The Structure of Chlorophyll c_3, a Novel Marine Photosynthetic Pigment

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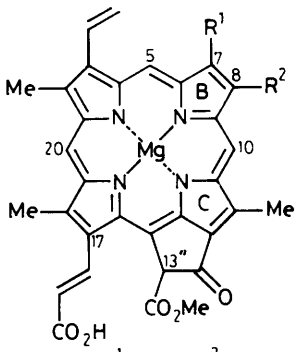
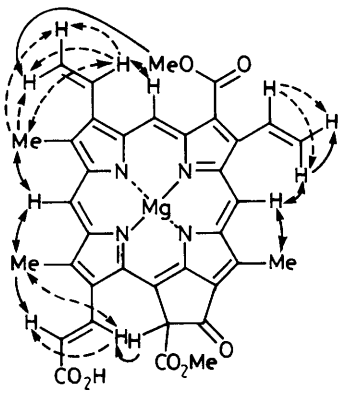
Chlorophyll c_3, isolated from the microalga *Emiliania huxleyi*, is tentatively identified as 7-demethyl-7-methoxycarbonyl chlorophyll c_2 (**1c**)

Chlorophyll *c*, a photosynthetic pigment widely distributed among the chromophyte algae,[1,2] usually consists of a mixture of two components c_1 and c_2.[3,4] The structures of these chlorophylls [(**1a**) and (**1b**) respectively[5]] are unusual in that they are porphyrins rather than chlorins with an acrylic rather than propionic acid side chain, and not esterified to phytol or other alcohols. Recent work has revealed the existence in some organisms of a third, more polar component, named chlorophyll c_3.[6,7] We now describe the first structural investigation of this compound.



	R^1	R^2
(**1a**)	Me	Et
(**1b**)	Me	$CH{=}CH_2$
(**1c**)	CO_2Me	$CH{=}CH_2$



(**2**)

——→ NOE

- - - - - - → decoupling

Table 1. ^1H NMR signal assignments for chlorophyll c_3 in $[^2H_5]$pyridine (0.4 mM) (δ values).

3-CH_2=CH	6.21, 6.68, 8.47	2-Me	3.58
8-CH_2=CH	6.34, 6.47, 8.63	12-Me	3.79
17-HO_2CCH=CH	7.15	18-Me	3.61
17-HO_2CCH=CH	9.63	5-H	11.71
7-MeO_2C	4.37	10-H	10.64
13″-MeO_2C	4.06	20-H	10.20
		13″-H	7.64

Chlorophyll c_3 was isolated from the coccolithophorid *Emiliania huxleyi* by methods outlined in refs. 4 and 7. The molecular weight, determined by FAB mass spectrometry in pyridine/3-nitrobenzyl alcohol was 652, 44 higher than that of chlorophyll c_2 (**1b**). Although the ^1H NMR spectra (400 MHz, $[^2H_5]$pyridine) of the two compounds were superficially similar, key differences were (a) an apparent downfield shift of β-methyl signal, from around δ 3.6 in chlorophyll c_2 to δ 4.37 in c_3, and (b) an even larger shift of either H-5 or H-10 to δ 11.71 in the chlorophyll c_3 spectrum. These shifts, together with the molecular weight data, indicated replacement of a ring methyl by a CO_2Me substituent.

Clarification of the chlorophyll c_3 structure was obtained using nuclear Overhauser enhancement (NOE) difference spectroscopy,[8] plus decoupling experiments to identify long-range couplings between the protons of β-methyls and adjacent unsaturated substituents.[9] The results, consistent with all the available data, are summarized in (**2**) (≡ **1c**); NMR parameters are given in Table 1.

It should be noted, however, that no connection between the two ring-*B* substituents was established, so that in addition to (**1c**) the structure in which the ring-*B* vinyl and ring-*C* methyl are interchanged is also formally possible. Because there is no precedent for this reversed arrangement of one- and two-carbon substituents in natural tetrapyrroles, we consider structure (**1c**) to be overwhelmingly more likely. Confirmation of the structure of chlorophyll c_3 is expected to come from total synthesis, which is currently in progress.

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