faint absorptions at 136.6, 126.8, 85.1, 82.2, and 41.5 ppm in the ^{13}C NMR spectrum of **1** suggested the presence of a small amount of such an isomeric peroxide. Careful high-pressure LC (10% EtOAc/hexane, μ-Porasil) of this fraction resolved a minor, faster moving component from **1** whose spectral features were consistent with the missing *trans*-dioxolane fraction.[17] Quantitatively, it accounts for 5% of the total endoperoxide mixture (**1** + **2**), making the cis/trans selectively 19:1.

Although cis selectivity in alkenylperoxy radical cyclizations has just recently been reported,[18] the exceptional preference exhibited in the linoleate system and the similarity of these materials to the proposed intermediates in prostaglandin biosynthesis make our results especially noteworthy. We have also shown that hydroperoxides of the triunsaturated fatty ester, methyl linolenate, form *cis*-dioxolanes analogous to **1** and **2** with the same degree of selectivity.[19] We conclude that it is a general property of β,γ-unsaturated lipid hydroperoxides to cyclize stereoselectively to *cis*-1,2-dioxolanes and that this preference may be an implicit step in the enzymatic formation of prostaglandin endoperoxides.

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(17) Only enough of this material could be collected for preliminary ^1H and ^{13}C FT-NMR evaluation. Comparison to model compounds proved helpful in this structure assignment and this work will be described in the full paper.

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(19) O'Connor, D. E.; Mihelich, E. D.; Coleman, M. C. unpublished results. Autoxidation and singlet oxygenation of methyl α-linolenate yielded two diastereomeric dioxolanes each of which consisted of 9,10,12 and 13,15,16 positional isomers.[20] Relative stereochemistry was strongly implicated by comparison of their NMR spectral features to those of **1** and **2** and proven by conversion to triols as described for the linoleate diperoxides. Autoxidation of 13-hydroxyperoxylinolenate (obtained from the action of soybean lipoxygenase on α-linolenic acid followed by diazomethane esterification) afforded two pure 16-hydroperoxy 13,15-endoperoxides. The major and less polar isomer has also been isolated by Chan[23] and can now be assigned the 13*S*,15*R*,16*S* configuration. The less abundant, more polar isomer has the 16*R* configuration.

(20) These compounds have TLC mobilities identical with those reported for cyclic peroxides isolated from both an enzymatic oxidation[21] and autoxidation[22] of methyl linolenate. Our results indicate that the claim of 1,2-dioxane formation in the latter case, which was based on some minor hydrogenation byproducts,[22] is in error. This is in agreement with the extensive model studies of Porter[15] where no trace of dioxane formation was observed even in "thermodynamically biased" cases.

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Primary Electron Acceptors in Plant Photosynthesis

Sir:

Recent spectroscopic evidence indicates that short-lived transients mediate the light-induced charge separation in photosystems (PS) I and II of plant photosynthesis.[1-8] These intermediates, labeled A_1 (first acceptor) in PS I and I (intermediary acceptor) in PS II, transfer an electron in a picosecond time domain from the chlorophyll phototraps to secondary acceptors, iron–sulfur proteins in PS I and plastoquinone (Q) in PS II. Chlorophyll *a* (Chl)[3-6,9-11] and pheophytin *a* (Pheo, a metal-free Chl)[6-8] have been proposed as A_1 and I, respectively. We present here electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) results which establish that in subchloroplast fragments enriched in PS II reaction centers, the trapped primary electron acceptor (I^-) exhibits magnetic characteristics (*g* value, ESR line width, saturation behavior, and ENDOR transitions) very similar to those of the monomeric anion radical of Pheo in vitro. In addition, the midpoint potential[12] and the optical changes[7,8,12] that accompany the reduction of I in vivo closely parallel those observed for monomeric Pheo in vitro.[6] We conclude that pheophytin *a* is the most likely candidate as the primary electron acceptor of the charge separation induced by light in PS II.

Parallel ESR and ENDOR results on subchloroplast fragments enriched in PS I, taken in conjunction with recent optical data obtained by picosecond[3-5] and other flash-kinetic[3,11] techniques, suggest that a monomeric chlorophyll[6] acts as the primary electron acceptor in PS I.

The intermediate I^- was trapped in subchloroplast fragments (TSF-IIa) highly enriched in PS II reaction centers[13] by a technique[8] which takes advantage of the fast reaction of endogenous donors (D) with $P680^+$, the phototrap of PS II. Under continuous illumination at 210 K and at redox potentials low enough to reduce the secondary acceptor Q (−0.45 V vs. NHE), the rapid, reversible photooxidation of P680

$$\mathrm{D\ P680\ I\ Q^-} \underset{2\text{–}4\ \mathrm{ns}}{\overset{h\nu,\ S_2O_4^{2-}}{\rightleftharpoons}} \mathrm{D\ P680^+ I^- Q^-}$$

is terminated by the eventual reduction of $P680^+$ by the donor D:

$$\mathrm{D\ P680^+ I^- Q^-} \xrightarrow[\leq 1\ \mu s]{} \mathrm{D^+\ P680\ I^-\ Q^-}$$

Under the strongly reducing conditions used, D^+ is reduced by the medium with the net photoreaction:

$$\mathrm{D\ P680\ I\ Q^-} \xrightarrow{h\nu} \mathrm{D\ P680\ I^-\ Q^-} + \text{oxidized medium (prepn A)}$$

If the photoillumination is carried out at 273 K, an additional product accumulates:

$$\mathrm{D\ P680\ I^-\ Q^-} \rightarrow \mathrm{D\ P680\ I\ Q^{2-}}$$

Repetition of the above reactions leads to a trapped I^-,Q^{2-} configuration:

$$\mathrm{D\ P680\ I\ Q^{2-}} \xrightarrow[273\ \mathrm{K}]{h\nu} \mathrm{D\ P680\ I^-\ Q^{2-}}\ \text{(prepn B)}$$

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(13) The preparations, obtained by Triton treatment of spinach chloroplasts, contained ~1 PS II reaction center per 30–40 Chl molecules and were free of PS I reaction centers. The fragments were suspended in 0.1 M tricine–NaOH (pH 8) which contained 50% glycerol.[8]

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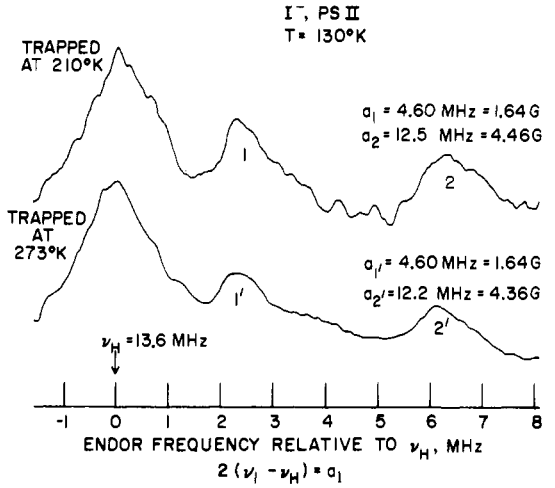

Figure 1. ENDOR spectra, at 130 K, of PS II subchloroplast particles containing I^- trapped at 210 K (I^-, Q^- configuration, preparation A) and at 273 K (I^-, Q^{2-} configuration, preparation B). The data are presented relative to the free proton frequency, ν_H = 13.6 MHz.

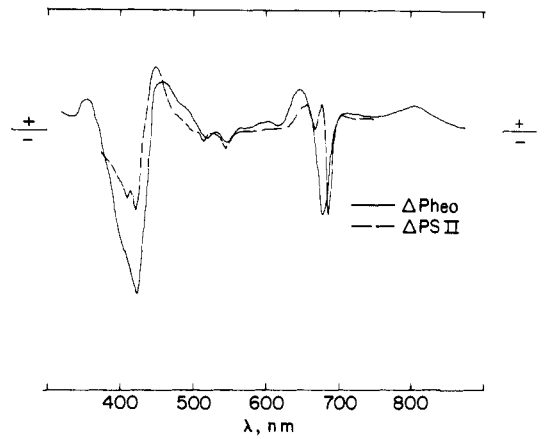

Figure 2. Comparison of the optical changes caused[8] by the reduction of I (ΔPS II) and the difference spectrum obtained[6] on electrochemical reduction of Pheo *a* in dimethylformamide (Δ Pheo). The spectra have been normalized at ~680 nm and the Pheo spectrum has been red-shifted ~20 nm.

This reaction can be prevented by performing the irradiation at 210 K (preparation A). In each preparation, the final product is trapped by quenching in liquid nitrogen.

The two preparations yield singlet ESR signals with *g* values of 2.0033 (±0.0002). The signals saturate easily (ΔH = 13 and 14 G at 0.01 and 1 mW, respectively; see Table I) and reveal proton ENDOR resonances at 1.64 and 4.46 G for preparation A and 1.64 and 4.36 G for B (Figure 1).

Comparison of these parameters with those of the anion radicals of chlorophyll and pheophytin in vitro (Table I) indicates that the *g* values, line widths, saturation behavior, and ENDOR responses of I^- are clearly consonant with those of monomeric anion radicals of Pheo or Chl. (Electron sharing, *on the ESR time scale*, between two or more molecules such as $(Chl)_2^-$, $(Pheo)_2^-$, or $(Chl\text{–}Pheo)^-$ would reduce the ESR line width and the hyperfine splittings observed by ENDOR.) I^- must therefore be $Pheo^-$ or Chl^- (or possibly a heterogeneous array of the two) but not a dimeric complex. Comparison of the optical difference spectra obtained on reduction of Pheo and Chl in vitro[6] with those observed[7,8,12] on reduction of I in PS II fragments and in chloroplasts indicates that many of the optical changes observed in vivo mirror those found upon reduction of Pheo in vitro (Figure 2). In addition, the midpoint potential estimated[12] for the reduction of I, E_m = –0.61 V, is nearly identical with the half-wave potential found[6] for the reduction of Pheo in dimethylformamide, –0.64 V, whereas reduction of Chl in the same solvent occurs[6] at –0.88 V. The combination of ESR, ENDOR, optical, and redox data thus leads to the conclusion that I^- in PS II exhibits many of the properties of a monomeric anion radical of Pheo.

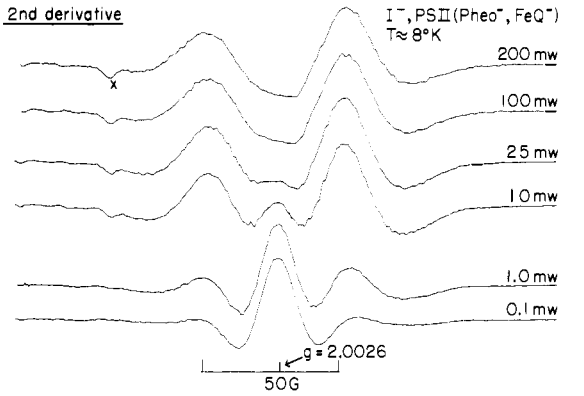

Figure 3. Second-derivative ESR spectra at 8 (±1) K of I^- trapped in the I^-, $[Fe\text{–}Q]^-$ configuration (preparation A). The center line observed at low microwave power is attributed to $Pheo^-$ and saturates easily to reveal a doublet spectrum separated by 52 (±2) G. The doublet spectrum is only observed when $[Fe\text{–}Q]^-$ is present. The origin of the small peak marked X is undetermined.

The question arises as to whether the Pheo anion observed is not simply an artifact of the preparation. The following observations render this possibility unlikely. The reducing conditions used in preparation A result in the trapping of I^- and Q^-, the subsequent acceptor in the electron-transport chain. This latter species has recently been shown[19] to comprise an iron–plastoquinone complex (Fe–Q) analogous to the iron–quinone acceptors found[20] in photosynthetic bacteria. At 10 K, in preparation A, interactions between the Pheo and [Fe–Q] radicals give rise[8] to a doublet ESR signal (Figure 3) which is difficult to saturate and exhibits no ENDOR response. This signal disappears if the integrity of the $[Fe\text{–}Q]^-$ complex is destroyed by extraction of Q or Fe[19] or by reduction at room temperature, presumably to $[Fe\text{–}Q]^{2-}$ (preparation B). These results indicate therefore that the Pheo anion observed is in close proximity to the quinone and is indeed an integral part of the reaction center and not simply an aberration induced by the experimental techniques employed to isolate the reaction center and generate $Pheo^-$. A similar doublet signal has been detected[21] under comparable conditions in photosynthetic bacteria and has been attributed to an analogous interaction between a bacteriopheophytin anion[22] and a reduced iron–menaquinone complex.[21] Somewhat surprisingly, then, the initial sequence of electron acceptors in PS II, which mediates oxygen evolution in green plants, seems to mirror that found in

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Table I. Comparison of the Properties of I^- and A_1^- and Pheo$^-$ and Chl$^-$

	I^-, PS II	Pheo$^-$ [a]	Chl$^-$ [a]	A_1^-, PS I
g value	2.0033 (±0.0002)	2.0030 (±0.0001)	2.0029 (±0.0001)	2.0033 (±0.0002)
ΔH, $T = 130$ K[b]	13.2–13.9 G	12.2–13.1	12.1–13.5	13.2–13.9
ENDOR, a_H, G	Prepn A: 1.64, 4.46	1.95, 3.75	1.95, 4.05	1.7, 4.9
$T = 130$ K[c]	Prepn B: 1.64, 4.36			
reduction potential V vs. NHE	−0.61[8]	−0.64	−0.88	>−0.73[18]
optical spectra	similar to Pheo$^-$,[8,12] red shifted ~20 nm			similar to Chl$^-$,[3,11] red shifted ~20 nm

[a] In dimethylformamide.[6] [b] Minimum and maximum peak to peak line width of the first-derivative ESR spectra obtained in the range 0.01–1 mW of microwave power. [c] The small and large proton splittings of Pheo$^-$ and Chl$^-$ in vitro have been assigned[6] to the 1- and 5-methyl groups, respectively, on the basis of selective deuterations and molecular orbital calculations. The ENDOR coupling constants obtained for PS I and II are about 16% lower for the 1-CH_3 and 20% larger for the 5-CH_3 than the corresponding values in dimethylformamide and are reflected in the slightly larger in vivo line widths. Iterative extended Hückel calculations for Chl$^-$ indicate that if the 2-vinyl group is rotated to be perpendicular to the plane of the Chl,[14] the unpaired spin densities decrease by 23% at the 1-carbon and increase by 6% at the 5-carbon compared to the densities computed[15] by using the crystal coordinates of ethyl chlorophyllide *a* where the 2-vinyl group makes a torsional angle of 30° to the Chl plane.[16] These results suggest that, as in heme proteins,[17] neighboring molecules or protein residues impose specific orientations on the substituent groups of the Chl and Pheo within the reaction center.

purple bacteria, which do not liberate oxygen in their photosynthetic cycle:[23]

$$(B)Chl_n + (B)Pheo + FeQ \xrightarrow{h\nu}$$
$$(B)Chl_n^+ + (B)Pheo^- + FeQ \rightarrow (B)Chl_n^+ + (B)Pheo + FeQ^-$$

where B = bacterio and Q = plastoquinone in PS II and mena- or ubiquinone in bacteria.

Comparable ESR and ENDOR experiments performed on the primary acceptor of PS I, A_1^-, trapped[26] in subchloroplast fragments enriched in PS I (TSF I)[27] yielded a g value of 2.0033, ΔH = 13–14 G, and ENDOR resonances of 1.7 and 4.9 G at 130 K (Table I). Comparison of these results and of recent flash photolysis optical spectra of A_1^-[3-5,11] with the properties of Chl$^-$ in vitro[6] suggests that a monomeric chlorophyll[28] acts as the primary electron acceptor in PS I, as originally proposed by Fujita et al.[6] on the basis of in vitro studies.

The 1.8-eV photons incident on the reaction centers of green plants are thus transduced in PS II into a strong chlorophyll oxidant (P680$^+$) with a midpoint potential, E_m, estimated at ~1 V vs. NHE and a pheophytin reductant with E_m ~−0.6 V, whereas in PS I, the chlorophyll donor (P700$^+$) has a lower oxidation potential, E_m ~0.4–0.5 V, and the chlorophyll acceptor is a powerful reductant with E_m ~−0.9 V. Photosynthetic bacteria, limited by the 1.4 eV of energy reaching the reaction center, appear to straddle the two plant systems with a bacteriochlorophyll donor (P870$^+$) of E_m ~0.45 V and a bacteriopheophytin acceptor with E_m ~−0.5–0.6 V.[29]

If the postulated identity of the transient acceptors is correct, it is attractive to speculate that the interposition of chlorophyll-like molecules between the chlorophyll donors and the subsequent quinone (PS II) or iron–sulfur (PS I) acceptors in the electron-transport chain favors the picosecond transfer of electrons because of the similar electronic configurations of the primary donors and acceptors, whereas the very different orbital symmetries[6,22,24,30] of the resulting cation and anion radicals minimize orbital overlap and thereby inhibit wasteful back reactions.

Supporting evidence for the above premises is found in picosecond data[31] for a biomimetic model of PS II consisting of a diporphyrin in which a magnesium and a free base porphyrin are cofacially linked by two five-membered bridges and are separated by ~4 Å. Within 6 ps of excitation, the diporphyrin displays optical changes consistent with electron transfer from the magnesium porphyrin to the free base, and the charge-transfer state decays back to the ground state with lifetimes of 0.4 ns in dichloromethane and 2 ns in dimethylformamide. Thus, in the synthetic model predicated on the molecular architecture and primary charge separation proposed for PS II, i.e.,

$$Chl + Pheo \underset{\sim 3\ ns}{\overset{h\nu,\ ps}{\rightleftharpoons}} Chl^+ + Pheo^-$$

the rise and decay times approach those found in vivo for both the forward and back electron transfers.

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(23) The ability of PS II to evolve oxygen derives from the high oxidation potential of P680$^+$, which must have a minimum thermodynamic oxidation potential of +0.8 V vs. NHE at physiological pHs. This potential has been estimated[12] to be as high as 1.1 V. Davis et at.[24] have suggested that such a high potential is attained because P680 is a ligated Chl monomer, unlike the phototraps of PS I and photosynthetic bacteria which have been shown[25] to be dimeric chlorophylls by ENDOR experiments.

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(26) TSF I preparations[27] were illuminated in an ESR tube in the presence of 10^{-2} M dithionite with intense white light (5×10^5 erg/cm^2/s) for ~1 min and the sample quenched in liquid nitrogen. See: Ke, B.; Hanson, R. E.; Beinert, H. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2941–2945.

(27) The Triton-fractionated fragments contained 1 PS I reaction center per 26–28 Chl molecules and were prepared according to Vernon et al. (Vernon, L. P.; Shaw, E. R. *Methods Enzymol.* **1971**, *23*, 277–289). See also ref 7.

(28) A broad range of g values (2.0025–2.005) and ESR line widths (10–14 G) has been reported[3,10,11] for A_1^-, and a dimeric chlorophyll configuration has been suggested[3] for this acceptor. The detergents used in the preparations and removal of the next electron acceptor, an [Fe–S] cluster, seem to cause these significant variations.[10] The detergents may interfere with the steric or chemical interactions that orient the substituent groups (see discussion in Table I) or that exist between adjacent chlorophyll molecules, and may also disrupt magnetic interactions between A_1^- and the reduced [Fe–S] group present when A_1^- is trapped. If the [Fe–S] complex is absent, the g values and line width of A_1^- resemble[11] those of Chl$^-$ in vitro.[6]

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