Under the same reducing conditions the analogous rhodium(I) complex (VIII) forms a dicarbonyl anionic complex (IX) in which neither triphenylphosphine is replaced. The origin of this disparity is not clear. This complex combines readily with trimethyltin chloride to form an air-stable crystalline compound, X.

$$\underset{\mathrm{VIII}}{[\mathrm{RhL_2(CO)Cl}]} \xrightarrow[\mathrm{CO,\ THF}]{\mathrm{Na(Hg)}_x} \underset{\mathrm{IX}}{\mathrm{Na^+[RhL_2(CO)_2]^-}} \xrightarrow{\mathrm{(CH_3)_3SnCl}} \underset{\mathrm{X}}{\mathrm{(CH_3)_3Sn{-}RhL_2(CO)_2}}$$

The $\mathrm{Sn^{119}}$–H coupling constants (Table II) for methyltin derivatives containing iridium and rhodium are similar to those reported[9] for other complexes containing transition metal–tin bonds.

It was anticipated that these five-coordinate complexes containing iridium or rhodium bound to another metal might undergo stepwise oxidative addition reactions in the manner of similar five-coordinate complexes having a d^8 configuration.[10] Unfortunately reaction with mercuric halides, iodine, and bromine occurs with concomitant cleavage of iridium–tin or iridium–gold bonds. Unless an excess of oxidizing agents is used, intractable mixtures result. This type of process is illustrated by the reaction of IV with excess bromine to yield 1 equiv of CO (gas buret analysis), bromobenzene (gas chromatographic analysis), and an iridium(III) complex, XI.

$$\underset{\mathrm{IV}}{\mathrm{Ir(CO)_3LSn(C_6H_5)_3}} + 5\mathrm{Br_2} \longrightarrow \mathrm{CO} + \underset{\mathrm{XI}}{[\mathrm{IrL(CO)_2Br_3}]} + 3\mathrm{C_6H_5Br} + \mathrm{SnBr_4}$$

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[9] H. R. H. Patil and W. A. G. Graham, *J. Am. Chem. Soc.*, **87**, 673 (1965).

[10] J. P. Collman and W. R. Roper, *ibid.*, **87**, 4008 (1965); **88**, 3504 (1966).

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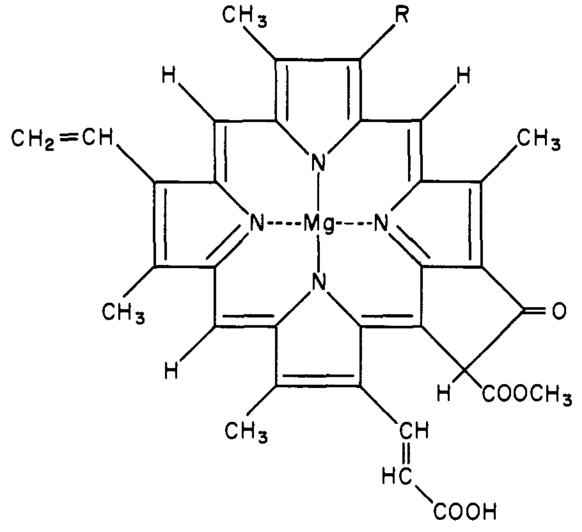
Structure of Chlorophyll *c*[1]

Sir:

Chlorophyll *c*, a widely distributed constituent of marine algae,[2] has been the least investigated of the major photosynthetic pigments. The following evidence now indicates that chlorophyll *c*, isolated from the marine diatom *Nitzschia closterium* by a recently described procedure,[3] is a mixture of magnesium hexadehydropheoporphyrin a_5 monomethyl ester (Figure 1a) and magnesium tetradehydropheoporphyrin a_5 monomethyl ester (Figure 1b).



(a) R = $-\mathrm{CH{=}CH_2}$
($\mathrm{C_{35}H_{28}N_4O_5Mg}$)
(b) R = $-\mathrm{CH_2{-}CH_3}$
($\mathrm{C_{35}H_{30}N_4O_5Mg}$)

Figure 1. Proposed structures for chlorophylls *c*.

Chlorophyll *c*, crystallized from tetrahydrofuran (THF) and petroleum ether,[3] proved to be the bis-tetrahydrofuranate, as shown by the characteristic high-field THF resonance[4] near 2 ppm (relative area 8) in the nmr and by elemental analysis (*Anal.* Calcd for $\mathrm{C_{35}H_{30}N_4O_5Mg{\cdot}(C_4H_8O)_2}$: C, 68.34; H, 6.09. Found: C, 68.60; H, 6.16; one $\mathrm{CH_3O}$ group/mole).[5]

Chlorophyll *c* without THF has no resonances above 3 ppm except for a variable intensity triplet at 1.7 ppm; hence this chlorophyll contains no lipophile group and is a free acid.[6] The chemical shift (1.7 ppm) and the relative area (~1.5) of the triplet ($|J| = 7.2$ cps) in the chlorophyll *c* dissolved in trifluoroacetic acid (TFA) indicate the presence of a porphyrin ethyl group in one component of the preparation.

The low-field methyl region[7] of the chlorophyll *c* nmr is very narrow in TFA (3.77–4.09 ppm, relative area 15), indicating the absence of chlorin hydrogen or oxygenated side chains[7] such as $-\mathrm{C}H\mathrm{OHCH_3}$, $-\mathrm{CH_2COOR}$, or $-\mathrm{CH_2CH_2COOR}$. The chemical shifts of the ring methine protons also exclude the presence of chlorins and formyl-substituted porphyrins.

Assignment of the resonances below 4.1 ppm in the chlorophyll *c* nmr spectrum (Table I) followed directly from nmr studies of other porphyrins and chlorins.[7]

Crystalline chlorophyll *c* is infusible;[8] consequently more volatile derivatives were required for determination of the mass spectrum. Treatment of solutions of chlorophyll *c* with dilute hydrochloric acid yielded pheoporphyrin c_5 monomethyl ester derivatives (formerly called pheophytin c) in quantitative yield. The nmr and infrared spectra of this material were

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission. Supported in part by a grant to R. C. D. from the Research Corporation.

[2] H. H. Strain and W. M. Manning, *J. Biol. Chem.*, **144**, 625 (1942); H. H. Strain, W. M. Manning, and G. Hardin, *ibid.*, **148**, 655 (1943).

[3] H. H. Strain and W. A. Svec in "The Chlorophylls," L. P. Vernon and G. R. Seely, Ed., Academic Press Inc., New York, N. Y., 1966, p 57 ff.

[4] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 77.

[5] By Crobaugh Laboratories.

[6] The diatoms were treated with rapidly boiling water prior to extraction, thus minimizing the possibility of enzymatic deesterification of native chlorophyll *c*. The extraction conditions were so mild that an acrylate ester would certainly have survived after the death of the cell (*cf.* ref 1 and 2).

[7] J. J. Katz, R. C. Dougherty, and L. J. Boucher in ref 3, p 230.

[8] *Cf.* magnesium pheoporphyrin a_5 monomethyl ester which is also infusible. H. Fischer and A. Stern, "Die Chemie des Pyrrols," Akademische Verlag, Leipzig, 1940, p 170.

Table I. Low-Field Nuclear Magnetic Resonance Assignments for Chlorophyll *c* (approximately 0.1 *M* in TFA or TFA-*d*)

Chemical shift[a]	$\lvert J \rvert$, cps	Relative area	Assignment
A_1 = 6.64[b]	A_1B_1, < 1.8[b]		Porphyrin vinyl
A_2 = 6.64[b]	A_2B_2, < 1.8[b]		methylenes
B_1 = 6.51[b]	A_1X_1, = 12.0[b]	3	(–CH=C*H*$_2$)
B_2 = 6.42[b]	A_2X_2, = 11.7[b]		
7.28	16.8, doublet	1	Porphyrin *trans*-acrylate (–CH=C*H*COOH)
7.62	Singlet	1	Porphyrin carbomethoxycyclopentanone (C-10)
X_1 = 8.27	Multiplet[b]	1.5	Porphyrin vinyl
X_2 = 8.24			methine (–C*H*=CH$_2$)
9.30	16.8, doublet	1	Porphyrin *trans*-acrylate (–C*H*=CHCOOH)
11.01	Singlets	3	Porphyrin methine
11.03			protons
11.16			

[a] Nmr spectra were determined with a Varian HA-100 nmr spectrometer. Chemical shifts are in parts per million from internal TMS (δ). [b] The observed resonances were superimposed ABX patterns. It was not possible to solve the ABX problem (J. A. Pople, W. S. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132) explicitly; however, the assignments of chemical shift and coupling parameters are self-consistent with the observed spectrum. These parameters were obtained by assuming that only two different vinyl groups were present in the sample. [c] This resonance was absent in spectra taken in TFA-*d*, due to ready exchange of the ring V proton.

entirely analogous to the parent substance. The mass spectrum[9] of this chlorophyll *c* derivative did not give a strong parent ion because of the free carboxylic acid group. Thus, esterified derivatives were prepared.

Treatment of chlorophyll *c* with dry methanolic hydrochloric acid under reflux for 18 hr produced a methylated pheoporphyrin c. The nmr spectra of the methylated pheoporphyrin c were consistent with electrophilic addition of methanol to the acrylic ester (a broad one-proton multiplet, 5.0 ppm in TFA, porphyrin -C*H*(OCH$_3$)CH$_2$COOCH$_3$). Mass measurement of the parent (base) peaks at *m*/*e* 632 and 634 required empirical formulas of $C_{37}H_{36}N_4O_6$ and $C_{37}H_{38}N_4O_6$. The relative intensity of these two ions was roughly equal, suggesting that chlorophyll *c* may be an approximately 1:1 mixture of two pigments that differ only in the degree of hydrogenation.

Hydrogenation at 1 atm of pheoporphyrin c$_5$ in TFA with palladium followed by methylation with methanolic hydrochloric acid produced one compound (by thin layer chromatography) in high yield. Under these reduction conditions, chlorins were not formed and acrylic acid residues were not reduced to propionic acid side chains. The mass spectrum of this pheoporphyrin c$_6$ derivative showed only one parent ion (*m*/*e* 636, formula $C_{37}H_{40}N_4O_6$). The observed intense fragment ions, 605, 604, 578, and 577, correspond to loss of CH_3O, CH_3OH, $C_2H_2O_2$, and $C_2H_3O_2$, as would be anticipated for a structure similar to pheoporphyrin a$_5$.[10] The absence of a peak (intensity >0.1% base) at *m*/*e* 297 in the doubly ionized portion of the spectrum suggested that no propionic ester side chain is present in this compound. The most intense peak in the doubly ionized portion of the spectrum corresponded exactly to loss of $C_4H_6O_4$ from M^{2+}. This observation is consistent with the proposed structure for this compound, 7′-methoxypheoporphyrin a$_5$ dimethyl ester. The nmr spectrum in TFA was also highly consistent with this structure.

Reduction of chlorophyll *c* with hydriodic acid yielded a single product indistinguishable from authentic pheoporphyrin a$_5$ monomethyl ester.[8]

The data presented above, in addition to previously reported information,[3,11,12] suggest that chlorophyll *c* obtained by our procedure is a mixture of compounds Ia and Ib. These structures are in close agreement with Granick's original surmise[11] about the nature of chlorophyll *c*. The groups around the ring were located only by analogy with those of other known porphyrin natural products.[13]

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(9) Measured on an AEI MS-9 mass spectrometer at Battelle Memorial Institute, Columbus, Ohio, by Dr. R. Foltz.

(10) A. H. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, **21**, 2913 (1965).

(11) S. Granick, *J. Biol. Chem.*, **179**, 505 (1949).

(12) A. S. Holt in ref 3, p 116.

(13) J. Lascelles, "Tetrapyrrole Biosynthesis," W. A. Benjamin, Inc., New York, N. Y., 1964.

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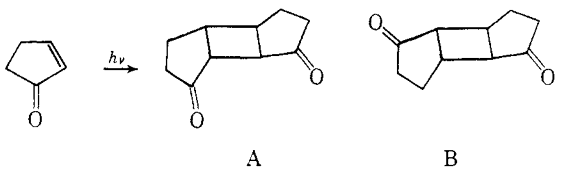
Received August 8, 1966

Photodimerization of Cyclopentenone. Singlet or Triplet?[1]

Sir:

We wish to establish here that the photodimerization[2] of 2-cyclopentenone is an excited triplet state reaction. It is our hope that this communication will erase the uncertainties that now exist on this point.[3]



The quantum yield for the photodimerization of cyclopentenone is reduced toward zero if the reaction is carried out in the presence of such triplet quenching agents as piperylene. A plot (Figure 1) of the inverse of the relative quantum yield against the concentration of added piperylene is linear over the concentration range studied. If the singlet excited state of cyclopentenone accounted for even 5% of the reaction, the line would curve distinctly in the higher concentration region.

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(1) This work was supported by generous grants from the National Institutes of Health (GM 10572 and GM 13451).

(2) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(3) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 537; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 203; G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); J. Saltiel in "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, p 302; P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962); J. L. Ruhlen and P. A. Leermakers, private communication.