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COMMENTS ON "CONTRIBUTION TO THE PROBLEM OF CAROTINOID FUNCTION IN PHOTOSYNTHESIS"

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ABSTRACT

The suggestion is made and the evidence adduced that carotinoids function to transport or convert the energy absorbed by chlorophyll.

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In the foregoing article[1] some observations are described on the photosynthetic bacterium Rhodopseudomonas spheroides and some of its mutants which indicate quite clearly that the presence of visibly colored carotinoid within the cell prevents the killing of the cell when it is exposed simultaneously to oxygen and light and that this killing is produced by light adsorbed by the bacteriochlorophyll in the absence of colored carotinoid. It may be associated with a similar phenomenon described for carotinoid-deficient mutants of Chlorella.[2] For the latter, however, the requirement of the presence of oxygen for the photokilling of the cell has not yet been demonstrated, although it seems likely that it will be.

The suggestion is made therein that this "protective action" of the carotinoid may represent a significant primary positive biological function of the carotinoid which has survival value and therefore, by implication, was and is a variable upon which evolutionary selection was based. When an attempt is made to formulate the molecular basis for this phenomenon (protection against photooxidative destruction), a somewhat different point of view regarding the reasons for its existence presents itself.

If one interprets the phenomenon in terms of an ability or function of the carotinoid to remove the 25 to 40 kcal of excitation energy from the chlorophyll in some useful way prior to its use in the activation of some oxidation reaction by molecular oxygen, the protective action arises as an incidental result. Photosensitized oxidations by molecular oxygen and dyestuffs of the type of chlorophyll and by chlorophyll itself, in fact, are very well known. The photosensitized oxidation of thiourea by chlorophyll has indeed been used in actinometry and the more general photosensitized oxidation of a large variety of unsaturated compounds by molecular oxygen has been studied in some detail.

The mechanism for this sensitized oxidation, as formulated by Schenck[3,4] has been used by others[5,6] to account for a variety of photooxidations sensitized by porphyrins, involves the transition of the first excited singlet state of the porphyrin into a long-lived (longer than 10^{-3} second) triplet state of the porphyrin.[7,8,9] This triplet state, then, is presumed to combine with the

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1 R. Y. Stanier et al., Nature
2 H. Claes, Z. Naturforsch 9b, 461 (1954)
3 G. O. Schenck, Ann. 584, No. 2/3, 125-238 (1953)
4 G. O. Schenck, Die Naturwissenschaften 19, 452 (1954)
5 J. A. Barltrop, P. M. Hayes, and M. Calvin, J. Am. Chem. Soc. 76, 4348 (1954)
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7 G. N. Lewis and M. Calvin, J. Am. Chem. Soc. 67, 1232 (1954)
8 G. D. Dorough and M. Calvin, Science 105, 433 (1947); J. Am. Chem. Soc. 70, 699 (1948)
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paramagnetic oxygen molecule to form a reactive peroxide.[3] The reactive peroxide can then transfer its oxygen to a suitable reductant, leaving the sensitizer to return to its original ground state. Such reductants have been substances such as ascaridol, etc.,[2] and other oxidizable materials such as the thioctic acid disulfide.[5]

There is evidence that precisely such a process of absorption and transition to a long-lived (longer than 10^{-2} second) state by chlorophyll takes place in the plastids of photosynthetic organisms.[10, 11, 12] If the carotinoid were to play a part in the transport or transformation of the energy from this state so that in the absence of carotinoids this state would have a greater probability of active peroxide formation in the presence of molecular oxygen, the phenomena above described would be expected to follow. Indeed, evidence for the likelihood of such a function for the carotinoid is also found in another observation described in the previous paper.[1] This is the great reduction amounting almost to the disappearance of the absorption bands at 8000 and 8550 Å from the mutant lacking colored carotinoid without any concomitant change in the porphyrin composition of the cell to which this might be attributed. As suggested in the previous manuscript, the disappearance of these absorption bands appears to be due to some change in the geometry of the plastids. More specifically, we would suggest that this absorption band is associated with the existence of a pi-complex between the carotinoid and the chlorophyll, models for which are to be found in the several systems that have been described by Scheibe[13] over the past twenty years. Such an interaction would indicate a close coupling between the electronic systems of the two molecules and provide a very effective pathway for energy transport or transformation. That such a transfer may take place in the reverse direction was demonstrated by the observation of chlorophyll fluorescence induced by carotinoid light absorption.[14]

In this view the "normal" function of the carotinoid would be in one of the following steps: (a) in the conversion of the long-lived electronic chlorophyll excitation into reducing and oxidizing agents (electrons and holes);*, [10] (b) in the succeeding separation of these agents by a process of conduction in the conjugate chain; or (c) as a coenzyme in the conversion of the initially formed oxidant (to oxygen in the green plant or to oxidize the hydrogen donor in the photosynthetic bacteria). In performing any of these energetically useful functions it would, of course, inhibit the photosensitized oxidation of such essential sensitive cell constituents as disulfides and mercaptans. An apparently alternative mechanism for the "protection" would be for the carotinoid to act as "most favored" oxygen acceptor from the reactive peroxide. This would require a

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10 D. F. Bradley and M. Calvin, Proc. Nat. Acad. Sci. (submitted).

11 J. A. Bassham and M. Calvin, University of California Radiation Laboratory Report No. UCRL-2853. Paper on "Photosynthesis" for Currents in Biochemical Research. Vol. II, Interscience Publishers, in press.

12 H. T. Witt, Z. Physik. Chem. 4, 120 (1955).

13 G. Scheibe, Z. Elektrochem. 52, 283 (1948).

14 E. C. Wassink and J. A. H. Kersten, Enzymologia 11, 782 (1945).

* It is not unlikely that the extra absorption bands mentioned in the previous paragraph are charge-transfer spectra related to this process.

a reductive process for the regeneration of carotinoid and it might even be an energy-yielding process, in which case it would correspond to the third possibility mentioned above.

Since all of these functions would be considered essential steps in the ability of a cell to use light energy for growth, it is necessary to recognize the requirement for something able to perform these functions, albeit less efficiently, in the case of the anaerobic photosynthetic growth of the blue-green mutant. This may be the less conjugated phytoene, or some other as yet unrecognized cell constituent.

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