The Effect of Sensitizing Dyes for Photo as Antioxidants on the Autoxidation of Methyl Linoleate

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ABSTRACT

The sensitizing dyes for photo which are cyanine homologues have been used as medicine and cosmetics. Their uses are widespread. The authors expected that these dyes might serve as antioxidants by a radical termination mechanism such as hydroperoxy radicals added to the many conjugated double bonds which exist in the dyes. Determination of the induction period by the weighing method confirmed that some sensitizing dyes for photo are available as antioxidants in the autoxidation of methyl linoleate. Therefore, these dyes may serve as new types of antioxidants.

INTRODUCTION

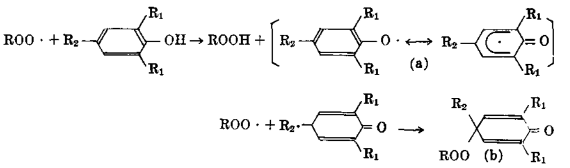
The autoxidation of lipids proceeds through the following chain reactions:

$$RH + O_2 \rightarrow R^\bullet + {}^\bullet OOH \qquad [1]$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad [2]$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \qquad [3]$$

where RH is a substrate. The first is the chain initiation reaction, and the second and third are the chain propagation steps. Thus ROOH is formed by the autocatalytic reaction of the trace of ROO• (1). The reaction mechanism of phenolic antioxidants in the autoxidation of lipids is as follows (2-4):



[4]

[5]

The phenoxy radical, formed from the phenol by donating its hydrogen atom to the hydroperoxy radical, is stabilized by such resonance structures as (a). Therefore, such a phenoxy radical cannot feasibly work as a chain initiator. This phenoxy radical is terminated by the attack of the hydroperoxy radical to form stable compounds (b).

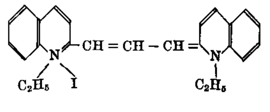
The sensitizing dyes for photo have many conjugated double bonds. If the hydroperoxy radicals add to these conjugated double bonds to form radicals, they may be stabilized by the resonance effect of the remaining conjugated double bonds. Thus the occurrence of the chain reactions [2] and [3] are unlikely to occur. With the expectation mentioned above, the sensitizing dyes for photo, which are cyanine homologues, were used as antioxidants in the autoxidation of methyl linoleate. The induction period in this autoxidation was determined by the weighing method. The reaction mechanism is then discussed.

EXPERIMENTAL PROCEDURE

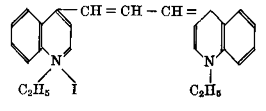
Sample

Preparation of Methyl Cis-9, Cis-12-Octadecadienoate (Methyl Linoleate) (5). Methyl linoleate was prepared by treating safflower oil fatty acid with methanol containing sulfuric acid,and by fractionating the obtained esters by the urea-adduct formation. Methyl linoleate, having a purity of 99% by gas liquid chromatography, was prepared in this manner. It was confirmed that this samples is free from natural antioxidants (6). The following are sensitizing dyes for photo as antioxidants: 1,1′-Diethyl-2,2′-quinocarbocyanine iodide (A), 1,1′-diethyl-4,4′-quinocarbocyanine iodide (B), 1,1′-di-n-butyl-4,4′-quinocarbocyanine iodide (C), 1,1′-di-isopentyl-4,4′-quinocarbocyanine iodide (D), 1,1′-di-isopropyl-4,4′-quinocarbocyanine iodide (E), 3,3′-diethyl-9-methyl-2,2′-thia carbocyanine iodide (F), 1,3,3,1′,3′,3′-hexamethyl-2,2′-indocarbocyanine iodide (G), 1,1′-dimethyl-11-bromo-2,2′-quinodicarbocyanine iodide (H), 1,1′-diethyl-2,2′-quinotricarbocyanine iodide (I), 1,1′-diethyl-4,4′-quinotricarbocyanine iodide (J), 3,3′-diethyl-2,2′-thiatricarbocyanine iodide (K), 1,1′-di-n-octyl-4,4′-quinocarbocyanine iodide (L), 1,1′-di-n-heptyl-2,2′-quinocarbocyanine iodide (M), 1,1′-diethyl-4,4′-quinocarbocyanine tosilate (N), 1,1′-di-*n*-heptyl-2,2′-quinotricarbocyanine iodide (O), 1,1′-di-*n*-heptyl-4,4′-quinotricarbocyanine iodide (P), 3,3′-diethyl-2,2′-selena carbocyanine iodide (Q), 3,3′,9-triethyl-2,2′-thiacarbocyanine iodide (R), 1,1′-diethyl-4,4′-quinodicarbocyanine iodide (S), 1,1′-diethyl-11-chloro-2,2′-quinodicarbocyanine chloride (T), and 1,1′-diethyl-11-chloro-4,4′-quinocarbocyanine tosilate (U). The constitutional formulas for A, B, I, J, M, O and P follow:

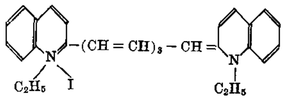
(A)



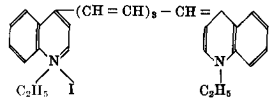
(B)



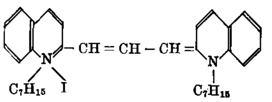
(I)



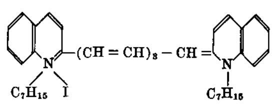
(J)



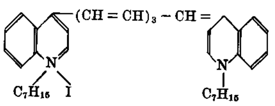
(M)



(O)



(P)



The data for the elementary analysis for these dyes almost agree with the theoretical values. These products were supplied by the Sensitizing Dye for Photo Research Institute in Japan and used as antioxidants.

Autoxidation of Methyl Linoleate and the Sample Containing the Sensitizing Dye for Photo as the Antioxidant

The autoxidation procedure was carried out as described in the preceding paper (5). In this study, each samples was mixed with 0.01, 0.05, or 0.1 wt % sensitizing dye for photo as the antioxidant (7,8).

Determination

The weight increase in the autoxidation of the samples was measured by the weighing procedure, which is the most

TABLE I

Effect of Sensitizing Dyes for Photo on the Induction Period in the Autoxidation of Methyl Linoleate

Sensitizing dyes for photo	0.01%		0.05%		0.10%	
	Induction period, hr	Effect, ratio[a]	Induction period, hr	Effect, ratio[a]	Induction period, hr	Effect, ratio[a]
A	210	6.0	230	6.6	250	7.1
B	230	6.6	240	6.9	310	8.9
C	170	4.9	200	5.7	220	6.3
D	190	5.4	240	6.9	300	8.6
E	190	5.4	220	6.3	240	6.9
F	31	0.9	220	6.3	270	7.7
G	19	0.5	60	1.7	80	2.3
H	220	6.3	230	6.6	270	7.7
I	210	6.0	240	6.9	360	10.3
J	250	7.1	260	7.4	450	12.9
K	220	6.3	230	6.6	330	9.4
L	190	5.4	260	7.4	320	9.1
M	140	4.0	180	5.1	220	6.3
N	150	4.3	220	6.3	240	6.9
O	200	5.7	210	6.0	240	6.9
P	220	6.3	350	10.0	560	16.0
Q	25	0.7	69	2.0	96	2.7
R	37	1.1	62	1.8	90	2.6
S	220	6.3	240	6.9	370	10.6
T	180	5.1	190	5.4	210	6.0
U	240	6.9	280	8.0	320	9.1
Control	35	1.0	------	------	------	------
BHT	290	8.3	------	------	------	------

[a] Ratio of the induction period of the sample containing the sensitizing dye for photo to that of the control.

convenient method for estimating autoxidation (7,8). In this paper, the weight gain chosen as the end of the induction period was 10 mg/1.5 g as in the preceeding paper (5). IR spectra were recorded on a usual NaCl prism type, Schimazu spectrometer Model IR-27B (cell 0.1 mm or 10 mm NaCl; solvent, carbon tetrachloride, carbon disulfide). Peroxide value (m.eq./kg) were estimated by the iodometry (9). Conjugated *cis, trans* and *trans, trans* dienes contents were calculated from the IR spectra (10).

TABLE II

Conjugated Diene Contents for the Samples (Containing Sensitizing Dyes for Photo)[a] Gaining Weight, 10 mg/1.5 g, and That (Containing BHT)[a] Gaining the Same Weight

Sensitizing dyes for photo	*Cis, trans* conjugated diene, %	*Trans, trans* conjugated diene, %	Ratio[b]
A	2	1	2
B	3	4	1
C	8	3	3
D	2	4	1
E	2	7	0
F	6	4	2
G	5	4	1
H	2	2	1
I	1	3	0
J	2	3	1
K	5	3	2
L	3	4	1
M	2	3	1
N	3	3	1
O	8	3	3
P	5	3	2
Q	7	3	2
R	3	2	2
S	4	2	2
T	6	3	2
U	4	3	1
BHT	6	1	6

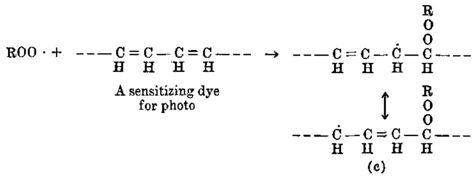
[a] 0.01 wt %.

[b] Radio of *cis, trans* conjugated diene per cent to *trans, trans* conjugated diene per cent.

RESULTS AND DISCUSSION

The autoxidation induction period was determined for methyl linoleate and for each sample containing the sensitizing dye for photo as the antioxidant. These results are shown in Table I. The sensitizing dyes for photo used in this study are not all as effective as the antioxidant. Some of them indicated an ability to be the prooxidant, e.g., the dyes, F, G and Q acted as the prooxidant. This is explained as follows: (a) The more conjugated double bonds the dyes have, the more effective they are as an antioxidant. In the dyes which have similar compositions but differ from each other in the unsaturated hydrocarbon side chain length, the longer the side chain they have, the more effective they are, that is, J or O is superior to B or M, respectively. (b) The sensitizing dyes for photo as the antioxidant, which have a normal unsaturated hydrocarbon side chain on the 4 position, are superior to those which have it on the 2 position. For example, B, J or P is superior to A, I or O, respectively. As the autoxidation proceeds, the color of the sensitizing dyes for photo becomes lighter and then disappears. When 0.01 wt % of the sensitizing dye for photo was added to methyl linoleate, the amount of the dye consumed in the autoxidation was estimated by its visible spectra. In the samples gaining 10 mg/1.5 g at the end point of the induction period, 77-100% of the dye was consumed.

Therefore, in reaction [2], ROO• may add to the sensitizing dye for photo as follows:

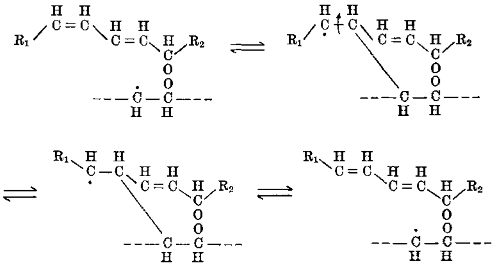


[6]

The radical (c) may be stabilized by the resonance effect of the remaining conjugated double bonds extending to the heterocyclic ring. Thus the chain reactions [2] and [3] are inhibited. This new type of mechanism for the antioxidant may reasonably explain the phenomena (a) and (b), mentioned above, through a resonance effect or steric hindrances. Therefore, such sensitizing dyes for photo, which have many conjugated double bonds in the normal unsaturated hydrocarbon side chain and have little steric hindrances, may be effective as the antioxidant. In the range of 0.01-0.1 wt %, the larger the amount of dye added to the sample, the more effective it is as the antioxidant. On the addition of 0.05 or 0.1 wt % of the dye, the greater part is not soluble but disperses in the substrate. As the autoxidation proceeds, the precipitated dye begins to dissolve into the substrate.

Peroxide values for the control and sample (v) (containing butylated hydroxytoluene, BHT) gaining 10 mg/1.5 g weight were 5.0 x 10^2 and 4.8 x 10^2 (m.eq./kg.), respectively, but those for samples (w) (containing the dyes) gaining the same weight were generally somewhat larger than the above values. For example, the value for O is 7.7 x 10^2. After the determination of the peroxide values, the lipids were extracted with ether. IR spectra for these lipids were determined to estimate the OH group, using 10 mm NaCl cell (11). The OH band in the lipid from samples (v) was stronger than that from (w). This fact suggests the following reactions: in the control and the sample (v), ROOH converts to ROH through the iodometric measurement, but in the samples (w), ROOH may at least partly convert to RH.

IR spectra for samples (w) and gaining weight 10 mg/1.5 g in the early stage of the autoxidation were similar to each other but different from those for samples (v). Generally, samples (w) had a lower ratio of *cis, trans* conjugated diene to *trans, trans* than samples (v), as shown in Table II. The reason why the large amount of *trans, trans* conjugated diene exists in samples (w) may be found in the following reaction (12).



[7]

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