TABLE III

Effect of Increasing Amounts of Sorbitol on Stability of Lard

Sample	Peroxide values—AOM[a] conditions (6 hrs.) Levels of sorbitol used				PF[a] (0.05%)
	None	0.01%	0.05%	0.10%	
1	200	210	75	11	18
2	380	120	36	58	10
3	18	9.3	12	16	2
4	100	180	4.9	8.9	20

[a] See Table I for key.

of tocopherol increased the stability considerably, but only a small difference is observed between the tocopherol sample treated with sorbitol plus citric acid and the tocopherol sample treated with sorbitol alone.

It could be argued that sorbitol forms acidic materials when it is added to an oil during deodorization. Samples of methyl esters of cottonseed fatty acids were treated under deodorization conditions with 0.15% sorbitol, 0.1% citric acid, and with both 0.15% sorbitol and 0.005% citric acid added prior to or during deodorization, not on the downgrade. The acid values as compared to the acid value of the sample with no additive did not increase. Indeed it decreased (?) from 1.7 to 1.6 (calculated as oleic acid) for all treated samples. Since both citric acid and sorbitol samples gave slightly reduced acid values, it does not seem likely that an acid synergist is formed from sorbitol. Since sorbitol is comparatively neutral, it cannot act as an acid synergist.

Methyl esters rather than oil were used in these experiments for attempted concentration of any acidic product. Citric acid was normally added on the downgrade, and much of its acidity was retained. For example, in tests with 0.01% of added citric acid, 60 to 85% of the citric acid was retained in the oil as titratable acidity. In experiments with sorbitol and citric acid reported in Table I and Figures 2 and 3, citric acid was retained in the fat to act as a synergist or metal-inactivating agent.

Sorbitol might act in some unknown way to serve as a neutral synergist, form *in situ* an acidic synergist or a new antioxidant. If it does not, the antioxidant properties of citric acid must be attributed to its inactivating capacity for metals. Further work on the effect of sorbitol and its mode of action is beyond the present scope of our investigations.

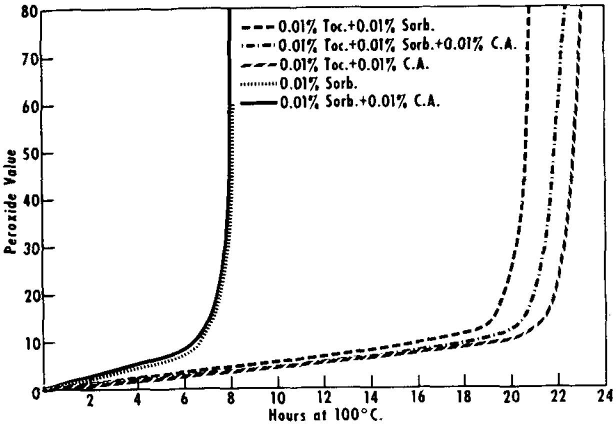

FIG. 3. Stabilizing effect of 0.01% sorbitol (Sorb.) and 0.01% sorbitol plus 0.01% citric acid (C.A.) in lard and in lard containing 0.01% added α-tocopherol (Toc.) oxidized at 100°C. under Active Oxygen Method conditions.

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The Effect of Heat on Pure Triglycerides

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A knowledge of the mechanism of the degradation of triglycerides at temperatures from 190°C. is important in predicting the type of breakdown products likely to be formed in processing oils at elevated temperatures, or in the usage of oils and fats in frying or baking.

The effect of heat on tricaprin and 2-oleo-dipalmitin has been studied both in the absence and in the presence of oxygen. The results show that even a pure fully saturated triglyceride is rendered organoleptically unacceptable, due to breakdown in the temperature range studied, although the mechanism differs according to whether oxygen is present or not. Unsaturated glycerides are more readily degraded, fission at or near the double bonds being superimposed on the processes previously established for saturated triglycerides. Many of the degradation products have been identified.

Degraded triglycerides can be refined to an acceptable standard by conventional means but their keeping times, in the refined state, are considerably less than those of the original pure materials. Hence, it is inferred that precursors of off-flavors persist in the products and survive the refining operations.

EXPERIENCE in handling oils and fats for culinary use has shown that it is difficult to maintain a bland flavor when they are used for long periods. Much is known of the general means by which fatty materials are oxidized or otherwise decomposed in the course of heating during frying or baking conditions, but hitherto such studies have been confined to natural oils and fats, or to blends of such materials. Even if highly sophisticated techniques are used in isolating degradation products to elucidate the mechanism of degradation, such products must be so numerous that interpretation of the mechanism of degradation will be difficult. For this reason, in the present study, use has been made of two pure synthetic triglycerides.

TABLE I

Effect of Heat on Tricaprin

Conditions of heating	Time (hr.)	F.F.A. %	Flavor etc.	Effect of refining	Major Products	
					Volatile	Nonvolatile
Nitrogen atmosphere 240–260°C.	4½	......	Harsh, unacceptable	......	Capric acid (only acid)	......
	15½	0.12	Paint-like, burnt	Acceptable products	Traces of neutral products	
	35	0.22				
Nitrogen atmosphere 300°C.	1	1.2	Strong, paint-like, unacceptable	......	Capric acid (only acid) Di-nonyl ketone	No polymers (Hügel test) (14)
	10	8.8	Very strong, choking Dark brown	Still unpleasant	Traces of lower symmetrical ketones Acrolein. Methyl vinyl ketone (?)	
Slow stream of dry air at 190°C.	½	....	Strong, burnt, unacceptable	......	Water	No polymers Keto-glyceride residue
	3	2.5	......	......	Valeric, caproic, heptanoic, caprylic, nonanoic, and capric acids, with traces of lower acids	
	30	4.0	......	Almost tasteless but deteriorates to unacceptable standard after 1 week. Addition of 0.2% BHA prolongs keeping time slightly	Methyl heptyl ketone, with smaller amounts of methyl octyl and hexyl ketones, diamyl ketone and n-decanal	

To ascertain whether a pure, fully saturated triglyceride breaks down under the conditions encountered in cooking, a study was made of the effect of heat on tricaprin. This triglyceride was selected because its low melting point (31.1°C.) makes organoleptic assessment possible, and at the same time its molecular weight approaches those of the triglycerides important in practice. The second pure triglyceride studied was 2-oleo-dipalmitin, synthesized by the method of Chapman, Crossley, and Davies (1). This compound (m.p. 36.5°C.) is typical of the triglycerides present in various vegetable oils and, being unsaturated, may be expected to decompose, at least in part, in a different manner from tricaprin.

The literature on the thermal oxidation and decomposition of fats lies mainly in the fields of pyrolysis of fatty acids and esters and in the "heat-bodying" of drying oils. Krafft (2) showed that olefins and fatty acids could be obtained by the pyrolysis of esters, and Ralston (3) records the production of symmetrical ketones and hydrocarbons from fatty acids. It is well recognized that the gross pyrolysis of fats commences at about 300°C. with the production of fatty acids and acrolein. At higher temperatures (400 to 500°C.) "cracking" occurs, producing short chain hydrocarbons as the main products (4). Dependent on the degree of unsaturation and the temperature, polymerization will also occur, both in the presence and in the absence of oxygen.

Experimental

The pure glycerides were heated, either in a slow stream of oxygen-free nitrogen, *in vacuo,* or in a slow stream of air, with stirring, the reaction flask being heated by means of an external bath. Volatile decomposition products passed through a vertical condenser and were returned to the heated oil, except for the most volatile material, which was condensed in a cold trap after escape through the water condenser.

At the end of the heating period the following procedures were found most satisfactory. The volatile decomposition products were removed from the oil either by conventional deodorization or by a degassing technique (5). The volatile products thus obtained were separated into acidic and neutral components.

The neutral volatile materials were separated from the mixture by adding degassed medicinal paraffin and solid sodium carbonate to the contents of the degassing flask. The acidic components were thus converted to the sodium salts and the neutral components were removed by degassing into a capillary tube. The sodium salts of the acidic components were then washed out of the paraffin and the acids regenerated and analyzed by gas/liquid chromatography (GLC) as the methyl esters by conventional means (Fig. 1).

The capillary tube containing neutral volatiles was broken on a GLC column and an analytical trace obtained (Fig. 2). Carbonyl components were identified by comparing their retention volumes on the GLC column with those of model compounds, and confirmations were obtained by chromatographic comparisons of their 2:4 dinitrophenyl hydrazones (DNPH's) with those of the same standard compounds. These derivatives were prepared by standard methods and separated either on a silica/nitromethane column (6) or on paper (7). In examining mixed carbonyl compounds, aldehydes were distinguished from ketones by oxidation of the former to acids with silver oxide. Identities were established for a number of products (Tables III, IV, and V).

In addition to the volatile products, some investigations were made into the nature of nonvolatile carbonyl compounds produced. After refining and

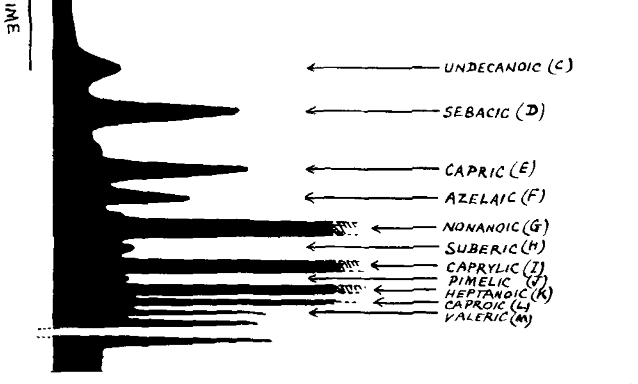


FIG. 1. GLC chromatogram of fatty acids (as methyl esters) from the degassate resulting from heating 2-oleo-dipalmitin in air at 190°C. (Column: apiezon/celite, temperature: 160°C.)

TABLE II

Effect of Heat on 2-Oleo-Dipalmitin

Conditions of heating	Time (hr.)	F.F.A. %	I.V.	Flavor etc.	Effect of refining	Major products
Slow stream of nitrogen at 190°C.	3	....	30.5	Paint-like Unacceptable	....	Volatile Oleic/palmitic acids (1:2) (no isomerization)
	10	....	30.5	Strong, burnt	....	
	20	1.6	30.5			
Vacuum, 250°C.	10	0.13	30.5	Paint-like, strong	....	Volatile Acids, acrolein
Slow stream of dry air at 190°C.	Start	nil	30.5	Bland, colorless	After refining, an oil of good quality was obtained but this reverted after 6 days, whether or not autoxidant (0.02% BHA) was present. 2-Oleo-dipalmitin will keep for 4 weeks.	Volatile Nonanoic, caprylic and heptanoic acids (large), capric, caproic, and sebacic acids (moderate), other dibasic (C_7 to C_{11}) and monobasic (C_5 to C_{12}) acids in traces. C_9 to C_{10} unsaturated ketones (large). Methyl n-octyl and n-heptyl ketones (moderate). Other C_8 to C_{11} ketones (small). n-Nonanal (small). Nonvolatile Acid compositions of the glycerides change from oleic/palmitic (1:2) to (1:4).
	½	....	30.4	Very strong, paint-like		
	5	2.3	26.7	Burnt Unacceptable, pale yellow		
	15	5.5	22.9	Unacceptable, deep yellow		
	20	8.3	22.1	Unacceptable, orange		

deodorization, heated fat samples were hydrolyzed and the fatty acids converted to methyl esters. These were submitted to GLC analysis and it was found that, in addition to the expected caprate palmitate and oleate, other components were present in minor amounts. These were separated on a preparative scale from the GLC column and were found to form DNPH's, which exhibited UV absorption maxima at 363 and 376 mμ, indicative of methyl keto-esters. Examination of the DNPH's by paper chromatography showed that they were complex mixtures and their complete identification was not undertaken. Indications from R_f. values however, were that they were derived from the original glycerides by oxidative attack at carbon atoms beyond the alpha- and beta-positions.

Effect of Heat on Tricaprin

Tricaprin was heated under four sets of conditions, as outlined in Table I. At 240–260°C. in a nitrogen atmosphere, the oil is relatively stable. After 4½ hr. the taste of the oil had become unacceptable, but it was possible to restore the originally bland taste by conventional refining processes, i.e., by neutralization and deodorization. The only decomposition product detected in significant quantity was capric acid.

Under similar conditions, but at 300°C., decomposition is much more drastic. Larger quantities of free fatty acid are produced and an unpleasant oil results which cannot be refined to a bland fat. Again capric acid is the major decomposition product, and is the only acid formed. In addition, various neutral products were detected, particularly di-n-nonyl ketone, amounting to 0.15% of the original tricaprin.

TABLE III

Volatile Acids Produced During the Heating of 2-Oleo-Dipalmitin at 190°C. in the Presence of Air (see also Fig. 1)

GLC peak number	Chain length	Relative quantity	Identity of acid
A.	C_{12}	Trace	Lauric
B.	C_{11} dibasic	Small	Nonane dicarboxylic
C.	C_{11}	Small	Undecanoic
D.	C_{10} dibasic	Moderate	Sebacic
E.	C_{10}	Moderate	Capric
F.	C_9 dibasic	Small	Azelaic
G.	C_9	Large	Nonanoic
H.	C_8 dibasic	Trace	Suberic
I.	C_8	Large	Caprylic
J.	C_7 dibasic	Trace	Pimelic
K.	C_7	Large	Heptanoic
L.	C_6	Moderate	Caproic
M.	C_5	Small	Valeric

(Compounds identified as dibasic acids may be in part unsaturated.)

Though quantitatively of less importance, the symmetrical ketones di-n-butyl, di-n-amyl, and di-n-hexyl ketones were also formed. An important and very volatile component was found to be acrolein, possibly contaminated with methyl vinyl ketone.

In a further experiment, tricaprin was heated in vacuo at 250°C. The course of decomposition was similar to that observed in a nitrogen atmosphere with capric acid and acrolein being readily detected. The harsh paint-like taste that developed could be reproduced by mixing capric acid (0.2%) and acrolein (0.002%) in Nujol solution.

For heating in air, a lower temperature, 190°C., was chosen. Under these conditions the oil acquired a strong burnt taste after half an hour and was organoleptically unacceptable. Heating was continued up to 30 hr., during which time water was produced, and the product analyzed as before. In addition to capric acid, nonanoic, caprylic, heptanoic, caproic, valeric acids, and traces of lower acids were formed. The neutral products were dominated by methyl n-heptyl ketone, though smaller quantities of methyl n-octyl, methyl n-hexyl, di-n-amyl ketones, and a trace of n-decanal were also present.

The oil obtained under these conditions of oxidative degradation could be refined to a fairly satisfactory product, but in this form it deteriorated to an unacceptable grade after one week; this keeping period could be extended by the addition of 0.2% BHA. However, even this extended keeping period was inferior to that of the original tricaprin, which remained bland for six weeks under similar conditions. It was of interest, therefore, that examination of the nonvolatile oxidation products indicated the presence of keto-glycerides, which could possibly act as off-flavor precursors.

TABLE IV

Nonvolatile Acids Produced During the Heating of 2-Oleo-Dipalmitin at 190°C. in the Presence of Air

GLC peak number	Chain length	Relative quantity	Identity of acid
A.	C_{18} unsat.	Large	Oleic
B.	C_{16}	Very large	Palmitic
C[a].	C_{15} ?	Moderate	?
D[a].	C_{13} ?	Small	?
E.	C_{12}	Moderate	Lauric
F.	C_{11}	Small	Undecanoic
G.	C_{10}	Trace	Capric
H.	C_9	Small	Nonanoic
I.	C_8	Small	Caprylic
J.	C_7	Trace	Heptanoic

[a] Possibly hydroxy acids or lactones as some OH was detected in the combined product by infrared spectroscopy.

TABLE V

Carbonyl Compounds Produced by Heating 2-Oleo-Dipalmitin in Air at 190°C. (see also Fig. 2)

GLC peak	Compound type	Relative quantity	Identification
A	C_{11}+ (?)	Small	....
B	C_{11} (ketone)	Small	....
C	C_{10} (unsat. ketone)	Large	See note 1.
D	C_{10} (ketone)	Moderate	Methyl n-octyl ketone (R_f of DNPH = 0.44, UV maximum = 365 mμ)
E	C_9 (unsat. aldehyde)	Small	Non-2-en-1-al (R_f of DNPH = 0.62, UV maximum = 375 mμ)
F	C_9 (unsat. ketone)	Large	See note 2.
G	C_9 (aldehyde)	Small	Nonan-1-al (R_f of DNPH = 0.60, UV maximum = 358 mμ)
H	C_9 (ketone)	Moderate	Methyl n-heptyl ketone (R_f of DNPH = 0.55, UV maximum = 365 mμ)
I	C_9 (ketone)	Small	Di-n-butyl ketone (R_f of DNPH = 0.46, UV maximnm = 365 mμ)
J	C_8 (ketone)	Small	....
K	C_9 (ketone)	Moderate	....
L	C_8 (ketone)	Moderate	....
M	C_8 (ketone)	Small	Methyl n-hexyl ketone (R_f of DNPH = 0.58, UV maximum = 365 mμ)
N	C_7 (ketone)	Small	....
O	C_7 (ketone)	Small	Methyl n-amyl ketone
P	C_7 (aldehyde)	Trace	....
Q	C_6 (aldehyde)	Moderate	....
R	C_5 (ketone)	Small	....

NOTE 1—Peak C (R_f of DNPH = 0.42, UV maximum = 375 mμ) is very closely related to, but not identical with, n-heptylidene acetone (0.46 and 376 mμ, respectively).

NOTE 2—Peak F is similarly related to, but not identical with, n-hexylidene acetone.

Effect of Heat on 2-Oleo-dipalmitin

2-Oleo-dipalmitin was heated under three sets of conditions, as outlined in Table II. In an inert atmosphere, this triglyceride decomposed at a lower temperature than tricaprin. Heat in a nitrogen atmosphere at 190°C. and *in vacuo* at 250°C. readily gave rise to the development of an objectionable flavor, with the formation of free oleic and palmitic acids in the same ratio (1:2) as these are present in the pure glyceride. The oleic acid formed contained no *trans*-isomers, judging from infrared spectroscopic analysis. The temperatures involved were not high enough to form long-chain ketones (cf. the formation of di-n-nonyl ketone from tricaprin at 300°C.), though acrolein was detected.

The effect of heat in the presence of oxygen proved to be very complex. Oxidative degradation occurred, but it was evident since the oleic:palmitic acid ratio in the residual nonvolatile glycerides after heating had changed from 1:2 to 1:4 that oleic acid had been preferentially oxidized. Swern *et al.* reached a similar conclusion in the course of their studies on methyl oleate (8). The volatile fatty acids (see Table III and Fig. 1) were isolated by the degassing procedure and proved to consist of both mono- and dicarboxylic acids with up to 12 carbon atoms. The nonvolatile fatty acids (Table IV) were primarily those of longer chain-length. Evidently the acids arise both by oxidative degradation of palmitic acid and by scission of oleic acid.

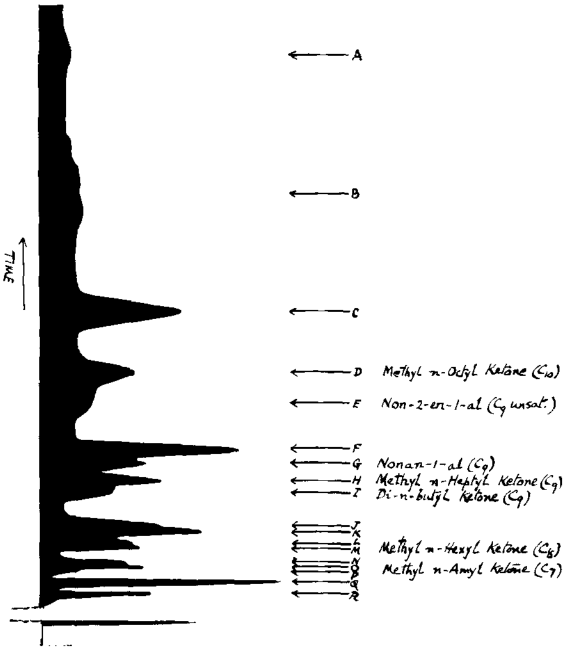


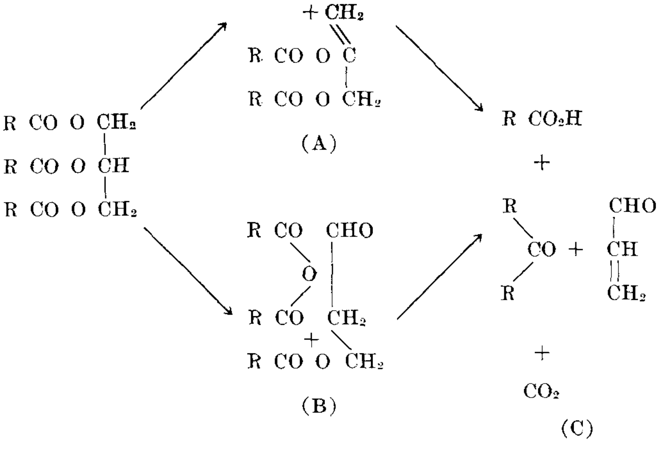
FIG. 2. GLC chromatogram of carbonyl fraction from the degassate resulting from heating 2-oleo-dipalmitin at 190°C., 20 hr. (Column: apiezon/celite, temperature: 119°C.)

The neutral part of the degassate presented a very complex picture (see Table V and Fig. 2). The oxidation with silver oxide identified certain components as aldehydes, the unaffected ones being ketones. The individual components were isolated from the GLC column and converted to DNPH's, which were then examined by paper chromatography and by ultraviolet spectrophotometry. By comparison with model compounds, identities could be firmly established in a number of cases. The two major components C and F, which were unsaturated ketones, were not positively identified.

After removal of the volatile products and the residual nonvolatile free fatty acids the remaining oil gave DNPH's. The latter were complex in type, giving streaks when submitted to reverse-phase paper chromatography. They indicated the presence in the oil of mixed keto-glycerides.

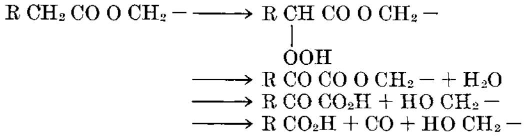
Discussion of Degradation Mechanisms

Evidence indicates that triglycerides decompose at high temperatures in different ways, according to the presence or absence of oxygen. In the absence of air even a fully saturated triglyceride has only limited stability, and the first important degradation product that appears is the component fatty acid (at 240–260°C.). This suggests that the first stage is one of the two alternative initial steps in the reaction sequence:



The breakdown products (A) and (B) represent possible intermediate stages and (C) the final products. The early appearance of saturated acids is accounted for by (A), but (B) accounts for acrolein appearing before the ketone, and this can most easily be envisaged as a breakdown of the aldehydo-ester with the simultaneous formation of fatty acid. However, the final products (C) are not in doubt, though the last stages of the degradation, in particular the formation of ketone, probably only take place at temperatures little below 300°C.

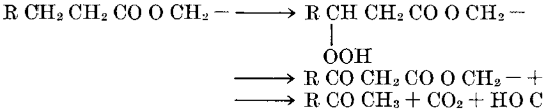
In the presence of oxygen, oxidative types of degradation ensue at lower temperatures and even at 190°C. the breakdown is complex. Judged from the products isolated from tricaprin, these arise from the initial formation of hydroperoxides. If the α-carbon atom of the acid radical is first attacked, and from the products formed this seems to be the dominant reaction, the sequence seems likely to be:



$$\begin{aligned} & R\,CH_2\,CO\,O\,CH_2 - \longrightarrow R\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,CO\,O\,CH_2 - \\ & \longrightarrow R\,CO\,CO\,O\,CH_2 - + H_2O \\ & \longrightarrow R\,CO\,CO_2H + HO\,CH_2 - \\ & \longrightarrow R\,CO_2H + CO + HO\,CH_2 - \end{aligned}$$

The thermal decomposition of α-keto acids in the manner shown in the last stage has been described by Claisen (9), and accounts for the formation of nonanoic acid from tricaprin, and hence, by similar further stepwise α-oxidations, for the formation from nonanoic acid of the series of lower acids. This form of attack is probably more effective with free fatty acids than with glycerides (10).

The consequence of oxidative attack at the β-carbon atom of the acid radical can be seen to be the formation of methyl ketones:



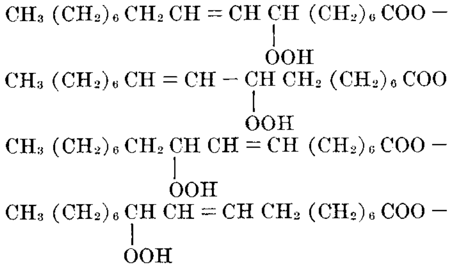
$$\begin{aligned} & R\,CH_2\,CH_2\,CO\,O\,CH_2 - \longrightarrow R\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,CH_2\,CO\,O\,CH_2 - \\ & \longrightarrow R\,CO\,CH_2\,CO\,O\,CH_2 - + H_2O \\ & \longrightarrow R\,CO\,CH_3 + CO_2 + HO\,CH_2 - \end{aligned}$$

This mechanism is strongly supported by the formation of methyl n-heptyl ketone as the principal neutral breakdown product of tricaprin. The formation of the lower homologues, methyl hexyl ketone and so on, can be explained by β-oxidation of nonanoic acid and its lower homologues. Again, attack will take place both on glycerides and free acids, but principally on the latter.

In addition to α- and β-oxidation it is likely that progressively diminishing oxidative attacks occur further along the chain. The thermostable carbonyl compounds so formed are probably not split off from the glyceride molecule, and hence they are detectable as nonvolatile oxidation products. They are probably precursors of the volatile off-flavors which are generated on prolonged storage of refined fats containing such keto-glycerides. The absence of dibasic acids as oxidation products from saturated triglycerides such as tricaprin, shows that scission of saturated carbon chains does not occur in the positions adjacent to the carboxyl.

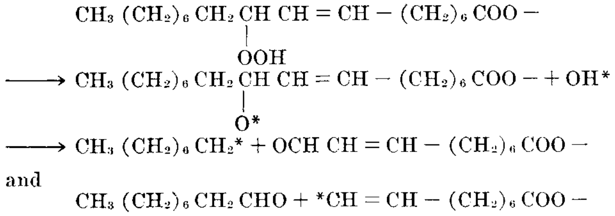
Consideration of the volatile products obtained by heating 2-oleo-dipalmitin at 190°C. in air shows that when double bands are present in the molecule, oxidation takes place in the vicinity of such bonds in preference to attack in the proximity of the carbonyl function. This is confirmed by the progressive fall in the proportion of oleic acid radicals relative to palmitic radicals in the residual glyceride molecules. Scission of the oleic acid radical is established by the presence of dibasic acids in the volatile reaction products.

According to Farmer *et al.* (11) the oleic acid radical at lower temperatures forms principally four primary autoxidation products:



$$\begin{aligned} & CH_3\,(CH_2)_6\,CH_2\,CH = CH\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,(CH_2)_6\,COO - \\ & CH_3\,(CH_2)_6\,CH = CH - \underset{\displaystyle OOH}{\underset{|}{CH}}\,CH_2\,(CH_2)_6\,COO - \\ & CH_3\,(CH_2)_6\,CH_2\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,CH = CH\,(CH_2)_6\,COO - \\ & CH_3\,(CH_2)_6\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,CH = CH\,CH_2\,(CH_2)_6\,COO - \end{aligned}$$

It seems likely that such materials are also the primary oxidation products of the high temperature reaction. This type of hydroperoxide is believed to decompose according to the free radical mechanism, which is here illustrated for the third of the above hydroperoxides:



$$\begin{aligned} & CH_3\,(CH_2)_6\,CH_2\,\underset{\displaystyle OOH}{\underset{|}{CH}}\,CH = CH - (CH_2)_6\,COO - \\ \longrightarrow\ & CH_3\,(CH_2)_6\,CH_2\,\underset{\displaystyle O^*}{\underset{|}{CH}}\,CH = CH - (CH_2)_6\,COO - + OH^* \\ \longrightarrow\ & CH_3\,(CH_2)_6\,CH_2^* + OCH\,CH = CH - (CH_2)_6\,COO - \\ \text{and}\ & \\ & CH_3\,(CH_2)_6\,CH_2\,CHO + {}^*CH = CH - (CH_2)_6\,COO - \end{aligned}$$

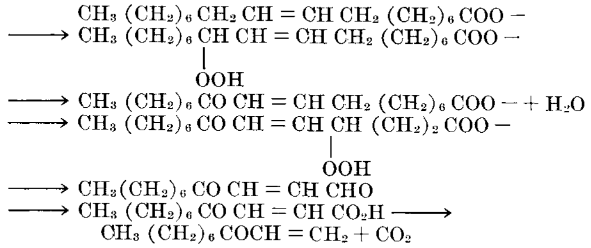
Such free radicals interact with more oxygen, form hydroperoxides by the chain propagation mechanism, and eventually yield lower aldehydes:

$$\begin{aligned} CH_3\,(CH_2)_6\,CH_2^* & \longrightarrow CH_3\,(CH_2)_6\,CH_2\,OO^* \\ & \longrightarrow CH_3\,(CH_2)_6\,CH_2\,OOH \\ & \longrightarrow CH_3\,(CH_2)_6\,CHO + H_2O \\ \text{or}\ \ & CH_3\,(CH_2)_6\,CH_2O^* \longrightarrow \\ & \quad CH_3\,(CH_2)_5\,CH_2^* + HCHO \end{aligned}$$

Assuming this mechanism, it is possible to account for the mono- and dibasic acids, produced from aldehydes in the oxidation of 2-oleo-dipalmitin, listed in Table III and traced in Fig. 1. Theoretically some of these acids will be unsaturated as well as saturated but under the conditions of running the GLC column, it would not be possible to detect unsaturation.

In the oxidation of 2-oleo-dipalmitin the acids are much more important quantitatively than the carbonyl compounds (Table IV, Fig. 2), but the formation of the latter must nevertheless be explained on theoretical grounds. The carbonyl compounds, almost exclusively ketones, whose occurrence as scission products has not hitherto been reported, are evidently produced by a secondary oxidative mechanism. As C_{17} unsaturated or C_{15} saturated ketones do not occur it is evident that those formed are by oxidative scission in the neighborhood of the double bond which is a preferred reaction to the α- or β-oxidations observed with tricaprin. The production of ketones by oxidative scission has received little attention, and hence a speculative mechanism is put forward here to account for their formation.

In general the literature is confined to studies of oxidation at lower temperatures, cf. Swift *et al.* (12) and Ellis (13), when α:β-unsaturated carbonyl compounds or aldehydes are formed. At higher temperatures it seems reasonable to suppose that the former will be further oxidized, then suffer scission, and that finally unsaturated ketones will result:



$$\begin{aligned} & CH_3(CH_2)_6CH_2CH = CHCH_2(CH_2)_6COO- \\ \longrightarrow\ & CH_3(CH_2)_6\underset{\substack{|\\ OOH}}{CH}CH = CHCH_2(CH_2)_6COO- \\ \longrightarrow\ & CH_3(CH_2)_6COCH = CHCH_2(CH_2)_6COO- + H_2O \\ \longrightarrow\ & CH_3(CH_2)_6COCH = CH\underset{\substack{|\\ OOH}}{CH}(CH_2)_2COO- \\ \longrightarrow\ & CH_3(CH_2)_6COCH = CHCHO \\ \longrightarrow\ & CH_3(CH_2)_6COCH = CHCO_2H \longrightarrow \\ & \quad CH_3(CH_2)_6COCH = CH_2 + CO_2 \end{aligned}$$

This last compound is suspected to represent Peak C (Fig. 2) but this has not yet been checked against an authentic sample. Its elution time is very close to, but not identical with, that of the isomeric heptylidene acetone,

$$CH_3(CH_2)_5 - CH = CH\,COCH_3.$$

The other major "unknown" peak, F, could be the lower homologue, vinyl hexyl ketone,

$$CH_3(CH_2)_5\,CO\,CH = CH_2,$$

produced via a double bond shift in the oxidizing oleic radical.

Finally, the production of the quantitatively less important, but positively identified, methyl ketones could be accounted for by the oxidation of the vinyl ketones by some such mechanism as the following:

$$\begin{aligned} & COCH = CH_2 \xrightarrow{O_2} -COCH^* - CH_2OO^* \\ \longrightarrow\ & -COCH^* - CHO + OH^* \xrightarrow{RH} -COCH_2CHO + R^* \\ \xrightarrow{O}\ & -COCH_2CO_2H \longrightarrow -COCH_3 + CO_2 \end{aligned}$$

In this way vinyl hexyl and vinyl heptyl ketones would give rise to methyl hexyl and methyl heptyl ketones, respectively, both of which are positively identified in the neutral reaction products. When the initial formation of a carbonyl group occurs on the side of the oleic double bond nearer to the glycerol residue this mechanism implies the formation of thermostable keto glycerides, which are also found in practice.

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Selectivity and Isomerization During Partial Hydrogenation of Cottonseed Oil and Methyl Oleate: Effect of Operating Variables

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Results are now available for hydrogenation of cottonseed oil and methyl oleate in which sufficient agitation was provided to eliminate mass transfer resistances from the catalyst surface. The ratio of the *trans*-to-*cis* isomers of oleic acid groups approaches 2.0 even at high pressures and high degrees of agitation. The rates of hydrogenation for both *cis* and *trans* isomers and for positional isomers are all essentially identical. A reaction scheme has been devised that is consistent with extensive experimental data, and the method of evaluating the relative reaction rate constants for each step is outlined. Using these rates constants, selectivity can be quantitatively evaluated.

HYDROGENATION of vegetable oils and animal fats (which are predominantly triglycerides) involves several consecutive and simultaneous reactions. Changes of the operating variables often affect the rates of the individual reactions and hence the overall course of the reaction. Selectivity of hydrogenation as defined here refers to the preferential hydrogenation of the polyunsaturated acid groups, such as linolenic or linoleic acid groups, relative to monounsaturated acid groups, such as oleic acid groups. Two types of isomerization also always occur during hydrogenation. *Cis-trans* geometrical isomerization of the carbon-carbon double bonds has a significant effect on the softening point and consistency of the fats. Positional isomerization also occurs as the double bonds migrate along the fatty acid chain (2,3,7,8), but presumably this isomerization does not have too much effect on the physical properties unless perhaps when the double bonds migrate close to the ends of the fatty acid chains.

Operating variables which affect the selectivity of the hydrogenation also affect both the *cis-trans* and positional isomerization (6). Those operating variables which increase the concentration of hydrogen at the catalyst surface decrease selectivity and both types of isomerization (9). Mass transfer of the reactants and products to and from the surface is obviously of importance, and changes in the degree of agitation will affect the resistances to mass transfer. The true effect of the operating variables, such as temperature, pressure, and catalyst concentration, on the reactions occurring on the catalyst surface can only be evaluated when mass transfer resistances are eliminated. Only three investigations (1,9,13) are known in which these resistances were eliminated, and the results of these studies should be especially important for evaluating the effect of operating variables on the rates of the various reactions that occur during hydrogenation.

Several reaction schemes have been proposed previously, and reaction rate constants were evaluated for the various reactions (6,9,11,12). All of the re-

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