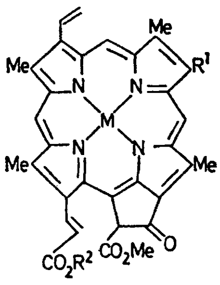
Synthesis of the Methyl Ester of the Magnesium-free Derivative of Chlorophyll c_2

By Peter S. Clezy* and Christopher J. R. Fookes

(Department of Organic Chemistry, University of New South Wales, P.O. Box 1, Kensington N.S.W., 2033, Australia)

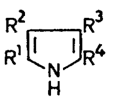
Summary The synthesis is reported of 7′,7″-dehydro-2,4-dide-ethyl-2,4-divinylphaeoporphyrin a_5 dimethyl ester (**1c**) which is the methyl ester of the magnesium-free derivative of chlorophyll c_2 (**1b**).

The chlorophyll *c* component of many marine algae has been shown to consist of a mixture of two components (c_1 and c_2), while in some species chlorophyll c_2 occurs without chlorophyll c_1.[1] The structures of the chlorophylls c_1 and c_2 have been reported[2,3] as (**1a**) and (**1b**) respectively. We now describe the synthesis of (**1c**), a derivative of chlorophyll c_2.



(1)

	R^1	R^2	M
(a)	Et	H	Mg
(b)	CH:CH$_2$	H	Mg
(c)	CH:CH$_2$	Me	2H

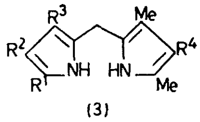


(2)

	R^1	R^2	R^3	R^4
(a)	CO$_2$CH$_2$Ph	Me	CH$_2$CH$_2$OAc	Me
(b)	H	Me	CO$_2$Et	Me
(c)	CO$_2$CH$_2$Ph	Ac	Me	Me
(d)	CO$_2$CH$_2$Ph	CH$_2$CO$_2$Me	Me	Me
(e)	CO$_2$CH$_2$Ph	CH$_2$CH$_2$OAc	Me	CH$_2$OAc
(f)	H	Me	Ac	Me

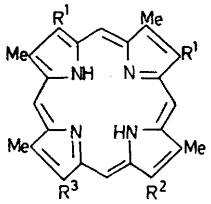
The acetoxymethyl derivative of the pyrrole (**2a**)[4] was condensed in MeCO$_2$H with the α-free pyrrole (**2b**)[5] to yield the dipyrrylmethane (**3a**). The aldehyde derivative (**3b**) was obtained by established procedures.[6] Rearrangement of pyrrole (**2c**)[7] with thallium(III) nitrate in methanol[8] produced (**2d**) which, after reduction, acetylation and acetoxylation furnished (**2e**). Condensation of (**2e**) with the α-free pyrrole (**2f**)[5] in MeCO$_2$H yielded the dipyrrylmethane (**3c**) from which the acid (**3d**) was derived by hydrogenolysis.

Condensation of the dipyrrylmethanes (**3b**) and (**3d**) in CF$_3$CO$_2$H–MeOH produced a bilene-*b* salt which, without isolation, was heated with copper acetate in MeCO$_2$H–MeOH.[9] Treatment of the resultant porphyrin copper complex with H$_2$SO$_4$ not only removed the metal but also hydrolysed the acetoxyethyl substituents. The derived porphyrin diol was a sparingly soluble compound and hence difficult to handle. Thus, the crude product was transformed by treatment with *NN*-dimethylformamide–PhCOCl[10] into the dichloro analogue (**4a**), m.p. 247—249 °C, (25% yield from the dipyrrylmethanes) for purification and characterisation.† Reduction of the acetyl group in (**4a**) with NaBH$_4$, and dehydration of the derived hydroxyethylporphyrin with PhCOCl–*NN*-dimethylformamide[11,12] gave the vinyl compound (**4b**), m.p. 247—248 °C (decomp.), 86%. Treatment of (**4b**) with OsO$_4$ in pyridine followed by periodate[13] produced the formylporphyrin (**4c**), m.p. 268—270 °C, 88%. When (**4c**) was refluxed under nitrogen in aqueous pyridine containing NaOH, the ester group was hydrolysed and vinyl substituents were generated at positions 2 and 4 to yield (**4d**). Condensation of (**4d**) with methyl hydrogen malonate in pyridine containing piperidine gave the acrylate ester (**4e**), m.p. > 300 °C, 35% yield from (**4c**). Oxalyl chloride converted (**4e**) into its acid chloride derivative from which the β-ketoester (**4f**), m.p. 300 °C, 40%, was obtained as a mixture of keto and enol tautomers by reaction with the magnesium chelate (**5**).[14] A solution of (**4f**) in CH$_2$Cl$_2$ was treated with thallium(III) trifluoroacetate (2·5 equiv) in tetrahydrofuran containing CF$_3$CO$_2$H, and the mixture irradiated for 15 min by exposure to sunlight.[15] Demetallation[16] of the product yielded (**1c**), m.p. 290 °C (decomp.), 27% yield from (**4f**); δ (CF$_3$CO$_2$D): 11·14 (1H), 11·04 (1H), 11·01 (1H, CH), 9·22 (1H, d, *J* 16 Hz, C*H*:CHCO$_2$Me), 8·25 (2H, m, C*H*:CH$_2$), 7·24 (1H, d, *J* 16 Hz, CH:C*H*CO$_2$Me), 6·52 (4H, m, CH:C*H*$_2$), 4·24 (3H), 4·01 (3H), 3·93 (6H), and 3·83 (6H, 4 × Me, 2 × OMe); in CF$_3$CO$_2$H the enolic proton at C-10 was observed at δ 7·61; λ_{max} (CHCl$_3$)(log ε): 440 (5·22), 535·5 (4·05), 540 (4·09), 597·5 (4·10), and 656 (3·15) nm.



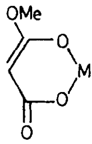
(3)

	R^1	R^2	R^3	R^4
(a)	CO$_2$CH$_2$Ph	Me	CH$_2$CH$_2$OAc	CO$_2$Et
(b)	CHO	Me	CH$_2$CH$_2$OAc	CO$_2$Et
(c)	CO$_2$CH$_2$Ph	CH$_2$CH$_2$OAc	Me	Ac
(d)	CO$_2$H	CH$_2$CH$_2$OAc	Me	Ac



(4)

	R^1	R^2	R^3
(a)	CH$_2$CH$_2$Cl	CO$_2$Et	Ac
(b)	CH$_2$CH$_2$Cl	CO$_2$Et	CH:CH$_2$
(c)	CH$_2$CH$_2$Cl	CO$_2$Et	CHO
(d)	CH:CH$_2$	CO$_2$H	CHO
(e)	CH:CH$_2$	CO$_2$H	CH:CHCO$_2$Me
(f)	CH:CH$_2$	COCH$_2$CO$_2$Me	CH:CHCO$_2$Me



(5)

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† All new compounds had spectroscopic and analytical data in agreement with the proposed structures.

Much of the structural work on the chlorophylls *c* was carried out on a mixture of the two components and extensive data on the pure magnesium-free derivatives are not available in the literature. However, the n.m.r. and electronic spectra of our synthetic material agree closely with published results.[2,3]

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