Effect of Some Terpenyl Oleates on Soybean Oil Oxidation at 180°C

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ABSTRACT: The ability of linalyl oleate (LO) to act as an autoxidation inhibitor in soybean oil at 180 ± 5°C was compared with the oleates of geraniol (GeO), menthol (MenO), perillyl alcohol (PeO), farnesol (FaO), phytol (PhO), and cholesterol (ChO) at levels of 0.1% by weight in the oil. Changes in FA composition and conjugated dienes were monitored. Logarithmic plots of the decreasing ratios of linoleate/palmitate and linolenate/palmitate vs. time were linear for soybean oil controls, but plots for LO, GeO, MenO, PeO, FaO, and ChO had inflection points (IP) at times between 5 and 11.4 h. These terpenyl oleates had smaller rate constants before the IP than the control oil. Thus, these esters all exhibited autoxidation inhibition, which was confirmed by conjugated diene values. Plots for PhO had no IP and very limited inhibitory effect relative to the controls. LO originally was chosen for study because it has a double bond structure similar to that of the side chain of avenasterol, which also shows an ability to inhibit oxidation. The ability of terpenyl oleates having widely different structures to inhibit autoxidation suggests that LO's double bond structure is not the cause of its inhibitory activity.

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Vegetable oils containing PUFA oxidize rapidly at frying temperatures (~180°C). Both physical and chemical changes occur in the frying oil while exposed to air, and these changes reduce the nutritional value of the oil, and consequently, the food fried in the oil (1,2). Substances that retard oxidation, polymerization, darkening, and foaming may be added to the frying medium. Phenolic antioxidants that are effective in protecting against oxidation at ambient temperatures usually undergo distillation or destruction under frying conditions (3) and quickly lose their antioxidant activity.

The use of methyl silicone (MS) or polydimethylsiloxane as an antifoaming agent in frying oils is permitted in many countries at levels up to 10 ppm. MS also is effective in extending the life of frying oils. Some people believe that MS forms an inert layer between air and oil surfaces, which slows heat loss and convection in the oil, thus minimizing foaming and also oxidation (4). However, surface tension measurements of oils containing MS (5) did not detect the accumulation of MS in the oil surface at room temperature.

Various plant extracts (6–8) and several plant sterols, including Δ^5- and Δ^7- avenasterol, vernosterol and citrostadienol, reduce the oxidative changes that occur in vegetable oils during frying (9,10). Gordon and Magos (9) theorized that the ethylidene side chain present on these sterols reacts rapidly with lipid free radicals to form "stable" allylic tertiary free radicals that cannot extract hydrogen radicals from unsaturated fat and continue the oxidation chain. This theory was further tested by examining the inhibitory effects of compounds containing an ethylidene-like group, but without sterol-like structures. The inhibitory activities of linalyl acetate (LA), linalyl oleate (LO), and undecylenic acid, a terminally unsaturated FA, have been reported (5,8,11). LO at 0.05 and 0.1% was as effective as MS at 5 and 10 ppm. The use of LO eliminated the relatively strong flavor of LA and decreased LA's tendency to distill from the oil at frying temperature.

The purposes of the present study were to optimize the synthesis of LO and other terpenyl esters, to determine whether the autoxidation inhibition shown by LO depended on its double bond structure, and to understand better the oxidation inhibition mechanisms of LO. First we tested the effect of other terpenols. Geranyl oleate (GeO) was chosen because the structure of one of its double bonds was similar to LO and the other was quite different. Perillyl oleate (PeO) had two double bonds different from LO; one was in a cyclohexane ring and the other was a terminal double bond. Menthyl oleate (MenO) was chosen because it had no double bonds in the terpenol moiety. After the experiment with terpenols, we wished to see how sesquiterpenyl and diterpenyl oleates would affect the activity. Farnesol and phytol were selected because of their availability. Cholesteryl oleate (ChO) was chosen as a compound related to terpenes and sterols previously reported to inhibit oxidation during frying (10).

EXPERIMENTAL PROCEDURES

Materials. Bleached, deodorized soybean oil, containing only citric acid as an additive, was a gift from ADM (Decatur, IL). PV of the soybean oils as received were 0.1–0.6 mequiv/kg by AOCS method Cd 8-53 (12). Olive oil used for methyl oleate (MO) production was purchased from a local market. Silica gel (40–140 mesh) was from J.T. Baker Inc. (Phillipsburg, NJ). Urea and sodium methoxide solution in methanol (~5.4 M)

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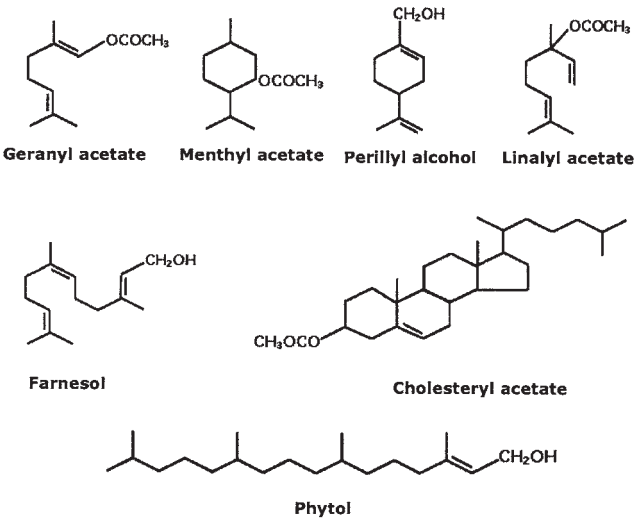

SCHEME 1

were purchased from Fluka (Milwaukee, WI). LA, geranyl acetate, DL-menthyl acetate, *S*-(–)-perillyl alcohol, cholesteryl acetate, methyl heptadecanoate, and mixed isomers of farnesol and phytol were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Their structures are shown in Scheme 1. Other chemicals were reagent grade and from Fisher (Fairlawn, NJ).

Concentration of MO. MO was concentrated from olive oil methyl esters by urea fractionation (13) as described by Onal-Ulusoy *et al*. (5) and used for synthesis of oleate esters. The MO concentrate was 84–90% MO, 7–10% methyl linoleate, and 0.4–2% methyl palmitate. Other compounds were at concentrations of less than 1%. The yield, based on the oleate in the olive oil, was 34–38%.

Synthesis of terpenyl and cholesteryl oleates. LO was synthesized by interesterification of LA and a 10% molar excess of MO using 0.5 mL of 5.4 M methanolic sodium methoxide solution as a catalyst (5). The methanol was removed from the sodium methoxide under vacuum before the other reagents were added. The reaction mixture was held at atmospheric pressure and room temperature for 15 min to allow the interesterification to proceed. After 15 min, the pressure was reduced slowly until no bubbles were seen in the reaction mixture, and then the reaction mixture was heated to 55°C for 30 min to facilitate removal of methyl acetate and drive the reaction to completion. When LO was synthesized by this procedure, the resulting mixture contained 35.1% FAME and 58.6% long-chain linalyl esters. Various modifications were tried to improve the yield of long-chain linalyl esters. These included (i) drying the LA with calcium sulfate to remove water, (ii) degassing the LA and MO under vacuum to remove soluble carbon dioxide before adding sodium methoxide, (iii) stirring the reaction mixture at atmospheric pressure for 15 min to give the volatile LA more time to react before applying vacuum to remove the methyl acetate formed by interesterification and drive the reaction to completion, and (iv) applying the vacuum to the reaction mixture as soon as possible for 10 min before heating the reaction mixture to 55°C for 30 min to remove volatiles, and (v) extending the reaction time at 55°C. The important factor for improving the yield was applying the vacuum to the reaction mixture as soon as possible for 10 min before heating the reaction mixture to 55°C for 30 min to remove volatiles. The revised method gave 76.9% yields of long-chain linalyl esters, of which 71.1% was LO.

The oleates of Experiment 1 were synthesized by the unmodified method used previously (5) whereas those of Experiment 2 were synthesized by this optimized procedure. LA, geranyl acetate, menthyl acetate, perillyl alcohol, farnesol, phytol, and cholesteryl acetate were used as reactants in the interesterification reactions. Reaction mixtures containing 90.8–92.8 % of farnesyl oleate (FaO), phytyl oleate (PhO), and ChO by GC were obtained and used without further purification. For ChO synthesis, only the volatile impurities could be measured by GC using methyl heptadecanoate as an internal standard.

Column purification of LO, GeO, MenO, and PeO. These reaction mixtures were fractionated by LC, primarily to remove unreacted MO. One gram of the reaction mixture was added to a column (20 mm i.d. × 18 cm) containing 10 g of silica gel. The eluent consisted of hexane/diethyl ether in a ratio of 1:0.005 vol/vol for LO and GeO and 1:0.006 vol/vol for PeO. The ether was distilled from lithium aluminum hydride before use to remove peroxides and the BHT that it contained as a stabilizer. The eluate was collected in 20-mL fractions. For purification of MenO, the first three fractions were eluted by using hexane/diethyl ether 1:0.005 vol/vol and the last four fractions with 1:0.006 vol/vol. For all the terpenol preparations, fractions rich in the desired product were identified by GC and were generally the fourth through the eighth fractions.

Verification of ChO. Because ChO could not be detected by GC, its synthesis was verified by TLC. The reaction mixture and MO and cholesteryl acetate standards were applied to a silica gel TLC plate having a 0.25 mm thick layer. The plate was developed with hexane/diethyl ether 95:5 vol/vol and viewed under UV light after spraying with a 0.1% solution of 2′,7′-dichlorofluorescein in methanol.

Frying procedure and oil sampling. The compounds to be tested as oxidation inhibitors were dissolved in distilled ethanol and added to a FryDaddy® 05422 (National Presto Industries, Eau Claire, WI) deep-fat fryer, and the ethanol was vaporized. The amount of these compounds was 0.1% of the oil weight, which was 252 g. A control without additives also was prepared. After addition of the oil, the fryers were heated continuously at 180 ± 5°C for 32 h. The temperature of each fryer was maintained by a variable transformer and monitored with a thermocouple. Three grams of oil was removed at 2, 4, 8, 12, 24, and 32 h for analyses and stored under nitrogen at 5°C until analyzed. The oil removed for samples was not replenished.

Conjugated dienoic acids (CD). Conjugated dienes were measured by AOCS method Ti 1a-64 (12) with a Hitachi U-2000 model spectrophotometer.

GC analyses. FAME of the frying oils were prepared by transesterifying the oils with sodium methoxide in methanol as

described by Hammond (14). An HP 5890 Series II gas chromatograph equipped with an FID and an SP-2330 capillary column (15 m × 0.25 mm × 1.0 μm film thickness; Supelco, Bellefonte, PA). Helium was the carrier gas (3 mL/min), and the injection port and detector temperatures were 230°C. For FA compositions of the heated oil samples, the column temperature was maintained at 190°C. For the MO fractions obtained during urea fractionation, the column temperature was programmed at 10°C/min from 140 to 225°C and maintained at 225°C for 5 min. For the terpenyl oleates, the column was programmed at 10°C/min from 100 to 225°C. The impurities in the ChO reaction mixture (FAME, especially unreacted MO and cholesteryl acetate) were analyzed on a HP-5 capillary column (30 m × 0.25 mm × 0.25 mm film thickness). The injection port and detector temperatures were 300°C, and the column was programmed at 10°C/min from 60 to 300°C.

NMR spectra. ^{1}H NMR spectra were obtained in chloroform-D (Cambridge Isotope Laboratories, Andover MA) on a Varian VXR 300-MHz instrument.

Statistical analysis. The frying data are the average of two replicate experiments. Data were analyzed statistically by using ANOVA by means of the general linear models procedure of an SPSS 9.0 software package (15). A confidence level of 0.05 was considered significant.

RESULTS AND DISCUSSION

The yield of LO was not affected by treatments to remove residual moisture or carbon dioxide from the reactants. Delay in the application of the vacuum to the reaction mixture to remove volatile products and drive the reaction resulted in a significant increase of free linalool and a decrease in yield of LO. The yield of LO was increased significantly by applying the vacuum quickly but keeping the reaction mixture at room temperature for about 10 min before increasing the temperature to 55°C. Holding the reaction mixture at 55°C for 3 h rather than 0.5 h also increased the yield of LO. By using these measures and holding the reaction mixture at 55°C for 30 min under vacuum, we increased the yield of long chain linalyl esters (linalyl oleate, palmitate, and linoleate) from 58.6% by our previous method (5) to 76.9%. The yield of LO was 71.1%. Holding the reaction mixture at 55°C for 3 h rather than 0.5 h also increased the yield of LO by ~5%. The yields of other terpenyl esters was not affected as strongly as LO by interesterification conditions. In using the unmodified method (5), the yield of the other terpenyl oleates was 77.5% GeO, 76.1% MenO, or 78.4% PeO. After silica gel chromatography, the purities of the products were 93.2, 91.9, and 85.1%, respectively. The other individual reaction mixtures contained 90.8% FaO, 92.8% PhO, and 91.5% ChO. Because of their high purity, we dispensed with further purification. Seemingly, the perillyl alcohol, farnesol, and phytol reacted almost as well as the terpenyl acetates.

The presence of ChO in the reaction mixture was verified by a TLC spot with an R_f greater than those of cholesteryl acetate and MO. Other spots were not observed in the reaction mixture. The concentration of ChO in the reaction mixture was estimated by determining the amount of cholesteryl acetate and MO in the reaction mixture by GC with methyl heptadecanoate as an internal standard and subtracting their amounts from the total amounts by weight in the reaction mixture.

NMR. The NMR results for LO are given in our previous paper (5). The identities of the new oleate esters also were verified by ^{1}H NMR: GeO ($CDCl_3$ 300 MHz): δ 5.34 (*t*, 3H), 5.08 (*t* 1H), 4.60 (*s*, 1H), 4.57 (*s*, 1H), 2.29 (*t*, 2H), 2.01 (*m*, 8H), 1.7 (*d*, 6H), 1.57 (*m*, 6H), 1.30 (*d,* 3H), 1.26 (*d*, 22H), 0.88(*t* 3H). MenO: δ 5.34 (*t*, 2H), 4.68 (*t*, 1H), 2.27 (*t*, 2H), 2.00 (*t*, 4H), 1.57 (*m*, 3H), 1.27 (*t*, 28H), 0.87, 0.76, 0.74 (*m*, 12H). PeO: δ 5.75 (*t*, 1H), 5.34 (*qn*, 2H), 4.73 (*d*, 2H), 4.46 (*s*, 2H), 2.32 (*t*, 2H), 2.21 (*m*, 9H), 1.74 (*s*, 3H), 1.57 (*m*, 2H), 1.27 (*m*, 22H), 0.88 (*t*, 3H). FaO: δ 5.34 (*t*, 2H), 5.09 (*t*, 2H), 4.57 (*d*, 2H), 2.30 (*t*, 2H), 2.03 (*m*, 13H), 1.76, 1.68, 1.60 (*m*, 12H), 1.30, 1.26 (*m*, 22H), 0.88 (*t*, 3H). PhO: δ 5.34 (*s*, 2H), 5.32 (*t*, 1H), 4.57 (*t*, 2H), 2.30 (*t,* 2H), 1.99 (*m*, 6H), 1.69 (*s*, 3H), 1.63 (*t*, 1H), 1.21, 1.27 (*m*, 40H), 0.88 (*m*, 15H). ChO: δ 5.35 (*m*, 3H), 4.63 (*t*, 1H), 2.26 (*t*, 2H), 2.00 (*m*, 8H), 1.83 (*m*, 1H), 1.30 (*m*, 48), 0.88 (*m*, 15H). All the ^{1}H NMR spectra agreed well with computer-predicted values. All the spectra except that of MenO showed a small peak at 3.66, which can be attributed to methyl carbamate produced during the concentration of the MO from olive oil with urea. Presumably, the altered column purification steps for MenO removed this impurity.

Comparison of fryers. In the previous study (5), the inhibitory effect of LO on autoxidation at 180°C at various levels was determined in FryBaby® 05430 fryers (National Presto Industries). In these fryers, 200 g of soybean oils was used. After considerable use, the Teflon™ layers on the inside surface of the fryers were damaged. Model 05430 was no longer available, so we purchased the most similar option, the FryDaddy 05442 deep-fat fryer, which had a diameter of 17.9 cm compared with 16 cm in the FryBaby. To keep the surface-to-volume ratio of the oil constant with respect to our previous study, we used 252 g of SBO in FryDaddy 05442. We found that LO at 0.05% was not as effective in the FryDaddy as it had been in the FryBaby. So, for the present experiments we used 0.1% by weight of the oil of the additives rather than 0.05% used previously. The change in fryers did not seem to affect the effectiveness of MS.

CD values. Figure 1 shows the percentages of CD in the control (oil without additives) and oils with 0.1% of LO, GeO, MenO, or PeO (the first experimental group) during the 32-h heating period. The percentage of CD in the control increased for 24 h, reached a plateau, and then decreased so that at the end of 32 h, the control had the lowest CD percentage of all the treatments. The additives retarded the increase in percentage CD, and at the end of 32 h their CD percentages were close to that of the control at 24 h. The statistical treatment of the data showed that at 2 and 8 h all the treatments were different from the control, but by 24 and 32 h none of the treatments was different from the control.

Figure 2 shows the changes in percent CD in the second experimental group (control, and oils with 0.1% LO, FaO, PhO, or ChO). Oil with LO, FaO, and ChO showed similar retardation of the increase in percentage CD through 24 h compared

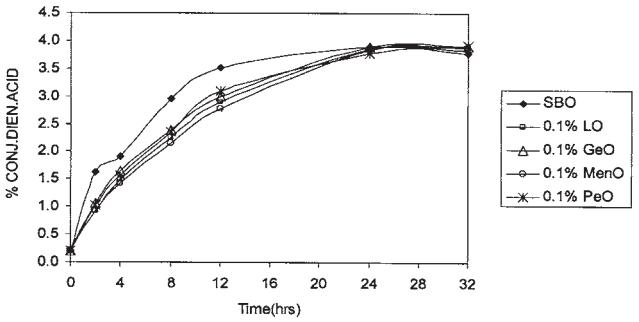

FIG. 1. Percentages of conjugated dienoic acid in soybean oil (SBO) protected with 0.1% linalyl oleate (LO), geranyl oleate (GeO), menthyl oleate (MenO), and perillyl oleate (PeO)

with the control. ChO had the lowest percentage CD at 24 h but eventually reached the same value of CD as LO. PhO only slightly decreased the rate of formation of CD compared with the control. After 24 h, the CD% in the control, FaO-, and PhO-treated oils started to decrease, whereas CD% in oils with LO and ChO were still increasing. The statistical treatment showed that at 2 h all the treatments were different from the control. At 8 h all except PhO were different from the control, and at 32 h none of the treatments was different from the control or each other. Thus, compared with the controls, all the treatments significantly retarded the generation of CD, but the retardation by PhO was much less than the other treatments.

CD formation has been shown to parallel polymer formation in heated oils (16,17) and increase linearly with total polar compounds, which provides a reliable measure of the extent of deterioration (2,16).

The ratio of linoleate%/palmitate% (18:2%/16:0%) and linolenate%/palmitate% (18:3%/16:0%). The ratio of 18:2%/16:0% can be used as an indicator of the extent of fat deterioration, and these ratios have been reported to correlate with changes in iodine value and dielectric constant (17,18). The ratios of 18:2%/16:0% and 18:3%/16:0% are measures of the survival of 18:2 and 18:3 with frying time because linoleate and linolenate are quite susceptible to oxidation, whereas palmitate is stable.

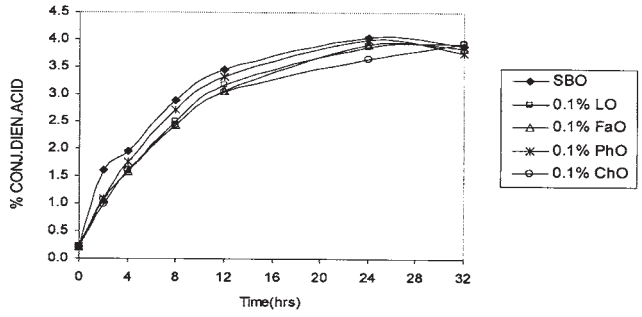

FIG. 2. Percentages of conjugated dienoic acid in SBO protected with 0.1% LO, farnesyl oleate (FaO), phytyl oleate (PhO), and cholesteryl oleate (ChO). For other abbreviations see Figure 1.

Logarithmic plots of decreasing ratios of 18:2%/16:0% and 18:3%/16:0% vs. time for controls and PhO were linear, but in oils with the other additives, plots for both these ratios had inflection points (IP) between 5–8.3 h and 5.2–11.4 h, respectively. The plots were linear both before and after the IP (R^2 = 0.99–1.0), and all could be fitted by first-order kinetics. The reaction rate constants before the IP were less than the reaction rate constants after the IP. Rate constants for 18:2%/16:0% and 18:3%/16:0% of control and oils with 0.1% of the various additives are given in Table 1.

In experimental group one, LO and MenO had the same rate constants for 18:2%/16:0% before the IP, but MenO's IP occurred earlier than LO's. Although GeO had an IP similar to LO's, GeO's rate constant was slightly higher than LO's, but this difference was not significant. Before the IP, oils with GeO, LO, MenO, and PeO reduced the disappearance of linoleate by 1.5-, 1.9-, 1.9-, and 2.1-fold, respectively, compared with the control. The reaction rate constant of oil with PeO was the lowest among the treatments, but its IP came earlier in frying than that of any of the other treatments.

In experimental group one, the rate constant of 18:3%/16:0% for oils with LO and MenO were lower than that of the control as shown in Table 1. But as with 18:2%/16:0%, the IP of oil with MenO occurred earlier than with LO. In contrast to the results with 18:2%/16:0%, the IP of oil with PeO occurred later in frying than with any of the other treatments, but its reaction rate was second highest among treatments. After the IP, the rates for all treatments were not different from the control.

In Experiment 2, the rate constants of 18:2%/16:0% and 18:3%/16:0% for the control and PhO were almost identical (0.025/h, 0.026/h, and 0.046/h, 0.047/h, respectively). The values for PhO were greater than the constants for oils with LO, FaO, and ChO prior to their IP. Thus, the limited ability of PhO to inhibit oxidation revealed by the CD data could not be detected in the kinetic data. The rate constants of FaO, ChO, and LO were not different from each other, but the IP of ChO and LO occurred at considerably longer times than that of FaO. After the IP, the 18:2%/16:0% rate constant of oil with FaO was less than those for ChO and LO, but not different from the control and PhO. The 18:3%/16:0% rate constant after the IP showed similar trends, but only the differences in rates for FaO and ChO were statistically significant.

The rate of decrease of 18:3 in the soybean oil control was about 1.8 times that of 18:2, which is close to the value found in a previous study (5). LO had greater rate constants before its IP for both 18:2%/16:0% and 18:3%/16:0% than those found previously (5), but LO reduced the rate of oxidation of 18:3/18:2 by 2.3- to 2.4-fold, which is similar to the value found previously.

Linalool esters originally were chosen for study because linalool has a double bond structure similar to that of the side chain of avenasterol, which also shows an ability to inhibit oxidation under frying conditions. This study shows that terpenyl oleates with widely different structures, or with no double bonds in the terpene portion in the instance of MenO, inhibited autoxidation at frying temperatures. These results suggest that

TABLE 1
The Inflection Points and Numerical Values of the Rate Constants for the Disappearance of 18:2% and 18:3%, Relative to 16:0%, vs. Time in Soybean Oil Controls and Treatments with 0.1% of Linalyl Oleate (LO), Geranyl Oleate (GeO), Menthyl Oleate (MenO), Perillyl Oleate (PeO), Farnesyl Oleate (FaO), Phytyl Oleate (PhO), or Cholesteryl Oleate (ChO) Heated to 180°C

Treatments	Before inflection point	After inflection point	Time of inflection point
18:2%/16:0%	k (h^{-1})	k (h^{-1})	h
Experiment 1			
Control	0.025^{b}	0.025^{a}	None
LO	0.013^{a}	0.025^{a}	7.0
GeO	0.017^{a}	0.024^{a}	7.1
MenO	0.013^{a}	0.027^{a}	6.4
PeO	0.012^{a}	0.025^{a}	5.0
Experiment 2			
Control	0.025^{b}	$0.025^{a,b,c}$	None
LO	0.014^{a}	$0.027^{b,c}$	7.0
FaO	0.018^{a}	0.025^{a}	6.3
PhO	0.026^{b}	$0.026^{a,b}$	None
ChO	0.019^{a}	0.028^{c}	8.3
18:3%/16:0%			
Experiment 1			
Control	0.047^{b}	0.047^{a}	None
LO	0.032^{a}	0.046^{a}	10.3
GeO	$0.037^{a,b}$	0.044^{a}	9.9
MenO	0.031^{a}	0.048^{a}	7.9
PeO	$0.036^{a,b}$	0.046^{a}	11.4
Experiment 2			
Control	0.046^{b}	$0.046^{a,b}$	None
LO	0.032^{a}	$0.047^{a,b}$	7.7
FaO	0.036^{a}	0.044^{a}	5.2
PhO	0.047^{b}	$0.047^{a,b}$	None
ChO	0.035^{a}	0.050^{b}	8.2

^{a,b,c}Constants within a column, experiment, and FA type with the same superscript are not significantly different ($P > 0.05$).

linalool's double bond structure is not the cause of its inhibitory activity. Although the data reported in this paper weaken the hypothesis that the oxidation inhibition activity of various sterols and LO can be attributed to their double bond structures, the data does not suggest any particular alternate theory. Our current working hypothesis is that MS and some of the compounds we have tested inhibit oxidation by accumulating on the surface of oils and forming an oxygen barrier. MS appears to accumulate on oil surfaces at a lower concentration than the compounds we have tested, but compounds more "natural" than MS and with more effective structures might be designed.

Gordon and Magos (5) reported that cholesterol had no significant antioxidant activity on oxidation of a model TG mixture, so esterification of cholesterol's hydroxy group may be necessary for activity. LA was reported to be ineffective in preventing the oxidation of cholesterol and TG in heated lard, although LA was effective in soybean oils (3). In our previous paper, we speculated that tocopherols might be necessary for the inhibitory effect of LO and MS. Lard contains 12 and 7 ppm of α-tocopherol and γ-tocopherol, respectively, which is lower than that of most vegetable oils (19). The limited activity of PhO as an oxidation inhibitor is unexplained. Possibly, if the accumulation of the terpene portion of the molecule in the air/oil interface is important, the length of the terpene portion should not exceed that of the straight-chain FA portion. Further work needs to be done to better understand the inhibitory mechanism of terpenyl and steryl esters.

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