Synthesis and Properties of Pheophorbide-Quinone Compounds

Victor V. Borovkov,*,# Alexander A. Gribkov,† Andrei N. Kozyrev,† Alexander S. Brandis,†
Akito Ishida, and Yoshiteru Sakata
The Institute of Scientific and Industrial Research, Osaka University, Mihoga-oka, Ibaraki. Osaka 567
†M.V. Lomonosov Institute of Fine Chemical Technology,
pr. Vernadskogo 86, Moscow 117571, Russia
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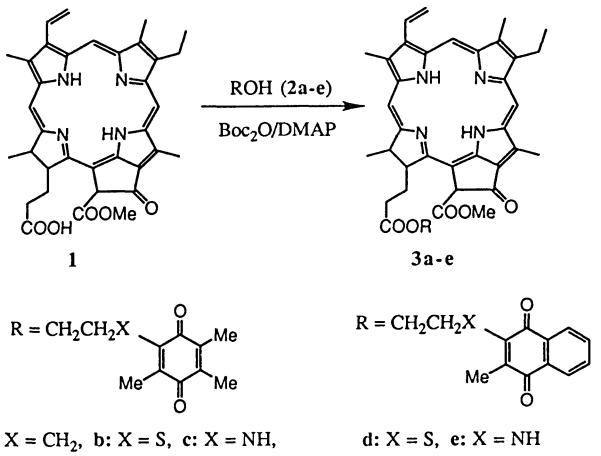
New pheophorbide-quinone derivatives with a different kind of quinone moieties were synthesized by mixed anhydride method. The structures of these compounds were confirmed by UV, IR, ^{1}H NMR, fluorescence, and mass spectra. Effective fluorescence quenching of the pheophorbide chromophores in the synthesized molecules was observed depending on the electron-accepting properties of the quinone fragment and spatial disposition of the donor and acceptor. Electron-transfer rate constants were calculated based on fluorescence decay measurements. The role of energetic and conformational changes of pheophorbide-quinones in the electron-transfer processes is discussed.

Since the X-ray analysis and femtosecond spectroscopic data of the photosynthetic reaction center were reported, a new class of donor–acceptor compounds constituted of covalently linked porphyrin and quinone fragments for modelling of the primary step of electron transfer in photosynthesis has been intensively investigated.[1,2] Among a lot of these models, however, only a few pheophorbide-quinone molecules based on natural chlorin chromophores were synthesized.[1–4] In this connection the synthesis of quinone-linked pheophorbide compounds, in which pheophorbide is a naturally occurring chromophore, seems important for further investigation of the light induced electron-transfer processes. A comparison of intramolecular electron-transfer parameters of porphyrin with these of chlorophyll-based models would allow us not only to understand more clearly the nature of the charge separation in photosynthesis, but also to choose more effective chromophores for possible application of such kind of systems in molecular electronic devices or systems for utilization of solar energy.



Scheme 1.

We have synthesized new models **3a**—**e** where pheophorbide *a* is linked to a quinone group by an ester bond. For all pheophorbide-quinones **3a**—**e** the pheophorbide and quinone moieties are connected by a covalent spacer consisting of 7 atoms. Although the spacers are flexible, **3a**—**e** have similar spatial structure with each other due to the same number of atoms in the chain and the same bridging positions of the two chromophores. Since CH_2, S, and NH groups are directly attached to the quinones in **3a**—**e**, the electron-accepting properties of the quinone moieties change considerably. Therefore, these models are expected to allow us to investigate the influence of the heteroatoms on the charge separation process.

Results and Discussion

Synthesis of Pheophorbide-Quinone Compounds. Initial quinonyl-substituted alcohols **2a**—**e** were synthesized by the described methods.[5–7] Pheophorbide **1** was obtained by the new developed method[8] from blue-green seaweed—*Spirulina platensis*. The preparation includes separation of water-soluble proteins, acid treatment of chlorophyll extracts followed by the isolation of the desired product in 55% yield. The investigation of the obtained product by ^{1}H NMR spectroscopy has shown the existence of two epimeric forms (*a* and *a'*) of pheophorbide relative to the carbon atom at 13^2 position of the macrocycle in 3 : 1 relationship. This ratio corresponds to the equilibrium state as described previously.[9]

To form an ester bond in **3a**—**e** we have applied mixed anhydride method by using di-*t*-butyl dicarbonate with a catalytic amount of 4-dimethylaminopyridine.[5–7] Previously we have found that this method is quite suitable for the synthesis of porphyrin-quinones based on natural porphyrins (such as deutero-, proto-, hemato-, mesoporphyrins, and etc.) with an ester bond between porphyrins and quinones.[4–6] The synthesis of **3a**—**e** was performed in a mixture of chloro-

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form–pyridine at 0 °C. After purification by preparative TLC yields of the products were 14.8—25.7% (see Experimental part). Low yields of **3a**—**e** by comparison with the porphyrin-quinones obtained previously by the similar method are apparently explained by the lability of **3a**—**e** at separation stage, because before purification the main product of this reaction was pheophorbide-quinone based on TLC control of the reaction mixture.

Spectroscopic Properties of Pheophorbide-Quinone Derivatives. In fast atom bombardment (FAB) mass spectra of **3a**—**e** peaks of the proper molecular ions M^+ and followed peaks $(M-H)^+$ and $(M+H)^+$ were observed.

The absorption spectra of **3a**—**e** were a superposition of its phorbine and quinone components without any changes. It indicates that there are no appreciable interactions between the chromophores in the ground state.[5–7,10–12]

In ^{1}H NMR spectra (see Experimental part and Table 1) the positions of the proton signals of the phorbine cycle in **3a**—**e** are practically unchanged comparing with the initial pheophorbide **1** ($\Delta\delta$=0.01—0.18 ppm) while the all proton signals of the quinone residues in **3a**—**e** are shifted to upfield ($\Delta\delta$: **3a**, 0.05—0.68 ppm; **3b**, 0.17—0.99 ppm; **3c**, 0.1—0.8 ppm; **3d**, 0.23—0.77 ppm; **3e**, 0.05—0.83 ppm) in comparison with those of the corresponding protons of the starting quinones **2a**—**e** (The δ data for the initial quinones **2a**—**e** have been reported previously.[6,7]). Such changes are attributable to the ring current effect of the phorbine cycle. This is an indication of the quinone fragment being located over the phorbine ring plane. The similar folded structure was suggested for porphyrin-quinones compounds with flexible spacer.[2] In **3d** and **3e** the signals of the aromatic protons in the naphthoquinone residues show upfield shifts only by 0.05—0.26 ppm, whereas the quinone methyl group has larger shift (0.68—0.76 ppm). In **3c** relatively large upfield shifts were observed for the methylene protons adjacent to NH group (0.8 ppm) and for one of the three methyl groups at the quinone ring (0.68 ppm). The signals of the other methyl groups in the quinone fragment show only small upfield shifts (ca. 0.1 ppm). These results indicate more close disposition of the methylene group adjacent to X and the methyl group at 3-position of the benzoquinone ring to the pheophorbide plane. The signals of the NH protons directly attached to the quinone ring in **3c** and **3e** are also shifted to upfield by 0.33 and 0.83 ppm, respectively. In **3b** and **3d**, which contain a sulfur atom in the covalent bridge the maximum shifts of the quinone methyl group are 0.99 and 0.77 ppm. On other hand, the upfield shifts of the corresponding protons for the quinone aromatic system of **3d** and the other two methyl groups of **3b** are not so large ($\Delta\delta$=0.16—0.26 ppm). Pheophorbide-quinone **3a** without heteroatom in the covalent bridge is assumed to have such folded conformation that one of the methyl groups of the quinone ($\Delta\delta$=0.65 ppm) and β-methylene group of the quinone covalent bridge ($\Delta\delta$=0.44 ppm) have the closest distance to pheophorbide plane. Based on these data we can assume that the distances between the pheophorbide and quinone moieties in **3a**—**e** do not differ very much, but relative orientation of the two chromophores is changed depending on the X group and on the substitution pattern in quinone moieties.

A comparison of ^{1}H NMR data of **3a**—**e** with the previous synthesized analogs based on the porphyrin structure[4–6] shows that $\Delta\delta$ values of the quinone protons for **3a**—**e** are smaller than those for the porphyrin derivatives ($\Delta\delta$: **3a**—**e**, 0.05—0.99 ppm; porphyrin derivatives, 0.23—2.10 ppm). Decreasing of $\Delta\delta$ values for **3a**—**e** apparently results from the smaller ring current of a chlorin cycle comparing with a porphyrin. Also it could be caused by some increased distance between the pheophorbide and quinone moieties due to the absence of a double bond in IV ring of the

Table 1. Selected ^{1}H NMR Chemical Shift Data (δ ppm, in $CDCl_3$) of the Quinone Moiety for **3a**—**e**

Compound	CH arom.	CH_3	$NHCH_2$	$CH_2CH_2CH_2O$,$NHCH_2CH_2O$, SCH_2CH_2O	CH_2O
3a[a]	—	1.90(3H,q,J=1.2 Hz),1.81(3H,q, J=1.2 Hz), 1.37 (3H,s)	—	2.57(2H,t,J=7.4 Hz)	3.67(2H,t,J=6.0 Hz)
3b	—	2.04(3H,s),1.82 (3H,s),1.25(3H,s)	—	3.00(2H,t,J=6.3 Hz)	4.04(1H,t,J=6.3 Hz), 3.99(1H,t,J=6.3 Hz)
3c	—	1.93(3H,q,J=1.2 Hz),1.86(3H,q, J=1.2 Hz),1.24 (3H,s)	5.33(1H,t, J= 6 Hz)	2.85—2.55(2H,m)	4.28—3.98(2H,m)
3d	7.90—7.80(2H,m), 7.60—7.40(2H,m)	1.68(3H,s)	—	3.07(2H,t,J=6.0 Hz)	4.06(2H,t,J=6.0Hz)
3e	7.96(1H,dd,J_1=8 Hz,J_2=1.5 Hz), 7.73(1H,dd,J_1=8 Hz,J_2=1.5 Hz), 7.54(1H,dt,J_1=8 Hz,J_2=1.5 Hz), 7.40(1H,dt,J_1=8 Hz,J_2=1.5 Hz)	1.76(3H,s)	5.16(1H,t, J=6 Hz)	3.22(2H,q,J=6.5 Hz)	3.80(2H,t,J=6.5 Hz)

a) There is additional signal at 1.25 ppm (2H, $CH_2CH_2CH_2O$, tt, J_1=6.0 Hz, J_2=7.4 Hz).

Table 2. Polarografic Half-Wave Potentials of Quinone Moieties and Fluorescence Spectroscopic Data for **1** and **3a—e**

Compound	$-E_{1/2}$/eV[a]	$I_{em}\times10^{-2}$ [b]	Lifetime[c] τ_1/ns	Quantum yield ϕ_1 of τ_1 exponent/%	Lifetime[c] τ_2/ns	Quantum yield ϕ_2 of τ_2 exponent/%	$k_{et}/10^8$ s^{-1}
1	—	100	—	—	6.24	100	—
3a	0.84	18	2.08	51.5	6.54	48.5	3.3
3b	0.70	13.6	1.27	64	6.45	36	6.3
3c	0.96	55	2.33	18.2	6.87	81.8	2.8
3d	0.74	5	1.03	53	6.45	47	8.2
3e	0.99	40	2.20	41.4	6.44	58.6	3.0

a) Measured for **2a—e**. b) λ_{em}=670 nm, λ_{ex}=410 nm, C=10^{-6} mol L^{-1}, acetone. c) λ_{em}>560 nm (by 0—560 filter), λ_{ex}=410 nm, C=10^{-6} mol L^{-1}, solvent: Ar saturated acetone.

pheophorbide.

A comparison of the initial pheophorbide *a* with **3a—e** by TLC has also shown the existence of two epimeric forms for the pheophorbide moieties. Based on ^{1}H NMR data the relationship between *a* and *a'* epimers is not changed from the initial pheophorbide **1**.

In fluorescence spectra the intensities of **3a—e** are considerably decreased comparing with the initial pheophorbide **1** (Table 2). The fluorescence quenching is reduced in the following sequence: **3d>3b>3a>3e>3c** and these values relative to the fluorescence of the initial pheophorbide **1** are: 20, 7.4, 5.6, 2.5, and 1.8 respectively. This order is similar to that of the quinone redox potentials measured in DMF for **2a—e**. Thus, polarografic half-wave potentials $E_{1/2}$, which characterize the electron acceptor properties of the quinones, decrease in the series: **2b>2d>2a>2c>2e** (Table 2). Small differences between the order of fluorescence quenching and quinone redox potentials in naphtho- and benzoquinone-substituted pheophorbides may be caused by small conformational changes as described above. In comparison with the porphyrin-quinones the fluorescence quenching of pheophorbide-quinones is smaller apparently due to less efficiency of the electron transfer from a pheophorbide to a quinone acceptor ($I_{em}\times10^{-2}$ values of porphyrin-quinones corresponding to **3a—3e** are 1.56, 3.3, 27, 3.1, and 6.3, respectively).

In order to evaluate electron-transfer rates more quantitatively the measurements of fluorescence lifetimes were carried out. All decay curves of **3a—e** are well fitted by a sum of two exponents with fast component τ_1 and slow component τ_2, while the initial pheophorbide *a* clearly shows single exponential decay with a lifetime τ, which is very close to τ_2. Values τ_1 and τ_2 together with the quantum yields are summarized in Table 2. It is possible to conclude that the fast component τ_1 is connected with the quenching of the pheophorbide fluorescence by intramolecular electron-transfer process due to the presence of a quinone electron acceptor moiety.

$$P\text{-}Q \xrightarrow{h\nu} P^*\text{-}Q \xrightarrow{k_{et}} P^+\text{-}Q^-$$

Values of τ_1 and τ_2 allowed us to determine the rate constants (k_{et}) of electron-transfer from photo-excited pheophorbide to quinone. We have calculated k_{et} values according to the equation: $k_{et}=1/\tau_1-1/\tau_2$ and listed them in Table 2. These data show that intramolecular electron-transfer rates of **3b** and **3d** with the highest reduction potential of quinone moiety are faster than those of **3a**, **3c**, and **3e**. This agrees completely with the results of fluorescence quenching for these compounds (Table 2). When k_{et} values are plotted against $E_{1/2}$ data of initial quinones, approximately linear relationship was observed (Fig. 1). Some deviations for naphtho and benzo series from the linearity may be caused from different spatial orientation of pheophorbide and quinone moieties. It is worth while to note that the electron-transfer rate of **3a—e** is dependent upon $E_{1/2}$ values of quinone, i.e. free energy difference of the reaction, with some relationship, although the both chromophores in a molecule are not rigidly fixed.

Comparison of k_{et} value of pheophorbide-quinone **3d** with porphyrin-quinone[13] shows that intramolecular

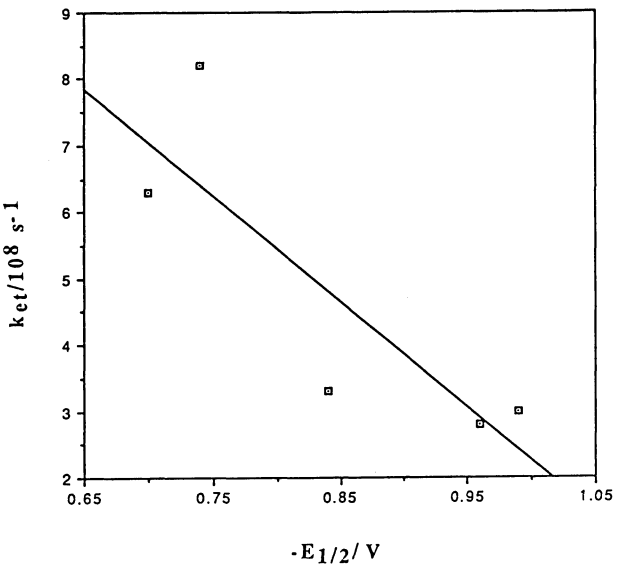

Fig. 1. The relationship between electron transfer rate constants (k_{et}) of **3a—e** and reduction potentials of **2a—e** ($E_{1/2}$).

electron transfer rate for **3d** is slower by 1.8 times. This may be explained by the larger distance between photosensitizer and acceptor in pheophorbide contained model (based on ^{1}H NMR data) and the different nature of electronic structures of its chromophores.

Experimental

General. For the condensation reactions pyridine was stored over potassium hydroxide followed by distillation over barium oxide and chloroform was treated with conc. sulfuric acid to remove ethanol as stabilizer, washed thoroughly with water, then with sodium hydrogencarbonate solution, dried over calcium chloride, and distilled over phosphorus pentaoxide. Column chromatography was carried out on silica gel (L 40/100) and preparative thin-layer chromatography was done on 20×20 cm glass plates coated with Kieselgel 60F (0.08 mm size of the particles, Merck). Reactions were monitored and the purity of **3a**—**e** was determined by thin-layer chromatography on Silufol UV-254 (Kavalier) with chloroform–methanol, 15:1 (1); on Kieselgel 60F (Merck) with chloroform–methanol, 15:1 (2); on alumina with chloroform–hexane, 1:1 (3); chloroform–hexane, 1:2 (4). The ^{1}H NMR spectra were obtained on a Bruker MSL-200 spectrometer (200 MHz) in chloroform-*d* with hexamethyldisiloxane as an internal reference. The UV-vis and IR spectra were recorded on a Shimadzu UV-240 (in acetone) and Shimadzu IR-435 (in vaseline film on KBr plate) spectrophotometers, respectively. Fluorescence spectra were measured on a Shimadzu RF-540 spectrofluorimeter in acetone. Fluorescence lifetimes were measured on a Horiba NAES-1100 time-resolved spectrofluorimeter. Mass spectra were obtained on a Kratos MS-50 mass-spectrometer by using a FAB method (Xe atoms, energy 6—8 keV). Polarografic half-wave potentials $E_{1/2}$ were measured in DMF relatively to Hg_2Cl_2 electrode.

Pheophorbide *a* (1). Paste of blue-green seaweed *Spirulina platensis* (600 g) preliminary frozen at −10 °C was defrost and mixed with phosphate buffer (pH 6, 6 l). Water-soluble proteins were separated by centrifugation. To the residue acetone (1.5 l) was added, the suspension was filtered under reduced pressure. The resulted extract was concentrated in three times by evaporating. Then concentrated hydrochloric acid was added (0.75 l) and the mixture was stirred for 1.5 h. After neutralization of the mixture by 10% aqueous ammonia solution to pH 6 product was extracted with chloroform (2×300 ml) and dried over anhydrous sodium sulfate. Solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (3.5×20 cm) with chloroform–acetone (7:1) to give: 750 mg (55%) of **1**; mp 190—195 °C; R_f=0 (3), 0 (4); UV-vis λ_{max} ($\log\varepsilon$) 665.5 (4.46), 608.1 (3.54), 532.9 (3.66), 503.3 (3.81), 466.9 (3.23), and 408.3 nm (4.86); IR 3300 (NH), 1705 (C=O in COOH), 1685 (ketone C=O), 1605 cm^{-1} (C=CCO); ^{1}H NMR δ=9.53 (1H, s, *meso*-H), 9.38 (1H, s, *meso*-H), 8.59 (1H, s, *meso*-H), 7.98 (1H, X in ABX, J_{AX}=18 Hz, J_{BX}=11.2 Hz, C*H*=CH$_2$), 6.30 (1H, A in ABX, J_{AB}=1.5 Hz, J_{AX}=18 Hz, CH=C*H*$_2$), 6.24 (1H, s, 10-H), 6.17 (1H, B in ABX, J_{AB}=1.5 Hz, J_{BX}=11.2 Hz, CH=C*H*$_2$), 4.52—4.40 (1H, m, 8-H, 7-H), 4.24—4.10 (1H, m, 8-H, 7-H), 3.87 (3H, s, OCH$_3$), 3.68 (3H, s, CH$_3$), 3.66 (2H, q, J=7.5 Hz, C*H*$_2$CH$_3$), 3.42 (3H, s, CH$_3$), 3.23 (3H, s, CH$_3$), 2.60—2.20 (4H, m, CH$_2$CH$_2$), 1.82 (3H, d, J=7.0 Hz, CH$_3$), 1.68 (3H, t, J=7.5 Hz, CH$_2$C*H*$_3$).

General Method for the Synthesis of 2,7,12,18-Tetramethyl-3-vinyl-8-ethyl-13^2-methoxycarbonyl-17-[2-[3-(3,5,6-trimethyl-*p*-benzoquinonyl)propoxycarbonyl]ethyl]phorbine (3a), 2,7,12,18-Tetramethyl-3-vinyl-8-ethyl-13^2-methoxycarbonyl-17-[2-[2-(3,5,6-trimethyl-*p*-benzoquinonylthio)ethoxycarbonyl]ethyl]phorbine (3b), 2,7,12,18-Tetramethyl-3-vinyl-8-ethyl-13^2-methoxycarbonyl-17-[2-[2-(3,5,6-trimethyl-*p*-benzoquinonylamino)ethoxycarbonyl]ethyl]phorbine (3c), 2,7,12,18-Tetramethyl-3-vinyl-8-ethyl-13^2-methoxycarbonyl-17-[2-[2-(3-methyl-1,4-naphthoquinon-2-ylthio)ethoxycarbonyl]ethyl]phorbine (3d), 2,7,12,18-Tetramethyl-3-vinyl-8-ethyl-13^2-methoxycarbonyl-17-[2-[2-(3-methyl-1,4-naphthoquinon-2-ylamino)ethoxycarbonyl]ethyl]phorbine (3e). To a stirred solution of pheophorbide *a* (100 mg, 0.17 mmol) in a mixture of pyridine (3 ml) and chloroform (20 ml) was added **2a**—**e** (0.20 mmol) and the solution was cooled to 0 °C. Then di-*t*-butyl dicarbonate (74 mg, 0.34 mmol) was added and after 10 min a catalytic amount of 4-dimethylaminopyridine (5 mg, 0.04 mmol) was added. The reaction mixture was stirred for 1 h at 20 °C, then poured onto 2% solution of hydrochloric acid (300 ml), and it was extracted with chloroform (50 ml). The extract was washed with water (3×200 ml), dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by preparative TLC on Kieselgel with chloroform–hexane (2:1). The product was collected, precipitated by pentane, washed with pentane, dried over phosphorus pentaoxide and paraffin in a vacuum desiccator. Data of ^{1}H NMR spectra of quinone moieties and fluorescence spectra are given in Tables 1 and 2, respectively.

3a: 23.1% yield; R_f=0.73 (1), 0.77 (2); UV-vis λ_{max} ($\log\varepsilon$) 666.1 (4.65), 608.5 (3.86), 534.3 (3.95), 505.3 (4.04), 467.3 (3.64), and 407.9 nm (5.02); IR 3300 (NH), 1730 (ester C=O), 1685 (ketone C=O), 1645 (quinone C=O), 1605 (C=CCO), 1580 cm^{-1} (quinone C=C); ^{1}H NMR δ=9.52 (1H, s, *meso*-H), 9.31 (1H, s, *meso*-H), 8.58 (1H, s, *meso*-H), 7.95 (1H, X in ABX, J_{AX}=18 Hz, J_{BX}=11 Hz, C*H*=CH$_2$), 6.31 (1H, s, 10-H), 6.26 (1H, A in ABX, J_{AB}=1.5 Hz, J_{AX}=18 Hz, CH=C*H*$_2$), 6.15 (1H, B in ABX, J_{AB}=1.5 Hz, J_{BX}=11 Hz, CH=C*H*$_2$), 4.47 (1H, dq, J_1=7 Hz, J_2=2 Hz, 8-H, 7-H), 4.30—4.18 (1H, m, 8-H, 7-H), 3.86 (3H, s, OCH$_3$), 3.68 (3H, s, CH$_3$), 3.67 (2H, q, J=7.5 Hz, C*H*$_2$CH$_3$), 3.39 (3H, s, CH$_3$), 3.19 (3H, s, CH$_3$), 2.70—2.24 (4H, m, CH$_2$CH$_2$), 1.80 (3H, d, J=7.0 Hz, CH$_3$), 1.69 (3H, t, J=7.5 Hz, CH$_2$C*H*$_3$); MS m/z 784 ((M+H)$^+$, 79%), 783 (M$^+$, 100), 782 ((M−H)$^+$, 35).

3b: 14.8% yield; R_f=0.60 (1), 0.61 (4); UV-vis λ_{max} ($\log\varepsilon$) 665.5 (4.58), 608.1 (3.75), 533.7 (3.86), 503.9 (3.96), 467.5 (3.54), and 408.3 nm (4.98); IR 3300 (NH), 1730 (ester C=O), 1685 (ketone C=O), 1640 (quinone C=O), 1605 (C=CCO), 1580 cm^{-1} (quinone C=C); ^{1}H NMR δ=9.49 (1H, s, *meso*-H), 9.33 (1H, s, *meso*-H), 8.56 (1H, s, *meso*-H), 7.96 (1H, X in ABX, J_{AX}=18 Hz, J_{BX}=11 Hz, C*H*=CH$_2$), 6.27 (1H, A in ABX, J_{AB}=1.5 Hz, J_{AX}=18 Hz, CH=C*H*$_2$), 6.24 (1H, s, 10-H), 6.16 (1H, B in ABX, J_{AB}=1.5 Hz, J_{BX}=11 Hz, CH=C*H*$_2$), 4.45 (1H, q, J=6.9 Hz, 8-H, 7-H), 4.26—4.16 (1H, m, 8-H, 7-H), 3.86 (3H, s, OCH$_3$), 3.68 (2H, q, J=7.5 Hz, C*H*$_2$CH$_3$), 3.67 (3H, s, CH$_3$), 3.46 (3H, s, CH$_3$), 3.22 (3H, s, CH$_3$), 2.68—2.28 (4H, m, CH$_2$CH$_2$), 1.79 (3H, d, J=7.1 Hz, CH$_3$), 1.67 (3H, t, J=7.5 Hz, CH$_2$C*H*$_3$); MS m/z 802 ((M+H)$^+$, 83%), 801 (M$^+$, 100), 800 ((M−H)$^+$, 33).

3c: 25.7% yield; R_f=0.56 (1), 0.34 (4); UV-vis λ_{max} ($\log\varepsilon$) 665.1 (4.35), 608.1 (3.62), 534.5 (3.71), 504.3 (3.76), 470.4 (3.32), and 408.3 nm (4.81); IR 3300 (NH), 1730 (ester C=O),

1680 (ketone C=O), 1660 (quinone C=O), 1605 (C=CCO), 1580 cm^{-1} (quinone C=C); ^1H NMR δ=9.52 (1H, s, *meso*-H), 9.40 (1H, s, *meso*-H), 8.57 (1H, s, *meso*-H), 7.99 (1H, X in ABX, J_{AX}=18 Hz, J_{BX}=11 Hz, C*H*=CH_2), 6.29 (1H, A in ABX, J_{AB}=1.5 Hz, J_{AX}=18 Hz, CH=C*H*$_2$), 6.24 (1H, s, 10-H), 6.19 (1H, B in ABX, J_{AB}=1.5 Hz, J_{BX}=11 Hz, CH=C*H*$_2$), 4.52—4.38 (1H, m, 8-H, 7-H), 4.28—4.05 (1H, m, 8-H, 7-H), 3.85 (3H, s, OCH_3), 3.68 (3H, s, CH_3), 3.67 (2H, q, J=7.5 Hz, C*H*$_2$$CH_3$), 3.40 (3H, s, CH_3), 3.22 (3H, s, CH_3), 2.68—2.28 (4H, m, CH_2CH_2), 1.81 (3H, d, J=7.5 Hz, CH_3), 1.68 (3H, t, J=7.5 Hz, CH_2C*H*$_3$); MS m/z 785 ($(M+H)^+$, 63%), 784 (M^+, 100), 783 ($(M-H)^+$, 33).

3d: 18.3% yield; R_f=0.67 (1), 0.83 (2), 0.38 (4); UV-vis λ_{max} ($\log\varepsilon$) 665.7 (4.76), 607.9 (3.94), 534.1 (4.06), 505.1 (4.14), 466.5 (3.76), and 408.3 nm (5.13); IR 3300 (NH), 1729 (ester C=O), 1680 (ketone C=O), 1650 (quinone C=O), 1605 (C=CCO), 1580, 1530 cm^{-1} (quinone C=C); ^1H NMR δ=9.51 (1H, s, *meso*-H), 9.35 (1H, s, *meso*-H), 8.54 (1H, s, *meso*-H), 7.97 (1H, X in ABX, J_{AX}=18 Hz, J_{BX}=11 Hz, C*H*=CH_2), 6.28 (1H, A in ABX, J_{AB}=1.5 Hz, J_{AX}=18 Hz, CH=C*H*$_2$), 6.21 (1H, s, 10-H), 6.17 (1H, B in ABX, J_{AB}=1.5 Hz, J_{BX}=11 Hz, CH=C*H*$_2$), 4.45—4.25 (1H, m, 8-H, 7-H), 4.22—4.10 (1H, m, 8-H, 7-H), 3.85 (3H, s, OCH_3), 3.69 (3H, s, CH_3), 3.67 (2H, q, J=7.5 Hz, C*H*$_2$$CH_3$), 3.40 (3H, s, CH_3), 3.21 (3H, s, CH_3), 2.70—2.22 (4H, m, CH_2CH_2), 1.77 (3H, d, J=7.5 Hz, CH_3), 1.68 (3H, t, J=7.5 Hz, CH_2C*H*$_3$); MS m/z 824 ($(M+H)^+$, 77%), 823 (M^+, 100), 822 ($(M-H)^+$, 33).

3e: 24.5% yield; R_f=0.51 (1), 0.55 (2), 0.45 (3); UV-vis λ_{max} ($\log\varepsilon$) 665.3 (4.62), 607.9 (3.85), 533.9 (3.69), 504.9 (4.05), 470.1 (3.76), and 409.7 nm (4.99); IR 3300 (NH), 1730 (ester C=O), 1679 (ketone C=O), 1650 (quinone C=O), 1600 (C=CCO), 1580, 1545 cm^{-1} (quinone C=C); ^1H NMR δ=9.50 (1H, s, *meso*-H), 9.31 (1H, s, *meso*-H), 8.54 (1H, s, *meso*-H), 7.92 (1H, X in ABX, J_{AX}=18 Hz, J_{BX}=11 Hz, C*H*=CH_2), 6.31 (1H, s, 10-H), 6.26 (1H, A in ABX, J_{AB}=1.5 Hz, J_{AX}=18 Hz, CH=C*H*$_2$), 6.14 (1H, B in ABX, J_{AB}=1.5 Hz, J_{BX}=11 Hz, CH=C*H*$_2$), 4.54—4.36 (1H, m, 8-H, 7-H), 4.28—4.05 (1H, m, 8-H, 7-H), 3.85 (3H, s, OCH_3) 3.66 (3H, s, CH_3), 3.65 (2H, q, J=7.5 Hz, C*H*$_2$$CH_3$), 3.38 (3H, s, CH_3), 3.18 (3H, s, CH_3), 2.68—2.28 (4H, m, CH_2CH_2), 1.78 (3H, d, J=7.5 Hz, CH_3), 1.67 (3H, t, J=7.5 Hz, CH_2C*H*$_3$); MS m/z 807 ($(M+H)^+$, 56%), 806 (M^+, 100), 805 ($(M-H)^+$, 24).

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