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(11) ^{1}H NMR ($CDCl_3$) for the following compounds: (a) **4,** δ 1.8–2.9 (m, 2 H), 3.5–4.2 (m, 2 H), 5.4–5.9 (m, 2 H); (b) **5,** δ 1.9–3.1 (m, 2 H), 4.0–4.6 (m, 2 H), 4.73 (s, 2 H), 5.5–6.1 (m, 2 H), 6.65–7.0 (m, 1 H); (c) **6,** δ 2.7–3.0 (m, 2 H), 4.78 (s, 2 H), 4.8–5.15 (m, 2 H), 5.7–6.1 (m, 2 H), 6.1–6.7 (m, 1 H), 7.82 (s, 4 H); (d) **8,** δ 2.35–2.7 (m, 2 H), 4.2–4.8 (m, 2 H), 4.72 (s, 2 H), 5.13 (s, 2 H), 5.5–6.1 (m, 2 H), 7.32 (s, 5 H), 8.46 (s, 1 H); (e) **10,** δ 2.65–3.0 (m, 2 H), 4.55–5.5 (m, 2 H), 5.0 (s, 2 H), 5.6–6.2 (m, 2 H), 7.27 (s, 5 H), 7.5–7.95 (m, 4 H); (f) **11** ($(CD_3)_2CO$), δ 3.17 (d, J = 7 Hz, 2 H) 5.21 (s, 2 H), 5.1–5.8 (m, 2 H), 7.37 (s, 5 H), 7.90 (s, 4 H), 9.5 (br s, 1 H); (g) **12,** δ 3.10 (d, J = 5 Hz, 2 H), 5.40 (s, 2 H), 5.1–5.7 (m, 2 H), 7.38 (m, 5 H), 7.85 (s, 4 H), 8.4 (br, s, 1 H); (h) **15,** δ 2.77 (d, J = 7 Hz, 2 H), 5.15–5.7 (m, 2 H), 6.91 (s, 1 H), 7.15 (s, 5 H), 7.26 (s, 5 H), 7.75 (m, 4 H), 8.1 (br s, 1 H); (i) **16,** δ 2.94 (d, J = 5 Hz, 2 H), 5.1–5.4 (m, 2 H), 6.80 (s, 1 H), 7.23 (s, 10 H), 7.72 (m, 4 H), 8.0 (br s, 1 H); (j) **18,** δ 3.33 (d, J = 9 Hz, 2 H), 5.2–5.9 (m, 2 H), 6.94 (s, 1 H), 7.21 (s, 5 H), 7.31 (s, 5 H), 7.80 (m, 4 H); (k) **19,** δ 3.41 (d, J = 9 Hz, 2 H), 5.2–5.8 (m, 7 H), 7.83 (m, 4 H); (l) **20** (D_2O), δ 3.40 (d, J = 9 Hz, 2 H), 3.92 (d, J = 4 Hz, 1 H), 5.15 (m, 2 H); (m) **21** ($(CD_3)_2CO$), δ 3.57 (d, J = 9 Hz, 2 H), 5.2–5.7 (m, 2 H), 7.95 (m, 2 H).

(12) To our knowledge, cyclopentadiene monoepoxide had not been opened by any amine at the start of our work. Recently, G. H. Posner and D. Z. Rogers, *J. Am. Chem. Soc.*, **99,** 8214 (1977), reported on the opening with *N*-butylamine.

(13) The free amine was readily regenerated by passage of a MeOH solution of the salt through a quaternary ammonium hydroxide ion exchange resin.

(14) This two-stage resolution is necessary since direct resolution with L-(+)-tartartic acid gives a poor yield of resolved material. The deoxycholic acid on the other hand gives about a 90% yield of optically pure ent isomer in a single crystallization from MeOH.

(15) The 3*R*,4*R* and 3*S*,4*S* isomers of **4** were assigned to their respective series after application of the benzoate sector rule (N. Harada and K. Nakanishi, *J. Am. Chem. Soc.*, **91,** 3989 (1969)) to the data obtained from their respective benzoate benzamides. The validity of the extension of this rule from vicinal glycols to vicinal hydroxy amines is shown herein by conversion of the material assigned 3*R*,4*R* to natural AT-125.

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(19) The ratio was determined by chromatographic separation of the products. The structures were assigned to the products on the basis of their NMR spectra and the fact that the major product was converted to AT-125.

(20) When the corresponding TCEC–Cbz protected compound **8** was oxidized, a 1:1 ratio of natural to iso product was obtained.

(21) Acid deprotection of **11** or other protected derivatives such as those with R_8 = *t*-Boc or *p*-MeO–Cbz was not feasible owing to the fact that even such mild acids as 85% formic nearly quantitatively isomerized **13** to **14** in <1 h.

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(23) We thank D. G. Martin for this procedure.

(24) Private communication from L. Hanka and D. G. Martin of The Upjohn Co.

R. C. Kelly,* I. Schletter, S. J. Stein, W. Wierenga*
Experimental Chemistry Research, The Upjohn Company
Kalamazoo, Michigan 49001

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Photodisaggregation of Chlorophyll *a* and *b* Dimers

Sir:

We have recently demonstrated reversible unfolding of excited "dimers", formed by two covalently linked pyrochlorophyllide molecules, in benzene containing methanol.[1] This structure, in which the two macrocycles are pinned by OH bridges between Mg of one unit and keto carbonyl of the other,[2-5] shows characteristic absorption near 700 nm and is of special interest in view of proposals that it is a model for the reaction center, P-700, in photosynthesis.[2,3] We now report related work on 700-nm-absorbing chlorophyll *a* and *b* dimers, formed by direct aggregation of monomers at low temperature.[4,6-8]

At room temperature, chlorophyll *a* (~10^{-4} M) in dry methylcyclohexane containing 0.01 M methanol shows only the monomer peak at 661 nm. At −78 °C, this is partially converted to dimer, absorbing at 695 nm (Figure 1a). Flash photolysis using a 30-ns ruby laser pulse (694.3 nm)[1] selectively excites and bleaches the dimer (Figures 1b and 2). The initial difference spectrum (Figure 1b) shows also smaller bleaching in the Soret region and positive transients at 670 nm and in the triplet region, 470-600 nm.[9] These changes are completely reversible and correspond, at least semiquantitatively, to cleavage of a dimer to give triplet and ground-state units.[1] We note that the nascent monomer band at 670 nm is distinctly different from the original monomer (662), indicating a dif-

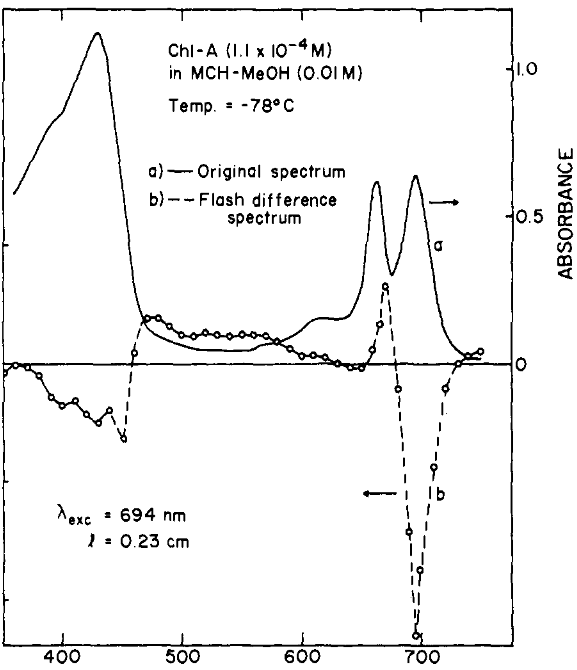

Figure 1. Absorption spectrum (curve a) and flash difference spectrum (curve b) immediately after laser flash (694.3 nm) excitation of chlorophyll *a* (1.1 × 10^{-4} M) in methylcyclohexane-methanol (0.01 M) at −78 °C; l = 0.23 cm; the sample was deoxygenated by argon bubbling. Arrows indicate absorbance scales for curves a and b.

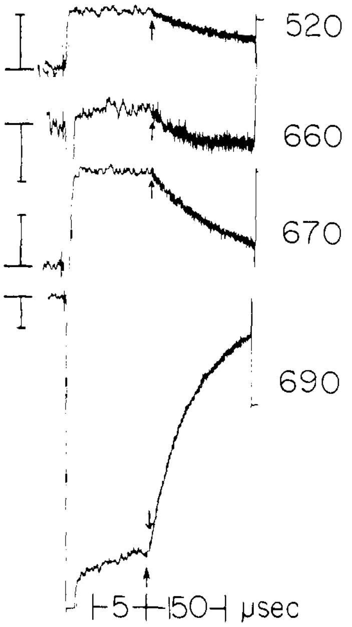

Figure 2. Flash profiles of chlorophyll *a* at 520, 660, 670, and 690 nm. The experimental conditions are as given in Figure 1. I indicates 10% change in transmission. Note composite time base.

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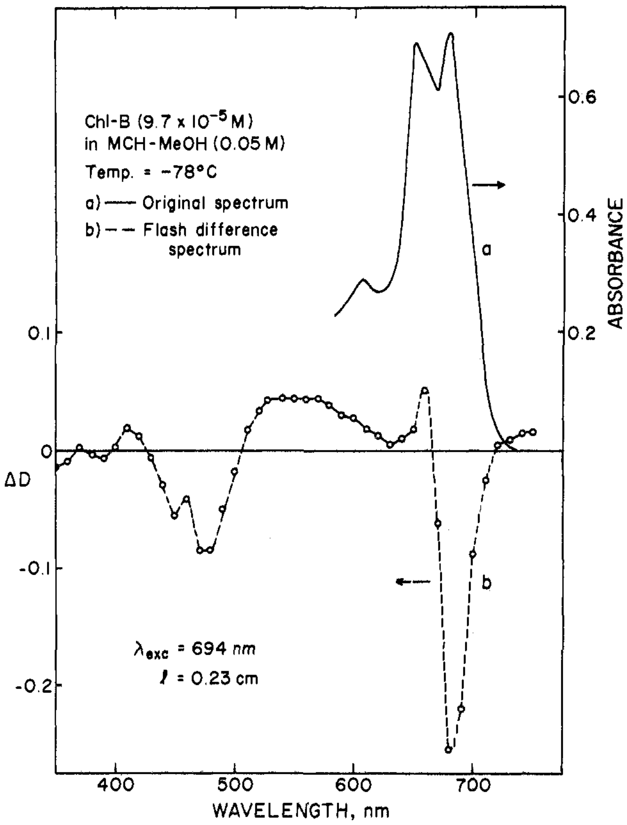
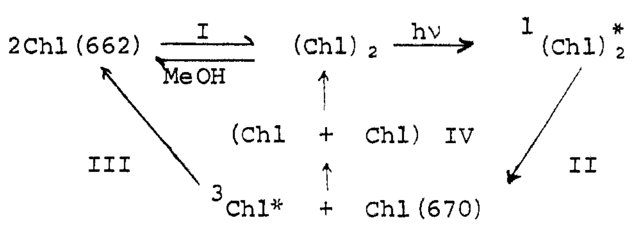


Figure 3. Absorption spectrum (curve a) and flash difference spectrum (curve b) immediately after laser flash (694.3 nm) excitation of deoxygenated chlorophyll *b* (9.5×10^{-5} M) in methylcyclohexane-methanol (0.05 M) at −78 °C; l = 0.23 cm. Arrows indicate absorbance scales for curves a and b.

Scheme I



ferent mode of solvent coordination. The disaggregation demonstrated in Figure 1 accompanies a decrease in acidity of Mg^{2+} in the excited state.[1]

Figure 3 shows similar results with Chl *b*. In methylcyclohexane-methanol (0.05 M) the room temperature monomer band at 644 shifts to 652 nm at −78 °C and is partially converted to dimer at 680 nm. Flashing (absorption in the dimer tail at 694 nm) selectively bleaches the 680-nm band, giving a broad triplet absorption[9] and red-shifted ground-state peak at 660 nm.

The transient absorption at 520 (Chl *a*, Figures 1 and 2) decays with mixed kinetics, as expected for a triplet.[9] However, the recovery at 695 nm is faster (Figure 2) and is close to first order throughout. In a typical experiment at ~0.01 M methanol, initial half-lives were 190 μs at 520 nm and 85 μs at 695 nm. In addition, at low methanol concentrations, a slight bleaching *after* the flash, followed by recovery, is seen around 660 nm (Figure 2). These observations fit Scheme I. The rapid recovery at 695 nm and slight reversible loss at 660 nm is interpreted as initial relaxation, via reaction I, of the perturbed monomer-dimer equilibrium. This will approach first order for small displacements from equilibrium, although the changes in Figure 1 are appreciable.

Attempts to isolate reaction I were made by using reversible quenchers to shorten the triplet lifetime. However, dimer recovery at 695 nm kept pace with triplet decay even down to lifetimes of 10 μs (with chloranil) or 1 μs (in presence of oxygen) and at methanol concentrations of ~0.01 M. This indicates another pathway for dimerization via geminate monomers (reaction IV), which appear to diffuse apart relatively slowly forming a Chl population distinct from the 662-nm species.

These experiments show that photodisaggregation of the 700-nm dimer in fluid hydrocarbon solvent occurs in <50 ns after excitation both at room temperature and −78 °C. However, reaction II is slow enough to permit observation of dimer fluorescence[6] even at room temperature.[2] Whether these results apply to P-700 is, of course, an open question and depends on both the validity of the model[2,3] and speed of P-700 oxidation in vivo.[10] Until this is resolved, the possibility of complications arising from dimer cleavage and shifted monomer bands should be recognized in interpreting light-dark difference spectra of algae or chloroplasts, particularly those which show positive transients or complex spectral shifts in the red, accompanying bleaching of P-700.[11] A blocked electron-transport path from P-700 may also permit unfolding to the triplet,[12] offering a possible means of short-term energy storage. Photodisaggregation may function in mediating the response of chloroplast membranes to light.

The photodissociation of pheophytin *a* aggregates has been described by Sagun and Dhzagarov.[13]

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N. Periasamy, H. Linschitz*
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154

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Total Synthesis of (R_C)-Sparsomycin[1]

Sir:

Seventeen years have passed since the isolation of sparsomycin (**1**) from *Streptomyces sparsogenes* was reported by Argoudelis and Herr.[2] This compound exhibits anticancer activity[4,5] and is active against various bacteria,[3,4] fungi,[6] and viruses.[7] Wiley and MacKellar, through their structure proof of **1**, demonstrated that the chiral carbon atom has the *S* configuration,[8] but the configuration of the sulfinyl group has not been determined. Several analogues of **1** have been syn-