Chemical Reactions Involved in the Deep-Fat Frying of Foods: IX. Identification of the Volatile Decomposition Products of Triolein

WILLIAM A. MAY[1], ROBERT J. PETERSON[2] and STEPHEN S. CHANG*, Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903

ABSTRACT

The acidic and nonacidic volatile decomposition products (VDP) produced by pure triolein maintained at 185 C with periodic injection of steam were collected, fractionated and identified. A total of 93 compounds were positively or tentatively identified. A number of the compounds found were identified for the first time in fats or oil VDP. Among these newly identified compounds are: unsaturated acids, keto-substituted unsaturated acids, ω-enals, unsaturated esters and an unsaturated γ-lactone.

The volatile decomposition products (VDP) derived from oleic acid and its ester derivatives have been investigated by a number of researchers over many years (1-6). This interest in oleic acid and its derivatives is due, in large part, to the significant amounts of this fatty acid found in the glycerides of commercial fats and oils.

A great many volatile compounds have been identified as thermal and/or oxidative decomposition products of the various oleates investigated. The classes of compounds to which the identified volatiles belong include: hydrocarbons, alkanals, 2-alkenals, alcohols, ketones, mono- and dibasic acids, esters and lactones.

A large proportion of edible fats and oils consumed in the United States is used in commercial or home deep-fat frying procedures. Therefore, it would be of interest to know what VDP are produced from oleates during the deep-fat frying process. However, the past investigations of the oleate VDP were performed under conditions which do not precisely simulate the deep-fat frying process. The conditions used in the previous work generally involved either autoxidative conditions, such as oxidation under ultraviolet (UV) light at room temperature (1) or thermal oxidative conditions, such as heating to relatively high temperatures (165-200 C) in the presence of air (1,2). Fats and oils used in deep-fat frying are not only exposed to relatively high temperatures in the presence of air, but come in contact with a significant amount of steam derived from the fried food product. Therefore, as part of a continuing series on the chemical reactions involved in deep-fat frying, triolein was subjected to simulated frying conditions and the generated VDP analyzed. A relatively large amount of triolein (2,128 g.) was processed in this manner in order to increase the possibility of identifying minor VDP which may have significant odor properties.

EXPERIMENTAL PROCEDURES

Materials

The composition, synthesis and chemical properties of triolein used in this investigation have been previously reported (7).

Simulated Deep-fat Frying and Isolation of VDP

The frying apparatus and isolation procedures used in this investigations were the same as those reported previously for trilinolein (8). The triolein (2128 g) was treated under simulated deep-fat frying conditions at 185 C with periodic injection of steam for 75 hr. The extraction of the isolated VDP with reagent grade ethyl ether, their concentration, their separation into acidic and nonacidic fractions, and the conversion of the acidic compounds into their methyl esters were conducted in the same manner as reported previously for trilinolein (9). Since both the acidic and nonacidic VDP solutions were contaminated with some entrained triolein, they were molecularly distilled at 150 C and 10^{-3} torr for 5 hr (10).

Fractionation of Acidic VDP by Gas Chromatography

The methyl esters of the acidic VDP were separated into 16 fractions by gas chromatography (GC) using an Aerograph A-90P with a 10 ft × ¼ in. id aluminum column packed with 20% DEGS on Anakrom ABS 60/70 mesh (Fig. 1). The temperature was nonlinearly programmed from 60 to 190 C for 16 min. The He flow rate was 60 mL/min. Each of the 16 fractions was accumulatively collected in one trap according to the method of Deck et al. (11). The chromatography was repeated until the sample was exhausted.

Each of the 16 preliminary fractions of the acidic VDP

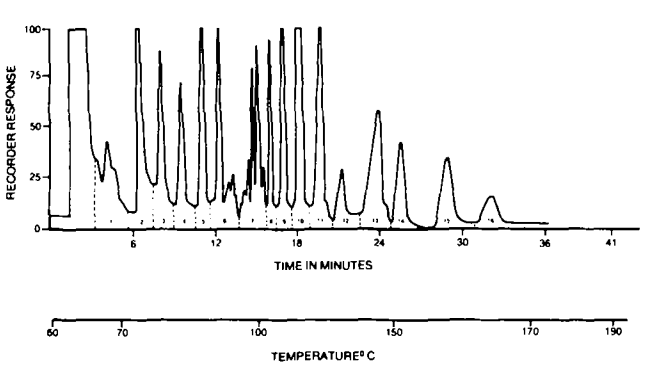

FIG. 1. Gas chromatogram of the acidic volatile decomposition products from thermally oxidized triolein.

[1]Current address: Moxie Industries, Ltd., Atlanta, GA.
[2]Current address: Firmenich, Inc., Princeton, NJ 08536.
*To whom correspondence should be addressed.

was rechromatographed with an Aerograph 202 using a 20 ft × 1/8 in. id stainless steel column packed with 15% SE-30 on Anakrom ABS 60/70 mesh. The He flow rate was 48 mL/min. For each fraction, the temperature was linearly programmed after an initial 6-min, 50 C isothrmal period, at 6 C/min to 200 C and held. The subfractions in the second and subsequent chromatographies were accumulatively collected in "hairpin" traps according to the method of Thompson et al. (9).

Each subfraction resulting from the second chromatography was chromatographed for a third time with the Aerograph 202 using a 20 ft × 1/8 in. id stainless steel column packed with 15% stabilized DEGS on Anakrom ABS 60/70 mesh. The conditions used for the rechromatography of each subfraction were chosen for maximum resolution. The final subfractions obtained were subjected to the identification procedures described below.

Fractionation of Nonacidic VDP by Gas Chromatography

The nonacidic VDP were separated into 19 fractions by gas chromatography using the Aerograph A-90P with a 20 ft × 3/8 in. id aluminum column packed with 20% SE-30 on Anakrom ABS 60/70 mesh (Fig. 2). The temperature was nonlinearly programmed from 60 to 190 C and held at 190 C for 24 min. The He flow rate was 70 mL/min. Each of the 19 fractions were accumulatively collected in one trap according to the method of Deck et al. (11). The chromatography was repeated until the sample was exhausted.

Each of the 19 preliminary fractions of the nonacidic VDP was rechromatographed with an Aerograph 202. Fractions 1-5 were chromatographed using a 10 ft × ¼ in. id aluminum column packed with 20% Carbowax 20M on Anakrom ABS 70/80 mesh. The He flow rate was 40 mL/min. For each of these fractions, the temperature was linearly programmed, after an initial 6-min, 50 C isothermal period, at 4 C/min to 150 C and held. Fractions 6-19 were chromatographed using a 20 ft × 1/8 in. id stainless steel column packed with 10% Carbowax 20M on Anakrom ABS 60/70 mesh. The He flow rate was 50 mL/min. For each of these fractions, the temperature was linearly programmed, after an initial 2-min, 50 C isothermal period, at 6 C/min to 195 C and held. The subfractions obtained in the second and subsequent chromatographies were accumulatively collected in "hairpin" traps.

Each subfraction resulting from the second chromatography was chromatographed for a third time with the Aerograph A-90P using a 20 ft × 1/8 in. id stainless steel column packed with 10% SE-30 on Anakrom ABS 60/70 mesh. The conditions used for the rechromatography of each subfraction were chosen for maximum resolution. The final subfractions obtained were subjected to the identification procedures described below.

Identification of Gas Chromatographic Fractions and Peak Size

The subfractions obtained from the third preparative gas chromatography of the triolein VDP were in the majority of cases pure compounds, as indicated by the chromatographic peak shapes and by the subsequent spectral data. These subfractions were identified by a combination of infrared (IR) and mass spectrometry and GC retention time data according to the method of Kawada et al. (12). The infrared specta were recorded as CCl_4 solutions on a

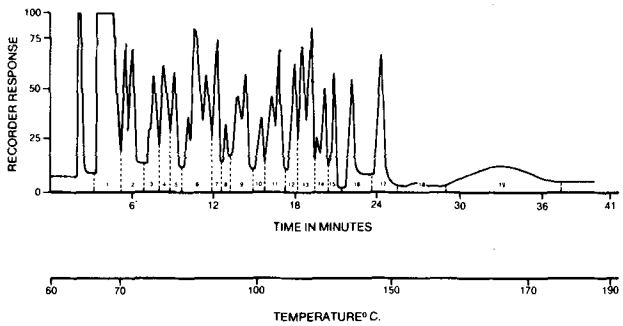

FIG. 2. Gas chromatogram of the nonacidic volatile decomposition products from thermally oxidized triolein.

Beckman IR-8 employing an ultramicro cavity cell according to the procedure reported by Kawada et al. (12). The pure components from the repeated chromatography were introduced into the heated, glass batch inlet of a Hitachi-Perkin-Elmer RMU-7 mass spectrometer for analysis. A compound was considered to be positively identified if both the IR and mass spectra agreed with the published spectra. An identification was considered tentative if only one type of spectral data was available. The peak size of each subfraction was obtained according to the method of Krishnamurthy and Chang (13).

RESULTS AND DISCUSSION

A total of 93 compounds were either positively or tentatively identified from the acidic and nonacidic VDP produced by triolein during simulated deep-fat frying (Tables I and II). The identified compounds included: 10 hydrocarbons, 5 alcohols, 6 esters, 9 saturated aldehydes, 11 unsaturated aldehydes, 9 ketones, 7 lactones, 11 saturated acids, 16 unsaturated acids, 2 dibasic acids, 4 keto acids and 3 miscellaneous compounds.

A number of compounds not previously identified in the VDP of fats and oils were found in this study. These are indicated in Tables I and II. This area deserves additional study. The infrared and mass spectra of some of these compounds are presented in Figures 3-5. Figure 3 shows the IR and MS of the subfraction identified as 8-oxo-*cis*-2-nonenoic acid as the methyl ester. The IR shows characteristic conjugated, *cis*, double bond absorptions at 3.3, 6.1 and 14.6μ (14). The strong doublet at 5.80 and 5.85μ indicates the presence of two types of carbonyl groups, an unsaturated ester and saturated ketone carbonyl, respectively, within the molecule. The series of strong absorptions at ca. 8.5μ is indicative of the ester linkage. The mass spectrum shows a molecule ion at m/e 184, suggesting a molecular formula of $C_{10}H_{16}O_3$. The peak at m/e 169 is due to loss of a CH_3 group and the base peak at m/e 141 is probably due to loss of CH_3-C=O (M-43). The existence of, and relative intensity of these latter two peaks leads to the assignment of the keto group at carbon number eight of the molecule. Further evidence for a C_8 keto group is the peak at m/e 126 (M-58) which is probably due to loss of CH_3-C(OH) = CH_2 from a McLafferty rearrangement with charge retention on the unsaturated ester fragment. The peaks at m/e 81, 74, 55, 41, and 39 are typical of unsaturated esters (15).

Figure 4 shows the IR and MS of the subfraction identi-

TABLE I

Compounds Positively Identified in the Volatile Decomposition Products of Thermally Oxidized Triolein

Fraction[a]	Identified as	Peak size[b]
Saturated aldehydes		
B-1-2-1	Propanal	L
B-3-2-1	Butanal	M
B-5-3-1	Hexanal	M
B-8-3-1	Heptanal	L
B-10-3-1	Octanal	XL
B-11-6-3	Nonanal	XL
B-11-6-4	Decanal	M
B-14-2-2	Undecanal	L
B-16-1-2	Dodecanal	M
Unsaturated aldehydes		
B-7-2-3	*trans*-2-Hexenal	S
B-10-4-1	*trans*-2-Heptenal	M
B-13-2-1	*trans*-2-Octenal	M
B-15-3-3	*trans*-2-Nonenal	L
B-17-1-2	*trans*-2-Decenal	XL
B-18-2-1	*trans*-2-Undecenal	XL
B-16-2-1	*trans*-3-Decenal	M
B-4-1-1[c]	5-Hexenal	M
B-5-3-2[c]	6-Heptenal	M
B-6-2-3[c]	7-Octenal	L
B-11-5-3	*trans*-2-*cis*-4-Nonadienal	M
Ketones		
B-10-4-2	2-Heptanone	S
B-10-2-1	3-Heptanone	S
B-11-4-1	3-Octanone	S
B-11-3-1	4-Octanone	M
B-15-1-3	2-Nonanone	M
B-15-1-1	3-Nonanone	S
B-16-1-1	2-Decanone	L
Dibasic acids		
A-7-4-1	Octanedioic acid	S
A-11-3-1	Nonanedioic acid	M
Keto acids		
A-12-3-1[c]	4-Oxo-*trans*-2-octenoic acid	L
A-13-5-1	8-Oxo-*cis*-2-nonenoic acid	M
A-14-3-1	4-Oxo-*trans*-2-decenoic acid	S
Saturated hydrocarbons		
B-4-3-2	Hexane	XS
B-5-1-1	Heptane	M
B-7-1-1	Octane	S
B-7-2-1	Nonane	XL
B-7-3-1	Decane	M
B-8-1-3	Undecane	S
B-10-1-1	Dodecane	L
Unsaturated hydrocarbons		
B-8-1-1	1-Octene	M
B-8-1-2	1-Nonene	M
B-11-4-2	1-Decene	S
Alcohols		
B-1-1-1	1-Propanol	L
B-3-1-1	1-Butanol	M
B-8-5-1	1-Hexanol	L
B-11-7-1	1-Heptanol	L
B-14-3-1	1-Octanol	L
Esters		
B-2-3-1	Ethyl acetate	XL
B-11-5-2	Hexyl formate	L
B-14-2-3	Octyl formate	L
B-17-1-1[c]	*trans*-2-Octenyl formate	S
B-10-4-2	Ethyl octanoate	S
Saturated acids		
A-2-2-1	Butanoic acid	M
A-4-1-1	Pentanoic acid	L
A-4-3-2	Hexanoic acid	L
A-5-4-1	Heptanoic acid	M
A-7-6-1	Octanoic acid	XL
A-11-3-1	Nonanoic acid	XL
A-12-2-1	Decanoic acid	L
A-12-3-1	Undecanoic acid	M
A-13-2-1	Dodecanoic acid	M
A-13-3-1	Tridecanoic acid	S
A-15-1-1	Tetradecanoic acid	S

(Table I continued next page)

TABLE I (continued)

Fraction[a]	Identified as	Peak size[b]
Unsaturated acids		
A-7-5-2	*trans*-2-Octenoic acid	M
A-7-7-1	*trans*-2-Nonenoic acid	M
A-7-9-1[c]	*trans*-2-Decenoic acid	M
A-7-11-1	*trans*-2-Undecenoic acid	L
A-15-3-1	*trans*-2-Dodecenoic acid	S
A-16-3-1[c]	*trans*-2-Tridecenoic acid	S
A-7-8-1	*cis*-3-Octenoic acid	M
A-7-9-3	*cis*-3-Nonenoic acid	S
A-7-10-1	*trans*-3-Decenoic acid	XS
A-13-5-2	*cis*-3-Decenoic acid	XS
A-14-1-1[c]	*cis*-3-Dodecenoic acid	M
A-5-2-1	5-Hexenoic acid	L
A-6-2-1	6-Heptenoic acid	L
A-7-6-2	7-Octenoic acid	L
A-16-4-1	*trans*-9-Octadecenoic acid	M
Lactones		
B-13-2-1	4-Hydroxyheptanoic acid lactone	XS
B-15-1-1	4-Hydroxyoctanoic acid lactone	S
B-15-3-1	4-Hydroxynonanoic acid lactone	M
B-17-3-1	4-Hydroxydecanoic acid lactone	S
B-15-2-2	4-Hydroxy-2-octenoic acid lactone	M

[a]A = Acidic VDP; B = nonacidic VDP. The first, second and third numerals indicate the peak number of the GC fraction during the first, second and third chromatographies, respectively.

[b]XS = extra small; S = small; M = medium; L = large; XL = extra large.

[c]Compound identified for first time in VDP of fats and oils.

TABLE II

Compounds Tentatively Identified in the Volatile Decomposition Products of Thermally Oxidized Triolein

Fraction[a]	Identified as	Peak size[b]
Unsaturated acid		
A-7-8-2	*cis*-2-*trans*-4-Octadienoic acid	S
Keto acid		
A-15-2-1[c]	4-Oxo-*cis*-2-dodecenoic acid	XS
Ester		
B-19-5-3[c]	Ethyl-*cis*-2-dodecenoate	S
Ketones		
B-14-3-2	a Nonenone	XS
B-19-5-1	a Dodecenone	XS
Lactones		
B-13-5-2	4-Hydroxy-2-hexenoic acid lactone	XS
B-17-2-2[c]	4-Hydroxy-3-octenoic acid lactone	S
Miscellaneous		
A-16-2-1[c]	10-Hydroxy-*cis*-8-hexadecenoic acid	XS
A-7-4-1	Octanedioic acid semialdehyde	S
B-15-2-1[c]	4-Oxo-*trans*-2-octenal	L

[a]A = Acidic VDP; B = nonacidic VDP. The first, second and third numerals indicate the peak number of the GC fraction during the first, second and third chromatographies, respectively.

[b]XS = Extra small; S = small; M = medium; L = large; XL = extra large.

[c]Compound identified for the first time in VDP of fats and oils.

fied as 4-oxo-*trans*-2-octenal. The IR shows characteristic conjugated, *trans* double bond absorptions at 3.3, 6.1 and 10.3μ (13). Absorption bands due to the aldehydic hydrogen are apparent at 3.55 and 3.65μ. The strong absorption band at 5.80μ is due to the unsaturated aldehyde carbonyl, while the band at 5.9μ is due to the unsaturated ketone carbonyl (14). The mass spectrum shows the molecular ion at m/e 140, which is consistent with a molecular formula of $C_8H_{12}O_2$. The peaks at m/e 112 (M-28) and 111 (M-29) may be due in part to loss of CO and CHO, respectively, from the aldehyde group. The peak at m/e 98 (M-42) is probably due to a McLafferty rearrangement involving the ketone group on C_4 with charge retention on the unsaturated keto-aldehyde fragment. The large peak at m/e 83 (M-57) indicates that the ketone group is located on C_4. The large peaks at m/e 55, 43, 42 and 41 are typical of

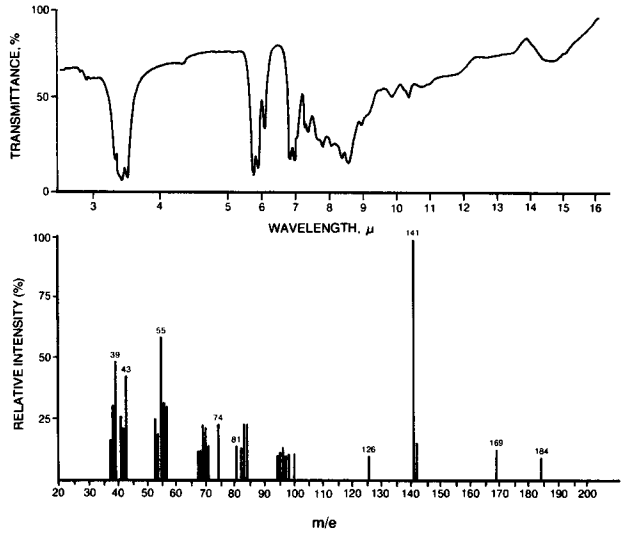

FIG. 3. IR and mass spectra of subfraction identified as methyl 8-oxo-*cis*-2-nonenoate.

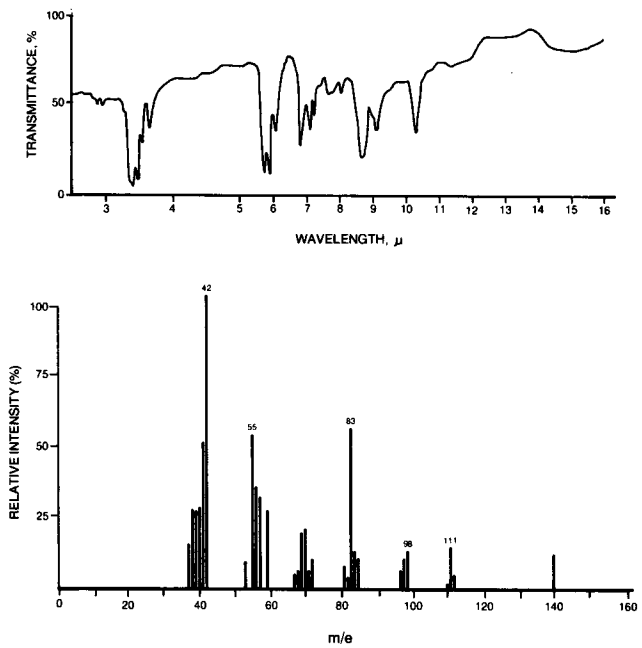

FIG. 4. IR and mass spectra of subfraction identified as 4-oxo-*trans*-2-octenal.

unsaturated compounds in general (15).

Figure 5 shows the IR of the subfraction identified as 7-octenal. The IR shows characteristic vinylic double bond absorptions at 3.22, 6.08, 10.05 and 10.97μ (14). The aldehydic hydrogen absorption bands are apparent at 3.53 and 3.76μ. The strong absorption band at 5.75μ is due to the nonconjugated aldehyde carboxyl (14).

The total number of compounds identified in the VDP of triolein was less than the total number identified in previous work on the VDP of trilinolein (9). This follows from the larger number of sites for initial attack by oxygen in the more highly saturated trilinolein as compared with triolein. The present work supports some of the findings of Selke et al. (6) with respect to the relative abundance in which the compounds heptanal, octanal, nonanal, 2-decanal and

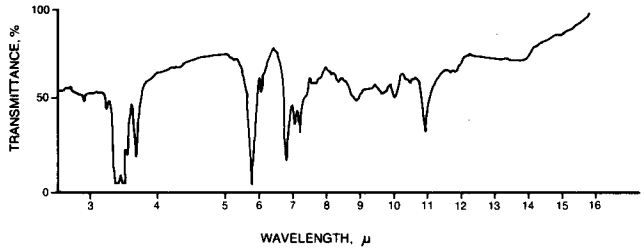

FIG. 5. IR spectrum of subfraction identified as 7-octenal.

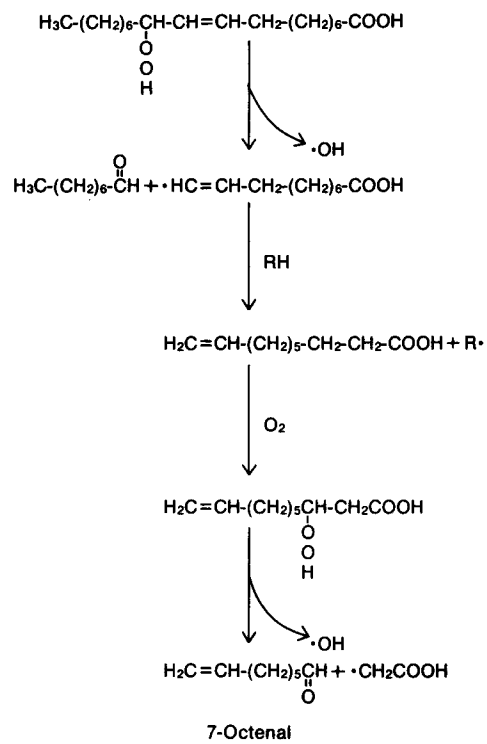

FIG. 6. Possible mechanism for the formation of 7-octenal from the 11-hydroperoxide of oleic acid.

2-undecanal were found. However, since the conditions used and amounts of triolein employed were different in the present study compared to the work of Selke et al., there are a number of qualitative and quantitative differences in the VDP found. Selke et al. found that heptane and octane were major VDP of triolein; however, nonane was found to be the only major hydrocarbon VDP in the present work. Octanoic and nonanoic acids were identified as additional major VDP of triolein in the present study.

The finding of a particular volatile constituent in a relatively small amount in a sample does not necessitate that this compound make an insignificant contribution to the odor characteristics of the sample. Therefore, the compounds identified in lesser amounts in this study, and others, may play a role in the odor of thermally oxidized triolein and in the odor of fats and oils used for deep-fat frying in general. Among the VDP found in small amounts were 2 and 3-enoic acids, terminal unsaturated acids and aldehydes, keto-2-enoic acids and saturated and unsaturated γ-lactones.

In agreement with the results of Selke et al. (6), the carbon chain length of the majority of the VDP of triolein

did not exceed 11 carbon atoms. However, the identification of a number of compounds with more than 11 carbon atoms, e.g., 2-dodecenoic acid, indicates that an apparent double bond migration may take place when triolein is treated under the conditions used in this study. The possibility of double bond migration in trilinolein, treated under conditions identical to those reported here, has been previously reported by Thompson et al. (9).

Three terminally unsaturated aldehydes and the three corresponding terminally unsaturated acids were identified for the first time in the VDP of an oil system. One possible mechanism for the formation of one of these terminally unsaturated compounds, starting from the 11-hydroperoxide of oleic acid, is given in Figure 6. Levy and Paul (16) have demonstrated the possibility of oxidation of a carbon atom, β- to a carboxylate group. A number of other possible mechanisms for the formation of these compounds exists. This area deserves additional study.

The lack of a large number and large amount of dienals, especially the 2,4-decadienals, demonstrates the limited extent of dehydrogenation during thermal oxidation of triolein, and helps explain the lack of a strong, deep-fat fried aroma in the treated triolein.

ACKNOWLEDGMENTS

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Biochemistry of Unsaturated Fatty Acid Isomers[1]

E.A. EMKEN, Northern Regional Research Center, Agricultural Research Service, US Department of Agriculture, Peoria, IL 61604

ABSTRACT

Recognition that catalytic hydrogenation changes the configuration and position of double bonds and alters the physical properties of unsaturated fats prompted numerous early investigations on the biochemical effects of "*trans* isomers." Recent research has provided data on positional isomer metabolism. Some aspects of fatty acid isomer metabolism are now reasonably well understood, but other issues are not resolved. Human and animal data have provided good evidence that isomers in partially hydrogenated oils are well adsorbed and incorporated into all organs and tissues. Analyses of human tissues also indicate that hydrogenated oils are the major source of fatty acid isomers in the US diet. Tissue composition data combined with isolated enzyme studies and isotope tracer experiments with whole organisms show unquestionably that structural differences between various fatty acid isomers influence specific biochemical transformations. Examples are differences in the reaction rates and/or specificities of acyl transferase, lipase, desaturase and cholesteryl esterase/hydrolase for various positional fatty acid isomers. Isolated microsomes and mitochondria also have been used to identify differences in acyl CoA activation, oxidation, and elongation of positional isomers. In addition, isotope tracer experiments show that preferential metabolism of individual positional isomers occurs in vivo. In vivo studies with hydrogenated vegetable oil diets containing adequate levels of linoleic acid produced no obvious physiological changes. Experiments with specific polyunsaturated isomers have produced changes in blood cell properties, pulmonary weight, linoleic acid requirements and tissue lipid composition. These changes may be related to a number of factors such as membrane fluidity and permeability, cell function, synthesis of arachidonic acid, homo-gamma-linoleic acid or prostaglandins. Whether differences in the biochemistry of fatty acid isomers are desirable or undesirable and whether these differences contribute to long-term or subtle effects important to the etiology of atherosclerosis and cancer are not resolved.

INTRODUCTION

Research on the biochemistry of unsaturated fatty acid isomers began in the 1930s (1) and dealt with the deposition in rat tissue of "isooleic acid" present in hydrogenated oils. Since that time, interest in the biochemistry and metabolism of fatty acid isomers has paralleled the steady increase in consumption of partially hydrogenated vegetable and marine oils.

During the 1960s, analytical methods were developed and used to identify a wide range of both *cis* and *trans* positional isomers in partially hydrogenated oils that are formed as a side reaction in the hydrogenation process. *cis* and *trans*

[1] Presented at the 73rd AOCS annual meeting, Toronto, 1982.