Improved Oxidative Stability of Sunflower Oil in the Presence of an Oxygen-Scavenging Film

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ABSTRACT: The oxidative stability of sunflower oil (SFO) was measured during storage at 23 and 37°C in the presence of a novel oxygen-scavenging film that contained polyfuryloxirane (PFO). Commercially refined and deodorized SFO was stored in a lighted room in sealed transparent packages containing either PFO film or an antioxidant, 0.02% butylated hydroxytoluene (BHT). Oxidative stability was evaluated by determination of peroxide values and gas-chromatographic measurement of headspace hexanal. SFO stored in the presence of the oxygen-scavenging film was more stable than oil stored without the film, or than film stored with 0.02% BHT. The PFO film scavenges oxygen through energy-transfer sensitization of singlet oxygen. The film is doped with eosin and the naturally-occurring dye, curcumin, which absorb over a wide range of visible wavelengths. Curcumin transfers its absorbed energy to eosin, which sensitizes the production of singlet oxygen. The singlet oxygen is scavenged by PFO. The use of two dyes increases the efficiency of the sensitization process, reducing the illumination time and intensity required for effective oxygen scavenging.

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Oxygen is a major determinant of food shelf life, because it contributes to the oxidation of lipids and is essential for the growth of aerobic food spoilage microorganisms and insect pests. One or more of these factors can cause an overall deterioration in food quality (1) and, obviously, it is highly desirable to minimize this. Methods that have been used to slow or inhibit oxygen-related degradation include chilled storage, freezing, heat processing, drying, modified-atmosphere packaging (MAP), and the use of chemical additives and preservatives, including antioxidants.

Deterioration of lipid foods as a result of oxidation is a particular problem for polyunsaturated oils, such as sunflower oil (SFO). There have been a number of studies on the stability of SFO (2,3), and it has been found that oxidation and the development of rancidity may be retarded by antioxidants. As mentioned previously, an alternative approach would be to use MAP, in which the food product is stored in a gas-barrier material, and the gaseous environment is changed so as to retard oxidation and also to reduce microbiological growth. Although MAP methods extend food shelf life, they lose effectiveness when there are problems with oxygen permeability of packaging materials, leakage of air through poor seals and pinholes, outgassing of foodstuffs, and inadequate evacuation and/or gas flushing. There is thus a need for active packaging materials that can scavenge residual oxygen from package headspaces, and any that subsequently diffuses into the package.

There have been many suggestions of oxygen scavengers for use in packaging. The Mitsubishi Chemical Company (Tokyo, Japan) has developed a range of oxygen absorbers, that are based on the oxidation of iron, immobilized in sachets, to form nontoxic iron oxide (4). Other films incorporate reducing agents, such as ascorbates and isoascorbates, and oxygen scavenging is accelerated by heat (5) or a transition-metal catalyst (6). Koyama *et al.* (7) have developed an approach that combines heating and reduction by iron or zinc powder, and Speer *et al.* (8) have used unsaturated hydrocarbons to scavenge oxygen in the presence of a metal-ion catalyst and ultraviolet or visible radiation. The latter process relies on autoxidation of the polymer by ground-state oxygen following initiation by the metal ions and light.

A disadvantage of many oxygen-scavenging systems is that they are relatively slow. For example, some of the iron-based scavengers take from one to four days to reduce the residual oxygen levels in a package to less than 100 ppm. A similar limitation applies to many other recent patents in this area, because they rely on the relatively slow reaction rates associated with ground-state oxygen, which is in a triplet electronic state ($^3O_2$).

This paper describes a MAP approach to improve the oxidative stability of SFO through the use of a novel oxygen-scavenging film that incorporates recent developments in energy-transfer theory and polymer chemistry. The film uses energy transfer to convert triplet oxygen to highly reactive singlet oxygen ($^1O_2$), which is absorbed irreversibly by the film. The film, which is a development from our earlier studies of polymer-based, light-sensitive films (9–11), contains

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the common organic dyes—eosin and curcumin—and polyfuryloxirane (PFO), a recently synthesized polyether that we have found can be used as a singlet-oxygen scavenger. When exposed to light, the dyes absorb over a wide range of wavelengths. Direct absorption by eosin, and energy transfer from curcumin to eosin cause triplet oxygen to be converted to singlet oxygen, which is rapidly scavenged by the PFO. Bleached, deodorized SFO was stored in the presence of the oxygen-scavenging film and evaluated for rancidity.

MATERIALS AND METHODS

Materials. Bleached, deodorized SFO was obtained from Meadow Lea Foods Limited (Sydney, NSW, Australia). Butylated hydroxytoluene (BHT), (laboratory reagent; Aldrich, Milwaukee, WI) was used as received. Eosin (Gurr microscopy-grade, C.I. 45380) and curcumin (1,6-heptadiene-3,5-dione, laboratory reagent, C.I. 75300) were recrystallized from ethanol and water, respectively. Ethyl cellulose was supplied by BDH Chemicals (Melbourne, Victoria, Australia).

Methods. The polymer PFO was synthesized by the method of Amri (12) and Salon *et al.* (13). The PFO had a degree of polymerization (average number of monomer units per molecule of polymer) between 33 and 55, and was gum-like in consistency. It was blended with ethyl cellulose, which has relatively high permeability to oxygen, and appropriate physical properties for producing films. A blend of 20% w/w PFO in ethyl cellulose was prepared by dissolving both polymers in ethyl acetate, and after solutions of eosin and curcumin in ethanol had been added, films were cast on a laboratory film-casting machine (Unit No. 41889-V; RK Print-Coat Instruments Ltd., Royston, Herts, United Kingdom) on a Mylar release film.

Samples of SFO (20 mL) were placed in 7.5-cm covered glass petri dishes, each of which was wrapped with a PFO/ethyl cellulose polymer film (17 × 13 cm). The dishes were then sealed in plastic pouches made of high barrier film (Nylon/EVOH/polyethylene). BHT (0.02%) was added to similar oil samples, which were stored in pouches without PFO. To test for the effect of light, some samples were wrapped with aluminum foil to exclude light. Control samples were stored in petri dishes without PFO or BHT. The samples were irradiated for two days with light from two sources—an Osram 20W/RS white fluorescent tube (Osram Australia Pty. Ltd.; Sydney, NSW, Australia), and a Philips TL 20 W fluorescent tube (Philips Electronics Australia Ltd.; Sydney, NSW, Australia). These lamps emitted strongly at wavelengths that were absorbed by eosin and curcumin, respectively. The overall light intensity was 2000 lux. After the initial irradiation period, the samples were left under continuous illumination with normal fluorescent room light (500 lux) in temperature-controlled rooms at 23 and 37°C. The two-day irradiation period was chosen to ensure that minimal levels of oxygen remained; we have found that irradiation periods of 1–2 h can reduce headspace oxygen levels to less than 1% (14).

Analysis of the oil. Stability of the oil samples was evaluated by two methods—peroxide value (PV) determination on 5-g aliquots of oil by AOCS method Cd 8-53 (16, as reported in 15), and gas-chromatographic analysis of headspace hexanal. The presence of hexanal was confirmed by gas chromatography/mass spectrometry (GC/MS) and by spiking with an authentic sample. Other volatile compounds were identified in the headspace gas, as described later. The headspace analysis was calibrated with external standards of hexanal in paraffin oil. The average response factor, determined as the ratio of the hexanal concentration area in paraffin oil and in fresh unoxidized oil, was 1.5×10^{-3}. The concentration of hexanal in oil samples was determined by multiplying this value by the area of the hexanal peak for the sample.

Gas-chromatographic analysis of headspace hexanal. Hexanal was analyzed in a Hewlett-Packard (Avondale, PA) 5890 A gas chromatograph equipped with a Hewlett-Packard 19395 A headspace sampler. A fused-silica capillary column (30 m × 0.32 mm i.d. with 0.32 μm film thickness, DBI column; J&W Scientific, Folsom, CA) and a flame-ionization detector were used. For hexanal analysis, 1.0-g samples of oil were taken from each of three identical petri dishes at the end of each storage period and placed in 10-mL headspace vials. The vials were purged with nitrogen gas and sealed with a teflon-lined septum and aluminum cap (17,18). Each vial was placed in the headspace analyzer and heated at 95°C for 45 min to generate volatiles; 1 mL of the headspace gas was then automatically injected into the column. The GC oven was held at 45°C for 5 min and programmed to reach 200°C at a rate of 5°/min. Other instrumental conditions were: injector temperature, 200°C; detector temperature, 220°C; nitrogen carrier gas, column head pressure of 70 kPa. Hexanal, pentanal, pentane, nonane, 2,4-decadiene, and nonanal were identified by spiking with authentic samples. The volatiles were also analyzed by GC/MS.

GC/MS. A Hewlett-Packard 5890 Series II gas chromatograph, interfaced to a 5971 A mass-selective detector was used with a fused-silica capillary column (DBI column, 30 m × 0.25 mm i.d. with 1.0 μm film thickness; J&W) to confirm the identity of the volatiles. Volatiles generated in the headspace GC were sampled with a gas-tight syringe. The GC oven was held at –5°C for 1 min and programmed to reach 240°C at a rate of 5°C/min. Other instrumental conditions were: injector temperature, 200°C; source temperature, 220°C; electron impact ionization, 70 eV; helium carrier gas, column head pressure of 50 kPa. Peaks in the mass spectra were identified by means of a Wiley mass-spectral library. To reduce interference by air peaks on early-eluting species, such as acetaldehyde, a nitrogen atmosphere was maintained in the vials during temperature equilibration of samples in the headspace magazine.

RESULTS

Identification of volatiles. Fresh SFO gave "clean" headspace chromatograms and contained less than 1 ppm of oxidation volatiles. As expected, the number and concentration of volatile compounds increased with the degree of oxidation. These compounds, which were identified by spiking with authentic samples, included acetaldehyde, butanal, pentanal, pentane, hexanal, nonanal, and 2,4-decadiene, with hexanal and pentanal occurring at higher concentrations due to the linoleate and oleate content (19) of SFO. The GC/MS results showed the presence of propanal, pentanal, hexanal, nonanal, and 2-decenal; minor components included formic acid, butanal, 2-pentanol, 1-hexene, hexanoic acid, pentanoic acid, and 2-pentylfuran. The formation of these volatiles is consistent with the autoxidation of linoleic and oleic acids, which are the major fatty acids in SFO (17). The more polar volatiles, hexanoic and pentanoic acids, are characteristic of advanced rancidity and arise due to oxidation of the corresponding aldehydes. The absence of 2,4-decadienal, a major autoxidation product of linoleate, in the oxidized sample is attributed to its further ready oxidation to hexanal and, ultimately, to hexanoic acid (19,20).

Development of rancidity. Figure 1 shows plots of PV against time for the development of rancidity in SFO at 23 and 37°C. The control samples that had been stored without either the oxygen-scavenging film or BHT showed more rapid increases in PV with time than the samples containing BHT or the film. The SFO at 37°C became rancid more rapidly, owing to increased reaction rates at the higher temperature. At both temperatures the control samples showed a rapid increase in the number and intensity of the volatile peaks in the headspace chromatograms.

Oil that had been stored with BHT was oxidized more slowly than the control. The rate of oxidation is similar to that of SFO covered with aluminum foil, which indicates that the presence of light affects the development of rancidity. Although the unsaturated fatty acids are colorless and are not normally subjected to ultraviolet irradiation at wavelengths that they can absorb, they can undergo photosensitized oxidation owing to light absorption by coloring matter in the foodstuff. The reaction may be a type I or type II photooxidation (21).

Plots of hexanal concentration vs. time (shown in Fig. 2) demonstrate the same trend as the PV values. Thus, under similar test conditions, SFO stored with the oxygen-scavenging film shows greater stability than the oils stored without it. A correlation coefficient for the comparison between the PV and gas-chromatographic studies is high ($r > 0.95$), indicating good correlation between the two methods for measuring rancidity.

DISCUSSION

Potential usefulness of the oxygen-scavenging film. The results described here point to the potential usefulness of an oxygen scavenger in the form of a film. In this case, the film was an insert in the food package, but its greatest potential use would probably be as part of a laminate. This would allow it to be used in packaging of the wide range of foods that contain polyunsaturated oils as ingredients.

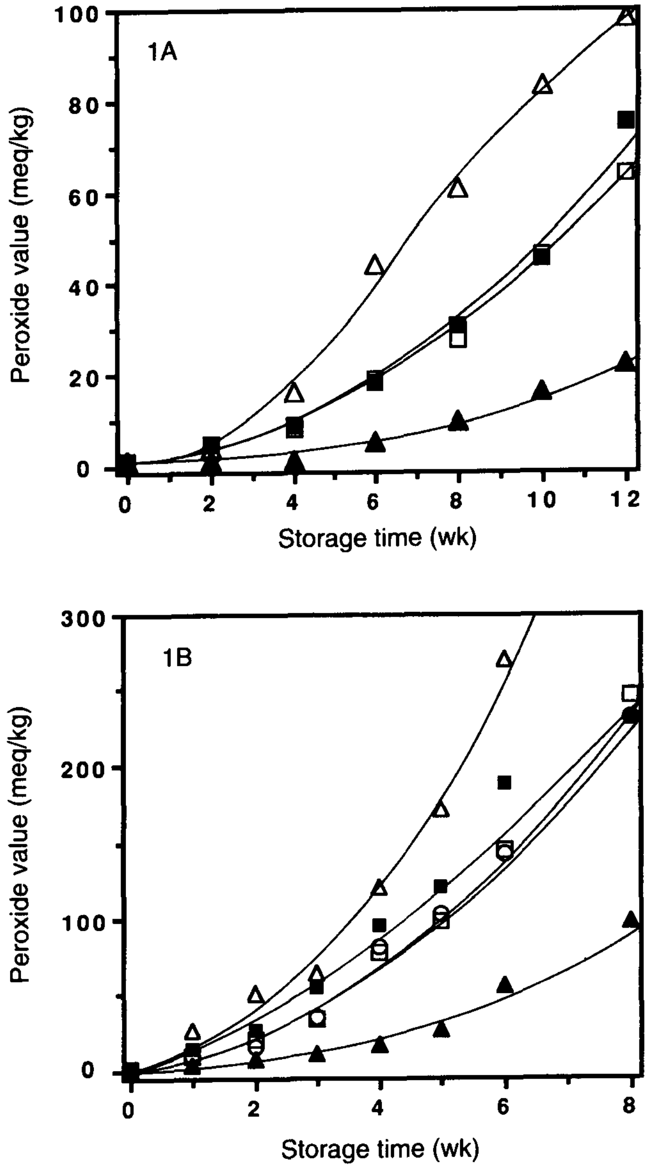

FIG. 1. A. Peroxide values for sunflower oil (SFO) stored at 23°C. B. Peroxide values for SFO stored at 37°C. △, SFO alone; ■, SFO with 0.02% butylated hydroxytoluene; □, SFO covered with aluminum foil; ○, SFO with polyfuryloxirane (PFO) film and covered with aluminum foil; ▲, SFO with PFO film.

The oxygen-scavenging film works as follows: A dye (D, e.g., eosin) is immobilized in a polymer film and illuminated with light of suitable wavelength. Absorption of light, $h\nu$, excites the dye to an excited singlet state, ^1D, which may then produce a triplet-state molecule, ^3D, if intersystem crossing is efficient. If the triplet-state dye interacts with ground-state oxygen ($^3O_2$), transfer of energy generates singlet oxygen, $^1O_2$, which rapidly reacts with a suitable trap or acceptor, A, which is also immobilized in the film. This effectively removes O_2 from the system. Dye excitation continues as long as the system is being illuminated, and oxygen will continue to be scavenged as long as the acceptor is not exhausted, and

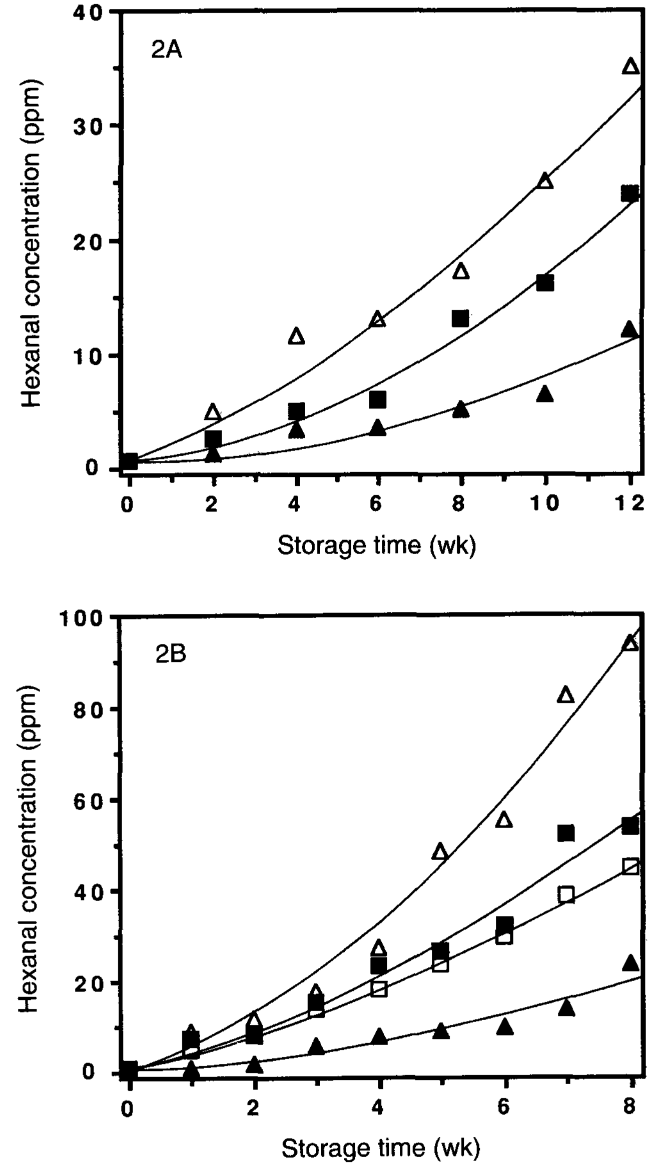

FIG. 2. A. Development of headspace hexanal for SFO stored at 23°C. B. Development of headspace hexanal for SFO stored at 37°C. △, SFO alone; ■, SFO with 0.02% BHT; □, SFO covered with aluminum foil; ▲, SFO with PFO film. Abbreviations as in Figure 1.

the singlet oxygen can diffuse to it. Other processes, such as decay of singlet oxygen to the ground state, also occur, but a simplified photochemical sequence is as follows:

$$\begin{aligned} &D + h\nu \rightarrow {}^1D \qquad [1]\\ &{}^1D \rightarrow {}^3D\\ &{}^3D + {}^3O_2 \rightarrow D + {}^1O_2\\ &{}^1O_2 + A \rightarrow AO_2 \end{aligned}$$

A potential problem with this type of film is that the dyes absorb over relatively narrow bands of wavelengths, so the films may have to be irradiated with special light sources, or at high light intensities, or for prolonged periods. We have overcome this problem by using combinations of dyes that are good sensitizers of singlet oxygen production (e.g., eosin) in combination with other dyes that are poor sensitizers but that absorb at other wavelengths. These other dyes, *D′* (e.g., curcumin), can transfer energy to the sensitizing dye, *D*, by the Förster mechanism of energy transfer (22), as summarized below.

$$\begin{aligned} &D' + h\nu \rightarrow {}^1D' \qquad [2]\\ &{}^1D' + D \rightarrow D' + {}^1D\\ &{}^1D \rightarrow {}^3D \textit{ etc.} \end{aligned}$$

Thus, a larger proportion of the available light is used to sensitize oxygen scavenging. A judicious choice of dyes ensures that scavenging will occur under normal indoor lighting conditions, and may be accelerated by using commonly available fluorescent tubes, rather than specialized high-intensity lamps. To ensure that there is an adequate supply of acceptor, we prepared polymer films that contain PFO, a polyether with furan side-groups that are highly reactive to singlet oxygen. Provided a large enough piece of film is incorporated in the package, all of the oxygen in the headspace gas will be scavenged, and there is enough reserve capacity to absorb any oxygen that subsequently diffuses in. The films that were used had dimensions of 17 × 13 cm, and had the capacity to absorb all the oxygen from 200 mL of air.

The furan groups in the PFO film are so reactive toward singlet oxygen that they permit a higher rate of oxygen-scavenging than is achievable with other systems that are based on reactions of ground-state oxygen. The rate is limited in practice by the light intensity and the permeability to oxygen of either the scavenging film itself or any additional film that lies between the scavenging film and the headspace (for example, if the PFO is incorporated in a laminate). The extreme case of this retardation is the use of an oxygen barrier film on the outside of the package to prevent oxygen ingress, as used previously (9).

The high scavenging rate achievable by this type of film and either high light intensity (10) or energy transfer at low intensity (14) means that some food packs might be scavenged of most of their oxygen while on the filling line. The light intensity (500 lux) used in the present study is lower than that used previously (9–11) because of the higher sensitization efficiencies produced by broad-band absorption and energy transfer from curcumin. Light intensities, such as those used in the present work, are found in the commercial display of foods. In preliminary experiments, this intensity has also been found to cause the scavenging of oxygen by ethyl cellulose films that contained *bis*(furfurylidene)pentaerythritol (PEF; 0.4 M) and erythrosine (10^{-3} M). It would be necessary for a package on display to have at least some of its active layer exposed to light in order for this process to function as an oxygen scavenger during retailing, to combat any permeability of the package.

The period of illumination required to remove the headspace oxygen present at package sealing will depend on a wide range of variables, including reagent concentration, scavenger-film permeability, film surface-to-headspace volume ratio, light intensity, and the characteristics of the scavenging components. An example of a simple system, which was not optimized, showed that 150 cm^2 of a scavenger film could essentially deoxygenate 25 mL of air in about 15 min (10). Packages with small headspaces, such as meat or cheese packs, might be treated with shorter times.

A detailed toxicological study would be required before the PFO/ethyl cellulose film could be used for food applications, but encapsulation in a laminate could help to make the material compatible with foodstuffs. In earlier work, we showed that oxygen may also be scavenged efficiently by a cheap, unpolymerized furan compound, such as PEF, dissolved in a polymer film (10). However, even though the furan components of this compound are derived from oats, the remainder is synthetic, and its use would also require regulatory approval. Furthermore, the compound was found to diffuse sufficiently rapidly in ethyl cellulose that it crystallized in the polymer film within two months at 25°C and 12 mon at −20°C. An alternative of a cheap commodity polymer, such as natural rubber, was also evaluated (9). The double bonds in natural rubber reacted readily with singlet oxygen and underwent chain scission in a manner similar to that found in the autoxidation of polyunsaturated fatty acids. However, after oxygen scavenging, the packages had a strong taint of oxidized hydrocarbon when opened. Also, the rubber film, which was initially tacky, became tack-free and finally powdery, like the surface of an aged house-paint film.

Given these problems with diffusion and decomposition of acceptors, we chose in the present investigation to use a high-molecular-weight acceptor that would be unlikely to diffuse, and that would not decompose upon oxidation. These conditions were met by PFO, in which the reactive furan component is pendant from a poly(ethylene oxide) chain, which appears to resist oxidation. When this acceptor was blended with ethyl cellulose, its performance was most satisfactory.

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