

Thermal Oxidation of a Series of Saturated Triacylglycerols

Eliana D. Crnjar, Arbsook Witchwoot, and Wassef W. Nawar*

The products from a series of triacylglycerols containing the even-numbered saturated fatty acid chains C_6 to C_{18} , after heating in air for 1 h at 180 and 250 °C, were studied qualitatively and quantitatively. The major decomposition products were alkanes, methyl ketones, alkanals, and γ - and δ -lactones. Among the hydrocarbons and particularly at the higher temperature, the C_{n-1} *n*-alkane was the most abundant. At the lower temperature, samples containing the longer fatty acid chains produced the C_{n-4} alkane in greater amounts than the decarboxylation product. In all cases the C_{n-1} methyl ketone was the major carbonyl compound, and the most abundant γ -lactone was the compound having a carbon number equal to that of the parent fatty acid. Only C_n δ -lactones were produced from each fatty acid. Mechanisms of thermal decomposition are discussed.

Heat, to which foods are subjected during processing, produces various chemical changes, many of which are of significant importance from the standpoint of flavor, appearance, nutrition, and toxicity. Not only do the different nutrients in food undergo decomposition reactions but also extremely complex interactions between these nutrients simultaneously take place, leading to the formation of a very large number of new compounds. It is obvious that a clear understanding of the mechanisms involved, and of the effects of treatment conditions on reaction pathways, is of paramount importance for proper control of food quality.

Since food systems are extremely complex, we have been studying effects of heat on the major food components, i.e., lipids, proteins, and carbohydrates, separately and in mixtures. Fats are important constituents of most foods and are used extensively for frying. The bulk of the naturally present lipids is in the form of triacylglycerols. A number of studies have been reported on thermal decomposition of saturated triacylglycerols (Crossley et al., 1962; Endres et al., 1962; Kleinau and Neitzel, 1970; Lien and Nawar, 1973; Selke et al., 1975). Different workers, however, used different substrates (e.g., short- and long-chain fatty acid; mono- and diacid triacylglycerol), different conditions of heating, and different techniques of analysis. Consequently the results varied and at times were incomplete or appeared contradictory.

Crossley et al. (1962) and Endres et al. (1962) reported that the major oxidative products of triacylglycerols consist of homologous series of carboxylic acids, methyl ketones, and *n*-alkanals. In addition to these compounds, Selke et al. (1975) identified homologous series of *n*-alkanes, 1-alkenes, *n*-alcohols, and γ -lactones. They concluded that the principal mechanism in thermal oxidation of saturated triacylglycerols involved the formation of monohydroperoxides and that oxygen attack occurred at all the methylene groups of the fatty acids of the glyceride molecules. Selke et al. (1975), however, suggested that oxygen attack toward the center of the molecule was more favored. In contrast, Crossley et al. (1962) and Endres et al. (1962) concluded that oxidation occurred preferentially at the α , β , and γ positions of the glyceride molecules. The effects of the various parameters of the heat treatment on the decomposition pattern have not been thoroughly investigated.

The present work was therefore designed to provide a more detailed insight regarding mechanisms of thermal decomposition and the influence of heating conditions by

using a series of substrates containing the even-numbered C_6 to C_{18} saturated fatty acid chains. Thermal decomposition of unsaturated fats and their interaction with other food components will be reported elsewhere.

EXPERIMENTAL SECTION

Triacylglycerols were purchased commercially and purified by cold-finger distillation as previously described (Nawar et al., 1969). One-gram samples were heated separately in 250-mL round-bottom flasks for 1 h at 180 °C and at 250 °C. A portion of 0.6 mL of the heated sample was transferred to another 250-mL round-bottom flask, and known amounts of 1-nonyne and 10-undecenal were added as internal standards. Collection of the volatile decomposition products was accomplished by cold-finger distillation at 80 °C under vacuum (10^{-3} torr) for 1 h. The distillate was fractionated into polar and nonpolar fractions on silica. Pentane was used to extract the nonpolar compounds; the polar components eluted with anhydrous diethyl ether. After concentration under a mild flow of N_2 , the polar compounds were separated by gas chromatography using a Varian Aerograph Model 3700 equipped with temperature programming and a flame ionization detector. The column, consisting of a 500 ft \times 0.02 in. o.d. stainless steel capillary, coated with Carbowax 20M, was temperature programmed from 60 to 200 °C at 4 °C/min and maintained until the completion of the analysis. The injection port was kept at 250 °C and the flame ionization detector maintained at 300 °C. The N_2 carrier gas flow rate was 5 mL/min at 60 °C. The quantitative analysis of the compounds was performed by electronic integration of the gas chromatographic peaks using a Varian Chromatography Data System IIIC.

A Perkin-Elmer Model 3920 gas chromatograph with a flame ionization detector, a temperature programmer, and a 250 ft \times 0.02 in. o.d. stainless steel capillary column coated with Carbowax 20M was used for the separation of the nonpolar components. Gas chromatographic conditions were as follows: temperature program, 60–200 °C at 4 °C/min and held until the analysis was completed; flow rate, 5 mL/min at 60 °C; injection port and detector temperatures, 250 °C.

Qualitative identification of all components was accomplished by combined gas chromatography-mass spectrometry. A Perkin-Elmer Model 3920 gas chromatograph interfaced with a Hitachi Perkin-Elmer Model RMU-6A mass spectrometer were used. The ion source was operated at 80 eV.

RESULTS AND DISCUSSION

The decomposition products identified in triacylglycerols after heating at 180 and 250 °C and the quantitative

Department of Food Science & Nutrition, University of Massachusetts, Amherst, Massachusetts 01003.

Table I. Quantitative Analysis of *n*-Alkanes and 1-Alkenes Formed in Triacylglycerols after Heating in Air for 1 h at 180 and 250 °C^a

	quantitative analysis, $\mu\text{mol}/100\text{ g}$									
	Tri-10		Tri-12		Tri-14		Tri-16		Tri-18	
	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C
9	<u>91</u>	<u>968</u>	75	86	342	516	110	523	277	325
9:1	07	31			61	16		18	7	43
10			170	290	405	620	159	619	368	470
10:1			16	128	50	36	02	67	13	49
11			<u>188</u>	<u>852</u>	236	426	201	593	392	547
12					300	524	<u>370</u>	495	401	584
12:1					87	317	09	32	11	31
13					<u>421</u>	<u>1284</u>	128	348	451	624
13:1					29	44	06	139	13	30
14							209	411	<u>549</u>	476
14:1							18	215	9	22
15							254	<u>833</u>	195	279
15:1							36	42	8	16
16									318	382
16:1									19	130
17									312	<u>1669</u>
17:1									35	

^a The most abundant hydrocarbon is underlined.

Table II. Quantitative Analysis of *n*-Alkanals and 2-Ketones Formed in Triacylglycerols after Heating in Air for 1 h at 180 and 250 °C

	quantitative analysis, $\mu\text{mol}/100\text{ g}$											
	Tri-6		Tri-8		Tri-10		Tri-12		Tri-14		Tri-16	
	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C
5 K + A ^a	233	238	113	135	182	186	139	260	160	200	247	198
6 K + A ^a			171	191	153	169	100	170	90	180	162	174
7 K + A ^a			231	312	117	93	80	140	35	170	103	100
8 K					66	95	43	44	28	80	89	88
8 A					33	35	31	68	44	81	23	23
9 K					151	180	24	26	32	56	80	81
9 A						70	32	36	31	76	17	18
10 K							57	71	27	43	78	78
10 A							27	27	18	65	11	11
11 K							100	208	13	25	79	77
11 A							26	84	35	61	09	09
12 K									40	62	59	66
12 A									19	23	10	12
13 K									80	180	18	16
13 A									21	97	20	17
14 K											70	59
14 A											10	09
15 K											130	121
15 A											07	07

^a Ketone and aldehyde peaks unresolved. K = ketone; A = aldehyde.

amounts for each compound are presented in Tables I–III. Qualitatively, the oxidative pattern was similar for samples heated at the two temperatures. It consisted mainly of hydrocarbons, methyl ketones, alkanals, and lactones. Generally, higher amounts of the decomposition products were formed at 250 °C.

The hydrocarbon series being the major nonpolar compounds were the same as those produced in the absence of oxygen, i.e., homologous series of *n*-alkanes and 1-alkenes with the alkanes predominating and the decarboxylation product of the parent fatty acid produced in substantial amounts (Lien and Nawar, 1973; Witchwoot and Nawar, 1980). However, the amounts formed were much more significant under the oxidative conditions, indicating that in addition to thermolytic reactions, oxidative decomposition is partly responsible for the hydrocarbons produced upon heating in air.

The data in Table I also show that both fatty acid chain length and temperature of heating have a decided effect

on the quantitative pattern of the hydrocarbons formed. For all samples treated at 250 °C, the C_{*n*-1} alkane was the hydrocarbon produced in the greatest quantity. In the case of the 180 °C oxidation, however, the quantitative pattern was dependent on the chain length of the component fatty acid, with C_{*n*-4} becoming more prominent for the longer chains. Thus, the C_{*n*-1} was the major hydrocarbon from substrates containing up to C₁₂ acids, but decane and tridecane were produced in almost equal quantities from trimyristin, and the C_{*n*-4} became the most abundant alkane from the C₁₆ and C₁₈ acids. It is interesting to note that in all cases the C_{*n*-3} alkane was the least abundant alkane formed.

In the case of polar compounds, methyl ketones were generally produced in larger quantities than the alkanals (Table V). In nearly all cases the C_{*n*-1} methyl ketone was the major carbonyl compound formed. The C_{*n*-2} methyl ketone was also abundant while the C_{*n*-3} member of the series was relatively small.

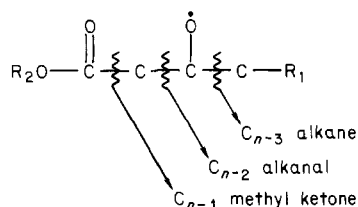
Table III. Quantitative Analysis of the Lactones Formed in Triacylglycerols after Heating in Air for 1 h at 180 and 250 °C

compd C no.	quantitative analysis, $\mu\text{mol}/100\text{ g}$											
	Tri-6		Tri-8		Tri-10		Tri-12		Tri-14		Tri-16	
	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C	180 °C	250 °C
6 γ	316	338	42	82	38	41	56	26				
6 δ	408	463	—	—	—	—	—	—				
7 γ			81	239	48	58	73	73			52	54
7 δ			—	—	—	—	—	—			—	—
8 γ			218	346	98	92	27	32	62	43	32	41
8 δ			224	284	—	—	—	—	—	—	—	—
9 γ					48	47	44	15	28	29		
9 δ					—	—	—	—	—	—		
10 γ					192	231	14	10	20	18	31	28
10 δ					230	176	—	—	—	—	—	—
11 γ							13	12	10	10	31	40
11 δ							—	—	—	—	—	—
12 γ							176	206	10	07	30	19
12 δ							24	170	—	—	—	—
13 γ									13	25	14	10
13 δ									—	—	—	—
14 γ									108	192	12	06
14 δ									89	172	—	—
15 γ											12	01
15 δ											—	—
16 γ											67	71
16 δ											52	72

Heating at both temperatures produced a homologous series of γ -lactones from each triacylglycerol, with the C_n lactone consistently being the most abundant. However, the only δ -lactones formed were those having a carbon number equal to that of the parent fatty acid. The amounts of the C_n γ - and δ -lactones appeared to decrease with increased fatty acid chain length.

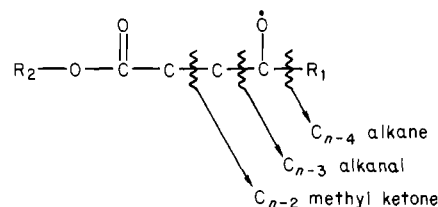
It is generally accepted that the principal mechanism in thermal oxidation of saturated fatty acids involves the formation of monohydroperoxides and that oxygen attack occurs at all the methylene groups of the fatty acid (Brodnitz et al., 1968; Crossley et al., 1962; Selke et al., 1975). The observation, made by many investigators, that the dominant oxidative products of saturated fatty acids are those with chain lengths near or equal to the parent fatty acids led to the conclusion that oxidation occurs preferentially at the α , β , and γ positions (Crossley et al., 1962; Endres et al., 1962; Jewell and Nawar, 1980).

Oxidative attack at the β -carbon of the fatty acid, for example, results in the formation of β -keto acids which produce the C_{n-1} methyl ketones upon decarboxylation. Cleavage between the α - and β -carbons of the alkoxy radical intermediate gives rise to the C_{n-2} alkanal while scission between the β - and γ -carbons produces C_{n-3} hydrocarbons:



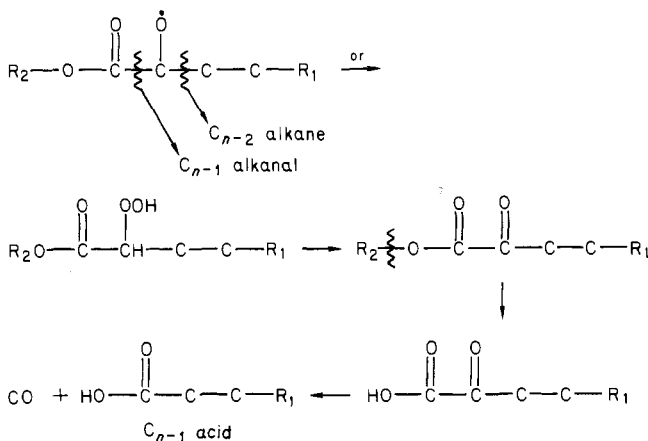
The quantitative data obtained in the present study showing relatively large amounts of C_{n-1} methyl ketone and small quantities of the C_{n-3} alkane and the C_{n-2} alkanal indicate that loss of CO_2 is more favored at higher temperatures than cleavages between the α - and β -carbons or the β - and γ -carbons. Loss of CO_2 occurring at higher heating temperature is also responsible for the larger quantities of C_{n-1} alkane produced at 250 °C than those at 180 °C.

Oxygen attack at the γ position would give rise to the C_{n-4} hydrocarbon, C_{n-3} alkanal, and C_{n-2} methyl ketone.



Results from this work showing C_{n-4} alkane as the most abundant hydrocarbon for C_{16} and C_{18} triacylglycerols heated at 180 °C indicate a preferential cleavage between carbons 3 and 4 at the lower temperatures. In addition, hydroperoxide formation at the γ position is believed to be responsible for the production of the C_n γ -lactones via cyclization of the resulting hydroxy acids.

Oxygen attack at α -carbons accounts for the production of the C_{n-1} fatty acid (via formation of the α -keto acid), the C_{n-1} alkanal, and the C_{n-2} hydrocarbon.



Further stepwise oxidations would give rise to a series of the lower acids which may themselves undergo oxidation, producing typical decomposition products of their own. This may explain the formation in small amounts of the shorter chain hydrocarbons, lactones, and carbonyl compounds. Although oxidation at δ positions is the only

logical route for the formation of the C_n δ -lactones, it is not clear why, in contrast to γ -lactones, the only δ -lactones observed were those of equal carbon numbers to the parent fatty acids.

In contrast to the above argument, preferential oxygen attack toward the center of the fatty acid chain was concluded by Brodnitz et al. (1968), who chemically cleaved the reduced esters of oxidized methyl palmitate and analyzed the resulting mono- and dibasic acids, and by Selke et al. (1975), who heated tristearin in a stainless steel "microroom" and analyzed the volatiles by gas chromatography. The apparent contradiction may be due to the different oxidative conditions and analytical techniques employed by different investigators. On the other hand, it should also be kept in mind that hydroperoxides decompose rapidly at elevated temperatures. Higher amounts of specific hydroperoxides collected after thermal oxidation may reflect their relative stability rather than their selective formation.

ACKNOWLEDGMENT

The authors thank Regina Whiteman and Francois

Gouin for their technical assistance.

LITERATURE CITED

- Brodnitz, M. H.; Nawar, W. W.; Fagerson, I. S. *Lipids* 1968, 3, 65.
 Crossley, A.; Heyes, T. D.; Hudson, J. F. *J. Am. Oil Chem. Soc.* 1962, 39, 9.
 Endres, J. G.; Bhalerao, V. R.; Kummerow, F. A. *J. Am. Oil Chem. Soc.* 1962, 39, 159.
 Jewell, N. E.; Nawar, W. W., submitted for publication in *J. Am. Oil Chem. Soc.*, 1980.
 Kleinau, H. J.; Neitzel, C. *Fette, Seifen, Anstrichm.* 1970, 72, 1025.
 Lien, Y. C.; Nawar, W. W. *J. Food Sci.* 1973, 39, 911.
 Nawar, W. W.; Champagne, J.; Dubravac, M.; LeTellier, R. *J. Agric. Food Chem.* 1969, 17, 645.
 Selke, E.; Rohwedder, W. K.; Dutton, H. J. *J. Am. Oil Chem. Soc.* 1975, 52, 232.
 Witchwood, A.; Nawar, W. W., University of Massachusetts, unpublished data, 1980.

Received for review April 17, 1980. Accepted August 11, 1980. The work was supported in part by University of Massachusetts Experiment Station Project No. 443 and a grant from the Army.

Isolation and Identification of Volatile Compounds from Baked Potatoes

Edward C. Coleman,¹ Chi-Tang Ho,* and Stephen S. Chang

The volatile flavor components were isolated from 540 lb of Idaho Russet Burbank baked potatoes. Extensive gas chromatographic analysis yielded 420 fractions. The odor of each chromatographic fraction was evaluated, and the fractions were identified by infrared and mass spectrometry. A total of 228 compounds was identified. The compounds identified in the volatiles of baked potatoes included hydrocarbons, acids, alcohols, aldehydes, esters, lactones, ethers, furans, halogenated hydrocarbons, ketones, pyrazines, oxazoles, thiazoles, and miscellaneous heterocycles. The most important compounds in baked potato flavor are the pyrazines, oxazoles, thiazoles, and a furanone.

The volatile flavor compounds isolated from baked potatoes have not been extensively studied because of the difficulty involved in obtaining an isolate from such a mild but characteristic flavor. Self and Rolley (1963) compared the total number of volatiles produced by baking with the total number of volatiles produced by boiling potatoes. They reported an increase in the amount of 2- and 3-methylbutanal during baking, which were thought to arise from the Strecker degradation of isoleucine and leucine, respectively.

Buttery et al. (1973) reported the identification of 45 compounds, mostly pyrazines and aliphatic aldehydes, as volatile flavor components of Washington Russet Burbank potatoes. The authors consider the following compounds to be the most important to baked potato aroma: 2-ethyl-3,6-dimethylpyrazine, methional, deca-*trans,trans*-2,4-dienal, and, possibly, 2-ethyl-3,5-dimethylpyrazine. These compounds have been previously identified by Deck et al. (1973) in potato chip aroma.

Pareles and Chang (1974) identified 16 compounds in the volatiles of baked potato. They have found that 2-isobutyl-3-methylpyrazine, 2,3-diethyl-5-methylpyrazine,

and 3,5-diethyl-2-methylpyrazine, taken as a mixture, have an odor close in character to baked potato aroma.

The present study is a systematic chemical analysis of the volatile flavor components isolated from a natural baked potato flavor.

EXPERIMENTAL SECTION

Isolation of the Volatile Compounds from Baked Potatoes. The potatoes used for this study were Idaho Russet Burbank potatoes purchased from a local supermarket.

The potatoes used for baking were freed from adhering soil particles by thorough washing and scrubbing. After potatoes were baked whole with skin wrapped with aluminum foil at 205 °C for 105 min, the volatile compounds were isolated by the apparatus previously described by Chang et al. (1977). Nitrogen gas was used to remove the volatile compounds from baked potatoes. The samples and nitrogen gas were kept at 65 °C during the isolation period. The true aroma of baked potatoes was collected from the head space of the food as it exists under normal conditions; the flavor was not isolated from a water slurry of baked potatoes. Since the concentration of the flavor components in the space above the food is extremely low and a genuine baked potato aroma is very mild, it became necessary to run 18 isolations of 30 lb each. Isolations were run for 48 h. A total of 540 lb of baked potatoes was used. The total volatile isolate collected in traps cooled with dry ice and

Department of Food Science, Cook College, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903.

¹Present address: Whitestone, NY 11357.