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9-DESOXO-9,10-DEHYDROCHLOROPHYLL a
A NEW CHLOROPHYLL WITH AN EFFECTIVE
20-PI ELECTRON MACROCYCLE

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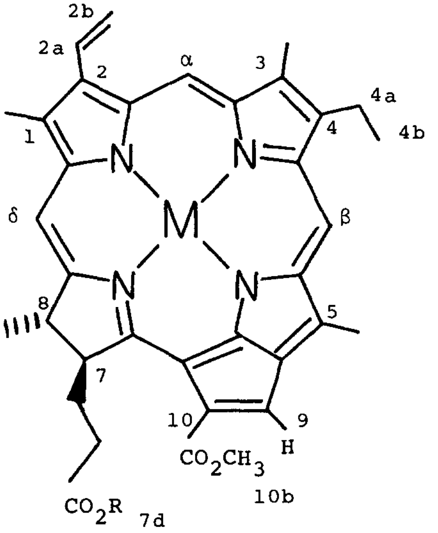
The enolic tautomer of the β- keto ester in ring V of chlorophyll a, Chl a, has been suggested as a possible intermediate in the photochemistry of P700 Chl a special pairs in green plant photoreaction centers.[2] Moreover, this tautomer may be involved in the photo-oxidation of Chl a by molecular oxygen.[3] Attempts to trap the Chl a enol as an enol ester or a silyl enol ether lead to very unstable products.[4] In order to investigate these phenomena we have prepared a new stable Chl a derivative, <u>4</u> in which ring V is fully unsaturated. The resulting macrocycle possesses a π electronic system very similar to that of the enol and thus serves as a useful model for photochemical studies.

9-Desoxo-9,10-dehydrochlorophyll a, <u>4</u> was prepared by the following route: The 9-keto group of pheophytin a, <u>1</u> was reduced with $NaBH_4$ in CH_3OH to yield a diastereomeric mixture of 9-desoxo-9-hydroxy-pheophytins a, <u>2</u> (87%).[5] Mild elimination of H_2O from ring V was effected by treating the mixture of alcohols (1.5 mmoles) in pyridine at 0° with excess trifluoroacetylimidazole over 5 minutes. Addition of 1,8-bis(dimethylamino)naphthalene (3 mmoles) followed by 30 minutes stirring at 0°, 3 hours at 25°, and conventional work up yielded 9-desoxo-9,10-dehydropheophytin a, <u>3</u> (93%; MS: m/e 854, M^+; $\lambda_{max}(\varepsilon)$ acetone : 800 (1330), 625 (4000), 425 (55200), 350 (38800); ^1H nmr: see Table I; ir: (CCl_4) 1710, 1738 cm^{-1} C=O).

Magnesium insertion into 3 was carried out with excess Mg(ClO$_4$)$_2$ in refluxing pyridine.[6] The resulting solutions of 4 were maintained at 0-5° during work up of the reaction mixture to prevent demetallation (60%).



	3	4
M =	H$_2$	Mg
R =	phytyl	phytyl

The proton chemical shifts in the nmr spectrum of 4 differ substantially from those of Chl a, Table I. For example, the α, β, and δ methine protons of Chl a exhibit large downfield shifts characteristic of an effective 18 π electron macrocycle.[7] However, the resonances of the corresponding protons in 4 are shifted upfield by nearly 2 ppm relative to those in Chl a. A similar effect of lesser magnitude has been observed in the magnesium enolate of methyl pheophorbide a.[8] The nmr data for this chelated enol may be compared directly with that obtained for 3 (Table I). Compound 3 is somewhat less diatropic than the chelated enol. This indicates that the 9,10 double bond in 4 significantly perturbs the π electronic structure of the macrocycle.

This view is further supported by a comparison between the electronic spectra of 4 and Chl a (Figure 1). The Soret band of 4 is split into two distinct maxima at 445 nm and 363 nm. This is quite different from the single broad Soret band of Chl a at 430 nm. The magnesium enolate of methyl pheophorbide a also exhibits a split Soret band. The 650 nm absorption band of 4 is tentatively assigned to the $Q_y(0,0)$ transition and is substantially blue shifted from the corresponding 663 nm band in Chl a. In addition, the oscillator strength of this band is only about 10% that of the band in Chl a. This loss in oscillator strength is consistent with a decrease in the dipole moment of 4 along the ring I - ring III axis due to the absence of the 9-keto group. The most interesting feature in the spectrum is the broad, low energy absorption centered at 800 nm. This band is unique to this π electronic system and is notably absent in the magnesium enolates.[8] No fluorescence emission directly attributable to 4 was detected at wavelengths < 825 nm when the molecule was excited with 400 nm light. This behavior is similar to that observed for the magnesium enolates.[8] Either radiationless deactivation to the ground state or efficient intersystem crossing to the triplet state may account for this result. We are currently examining the triplet state properties of 4 to elucidate this point.

TABLE I

Proton Chemical Shifts*

proton	Chl a	Mg enolate	3	4	proton	Chl a	Mg enolate	3	4
β-H	9.75	9.01	8.37	7.87	10b-CH_3	3.76	3.83	3.86	3.63
α-H	9.57	8.83	8.28	7.69	8-H	4.42	4.10	3.75	?
2a-H	8.08	7.77	7.54	7.32	7d-CH_3	-	3.38	-	-
δ-H	8.71	8.00	7.53	6.71	4a-CH_2	3.54	3.29	3.22	3.04
9-H	-	-	7.11	6.49	5-CH_3	3.42	3.11	2.91	2.63
2b-H_A	6.23	6.06	6.00	5.69	3-CH_3	3.21	2.95	2.87	2.56
2b-H_B	6.05	5.87	5.93	5.53	1-CH_3	3.08	2.83	2.76	2.48
7-H	4.29	4.65	4.73	?					

*δ ppm The chemical shifts of the phytyl resonances and that of 4b-CH_3 are not given. They are identical for each compound with those reported for Chl a (Ref.7). All nmr spectra were recorded in 10% pyridine-d_5 in benzene-d_6 at concentrations of 0.02-0.03 M.

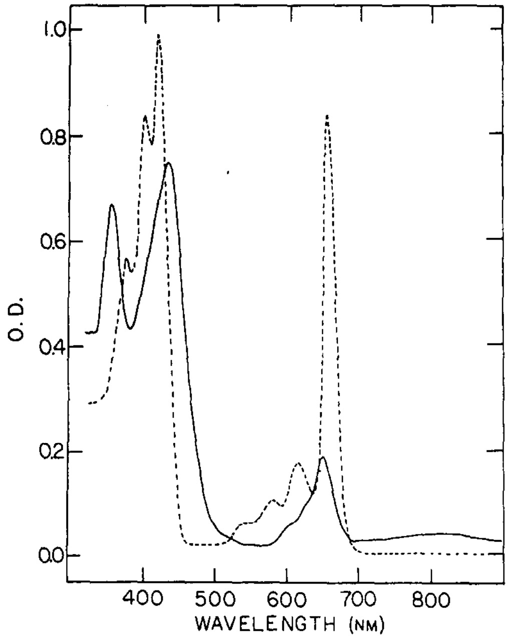


Figure 1. Electronic spectra of 10^{-5} *M* Chl a ---- and 10^{-5} *M* *4* —— in acetone

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