The 2,3-Secochlorin-2,3-dione System

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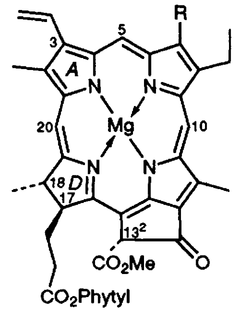
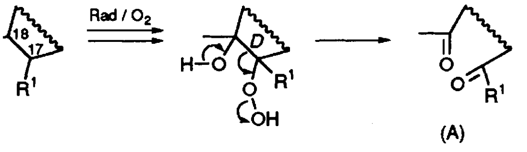
Cleavage of nickel(II) octaethyl-2,3-dihydroxychlorin **3** with lead tetraacetate gives the novel octaethyl-2,3-secochlorin-2,3-dione system as its nickel(II) complex **4**, which on treatment with base cyclises to a novel homoporphyrinone structure **5**; electronic spectra are presented: **4** and **5** are seen as representing chromophores that may arise in chlorophyll catabolism.

The catabolic fate of chlorophyll has received increasing attention recently.[1–3] Although in the form of metalloporphyrins, a small fraction persists in sedimentary organic deposits, most of it must be destroyed during senescence. On chemical grounds the major reactive sites (shown in **1**) of chlorophyll a are expected to be (*a*) C-13^2, a pseudobenzylic acidic (β-keto ester) position; (*b*) the metal-π system, readily oxidised and readily demetallated; (*c*) the ring *A*-C-3 vinyl system; (*d*) the unsubstituted *meso* positions (C-5,10,20-electrophilic substitution, addition); and the tertiary pseudobenzylic C-17 and C-18 positions. Adams[4] postulated (Scheme 1) that radical reactions at the 17 and 18 positions could lead to cleavage of the 17–18 bond to give the secochlorindione (A). We now describe this dione in a model system, which may allow this chromophore to be recognised should it occur naturally.

Osmylation of octaethylporphyrin gave the dihydroxychlorin **2**.[5] Attempted cleavage of the glycol function of this gave complex mixtures, but the nickel(II) complex **3** reacted smoothly with lead tetraacetate in anhydrous benzene (20 °C, 15 min) to give 76% of the secochlorindione **4** as tiny green needles, $C_{36}H_{44}N_4NiO_2$ (elemental analysis, accurately measured M^+). The electronic spectrum (Fig. 1) showed strong broad bands at 444 nm (ε 49 000) and 648 nm (ε 13 300), while in the IR the conjugated carbonyl groups appeared as a single band at ν 1676 cm^{-1} (KBr). In the ^{1}H NMR spectrum the *meso* signals at δ 9.03 (s) and δ 8.17 (s) showed marginal changes compared with the corresponding singlets (δ 9.12, 8.25) in the spectrum of the precursor **3**. The structure **4** was confirmed by X-ray crystal analysis.[6] In the crystal the carbonyl groups point in opposite directions: thus the C-2 carbonyl group, for instance, lies in a plane (C-1, C-2, C-2^1, O) which makes a dihedral angle of 62° to the mean plane determined by C-1, C-2, C-20 and N-21. As a consequence, the two hydrogens of each methylene group adjacent to a carbonyl are inequivalent, and in the ^{1}H NMR spectrum appear as double quartets at δ 2.04 and 2.75.

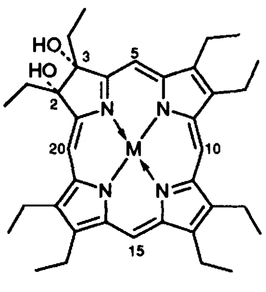


1 Chlorophyll *a*, R = Me
Chlorophyll *b*, R = CHO

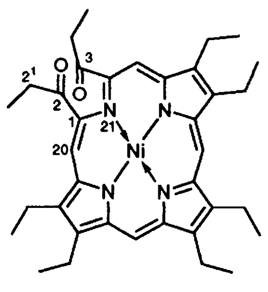


Scheme 1 R^1 = $CH_2CH_2CO_2$Phytyl

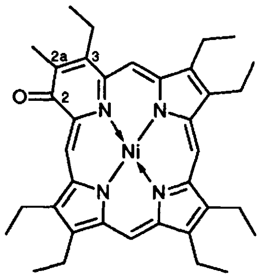
The secochlorindione **4** shows normal carbonyl reactions, and gave a bis(2,4-dinitrophenylhydrazone). Treatment of **4** with potassium *tert*-butoxide at 40 °C caused aldol condensation to give the novel homoporphyrinone system **5**, obtained as small blue prisms ($C_{36}H_{42}N_4NiO$, elemental analysis, accurately measured M^+). The same product was obtained on treating **4** with primary aliphatic amines. The electronic spectrum of **5** was of a metallochlorin type (Fig. 2), while the ^{1}H NMR spectrum indicated that the ring current (*meso* protons at δ 9.25, 9.04, 9.03, 8.81) was maintained. The methyl group substituted at C-2a appeared as a singlet at δ



2 M = 2H
3 M = Ni^{II}



4 Nickel(II) 2,3,7,8,12,13,17,18-octaethyl-2,3,-secochlorin-2,3-dione



5 Nickel(II) 3,7,8,12,13,17,18-heptaethyl-2a-methyl-2a-homoporphyrin-2-one

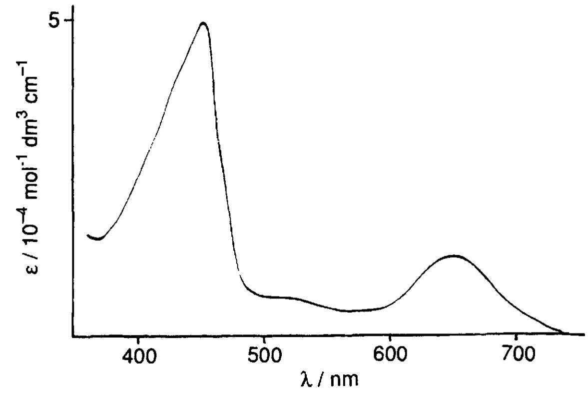


Fig. 1 Electronic spectrum of nickel(II) octaethyl-2,3-secochlorin-2,3-dione **4** in chloroform

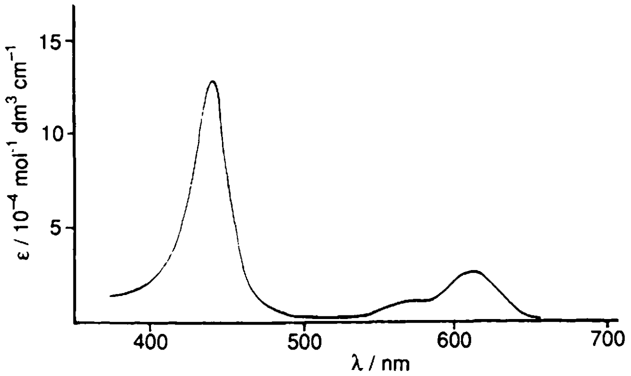


Fig. 2 Electronic spectrum of nickel(II) heptaethyl-2a-methyl-2a-homoporphyrin-2-one **5** in chloroform

2.72. The carbonyl group of **5** proved to be strongly conjugated and unreactive. Thus the IR stretching mode occurred at ν 1636 cm^{-1}, while the ^{13}C chemical shift assigned to the carbonyl group appeared at δ 191.2 (*cf.* δ 201.6 for **4**). The conjugated carbonyl system did not form derivatives with common carbonyl reagents, nor did it react with lithium dibutylcuprate, nor with 2,3-dimethylbuta-1,3-diene. This kinetic stability (for **5**) and enhanced absorption in the red (for **4** and **5**) makes these systems potential candidates (as free bases, or coordinated to non-transition metals) as photosensitisers for photodynamic therapy.[5]

This work was supported by the SERC, the NERC and the Ministerio de Educación i Ciencia (Madrid). M. A. V. was supported by a short-stay grant from CIRIT (Generalitat de Catalunya). Mass spectrometric services at Swansea (SERC) and NMR services in London (ULIRS) are gratefully acknowledged.

Received, 2nd August 1993; Com. 3/05063G

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