

Figure 1. Oxygen 1s spectrum of Chl a. The ΔE_b is defined as the difference between the binding energy of the O 1s peak and the C 1s peak: (a) 30 °C, (b) 90 °C, (c) 120 °C, (d) 150 °C, (e) 180 °C, (f) 210 °C, (g) 250 °C, (h) gold blank.

A computer deconvolution of the O 1s spectrum (30–120 °C) reveals an approximate 5:1 area ratio for the main band and the high binding energy shoulder, consistent with the monohydrate stoichiometry of Chl a·H₂O.^{2,13,14} The sample chlorophyll after heat treatment at 250 °C was redissolved in diethyl ether. The absorption spectrum of this solution had maxima at 428.2 and 660.2 nm reproducing those expected of pure Chl a solutions in ether.^{2a} However, a blue-red peak absorbancy ratio of 3.2 (instead of the corresponding value 1.29 ± 0.01 observed^{2a} for the sample prior to the heat treatment) was obtained. In addition, an onset at 380 nm of a pronounced absorption edge (absent in the case of pure Chl a) into the near-uv region was also found. These optical measurements are indicative of probable Chl a degradation as a result of the dehydration of the tightly bound² water of hydration.^{6,7} We believe the present determination to be the first direct spectroscopic observation of the water of hydration bound to Chl a. Earlier conclusions of the stoichiometric formulas for Chl

a-H₂O complexes had been derived from optical measurements interpreted in terms of an equilibration of multiple Chl a-Chl a and Chl a-H₂O aggregates.^{2,15}

Acknowledgment. The above work was supported by the National Science Foundation (Grant Nos. BMS7411919 and GP37017X).

References and Notes

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- (3) (a) Recent developments have been summarized in F. K. Fong, "Theory of Molecular Relaxation: Applications in Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1975, Chapter 9. (b) The history of the question of Chl a-H₂O complexes and their role in photosynthesis can be traced to a 1931 article: K. Shibata, "Carbon and Nitrogen Assimilation", translated by H. Gest and R. K. Togasaki, Japan Science Press, 1975, pp 74–76.
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- (6) The "tightly bound" water refers to the remaining water of hydration as the dihydrate Chl a·2H₂O loses one H₂O molecule to yield the corresponding monohydrate.² It appears reasonable to suppose that the tightly bound water molecule plays a role in the stabilization of the five-coordinated Mg atom in Chl a-H₂O, and that the removal of this water may be concomitant to degradation of the chlorophyll molecule.⁷
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- (13) The neglect to recognize the presence of the tightly bound water of hydration by several earlier workers had led to the notion that Chl a could be prepared in an anhydrous state upon heat treatment at 80 °C under vacuum. For a review of Chl a-H₂O interactions, see ref 3a, pp 284–297.
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Received December 22, 1975

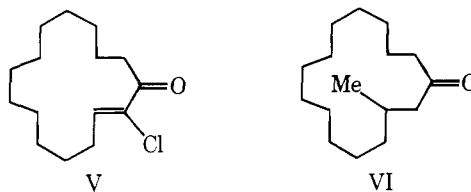
Additions and Corrections

A Synthesis of *d,l*-Muscone from Cyclododecanone [*J. Am. Chem. Soc.*, **97**, 1264 (1975)]. By GILBERT STORK* and T. L. MACDONALD, Department of Chemistry, Columbia University, New York, New York 10027.

On page 1264, line 2, instead of muscone (V), read muscone (VI).

On page 1265, line 9, instead of δ 4.42 quintet, $J = 7.0$ Hz, 1 H, read NMR δ 4.35 t, $J = 7.0$ Hz, 0.8 H (cis isomer), 4.58 t, $J = 7.0$ Hz, 0.2 H (trans isomer).

Structures V and VI should be:



Reference 2: Instead of 6.18 (m, 1 H), read 6.18 (d, $J = 15.5$ Hz, 1 H). Instead of "the β,γ isomer", read the (cis and trans) β,γ isomer.