Evaluation of the Mechanism of Dilauryl Thiodipropionate Antioxidant Activity

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Dilauryl thiodipropionate (DLTDP) was ineffective as an antioxidant for decomposing lipid hydroperoxides when incorporated into fish oil at concentrations less than 50,000 ppm (0.1 M) at 50 C. However, some general antioxidant properties for DLTDP were observed in fish oil containing 200 ppm DLTDP at 50 C under oxygen for 72 hr. An anomolous prooxidant behavior for DLTDP in fish oil was observed under some conditions of accelerated oxidation which was attributed to the formation of the bisulfite ion free radicals derived from DLTDP degradations. DLTDP was effective for inactivating peracids in model systems containing performic acid and nonanal, ethyl oleate or cholesterol. In these systems DLTDP (2:1 DLTDP:performic acid mole ratio) was preferentially oxidized to the sulfoxide, and prevented the formation of nonanoic acid, 9-epoxy ethyl oleate and 5,6-epoxy cholesterol, respectively.

Primary antioxidants currently used in foods in the U.S. include the synthetic phenolics and tocopherols that rely on free radical termination and singlet oxygen scavenging to provide lipid stabilization (1, 2). These antioxidants significantly retard the rate of deterioration in many foods and oils, but oxidative degradation of lipids and flavor components often occurs in the presence of these compounds after relatively short times. Therefore, improved antioxidant protection is sought continually by the industry.

Thiodipropionic acid and its dilauryl ester have been approved for food use for some time (3), but few applications have been described (4,5). For foods, the thiodipropionates generally are regarded as synergists rather than primary antioxidants (6–10). This activity generally has been attributed to an ability to chelate metals by free thiodipropionic acid (8) and the general sulfide function of decomposing alkyl hydroperoxides into more stable compounds (4, 5, 11). However, sulfides also inactivate peroxyacids (peracids) (12) which are capable of oxidizing aldehydes, ketones (13–17) and olefins (12–15, 18).

Because thiodipropionates should possess useful antioxidant properties for foods, wider application of these approved food additives might result from a more thorough evaluation of their mechanism of action. Therefore, the purposes of this research were to determine the ability of dilauryl thiodipropionate (DLTDP) to degrade hydroperoxides in fish oil and to evaluate its ability to protect olefinic and carbonyl groups from oxidation by peracids in compounds significant to food quality.

MATERIALS AND METHODS

Model systems for hydroperoxide decomposition. Various concentrations of DLTDP (dilauryl thiodipropionate; 0, 200, 500, 1,000, 2,500, 5,000, 50,000 and 200,000 ppm) (Evans Chemetics, W.R. Grace and Co., Lexington, Massachusetts) were added as methylene chloride (HPLC; J.T. Baker Chemical Co., Phillipsburg, New Jersey) solutions to one g of dry, freshly-prepared, heat-rendered (100 C for 10 min) oil from siscowet lake trout (*Salvilinus namaycush* siscowets) obtained commercially (Bodin Fisheries, Inc., Bayfield, Wisconsin). Samples of oil were placed in a vacuum desiccator (250 mm) containing a five-cm bed of sand, evacuated to 2–3 mm Hg, and then were incubated quiescently in the closed vessel while it was positioned in a waterbath (Model 02156; American Optical Corp.) held at 50 C for 24 hr. The vacuum desiccator was opened at 3-, 6-, 12-and 24-hr intervals for sampling of oils. Samples were taken quickly, and the vessel was again closed and evacuated (2–3 mm Hg).

Duplicate samples from each vial were analyzed for hydroperoxide content by the method described by Buege and Aust (19).

Model systems for general antioxidant behavior. One-g samples of the heat-rendered siscowet lake trout oil containing either no added antioxidant, 200 ppm DLTDP, 200 ppm butylated hydroxytoluene (BHT; Eastman Chemical Products, Inc., Kingsport, Tennessee) or 200 ppm DLTDP plus 200 ppm BHT were prepared. Samples were oxidized under accelerated conditions (50 C) by placing open vials in a chamber with a five-cm bed of sand where an excess of pure oxygen was bubbled through the oil (ca. 240 ml/min). The temperature of the bed of sand was maintained by immersing the chamber in a waterbath.

Model systems used to evaluate the effect of elevated levels of antioxidants on the rate of oil oxidation used vacuum, steam-stripped (laboratory apparatus, 20; 125 C for 1.5 hr at 4 mm Hg) cod liver oil (McKesson Corp., Dublin, California) which initially had been stabilized in the laboratory with 100 ppm butylated hydroxyanisole (BHA), 100 ppm tertiarybutyl hydroquinone (TBHQ; Eastman Chemical Products, Inc., Kingsport, Tennessee) and 200 ppm DLTDP as the control oil. To this stabilized control oil, either 200 ppm BHT, 200 ppm DLTDP or 200 ppm DLTDP plus excess sodium bicarbonate (Fisher Scientific Co., Fairlawn, New Jersey) was added; then, it was exposed to accelerated oxidation conditions of 50 C and excess oxygen. Each oil sample was evaluated over time and analyzed for hydroperoxide content (19).

Synthesis of performic acid in model systems. Freshly synthesized performic acid for model systems was prepared by reacting excess formic acid (A.C.S. grade, 98%, Aldrich Chemical Co., Milwaukee, Wisconsin) with 30% hydrogen peroxide (Fisher Scientific Co., Fairlawn, New Jersey) in a ratio of 4:1 (vol:vol), respectively (15). The solution was mixed using a rocker-arm shaker (Model BB; Burrell Corp., Pittsburg, Pennsylvania) at 21 C for five min before addition of aliquots of performic acid to each model system. Because techniques were unavailable for measurement of concentra-

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tions of synthesized performic acid, these were estimated based on the concentration of the limiting reactant (H_2O_2) assuming a 1:1 mole production of performic acid for each mole of hydrogen peroxide.

Performic acid oxidation of dilauryl thiodipropionate. DLTDP (2500 ppm) and ethyl palmitate (Eastman Chemical Products Inc., Kingsport, Tennessee; internal standard, 2500 ppm) were dissolved in one ml of n-butyl chloride (Fisher Scientific Co., Fairlawn, New Jersey). A 10-μl aliquot of performic acid mix was added to each three-dram reaction vial, and vials were tightly capped to minimize solvent loss, then agitated at 21 C.

Samples (20 μl) were withdrawn at each sampling point for HPLC analysis using a SupelcoSil LC-18 reverse phase column (250 mm × 6.25 mm i.d., Supelco, Inc., Bellefonte, Pennsylvania) which was protected with a guard column of the same packing. The mobile phase was degassed acetonitrile (HPLC grade, Fisher Scientific, Co., Fairlawn, New Jersey) which was delivered with an ISCO pump (Model 2300, Instrument Specialties Co., Lincoln, Nebraska) at a flow rate of 1.6 ml/min. Samples were introduced with a Rheodyne injection valve fitted with a 20-μl loop (Model 7125, Rheodyne Inc., Cotati, California). A variable wavelength absorbance detector (ISCO Model 1840; Instrument Specialties Co., Lincoln, Nebraska) equipped with a 19-μl flow cell was set at 210 nm. Chromatographic data were processed with a computing integrator (Model SP 4100, Spectra Physics, San Jose, California).

Identification of peaks in oxidized DLTDP was accomplished by coincidence of HPLC retention times of unknowns with authentic compounds and by solid probe mass spectrometry. Fractions eluting under peaks were collected and were analyzed with a Finnigan 4500 mass spectrometer using either the chemical ionization mode (CI; isobutane, 50 C for one min, then to 300 C at 8 C/min; 70/ev) or the electron impact mode (EI; 50 C for one min, then to 300 C at 8 C/min; 70/ev) to determine molecular weights and mass fragmentation patterns, respectively. HPLC response factors for DLTDP (0.034), DLTDP sulfoxide (0.021) and DLTDP sulfone (0.59) were measured by determining the ratio of the area of ethyl palmitate (internal standard) to that of each compound for equivalent molar concentrations.

Performic acid oxidation of nonanal. Nonanal (Chemical Samples Co., Columbus, Ohio) was purified before oxidation by collecting fractions from GLC separations using a 3-m × 2-mm i.d. glass column packed with 7% Carbowax 20M on Chromosorb W AW/DMCS installed in a Varian 1740 GC (Varian Associates Inc., Sunnyvale, California). Measured amounts of nonanal (ca. 500 ppm), tridecane (Aldrich Chemical Co., Milwaukee, Wisconsin; internal standard; 18 ppm) and, where appropriate, DLTDP (ca. 230,000 ppm; 2:1; mole DLTDP:mole performic) were dissolved in one ml of hexane (HPLC grade, Mallinckrodt Inc., Paris, Kentucky). A 200-μl aliquot of performic acid mixture was added to each three-dram reaction container and tightly capped with a screw-cap to minimize solvent loss before agitating them at 21 C. Oxidized DLTDP was allowed to crystallize and separate from the reaction mixture. Concentrations of nonanal remaining in the hexane solvent were measured quantitatively compared to the internal standard (tridecane). A one-μl sample was withdrawn at each given interval and analyzed by GC.

Volatile compounds in hexane solvents were analyzed using a Varian 3700 gas chromatograph (Varian Associates Inc., Sunnyvale, California) equipped with an on-column injection system and FID/FPD detectors. Separations of volatile compounds were achieved using a Durabond 1 (60-m × 0.31-mm i.d.) fused silica capillary column (J & W Scientific, Inc., Rancho Cordova, California) operated with helium as the carrier gas. A program rate of 50 C (1-min hold) to 300 C at 6 C/min was used. Chromatographic data were processed with a computing integrator (Model SP 4200, Spectra Physics, San Jose, California).

Peak identifications were based on retention indices of authentic compounds (21). Response factors for nonanal (0.33) and nonanoic acid (0.40) were determined as before, based on equivalent molar concentrations compared to the internal standard (tridecane).

Performic acid oxidation of cholesterol. Cholesterol (500 ppm), 5α-cholestane (Sigma Chemical Co., St. Louis, Missouri; internal standard, 500 ppm) and, when appropriate, DLTDP (5800 ppm) were dissolved in four ml of hexane. A five-μl aliquot of performic acid mix (2:1 mole DLTDP:mole performic acid) was added to each reaction vial and tightly covered prior to agitation at 21 C. Oxidized DLTDP was allowed to crystallize and separate from the reaction mix leaving cholesterol, its oxidation products, and 5α-cholestane (internal standard) in the hexane solvent. A one-μl sample of the hexane solvent was withdrawn at each given interval and analyzed with a Hewlett Packard 6890A gas chromatograph (Hewlett Packard Co., Palo Alto, California) equipped with an automatic injector and a hot on-column injection system with a 1:10 split ratio. Separation of compounds was achieved using an HP-1 (5-m × 0.32-mm i.d.) fused silica capillary column (Hewlett Packard Co., Palo Alto, California) operated isothermally at 250 C with helium as the carrier gas. Chroma-

TABLE 1

Hydroperoxide Concentrations of Heat-rendered Fish Body Oil[a]

Dilauryl thiodipropionate concentration (ppm)	Hydroperoxide concentration[b] (μmol/mg oil)				
	0 hr	3 hr	6 hr	12 hr	24 hr
0 (no added $MeCl_2$)	5.5	—[c]	—	—	—
0 (added $MeCl_2$)	—	—	4.8	—	7.4
200	—	5.0	5.6	6.3	7.1
500	—	—	4.8	—	6.3
1000	—	5.4	5.6	6.3	5.6
2500	—	—	6.0	—	7.0
5000	—	5.2	5.5	5.8	6.5
50,000 (0.1 M)	—	—	5.3	—	4.1
200,000 (0.4 M)	—	3.7	3.4	2.1	1.3

[a]Oil from siscowet lake trout containing different levels of dilauryl thiodipropionate added as methylene chloride solutions and held overtime at 50 C quiescently under vacuum.

[b]Values reported are an average of two analyses. Analytic variation is ± 1.4.

[c]Sample not analyzed.

tographic data were processed using a Hewlett Packard 3393A integrator (Hewlett Packard Co., Palo Alto, California).

Peak identification of oxidized cholesterol (5,6-α-epoxy cholesterol, Sigma Chemical Co., St. Louis, Missouri) was based on coincidence of retention times with the authentic compound. The response factor for cholesterol (1.06) was determined with respect to the internal standard (5-α-cholestane) on an equal molar concentration basis.

Performic acid oxidation of ethyl oleate. Ethyl oleate (Aldrich Chemical Co., Milwaukee, Wisconsin; ca. 2300 ppm) and tridecane (internal standard; 47 ppm) each were added to 1.2 ml of hexane. A 100-μl aliquot of performic acid mix was added to the reaction mixture and allowed to react at 21 C for 46 hr. Samples (0.6 μl) were withdrawn at specified time intervals and analyzed by GC conditions reported for nonanal oxidation. The response factor for ethyl oleate (.78) was determined with respect to tridecane (internal standard) on an equal molar concentration basis.

Model systems used to demonstrate the protection of ethyl oleate by the addition of DLTDP were analyzed by HPLC. Ethyl oleate (ca. 1300 ppm), ethyl myristate (Aldrich Chemical Co., Milwaukee, Wisconsin; internal standard; 2500 ppm) and DLTDP (10,000 ppm) were dissolved in one ml of n-butyl chloride. Ten μl of peracid mix was added to the reaction mixture (2:1; mole DLTDP:mole performic) and allowed to react for 46 hr. A 20-μl sample was removed at each given time interval and analyzed by HPLC procedures described above. The response factor for ethyl oleate (0.024) was determined with respect to ethyl myristate (internal standard) on an equal molar concentration basis.

RESULTS AND DISCUSSION

Hydroperoxide decomposition by DLTDP. Results of experiments designed to evaluate the hydroperoxide-decomposing capability of different levels of DLTDP added to fish oil systems under vacuum (2–3 mm Hg) and at 50 C are presented in Table 1. Concentrations of DLTDP below 50,000 ppm (0.1M) did not significantly reduce the hydroperoxide concentration in 24 hr. However, when the level of DLTDP increased from 50,000 to 200,000 ppm (0.4M), a 76% reduction of total hydroperoxides was seen after 24 hr. These data indicate that the hydroperoxide-decomposing ability of DLTDP in lipids is limited to high concentrations where mass interaction between hydroperoxides and organic sulfides can proceed. Although these results are in agreement with those of Bateman and Hargrave (22), who showed substantial reduction of hydroperoxide content in the presence of 0.4M cyclohexylmethyl sulfide (66%), the level needed to obtain the desired hydroperoxide reduction in lipids far exceeds that of the maximum allowable level in foods (200 ppm) (3).

Even though these results show that DLTDP is an ineffective hydroperoxide decomposer at levels allowed in foods, 200 ppm of DLTDP provides limited antioxidant protection to fish oils exposed to accelerated oxidation conditions (50 C, pure O_2; Fig. 1). These data indicate that the very limited degree of protection was much less than that afforded by a traditional phenolic antioxidant (BHT). When DLTDP was added in conjunction with BHT (DLTDP + BHT; Fig. 1) no increase in antioxidant protection as indexed by hydroperoxide formation was observed which was not in agreement with earlier studies using free thiodipropionic acid (8–10). Because thiodipropionate esters cannot participate in chelation, their contribution to antioxidant protection would necessarily depend on chemical reactions involving the sulfidic functional group.

An anomalous prooxidant property of DLTDP was discovered in a highly antioxidized fish oil system which was used for accelerated oxidation studies. Oil samples containing 400 ppm DLTDP developed hydroperoxides more rapidly after 120 hr than oils containing 200 ppm DLTDP. However, when excess sodium bicarbonate was added to the system, the accelerated oxidation did not occur (Fig. 2). These data were interpreted as reflecting the involvement of free radical formation by the bisulfite anion after its formation through elimination from DLTDP sulfone.

Evidence for eliminations was seen when molecular weight determinations of DLTDP sulfone (MW = 546) and sulfoxide (MW = 530) were carried out using mass spectral chemical ionization analysis. Molecular

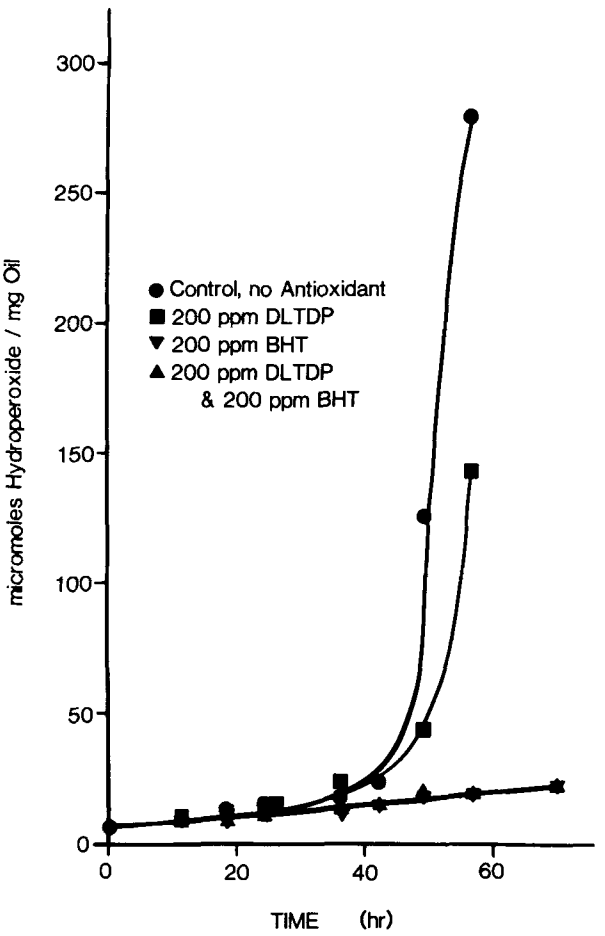

FIG. 1. Accelerated oxidation of siscowet lake trout oil at 50 C under excess oxygen purge containing no antioxidant (●), 200 ppm DLTDP (■), 200 ppm BHT (▼), or 200 ppm DLTDP plus 200 ppm BHT (▲).

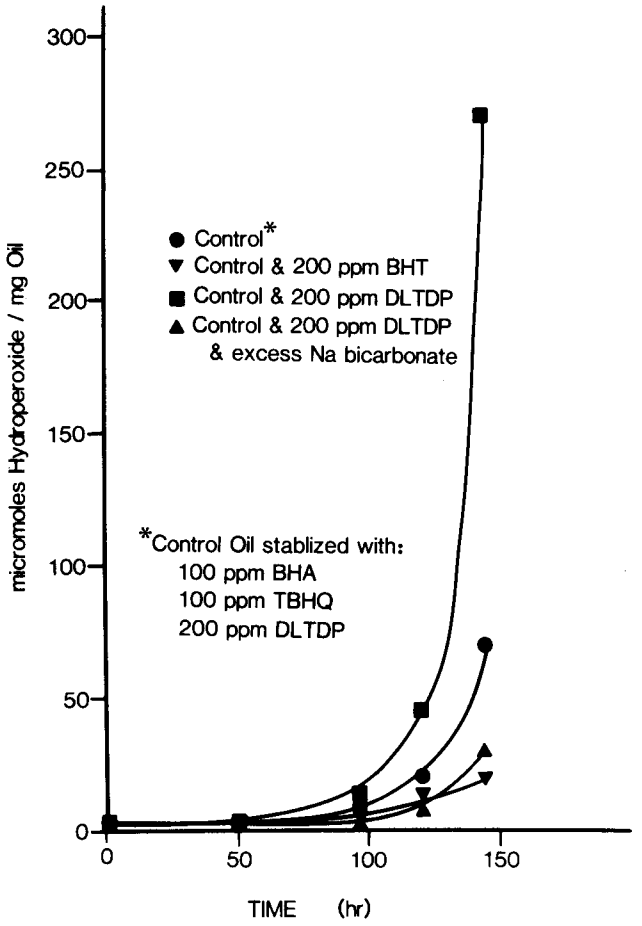

FIG. 2. Accelerated oxidation of stabilized cod liver oil (steam-stripped and containing 100 ppm BHA, 100 ppm TBHQ and 200 ppm DLTDP, ●) with additional DLTDP (200 ppm, ■), BHT (200 ppm, ▼) or DLTDP (200 ppm) plus excess sodium bicarbonate (▲) at 50 C and under excess oxygen.

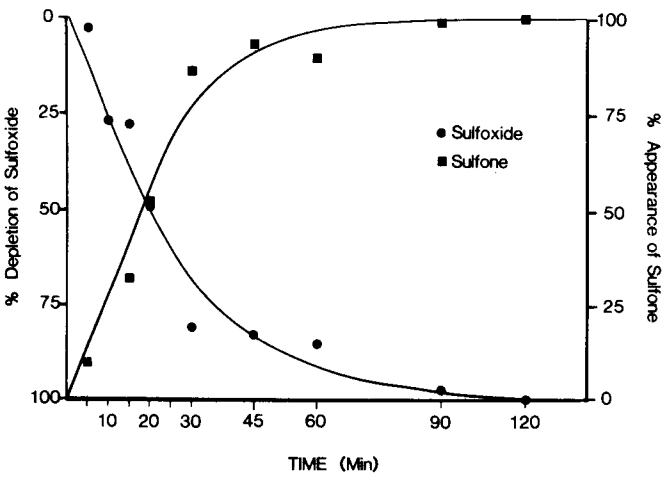

FIG. 3. Conversion of dilauryl thiodipropionate sulfoxide (●) to the sulfone (■) by excess performic acid oxidation of dilauryl thiodipropionate (DLTDP) in n-butyl chloride.

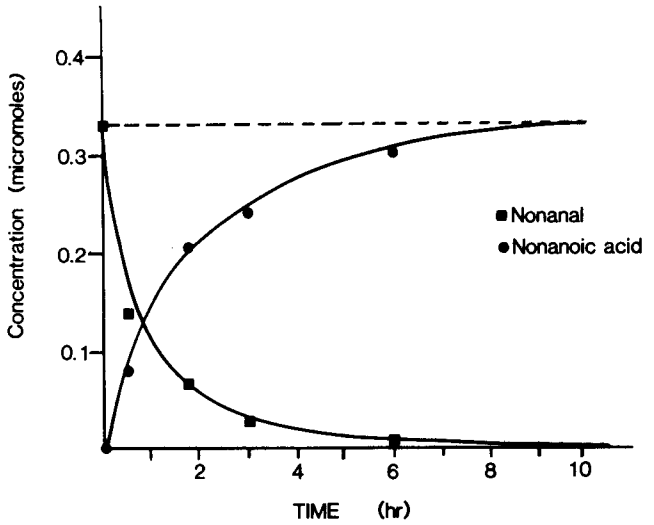

FIG. 4. Performic acid oxidation of nonanal (■) to nonanoic acid (●) in hexane solutions.

ions were not observed, but mass fragment peaks for the rearrangement derivatives were seen as 241(100), 243(54), 169(25) and 257(17) for the sulfone and 241(100), 242(19) and 275(13) for the sulfoxide. Because of the instability of the oxidized sulfur moiety (23, 24), elimination and recombination of the remaining fragments at elevated temperatures apparently occurred readily in the mass spectrometer as well as in the fish oil.

The formation of the free radicals which were believed to occur could result from the hydration of SO_2 in the presence of small amounts of water which proceeds to form the acid. The acid then ionizes to the bisulfite ion (25), and finally dismutates to form the $SO_2^{\bullet}$ free radical (26) or the $SO_3^{\bullet}$ free radical in the presence of excess H_2O_2 (27-29). These free radicals then can act as prooxidants in oxidizing lipid systems (30,31). Thus, these data and observations indicate that lower stability of oil systems could exist when high concentrations of DLTDP are involved. However, at concentrations of DLTDP in fish oil which are permitted by regulations, the prooxidant effect was not observed.

Peracid inactivation by DLTDP. The data presented in Figure 3 were obtained from the performic acid oxidation of DLTDP which proceeded step by step to form the sulfoxide (retention time = 14.5 min on SupelcoSil LC-18; EI mass spectrum: 55(100), 57(75), 43(62), 104(51), 71(41), 69(40), 122(34), 83(33), 97(27), 530 M^+ (not seen) within the first minute of reaction, and then the sulfone [retention time = 10.5 min on SupelcoSil LC-18; EI mass spectrum: 121(100), 193(99), 55(87), 57(75), 43(74), 379(60), 69(43), 211(39), 83(29), 547 M^{+1} (trace)].

The classic mechanism for sulfide oxidation by peracids initially involves a rapid concerted addition of oxygen from unionized peracid molecule to form the sulfoxide (12,13,32), followed by reaction of the sulfoxide with an ionized peracid to form the sulfone (13,33). In each step, one molecule of peracid is converted to the corresponding acid. Under conditions of this experiment the oxidation of the sulfide to the sulfoxide

occurred within one min, which was too rapid to quantify, but the conversion to the sulfone occurred at a slower rate (Fig. 3) which was regulated by the rate-limiting peracid ionization step (12,15).

Other sulfides which are commonly found in foods, such as methionine, cysteine and S-methyl cysteine, also may act as peracid inactivators. Earlier studies on the oxidation products of sulfur-containing amino acids have shown the presence of sulfoxide derivatives when elevated levels of hydrogen peroxide were introduced into the system (34-36). O'Keefe and Wartheson (35) demonstrated that the addition of excess hydrogen peroxide to free methionine resulted in the oxidation of the sulfide to the sulfoxide and sulfone, and concluded that this reaction proceeded by way of hydroperoxide decomposition. Based on the low hydroperoxide decomposing activity observed for DLTDP (Table 1) and the rapid peracid reaction with DLTDP (Fig. 3), it can be suggested that the H_2O_2-catalyzed reaction may have proceeded by formation of methionine peracid which quickly reacted with the sulfidic group of methionine to form sulfoxides. Ultimately, when high concentrations of H_2O_2 were used, sulfones were formed.

Antioxidant protection of aldehydes by DLTDP. Although selective peracid oxidations of aldehydes to acids and olefins to epoxides (13,15) are used routinely

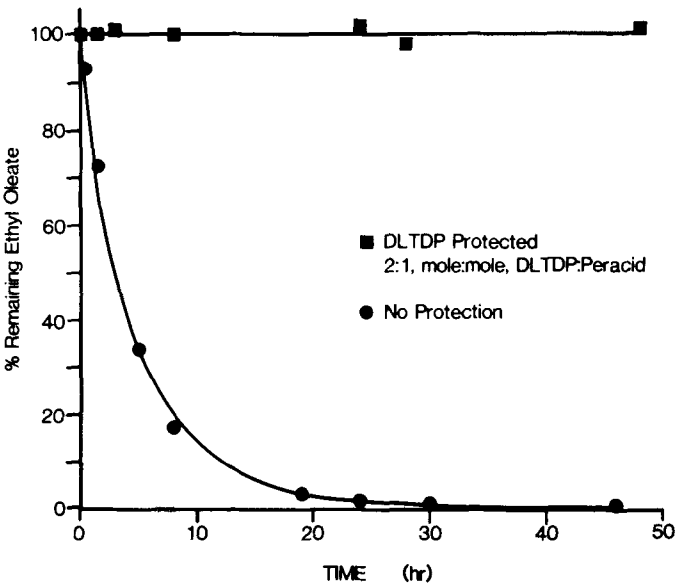

FIG. 6. Performic acid oxidation of unprotected ethyl oleate (●) and DLTDP-protected ethyl oleate (2:1 mole DLTDP:mole performic acid, ■) in hexane solutions.

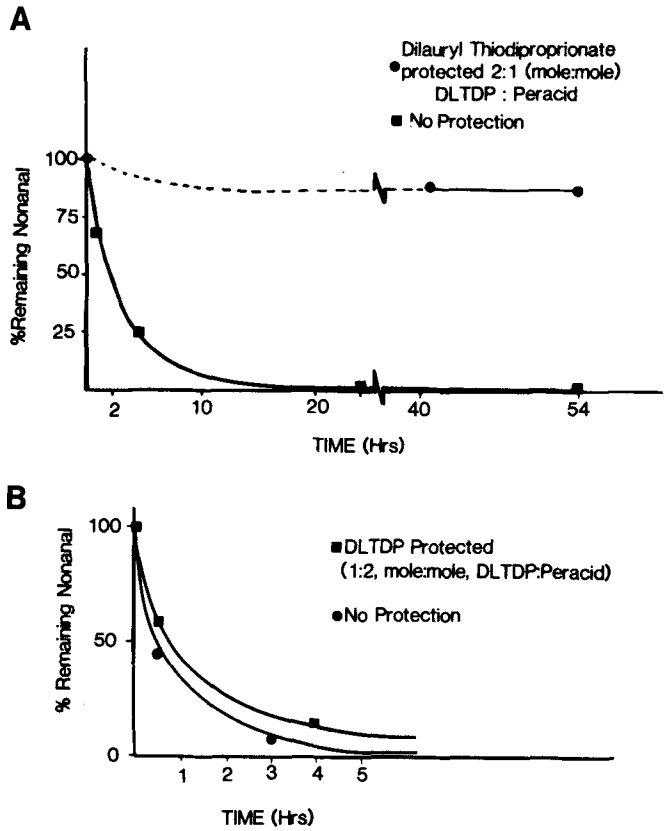

FIG. 5. Performic acid oxidations of unprotected nonanal and DLTDP-protected nonanal in hexane solutions. A, DLTDP protected at 2:1 mole DLTDP:mole performic acid concentration (●). B, DLTDP protected at 1:2 mole DLTDP:mole performic acid concentration (■).

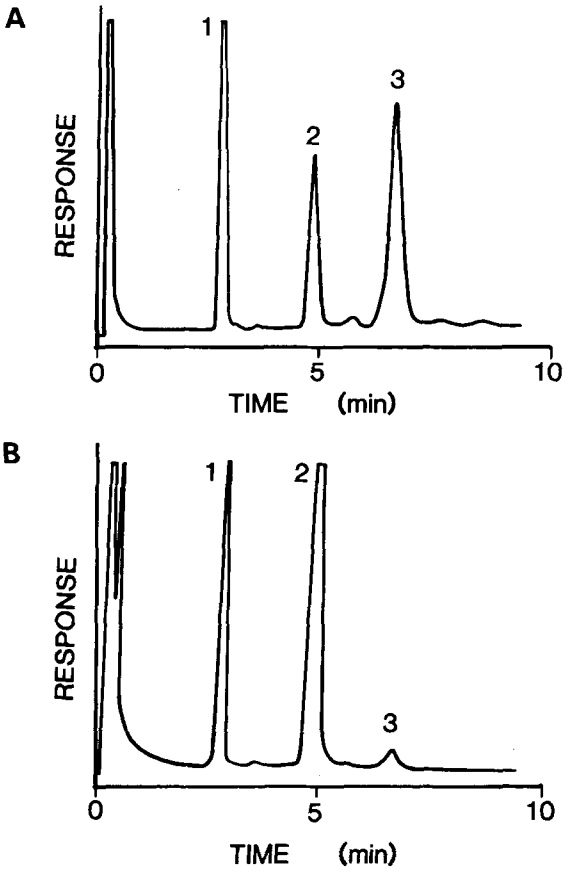

FIG. 7. Gas chromatograms of performic acid epoxidation of cholesterol (2) to 5,6α-cholesterol epoxide (3) without DLTDP protection (A) and in the presence of DLTDP (B; 2:1 mole DLTDP:mole performic acid) after 8 hr using an HP-1 (5-m × 0.32-mm i.d.) fused silica capillary column. 5-αcholestane (1) was incorporated as the internal standard.

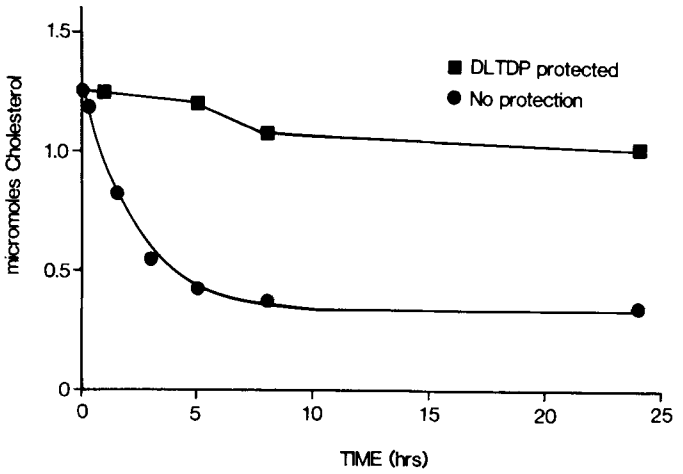

FIG. 8. Performic acid oxidation of unprotected cholesterol (●) and DLTDP-protected cholesterol (2:1 mole DLTDP:mole performic acid, ■) in hexane solutions.

in organic synthesis, the effects of peracid oxidations of sensitive flavor and nutritional components in foods have not been investigated to any extent. Peracids are formed from interactions between oxygen and aldehyde-derived free radicals (37) as well as by interactions of hydroperoxides with acids (13,15) in oxidizing lipid systems.

The data presented in Figure 4 for a model system show complete oxidation of nonanal by performic acid to nonanoic acid after 10 hr when DLTDP was omitted from the reaction mixture. When the model system was protected with DLTDP (2:1 mole ratio of DLTDP:performic acid; Fig. 5A), DLTDP was preferentially oxidized because of its rapid oxidation to the DLTDP sulfoxide, thus sparing nonanal from peracid oxidation. In studies where less concentrated DLTDP (1:2 mole DLTDP:mole performic acid) was incorporated, aldehyde oxidation was retarded but not prevented compared to unprotected samples (Fig. 5B). In this case, the sulfone-forming antioxidant activity developed at a much slower rate than for the sulfoxide-forming step. However, concentrations of peracids in foods would be expected to be much lower than the amount of DLTDP which would be provided, and ratios of at least 2:1 for DLTDP:peracid would exist. Therefore, effective rapid inactivation of peracids would be expected in foods.

Many flavor and aroma character-impact compounds are aldehydic (38,39), and much attention has been given to their stabilization to maintain flavor quality (40). Currently, physical oxygen barriers (41) or chemical derivatizations (40) provide the most effective means of protection against aldehyde oxidation. However, the incorporation of DLTDP as a peracid inactivator would provide an additional means of protection of the aldehydes from peracid oxidations and should result in an improvement of overall flavor quality and stability of many foods.

Antioxidant protection of olefinic bonds by DLTDP. Data presented in Figure 6 illustrate the reactive nature of performic acid in the epoxidation of the double in ethyl oleate. GC-MS analysis verified the oxidation product as 9-epoxy ethyl oleate [elution time = 32.4 min on DB-1; 55(100), 43(84), 69(81), 88(77), 155(69), 101(60), 83(55), 97(43), 326 M^+ (trace)]. When DLTDP was added (2:1 mole DLTDP:mole performic acid) to the reaction mixture, complete protection of the double bond resulted (Fig. 6) because of the sparing effect provided by preferential oxidation of DLTDP.

Results from similar experiments where performic acid was incorporated into model systems containing unprotected cholesterol showed that performic acid was a potent cholesterol epoxide generator (Fig. 7A). The oxidation of cholesterol to the 5,6α-cholesterol epoxide proceeds rapidly when exposed to performic acid, but cholesterol was spared in the presence of DLTDP (Fig. 7 and 8). The formation of cholesterol epoxides has also been reported for reactions of cholesterol with active oxygen species, such as singlet oxygen, superoxide anions, hydroxy radicals and ozone (42, 43). Because cholesterol oxides have been suspected as promoters of atherosclerosis or as carcinogens in laboratory animals (44-46), their presence in food has been a concern from the perspective of maintaining nutritional quality and safety under conditions that promote oxidation (47,48). The protection of cholesterol from peracid oxidation provided by DLTDP would appear to be a useful strategy in the prevention of cholesterol epoxide formation in vulnerable foods (49-54). Additionally, other sensitive olefinic components of foods, such as vitamin A and other unsaturated nutrients and flavor compounds, would be expected to be protected by DLTDP from epoxidation by peracids.

Thiodipropionates were found to be ineffective lipid hydroperoxide-decomposers at levels allowed in foods (200 ppm), but were found to effectively terminate peracid oxidations of aldehydes and epoxidation of olefins. Use of thiodipropionates with currently employed antioxidant systems should provide increased quality and flavor stability, especially in foods containing sensitive aldehydic flavor compounds, unsaturated nutrients, and compounds that are oxidized to potentially harmful substances.

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