic cone of the $Q2^1$ ester carbonyl group.

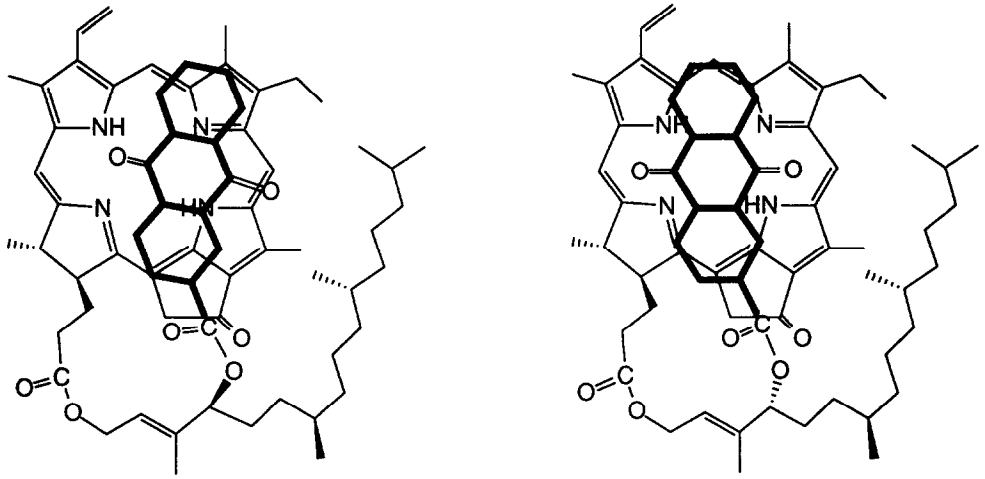


Figure 2. Proposed conformations of **5a** and **5b** in $CDCl_3$ solution.

The prominent downfield changes observed for the $2^1$, $8^2$, and $18^3$-$CH_3$ protons, as well as for the $17^1$ and $17^2$-$CH_2$ protons, presumably arise from the conformational alterations occuring in the phorbin macrocycle, particularly in ring D and its substituents. The positions of the side-chain protons probably change to more deshielding regions of the macrocyclic ring current[16], in consequence of the conformational alterations. The

latter may be attributed to the folding process induced by the π–π interactions between the tetrapyrrolic and anthraquinonic π-systems covalently linked to one another through a flexible ester linkage. This linkage is flexible enough to allow the formation of the folded conformations in consequence of the π–π interactions, but the rotational freedom of the propionic phytyl chain up to point P4 is reduced, *i.e.* the conformation of this side-chain fragment is more fixed as compared to the hydroxy derivatives (**3a** and **3b**).

Our very recent ROESY results show no correlation between the phorbin and anthraquinone rings, implying that the distance between the rings must exceed 4 - 5 Å. For the final verification of the above conclusions concerning the conformations of reduced ring D and its associated side-chains, high-field $^1$H NMR measurements, decoupling and spectral simulation techniques are needed[17,18].

The results of fluorescence studies have also shown differences between the two isomers (**5a** and **5b**). Though for both compounds, the fluorescence intensities were considerably decreased, the fluorescence quenching seemed to be more efficient in case of isomer **5a**: 9 and 17% of the fluorescence intensity of hydroxy-pyropheophytin *a* (**3a,b**) remained for isomers **5a** and **5b**, respectively. This significant difference in residual fluorescence intensities is consistent with our proposal concerning different mutual orientations of the aromatic π-systems for the **5a** and **5b** diastereomers.

In summary, $SeO_2$ is shown to be a regioselective reagent for the oxidation of the allylic position of pyrochlorophyll *a* phytyl chain. The P4-hydroxy diastereomers obtained appear to be very useful for binding with the different kinds of functionally active substituents. The esterification method applied for coupling between P4-hydroxy-pyropheophytin *a* and 9, 10-anthraquinone-2-carboxylic acid, is rather mild and seems to be suitable for the synthesis of molecules possessing really intrigue properties. The preliminary conformational studies that were accomplished for the two pyropheophytin-anthraquinone stereoisomers obtained, showed marked conformational differences between the diastereomers. Conceivably, the compounds obtained are of great value for the studies of photoinduced electron transfer, since they provide the possibility to investigate the dependence of the electron transfer rate on the distance and orientation between the donor and the acceptor. Such studies are now in progress and the results will be published elsewhere.

## ACKNOWLEDGEMENTS

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## EXPERIMENTAL

Silica gel 60 (230-400 mesh, ASTM, Merck, Darmstadt, Germany) was used for column chromatography. Analytical TLC was performed on Al-based, precoated silica-gel sheets (Merck 60 F254, layer thickness 0.2 mm) and on Al-based, precoated cellulose sheets (Merck, layer thickness 0.1 mm). The eluent for the silica sheets consisted of various mixtures of tetra- or dichloromethane and acetone, whereas *n*-heptane-pyridine was used for the cellulose sheets[19]. The $^1$H and $^{13}$C NMR spectra were measured on a 200 MHz Varian Gemini spectrometer in deuteriochloroform (D% 99.5, Aldrich, Milwaukee, USA); chemical shifts are expressed in ppm relative to the residual chloroform signal (7.258 ppm). The fast atom bombardment (FAB)

mass spectra were measured with a Finnigan MAT 95 high resolution mass spectrometer equipped with an Ion Tech FAB gun (Teddington, England). The samples were introduced into the ion source with a static FAB probe. 1 µl of sample solution (*ca* 1 mg/ml in $CH_2Cl_2$) and 1 µl of 1-thioglycerol (Fluka, Buchs, Switzerland) were injected on the stainless steel tip of the probe. The temperature of the ionization chamber was 50 °C, the xenon particle energy 8 kV, the emission current 10 mA, the accelerating voltage 5 kV and the magnetic field scanning rate was one scan through range m/z 400-1300/5 sec. The electronic absorption spectra were measured on a Shimadzu MPS-2000 spectrophotometer and the fluorescence spectra on a Shimadzu RF-5000 spectrofluorometer, in diethyl ether (*pro anal.*, Merck, dried and stabilized with 2,6-di-*t*-butyl-4-methylphenol). The other solvents used were of analytical grade; tetrachloromethane and dichloromethane were distilled through a Vigreux-column prior to use. Selenium (IV) oxide (99.8%) and anthraquinone-2-carboxylic acid (98%) were purchased from Aldrich. *N,N'*-dicyclohexylcarbodiimide (98 %) was obtained from Fluka.

**Chlorophyll *a* (1).** Chlorophyll *a* was isolated from clover leaves by the method described earlier[6], modified for large-scale preparation. The spectroscopic properties (UV-Vis, $^1H$ NMR) of the preparation were consistent with those reported previously[20].

**13²-Demethoxycarbonyl-chlorophyll *a* (pyrochlorophyll *a*) (2).** Chlorophyll *a* was quantitatively converted into pyrochlorophyll *a* by heating its degassed pyridine solution at 100 °C for 48 hours in a sealed tube[7]. The $^1H$ and $^{13}C$ NMR spectra of **2** were virtually identical with those reported earlier[8,9].

**13²-Demethoxycarbonyl-P4(*R, S*)-hydroxy-pheophytin *a* (3a,b).** 390 mg (0.48 mmol) of **2** were dissolved in 60 ml of 1,4-dioxane; 1.5 ml of water and 213 mg (1.92 mmol) of $SeO_2$ were then added to the solution. The reaction mixture was refluxed for 5 hours under argon and with magnetic stirring and the progress of the reaction was monitored by TLC on cellulose (eluent: *n*-heptane-pyridine, 9:1, v/v)[19]. After 5 h, the mixture was diluted with 500 ml of $CHCl_3$, washed thoroughly with water (4 x 400 ml) and dried over $MgSO_4$. Solvents were then evaporated and the residue, dissolved in 5 ml of $CHCl_3$, was passed through a silica layer (particle size 70-230 mesh; height of the layer 60 mm; 70 x 45 mm I.D. glass sinter, elution with chloroform-acetone, 1:1, v/v) and the effluent was evaporated to dryness. The products were chromatographed on silica gel (particle size 230-400 mesh; height of the layer 280 mm; 300 x 45 mm I.D. column, elution with $CCl_4$-acetone, 5:1, v/v). After the appearance of a minor component, the main product band was eluted out to yield hydroxy-derivative **3a,b** as a brownish-black wax-like solid: 127 mg (32%); $^1H$ NMR ($CDCl_3$), $\delta_H$ in ppm: 9.40 (s, 10-CH), 9.30 (s, 5-CH), 8.52 (s, 20-CH), 7.95 (dd, $^3J_{cis}$ = 12 Hz, $^3J_{trans}$ = 18 Hz, $3^1$-CH), 6.25 (dd, $^2J$ = 2 Hz, $^3J_{rans}$ = 18 Hz, $3^2$-$CH_2$, H *trans*), 6.14 (dd, $^2J$ = 2 Hz, $^3J_{cis}$ = 12 Hz, $3^2$-$CH_2$, H *cis*), 5.58 (m, P2-CH), 5.22 and 5.05 (AB spin system, $|^2J|$ = 20.5 Hz, $13^2$-$CH_2$), 4.68 (m, P1-$CH_2$), 4.44 (m, 18-CH), 4.21 (m, 17-CH), 4.01 (t, $^3J$ = 6.7 Hz, P4-CH), 3.62 (q, $^3J$ = 7.2 Hz, $8^1$-$CH_2$), 3.61 (s, $12^1$-$CH_3$), 3.38 (s, $2^1$-$CH_3$), 3.18 (s, $7^1$-$CH_3$), ~2.61 (m, $17^1$-$CH_2$), ~2.29 (m, $17^2$-$CH_2$), 1.80 (d, $^3J$ = 7.5 Hz, $18^1$-$CH_3$), 1.70 (br. s, $P3^1$-$CH_3$), 1.69-1.55 (m, P5-$CH_2$, P15-CH), 1.50 (t, $^3J$ = 7.2 Hz, $8^2$-$CH_3$), 1.45-0.95 (m, P7 and P11 CH-groups, P6, P8, P9, P10, P12, P13 and P14 $CH_2$-groups), 0.85 (d, $^3J$ = 6.7 Hz, $P15^1$ and P16 $CH_3$-groups), 0.83 (d, $^3J$ = 6.6 Hz, $P11^1$-$CH_3$), 0.80 (d, $^3J$ = 6.6 Hz, $P7^1$-$CH_3$), 0.47 (s, 21-NH), -1.70 (s, 23-NH); $^{13}C$ NMR ($CDCl_3$), $\delta_C$ in ppm: 196.7 ($13^1$), 172.8 ($17^3$), 171.5 (19), 160.4 (16), 155.2 (6), 150.7 (9) 149.0 (14), 145.0 (8), 144.5, 144.3 (P3), 141.6 (1), 137.8 (11), 136.2, 136.0, 135.8 (3, 7, 4),

131.5 (2), 130.2 (13), 129.1 ($13^1$), 128.3 (12), 122.5 ($13^2$), 118.8, 118.5 (P2), 105.9 (15), 104.0 (10), 97.1 (5), 93.0 (20), ~77.0, 76.8 (P4), 61.3 (P1), 51.6 (17), 50.2 (18), 48.2, 48.1 ($13^2$), 39.3 (P14), 37.3 (P6, P8, P10, P12), 32.7 (P7, P11), 32.4, 32.3 (P5), 31.6 ($17^1$), 30.1 ($17^2$), 29.7 (P15), 24.8 (P13), 24.4 (P9), 23.1 ($18^1$), 22.7 ($P15^1$), 22.6 (P16), 22.5 ($P3^1$), 19.7 ($P7^1$, $P11^1$), 19.4 ($8^1$), 17.4 ($8^2$), 12.1 ($2^1$), 12.0 ($12^1$), 11.2 ($7^1$); UV-Vis ($Et_2O$), $\lambda_{max}$ in nm ($\varepsilon \cdot 10^{-3}$ [$l \cdot mol^{-1} \cdot cm^{-1}$]): 318 (18.1), 408 (98.3), 506 (9.06), 534 (7.44), 607 (5.24) and 667 (46.5); FAB MS (1-thioglycerol): m/z 447 (54), 461 (68), 535 (58) and 829 (100, M+H$^+$); $C_{53}H_{72}N_4O_4$ requires 829.

**$13^2$-Demethoxycarbonyl-P4-oxo-pheophytin *a* (4).** 200 mg (0.25 mmol) of **2** were dissolved in 30 ml of 1,4-dioxane; 0.8 ml of water and 110 mg (1 mmol) of $SeO_2$ were then added to the solution. The reaction mixture was refluxed for 10 hours under argon and with magnetic stirring. The progress of the reaction was monitored by TLC on cellulose (eluent: *n*-heptane-pyridine, 9:1, v/v)[19] until the spot of the slowly moving hydroxy-derivative (**3a,b**) had disappeared completely. Work-up and purification procedures similar to those used for the compounds **3a,b**, yielded oxo-derivative **4** as a brownish-black wax-like solid: 42 mg (21%); $^1H$ and $^{13}C$ NMR ($CDCl_3$): the $\delta_H$, $J_{H\text{-}H}$ and $\delta_C$ values of the phorbin ring and its side-chains were virtually identical with those of derivative **3a,b**; $\delta_H$ in ppm for the phytyl group: 6.28 (m, P2-CH), 4.58 (m, P1-$CH_2$), 2.47 (t, $^3J$ = 6.8 Hz, P5-$CH_2$), 1.67 (br. s, $P3^1$-$CH_3$), 1.65-1.55 (m, P15-CH), 1.40-0.95 (m, P7 and P11 CH-groups, P6, P8, P9, P10, P12, P13 and P14 $CH_2$-groups), 0.85 (d, $^3J$ = 6.7 Hz, $P15^1$ and P16 $CH_3$-groups), 0.80 (d, $^3J$ = 6.6 Hz, $P11^1$-$CH_3$), 0.78 (d, $^3J$ = 6.6 Hz, $P7^1$-$CH_3$); $\delta_C$ in ppm for the phytyl group: 201.4 (P4), 139.1 (P3), 133.4 (P2), 61.3 (P1), 34.9 (P5), 27.9 ($P3^1$), the high field part of the phytyl carbon spectrum was virtually the same as for compound **3a,b**; UV-Vis ($Et_2O$), $\lambda_{max}$ in nm ($\varepsilon \cdot 10^{-3}$ [$l \cdot mol^{-1} \cdot cm^{-1}$]): 318 (2.0), 408 (112.1), 506 (10.5), 533 (8.56), 608 (6.14) and 667 (49.6); FAB MS (1-thioglycerol): m/z 447 (24), 461 (36), 535 (28) and 827 (100, M+H$^+$); $C_{53}H_{70}N_4O_4$ requires 827.

**$13^2$-Demethoxycarbonyl-P4-oxy-(9,10-anthracenedione-2-carbonyl)-pheophytin *a* (5a,b).** 50 mg (0.06 mmol) of **3a,b**, 23 mg (0.097 mmol) of 9, 10-anthraquinone-2-carboxylic acid and 94 mg (0.43 mmol) of *N,N'*-dicyclohexylcarbodiimide were dissolved in 20 ml of dry $CH_2Cl_2$. The reaction mixture was protected from moisture and while stirring magnetically, 5 mg of 4-(dimethylamino)pyridine were added to catalyse the esterification. Stirring was continued for 2 hours and the progress of the reaction was monitored by TLC on silica (eluent: $CH_2Cl_2$-acetone, 15:1, v/v). The solution was washed with water (3 x 30 ml), 5% acetic acid (3 x 30 ml), water (3 x 30 ml), dried over anhydrous $MgSO_4$ and the solvent was evaporated. The products were chromatographed on silica gel (particle size 230-400 mesh; height of the layer 330 mm; 350 x 25 mm I.D. column, elution with $CH_2Cl_2$-acetone, 5:1, v/v) to yield phorbin-antraquinone ester **5a,b**: 40 mg (62%). The phorbin-anthraquinone fraction was further chromatographed on silica gel (particle size 230-400 mesh; height of the layer 480 mm; 500 x 30 mm I.D. column, elution with $CH_2Cl_2$-acetone, 20:1, v/v) providing two fractions which were collected separately to give derivative **5a** (17 mg, 26%) and derivative **5b** (20 mg, 31%) as the brownish-black wax-like solids. Derivative **5a**: $^1H$ NMR ($CDCl_3$), $\delta_H$ in ppm: 9.15 (s, 5-CH), 9.13 (s, 10-CH), 8.56 (s, 20-CH), 7.96 (dd, $^3J_{cis}$ = 12 Hz, $^3J_{trans}$ = 18 Hz, $3^1$-CH), 7.87 (m, Q3-CH), 7.67 (m, Q8-CH, Q1-CH), 7.50 (d, Q4-CH), 7.38 (m, Q7-CH), 7.17 (m, Q6-CH), 6.76 (m, Q5-CH), 6.24 (dd, $^2J$ = 2 Hz, $^3J_{trans}$ = 18 Hz, $3^2$-$CH_2$, H *trans*), 6.17 (dd, $^2J$ = 2 Hz, $^3J_{cis}$ = 12 Hz, $3^2$-$CH_2$, H *cis*), 5.97 (t, $^3J$ = 7.5 Hz, P2-CH), 5.39 (t, $^3J$ = 7.2 Hz, P4-CH), 5.03 and 4.66 (AB spin system, $|^2J|$ = 20.3 Hz, $13^2$-

$CH_2$), 4.84 (m, P1-$CH_2$), 4.44 (m, 18-CH), 4.11 (m, 17-CH), 3.60 (q, $^3J$ = 7.3 Hz, $8^1$-$CH_2$), 3.53 (s, $12^1$-$CH_3$), 3.48 (s, $2^1$-$CH_3$), 3.11 (s, $7^1$-$CH_3$), ~2.73 (m, $17^1$-$CH_2$), ~2.53 (m, $17^2$-$CH_2$), 2.01 (s, $P3^1$-$CH_3$), 1.98 (d, $^3J$ = 7.5 Hz, $18^1$-$CH_3$), 1.80-1.62 (m, P5-$CH_2$, P15-CH), 1.66 (t, $^3J$ = 7.3 Hz, $8^2$-$CH_3$), 1.45-0.95 (m, P7 and P11 CH-groups, P6, P8, P9, P10, P12, P13 and P14 $CH_2$-groups), 0.84 (d, $^3J$ = 6.6 Hz, $P15^1$ and P16 $CH_3$-groups), 0.80 (d, $^3J$ = 6.6 Hz, $P11^1$-$CH_3$), 0.75 (d, $^3J$ = 6.5 Hz, $P7^1$-$CH_3$), -0.05 (s, 21-NH), -2.00 (s, 23-NH); $^{13}$C NMR ($CDCl_3$), $\delta_C$ in ppm: 195.8 ($13^1$), 181.1 (Q9), 180.0 (Q10), 172.7 ($17^3$), 171.5 (19), 163.9 ($Q2^1$), 160.8 (16), 154.9 (6), 150.6 (9) 148.7 (14), 144.7 (P3), 141.6 (1), 139.3 (8), 137.6 (11), 136.2, 135.8, 135.7 (3, 7, 4), 134.7 (Q12), 134.3 (Q11), 133.1 (Q3, Q6, Q7), 132.1 (Q2), 132.0 (Q13, Q14), 131.6 (2), 130.2 (13), 129.4 ($3^1$), 128.0 (12), 127.6 (Q1), 126.4 (Q4), 126.3 (Q8), 126.0 (Q5), 123.3 (P2), 122.3 ($3^2$), 105.7 (15), 103.9 (10), 97.0 (5), 93.2 (20), 80.6 (P4), 60.6 (P1), 51.3 (17), 50.4 (18), 47.9 ($13^2$) and the high field part of spectrum was virtually the same as for compound **3a,b**; UV-Vis ($Et_2O$), $\lambda_{max}$ in nm ($\varepsilon \cdot 10^{-3}$ [l·mol$^{-1}$·cm$^{-1}$]): 255 (54.6), 320 (24.3), 412 (89.3), 507 (9.61), 535 (7.30), 613 (6.63) and 670 (41.5); FAB MS (1-thioglycerol): m/z 447 (85), 461 (100), 535 (46), 811 (16) and 1063 (80, M+H$^+$); $C_{68}H_{78}N_4O_7$ requires 1063. Derivative **5b**: $^1$H NMR ($CDCl_3$), $\delta_H$ in ppm: 9.32 (s, 10-CH), 9.15 (s, 5-CH), 8.49 (s, 20-CH), 8.10 (m, Q1-CH), 7.92 (dd, $^3J_{cis}$ = 12 Hz, $^3J_{trans}$ = 18 Hz, $3^1$-CH), 7.73 (m, Q3-CH), 7.45 (m, Q8-CH), 7.22 (m, Q4-CH, Q7-CH), 7.02 (m, Q5-CH, Q6-CH), 6.23 (dd, $^2J$ = 2 Hz, $^3J_{trans}$ = 18 Hz, $3^2$-$CH_2$, H *trans*), 6.15 (dd, $^2J$ = 2 Hz, $^3J_{cis}$ = 12 Hz, $3^2$-$CH_2$, H *cis*), 5.94 (t, $^3J$ = 7.4 Hz, P2-CH), 5.47 (t, $^3J$ = 6.8 Hz, P4-CH), 5.11 and 4.83 (AB spin system, $|^2J|$ = 20.4 Hz, $13^2$-$CH_2$), 4.80 (m, P1-$CH_2$), 4.47 (m, 18-CH), 4.20 (m, 17-CH), 3.62 (q, $^3J$ = 7.3 Hz, $8^1$-$CH_2$), 3.60 (s, $12^1$-$CH_3$), 3.35 (s, $2^1$-$CH_3$), 3.15 (s, $7^1$-$CH_3$), ~2.78 (m, $17^1$-$CH_2$), ~2.53 (m, $17^2$-$CH_2$), 1.96 (d, $^3J$ = 7.5 Hz, $18^1$-$CH_3$), 1.91 (s, $P3^1$-$CH_3$), 1.80-1.62 (m, P5-$CH_2$, P15-CH), 1.70 (t, $^3J$ = 7.4 Hz, $8^2$-$CH_3$), 1.40-0.90 (m, P7 and P11 CH-groups, P6, P8, P9, P10, P12, P13 and P14 $CH_2$-groups), 0.82 (d, $^3J$ = 6.6 Hz, $P15^1$ and P16 $CH_3$-groups), 0.80 (d, $^3J$ = 6.6 Hz, $P11^1$-$CH_3$), 0.75 (d, $^3J$ = 6.4 Hz, $P7^1$-$CH_3$), -0.15 (s, 21-NH), -2.19 (s, 23-NH); $^{13}$C NMR ($CDCl_3$), $\delta_C$ in ppm: 195.7 ($13^1$), 180.7 (Q9, Q10), 172.8 ($17^3$), 171.1 (19), 163.7 ($Q2^1$), 160.1 (16), 154.9 (6), 150.7 (9) 148.7 (14), 144.9 (P3), 141.2 (1), 139.3 (8), 137.6 (11), 136.0, 135.8, 135.6 (3, 7, 4), 134.7 (Q12), 134.5 (Q11), 133.6 (Q3), 133.1 (Q6, Q7), 131.9 (Q2, Q13, Q14), 131.4 (2), 130.3 (13), 129.3 ($3^1$), 128.2 (12), 127.2 (Q1), 126.4 (Q4), 126.3 (Q8), 126.0 (Q5), 122.5 (P2), 122.3 ($3^2$), 105.9 (15), 104.0 (10), 97.1 (5), 92.9 (20), 80.1 (P4), 60.6 (P1), 51.6 (17), 50.1 (18), 48.0 ($13^2$) and the high field part of spectrum was virtually the same as for compound **3a,b**; UV-Vis ($Et_2O$), $\lambda_{max}$ in nm ($\varepsilon \cdot 10^{-3}$ [l·mol$^{-1}$·cm$^{-1}$]): 255 (49.6), 318 (22.6), 412 (89.6), 507 (9.73), 535 (7.02), 612 (6.34) and 670 (41.2); FAB MS (1-thioglycerol): m/z 447 (42), 461 (58), 535 (46), 811 (24) and 1063 (100, M+H$^+$); $C_{68}H_{78}N_4O_7$ requires 1063.

**9, 10-Anthracenedione-2-carboxylic acid methyl ester**(reference compound for NMR studies, see Table 1). The compound was prepared by esterifying the corresponding acid with 5% v/v $H_2SO_4$ in MeOH[21]. Crystallization from acetone - methanol gave faintly yellow needles; mp 166-167 °C (lit.[22] 165 °C); $^1$H NMR ($CDCl_3$), $\delta_H$ in ppm: 8.88 (m, Q1-CH), 8.37 (m, Q3-CH), 8.35 (d, Q4-CH), 8.30 (m, Q5-CH), 8.27 (m, Q8-CH), 7.81 (m, Q7-CH), 7.78 (m, Q6-CH), 3.99 (s, $Q2^2$-$CH_3$); $^{13}$C NMR ($CDCl_3$), $\delta_C$ in ppm: 183.1 (Q9), 182.9 (Q10), 166.1 ($Q2^1$), 136.8 (Q12), 135.9 (Q11), 135.2 (Q3), 135.1 (Q6), 135.0 (Q7), 134.3 (Q13), 134.2 (Q14), 134.1 (Q2), 129.3 (Q1), 128.2 (Q4), 128.1 (Q8, Q5), 53.4 ($Q2^2$).

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