Characterization of the Volatile Decomposition Products of Oxidized Methyl Arachidonate

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The volatile thermal and oxidative decomposition products of methyl arachidonate were separated by capillary gas chromatography and identified by mass spectrometry. Various aldehydes, ketones, aldehyde esters, hydrocarbons and alcohols were identified. The major products included hexanal, methyl 5-oxopentanoate, pentane, methyl butanoate and 2,4-decadienal, which could be important to off-odor development in oxidized food systems containing arachidonate.

KEY WORDS: Arachidonic acid, autoxidation, methyl arachidonate.

The search for the compounds responsible for the oxidized flavor in precooked meat has been an active field of study for over 20 yr. Improved techniques are now available for the analysis of volatile compounds that may be present at low concentrations and possess a significant flavor threshold. Current techniques favor headspace analysis of volatiles to minimize artifact formation; however, preconcentration is still often necessary.

Ruenger *et al.* (1) recognized the possible contribution of lipid oxidation products to off-flavor, based upon the identification of heptanal and 3,6-nonadienal in reheated turkey meat. Other studies with headspace analysis have confirmed the work of Ruenger *et al.* (1). St. Angelo *et al.* (2) identified 40 compounds from cooked beef, while Wu and Sheldon (3) found 32 compounds from heated turkey rolls. The changes in the concentrations of these compounds were positively correlated with off-flavor. In both studies, most of the compounds were secondary reaction products from the oxidation of unsaturated fatty acids. In spite of these recent findings, the contribution of specific oxidation products to the odor/flavor notes of meat remains unknown. It is apparent, however, that lipid oxidation products have an important role in flavor development.

The unsaturated fatty acid content, rather than the total fat content, is most important in off-flavor development. In meat, the polyunsaturated fatty acids (PUFA) contained in phospholipids are the primary substrates for the formation of oxidation products related to off-flavors (2). More than 50% of the total PUFA content of meat phospholipids consists of arachidonic acid (4). There are relatively few studies on the volatile oxidation products of arachidonate (5–7), although the origin of the major decomposition products from arachidonate hydroperoxides has been discussed in the literature (8,9). In contrast, a considerable amount of research on less unsaturated fatty acids has been completed. Frankel (10) and Grosch (11) have published extensive reviews in this area. The flavor aspects of the autoxidation products of marine oils have also been addressed (12). Although marine oils contain some arachidonate, the focus of that study (12) was primarily on the more unsaturated fatty acids present in greater concentrations than arachidonate. Hence, there is a need to further investigate the impact of arachidonate autoxidation on the formation of off-flavor components in cooked meat.

The specific objectives of this research were twofold: (i) to identify the thermal decomposition products of oxidized methyl arachidonate by gas chromatography/mass spectrometry (GC/MS) and (ii) to determine the effect of added *tert*-butylhydroquinone (TBHQ) to methyl arachidonate on the peroxide value and on the composition of the thermal decomposition products.

EXPERIMENTAL PROCEDURES

Treatment 1. Twenty milligrams of methyl arachidonate (methyl eicosa-5,8,11,14-tetraenoate, 99+% purity, Nu-Chek-Prep, Elysian, MN) was dissolved in 100 μL of chloroform and placed in 2-mL vials wrapped in aluminum foil to minimize light incursion. The chloroform was removed under a gentle stream of nitrogen to form a thin film of lipid on the bottom of each vial. The vials were flushed once with oxygen (hydrocarbon-free, ultra pure grade) for 10 s, capped and incubated at 37°C for 48 h (13). Three vials were removed after 6, 12, 18, 24, 36 and 48 h of incubation for peroxide value (PV) analysis. Samples from each vial were analyzed in triplicate.

Treatment 2. Vials containing 20 mg methyl arachidonate in 40 μL methylene chloride and 200 ppm TBHQ (Lancaster Synthesis, Windham, NH) were prepared. The vials were then treated in the same manner as the samples in Treatment 1.

Treatment 3. Vials were prepared as in Treatment 1 except that the vials were flushed with oxygen every 12 h up to 48 h for 10 s.

Peroxide value determination. The changes in the PV of methyl arachidonate during autoxidation at 37°C were monitored with the iodometric procedure of Lea and Swoboda (14).

GC analysis. The thermal decomposition products of oxidized methyl arachidonate (Treatments 1–3, after 48 h at 37°C) were analyzed with a capillary gas chromatograph (Hewlett-Packard Model 5840, Hewlett-Packard Co., Avondale, PA) equipped with a flame-ionization detector (FID). One-microliter samples were injected in triplicate. A 0.32 mm i.d. × 60 m SPB-5 fused silica column (5% diphenyl, 95% dimethyl, 1% vinyl polysiloxane) was used with a film thickness of 1 μm (Supelco, Inc., Bellefonte, PA). The operating conditions were: injector temperature, 200°C; detector temperature, 300°C; splitless injection for 0.7 min; column pressure, 18 psi; temperature program starting at −20°C (utilizing liquid nitrogen cryofocusing) for 4 min, then 5°C/min starting at 4 min, 2°C/min at 26 min, 5°C/min at 90 min and a final oven temperature of 280°C for 30 min. The carrier gas was helium with linear flow rates of 28.2 cm/s at −20°C, 24.7 cm/s at 40°C and 19.2 cm/s at 200°C. The volumetric flow rates of the FID

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gases were: air, 240 mL/min; hydrogen, 30 mL/min; and nitrogen, 30 mL/min.

GC/MS analysis. The identity of the thermal decomposition products was determined with a Hewlett Packard Model 5985 GC/MS system (Hewlett-Packard Co.). GC conditions were maintained as previously described, except that the column pressure was reduced to 10 psi (15).

The operating conditions for the MS were as follows: electron impact ionization mode with ion electron energy set at 70 eV and a source temperature of 200°C. Mass spectral data from the National Bureau of Standards (NBS) and the Wiley Mass Spectral libraries were used to aid in identification. Where possible, compound identification was confirmed by GC retention data from authentic standards.

RESULTS AND DISCUSSION

The changes in PV during the autoxidation of methyl arachidonate for each treatment are shown in Figure 1. Samples without added antioxidant displayed an induction period, followed by a period of rapid increase in the PV until a maximum was reached (16). As expected, a greater rate of oxidation was observed in the samples flushed with oxygen every 12 h as compared to the samples flushed once with oxygen. However, in the presence of TBHQ, the rate of methyl arachidonate oxidation was substantially reduced, relative to both the samples flushed with oxygen once and the samples flushed with oxygen every 12 h.

Thermal decomposition of the hydroperoxides present in the oxidized methyl arachidonate (Treatment 1, after 48 h at 37°C) occurred upon injection of the sample into the heated inlet of the GC (200°C) (17,18). The oxidized sample contained, after injection into the GC injection port, (i) thermal decomposition products from hydroperoxides, (ii) thermal decomposition products resulting from secondary oxidation products and (iii) secondary oxidation products formed during incubation of the sample prior to injection.

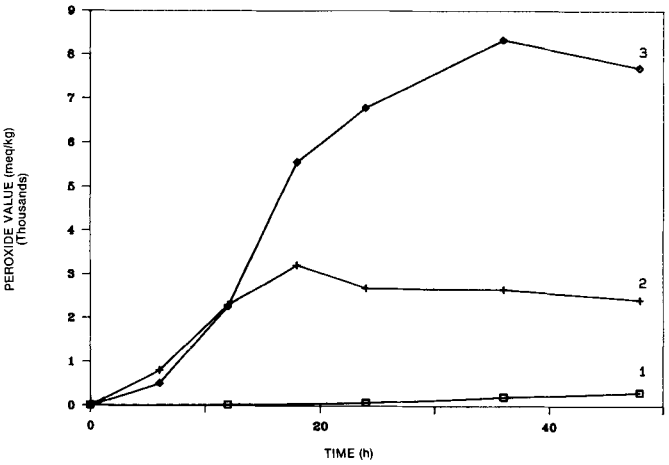

FIG. 1. Peroxide value of methyl arachidonate during storage at 37°C. Each analysis was done in triplicate, and the average was plotted. Sample (1) contained 200 ppm *tert*-butylhydroquinone and was flushed once with O_2; sample (2) was flushed once with O_2; sample (3) was flushed every 12 h with O_2.

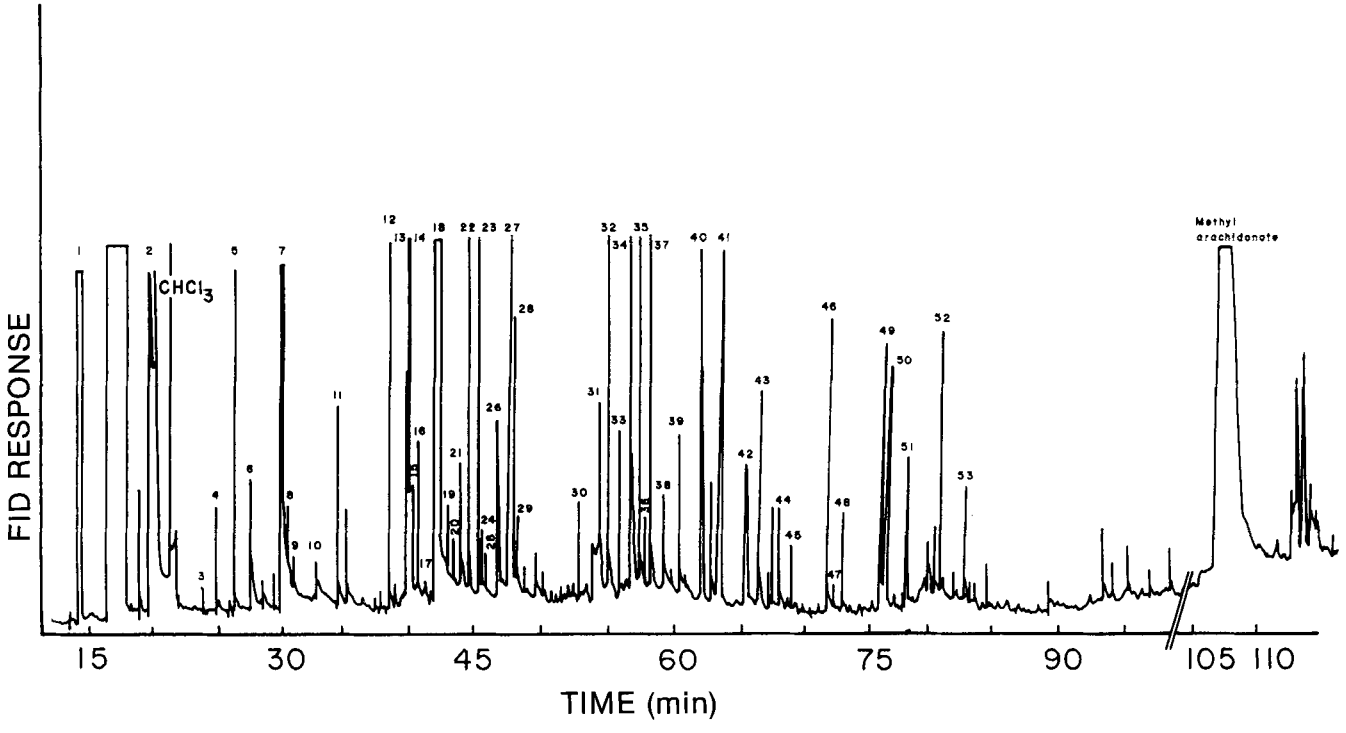

FIG. 2. Capillary gas chromatography chromatogram of methyl arachidonate (flushed once with oxygen and oxidized for 48 h at 37°C, Treatment 1). Conditions: SPB-5, df = 1.0 μm, 0.32 mm × 60 m, temp. program: −20°C for 4 min, 5°C/min at 4 min, 2°C/min at 26 min, 5°C/min at 90 min, final temp. 280°C, 1 μL inj. (0.4 mg/μL in CH_2Cl_2), splitless mode for 0.7 min; He at 18 psi. FID, flame-ionization detector.

The oxidized sample of methyl arachidonate, flushed once with oxygen and stored at 37°C for 48 h (Treatment 1), contained in excess of 200 major and minor components (Fig. 2). Peak numbers were assigned to the 53 components with interpretable mass spectra that eluted prior to methyl arachidonate. The unoxidized sample contained few, if any, contaminants or oxidation products (Fig. 3).

The total GC elution time was 120 min with the majority of the components eluting during the first 60 min of the analysis. A number of unresolved peaks may be observed in Figure 2, particularly for those areas containing large concentrations of compounds, *e.g.*, the areas between peaks 7-9, 13-16, 18-21, 23-29. One component (pentane) eluted prior to the solvent (methylene chloride). An artifact (chloroform) was also detected and confirmed by GC/MS. Several components eluted after methyl arachidonate (Fig. 2), indicating the presence of other, higher-molecular weight species.

The results of the GC/MS analysis of the thermal decomposition products of oxidized methyl arachidonate are shown in Table 1. Some compounds were only tentatively identified when authentic standards were unavailable for comparison. The interpretation of the mass spectra is discussed in detail elsewhere (19).

The compounds identified (Table 1) include aldehydes ranging from C3 to C10, ketones (C4 to C9), methyl esters (C4 to C9), hydrocarbons (C5 to C12), alcohols (C7 to C9), a furan, a fatty acid and a lactone. Many of these compounds have been previously reported in lipid-containing food materials. Hexanal is a common oxidation product from many foods, including soybean oil, beef, chicken and turkey (2,3,20-23). Animal tissues contain sufficient amounts of arachidonate in the phospholipid fraction to readily account for the formation of hexanal (24,25). 4-Nonenal was not reported in previous studies, although 2-nonenal has been identified in the volatiles of beef and chicken (2,20,26).

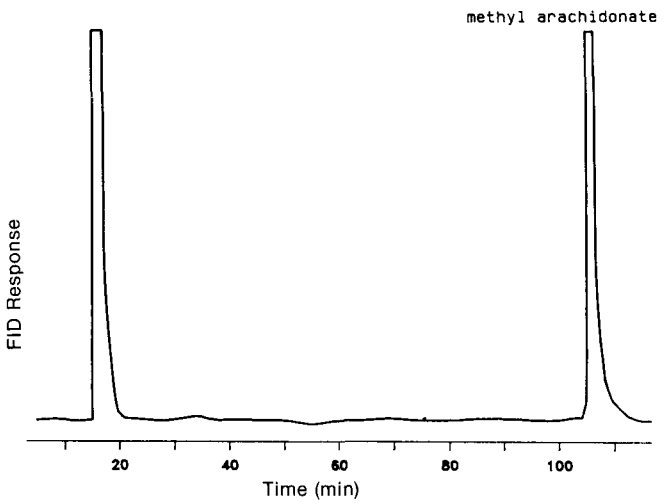

FIG. 3. Capillary gas chromatography chromatogram of unoxidized methyl arachidonate. Conditions: SPB-5, df = 1.0 μm, 0.32 mm × 60 m, temp. program: −20°C for 4 min, 5°C/min at 4 min, 2°C/min at 26 min, 5°C/min at 90 min, final temp. 280°C, 1 μL inj. (0.4 mg/μL in CH_2Cl_2), splitless mode for 0.7 min; He at 18 psi. FID, flame-ionization detector.

Ketones identified in the present study have also been reported from oxidized lipids and food materials (2,3). 2,3-Octanedione may be important, since its presence in cooked beef and turkey has been associated with the development of off-flavor (2,3).

Except for pentane, the hydrocarbons found in the present study have not been reported in previous studies. A large variety of lactones were found by Noleau and Toulemonde (26) in roasted chicken fat, including 4-hydroxypentanoic acid lactone, but no reports were found of its unsaturated isomer, 4-hydroxy-2-pentenoic acid lactone, tentatively identified in the present study.

Quantitation was limited to the 53 components that eluted prior to methyl arachidonate (Fig. 2). The peak area from the 53 identified components comprised more than 75% of the total peak area (Table 1), excluding those from the solvent (chloroform) and methyl arachidonate. The remaining 25% of the total area was due to minor components. The ratio of total volatiles to methyl arachidonate was approximately 0.2 to 0.25, based on peak area counts.

The relative concentrations of the identified components ranged from 0.025% (4-hydroxy-2-pentenoic acid lactone) to 28.0% (hexanal) (Table 1). Major compounds formed in addition to hexanal were pentane, methyl butanoate, methyl 5-oxopentanoate, and *(E,E)-* and *(E,Z)-*2,4-decadienal (Table 1).

Aldehydes. The majority of the identified volatiles consisted of aldehydes (43% of the total area of the identified components), then methyl esters (24%), aliphatic hydrocarbons (13%), ketones (3.6%) and alcohols (2.5%). Badings (5) isolated aliphatic aldehydes (approx. 92%) and a few ketones (approx. 8%) from arachidonic acid oxidized at 20°C. Similarly, Mottram *et al.* (27) found that aliphatic aldehydes tend to dominate the volatiles collected from oxidized lipids in beef and pork (30-50% of the total GC peak area). A large portion (>31%) of the volatiles isolated from autoxidized methyl arachidonate by Taylor and Mottram (7) were aldehydes, as expected (8,9). In the present study, hexanal was responsible for approximately 65% of the total aldehydes and 28% of the total volatiles.

Other major aldehydes found in the present study included the isomers of 2,4-decadienal (*E,Z-* and *E,E-*), which comprised approximately 14% of the total aldehydes. Both of these aldehydes are expected decomposition products from arachidonate hydroperoxides (8,9). Badings (5) also found smaller concentrations of the 2,4-decadienals as compared to hexanal. The ratio of hexanal to 2,4-decadienal in linoleate and arachidonate model systems has been addressed by various investigators. Taylor and Mottram (7) found two different 2,4-decadienal isomers, as well. Evidently, the nature of the low-molecular weight products formed at moderate temperatures in the presence of air can differ from that produced during the anaerobic pyrolysis of monohydroperoxides (11). In the presence of air, an increased ratio of the more saturated aldehydes is produced due to the greater oxidative susceptibility of the unsaturated aldehydes. 2,4-Decadienal is known to decompose further to 2-octenal, hexanal and other lower-molecular weight products (11).

Badings (5) reported that the ratio of hexanal to 2,4-decadienal was 1.4:1 from autoxidized arachidonate. In the present study, the ratio was 4.5:1. The higher ratio of hexanal to 2,4-decadienal in the present study may be

TABLE 1

Decomposition Products Identified from Oxidized Methyl Arachidonate[a]

Peak no.[b]	Gas chromatography trace (min)	Compound	Identification[c]	% of total[d]	SD
Aldehydes					
2	17.00	1,3-propanedial	I	3.11	±0.27
4	22.85	pentanal	M,G	0.19	±0.00
6	25.54	*(E)*-2-methyl-2-butenal	M,G	0.49	±0.06
7	27.93	hexanal	M,G	28.00	±1.26
12	36.52	*(E)*-2-heptenal	M,G	0.89	±0.06
22	42.38	*(Z)*-2-octenal	I	1.05	±0.02
23	43.22	*(E)*-2-octenal	M,G	1.28	±0.03
27	45.69	*(E)*-4-nonenal	L	1.92	±0.14
40	60.16	*(E,Z)*-2,4-decadienal	I	3.92	±0.14
41	61.79	*(E,E)*-2,4-decadienal	M,G	2.26	±0.01
Ketones					
3	21.60	2,3-butanedione	M,G	0.06	±0.00
11	32.55	2-heptanone	M,G	0.40	±0.03
14	38.01	3-octanone	M,G	0.94	±0.15
16	38.79	2-octanone	M,G	0.36	±0.03
21	51.87	3-octen-2-one	M,G	0.33	±0.01
24	43.48	2,3-octanedione	L	0.30	±0.03
26	44.83	4-nonanone	L	1.20	±0.14
Alcohols					
13	37.85	1-octen-3-ol	M,G	1.32	±0.16
25	43.85	*(E)*-2-octen-1-ol	M,G	0.24	±0.04
28	45.85	1,2-heptanediol	L	0.94	±0.04
34	53.95	2-methyl-3-octanol	L	2.06	±0.12
Methyl esters					
5	24.13	methyl butanoate	M,G	4.06	±0.21
18	40.30	methyl 5-oxopentanoate	I	9.60	±0.29
19	40.92	methyl*(E)*-5-heptenoate	I	0.11	±0.01
20	41.34	methyl *(Z)*-5-heptenoate	I	0.08	±0.00
30	50.81	methyl 3-heptenoate	L	0.40	±0.02
32	52.98	methyl 6-heptynoate	L	1.73	±0.27
33	53.95	methyl 7-nonynoate	L	0.66	±0.05
39	58.66	methyl 3-nonenoate	L	0.77	±0.08
Hydrocarbons					
1	11.95	pentane	M,G	6.41	±0.28
8	28.53	*(E)*-4-octene	M,G	0.37	±0.03
9	29.10	4-octyne	M,G	0.03	±0.00
29	46.32	2,4-undecadiene	I	0.25	±0.03
35	55.54	5,7-dodecadiene	L	3.40	±0.15
36	55.82	5,7-dodecadiene	L	0.26	±0.04
37	56.32	5,7-dodecadiene	L	1.68	±0.08
42	64.08	1-undecyne	L	0.44	±0.04
Others					
10	30.97	4-hydroxy-2-pentenoic acid lactone	L	0.03	±0.00
15	38.49	hexanoic acid	M,G	0.10	±0.01
17	39.42	2-pentyl furan	M,G	0.12	±0.00

[a] Flushed once with O_2 prior to incubation at 37°C for 48 h.

[b] Peak numbers according to Figure 2.

[c] M = MS (mass spectrometry) (complete spectrum) was consistent with that of authentic compound; G = GC (gas chromatography) retention data was consistent with that of authentic compound; L = tentative identification based on National Bureau of Standards and/or Wiley Mass Spectral Libraries; I = tentative identification based on an interpretation of mass spectral data.

[d] Mean of triplicate analyses.

attributed to differences in autoxidation conditions. The higher incubation temperature in this study (37°C), as compared to the work by Badings (5) (20°C), may have promoted the degradation of 2,4-decadienal to hexanal and favored the formation of hexanal over 2,4-decadienal. Except for 2-heptenal, Badings (5) also found minor amounts of aldehydes in autoxidized arachidonic acid. Aldehydes found by Taylor and Mottram (7), in addition to those identified in this study, included octa-2,4-dienal, dec-2-enal, nonenal and hex-2-enal.

Methyl esters. Methyl 5-oxopentanoate and methyl butanoate were the major methyl esters formed, which comprised approximately 20 and 4%, respectively, of the total volatiles. Only minor amounts of methyl 5-heptenoate were formed (0.2% of total volatiles). Taylor and Mottram (7) found several methyl esters, including methyl

hexanoate, methyl heptanoate and two methyl heptenoates, although they did not find methyl 5-oxypentanoate and methyl butanoate.

Hydrocarbons. Pentane was the major hydrocarbon isolated in this study (6.4% of total, 51% of its class), as expected (8,9,28). The change in pentane concentration can be a sensitive marker in predicting the deteriorative changes in oxidized food oils (29). The only noncyclic hydrocarbons Taylor and Mottram (7) identified from autoxidized methyl arachidonate were decane and an unspecified branched-chain hydrocarbon.

5,7-Dodecadiene (tentative identification) comprised 5.3% of the total volatiles (three isomers combined). It has not been reported in food materials, although other C12 unsaturated hydrocarbons were found in roasted chicken fat (26) and beef (2,30).

Only minor amounts of 4-octene, 4-octyne, 1-undecyne, and 2,4-undecadiene were found in the present study (0.03 to 0.44%) (Table 1). None of these compounds were reported in previous studies, although related C8-alkenes and 1-undecene were reported in minor amounts in beef (21,31), chicken (26) and turkey (3). Taylor and Mottram (7) found a large number of benzene derivatives, including naphthalene, from autoxidized methyl arachidonate, that were undetected in the present study.

Alcohols. Alcohols comprised 2.5% of the total volatiles. The amount of alcohol(s) reported in previous studies varied greatly. In roasted chicken fat, Noleau and Toulemonde (26) found that 6% of the total volatiles were alcohols; in beef, MacLeod and Ames (32) found 4% were alcohols, whereas Mottram *et al.* (27) found as much as 23%. Alcohols have also been isolated from turkey with warmed-over flavor, but they were not the principal volatiles (3,5). 1-Octen-3-ol (1.3% of total) was the major alcohol isolated in the present study. Taylor and Mottram (7) reported finding significant amounts of 1-octen-3-ol upon autoxidation of methyl arachidonate. The other major alcohol reported (pentanol) comprised 0.9 to 1.6% of the total volatiles (7). Wu and Sheldon (3) noted the importance of 1-octen-3-ol in warmed-over flavor development in turkey rolls. Short-chain alcohols are also expected oxidation products upon decomposition of arachidonate (8,9).

Ketones. The total concentration of ketones found in the present study was 3.6%. Badings (5) found approximately the same amount of ketones from autoxidized arachidonic acid (3.5%). Mottram *et al.* (27) examined beef and pork volatiles and found 7 and 8.4% ketones, respectively.

4-Nonanone was found in the greatest amount among the ketones identified (1.2% of total), followed closely by 3-octanone at 0.9%. With the exception of 2,3-butanedione (0.06%), the other ketones were present in nearly equal amounts, ranging from 0.3 to 0.4% of total. 2-Heptanone, 2-octanone and 3-octen-2-one have been previously reported as minor components in freshly cooked beef and chicken (26,32,33) as well as in beef and turkey with warmed-over flavor (2,3). Taylor and Mottram (7) identified several ketones among the oxidation products of methyl arachidonate, including 3-methylpentan-2-one, heptan-2-one, octan-3-one, a 2-ketone, oct-1-en-3-one, octan-2,3-dione, oct-3-en-2-one and acetophenone. The major ketone (oct-1-en-3-one) constituted from 5.22 to 9.49% of the major volatiles (depending upon the experimental conditions) (7).

Other compounds. Hexanoic acid, 4-hydroxy-2-pentenoic acid lactone and 2-pentyl furan were formed in minor amounts (0.025 to 0.12%) in the present study. Because these compounds are not expected cleavage products of unsaturated fatty acid hydroperoxides, their presence was an indication of further oxidation of the compounds produced from the decomposition of hydroperoxides (10). For example, Noleau and Toulemonde (26) found substantial amounts of hexanoic acid (4%) in roasted chicken fat. Taylor and Mottram (7) also found a substantial amount of hexanoic acid (1.59–5.5%) among the volatile oxidation products of methyl arachidonate.

Lactones are generally minor products of fat oxidation, and their presence cannot always be explained on the basis of the classical cleavage mechanisms. Minor amounts of lactones have been identified from oxidized oleate and linoleate (10). 4-Hydroxy-2-pentenoic acid lactone was found in small concentrations upon oxidation of methyl arachidonate (Table 1).

Addition of TBHQ and arachidonate oxidation. The GC profile of methyl arachidonate oxidized in the presence of 200 ppm TBHQ for 48 h at 37°C is shown in Figure 4. Only 4 major compounds were found: hexanal, methyl 5-oxopentanoate and the two isomers of 2,4-decadienal

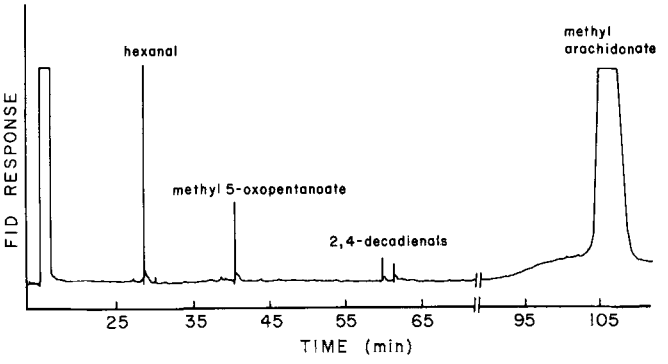

FIG. 4. Capillary gas chromatography chromatogram of methyl arachidonate (with added TBHQ, oxidized for 48 h at 37°C). Conditions: SPB-5, df = 1.0 μm, 0.32 mm × 60 m, GC temperature program: −20°C for 4 min, 5°C/min at 4 min, 2°C/min at 26 min, 5°C/min at 90 min, final temperature 280°C, 1 μL inj. (0.4 mg/μL in CH_2Cl_2), splitless mode for 0.7 min; He at 18 psi. FID, flame-ionization detector.

TABLE 2

Relative Concentrations of Arachidonate Oxidation Products in the Presence of 200 ppm TBHQ[a]

Peak no.	Compound[b]	% of total[c]	SD
7	Hexanal	50.70	±3.78
18	Methyl 5-oxopentanoate	32.60	±2.35
40	*(E),(Z)*-2,4-Decadienal	9.28	±0.89
41	*(E),(E)*-2,4-Decadienal	7.37	±0.87

[a] Contained 200 ppm *tert*-butylhydroquinone (TBHQ) and flushed once with oxygen prior to incubation at 37°C for 48 h.

[b] Identification based on gas chromatography/mass spectrometry.

[c] Based on the mean (triplicate analyses) of peak area counts.

(tentative identification). The small amount of volatiles formed in the presence of 200 ppm TBHQ confirmed the effectiveness of phenolic antioxidants in decreasing the oxidation of methyl arachidonate (34).

The ratio of hexanal/methyl 5-oxopentanoate/2,4-decadienal formed without TBHQ (52:36:12) (Treatment 1) was approximately the same as the sample with TBHQ (51:33:16) (Table 2). The fact that these two ratios were relatively close suggests that TBHQ did not drastically alter the pathway(s) leading to the formation of the major decomposition products. TBHQ simply limited the amount of hydroperoxides formed.

The effect of TBHQ may be similar to that of α-tocopherol, which is concentration-dependent (13,35,36). At lower concentrations (0.5%), α-tocopherol inhibited methyl linolenate oxidation; however, there was no change in the absolute amount of the 12- and 13-hydroperoxides formed as compared to the control (without added α-tocopherol). An increase in the absolute amount of 12- and 13-hydroperoxides was observed only after 2.5% α-tocopherol was added (37). Therefore, it is possible that, although the addition of 200 ppm (0.02%) TBHQ was antioxidative in the study, it was not sufficient to change the ratio of the peroxidic products formed from methyl arachidonate. This would explain the absence of any major change in the ratio of hexanal/methyl 5-oxopentanoate/2,4-decadienal.

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