acids, and cell membranes are also damaged in photo-
dynamic action, carotenoids also protect against these
effects, presumably by the same mechanism.

The behavior of these carotenoids in triplet MB
quenching also serves to explain the fact that shorter
carotenoid chains are effective in protecting against
anaerobic chlorophyll photoreduction, since triplet
carotenoids a is probably intermediate in this reaction,
and quenching of this triplet is effective even with
carotenoids of only 5 conjugated double bonds.

The implications of these observations for the mech-
anism of singlet oxygen quenching by carotenoids
are discussed in the accompanying communication.6

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Chemistry of Singlet Oxygen. XI. Cis—Trans
Isomerization of Carotenoids by Singlet Oxygen and a
Probable Quenching Mechanism

Sir:

Numerous reports of cis—trans isomerization of carot-
enoids by direct or sensitized irradiation have ap-
peared.2 The isomerization of carotenoids sensitized
by chlorophyll a appears to occur only in the direc-
tion cis → trans.2,3 We now report that isomerization
of 15,15′-cis-β-carotene (1) is sensitized by singlet oxy-
gen (1/2), as well as by triplet methylene blue (3MB)
with high efficiency. The product is, at least largely,
all-trans-β-carotene (2). Under the same conditions, 2
does not appear to undergo appreciable isomerization.

The apparatus and conditions used are similar to
those used for the quenching experiments, except
that 2-methyl-2-pentene was omitted from most ex-
periments (having been found not to affect the results),
and that changes in carotenoid composition were
monitored by absorption spectroscopy.5 All-trans-β-
carotene has strong (~114,000) absorption at 464 nm
and only weak (~7500) absorption at 345 nm; 15,15′-
cis-β-carotene has weaker absorption at 456 nm (~85,000) but much stronger absorption at 345 nm (~49,400); this latter absorption is referred to as the
“cis peak” and is much stronger for the symmetrical
15,15′-cis isomer than for other cis-carotenes.7,8

Solutions of 1 and methylene blue (MB) were ir-
adiated under O2 through a filter1 which ensured
that light was absorbed only by MB. The results are summarized in Table I, and show a rapid decrease
in the “cis peak” and a simultaneous increase in ab-
sorbance at 464 nm. The results are consistent with a
clean isomerization 1 → 2; the absorbance at 464 nm
calculated from the decrease at 345 nm on the
assumption that no other reaction occurs is in excellent
agreement with the observed values. Reaction under
N2 was equally rapid, but no reaction whatever oc-
curred under O2 without MB.

The carotene was isolated (in 80% yield) from an
isomerization run under the conditions of the quenching
experiments1 (containing 2-methyl-2-pentene) by Ca-
(OH)2 chromatography, and was found to be pure
all-trans-β-carotene by melting point and mixture melt-
ing point, Rf, uv-visible spectrum, and ir spectrum
(absence of cis band5 at 772 cm−1). Other cis isomers
were shown to be absent by tlc (isomerization of
2 with I2 produces a mixture which contains several
other cis isomers which are readily separable by chro-
matography7). Similar experiments using all-trans-β-
carotene gave no isomerization. From the amount
of 2-methyl-2-pentene peroxide produced in photo-
oxidation experiments1,4 and the rate of isomeriza-
tion, it can be calculated that each singlet oxygen
molecule produced causes isomerization of slightly less
than one molecule of 1 to 2.

A similar series of experiments was carried out
using O2 generated from NaOCl—H2O2 in CaH2:
CH3OH:diglyme (1:1:1); all experiments were car-
ried out in darkness to avoid photosomeration of
carotenoids. As in the photochemical experiments, 1
underwent smooth isomerization to the all-trans iso-
mer (identified as above), but 2 was not isomerized
detectably under identical conditions. No isomeriza-
tion of 1 occurred on addition of spent reagents nor
of H2O2 alone. The initial efficiency of isomerization

Table I. Absorbance of a Solution of 15,15′-cis-β-Carotene
and Methylene Blue

<table>
<thead>
<tr>
<th>Irradiation time, sec</th>
<th>Absorbance</th>
<th>Isomerization, %</th>
<th>A464 cm−1, calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.68</td>
<td>1.39</td>
<td>1.40</td>
</tr>
<tr>
<td>3</td>
<td>0.49</td>
<td>1.54</td>
<td>1.53</td>
</tr>
<tr>
<td>6</td>
<td>0.39</td>
<td>1.66</td>
<td>1.60</td>
</tr>
<tr>
<td>9</td>
<td>0.28</td>
<td>1.70</td>
<td>1.68</td>
</tr>
<tr>
<td>12</td>
<td>0.19</td>
<td>1.77</td>
<td>1.74</td>
</tr>
</tbody>
</table>

1 1.57 × 10−4 M. 4 × 10−3 M. 1 In CaH2:CH3OH (80:20);
irradiated through K2Cr2O7 filter; see ref 1. 4 Calculated from de-
crease in absorbance at 345 nm. 5 Calculated on assumption that reaction 1 → 2 is quantitative.
of 1 (moles of 1 isomerized/moles of \( \text{O}_2 \) generated\(^9\)) was 36\%. An attempt to measure the singlet \( \text{O}_2 \) quenching rate of 1 failed because complete isomerization to 2 occurred before sufficient product was formed from 2-methyl-2-pentene to be detected accurately by the usual techniques. The overall quenching rate measured in these runs agreed well with that previously determined for all-trans-\( \beta \)-carotene.

These results and those in the accompanying communication\(^1\) support the mechanism suggested\(^4\) for carotene quenching of singlet oxygen, in which energy transfer from \( \text{O}_2 \) to the carotene occurs, as shown below.

\[
\begin{align*}
\text{3MB} & \xrightarrow{k_{\text{O}_2}} \text{carotene} \\
& \quad \xrightarrow{A} \text{all-trans-\( \beta \)-carotene (2)}
\end{align*}
\]

In this scheme, all terms have the previous meaning: \(^1\) carotene is either cis- or trans-\( \beta \)-carotene, and \( \text{3carotene} \) is a carotene triplet. Radiationless decay processes for \( \text{3MB} \) and \( \text{O}_2 \) do not compete under these conditions and are omitted for clarity. \( \beta \)-Carotene must collapse largely to all trans-\( \beta \)-carotene, whether formed from 1 or 2 initially.

The presence or absence of \( \text{O}_2 \) was found not to affect the rate of photochemical isomerization, which is consistent with the above scheme since \( k_{\text{O}_2}[\text{car}] \gg k_{\text{A}}[\text{A}] \). On the other hand, if isomerization were caused only by \( \text{3MB} \), \( \text{O}_2 \) would inhibit the reaction whereas if \( \text{O}_2 \) were the sole cause, isomerization would not occur under \( \text{N}_2 \).\(^\text{10}\) In \( \text{O}_2 \) saturated solutions, isomerization occurs entirely by way of \( \text{O}_2 \), since \( k_{\text{O}_2}[\text{car}] \ll k_{\text{O}_2}[\text{car}] \).

The dependence of quenching rate on the length of the conjugated chain\(^1\) is consistent with the above scheme if the compounds with 5 and 7 double bonds have triplet energies above 22 kcal (the energy of \( \Delta_{\text{car}} \)) but below that of methylene blue. The triplet energy of the 9-double bond carotenoid would be near 22 kcal, and that of \( \beta \)-carotene (11 \( \text{C}=\text{C} \)) would be lower. No reliable energy data for any of these compounds are available.\(^1\)

Alternative mechanisms are not ruled out. For example, reversible electron transfer from carotene to \( \text{O}_2 \) could accommodate both the isomerization results and the chain-length dependence. Such mechanisms are well established for quenching,\(^\text{13}\) and the ionization potential of carotenoids should increase with decreasing conjugation, so that the rate should drop off, though perhaps not so sharply; furthermore, the carotene radical cation should isomerize relatively easily (although one might expect it to undergo other reactions as well). However, the energy-transfer mechanism seems more satisfactory.

The quenching of \( \text{O}_2 \) by carotenes not only explains at least part of the protective action of carotenes in natural systems, but also implicates singlet oxygen as a causative agent in photodynamic action, though probably not the sole one.

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Conformational Aspects of Polypeptide Structure.

XXXI. Helical Poly[(S)-thiazolidine-4-carboxylic acid] and Poly[(S)-oxazolidine-4-carboxylic acid].

Theoretical Results

Sir:

Conformational analysis of polypeptides has proven to be extremely useful in confirming and predicting ordered structures for isolated polymer chains.\(^1\)-\(^3\) We have calculated the structure for poly[(S)-thiazolidine-4-carboxylic acid], and believe that this polypeptide assumes a helical conformation. The structural relationship of this peptide to poly-L-proline is clear (Figure 1).

![Figure 1](image_url)

Another related polypeptide, namely, poly[(S)-oxazolidine-4-carboxylic acid], is also under investigation in our laboratory. Although we have not succeeded in

(1) (a) R. A. Scott and H. A. Scheraga, J. Chem. Phys., 45, 2091 (1966); (b) ibid., 46, 4410 (1967).
(2) G. N. Ramachandran and C. M. Venkatachalam, Biopolymers, 6, 1255 (1968).