Action of Tocopherol-Type Compounds in Directing Reactions Forming Flavor Compounds in Autoxidizing Fish Oils

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Menhaden and cod liver oils without additives or containing either α-tocopherol (670 ppm) or Trolox C (1000 ppm) with or without copper (II) cations (20 ppm) were oxidized under air at 65°C, and their headspace volatiles were quantitatively measured by capillary gas chromatography. Samples prepared without additives contained very little 1,5-octadien-3-one. Fish oils with Trolox C had distinct metallic, vinyl-ketone aromas, while those with α-tocopherol exhibited extremely fishy, cod liver-like aromas. High levels of 1,5-octadien-3-one and 1,5-octadien-3-ol and moderate levels of 2,4,7-decatrienals were found in samples with Trolox C, while moderate levels of the 8-carbon compounds and high levels of the 2,4,7-decatrienals were present in the α-tocopherol samples. Copper (II) greatly accelerated the overall rate of oxidation in samples, and in the presence of Trolox C it induced the formation of very high levels of 1,5-octadien-3-ol.

Oxidations of long-chain, highly unsaturated n-3 fatty acids found in marine oils notably develop distinct fishy flavors and aromas (1-4). Because these flavors are objectionable to consumers, there is considerable interest in developing antioxidant systems that will suppress or direct reactions away from the formation of fishy compounds.

α-Tocopherol and related compounds have often been suggested as antioxidants for fish oils because of their effective H-donor capability (5), but tocopherols can also act as prooxidants when high concentrations are added to oxidizing lipid systems (6-10). Studies evaluating the antioxidant effect of α, β, and γ-tocopherols have shown γ-tocopherol as the most effective, and α-tocopherol as the least effective antioxidant in oils (11,12). Of the tocopherol isomers, α-tocopherol is the most unstable because of its highly oxidizable nature, and this characteristic contributes to its low antioxidant capability (13).

Recently, studies evaluating the antioxidant properties of α-tocopherol in model systems containing polyunsaturated fatty acids have shown that α-tocopherol selectively affects the ratio of isomeric hydroperoxides in unsaturated fatty acids. Porter *et al.* (14) have outlined the mechanism responsible for the formation of *cis-trans* and *trans-trans* hydroperoxide isomers in autoxidizing fatty acids, and the reactions proceed as a series of reversible oxygenation and deoxygenation steps involving pentadienal radicals. Conditions allowing reversible reactions to proceed unhindered permit rotations of carbon-carbon bonds which yield both *cis-trans* and *trans-trans* hydroperoxides. The distribution of isomers is dependent upon the concentration and H-donating ability of the tocopherol-type compound in the system.

Peers *et al.* (15) have noted that only the *cis-trans* hydroperoxide isomers were formed when 5% α-tocopherol was present. When lower α-tocopherol concentrations were present, some *trans-trans* isomers were formed, although their concentrations diminished as the level of α-tocopherol increased. Thus, α-tocopherol quenched peroxy free radicals by readily donating a hydrogen atom, and this rapid quenching of peroxy radicals apparently stabilized the carbon-carbon backbone, which prevented formation of *trans-trans* hydroperoxides. These results have been confirmed by Koskas *et al.* (13) and Terao and Matsushita (16).

α-Tocopherol also inhibits the formation of diperoxides through its H-donating mechanism, and hydroperoxides thus stabilized are prevented from forming peroxy radicals that cyclize to the diperoxides (17,18). Inner rather than outer hydroperoxides are selectively formed in the pentadiene system of polyunsaturated fatty acids (17). In the presence of α-tocopherol, compounds from inner, *cis-trans* monohydroperoxides of n-3 fatty acids are favored among decomposition products.

Studies on fishy-metallic off-flavors in tainted butters which contain low levels of long-chain n-3 fatty acids have led to conclusions that α-tocopherol and copper were required in model systems for these off-flavors to form (19,20). Metallic taints in butters were attributed to 1,5-octadien-3-one (20,21). Low concentrations (<10 ppb) of this compound have been found to contribute green, fresh-like falvors and aromas to fresh fish (22) and fish oils (1). Neat preparations of 1,5-octadien-3-one exhibit heavy green, geranium leaf-like aroma qualities (21,22). Previous research (17,19) has indicated that 1,5-octadien-3-one can result from the directed oxidation of long-chain n-3 fatty acids in the presence of α-tocopherol through an inner, *cis-trans* hydroperoxide.

Trolox C is a synthetic antioxidant containing a chroman ring that has been proposed as a food antioxidant (23,24), but its use as a food additive has not yet been approved in the U.S. Trolox C is structurally-related to the tocopherols, and it exhibits some unique structural features that make it useful for studies of the antioxidant mechanism of α-tocopherol. Particularly, the Trolox C molecule lacks the long alkyl side chain of α-tocopherol, and it forms a stable oxidized quinone derivative more readily than the tocopherols (25,23).

Additional information on the mechanism of directing reactions in oxidizing fish oils should accelerate the development of antioxidant strategies that will minimize the formation of pronounced off-flavors in these oils. Thus, the purpose of this research was to investigate the effect of combinations of α-tocopherol or Trolox C with copper (II) on the production of volatile oxidation products in fish oils, and to relate these observations to the mechanisms of reactions that lead to the formation of characterizing fish compounds in n-3 oils.

MATERIALS AND METHODS

Preparation of steam deodorized fish oils. Commercially refined menhaden oil (26) (Zapata Hayne Corp., Reedville, VA) and cod liver oil (McKesson Corp., Dublin, CA) were low-temperature deodorized using a batch-type, vacuum laboratory apparatus (1,27) operated at 130°C at 4 mm Hg for 2 hr. Before initiating deodorizations, each 300 ml batch of oil was blended with 60 ml of water for 5 sec using a Waring Blendor (Dynamic Corp., New Hartfort, CT). Steam for deodorization was generated from distilled water for menhaden oil, and from dilute acetic acid solution (0.01N; J.T. Baker Chemical Co., Phillipsburg, NJ) for cod liver oil (1).

Preparation of model systems of fish oils. Samples composed of 20 ml portions of menhaden or cod liver oils were placed in 60 ml open glass (85 mm × 30 mm) bottles, and either 1000 ppm of Trolox C® (6,hydroxy-2,5,7,8 tetramethylchroman-2-carboxylic acid; Hoffman-La Roche, Inc., Nutley, NJ) or 670 ppm of d-α-tocopherol (670 mg/g soybean oil; 0.5%-2% non-α isomers; Sigma Chemical Co., St. Louis, MO), or 20 ppm of cupric palmitate (Pflatz and Bauer, Inc., Waterbury, CT) was added to each sample. Samples were also prepared with combinations of either cupric palmitate plus α-tocopherol or cupric palmitate plus Trolox C®. Control samples for each series were prepared without antioxidants. Uncapped bottles were then placed in an incubator (Blue M, Blue Island, IL) in the dark at 65°C, and held for up to 72 hr with samples periodically taken for analysis.

Analysis of headspace volatiles from oils. Volatile compounds in fish oil were quantitatively measured using the dynamic headspace procedure described by Olafsdottir *et al.* (28), with modifications. Aliquots of oil (15 ml) were added to cylindrical glass 30 ml reservoirs (3 cm × 10 cm) constructed with 24/40 ST glass joints (female), and assembled with a purging head described in the earlier procedure. Ethyl heptanoate was added as the internal standard at a level of 2.08 ppm of the oil. Headspace volatiles were purged from the oil by introducing nitrogen (270 ml/min for 3 hr at 75 ± 5°C) below the surface of the sample, and volatiles were entrained onto Tenax GC® (60-80 mesh, ENKA N.V., Holland). Volatile compounds were eluted from Tenax GC® traps with ca. 0.5 ml of redistilled diethyl ether (Fisher Scientific, Fairlawn, NJ), and extracts were then concentrated under a slow stream of nitrogen to about 30 μl at room temperature (21°C).

Volatile compounds were separated by capillary column gas chromatography using a Varian 3700 gas chromatograph (Varian Associates, Inc., Sunnyvale, CA) equipped with an on-column injector system and FID detector. A Carbowax 20M (60 m × 0.25 mm) fused silica capillary column (J&W Scientific, Inc., Rancho Cordova, CA) operated with helium as the carrier gas was employed. A program rate of 50°C (1 min hold) to 220°C at 4°C/min was used. Chromatographic data were processed with a computing integrator (Model 4200, Spectra Physics, San Jose, CA).

Mass spectra were obtained using a Finnegan 4500 mass spectrometer fitted with the same Carbowax 20M capillary column and temperature program rate. Identification of peaks was achieved by matching electron impact (70/ev) mass spectral data to those published in "EPA/NIH Mass Spectral Data Base" (29,30), or those of authentic compounds. Coincidence of retention indices of unknown compounds (I_E) (31) with authentic compounds was also employed for compound identification.

Assessments of fish oils. Oil samples were assessed by the authors for odor after equilibration to room temperature (21°C), and the samples were also assessed for flavor quality by placing a small drop of oil on the tip of the tongue (to prevent coating of the lips) (4). Samples were expectorated immediately after tasting, and lukewarm rinse water was available.

Determination of hydroperoxides. Hydroperoxides were determined by the method of Buege and Aust (32), and the mean of duplicate analyses were expressed as micromoles of hydroperoxide per mg of oil.

RESULTS AND DISCUSSION

Antioxidant behavior of α-tocopherol and Trolox C in fish oils. Characteristic data for hydroperoxide concentrations in oxidizing fish oil containing either Trolox C (1000 ppm) or α-tocopherol (670 ppm) are shown in Figure 1, and the data show that the two compounds behave differently with regard to antioxidant capability in fish oils. It has been well established that levels of α-tocopherol in excess of 1% (10,000 ppm; wt/wt basis) in lipid/water systems (6–9,17,33), and >0.1% (1000 ppm) in pure lipid systems (34) promote lipid autoxidation. In the present study, α-tocopherol (670 ppm) also accelerated the rate of hydroperoxide formation in menhaden oil, whereas the higher level of Trolox C (1000 ppm) exhibited an antioxidant effect. Similar prooxidant effects for α-tocopherol and antioxidant effects for Trolox C were observed for cod liver oil (Table 1).

The prooxidant activity of α-tocopherol (Fig. 2) apparently occurs because chroman ring free radicals formed by reactions with lipid radicals abstract hydrogen atoms from either unoxidized methylene carbon of unsaturated fatty acids or existing hydroperoxide (16,34). Thus, instead of retarding oxidation rates, α-tocopherol at high concentrations actually participates in the propagation of autoxidation. However, high concentrations of Trolox C suppress hydroperoxide formation because its chroman radical does not readily abstract hydrogen from hydroperoxide groups or unsaturated lipids, and it can scavenge a hydrogen radical from the medium to form a quinone (Fig. 3) (23,24). The carboxyl group in the 2-position on Trolox C provides an electron withdrawing group that

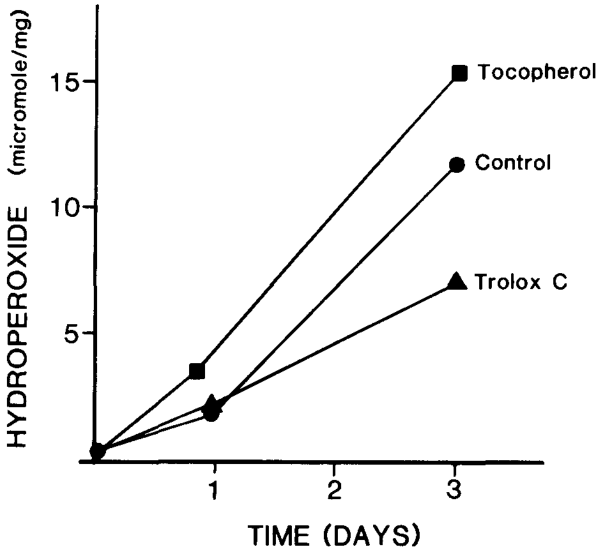

FIG. 1. Hydroperoxide concentrations in oxidizing menhaden oils held under air at 65°C for 72 hr. The control sample did not contain additives.

TABLE 1

Concentration of Selected Compounds Contributing to Fishy, Oxidized Flavors in Oxidized Cod Liver Oil Held for 16.5 Hours at 65°C

Sample description	*c*-4-heptenal	*t,c*-2,4-heptadienal	*t,t*-2,4-heptadienal	3,5-octadien-2-one	*t,c*-2,6-nonadienal	*t,c,c*-2,4,7-decatrienal	*t,t,c*-2,4,7-decatrienal	Hydroperoxide concentration[a] (μmol/mg oil)	Odor description
	Concentration (ppb)								
A. Control—no treatment—zero time	61	840	1630	58	tr[b]	22	tr	0.17	Fishy
B. Control—65°C	230	2220	2290	340	230	320	400	2.72	Green; fishy
C. 670 ppm α-tocopherol	210	10000	4260	540	230	1020	300	3.86	Green; fishy
D. 1000 ppm Trolox C	170	7940	3840	340	300	1300	200	1.40	Green; metallic; hay-like
E. 20 ppm Cu^{++}	810	14200	13800	1400	2100	2250	3140	9.30	Oxidized; painty straw-like
F. 670 ppm α-tocopherol + 20 ppm Cu^{++}	370	11500	9030	1100	980	2710	1370	5.06	Very cod liver oil-like; straw-like
G. 1000 ppm Trolox C + 20 ppm Cu^{++}	790	8250	3680	640	730	1200	390	1.27	Metallic; vinyl ketone-like

[a] Values represent the average of duplicate trials with a maximum coefficient of variation of 0.36.

[b] Trace.

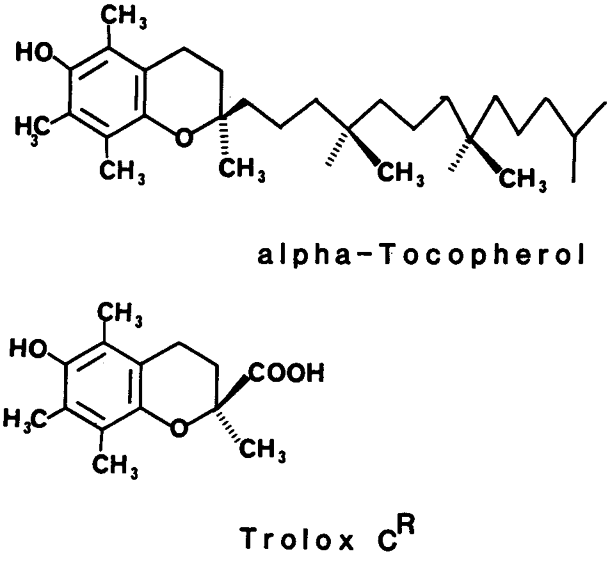

FIG. 2. Structures of chroman ring-type antioxidants evaluated in oxidizing fish oils.

encourages the opening of the phenoxyl ring radical to form the oxidized quinone (25).

Directed formation of 1,5-unsaturated-C-8 compounds. The two antioxidants influenced the relative amounts of individual volatile autoxidation compounds in fish oils in a manner that was not parallel to hydroperoxide concentrations. Although oxidizing menhaden oil containing Trolox C had low levels of hydroperoxides (Fig. 1), it exhibited higher concentrations of 1,5-octadien-3-one (Fig. 4, 125 ppb) and 1,5-octadien-3-ol (Fig. 5, 265 ppb) than either the control or the samples containing α-tocopherol. Menhaden oil containing α-tocopherol also developed substantial levels of these 1,5-unsaturated-C_8 compounds (Figs. 4 and 5), but since the degree of oxidation as measured by the hydroperoxide concentration was higher than the control (Fig. 1), some of the increased concentrations were probably contributed by non-directed autoxidations.

Cod liver oil containing copper ions as well as Trolox C produced the highest levels of 1,5-octadien-3-one (264 ppb) and 1,5-octadien-3-ol (3480 ppb) under accelerated oxidation conditions (Table 2) while maintaining a low hydroperoxide concentration (Table 1). These oils containing Trolox C (Table 1, treatments D and G) exhibited a green, metallic, vinyl ketone-like odor quality that was not as evident in the control, α-tocopherol or copper-containing oils which exhibitied green, fishy, or painty-oxidized odor qualities. Cod liver oil containing α-tocopherol plus copper also produced substantial levels of 1,5-octadien-3-one (75 ppb) and 1,5-octadien-3-ol (669 ppb). Overall, these findings are in agreement with those of Swoboda and Peers (19,20), who found elevated levels of 1,5-octadien-3-one in model systems containing butterfat, α-tocopherol and cupric palmitate (20).

A proposed mechanism for the tocopherol-type quinone-directed oxidation of n-3 fatty acids to form these 1,5-unsaturated-C_8 compounds is shown in Figure 6. Alignment of the pi-bond clouds of the quinone ring with the n-3 end of the fatty acid provides the desired geometry for positioning the available OH-group over the 3-position of the C_8 fragment (Fig. 6). It is not known whether the oxidized quinone facilitates cleavage of the fatty acid backbone, or if the hydroxylation occurs after the C_8 fragment has been released by an unrelated event. In any event, the alignment of the chroman ring over the n-3 end of the fatty acid would be responsible for directing the oxidation process.

In autoxidizing systems, the ability of the chroman free radical of α-tocopherol or Trolox C (Fig. 3) to undergo cleavage to form the corresponding quinone is increased when transition metal cations (Cu or Fe) (23) (Fig. 3) or acidic conditions (35) are present. Because of the

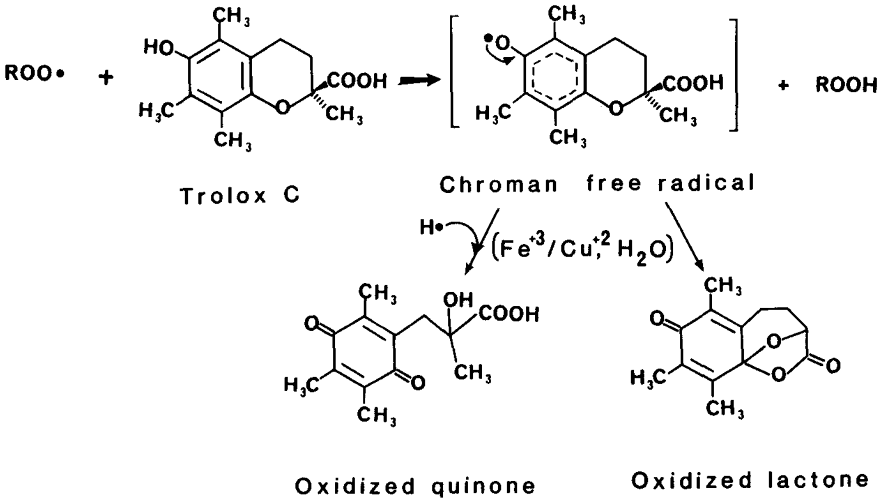

FIG. 3. Antioxidant mechanism of Trolox C showing the formation of stable oxidized products for participation in directed oxidations of n-3 fatty acids.

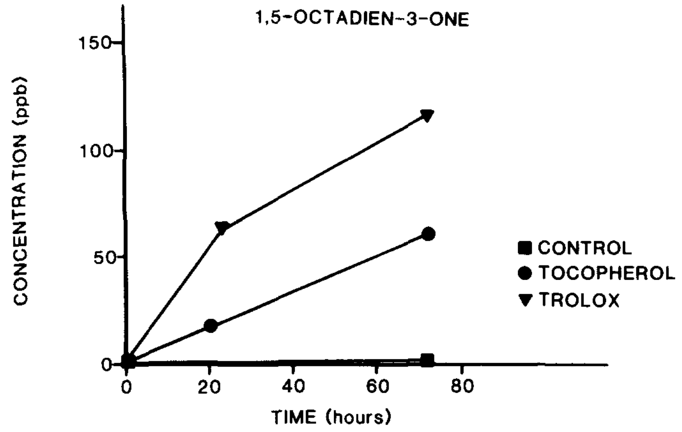

FIG. 4. Formation of 1,5-octadien-3-one in the presence of tocopherol-type antioxidants in menhaden oil under accelerated oxidation conditions. The control did not contain additives.

destabilizing effect of the carboxyl group on Trolox C, this antioxidant more readily undergoes conversion to the quinone than α-tocopherol, and thus allows higher concentrations of reactants to participate in directed oxidations.

In fish oil model systems (Table 1), copper alone exerted a distinct prooxidant effect on the polyunsaturated fatty acid, but when copper and Trolox C were both added, hydroperoxide formation was approximately equivalent to the sample where only Trolox C was added. Thus, copper was unable to accelerate the oxidation of polyunsaturated fatty acids to hydroperoxides in the presence of Trolox C like it did in the presence of α-tocopherol. This indicates that Trolox C was effective in intercepting oxidant species in the system.

In viewing the data for 1,5-octadien-3-ol (Table 2), it can be seen that much greater amounts of this compound was formed in the presence of Trolox C and copper than in the presence of Trolox C alone. Therefore, it appears that hydroperoxide formation is spared in the presence of copper and Trolox C, and Trolox-derived, quinone-mediated products (1,5-octadien-3-ol) result instead (Figs. 3 and 6).

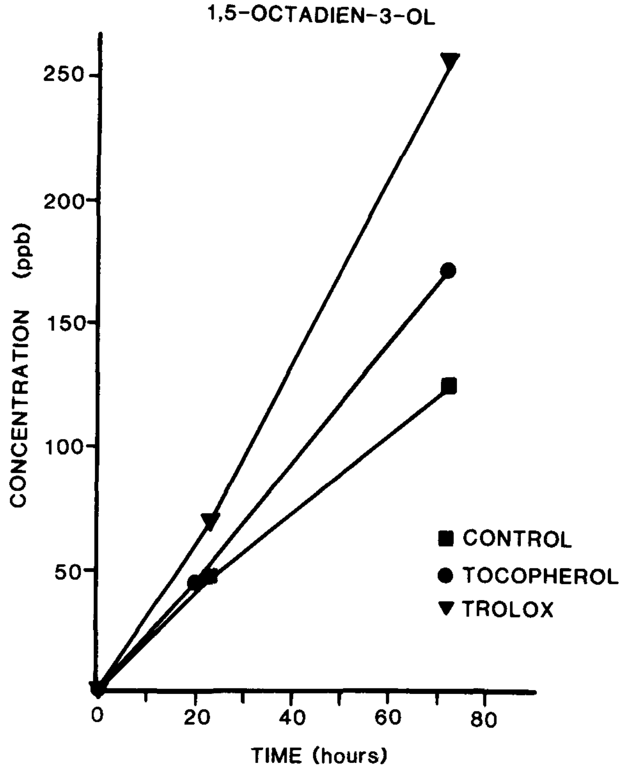

FIG. 5. Formation of 1,5-octadien-3-ol in the presence of tocopherol-type antioxidants in menhaden oil under accelerated oxidation conditions. The control did not contain additives.

Directed formation of cis-trans *hydroperoxide isomers and corresponding oxidation products.* Earlier studies have established that autoxidizing polyunsaturated fatty acids containing tocopherol-type compounds preferentially allow the formation of *trans-cis,* rather than *trans-trans,* hydroperoxide isomers (15-17,36). The H-donating capability of tocopherol-like compounds that prevents carbon-carbon bond rotations (Fig. 7, step 1) and translocation of the peroxy radical along the carbon backbone

TABLE 2

Concentration of Selected Unsaturated C_8 Compounds in Oxidized Cod Liver Oils Containing Selected Antioxidants and Held for 16.5 Hours at 65°C

Sample description	$1,5\text{-}C_8\text{-}3\text{-}ol$	$1,5\text{-}c_8\text{-}3\text{-}one$
	Concentration (ppb)	
A. Control—no treatment—zero time	18	nd[a]
B. Control—elevated temperature	65	nd
C. 670 ppm α-tocopherol	108	58
D. 1000 ppm Trolox C	118	205
E. 20 ppm Cu^{++}	318	100
F. 670 ppm α-tocopherol + 20 ppm Cu^{++}	669	75
G. 1000 ppm Trolox C + 20 ppm Cu^{++}	3480	264

[a]Not detected.

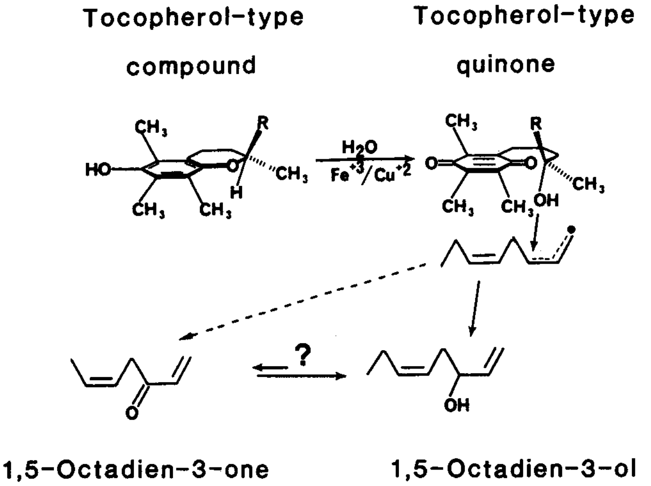

FIG. 6. A proposed mechanism for the directed oxidation by tocopherol-type antioxidants for n-3 fatty acid fragments leading to the formation of C_8 compounds.

(Fig. 7, step 2) has been proposed by Porter *et al.* (14) to be responsible for preferred *cis-trans* hydroperoxide isomer formations. Products formed from the decomposition of these hydroperoxides directly affect the final flavor and odor quality of oils containing n-3 fatty acids.

Although a trend for preferred *cis-trans* hydroperoxide decomposition products was generally observed for the 2,4-heptadienals and the 2,4,7-decatrienals (Table 1), the flavor and odor contributions of the 2,4,7-decatrienals were of most concern because of their influential role in providing burnt/fishy flavors to oxidized fish oils (1,2). In the current study, after 3 days *t,c,c*-2,4,7-decatrienal isomer was formed at high concentrations in menhaden oil containing either α-tocopherol or Trolox C (635 ppb and 415 ppb, respectively, Fig. 8) as compared to the control (310 ppb, Fig. 8). Non-directed oxidation of menhaden oil (control, 140 ppb, Fig. 9) produced higher levels of the *t,t,c*-isomer compared to oils containing either α-tocopherol or Trolox C (90 ppb and 65 ppb, respectively, Fig. 9) after a 3-day oxidation period. Thus, these results are in agreement with those of previous studies where initial formation of types of hydroperoxides was measured instead of specific oxidation products (15–17).

Cod liver oil containing α-tocopherol plus copper produced the highest level of *t,c,c*-2,4,7-decatrienal (2.71 ppm, Table 1) as compared to all other treatments. Samples containing Trolox C produced moderate levels of the decatrienals compared to samples with α-tocopherol, and the formation of the *t,c,c*-isomer was favored over the *t,t,c*-isomer (1.20 ppb and 0.39 ppb, respectively, Table 1). Samples that were allowed to oxidize without antioxidant additions (Cu [II] or control, Table 1) showed ratios of *t,c,c* to *t,t,c* isomers near 1:1.

The tocopherol-type compounds enhance the formation of both the C_8 and C_{10} unsaturated carbonyls, and both of these contribute characterizing flavors to oxidized fish oils. However, the ratio of the C_8 to C_{10} compounds formed with Trolox C favors the C_8 compounds (C_8:C_{10} =

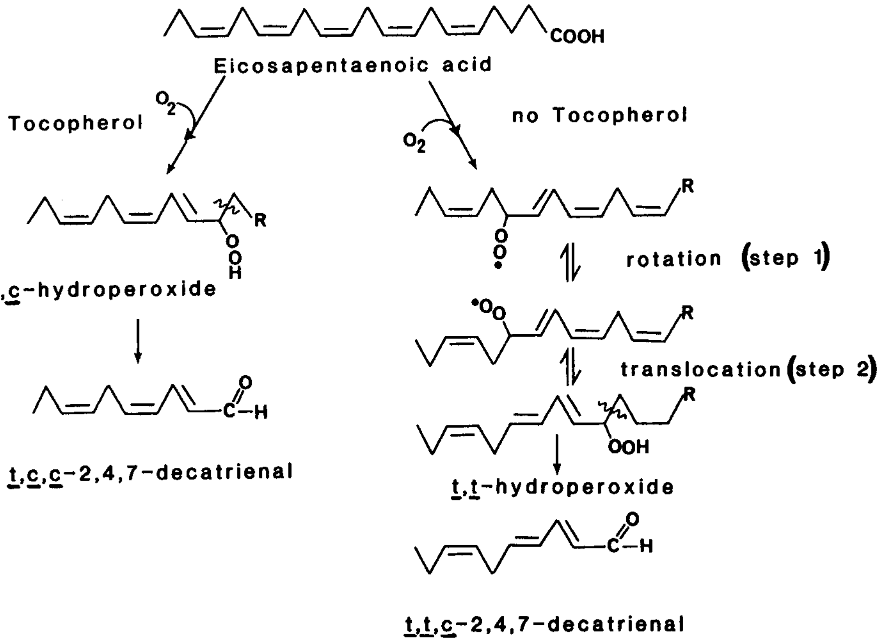

FIG. 7. Formation of isomeric hydroperoxides of polyunsaturated fatty acids.

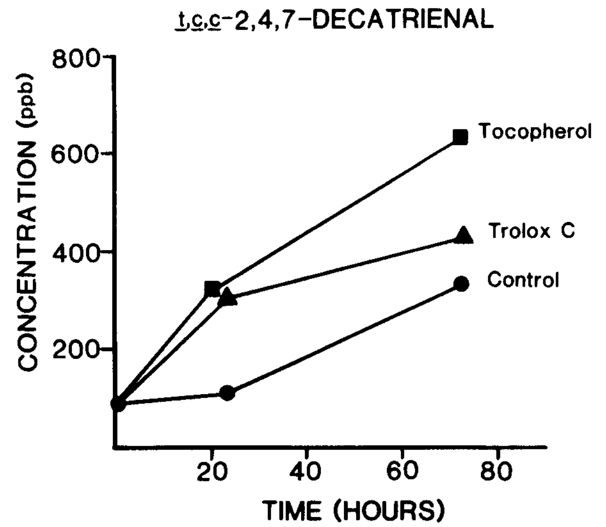

FIG. 8. Formation of *t,c,c*-2,4,7-decatrienal in the presence of tocopherol-type antioxidants in menhaden oil under accelerated oxidation conditions. The control did not contain additives.

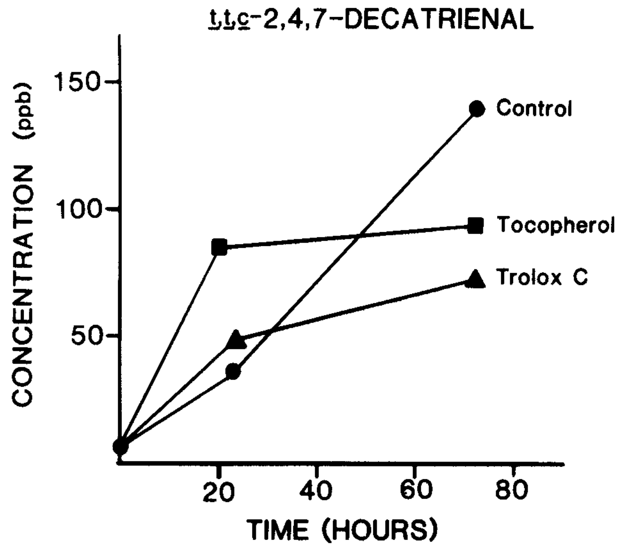

FIG. 9. Formation of *t,t,c*-2,4,7-decatrienal in the presence of tocopherol-type antioxidants in menhaden oil under accelerated oxidation conditions. The control did not contain additives.

2.35) compared to that for α-tocopherol (0.18) and copper (0.09). Therefore, less burnt/fishy aromas and flavors would result from the use of Trolox C than with the use of α-tocopherol. Metallic flavors that are expressed by the unsaturated C_8 compounds, however, may be more easily masked than the burnt/fishy flavors exhibited by the 2,4,7-decatrienals.

Formation of other oxidation products in the presence of tocopherol-type compounds. For many volatile compounds produced from autoxidation of fish oil in the presence of the two chroman ring antioxidants, the concentrations formed paralleled the overall degree of autoxidation expressed by peroxide values. Included were the 2,4-heptadienal isomers and 3,5-octadien-2-one which have been shown to be readily formed by autoxidation of n-3 fatty acids (21,37,38). Oxidized cod liver oil samples containing copper and α-tocopherol had the highest levels of 3,5-octadien-2-one (>540 ppb, Table 2, treatments C, E, F, and G). High degrees of oxidation reflected in the peroxide values (Table 1) would account for the high concentration of 3,5-octadien-2-one in these samples which contain prooxidant copper.

Concentrations of 2,4-heptadienal isomers in oxidizing cod liver oil also paralleled the rate of oxidation, and these concentrations were highest in samples containing copper or tocopherol (Table 1, treatments C, E, and F), mainly because of their prooxidant effects. Oils containing Trolox C had the lowest levels of 2,4-heptadienal (ca. 12 ppm, Table 1, treatment D and G) and hydroperoxide concentrations (1.40 μmol/mg oil, 1.27 μmol/mg oil, Table 1, treatments D and G, respectively), which was in agreement with the generally observed antioxidant behavior for this compound even in the presence of copper.

Combined effects of directed oxidations. The current study has provided results which show that the addition of Trolox C directs the oxidation of n-3 fatty acids to preferentially form 1,5-octadien-3-one and 1,5-octadien-3-ol instead of the 2,4,7-decatrienals. Odors of cod liver oil containing Trolox C lacked fishiness character that was expressed in the control or α-tocopherol-containing samples (Table 1). However, samples containing Trolox C possessed a very distinct green, metallic odor. Although samples containing α-tocopherol and copper had elevated levels of the C_8 unsaturated compounds (Table 2), the prooxidant effect of α-tocopherol allowed the formation of *t,c,c*-2,4,7-decatrienal to predominate, which resulted in the formation of distinct fishy odors (Table 1). In these samples, the green odor quality provided by 2,6=nonadienal and other green aldehyde contributors was suppressed because of the high concentrations of the decatrienals (Table 1).

These results indicate that although α-tocopherol has the ability to direct the formation of 1,5-unsaturated-C_8 compounds, its prooxidant character at high concentrations substantially increases the levels of burnt/fishy decatrienals that tend to dominate and overpower the contribution of the C_8 compounds. Alternately, Trolox C provided general antioxidant protection against autoxidation reactions and suppressed burnt/fishy flavors through directing the oxidation process in favor of 1,5-octadien-3-one and 1,5-octadien-3-ol. The green, metallic odors observed at high concentrations are modified at lower concentrations and elicit green, fresh fish-like responses in fish oils. Although Trolox C is not approved as a food additive, its effectiveness as an antioxidant and directing agent against fishy flavors should warrant attention and a re-evaluation as a food additive.

In summary, the addition of tocopherol-type compounds can direct oxidative processes in fish oils which modify characterizing flavors. Continued research on directing properties of other compounds in fish oils is needed to accelerate the development of antioxidant strategies that will minimize the formation of pronounced off-flavors in these oils.

ACKNOWLEDGMENTS

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