Soc., **98**, 5988–5996 (1976).
(15) Mass spectral analysis was performed on a Finnigan 4000 GC/MS/Data System by electron impact with a solid probe at 70 eV and at 250 °C ion source temperature. The diagnostic ions (with relative ion intensities shown in parenthesis) follow: **3** (at 185 °C probe temperature), *m/e* 290 (M^+, 100%), 275 (13), 272 (22), 257 (25), 244 (84), 229 (73), 215 (65), 202 (88), 189 (30); **4** (at 210 °C probe temperature), *m/e* 306 (M^+, 67%), 291 (5), 288 (26), 260 (38), 244 (43), 231 (59), 216 (83), 215 (100), 202 (89), 189 (37).
(16) NMR spectral analysis was performed on a Varian Model XL-200 NMR spectrometer at 24 °C. We thank Dr. George Gray of Varian Associates, Inc., for obtaining the NMR spectra.
(17) M. J. Karplus, *J. Am. Chem. Soc.*, **85**, 2870–2871 (1963). The results that $J_{1,2}$ = 4.5 Hz in *cis*-1,2-diacetoxy-1,2-dihydrophenanthrene,[14b] $J_{1,2}$ = 11.75 Hz in *trans*-1,2-dihydroxy-1,2-dihydrophenanthrene,[14b] $J_{1,2}$ = 1.7 Hz in *trans*-1,2-dihydroxy-1,2-dihydrobenz[*a*]anthracene,[14a] $J_{3,4}$ = 11.5 Hz in *trans*-3,4-dihydroxy-3,4-dihydrobenz[*a*]anthracene,[14a] and $J_{9,10}$ = 10 Hz in *trans*-9,10-dihydroxy-9,10-dihydro1-hydroxy-3-methylcholanthrene[6] are also consistent with our conclusions that **3** and **4** are *trans*-3,4-dihydrodiols.
(18) The bathochromic shifts of UV absorption maxima of **1**, **2**, **3**, and **4** relative to UV absorption maxima of benz[*a*]anthracene and benz[*a*]anthracene *trans*-3,4-dihydrodiol are apparently due to the presence of 7-CH_3 (or 7-CH_2OH) and the steric strain between the 12-CH_3 and H_1: M. A. Frisch, C. Barker, J. L. Margrave, and M. S. Newman, *J. Am. Chem. Soc.*, **85**, 2356–2357 (1963). Presumably the steric strain decreased the conjugation of 1,2 double bonds with anthracene nucleus in **3** and **4** compared with the 1,2 double bonds of *trans*-3,4-dihydroxy-3,4-dihydrobenz[*a*]anthracene and *trans*-9,10-dihydroxy-9,10-dihydro-1-hydroxy-3-methylcholanthrene and consequently the H_1 of **3** and **4** occurs at higher field. **1** is a nonplanar molecular with 1,2,3,4 ring inclined to that of anthracene nucleus at an angle of 18.5°: J. Iball, *Nature (London)*, **201**, 916–917 (1964).
(19) Under identical conditions, the *cis*-5,6-dihydrodiol of **1** yielded vicinal cis acetonide (M^+ at *m/e* 330) quantitatively.
(20) (a) M. W. Chou and S. K. Yang, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 5466–5470 (1978); (b) E. Huberman, M. W. Chou, and S. K. Yang, *ibid.*, in press.
(21) Since the submission of this manuscript, C. Malaveille et al. (*Biochem. Biophys. Res. Commun.*, **83**, 1468–1473 (1978)) reported high mutagenic activity of a chemically synthesized **3** (presumably the racemic trans isomer) toward *S. typhimurium* test strain TA100 in a rat liver microsome mediated mutagenicity assay.

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New Model Visual Pigments. Spectroscopy of Poly(ethylene glycol) Peptide Schiff Bases of Retinal

Sir:

Considerable knowledge is currently available[1-3] regarding the spectral and photochemical properties of various model visual pigment systems including retinals, retinols, and retinyl Schiff bases (RSB). However, as far as the understanding of the visual process itself is concerned, there are still many unresolved questions. Some of these concern the origin of the long-wavelength absorption maxima[4-6] of rhodopsin, the high photoisomerization quantum yield[7] of rhodopsin (both compared with protonated 11-cis RSB), and the mechanism of the primary photoprocesses.[8-10] Obviously, the environmental effect of the protein envelope and other internal interactions such as charge transfer and hydrogen bonding need to be investigated via models that more accurately mimic rhodopsin.

We have undertaken the spectroscopic study of a series of RSB complexes of poly(ethylene glycol) (PEG) amino acids and oligopeptides with selected amino acid sequencing. The absorption and emission spectral data for these systems under various conditions of solvents, cations, proton donors, and charge transfer agents will appear in the full paper. In this communication we report briefly the results for the all-trans

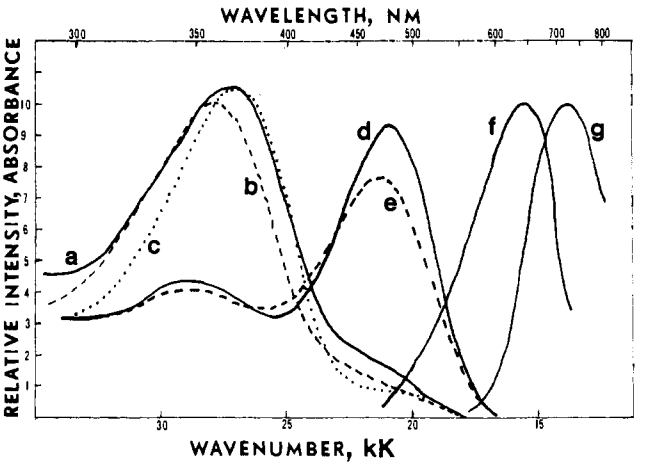

Figure 1. Absorption, emission, and excitation spectra of RSB of PEG-Ala-Lys-Glu in dichloromethane: (a) —, absorption spectrum of RSB at 193 K; (b) - - -, absorption spectrum of RSB at 298 K; (c) . . . , excitation spectrum of RSB at 193 K (monitored at 570 nm); (d) —, absorption spectrum of protonated RSB at 193 K; (e) - - -, absorption spectrum of protonated RSB at 298 K; (f) —, emission spectrum of RSB at 193 K (excited at 370 nm); (g) —, emission spectrum of protonated RSB at 193 K (excited at 470 nm).

RSB complexes of the italicized amino acids of PEG-*Ala* (I), PEG-Ala-Phe-*Lys* (II) (α-amino group of Lys protected by *tert*-butyl oxycarbonyl group), PEG-Ala-*Lys*-Glu (III) (ϵ-carboxylic group of Glu free), and PEG-Phe-*Lys*-Ala-Glu (IV) (ϵ-carboxylic group of Glu free), where Ala = alanine, Phe = phenylalanine, Lys = lysine, and Glu = glutamic acid. The PEG peptides were prepared using PEG of mol wt 6000 by the method of liquid-phase peptide syntheses described in detail elsewhere.[11]

At room temperature in EtOH-MeOH (4:1, v/v), the absorption spectra of all of the peptide RSB's are characterized by a broad band with maximum at 335–365 nm, which upon cooling to 77 K undergoes a red shift by 5–10 nm. On protonation with trichloroacetic acid (TCA) two bands develop, one at 330–340 nm and the other, more intense, at 440–450 nm. The latter band (long wavelength) undergoes a blue shift of 5–10 nm upon cooling to 77 K. Figure 1 shows the absorption spectra of an RSB complex of the peptide III, PEG-Ala-Lys-Glu, and its protonated form in dichloromethane at 298 and 193 K. It should be noted that the main absorption band of III is accompanied by a long-wavelength tail (430–520 nm) which upon cooling to 193 K increases in intensity by ~50% while the intensity at the band maximum increases by only ~9%. The spectral region of the increased absorption corresponds to the spectral region where the formally protonated RSB complex has its absorption maximum. Similar experiments done on all-trans RSB of peptide IV, PEG-Phe-Lys-Ala-Glu, in CH_2Cl_2–CHF_2Cl (1:1, v/v) at 298 and 173 K show that the long-wavelength tailing is present in both room- and low-temperature spectra, but to a much lesser extent.

Each of the RSB-peptide complexes exhibits a weak fluorescence ($\phi_F = 10^{-2}$–10^{-3}) at room temperature in EtOH-MeOH and CH_2Cl_2. The intensity of fluorescence becomes enhanced on cooling (ϕ_F = 0.1–0.2 in EtOH-MeOH at 77 K and ~0.02 in CH_2Cl_2 at 193 K). The protonated RSB's also fluoresce moderately strongly at low temperature ($\phi_F \sim 0.1$ in EtOH-MeOH at 77 K and ~0.01 in CH_2Cl_2 at 193 K). Both in EtOH-MeOH and CH_2Cl_2 at low temperature, the shape, position, and intensity of fluorescence of the RSB's of the peptides III and IV are found to show a marked dependence on the excitation wavelength. Thus, for the RSB of peptide III in CH_2Cl_2 at 193 K, as the excitation wavelength is changed from 350 nm to 430 nm, the emission maximum undergoes a red shift of ~1000 cm^{-1}; furthermore, the fluorescence spec-

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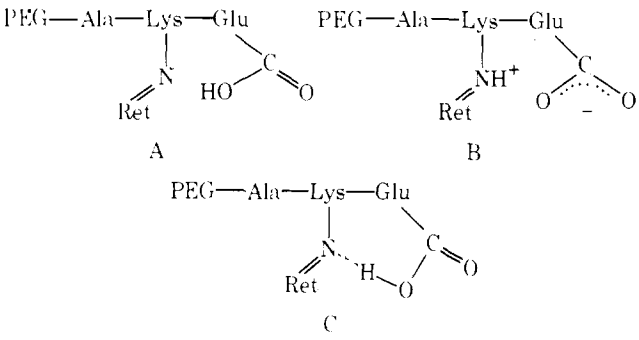
trum becomes more intense in its long-wavelength region (550–700 nm) where the formally protonated RSB has its emission maximum. The excitation spectrum monitored at the observed emission maximum (550–590 nm) of RSB's of peptides III and IV is composed of two distinct bands, one with a maximum at 340–440 nm (strong) and the other at 440–500 nm (weak), Figure 1.

Both the absorption and emission spectral data described above clearly indicate that, in the case of the RSB's of the peptides III and IV, more than one well-defined species is present in solution. The two bands observed in the excitation spectra are identifiable in position with the main absorption band of the nonprotonated and formally protonated forms. The latter data plus that of absorption and emission regarding the long-wavelength regions, vide supra, strongly indicate that the RSB's of the peptides III and IV contain at least two distinct species which we shall formally call nonprotonated (A) and protonated (B). A third viable possibility is an intramolecular



hydrogen-bonded form (C) which is expected to have spectral properties similar to those of B. Protonation could occur by dissociation of the H of the carboxyl group leading to the formation of a zwitterion involving the basic imino nitrogen of the Schiff base. H-bond formation between the different molecules is expected to be much less significant because of the expected large steric hindrance involved in the approach of the macromolecules to one another.

The question of whether a completely protonated form (B) or internally H-bonded form (C) (or possibly an intermolecularly H-bonded form) is predominantly involved remains to be settled by other means. However, in a relatively nonionizing solvent such as dichloromethane and at low temperature, the dissociation of the carboxyl group is expected to be small and the formation of an internally H-bonded species such as C is most likely. *To the best of our knowledge, this work represents the first study and observation of a molecular perturbation of known origin involving a peptide moiety of known sequencing that results in a significant alteration of the wavelength maximum of an RSB.* The presence of internal H-bonding protonation indicated in the present work may be exploited to resolve some of the issues involved in the mechanism of the visual processes including protonation–deprotonation.[8-10,12,13] In addition to the protein-like microenvironment offered by the polymeric PEG portion, it is possible for further study to have peptides containing suitable polar, polarizable, or aromatic groups which may take part in internal electrostatic or charge-transfer interactions with the polyene chain.[4,14,15]

It should be noted that, although the emission spectral maxima of the RSB's of peptides I and II show a *slight* dependence on excitation wavelengths, this behavior is much less pronounced compared with that of III (and IV) and is not explainable in terms of absorption of or emission from protonated–nonprotonated species.

The preparation of the RSB complexes was done by mixing dry methanol solutions of a PEG peptide and *all-trans*-retinal (Sigma, five–six times molar excess) over 3A molecular sieves and standing for 12 h at 0 ° under nitrogen in the dark. After the molecular sieves were removed by filtration, the RSB complex was precipitated from the methanol solution by adding ether (until the solution was opalescent) and cooling to 0 °C. This was filtered off, washed three times with cold, dry ether, and dried under high vacuum ($\sim 10^{-5}$ Torr). For spectral measurements, the RSB was dissolved in methanol followed by precipitation with ether, washing, and drying and this procedure was repeated twice to ensure the complete removal of unreacted retinal.

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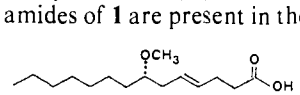
Malyngamide A, a Novel Chlorinated Metabolite of the Marine Cyanophyte *Lyngbya majuscula*

Sir:

(−)-7(*S*)-Methoxytetradec-4(*E*)-enoic acid (**1**) and chlorine-containing amides of **1** are present in the extracts of several shallow-water varieties of the marine blue-green alga *Lyngbya majuscula* Gomont.[1-3] Herein we report the structure of one of these amides, malyngamide A.



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Malyngamide A (**2**) was obtained as a neutral, colorless oil, $[\alpha]^{25}_D$ −6.5° (CH_2Cl_2, *c* 0.8) by gel filtration (Sephadex LH-20) and HPLC (μ-Bondapak-CN) of the dichloromethane extract of freeze-dried *L. majuscula* collected at Kahala Beach, Oahu. High resolution mass spectrometry established the molecular formula of **2** as $C_{29}H_{45}ClN_2O_6$. Negative re-

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