Participation of Singlet Oxygen in Photosensitized Oxidation of 1,4-Dienoic Systems and Photooxidation of Soybean Oil[1]

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ABSTRACT

Sensitized photooxidation of a model 1,4-diene, 4*cis*,7*cis*-undecadiene, was shown to yield 4-hydroperoxy-5*trans*,7*cis*-undecadiene and 5-hydroperoxy-3*trans*,7*cis*-undecadiene as initial products. Further irradiation (in the presence of the sensitizer) caused the isomerization of 4-hydroperoxy-5*trans*,7*cis*-undecadiene to 4-hydroperoxy-5*trans*,7*trans*-undecadiene. Oxidation of 4*cis*,7*cis*-undecadiene with chemically formed singlet oxygen gave the same initial products as the photosensitized oxidation. 5-Hydroperoxy-3*trans*,7*cis*-undecadiene is, however, not formed in the radical autoxidation of the diene. It is concluded that singlet oxygen is the reactive intermediate in the photooxidation. Comparison with this model reaction suggests that the photooxidation of refined soybean oil in propanol also proceeds via singlet oxygen: the photooxidations of both 4,7-undecadiene and soybean oil are inhibited by β-carotene and by triethylamine, but unlike radical chain autoxidation, they are not inhibited by 2,6-di-*t*-butyl-4-methylphenol. Also soybean oil can act as a sensitizer for the photooxidation of 4,7-undecadiene. Chlorophyl-like sensitizers are probably unimportant in the well refined soybean oil used in this work. The observed photooxidation of the skipped dienoic components of soybean oil, which is probably due to some other, unidentified sensitizer(s), absorbing below 500 nm, can be avoided by using a yellow filter.

INTRODUCTION

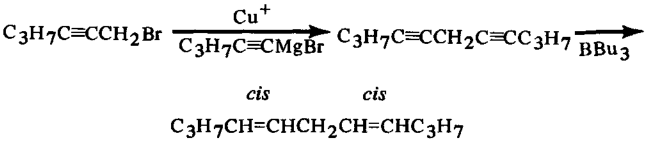
The effect of light has long been known to play a role in the flavor stability of vegetable oils (1), and other unsaturated fats and fat-containing products such as margarine (2), butter (3) and mayonnaise (4). The obvious solution of excluding light (5) is often not employed for marketing or economic reasons. Weak inhibition of photooxidative deterioration by phenolic or other inhibitors has been reported (5), but the effect of light cannot be eliminated. Thus the mechanism of photooxidation of fats and its inhibition remains a subject of current interest. One possible type of mechanism involves the catalysis of photooxidation by small quantities of pigments which absorb the incident light. Indeed it has long been known that small quantities of chlorophyl, derivatives of which are sometimes present in refined oils, can act as a sensitizer for fat and fatty acid oxidation (6).

After the discoveries of Foote and coworkers (7,8), who have shown that singlet oxygen is the intermediate in the dye-sensitized photooxidation of a number of monoenoic and dienoic compounds, both Khan (9) and Rawls and Van Santen (10) have presented evidence for the participation of singlet oxygen in the sensitized photooxidation of linoleic and oleic acids. In the present investigation, it was decided to first study in detail the photosensitized oxidation of a simple model system, and to confirm the participation of singlet oxygen, before examining the possibility that it might play a role in the more complicated photooxidation of oils. A 1,4-diene system was selected because of Rawls' observation that linoleic acid reacted much faster than oleic acid. A symmetrical compound, 4*cis*,7*cis*-undecadiene, was chosen to minimize the total number of photooxidation products.

METHODS AND RESULTS

Preparation of 4*cis*,7*cis*-Undecadiene

4*cis*,7*cis*-Undecadiene was prepared as shown:



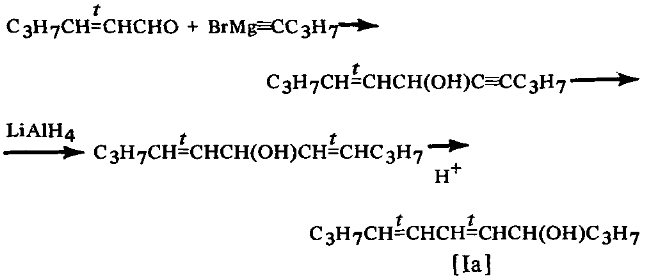
$$C_3H_7C{\equiv}CCH_2Br \xrightarrow[C_3H_7C\equiv CMgBr]{Cu^+} C_3H_7C{\equiv}CCH_2C{\equiv}CC_3H_7 \xrightarrow[BBu_3]{} C_3H_7\overset{cis}{CH{=}CH}CH_2\overset{cis}{CH{=}CH}C_3H_7$$

The use of tri-*n*-butyl boron for the reduction of the undecadiyne was found to yield a purer product than that obtained with the catalyst of Lindlar and Dubois (11) or with disiamylborane (12).

Photosensitized Oxidation of 4*cis*,7*cis*-Undecadiene

Photosensitized oxidations of this model diene were carried out with low dilutions (⩽0.05 M) in methanol. The reaction mixtures were irradiated with light of wavelengths greater than 330 nm to avoid light-induced hydroperoxide decomposition (13). Under these conditions no radical autoxidation was observed, even after the initial formation of hydroperoxide. If the light was switched off, oxidation ceased immediately.

With rose-bengal (7) as sensitizer, a mixture of unsaturated hydroperoxides was formed. This mixture was reduced with trimethylphosphite, and the resulting undecadienol mixture (54% isolated yield) hydrogenated to give a mixture of 4- and 5-undecanols, which were identified by comparison of the mass spectra with those of authentic alcohols. These results established the positions of the hydroperoxy group in the hydroperoxides originally formed. The two major components of the undecadienol mixture were isolated by preparative gas liquid chromatography (GLC) and identified as 4-hydroxy-5*trans*,7*trans*-undecadiene (Ia) and 5-hydroxy-3*trans*,7*cis*-undecadiene (II) by comparison (GLC retention time, NMR, IR and UV spectra) with authentic standards prepared by the following routes, using well established types of reactions:



$$C_3H_7CH\overset{t}{=}CHCHO + BrMg{\equiv}CC_3H_7 \longrightarrow C_3H_7CH\overset{t}{=}CHCH(OH)C{\equiv}CC_3H_7 \xrightarrow{LiAlH_4} C_3H_7CH\overset{t}{=}CHCH(OH)CH\overset{t}{=}CHC_3H_7 \xrightarrow[H^+]{} C_3H_7CH\overset{t}{=}CHCH\overset{t}{=}CHCH(OH)C_3H_7$$

[Ia]

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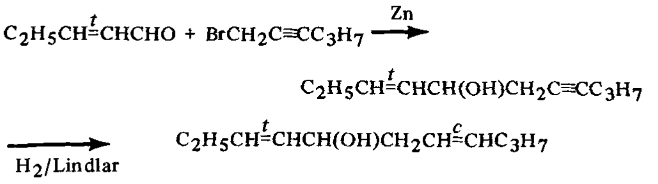
[1] Presented in part in the symposium "Oxidation Chemistry," New Chemical Society Meeting, Manchester, April 1972.



$$C_2H_5CH\overset{t}{=}CHCHO + BrCH_2C\equiv CC_3H_7 \xrightarrow{Zn} C_2H_5CH\overset{t}{=}CHCH(OH)CH_2C\equiv CC_3H_7 \xrightarrow[H_2/Lindlar]{} C_2H_5CH\overset{t}{=}CHCH(OH)CH_2CH\overset{c}{=}CHC_3H_7$$

[II]

The structures of all compounds formed during these preparations were confirmed by NMR (see Experimental Procedures).

Water-soluble "chlorophyl" (sodium chlorophillin) was also used as a sensitizer. The "chlorophyl"-sensitized photooxidation of 4,7-undecadiene carried out under the same conditions as the rose-bengal-sensitized reaction was shown to lead after reduction to a mixture of II and 4-hydroxy-5*trans*,7*cis*-undecadiene (Ib, identified by NMR). This result with "chlorophyl" prompted a reexamination of the rose-bengal-sensitized reaction, and it was found that in fact the initially formed *cis,trans*-hydroperoxide is slowly isomerized to the *trans,trans*-isomer (Table I).

Extended illumination times with "chlorophyl" as a sensitizer also caused this *cis*- to *trans*-isomerization. The isomerization could be carried out in the absence of oxygen and is presumably photosensitized (14).

When the *cis,cis*-undecadiene was oxidized with singlet oxygen, produced in situ by the reaction of hydrogen peroxide with sodium hypochlorite (7), the yields of oxidation products were extremely low (less than 1%). Using a 10-fold excess of singlet oxygen precursors, the reduced products were detectable with GLC. The alcohols II and Ib were found in a 40:60 ratio, which is very close to that observed initially in the photosensitized oxidation (Table I). Radical autoxidation, induced by bubbling oxygen through pure 4*cis*,7*cis*-undecadiene at room temperature for 1 day, gave after reduction the two isomeric conjugated alcohols Ia and Ib (identified by GLC), but no trace of II was detected.

Inhibition of Photosensitized Oxidation of 4*cis*,7*cis*-Undecadiene

The course of the sensitized photooxidation of 4*cis*,7*cis*-undecadiene was followed by UV measurements. Comparison with GLC results showed that during the initial stage of the reaction, the absorption at 234 nm (due to conjugated hydroperoxides) is proportional to the total yield of hydroperoxide, the ratio of conjugated to nonconjugated hydroperoxide remaining constant. At these low conversions, the photooxidation in the absence of inhibitor is linear with respect to the time (curve A, Fig. 1), as expected with either a singlet oxygen (16) or a nondegenerate radical chain reaction.

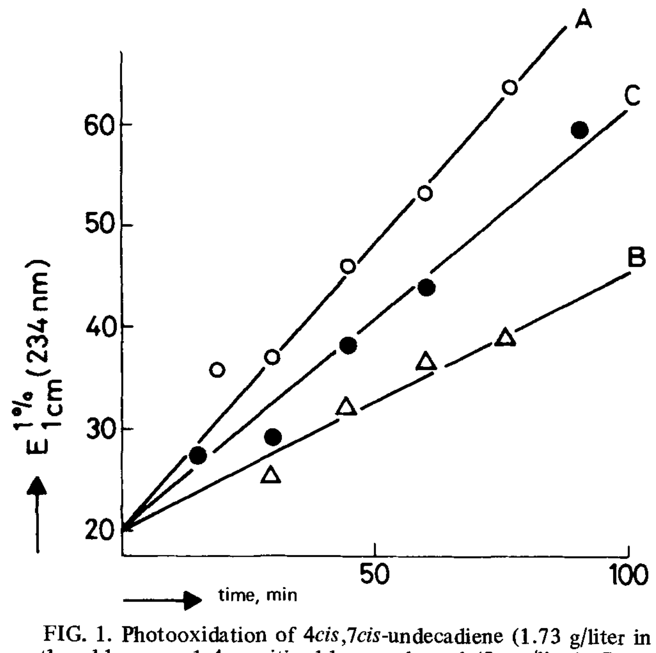


FIG. 1. Photooxidation of 4*cis*,7*cis*-undecadiene (1.73 g/liter in methanol-benzene 1:4 sensitized by rose-bengal (2 mg/liter). Curve A = in the absence of additives, B = in the presence of β-carotene (20 mg/liter), and C = in the presence of triethylamine (100 mg/liter).

The inhibiting effects of β-carotene and of triethylamine on the photooxidation of 4,7-undecadiene are also shown in Figure 1. These results agree with established inhibiting effects on singlet oxygen (14, 17-19). However 2,6-di-*t*-butyl-4-methyl phenol (BHT), a known autoxidation inhibitor, had no effect.

Photooxidation of Soybean Oil and Its Inhibition

Photosensitized oxidation of 4*cis*,7*cis*-undecadiene was still detectable after 5 hr of irradiation when sensitizer concentrations of 1 mg/liter rose-bengal in methanol or 10 mg/liter "chlorophyl" were used. These results suggest that singlet oxygen resulting from traces of sensitizers could be important in the photooxidative deterioration of oils and fats and related products. To establish whether singlet oxygen type oxidations could be observed in the photooxidation of a refined vegetable oil, soybean oil, which exhibits a particularly difficult stability problem, was subjected to photooxidation in propanol solution under conditions in which radical chain autoxidation was minimized. The photooxidation was followed by measuring the conjugated diene absorption in the UV, and was found to be linearly dependent on the time of exposure to light. While BHT had no effect on the reaction rate, β-carotene or triethylamine were observed to inhibit the reaction (Figs. 2-3).

The inhibition effects were confirmed by measurements of the peroxide values after 6 hr of photooxidation (Table II). Further, when a mixture of soybean oil and 4*cis*,7*cis*-undecadiene in propanol was photooxidized for 3 days, the GLC of the mixture, after reduction, showed (together with unidentified peaks) three peaks corresponding to the alcohols found in the rose-bengal-sensitized photooxidation of 4*cis*,7*cis*-undecadiene. The formation of the alcohol (II) can, as before, be rationalized only by a singlet oxygen mechanism and demonstrates that sensitizers are present in the soybean oil, which are able to produce singlet oxygen on photooxidation.

The nature of the major sensitizers in soybean oil was investigated by carrying out photooxidations with a yellow filter cutting off light with wavelength <500 nm. Such a filter virtually eliminates the photooxidation of the oil as such, indicating that the relevant absorption band of the sensitizer lies below this wavelength. The photooxidation induced by the addition of "chlorophyl" is, however, reduced but not eliminated by using this yellow filter (Table II and Fig. 4), which indicates that absorption of "chlorophyl" both below and above 500 nm leads to photosensitization.

EXPERIMENTAL PROCEDURES

NMR spectra (CCl_4) were carried out at 220 MHz and 13 C (Varian HR 220), or 60 MHz and 40 C (Varian A 60). δ-Values are in ppm from TMS. Decoupling experiments and measurements with the europium shift reagent Eu-$(DPM)_3$ were performed at 100 MHz and 30 C (Varian HA 100).

GLC analyses were carried out with a Type 409 Becker Multigraph apparatus (2 m x 4 mm column, 5% polyethyleneglycol adipate/gas-chrom Q, ex BDH). The same column was used for preparative GLC with a Becker cycloprep apparatus.

4,7-Undecadiyne: A procedure similar to that of Gensler and Mahadevan (20) for the preparation of 5,8-tridecadiyne was used for the synthesis of 4,7-undecadiyne, bp 99.5-103 C/15 mm; (89%) n^{24}_{D} 1.4628. Found: C, 89.00; H, 10.70. $C_{11}H_{16}$ requires: C, 89.10; H, 10.90. IR 1310 cm^{-1} (C≡C-CH$_2$).

4cis,7cis-Undecadiene: Reductions of monoalkynes were described by Hubert (21). All the operations were carried out in an atmosphere of dry oxygen-free nitrogen. 4,7-Undecadiyne (0.27 mol, 40.0 g) was added to tri-*n*-butyl boron (91.1 g, 0.5 mol prepared according to the method of Johnson et al. [22]), and the bath temperature of the rapidly stirred mixture was then raised as rapidly as possible from ca. 100 to 160 C. At 140 C, gas evolution suddenly began and 0.49 mol of butene was evolved, after which (ca. 1 hr) the unreacted tri-*n*-butyl boron and any diyne were distilled (bp 52 C/1 mm, 22.1 g) from the reaction mixture, to which acetic acid (40 g, 0.67 mol) was then added. The reaction mixture was stirred for ca. 2.5 hr at -10 to +8 C. Water (50 ml) was then added and the mixture extracted with hexane. The hexane extract was washed with water, dried ($MgSO_4$) and evaporated. Distillation of the residue gave 4*cis*,7*cis*-undecadiene, bp 80-81.5 C/16 mm, (purity [GLC] 99%), n^{22}_{D} 1.4415 (27.0 g, 66%). Found: C, 86.65; H, 13.04. $C_{11}H_{20}$ requires: C, 86.73; H, 13.27. IR 1650 (C=C nonconjugated), 705 cm^{-1} (CH=CH *cis*). NMR (60 MHz): δ 0.92, *t* (11,11-[CH$_3$]$_2$); 1.40, sextet (2,10-[CH$_2$]$_2$); 2.04, quartet (3,9-[CH$_2$]$_2$); 2.75, *t* (6-CH$_2$); 5.32, typical *cis* pattern (4,5,7,8-[olefinic H]$_4$).

Photooxidations: Photooxidations were carried out in a liquid-cooled "onion" apparatus similar to that described by Gollnick and Schenck (23), using a water-cooled Osram XBF1000 W2 (1,000 Watt) Xenon lamp. This lamp gives a continuous emission spectrum with a relative energy distribution which, in the UV region above 300 nm and in the visible region, is similar to that of daylight (24). Except where otherwise stated, the light was filtered through a 1 cm thick filter solution which cuts off the UV region below 340 nm. This solution was made up from 650 g NaBr.2 H_2O plus 3 g Pb $(NO_3)_2$ in 1 liter water. No problems were encountered due to decomposition of the filter solution (Rappoldt [25]).

Where stated, a yellow filter absorbing light below λ = 500 nm was used (30 g K_2CrO_4/liter). Solutions to be photooxidized were saturated with pure oxygen before the light was switched on, and the oxygen bubbled slowly through the solution during the reaction period so as to maintain saturation. The temperature of the cooling liquid was thermostatically controlled.

Photooxidation of 4cis,7cis-undecadiene: A solution of 4*cis*,7*cis*-undecadiene (3.86 g, 0.025 mol) in 500 ml methanol was photooxidized during 5 hr at 30 C in the presence of 50 mg rose-bengal. Evaporation of the methanol gave an oil (IR 860 [–O–O–], 3450 cm^{-1} [-OH]) which was taken up in ether and washed with water to remove the sensitizer. The ether extract was separated, dried ($MgSO_4$) and evaporated at reduced pressure. A few crystals of BHT were added (essential to avoid polymerization) and the mixture was dissolved in methanol. Trimethyl phosphite (4 g, 0.032 mol) in 50 ml methanol was then added dropwise to the stirred mixture over 1 hr (temperature between -5 and 0 C). Stirring was continued overnight at room temperature. The methanol was then evaporated and the residue dissolved in 50 ml ether. This ether solution was washed with water (3 x 10 ml), dried ($MgSO_4$) and evaporated. After addition of a few crystals of BHT, the residue was distilled to give a mixture of undecadienols, bp 68-75 C/0.5 mm (2.5 g, 54%).

The separation and identification of the two major components (Ia and II) of the undecadienol mixture are given under Methods and Results. Spectral data are given

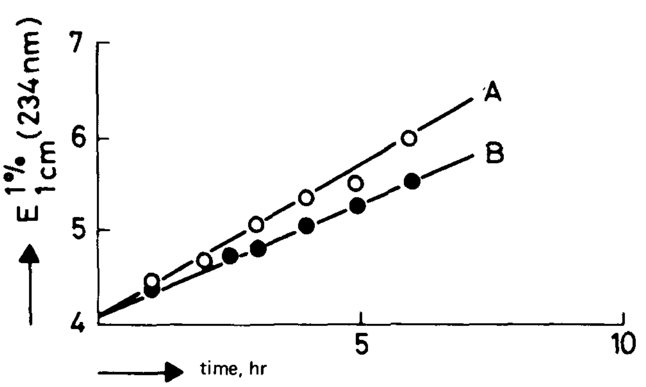


FIG. 2. Photooxidation of soybean oil (17.4 g/liter in propanol) in the presence of β-carotene (A = 0 mg/liter, B = 0.46 mg/liter).

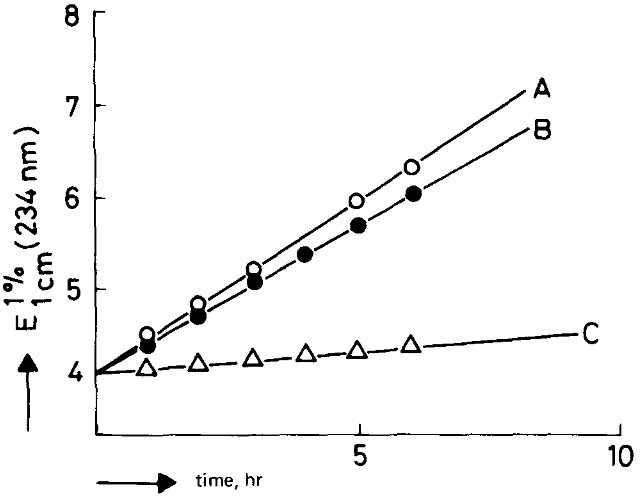


FIG. 3. Photooxidation of soybean oil (17.4 g/liter in propanol) in the presence of triethylamine (A = 0 mg/liter, B = 0.6 mg/liter, C = 6 mg/liter).

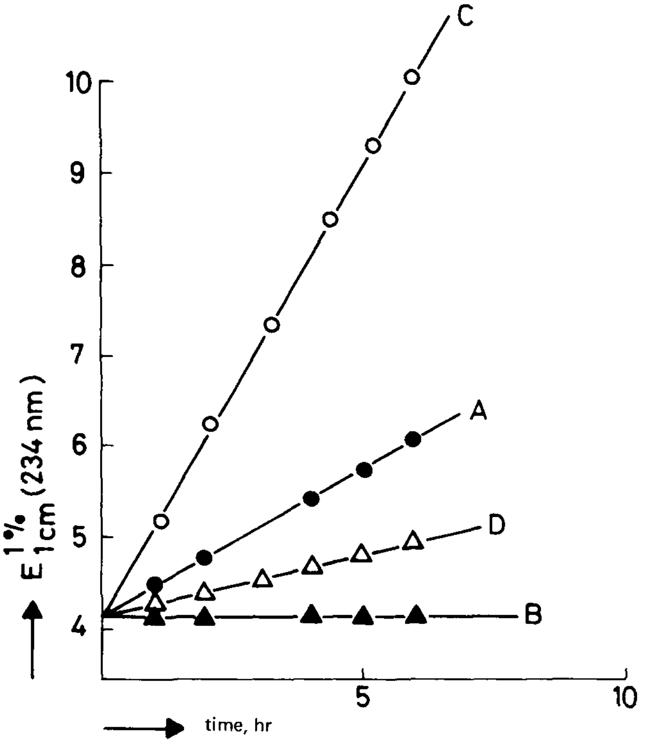
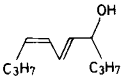
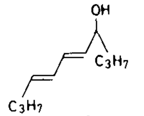
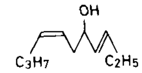


FIG. 4. Photooxidation of soybean oil (17.4 g/liter in propanol). Curve A = without addition of sensitizer, using light $\lambda > 330$ nm; B = without addition of sensitizer, using light of $\lambda > 500$ nm; C = with addition of "chlorophyl" (0.44 mg/liter), using light of $\lambda >$ 330 nm; D with addition of "chlorophyl" (0.44 mg/liter), using light of $\lambda > 500$ nm.

TABLE I

Products from Rose-Bengal Sensitized Photooxidation of 4*cis*,7*cis*-Undecadiene

Photooxidation time, min	Ratios of reduced photooxidation products		
	 [Ib]	 [Ia]	 [II]
15	57	0	43
30	56	1	43
60	48	10	42
90	21	38	41

under the authentic preparations. Hydrogenation at room temperature of a solution of this oil (0.10 g, 0.6 mmol) in 20 ml ethanol over 5 mg platinum oxide resulted in the uptake of 30 ml (1.3 mmol) hydrogen, to give a mixture of 4-undecanol and 5-undecanol (identified by mass spectrometry [MS]). Characteristic MS peaks of authentically prepared 4-undecanol: m/e 172 (M^+), 73 (C_3H_7 CHOH), 129 (C_7H_{15} CHOH); and peaks corresponding to loss of H_2O: m/e 55 and 111. Authentic 5-undecanol: m/e 172 (M^+), 87 (C_4H_9 CHOH), 115 (C_6H_{13} CHOH), 69 and 97.

The photooxidation in the presence of 30 mg "chlorophyl" (sodium chlorophillin ex Brocades, Haarlem, The Netherlands) similarly led to a mixture of undecadienols (1.96 g, 47%; bp 60-70 C/0.5 mm) separated and identified as II and 4-hydroxy-5*trans*,7*cis*-undecadiene (Ib), IR 3350 (-OH), 950 cm^{-1} (-CH=CH-*trans*); λ_{max} 234 (ϵ 20,900). NMR (220 MHz); δ 0.91, *t* $(1,11\text{-}[CH_3]_2)$; ca. 1.4, complex $(2,3,10\text{-}[CH_2]_3)$; 2.13, *q* (9-CH_2); 4.04, *q* (4-CH); 5.33 (8-CH); 5.56 (5-CH); 5.87 (7-CH); 6.35 (6-CH); $J_{67} = J_{78} = 11.0$ (*cis*); $J_{56} = 15.0$ (*trans*); $J_{45} = 6.5$ Hz.

The rose-bengal-sensitized reaction was also carried out with removal of 10 ml samples at the time intervals shown in Table I. These samples were reduced and worked up as before, but without distillation of the crude undecadienol mixtures, which were analyzed by GLC.

In the case of inhibition studies, a mixture of benzene and methanol was used as solvent to facilitate solution of the sensitizer and inhibitors at the stated (Fig. 1) concentrations.

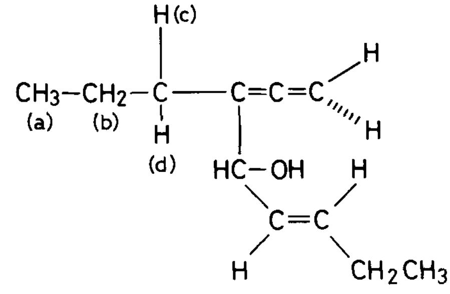
Photooxidation of soybean oil: A solution of refined 8.7 g soybean oil in 500 ml propanol was photooxidized at 20 C. One milliliter samples were taken and the UV absorption at 234 nm measured every hour. After 6 hr the solvent was evaporated and the peroxide value measured according to the method of Silbert and Swern (26).

Photooxidation of a mixture of soybean oil and 4cis, 7cis-undecadiene: A mixture of 10 g 4,7-undecadiene and 2 g refined soybean oil dissolved in 500 ml propanol was photooxidized for 3 days at 25 C. After reduction (with 4 g trimethylphosphite) and work-up, GLC of the product showed, together with other unidentified peaks, the three peaks corresponding to the three undecadienols Ia, Ib and II. Under the same experimental conditions, photooxidation of the 4,7-undecadiene or soybean oil alone did not give rise to these GLC peaks.

Oxidation of 4cis,7cis-undecadiene with chemically produced singlet oxygen: Aqueous sodium hypochlorite solution (35 ml, 0.020 mol) was added dropwise to an intensively stirred mixture of 4*cis*,7*cis*-undecadiene (300 mg, 0.002 mol) and hydrogen peroxide (5 ml, 0.025 mol) in 40 ml methanol. The temperature of the mixture was maintained between -5 and 0 C. After addition (ca. 1 hr), the reaction mixture was saturated with sodium chloride and extracted (5x) with petroleum ether (bp 40-60 C). The extract was separated, dried ($MgSO_4$) and, after addition of a few crystals of BHT, evaporated. The residue was treated with 3 g trimethyl phosphite in 25 ml methanol and worked up as described for the photooxidation product. The crude product was directly analyzed by GLC and shown to contain (together with other unidentified products) Ib and II (60:40). The yield, estimated by GLC, was less than 1%.

2trans-Pentenal: Condensation of 1-butyne magnesium bromide with triethylformate gave 2-pentynal diethylacetal, which was hydrogenated over Lindlar's catalyst and then treated with acid to give 2*trans*-pentenal. The procedures were analogous to those described by Sondheimer (27) for similar compounds. bp 71-71.5 C/115 mm (lit. [28], bp 110 C/760 mm). IR 2735, 2815 (-CHO), 1695 (C=C-C=O), 975 cm^{-1} (CH=CH *trans*); 97% pure (GLC).

5-Hydroxy-3trans-undecen-7-yne: Reformatsky-type condensation of 3-hexyne bromide with 2-butenal was carried out in benzene in a manner similar to that described by Henbest et al. (29) for similar reactions. An oil was obtained which was fractionated to give a clear liquid (bp 57-58 C/0.3 mm). One and one-half grams of this oil (purity by GLC: 60%) was chromatographed on neutral alumina (17 g, activated at 110 C for 1.5 hr). The separation was followed by thin layer chromatography (TLC) and GLC. Elution with 500 ml hexane gave impurities containing no alcohol groups (IR). Elution with 50 ml ether then gave a mixture (two components by GLC and TLC) containing the major product and an allenic impurity shown to be 4-hydroxy-3-propyl-1,2,5*trans*-octatriene (III). IR 3400 (OH): 1955 (C=C=C); 965 cm^{-1} (CH=CH *trans*). NMR (220 MHz): 0.91 (*a*-CH_3); 1.00 (8-CH_3); 1.43 (*b*-CH_2);



[III]

1.86 (*c*-CH); 1.92 (*d*-CH); 2.05 (7-CH_2); 4.36 (4-CH); 4.77 (1-CH_2); 5.40 (5-CH); 5.65 (6-CH); 2.45 (OH); $J_{1c} = J_{1d} = 3.5$, $J_{67} = 6.0$; $J_{14} = 2.0$; $J_{45} = 6.5$; $J_{46} \approx J_{57} \approx 1.3$ Hz. Further elution with 150 ml ether gave a pure sample of the major product 5-hydroxy-3*trans*-undecen-7-yne (300 mg). NMR (220 MHz): δ 0.97, *t* (11-CH_3); 1.01, *t* (1-CH_3); 1.50, sextet (10-CH_2); 2.05 (2-CH_2); 2.10 (9-CH_2); 2.20, *s* (OH); 2.28 (6-CH_2); 4.05, *q* (5-CH); 5.44 (4-CH); 5.67 (3-CH); $J_{23} = J_{45} = J_{56} = 6.2$; $J_{24} = 1.2$; $J_{34} = 15.5$ (*trans*); $J_{69} = 2.2$ Hz.

5-Hydroxy-3trans,7cis-undecadiene (II): One hundred

TABLE II

Effect of Additives and Filter on Final Peroxide Value of Soybean Oil after 6 hr Photooxidation

Additives and filters[a]	Concentration of additive, mg/liter	Final peroxide value[b] meq/kg
β-Carotene	0.46	30
Triethylamine	0.60	34
	6.0	24
BHT	14.0	36
"Chlorophyl"	0.44	86
"Chlorophyl" + yellow filter	0.44	14
Yellow filter	---	5

[a] Except where otherwise stated, light of $\lambda < 330$ nm was filtered out.

[b] The initial peroxide value was 0.6. A control photooxidation without additive or filter was always carried out; a final peroxide value of 36 was found in all cases.

milligrams 5-hydroxy-3*trans*-undecen-7-yne in 10 ml hexane was hydrogenated at room temperature over Lindlar's catalyst (7) at atmospheric pressure to give 5-hydroxy-3*trans*,7*cis*-undecadiene (found: C, 77.95; H, 11.74; 0, 10.32. $C_{11}H_{20}O$ requires: C, 78,49; H, 12.00; 0, 9.51). IR 3360 (OH), 965 (CH=CH *trans*). NMR (220 MHz): δ 0.91, *t* (11-CH_3); 1.00, *t* (1-CH_3); 1.28, *s* (OH); 1.38, sextet (10-CH_2); 2.01 (9-CH_2); 2.03 (2-CH_2); 2.17 and 2.21 (6-CH_2, nonequivalent); 3.97 (5-CH); 5.25-5.50, complex (7-CH, 8-CH); ca. 5.4 (4-CH); 5.61 (3-CH); $J_{23} = 6.5$; $J_{34} = 15.5$ Hz (*trans*). Irradiation of the CHOH absorption produced a sharpening of the 3-CH absorption, indicating long range coupling between those protons and confirming that the hydroxyl group is adjacent to the *trans*-double bond. On addition of tris(dipivalomethanato)europium (15), a clear separation was made of the absorption from the olefinic region, whereupon two doublets of triplets having a *cis*-coupling of 11 Hz were revealed due to the 7- and 8-vinyl hydrogens. This coupling constant contrasts with the *trans*-vinyl coupling (between 14.5 and 15.8 Hz), which is observed without addition of the shift reagent for all the other ethylenic double bonds in the series of compounds formed during the syntheses of the authentic specimens.

6-Hydroxy-trans-undecen-7-yne: The Grignard reaction between 2*trans*-hexenal and freshly prepared 1-pentyne magnesium bromide gave 6-hydroxy-4*trans*-undecen-7-yne (86%); bp 69-70 C/0.5 mm (purity [GLC] 98%). Found: C, 79.61; H, 10.83; 0, 9.59. $C_{11}H_{18}O$ requires: C, 79.45; H, 10.93; 0, 9.62. IR 3330 (OH), 2230 (C≡C), 965 cm^{-1} (CH=CH, *trans*). NMR (220 MHz); δ 0.93, *t* (1-CH_3); 1.00, *t* (11-CH_3); 1.44 (2-CH_2); 1.54 (10-CH_2); 2.03 (3-CH_2); 2.18 (9-CH_2); 2.37 (OH); 4.65 (6-CH); 5.47 (5-CH); 5.71 (4-CH); $J_{45} = 15.0$ (*trans*); $J_{56} = 5.5$ Hz.

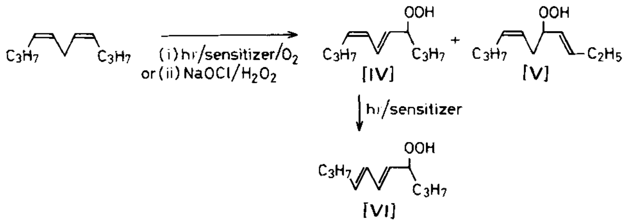
6-Hydroxy-4trans, 7trans-undecadiene: 6-Hydroxy-4*trans*-undecen-7-yne was reduced with lithium aluminium hydride, according to the procedures of Bates et al. (30) for the reduction of other acetylenic alcohols.

Fractionation gave 6-hydroxy-4*trans*-7*trans*-undecadiene (21 g, 52%), bp 103-104 C/6 mm. IR 3350 (OH), 965 cm^{-1} (CH=CH *trans*). Found: C, 78.96; H, 11.84; 0, 9.34. $C_{11}H_{20}O$ requires: C, 78.48; H, 11.98; 0, 9.51. NMR (220 MHz): δ 0.91 (1,11-$[CH_3]_2$); 1.40 (2,10$[CH_2]_2$); 1.99 (3,9-$CH_2]_2$); 5.52 (4-CH, 8-CH); 5.39 (5-CH, 7-CH); 4.40 (6-CH); 2.41 (OH); $J_{34} = J_{89} \sim 6.5$, $J_{4,5} = J_{7,8} = 15.8$ (*trans*); $J_{56} = 6.0$ Hz.

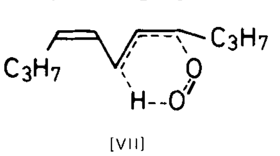
4-Hydroxy-5trans, 7trans-undecadiene (Ia): 6-Hydroxy-4*trans*,7*trans*-undecadiene was isomerized with sodium bisulfate by a method similar to that of Jones and McCombie (31) for the preparation of 2-hydroxy-3-hexen-5-yne. Fractionation gave 4-hydroxy-5*trans*,7*trans*-undecadiene (33%), bp 77-79 C/0.5 mm. Found: C, 78.70; H, 11.94; 0, 9.70. $C_{11}H_{20}O$ requires: C, 78.49; H, 11.98; 0, 9.51. IR 3450 (OH), 985 cm^{-1} (CH=CH, *trans*). NMR (220 MHz): δ 0.91 (1,11-$[CH_3]_2$); 1.4 (2-, 3-, 10-$[CH_2]_3$); 4.00 (4-CH); 5.49 (5-CH); 6.07 (6-CH); 5.94 (7-CH); 5.59 (8-CH); 2.04 (9-CH_2); 1.25 (OH); $J_{45} = 6.7$; $J_{56} = J_{78} = 14.5$ (*trans*); $J_{67} = 10.5$; $J_{89} = 7.0$ Hz. λ_{max} 231 nm (ε 22,000).

DISCUSSION

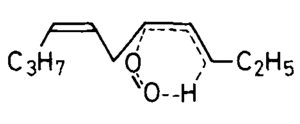
This work indicates that photosensitized oxidation and singlet oxygen oxidation of 4,7-undecadiene give the same initial hydroperoxide products in about the same ratio, and that one of these products (V) is not obtained by normal radical chain autoxidation. It is therefore concluded that singlet oxygen is an intermediate in the photosensitized oxidation of 4*cis*,7*cis*-undecadiene.



One current theory for the mechanisn of the singlet oxygen oxidation of alkenes favors a concerted reaction of $^1\Delta g$ O_2 via a six-membered ring transition state (8,32). Considering the two possible transition states (VII and VIII) from undecadiene, it can be seen that only in the transition state VII leading to the conjugated hydroperoxide is the unreacting double bond conjugated with the newly developing double bond.



[VII]



[VIII]

This delocalization in transition state VII could account for the slight preponderance of the conjugated hydroperoxide in the product. Foote and Denny (32) have observed a similar preference for the formation of conjugated isomers in the reactions of 1-aryl-3-methyl-2-butenes. The preferred formation of the conjugated hydroperoxide can be similarly rationalized by a mechanism involving perepoxide intermediates (33).

IR evidence has been noted for mixtures of *cis,trans*- and *trans,trans*-hydroperoxides from linoleic acid photooxidations (34), and it is possible that photosensitized isomerizations analogous to the *cis,trans*-isomerization IV to VI have occurred. This type of isomerization could be of importance in the deterioration of vegetable oils, for *cis,trans*- and *trans,trans*-isomers of aldehydes, believed to be formed from the corresponding dienoic hydroperoxides, often have odors and flavors which are quite different. For example, 2*trans*,4*cis*-decadienal is reported to have a sweet aldehydic odor, whereas 2*trans*,4*trans*-decadienal has a deep-fried fat odor (35). Both of those aldehydes are often formed in linoleic acid-containing oils (35).

The present work with soybean oil clearly indicates that the photooxidation of soybean oil in *solution* follows kinetics and inhibitor effects similar to the photooxidation of 4*cis*,7*cis*-undecadiene. Further, since soybean oil can act as a sensitizer for the photooxidation of 4*cis*,7*cis*-undecadiene, it is concluded that it contains sensitizers which lead to a photooxidation of the oil in solution, through a singlet oxygen intermediate.

The most important question remaining is: Does this singlet oxygen mechanism contribute significantly to the photooxidative deterioration of the flavor of *undiluted* soybean oil in practice? Recently Heiss et al. (36) have demonstrated a nonautocatalytic phase in the photooxidation of pure undiluted soybean oil, which is linearly dependent with time of irradiation and intensity of the absorbed light. These observations are consistent with a singlet oxygen mechanism (16). Further work is, however, necessary before we can say with certainty that the sensitizers present in soybean oil are having a decisive influence on its flavor stability.

The nature of the sensitizers in soybean oil remains unknown, but we believe that any small amounts of chlorophyl-like pigments present in the well refined soybean oil used in our experiments are probably unimportant, for when light of wavelength <500 nm is filtered off, the photooxidation of the skipped dienoic compounds of soybean oil virtually stops. Chlorophyl-like compounds have an absorption over 600 nm, which would be expected to lead to some photosensitization in the same way as our "chlorophyl" led to photooxidation (Fig. 4, curve D). Provided soybean oil is efficiently refined, so that chlorophyls are no longer detectable, the photosensitized oxidation in solution can be avoided by using a yellow filter that filters out all light below 500 nm. Many earlier workers, e.g. (5), have noted that the flavor stability of different vegetable oils is significantly improved by the use of filters that cut off light below 500 nm. When commercially applicable, removal of chlorophyls and then the use of an efficient yellow filter material may well be the easiest method of avoiding light-induced deterioration of oils, whether it is due to the formation of singlet oxygen or other causes.

We have shown that inhibition of the singlet oxygen reactions studied in this work is possible with triethylamine or β-carotene. Current studies (14,17) suggest that carotenes (not solely β-carotene) are natural inhibitors for singlet oxygen oxidations, just as the tocopherols are naturally occurring inhibitors of radical chain autoxidation (37). It is perhaps significant, from the point of view of flavor deterioration, that whereas the tocopherols (37) survive vegetable oil refining, the carotenes (38) are usually largely removed during the bleaching step. Indeed it has been stated that oils that have been neutralized, bleached and deodorized are known to become rancid much quicker than crude oils and even unbleached refined oils (6). Also β-carotene has in fact been reported (at 0.002% concentration) to be an inhibitor for photooxidative deterioration of corn and cottonseed oils (5). This inhibition was interpreted as being simply due to light absorption, i.e., an inbuilt filter. Inhibition of singlet oxygen provides an alternative explanation, and it may well be that other carotenes will similarly prove useful in inhibiting the photooxidation deterioration of vegetable oils.

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REFERENCES

1. Browne, C.H., Jr., J. Amer. Chem. Soc. 21:975 (1899).
2. Horovitz-Vlasova, L.M., M.I. Livshitz, E.E. Kacharova, I.A. Oberhard and A.B. Shalberova, Schriften Zentral. biochem. forsch. Inst. Nahr. u. Genussmitteling (USSR) 2:203 (1932); Chem. Abstr. 27:5435 (1933).
3. Horovitz-Vlasova, L.M., E.N. Morozova, I.A. Oberhard, E.L. Remennikova and E.A. Rodionova, Ibid. 2:315 (1932); Chem. Abstr. 27:5435 (1933).
4. Kozin, N.I., and L.S. Yastrebova, Vop. Pitan. 6:3 (3) (1937); Chem. Abstr. 32:3041 (1938).
5. McConnell, J.E.W., and W.B. Esselen, JAOCS 24:6 (1947).
6. Coe, M.R., Oil Soap (Chicago) 15:230 (1938).
7. Foote, C.S., S. Wexler, W. Ando and R. Higgins, J. Amer. Chem. Soc. 90:975 (1968).
8. Foote, C.S., Accounts Chem. Res. 1:104 (1968).
9. Khan, N.A., Oleagineux 25:281 (1970).
10. Rawls, H.R., and P.A. Van Santen, JAOCS 47:121 (1970).
11. Lindlar, H., and R. Dubois, Org. Syn. 46:89 (1966).
12. Brown, H.C., and G. Zweifel, J. Amer. Chem. Soc. 83:3884 (1961).
13. Calvert, J.G., and J.N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, 1966, p. 449.
14. Foote, C.S., Y.C. Chang and R.W. Denny, J. Amer. Chem. Soc. 92:5216 (1970).
15. Sanders, J.K.M., and D.A. Williams, Ibid. 93:641 (1971).
16. Gollnick, K., T. Franken, G. Schade and G. Dörhöfer, Ann. N.Y. Acad. Sci. 171:93 (1970).
17. Foote, C.S., and R.W. Denny, J. Amer. Chem. Soc. 90:6233 (1968).
18. Schenck, G.O., and G. Schade, Chimia 24:13 (1970).
19. Wilson, T., and C. Ouannès, J. Amer. Chem. Soc. 90:6527 (1968).
20. Gensler, W.J., and A.P. Mahadevan, Ibid. 77:3076 (1955).
21. Hubert, A.J., J. Chem. Soc. 6669 (1965).
22. Johnson, J.R., H.R. Snijder and M.G. van Campen, J. Amer. Chem. Soc. 60:118 (1938).
23. Gollnick, K., and G.O. Schenck, "1,4-Cycloaddition Reactions," Edited by J. Hamer, Academic Press Inc., New York, 1967, p. 255.
24. Schenck, G.O., "Preparative Organic Photochemistry," Springer-Verlag, Berlin, 1968, p. 477.
25. Rappoldt, M.P., Thesis, University of Leiden, 1958, p. 17.
26. Silbert, L.S., and D. Swern, Anal. Chem. 30:385 (1958).
27. Sondheimer, F., J. Amer. Chem. Soc. 74:4040 (1952).
28. Andrac, M., Ann. Chim. 9:287 (1964).
29. Henbest, H.B., E.R.H. Jones and J.M.S. Walls, J. Chem. Soc. 1949:2696.
30. Bates, E.B., E.R.H. Jones and M.C. Whiting, Ibid. 1854:1954.
31. Jones, E.R.H., and J.T. McCombie, Ibid. 261:1943.
32. Foote, C.S., and R.W. Denny, Pure Appl. Chem. 27:635 (1971).
33. Fenical, W., D.R. Kearns and P. Radlick, J. Amer. Chem. Soc. 91:7771 (1969).
34. Cobern, D., J.S. Hobbs, R.A. Lucas and D.J. MacKenzie, J. Chem. Soc. C. 1897:1966.
35. Hoffmann, G., "Symposium on Foods: Lipids and Their Oxidation," Avi Publishing Co. Inc., Westport, Conn., 1962, p. 215.
36. Heiss, R., R. Radka and P. Smits, Fette Seifen Anstrichm. 72:497 (1970).
37. Swern, D., "Bailey's Industrial Oil & Fat Products," Interscience Publishers, New York, 1964, p. 40.
38. Jefferson, M.L., "Soybeans & Soybean Products," Edited by K.S. Markley, Interscience Publishers, New York, 1950.

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