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Effect of α-Tocopherol and Trolox on the Decomposition of Methyl Linoleate Hydroperoxides

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ABSTRACT: To clarify the mechanisms of antioxidant action, the effect of α-tocopherol and its water-soluble carboxylic acid derivative, Trolox, was studied on the decomposition of methyl linoleate hydroperoxides (MeLoOOH). Decomposition rate and the distribution of autoxidation products formed from MeLoOOH were followed by analyzing the volatile and nonvolatile products by static headspace gas chromatography and normal-phase high-performance liquid chromatography, respectively. Both α-tocopherol and Trolox markedly inhibited the decomposition of MeLoOOH in a concentration-dependent way. In the absence of antioxidants, MeLoOOH was completely decomposed after incubation for 48 h at 60°C, and in the presence of equal molar concentration of antioxidants only 6–7% of initial MeLoOOH was decomposed even after 280 h of incubation. MeLoOOH produced 1.2% methyl linoleate hydroxy compounds (MeLoOH) in the presence of α-tocopherol and 3.8% in the presence of Trolox. Both antioxidants inhibited the formation of volatile decomposition products and the formation of ketodiene compounds. The hydroxy compounds may be formed by the reaction of alkoxy radical and hydrogen donating antioxidants. Conversion of MeLoOOH into stable MeLoOH demonstrated that the antioxidants α-tocopherol and Trolox trap alkoxyl radicals by H-donation.

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Major focus of the research on antioxidants has been directed on their ability to inhibit hydroperoxide formation (1–3), but less attention has been given on their effectiveness to inhibit the decomposition of lipid hydroperoxides. Phenolic antioxidants, such as tocopherols, not only inhibit the formation of lipid hydroperoxides, but also are known to have an effect on the decomposition of hydroperoxides. At high concentration, α-tocopherol can suppress further reactions of methyl linoleate (MeLo) and linolenate monohydroperoxides by donating hydrogen to peroxyl radical, thus inhibiting formation of *trans,trans* monohydroperoxide isomers in MeLo and cyclic hydroperoxides in methyl linolenate (4,5). α-Tocopherol (6) and other phenolic antioxidants (7) modify the proportions of volatile decomposition products of methyl linoleate hydroperoxides (MeLoOOH) and reduce the total amount of volatile decomposition products. During autoxidation of corn oil, α-tocopherol reduced the formation of hexanal derived from linoleate hydroperoxides (8). Previous research on the effect of tocopherols on the decomposition of hydroperoxides is conflicting, and this may be due to different experimental conditions and concentration of antioxidants. In 2.5 mM aqueous solution of free linoleic acid, the addition of 0.625 μM–0.625 mM of α-, γ-, and δ-tocopherols increased the stability of linoleic acid hydroperoxides (9). However, addition of 7 μmoles α-tocopherol to MeLoOOH in benzene solution (75 μmoles in 30 mL representing 2.5 mM solution) did not influence the amount decomposed by Cu(II) ions (10). Previous work on hydroperoxide decomposition was performed mainly using metal or radical catalysts (10,11), or on fatty acids (9,12–15). Very little work has been reported on the effects of antioxidants on thermal decomposition of hydroperoxides. Because the secondary decomposition products are mainly responsible for causing rancidity in foods, as well as damage in biological material, it is also of high importance to study the effect of antioxidants on decomposition of hydroperoxides and the formation of secondary decomposition products.

The aim of this work was to clarify the mechanisms of α-tocopherol and its water-soluble derivative, Trolox, in inhibiting the formation of volatile and nonvolatile decomposition products from MeLoOOH. The formation of selected volatile and nonvolatile decomposition products was followed by static headspace gas chromatography (GC) and by normal-phase high-performance liquid chromatography (HPLC), respectively.

MATERIALS AND METHODS

Materials. MeLo was supplied by Nu-Chek-Prep, Inc. (Elysian, MN), hexadecane and α-tocopherol by Sigma Chemicals Co. (St. Louis, MO), and Trolox by Aldrich Chemical Company, Inc. (Milwaukee, WI). Hexane and diethyl ether were purchased commercially (Fisher Scientific, Fairlawn, NJ). All the solvents were HPLC grade.

Preparation of MeLoOOH. Hydroperoxides of MeLo were prepared from autoxidized MeLo by chromatography (16) (Sep-pak silica cartridge; Waters Chromatography Division, Milford, MA). The hydroperoxide fraction was shown to be

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Abbreviations: GC, gas chromatography; HPLC, high-performance liquid chromatography; MeLo, methyl linoleate; MeLoOH, methyl linoleate hydroxy compounds; MeLoOOH, methyl linoleate hydroperoxides.

pure by thin-layer chromatography and had an absorptivity of 24,000 at 234 nm.

Decomposition of MeLoOOH. MeLoOOH or a 1:1 mixture of unoxidized MeLo and MeLoOOH (20 mM each) was dissolved in hexadecane solution in the absence or in the presence of 2 and 40 mM α-tocopherol or Trolox. MeLoOOH and α-tocopherol were soluble in hexadecane, but Trolox was only slightly soluble, and formed cloudy suspensions. Lipid solutions were incubated at 60°C for up to 282 h with continuous shaking. Sample aliquots for HPLC and GC analyses were taken at regular intervals.

HPLC analysis. Nonvolatile autoxidation products were analyzed by normal-phase HPLC, by a modified method of Tokita and Morita (17), using a Hewlett-Packard (Palo Alto, CA) model HP 1090 system equipped with a diode array detector. Particle size of the silica column was 5 μm (Supelco 25 cm × 2.1 mm; Bellefonte, PA). The solvent system was hexane/diethyl ether (85:15, vol/vol) with a flow rate of 0.3 mL/min. Ethanol used to stabilize diethyl ether was removed by silica column chromatography prior to the HPLC analysis. Autoxidation products were monitored at 233 nm (conjugated dienes), 210 nm (ester bond), and 268 nm (ketodienes). Tocopherols were monitored at 295 nm.

GC analysis of volatile decomposition products. Hexadecane solution (100 mg of 40 mM lipid solution) was weighed into 6-mL headspace vials. The hexanal formed was analyzed by static headspace capillary GC (16). The results were calculated as millimoles hexanal per kilogram hexadecane solution.

RESULTS

HPLC analysis of MeLoOOH decomposition products in the presence of α-tocopherol and Trolox. The main advantage of the HPLC method was the possibility of simultaneously monitoring MeLoOOH and formation of two important groups of decomposition products. The decomposition rate of hydroperoxides and formation of hydroxy compounds were monitored as total areas of four peaks (Fig. 1). Formation of ketodiene compounds was monitored as total areas of the two peaks in the chromatogram (Fig. 1A, peaks 1 and 2) having an absorption maximum at 268 nm in this solvent system (Fig. 2, spectrum 3), which is characteristic for ketodiene compounds (18). Total peak areas of these compounds were converted to percentage of the initial content of hydroperoxides by using the extinction coefficient of 28,600 for hydroperoxides (19), 27,200 for hydroxy compounds (19), and 28,000 for ketodiene compounds (18).

Elution order of the identified compounds was as follows: peaks 1 and 2, ketodienes; peaks 3–6, 13-*cis,trans* MeLoOOH, 13-*trans,trans* MeLoOOH, 9-*cis,trans* MeLoOOH, 9-*trans,trans* MeLoOOH; peaks 7–10, 13-*cis,trans* MeLoOH (methyl linoleate hydroxy compounds), 13-*trans,trans* MeLoOH, 9-*cis,trans* MeLoOH, 9-*trans,trans* MeLoOH (Fig. 1). Tentative identification of the MeLoOOH isomers was based on the ultraviolet spectra of the compounds (Fig. 2, spectras 1 and 2) and on the elution order reported in the literature (17,19). Retention times of the hydroxy compounds were confirmed with a reference sample prepared by reducing MeLoOOH mixture with $NaBH_4$. α-Tocopherol eluted before ketodienes (Fig. 1D, peak 11). Trolox could also be monitored by HPLC (Fig. 1C, peak 12). However, as it was only sparingly soluble in hexadecane, Trolox could not be measured quantitatively.

Effect of antioxidants on the decomposition of pure MeLoOOH. Both α-tocopherol and Trolox significantly inhibited the decomposition of MeLoOOH (Fig. 3). In the absence of antioxidants, 94% of initial MeLoOOH decomposed during the first 48 h at 60°C, whereas only 0–6% decomposed in the presence of antioxidants. After 282 h of incubation, MeLoOOH decomposed only 8.4% in the presence of 40 mM α-tocopherol and 11% in the presence of 40 mM Trolox. α-Tocopherol at 2 mM inhibited MeLoOOH decomposition up to 48 h, but Trolox was as effective at 2 mM as at 40 mM in inhibiting this decomposition for 282 h.

Antioxidants were detected in the samples until MeLoOOH started to decompose (Fig. 3). α-Tocopherol at 2 mM decomposed completely after 48 h incubation, and at 40 mM approximately 20% decomposed after 282 h incubation (Fig. 3B). Trolox was detected in the samples at 2 mM and 40 mM level, and samples also contained nonsolubilized Trolox after 282 h of incubation.

In the presence of antioxidants, the hydroxy derivatives (MeLoOH) produced represented 1.2–3.5% of initial MeLoOOH (Fig. 4A). Formation of MeLoOH was highest in the presence on 40 mM Trolox (3.5% of initial MeLoOOH), followed by 2 mM Trolox sample (2.1%) and 40 mM α-tocopherol (1.2%). With 40 mM Trolox, 1.5% MeLoOH was present initially after sample preparation. In the control sample, MeLoOH increased up to 0.5% during the first 20 h. However, the concentrations of MeLoOH compounds decreased rapidly in this sample during further incubation.

Ketodiene compounds were formed simultaneously with the rapid decomposition of hydroperoxides (Fig. 4B). In the control sample, ketodiene compounds increased from 0.3% of the initial MeLoOOH up to 4% after the first 20 h of incubation, and then decreased to 1.8% after 120 h of incubation. In the presence of α-tocopherol and Trolox, the formation of ketodiene compounds was inhibited together with the stabilization of hydroperoxides. Thus, after 282 h of incubation, 1.1% of ketodienes was formed in the presence of 40 mM Trolox, 0.9% in the 2 mM Trolox sample, and 1.6% in the 40 mM α-tocopherol sample (Table 1). In the presence of 2 mM α-tocopherol, the formation of ketodienes was inhibited during the first 48 h, increased rapidly to 2.8% when hydroperoxides started to decompose, and then decreased to 1.0% after 282 h of incubation.

Hexanal is a major volatile decomposition product of linoleate hydroperoxides (6,7). Both antioxidants inhibited hexanal formation effectively (Fig. 4C). Hexanal content increased initially in the control sample. In the presence of 2 mM α-tocopherol, hexanal increased simultaneously with

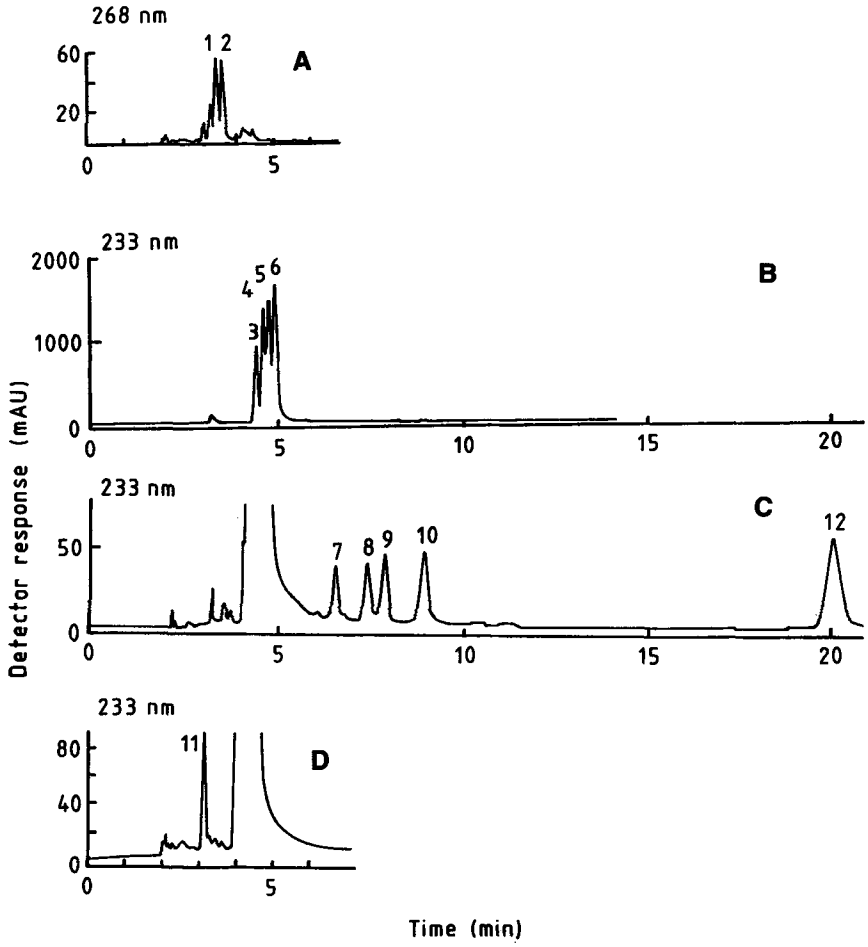

FIG. 1. High-performance liquid chromatographic (HPLC) chromatogram of oxidation products in the presence of antioxidants. Chromatographic conditions: silica column (5 μm, 25 cm × 2.1 mm), hexane/diethyl ether (85:15, vol/vol), flow rate of 0.3 mL/min. Autoxidation products were monitored at 233 nm (conjugated dienes) and 268 nm (ketodienes), and tocopherols and Trolox at 295 nm. Elution order of oxidation products: A, peaks 1 and 2, ketodienes; B, peaks 3–6, 13-*cis,trans* methyl linoleate hydroperoxides (MeLoOOH), 13-*trans,trans* MeLoOOH, 9-*cis,trans* MeLoOOH, 9-*trans,trans* MeLoOOH; C, peaks 7–10, 13-*cis,trans* methyl linoleate hydroxy compounds (MeLoOH), 13-*trans,trans* MeLoOH, 9-*cis,trans* MeLoOH, 9-*trans,trans* MeLoOH. Elution order of antioxidants: C, peak 12, Trolox; D, peak 11, α-tocopherol.

MeLoOOH decomposition after a lag period of 48 h. Hexanal formation was completely inhibited in the presence of 2 mM Trolox or 40 mM α-tocopherol and Trolox. After 282 h incubation, only 0.06 to 0.13 mmol/kg of hexanal was formed in the presence of 40 mM α-tocopherol or Trolox, compared to 2.24 mmol/kg after 48 h incubation in the absence of antioxidants.

Effect of antioxidants on the MeLo/MeLoOOH (1:1) mixture. The influence of unsaturated fatty acids as competitive hydrogen donors on the secondary reactions of hydroperoxides was investigated by decomposing MeLoOOH in the presence of unoxidized MeLo. In a mixture of MeLo (20 mM) and MeLoOOH (20 mM), changes in the rate of MeLoOOH decomposition, as well as formation of hexanal, MeLoOH, and ketodiene were similar, but lower than in pure MeLoOOH. After 282 h incubation, the amount of undecomposed MeLoOOH was 90.6% with 40 mM α-tocopherol, 88.9% with 40 mM Trolox, and 83.3% with 2 mM Trolox (Table 1). Oxidation of MeLo occurred in the sample containing 40 mM α-tocopherol, and the hydroperoxide content increased from 100% initially up to 123% during the first 114 h of incubation (Fig. 5A). α-Tocopherol apparently had a prooxidant effect at the 40 mM level. In the presence of 2 mM α-tocopherol, the hydroperoxides started to decompose after 114 h, and after 282 h of incubation only 15% of initial MeLoOOH was left undecomposed. Also, α-tocopherol was consumed after 120 h (Fig. 5B).

As with pure MeLoOOH, in the presence of MeLo, MeLoOH was produced in the presence of α-tocopherol and Trolox (Fig. 6A). After 330 h incubation, 3.17% MeLoOH

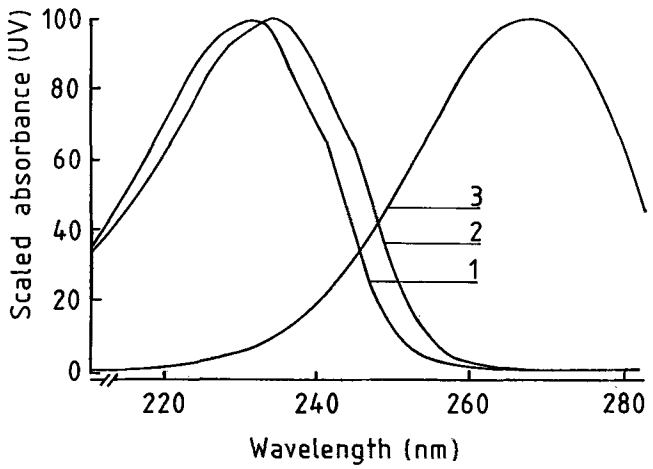

FIG. 2. Ultraviolet (UV) spectra of *trans,trans* (spectrum 1, combined peaks 4 and 6 in Fig. 1B) and *cis,trans* (spectrum 2, combined peaks 3 and 5 in Fig. 1B) hydroperoxides with absorption maximum of 230 and 235 nm, respectively, and ketodiene compounds (spectrum 3, combined peaks 1 and 2 in Fig. 1A) with absorption maximum at 268 nm.

was formed with 40 mM Trolox, 1.55% with 2 mM Trolox, and 0.54% with 40 mM α-tocopherol. In the presence of 2 mM α-tocopherol, MeLoOH content increased up to 0.54% after 282 h, but decreased after 330 h of incubation. Also in the MeLoOOH/MeLo mixture, the formation of ketodienes (Fig. 6B) and hexanal (Fig. 6C) increased together with MeLoOOH decomposition. Thus, ketodiene formation was highest in the control sample, reaching a maximum value of 5.6% after 48 h and 5.26% in the presence of 2 mM of α-tocopherol after 282 h of incubation. Ketodiene compounds were not formed initially in the presence of 40 mM α-tocopherol, 40 mM Trolox, or 2 mM Trolox. After 282 h incubation, 2.0% ketodiene compounds were formed in the presence of 40 mM α-tocopherol, 2.0% in 40 mM Trolox, and 1.5% in the presence of 2 mM Trolox (Fig. 6B).

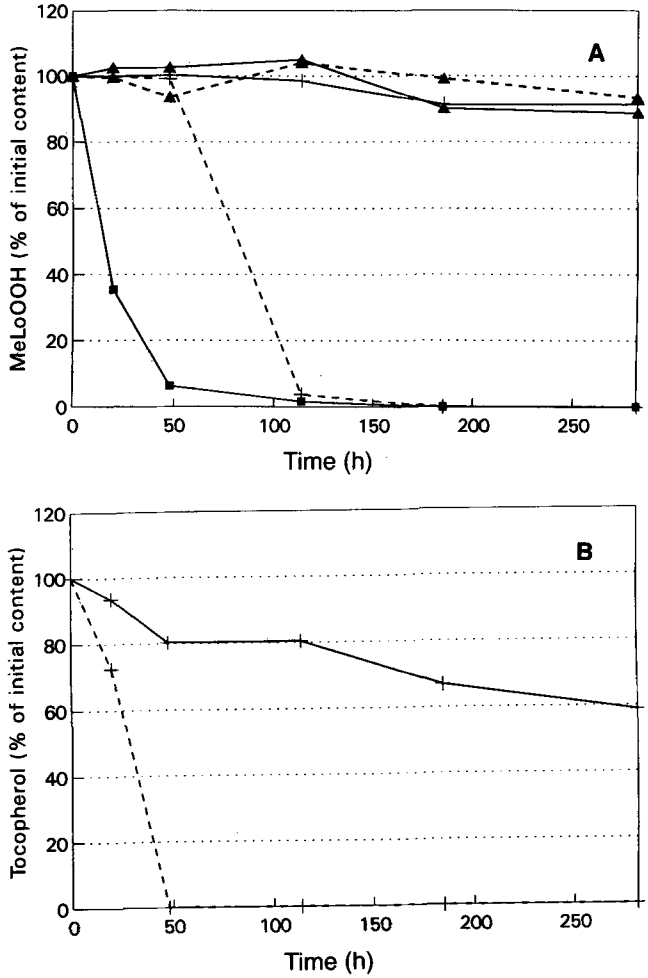

FIG. 3. Decomposition of methyl linoleate hydroperoxides (MeLoOOH) with or without antioxidant at 60°C in hexadecane solution: A, MeLoOOH; B, α-tocopherol. Legend: —■— = 40 mM MeLoOOH; —+— = 40 mM MeLoOOH + 40 mM α-tocopherol; ---+--- = 40 mM MeLoOOH + 2 mM α-tocopherol; —▲— = 40 mM MeLoOOH + 40 mM Trolox; ---▲--- = 40 mM MeLoOOH + 2 mM Trolox.

TABLE 1
Reaction Products Identified from the Decomposition of Methyl Linoleate Hydroperoxides After 282 h Incubation[a]

			Proportion of conversion products		
Sample	MeLOOH[b] (wt%)	Total conversion (wt%)	MeLoOH (%)	Ketodienes (%)	Conversion products[c] (%)
MeLoOOH (40 mM)	0	100	0	0.6	0.6
+ 40 mM α-Tocopherol	91.6	8.4	13.8	19.3	33.1
+ 2 mM α-Tocopherol	0	100	0	1.0	1.0
+ 40 mM Trolox	89.0	11.0	31.9	10.0	41.9
+ 2 mM Trolox	93.6	6.4	32.0	13.6	45.6
MeLoOOH/MeLo (20 mM each)	0	100	0	1.8	1.8
+ 40 mM α-Tocopherol	90.6	9.4	5.7	21.6	27.3
+ 2 mM α-Tocopherol	7.6	92.4	0	5.7	5.7
+ 40 mM Trolox	88.9	11.1	28.6	17.7	46.3
+ 2 mM Trolox	83.3	16.7	9.3	8.9	18.2

[a]MeLOOH, methyl linoleate hydroperoxides; MeLoOH, methyl linoleate hydroxy compounds; MeLo, methyl linleate. [b]Percentage of initial MeLOOH content. [c]All conversion products identified.

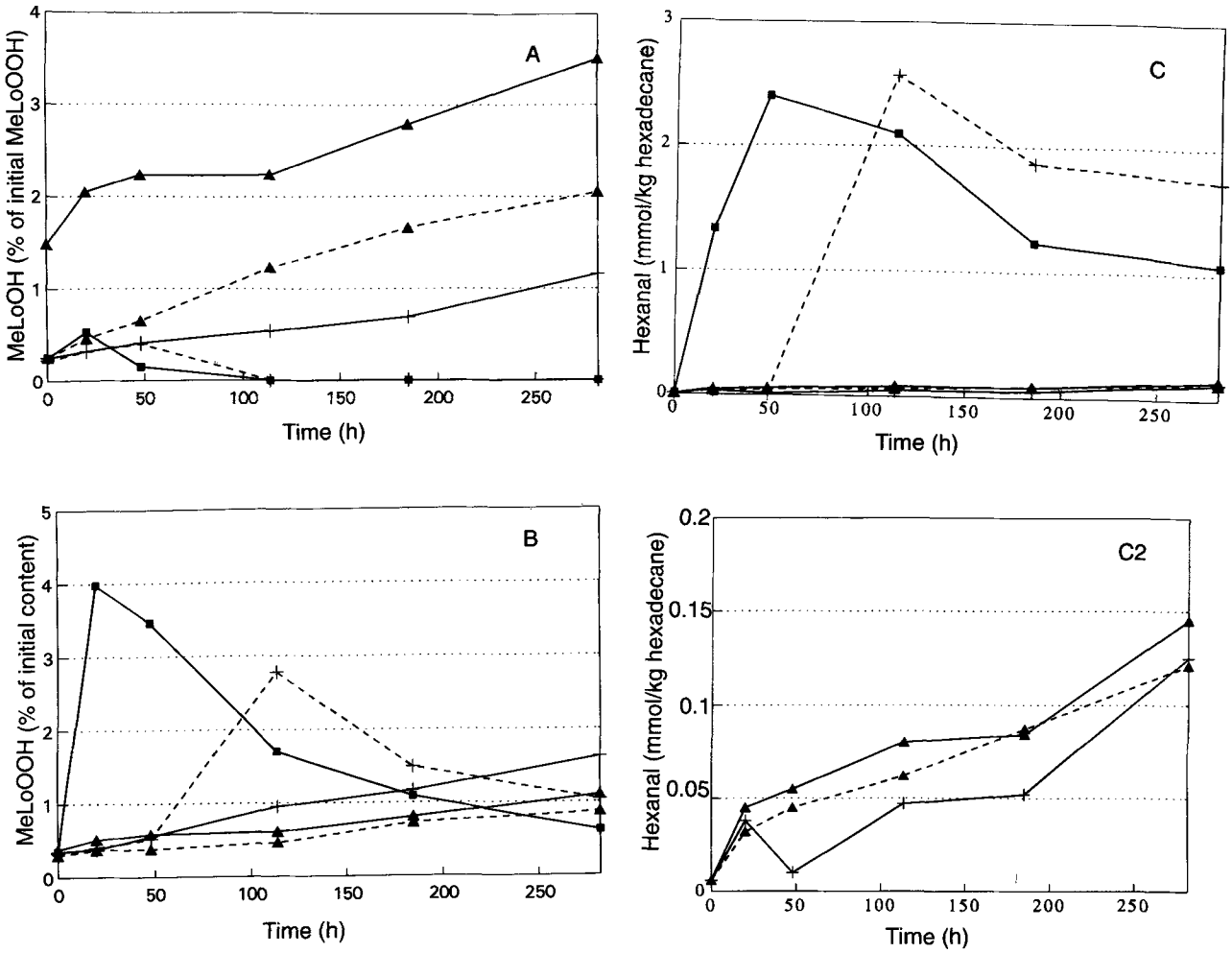

FIG. 4. A, Formation of hydroxy compounds; B, ketodiene compounds; C, hexanal, during decomposition of methyl linoleate hydroperoxides with or without antioxidant; C2, (C) with expanded y-axis. Samples in hexadecane solution. Legend as in Figure 3.

In the samples containing 40 mM α-tocopherol or Trolox and 2 mM Trolox, MeLoOH and ketodiene compounds were the major decomposition products of MeLoOOH, whereas in the highly decomposed samples a major part of the decomposition products was not detectable by the HPLC method used (Table 1). Thus, the conversion products that remained unidentified were 67% with 40 mM α-tocopherol, 99% with 2 mM α-tocopherol, 58% with 40 mM Trolox, and 54% with 2 mM Trolox (Table 1). More work is needed to further identify decomposition products other than hydroxy and ketodiene compounds.

DISCUSSION

The literature on decomposition of hydroperoxides deals mostly with lipids in the absence of antioxidants (10–15, 20,21). However, the pathways of decomposition would be expected to be markedly affected by the presence of hydrogen donating antioxidants. Decomposition of MeLoOOH leads to the same major products, such as ketodienes, hydroxy, epoxy and dimeric compounds, but in different ratios depending on whether the reaction proceeds through alkoxyl or peroxyl radical intermediates (10). Decomposition pathways of MeLoOOH depend markedly on the reaction conditions, and several mechanisms for lipid hydroperoxide decomposition have been suggested. According to the bond dissociation energies, the thermal decomposition of MeLoOOH may occur mainly through alkoxyl radical (44 kcal/mol) rather than through peroxyl radical (90 kcal/mol). However, the presence of transition metal ions may greatly affect the decomposition pathways. Peroxyl radicals may be produced by metal catalysts in their higher valence state, and alkoxyl radicals may be produced by metals in their lower valence state (22). MeLoOOH also have been shown to rearrange and decompose through pentadienyl radical (23). In this study no metal catalyst was added, but traces of metals are expected to be present in the reaction mixtures that would accelerate the decomposition of MeLoOOH at 60°C. Therefore, decomposition through alkoxyl radical is considered to be an important pathway.

The results of this study indicate that the phenolic antioxidants α-tocopherol and Trolox at high concentrations effi-

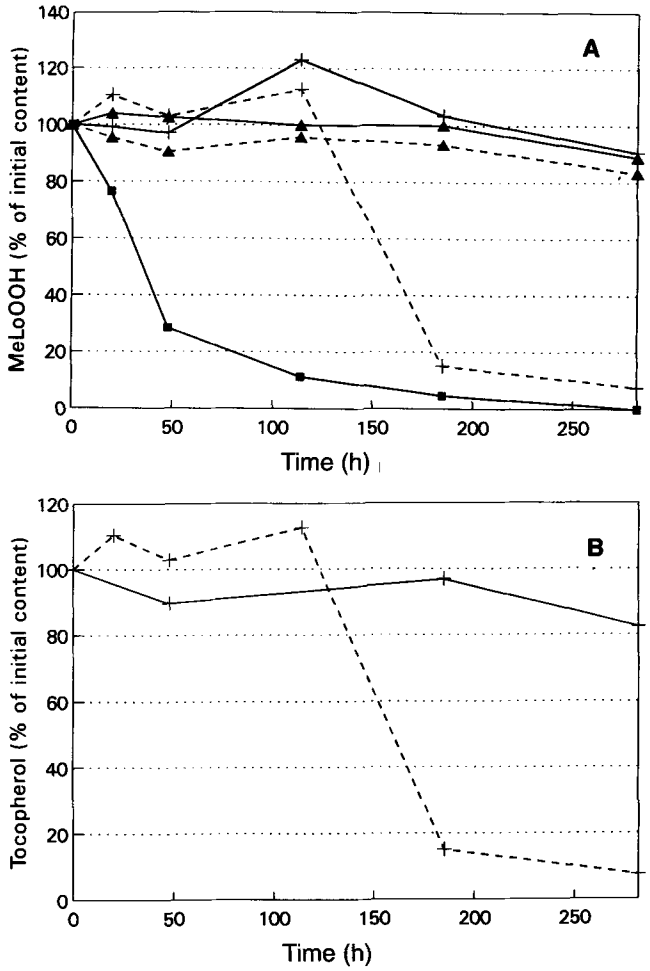

FIG. 5. Decomposition of methyl linoleate (MeLo) hydroperoxides (MeLoOOH) (A), and α-tocopherol (B), at 60°C. MeLoOOH/MeLo (20 mM each, 1:1) in hexadecane solution with or without antioxidants. Legend: —■— = 20 mM each of MeLoOOH and MeLo; —+— = 20 mM each of MeLoOOH and MeLo + 40 mM α-tocopherol; ---+--- = 20 mM each of MeLoOOH and MeLo + 2 mM α-tocopherol; —▲— = 20 mM each of MeLoOOH and MeLo + 40 mM Trolox; ---▲--- = 20 mM each of MeLoOOH and MeLo + 2 mM Trolox.

ciently inhibit the decomposition of MeLoOOH. This effect of α-tocopherol has been reported previously (6,9), but not for Trolox. This study provides, for the first time, evidence for the strong stabilizing effect of Trolox on lipid hydroperoxides. α-Tocopherol has been shown to inhibit decomposition of hydroperoxides in corn oil (8) and linoleic acid (9). Frankel and Gardner (6) observed that α-tocopherol at high concentrations decreases the total volatile products of MeLoOOH formed by thermal decomposition. They suggested that α-tocopherol at high concentration inhibits β-scission of alkoxyl radical (Eq. 1), leading to formation of aldehydes and hydrocarbons, by hydrogen donation.

$$R_2CH\text{–}O^{\bullet} \rightarrow RCHO + R^{\bullet} \quad [1]$$

Donation of the readily available hydrogen of α-tocopherol to alkoxyl radical would lead to formation of hydroxy compound (Eq. 2), through the following mechanism postulated by Bell *et al.* (24) and later by Hamberg (13) and Gardner (14):

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet} \quad [2]$$

Because the oxy radical of an alkoxy is allylic and the oxy radical is located at a secondary carbon, straight abstraction of hydrogen (Eq. 2) is considered to be fairly insignificant in the absence of strong hydrogen donors (25). β-Scission (Eq. 1) producing aldehydes and intramolecular rearrangements producing epoxy compounds and dimers, as well as disproportionation, are considered more probable reaction pathways (25,26). However, strong hydrogen donors, such as α-tocopherol and Trolox, may markedly affect the reaction pathway involving alkoxy radical, and the conversion of MeLoOOH into MeLoOH would be favored, as observed in this study. Previously, Schieberle and Grosch (10) observed that the decomposition of MeLoOOH was inhibited by ascorbyl palmitate with the simultaneous formation of MeLoOH. Formation of MeLoOH was also detected during autoxidation of MeLo in the presence of ascorbyl palmitate (27).

In the present study, the decomposition of MeLoOOH was effectively inhibited by Trolox and α-tocopherol with the simultaneous formation of MeLoOH and no hexanal formation. These results support the hypothesis that in the presence of the strong hydrogen donors α-tocopherol and Trolox, hydrogen abstraction by alkoxyl radicals (Eq. 2) becomes more favorable than β-scission of alkoxyl radicals (Eq. 1), resulting in effective inhibition of hexanal formation. Because MeLoOH formation also increased in the presence of unsaturated fatty acid, which is a competitive hydrogen donor in lipid systems (28), the hydrogen source in the reaction is mainly the antioxidant (AH) (Eq. 3) rather than the unsaturated lipid (RH) (Eq. 2).

$$RO^{\bullet} + AH \rightarrow ROH + A^{\bullet} \quad [3]$$

Thus, the conversion of MeLoOOH into MeLoOH shown in this study may provide a pathway to explain the antioxidant mechanism of α-tocopherol and Trolox in inhibiting the decomposition of hydroperoxides.

Ketodiene compounds, 13- and 9-oxo octadecadienoic acids are one major group of products known from the homolytic decomposition of linoleic acid hydroperoxides (10–13,29). Ketodienes were the main breakdown products formed during the aerobic breakdown of MeLoOOH in the presence of copper through alkoxy radical intermediate (10). Proposed mechanisms for ketodiene formation include the disproportionation of peroxyl radicals through a tetroxide intermediate in which hydrogen atom is transferred from one radical to another (30) (Eq. 4), the elimination of hydrogen from a tetroxide intermediate in which only ketodiene compounds are formed (10) (Eq. 5), and the elimination of hydrogen from an alkoxyl radical (13,14) (Eq. 6).

$$2\,R_2CHOO^{\bullet} \rightarrow R_2\text{–}CH\text{–}OOOO\text{–}HCR_2 \rightarrow R_2CHOH + R_2C{=}O + O_2 \quad [4]$$

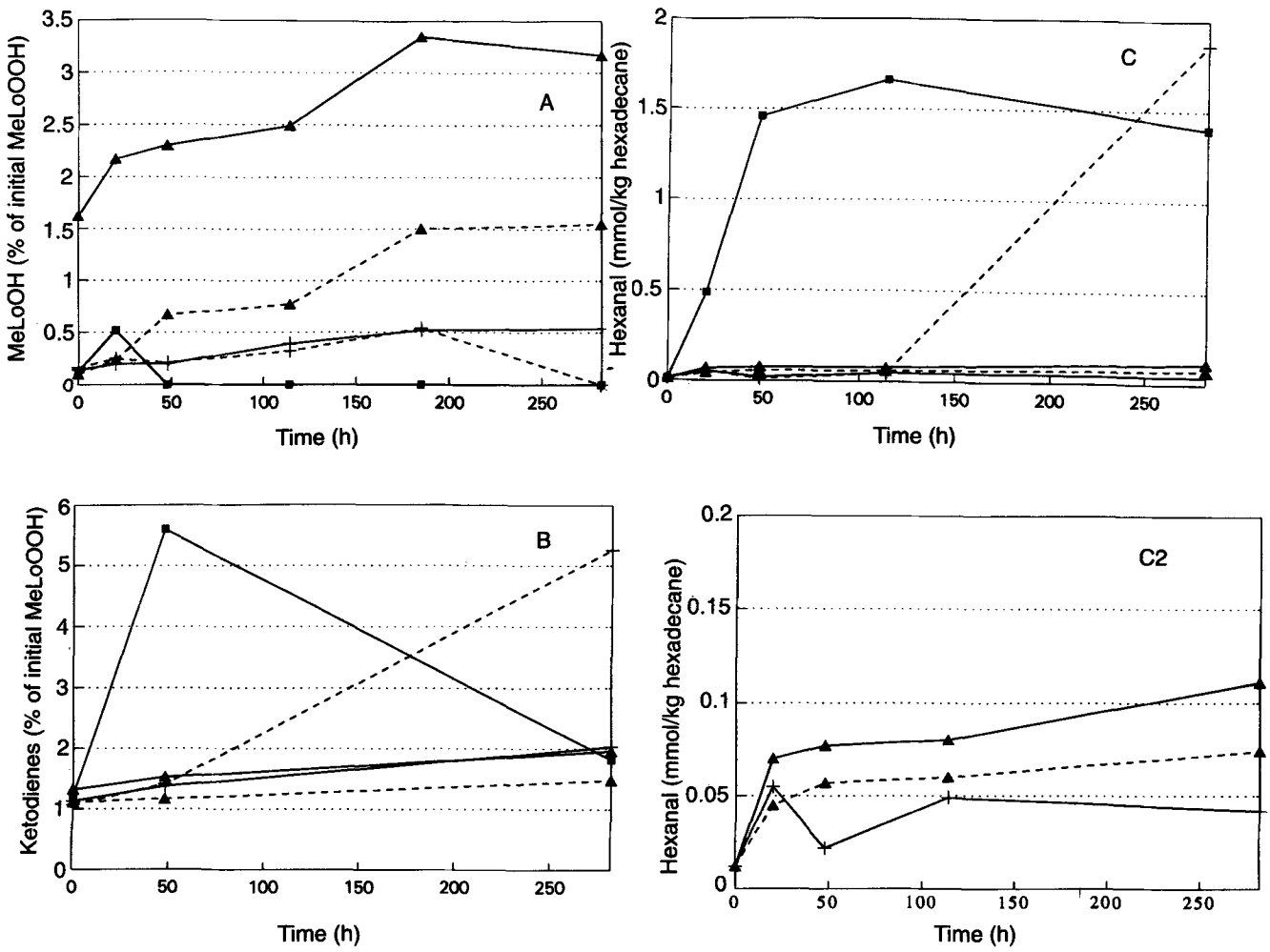

FIG. 6. A, Formation of hydroxy compounds; B, ketodiene compounds; C, hexanal, during decomposition of MeLoOOH with or without antioxidants; and C2, (C) with expanded y-axis. 40 mM solution of MeLoOOH/MeLo (1:1) in hexadecane solution. Legend and abbreviations as in Figure 5.

$$2\,R_2CHOO^{\bullet} \rightarrow R_2\text{–}CH\text{–}OOOO\text{–}HCR_2 \xrightarrow{-2H} 2\,R_2C{=}O + O_2 \quad [5]$$

$$R_2CHO^{\bullet} + X^{\bullet} \rightarrow R_2C{=}O + XH \quad [6]$$

Disproportionation of alkoxy radical (Eq. 4) would be expected to produce equal amounts of hydroxy and ketodiene compounds by the Russell mechanism (30). However, as discussed by Gardner (26), this pathway was not considered to be important.

In this work, antioxidants were shown to decrease the formation of keto dienes and increase the formation of hydroxy dienes. With Trolox, the ratio of hydroxy to ketodiene compounds was higher than with α-tocopherol. Therefore, hydrogen donating antioxidants can greatly influence the reaction pathways leading to stable hydroxy compounds.

Although the hydrophilic Trolox was only slightly soluble in hexadecane, it was more effective in inhibiting MeLoOOH decomposition than the lipophilic α-tocopherol. This phenomenon has not been previously reported for the decomposition of pure hydroperoxides, but it is consistent with our previous observations that these antioxidants have different effects on hydroperoxide and hexanal formation during autoxidation of corn oil (8). In a bulk corn oil system, even though the hydrophilic antioxidants Trolox and ascorbic acid were not completely soluble, they were more effective than the lipophilic antioxidants α-tocopherol and ascorbyl palmitate. However, in the corresponding corn oil-in-water emulsion system, the lipophilic antioxidants were more effective than their hydrophilic analogues in inhibiting hydroperoxide formation and decomposition. In emulsions, the higher protection of lipophilic antioxidants was explained by their higher affinity toward the oil–water interface. In bulk oils, the better protection of hydrophilic antioxidants was explained by their preferential orientation in the air–oil interface. This interfacial phenomenon supports our finding that the hydrophilic Trolox is more effective than the lipophilic α-tocopherol in inhibiting hydroperoxide decomposition in the nonpolar hexadecane solution. In our previous study (8), we also observed that α-tocopherol was more effective in inhibiting hydroperoxide formation at 232 than at 1161 μM, but the reverse trend was observed in inhibiting hydroperoxide decomposition based on hexanal determination. These results

support our previous study (6), showing that α-tocopherol is an effective inhibitor of the β-cleavage (Eq. 1) responsible for hexanal formation.

This study was limited to the formation of three groups of decomposition products formed at 60°C—hexanal, hydroxy, and ketodiene compounds, which can be formed *via* alkoxyl radicals by β-scission (Eq. 1), hydrogen abstraction (Eq. 2), and hydrogen elimination (Eq. 6). However, other reactions of lipid alkoxyl radicals may be significant under different conditions (25). During Fe(II)-induced decomposition of the 13-hydroperoxide of linoleic acid in methanol solution in the presence of a vitamin E model compound (2,2,5,7,8-pentamethyl chromanol-6-ol), under either aerobic or anaerobic conditions, the formation of epoxy compounds through epoxyallylic radicals, formed by rearrangement of alkoxyl radicals, was suggested as a possible pathway of decomposition (31). In another study (32), the decomposition of 13-MeLoOOH in air in the presence of equal molar concentrations of Fe(III) acetylacetonate and α-tocopherol in benzene solution at 37°C, produced mixtures of peroxy-α-tocopherones, epoxy-hydroperoxy-α-tocopherones, and tocopherol dimers. Under these conditions, the formation of both peroxyl and alkoxyl radicals, rearranging into allylic epoxy-hydroperoxyl radical intermediates, may account for the lipid–tocopherol adducts identified. Further research is under way to clarify the effect of antioxidants on the formation of other nonvolatile compounds, including polymeric products and epoxides, from the thermal decomposition of lipid hydroperoxides.

ACKNOWLEDGMENT

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