

Unexpected Methylation and Propylation of Porphyrin E-ring during the Hemisynthesis of Deoxyphylloerythroetioporphyrin (DPEP)

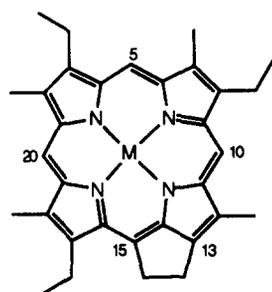
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Key Words: porphyrins, petroporphyrins, DPEP, synthesis, triazabicyclodecene, ring E alkylation.

Abstract: An improved hemisynthesis of DPEP from chlorophyll *a* is described. Hydrogenation of the vinyl group avoided the cleavage to a 3-H porphyrin, while heating in triazabicyclodecene performed the decarboxylation of the side-chain and the aromatization of ring D. Under these conditions extensive methylation and propylation of ring E occurred in the presence of CH₂X₂ (X = Cl, Br). © 1997 Elsevier Science Ltd.

Deoxyphylloerythroetioporphyrin **1** (DPEP) is a chlorophyll fossil found in most sediments containing organic matter, such as crude oils and oil shales.¹ Since this compound is often the major component of the mixture of porphyrins that can be isolated from geological sources, it is also a reference compound for all studies related to the structure determination of these fossil pigments.



DPEP **1**

M = H₂ (free base)
 or metal ion

The total synthesis of DPEP has been carried out by several groups,² but hemisynthesis from the readily available chlorophyll *a* provides by far the simplest access to DPEP.³ We carried out such a hemisynthesis,⁴ and have now improved several steps. During the initial work, a highly unexpected methylation of the five-membered ring E occurred, which was due to adventitious traces of dichloromethane interfering with the decarboxylation-dismutation reaction described by Kämpfen and Eschenmoser.⁵ Further work showed this reaction to give additional products, including propylated porphyrins. This article presents the full account of the improved hemisynthesis of DPEP as well as a reinvestigation of the alkylation processes occurring under Eschenmoser's conditions.

1. Hemisynthesis of DPEP

Crude chlorophyll *a* was extracted from *Spirulina*⁶ to avoid a separation from chlorophyll *b*, and was transformed in three classical steps (acid catalyzed demetallation, transesterification, refluxing in collidine) into methyl pyropheophorbide *a* **3**.⁷ Reduction⁸ of the keto group gave ester **4**.

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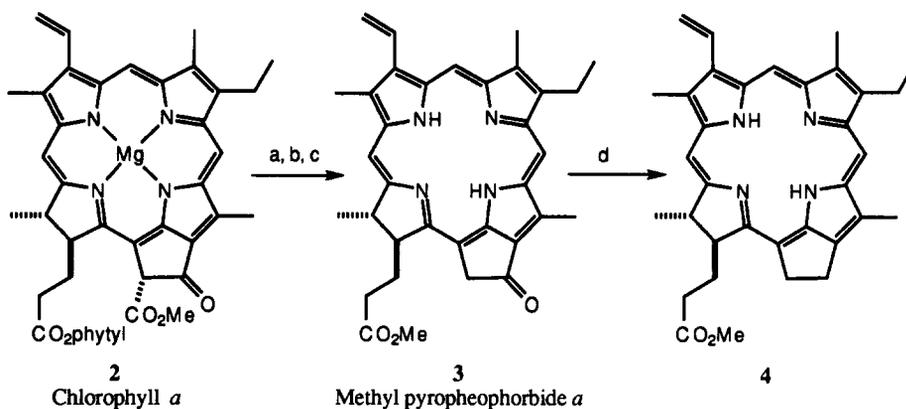


Figure 1. Reagents: a. 2N HCl; b. MeOH + 5% H₂SO₄; c. collidine, reflux; d. NaBH₄, CF₃CO₂H

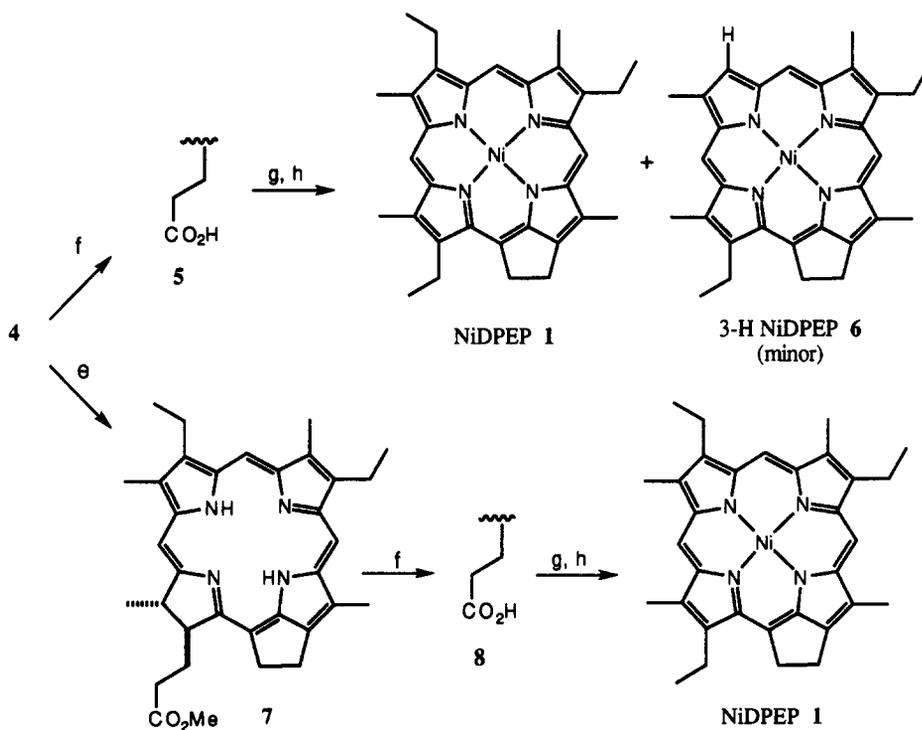


Figure 2. Reagents: e. Pd/C, H₂, THF; f. KOH, EtOH; g. TBD, 200°C; h. Ni(acac)₂, benzene, reflux.

The vinyl group could in principle be carried as such to the last step since, under Eschenmoser's conditions (triazabicyclodecene = TBD; 200°C),⁵ it is reduced to an ethyl group. However, a careful examination of the nickel complex of DPEP, produced at the end of our initial reaction sequence, revealed the presence of *ca* 10 % 3-H NiDPEP 6. HPLC purification of this compound allowed us to compare its NMR data and

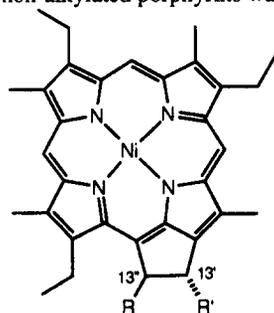
chromatographic behavior with those of a sample of 3-H NiDPEP, a widely distributed fossil porphyrin,¹ isolated from a natural source.⁹ This proved that, during the last step, the vinyl group of acid **5** could be cleaved, which recalls the Schumm reaction,¹⁰ *viz.* cleavage of vinyl groups of porphyrin free bases in hot resorcinol. It was suggested⁵ that the reduction of the vinyl group may proceed similarly, by way of an intermediate with TBD added at C-3' and we suggest that the cleavage of the C-3 side-chain may proceed *via* such an intermediate. To avoid this side-reaction the vinyl group of **4** was hydrogenated to an ethyl group to give **7**. We also found that the two reduction steps (reduction of the 13'-ketone and hydrogenation of the 3-vinyl group) can be reversed.

The three last steps, hydrolysis of the ester group to give acid **8** and reaction with TBD and immediate metallation with Ni(acac)₂ to avoid the oxidation of the very sensitive DPEP free base,¹ were carried out as reported earlier. DPEP, as its stable nickel complex **1**, was thus produced in 20 % overall yield from methyl pyropheophorbide *a*, in five highly reliable steps.

2. Methylation and propylation of DPEP under the conditions of Eschenmoser's reaction

In our preliminary report⁴ we drew attention to the fact that when traces of CH₂Cl₂ were inadvertently introduced into the reaction mixture, another product, 13''-methyl DPEP **9**, was obtained (the yield reported in our preliminary communication should read 6 % (/ starting material) and not 60 % which refers to the ratio of **9** / total porphyrin fraction). We suspected that the additional carbon originated from CH₂Cl₂ and wished to investigate further this new and unexpected reaction. We also noted that **9** is identical to a porphyrin isolated from an oil shale.¹¹

The results of preliminary experiments using CH₂Cl₂ proved to be erratic. This is likely due to the volatility of CH₂Cl₂, which was expected to be partially lost under the conditions required for sealing the reaction tube under vacuum. To control the amount of added reagent we used instead the less volatile CH₂Br₂ and found that alkylated porphyrins were also reproducibly produced and that the relative amount of alkylated / non-alkylated porphyrins was in the main sensitive to the relative amount of added CH₂Br₂.



1	R = H	R' = H
9	R = Me	R' = H
10	R = <i>n</i> -Pr	R' = H
11	R = Me	R' = Me
12	R, R' = Me, <i>n</i> -Pr	

Using 4 equivalents of CH₂Br₂, standard reaction conditions (ca 150 eq. TBD; 200°C; 4 h) and the usual work-up, including metallation with nickel, we recovered a porphyrin mixture (54 %, based on an average molecular weight of 560) containing five isolable products. NiDPEP **1** represented only 6.8 % of the mixture. The remaining components all contained one or more

additional CH₂ groups, as measured by mass spectrometry. HPLC separation allowed us to isolate two major components, Ni-13''-methyl DPEP **9** (62.6 %) and **10** (18.6 %) containing three additional carbons, while two minor porphyrins **11** (1.6 %) and **12** (3.8 %) contained respectively 2 or 4 additional CH₂. Mass spectra (12 and 70 eV) gave crucial information: peaks corresponding to the loss of methyl or propyl were observed and there was no evidence for loss of an ethyl group from **10**, **11** or **12**, or of a butyl group from **12** (under the conditions used the ethyl groups at C-3, C-8 and C-17 are almost untouched).

The NMR data (^1H and DEPT 135) for **9-12** confirmed the substitution patterns. In **9** and **10**, there remain 3 protons in the E ring, their relative chemical shifts indicating that substitution had occurred on carbon 13". In **11**, two doublets at high field indicated the presence of a $-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-$ substitution pattern on the ring, the absence of significant coupling between the two 13' and 13" protons confirming a trans stereochemistry. ^{13}C data also fully support the proposed structures for **9** and **10**. Product **12** is a mixture of the two isomers in a 5:1 ratio.

These results rule out a reaction mechanism involving successive methylations. Instead, we require a one carbon $-\text{CH}_2\text{Br}_2$ or CH_2Cl_2 being good candidates - and a 3 carbon unit to be added to the E-ring. The only 3 carbon fragment available is part of the TBD reagent.

TBD is a strong base, used in large excess under drastic thermal conditions; for example all the hydrogens of octaethylporphyrin are exchanged for deuterium under Eschenmoser's conditions.⁵ Accordingly, the formation of an anion at the benzylic positions 13' or 13" of DPEP should be easy. Moreover, the high reactivity at position 13" (or 15' if not cyclized) has been documented.¹² The porphyrin anion has then to react with an appropriate electrophile, generated by the reaction of CH_2X_2 ($\text{X} = \text{Cl}, \text{Br}$) with TBD. Alkylation of TBD would lead first to a iminium salt, which in turn may eliminate HX . The resulting iminium salt may then equilibrate with an endocyclic isomer. Attack of an anionic porphyrin on the iminium carbons would subsequently give intermediates in which the amine is bound to the porphyrin E ring.

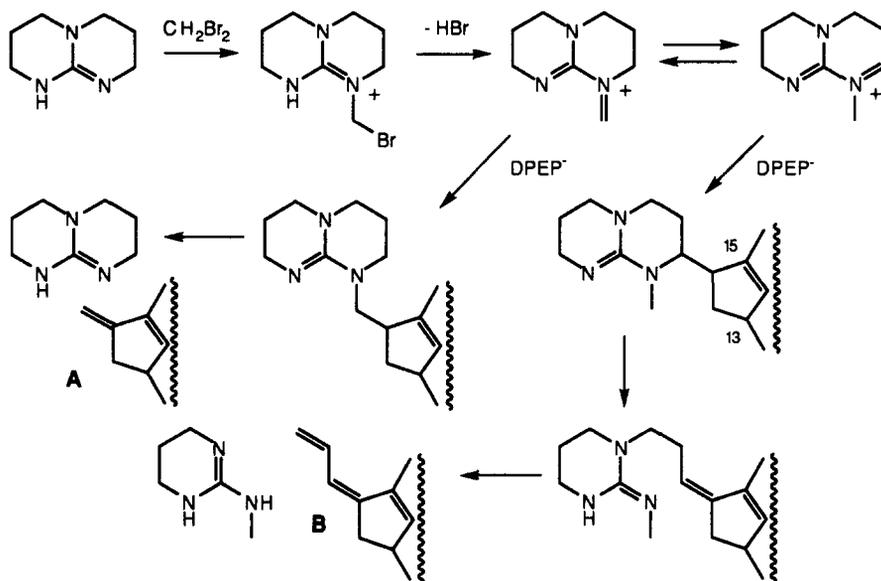


Figure 3. Proposed mechanism for the alkylation of DPEP by CH_2Br_2 / TBD (the cyclopentene represents DPEP E ring, attached to positions 13,15).

We suggest that the next steps are either elimination of TBD to give **A**, or two successive eliminations to give a monocyclic amine and **B**. **A** is comparable to β -vinylporphyrins, known to be reduced in hot TBD, while analogue **B** would be expected to behave similarly in two successive reduction steps. This sequence may then be

repeated at position 13', leading to dialkylation of DPEP. During the TBD reaction, the formation of very polar products possessing the porphyrin chromophore was observed. This not only accounts for the incomplete recovery of the alkylporphyrins, but also suggests that the cleavage of nitrogen containing highly basic intermediates was not complete.

Acknowledgments. The authors thank P. Wehrung, E. Mastio, J. Blanzat and R. Hueber for mass spectra measurements and Dr R. Ruppert for NMR help and fruitful discussions.

Experimental Section

General

NMR spectra were obtained in CDCl₃ (unless otherwise stated) on Bruker SY 200 (200 MHz) and Bruker AC 300 (300 MHz) instruments. Chemical shifts (δ) are expressed in ppm from TMS and coupling constants in Hz (vicinal coupling constants in ethyl groups are in the 7 Hz range). Mass spectra were recorded on a Finnigan TSQ 70 spectrometer, while high resolution data were measured on a VG Analytical ZAB-HF spectrometer (FAB mode). UV-visible spectra were obtained in CH₂Cl₂ using a Hewlett-Packard HP 8453 spectrometer. Elemental analyses were performed by the "Service de Microanalyse du Centre de Recherche Chimie de Strasbourg". Chromatographic separations were obtained using Merck 60 silica gel columns. HPLC separations were run on Waters 6000 A and 590 instruments (Hewlett-Packard DAD HP 1100 and Waters 440 detectors) using Du Pont RP-18 Zorbax ODS columns (analytical scale: 250 x 4.6 mm, 5 μ m, eluent: methanol-CH₂Cl₂ 96:4, 1mL/min; preparative scale: 250 x 21.6 mm, 8 μ m, eluent: methanol-CH₂Cl₂ 9:1, 19mL/min).

Methyl pyropheophorbide a 3 from Spirulina

Lyophilized *Spirulina*⁶ powder (500 g) was extracted overnight in refluxing acetone / ethanol (resp. 0.5 and 1.0 L). Filtration (paper) gave a green solution which was treated with 2 N HCl (150 mL) for 5 min, diluted with water (2 L) and extracted with CH₂Cl₂ (400 mL). The organic phase was dried over Na₂SO₄ and the solvent evaporated under vacuum. The residue was treated with methanol containing 5 % H₂SO₄ (250 mL). The resulting blue solution was kept overnight, filtered through sintered glass (por. 4) and extracted with CH₂Cl₂ (200 mL). The organic phase was washed with water (2 x 1 L), dried over Na₂SO₄ and concentrated. Crystallization (CH₂Cl₂-hexane) gave methyl pheophorbide *a* (2.6 g).

Methyl pheophorbide *a* (1.055 g) was dissolved in collidine (110 mL; redistilled and stored over KOH) and refluxed for 1 h. After cooling the solution was diluted with CH₂Cl₂ and washed with 2N HCl (4 x 200 mL) and water (2 x 200 mL). The solution was dried (Na₂SO₄) and evaporated. The residue was purified by silica gel chromatography (150 mL). Methyl pyropheophorbide *a 3* was eluted with CH₂Cl₂-AcOEt (9:1) and crystallized from CH₂Cl₂-hexane (887 mg; 93 %).

Methyl 13'-Deoxypyropheophorbide a 4 and methyl 13'-deoxomesopyropheophorbide a 7

A round-bottom flask containing trifluoroacetic acid (100 mL) was cooled to 0°C. Successively were added sodium borohydride (3.3 g; caution: gas evolution) and, dropwise, a solution of **3** in CH₂Cl₂ (16 mL). The mixture turned blue. At the end of the addition the ice bath was removed and the solution stirred overnight at

20°C. Dilution with CH₂Cl₂ (100 mL), addition of NaOH pellets until neutral, water washing (3 x 600 mL), drying (Na₂SO₄) and concentration under vacuum gave a solid residue which was chromatographed (silica gel; 200 mL). Elution with CH₂Cl₂-AcOEt (95:5), evaporation and crystallization from CH₂Cl₂-MeOH gave **4** (672 mg; 86 %). Compound **4** was used as such for the hydrogenation step.

4. ¹H NMR: 9.95, 9.59, 8.95 (3s, 1+1+1H, *meso*), 8.29, 6.29, 6.22 (3 dd, 1+1+1H, vinyl), 4.89 (m, 2H, 13''-CH₂), 4.67 (m, 1H, 18-H), 4.49 (m, 1H, 17-H), 4.07 (m, 2H, 13'-CH₂), 3.87 (q, 2H, 8-ethyl CH₂), 3.59 (s, 3H, ester CH₃), 3.58, 3.51, 3.44 (3s, 3+3+3H, 2-, 7-, 12-CH₃), 2.9-2.1 (m, 4H, 17-CH₂-CH₂), 1.85 (d, 3H, 18-ethyl CH₃), 1.77 (t, 3H, 8-ethyl CH₃), -1.6, -3.3 (2 broad s, 1+1H, NH). UV-visible: λ_{max} 404 (ε = 145 600), 504 (15 300), 532 (5 300), 594 (6 300), 648 (37 600).

To a solution of **4** (400 mg) in freshly distilled THF (100 mL) was added palladium on charcoal (10 %; 15 mg). After stirring at 20°C and normal hydrogen pressure for 1.5 h, the filtered solution was evaporated and product **7** purified on silica gel (200 mL; elution with CH₂Cl₂-AcOEt 95:5) and crystallized from CH₂Cl₂-MeOH (367 mg; 91 %). Its physical data were identical with those reported in the literature.¹³

7. ¹H NMR: 9.80, 9.63, 8.90 (3s, 1+1+1H, *meso*), 4.89 (m, 2H, 13''-CH₂), 4.67 (dq, 1H, 18-H), 4.57 (m, 1H, 17-H), 4.08 (m, 2H, 13'-CH₂), 4.06, 3.89 (2q, 2+2H, ethyl CH₂), 3.58 (s, 3H, ester CH₃), 3.53, 3.48, 3.47 (3s, 3+3+3H, 2-, 7-, 12-CH₃), 2.9-2.1 (m, 4H, 17-CH₂-CH₂), 1.85 (d, 3H, 18-CH₃), 1.80, 1.78 (2t, 3+3H, ethyl CH₃), -1.7, -3.5 (2 broad s, 1+1H, NH). UV-visible: λ_{max} 395 nm (ε = 153 000), 498 (12 300), 527 (3 600), 585 (4 300), 638 (37 700).

13'-Deoxomesopyropheorbide a 8

Ester **7** (928 mg) and KOH (195 mg) were dissolved in ethanol (350 mL) and refluxed overnight. After being diluted with CH₂Cl₂ (150 mL) and washed with water (500 mL) containing AcOH (5 mL), followed by pure water (500 mL), the solution was dried (Na₂SO₄) and evaporated. The residue was purified on silica gel (300 mL) and eluted with CH₂Cl₂-MeOH (95:5). Acid **8** did not crystallize and was pumped under vacuum (10⁻² Torr) and used as such.

8. ¹H NMR: 9.80, 9.62, 8.90 (3s, 1+1+1H, *meso*), 4.85 (m, 2H, 13''-CH₂), 4.66 (dq, 1H, 18-H), 4.51 (m, 1H, 17-H), 4.05 (m, 2H, 13'-CH₂), 4.05, 3.88 (2q, 2+2H, ethyl CH₂), 3.51 (s, 3H, 12-CH₃), 3.48, 3.46 (2s, 3+3H, 2-, 7-CH₃), 2.9-2.10 (m, 4H, 17-CH₂-CH₂), 1.85 (d, 3H, 18-CH₃), 1.81, 1.77 (2t, 3+3H, ethyl CH₃), -3.4 (very broad signal, 2H, NH). UV-visible: λ_{max} (rel. int.): 395 nm (1), 499 (0.100), 527 (0.053), 585 (0.053), 638 (0.232).

Nickel deoxophylloerythroetioporphyrin (NiDPEP) I (M = Ni)

A mixture of **8** (50 mg) and TBD (1.95 g) was sealed in a glass tube under argon vacuum and heated at 200°C for 4 h. The resulting product was dissolved in CH₂Cl₂ (150 mL), washed with water (3 x 250 mL), dried over Na₂SO₄ and evaporated under vacuum. The residue and Ni(acac)₂ (100 mg) were refluxed in benzene (15 mL) under argon for 6 h. The solution was filtered on a short silica gel column (eluent CH₂Cl₂) and the product purified on alumina (50 mL; eluent CH₂Cl₂-hexane 1:1) and crystallized from CH₂Cl₂-MeOH to give **1** (24 mg; 47 %). All physical data for this product were identical with those described in the literature.

1 (M = Ni) ¹H NMR: 9.76, 9.74, 9.73 (3s, 1+1+1H, *meso*), 5.06 (m, 2H, 13''-CH₂), 3.94, 3.92 (2q, 2+2H, 3,8-ethyl CH₂), 3.89 (m, 2H, 13'-CH₂), 3.78 (q, 2H, 17-ethyl CH₂), 3.50, 3.48, 3.44, 3.43 (4s, 3+3+3+3H, CH₃), 1.80, 1.79 (2t, 3+3H, 3-,8-ethyl CH₃), 1.63 (t, 3H, 17-ethyl CH₃). DEPT 135 (75 MHz) ¹³C: 97.1,

97.0, 95.8 (meso CH), 37.1, 24.3 (E ring CH₂), 20.8, 19.9, 19.8 (ethyl CH₂), 17.6, 17.5, 16.5, 12.3, 11.5, 11.3, ethyl CH₃). UV-visible: λ_{\max} 393 nm ($\epsilon = 186\ 000$), 514 (11 300), 552 (21 900).

Formation of NiDPEP 1 and 3-H-NiDPEP 6 from acid 5 in TBD

Ester **4** was hydrolyzed as described above (**7** to **8**). The crude acid **5** (80 %) did not crystallize and was pumped under vacuum (10^{-2} Torr) and used as such.

5. ¹H NMR: 9.95, 9.60, 8.96 (3s, 1+1+1H, *meso*), 8.28, 6.29, 6.21 (3dd, 1+1+1H, vinyl), 4.89 (m, 2H, 13''-CH₂), 4.68 (m, 1H, 18-H), 4.55 (m, 1H, 17-H), 4.07 (m, 2H, 13'-CH₂), 3.86 (q, 2H, 8-ethyl CH₂), 3.59, 3.51, 3.44 (3s, 3+3+3H, CH₃), 2.9-2.1 (m, 4H, 17-CH₂-CH₂), 1.86 (d, 3H, 18-CH₃), 1.76 (t, 3H, ethyl CH₃). UV-visible (rel. int.): λ_{\max} 402 (1), 502 (0.089), 516 (0.042), 646 (0.113).

Reaction in TBD under standard conditions (15 mg **5**, 625 mg TBD, sealed tube, 200°C, 4 h), followed by metallation with Ni(acac)₂ gave a mixture of nickel porphyrins **1** and **6** (ratio *ca* 9:1), which were separated by HPLC (conditions above). The products were identical to reference samples from various geochemical sources.

Reaction of 8 in the presence of TBD + CH₂Br₂

Acid **8** (50 mg), TBD (1.95 g) and CH₂Br₂ (27 μ l; 4 eq.) were placed in a glass tube, cooled to -78°C, sealed under argon vacuum, and heated to 200°C for 4h. After the isolation and metallation steps described above, the residue (29 mg) was analyzed by analytical HPLC to measure the relative abundance of the porphyrins (**1**, 6.8%; **9**, 62.6 %; **10**, 18.6 %; **11**, 1.6 %; **12**, 3.8 %). It was first purified on a silica gel plate (2 mm thick; eluent CH₂Cl₂-hexane 1:2) to eliminate **1**, then the individual alkylated porphyrins were separated by preparative HPLC. Nickel 13''-methylDPEP **9** and nickel 13''-*n*-propylDPEP **10** could be crystallized from CH₂Cl₂-MeOH (**9** and 3 mg; 17 and 5 % recovery respectively).

Nickel 13''-methyl DPEP 9. ¹H NMR: 9.79, 9.78, 9.76 (3s, 1+1+1H, *meso*), 5.80 (q, 1H, 13''-H, J = 6.8), 4.39 (dd, 1H, 13'-H, J = 16.8 and 5.3), 4.07 (m, 1H from 17-ethyl CH₂), 3.93 (m, 6H, 3-, 8-ethyl CH₂, 1H from 17-ethyl CH₂ and 13'-H), 3.51, 3.50, 3.48 (3s, 3+3+6H, 2-,7-,12-,18-CH₃), 1.82 (d, 3H, 13''-CH₃, J = 6.8 Hz), 1.79, 1.78 (2t, 3+3H, 3-,8-ethyl CH₃), 1.69 (t, 3H, 17-ethyl CH₃). DEPT 135 (75 MHz) ¹³C: 97.1, 97.0, 96.0 (meso CH), 44.7 (13''-CH), 34.2 (13'-CH₂), 27.2 (13''-CH₃), 21.0, 19.9, 19.0 (ethyl CH₂), 17.6, 17.5, 17.2, 12.3, 11.6, 11.5 (2-,7-,12-,18-CH₃ and ethyl CH₃). UV-visible: λ_{\max} 394 nm ($\epsilon = 177\ 000$), 515 (11 600), 553 (21 200). HRMS calcd for C₃₃H₃₆N₄⁵⁸Ni: 546.2293. Found: 546.2279.

Nickel 13''-n-propyl DPEP 10. ¹H NMR: 9.79, 9.77, 9.75 (3s, 1+1+1, *meso*), 5.67 (m, 1H, 13''-H), 4.27 (dd, 1H, 13'-H, J = 5.9 and 16.5 Hz), 3.94 (m, 6H, 3-,8-,17-ethyl CH₂), 3.67 (d, 1H, 13'-H, J = 16.5 Hz), 3.51, 3.50, 3.48 (3s, 3+3+6H, 2-,7-,12-,18-CH₃), 2.36 (m, 2H, propyl CH₂), 1.79, 1.78 (2t, 3+3H, 3-,8-ethyl CH₃), *ca* 1.8 (m, 2H, propyl CH₂), 1.67 (t, 3H, 17-ethyl CH₃), 0.98 (t, 3H, propyl CH₃). DEPT 135 (75 MHz) ¹³C: 97.1, 97.0, 96.0 (meso CH), 50.0 (13''-CH), 43.9 (13''-CH₂), 31.4 (13'-CH₂), 22.1 (13'''-CH₂), 20.9, 19.9, 19.8 (ethyl CH₂), 17.6, 17.5, 17.0, 12.3, 11.6, 11.5 (2-,7-,12-,18-CH₃ and ethyl CH₃), 14.3 (propyl CH₃). UV-visible: λ_{\max} 395 nm ($\epsilon = 200\ 000$), 515 (12 300), 553 (22 700). MS (70 eV): 574 (100 %, M⁺), 531 (36 %, M⁺-propyl). HRMS, calcd for C₃₅H₄₀N₄⁵⁸Ni: 574.2606. Found: 574.2606.

Nickel 13',13''-dimethyl DPEP 11. ¹H NMR: 9.78, 9.77, 9.75 (3s, 1+1+1H, *meso*), 5.35 (q, 1H, 13'- or 13''-H, J = 6.1 Hz), 5.25 (q, 1H, 13'- or 13''-H, J = 7.0 Hz), 3.93 (m, 6H, ethyl CH₂), 3.51, 3.50, 3.49, 3.48 (4s, 3+3+3+3H, 2-,7-,12-,18-CH₃), 1.95, 1.81 (2d, 3+3H, 13'- and 13''-CH₃), 1.79, 1.78 (2t, 3+3H, 3-,8-ethyl CH₃), 1.69 (t, 3H, 17-ethyl CH₃). UV-visible (rel. int.): λ_{max} 395 nm (1), 515 (0.58), 553 (0.114). MS (70 eV): 560 (100 %, M⁺), 545 (20 %, M⁺-CH₃), 530 (6 %, M⁺-2CH₃). HRMS, calcd for C₃₄H₃₈N₄⁵⁸Ni: 560.2449. Found: 560.2441.

Nickel methyl,n-propyl DPEP 12. The ratio between the two isomers was estimated at *ca* 5:1 and the signals were assigned to each isomer when possible and accordingly the number of H refer to each product or to the mixture of both. ¹H NMR: 9.78, 9.75 (2s, 2+1H, major, *meso*), 9.79, 9.77, 9.74 (3s, 1+1+1H, minor, *meso*), 5.35 (m, 13'- and 13''-H), 3.92 (m, 6H, ethyl CH₂), 3.53 (d, 3H, major, 12-CH₃, J = 0.6 Hz), 3.52, 3.50, 3.48 (3s, 3+3+3H, major, 2-, 7-, 18-CH₃), 2.3 and 2.0 (2m, propyl CH₂), 1.8 (m, 9H, 3-, 8-ethyl CH₃ and ring E CH₃), 1.70 (t, 3H, major, 17-ethyl CH₃), 1.69 (t, 3H, minor, 17-ethyl CH₃), 1.14 (t, 3H, minor, propyl CH₃), 1.12 (t, 3H, major, propyl CH₃). UV-visible (rel. int.): 395 nm (1), 515 (0.59), 553 (0.116). MS (70 eV): 588 (100 %, M⁺), 573 (4 %, M⁺-CH₃), 545 (15 %, M⁺-propyl). HRMS, calcd for C₃₆H₄₂N₄⁵⁸Ni: 588.2763. Found: 588.2744.

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(Received in Belgium 22 July 1997; accepted 9 September 1997)