Chemical Reactions Involved in the Catalytic Hydrogenation of Oils. III. Further Identification of Volatile By-Products[1, 2, 3]

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Abstract

Two distinct types of hydrogenation flavor may originate from catalytic hydrogenation of fats and oils. One is the characteristic flavor developed during hydrogenation. After it is removed by deodorization, the second type of hydrogenation flavor may develop during the storage of the bland deodorized hydrogenated fat.

The precursors of the characteristic flavor developed during catalytic hydrogenation were demonstrated as the hydroperoxides of the unsaturated fatty esters. A total of 37 compounds was chemically identified by the combination of infrared and mass spectrometry as the major components of the volatile by-products developed during catalytic hydrogenation of soybean oil with nickel as catalyst. Out of the 37 compounds, 14 were hydrocarbons, eight were alcohols, one was an ester, four were aldehydes, eight were ketones, and two were lactones. The seven largest peaks of the gas chromatogram of the volatile by-products were all alcohols and hydrocarbons. It was concluded that the characteristic flavor developed during catalytic hydrogenation appears to be due to the higher members of the aldehydes, ketones, and alcohols and the lactones.

Introduction

THE UNDESIRABLE FLAVORS originating from catalytic hydrogenation may be divided into two distinct types. One is the characteristic flavor developed during the catalytic hydrogenation of an oil. After the removal of this flavor by deodorization, the second type of hydrogenation flavor may develop during the storage of the bland deodorized hydrogenated fat. The first type of the hydrogenation flavor was isolated by Chang et al. (1) by vacuum steam distillation of a slightly autoxidized soybean oil hydrogenated to an iodine value of 71. Silveira, Masuda, and Chang (2) identified the ten major components of this isolated flavor as four hydrocarbons, three alcohols, two aldehydes, and one ketone. The second type of hydrogenation flavor was isolated by Keppler et al. (3) by autoxidizing a deodorized hydrogenated linseed oil and then isolating the volatile flavor compounds produced by stripping the oil under vacuum with a current of nitrogen. They concluded that 6-*cis*-nonenal and 6-*trans*-nonenal, and particularly the latter, are primarily responsible for the hydrogenation flavor developed in bland deodorized hydrogenated oils through autoxidation.

The present paper is an attempt both to determine the precursors of the volatile flavor compounds developed during catalytic hydrogenation and to systematically characterize these compounds.

Experimental

Oil Used for Hydrogenation

The oil used for this experiment was a commercially refined and bleached soybean oil with an iodine value of 131. It had a peroxide number of 10.5 meq/kg, which was developed during processing and during the storage in an oil tank in the plant. This type of oil therefore is sometimes used in industry for catalytic hydrogenation. It should be mentioned that most of the oils used for commerical hydrogenation in this country have peroxide value below 5, usually between 0.5–2.0 meq/kg.

Catalytic Hydrogenation of Soybean Oil

The procedures used were the same as reported previously (1).

Isolation of Volatile By-Products Developed During Hydrogenation

The semicontinuous counter current vacuum steam distillation method of Chang (4) was used. The hydrogenated oil was deodorized at 120C under a vacuum of 0.05 mm Hg with 3% of water. The isolated volatile by-products were separated into acidic and nonacidic compounds by dissolving them in ethyl ether and then extracting with 10% aqueous sodium carbonate solution.

Gas Chromatography

The ethyl ether solution of the volatile nonacidic by-products was fractionated with a Wilkens Model A-90-P gas chromatograph. The temperature was nonlinearly programmed from 55–200C in 45 min. An 8 ft aluminum column, ¼ in. I.D. packed with 15% Ucon Polar 50 HB 280 X on 80/100 mesh Chromosorb W, was used at a helium flow rate of 80 ml/min.

For rechromatography, an 8 ft aluminum column, ¼ in. I.D. packed with 20% of methyl silicone gum SE-30 on 70/80 mesh Anakrom ABS was used. Each fraction was rechromatographed isothermally at a temperature most suitable for that fraction, which varied between 60–180C.

The isolated volatile acidic by-products were converted into their methyl esters with the use of diazomethane (6) and then gas chromatographed with DEGS as stationary phase.

Identification of Gas Chromatographic Fractions

The nonacidic compounds of the isolated volatile by-products developed during hydrogenation were gas chromatographed with Ucon Polar as stationary phase. The eluent represented by each of the gas chromatographic peaks was collected with an espe-

[1] This investigation was supported in whole by Public Health Service Research Grant HE-06411, from the National Heart Institute.
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cially built fraction collector (5). The chromatography was repeated 26 times. Each peak material was accumulatively collected in one cold trap. The gas chromatographic fractions thus collected were then rechromatographed with methyl silicone gum SE-30 as stationary phase. Each of the rechromatographed fractions was again collected and its infrared spectrum determined with a Beckman IR-8 infrared spectrophotometer fitted with a beam condenser. A cavity cell of 0.1 mm path length was used to contain the carbon tetrachloride solution of the sample. An attenuated grid and a variable path wedge cell were used in the reference beam to compensate for the absorption due to solvent.

When infrared spectrum alone was insufficient for the chemical characterization of a gas chromatographic fraction, its mass spectrum was then determined. The carbon tetrachloride solution used for the infrared spectrum determination was gas chromatographed with methyl silicone gum SE-30 as stationary phase to remove the solvent. The pure gas chromatographic fraction was collected in a melting point capillary tubing, 1.0 mm I.D. and 100 mm in length. After both ends of the capillary tubing were sealed, the tubing was inserted into the heated inlet of a Consolidated Electrodynamics Corporation Model 21-103C mass spectrophotometer. The inlet tube was then evacuated to 10^{-4} torr and the capillary tubing broken by a steel bar inside the spectrophotometer to release the sample. The bar was lifted and dropped onto the sample tubing by manipulating a magnet from outside.

The chemical structure postulated for a gas chromatographic fraction by the interpretation of its infrared and mass spectra was confirmed by comparing its retention times on two different stationary phases with those of authentic compounds.

Catalytic Hydrogenation of n-Nonanal and 2-Pentanone

A refined, bleached, and deodorized cottonseed oil was redeodorized in the laboratory at 185C under 0.03 mm Hg for 3 hr with 2% by weight of water. One portion of this oil, 1 kg, was immediately hydrogenated for 30 min under the same conditions as those used for the hydrogenation of soybean oil (1). The volatile by-products thus produced were isolated by distillation at 150C under 0.03 mm Hg for 3 hr with 2% water. The distillate collected in traps cooled with solid carbon dioxide was extracted with ethyl ether. The ether extract was concentrated and gas chromatographed. The gas chromatogram thus obtained was used as the control.

To two other portions of this oil, 500 g each, was added 1 g of n-nonanal and 2-pentanone, respectively. The carbonyl compounds were purified by gas chromatography before they were used. Both oils were then hydrogenated and the volatile compounds isolated and gas chromatographed in the same manner as the cottonseed oil with no carbonyl compound added. The gas chromatographic peaks, which were, respectively, the hydrogenation products of n-nonanal and 2-pentanone, were chemically identified and then analyzed quantitatively.

Results and Discussion

The present results indicate that the precursors of the volatile by-products developed during catalytic hydrogenation are hydroperoxides of unsaturated fatty esters. One portion of the commercially refined and bleached soybean oil, 5 gal, was twice deodorized by a semicontinuous countercurrent vacuum steam distillation process (4) in order to remove all the volatile components present in the crude oil. Since during this continuous deodorization process, the oil was only heated to 110C for 6 min, the deodorized oil was free from volatile compounds but still had a peroxide number of 10.5 meq/kg. The deodorized oil was then hydrogenated to an iodine value of 70. The hydrogenated oil had a strong characteristic hydrogenation flavor. It was isolated and called A. Another 5 gallon portion of the oil, was deodorized by a batch steam distillation process under a vacuum of 0.05 mm Hg. Since during this batch deodorization process, the oil was heated to 180C for 2 hr, the deodorized oil was not only free from volatile compounds but also had a very low peroxide number of 0.3 meq/kg. The oil was then hydrogenated in exactly the same manner as before. The hydrogenated oil had only a faint characteristic hydrogenation flavor. It was also isolated and called B. Gas chromatographic analysis of A and B yielded similar chromatograms except that the peak areas of A were approximately 30 times larger than those of B. This seems to substantiate the observation of Merker and Brown (7) that a product with little hydrogenation flavor can be obtained by the hydrogenation of a freshly deodorized soybean oil.

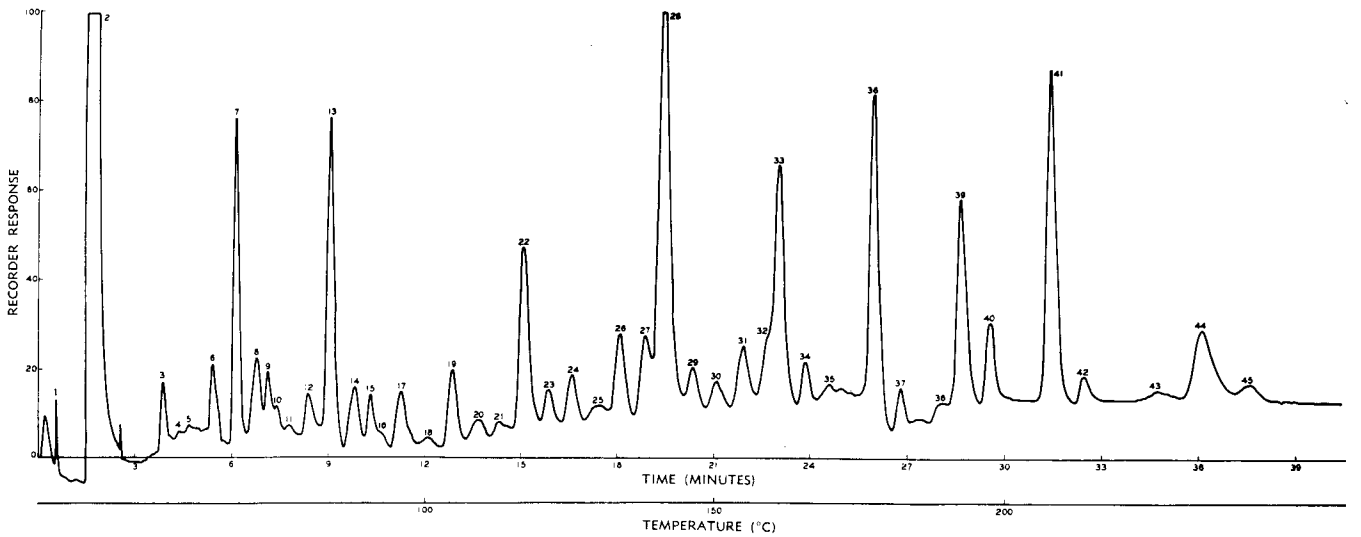


FIG. 1. Gas chromatogram of the volatile by-products developed during hydrogenation of soybean oil.

TABLE I

Compounds Identified as Volatile By-Products of Catalytic Hydrogenation

Peak No. in gas chromatograms	Size of peak	Identified as
1. Saturated hydrocarbons		
3-A	Small	n-Hexane
7-A	Medium	n-Octane
13-A	Medium	n-Nonane
19-A	Medium	n-Decane
24-B	Small	n-Undecane
29-A	Small	N-Dodecane
40-A	Medium	n-Tetradecane
42-A	Small	n-Hexadecane
44-A	Medium	n-Heptadecane
2. Unsaturated hydrocarbons		
8-A	Small	*trans*-Octene
10-A	Small	*cis*-2-Octene
14-A	Small	*trans*-Nonene
20-A	Small	*trans*-Decene
31-C	Small	*trans*-Dodecene
3. Saturated alcohols		
12-A	Small	n-Propanol
18-A	Small	n-Butanol
23-A	Small	n-Pentanol
28-A	Large	n-Hexanol
33-A	Large	n-Heptanol
36-A	Medium	n-Octanol
39-A	Medium	n-Nonanol
41-A	Large	n-Decanol
4. Esters		
6-A	Medium	Ethyl acetate
5. Carbonyl compounds		
11-A	Small	n-Butanal
17-A	Small	n-Hexanal
34-A	Small	n-Nonanal
38-A	Small	n-Decanal
22-A	Medium	2-Heptanone
27-A	Small	2-Octanone
32-A	Small	2-Nonanone
15-A	Small	3-Hexanone
26-A	Medium	3-Octanone
31-B	Medium	3-Nonanone
25-A	Small	4-Octanone
30-C	Small	4-Nonanone
6. Lactones		
37-A	Small	γ-Hexalactone
45-A	Small	γ-Nonalactone

Numerals indicate the number of gas chromatographic peaks with Ucon Polar as stationary phase (same as the numbers in Fig. 1).
Letters indicate the number of gas chromatographic peak when rechromatographed with SE-30 as stationary phase.

Gas chromatography of the methyl esters of the volatile acidic by-products showed no peak of significant size. The largest peak was that of methyl

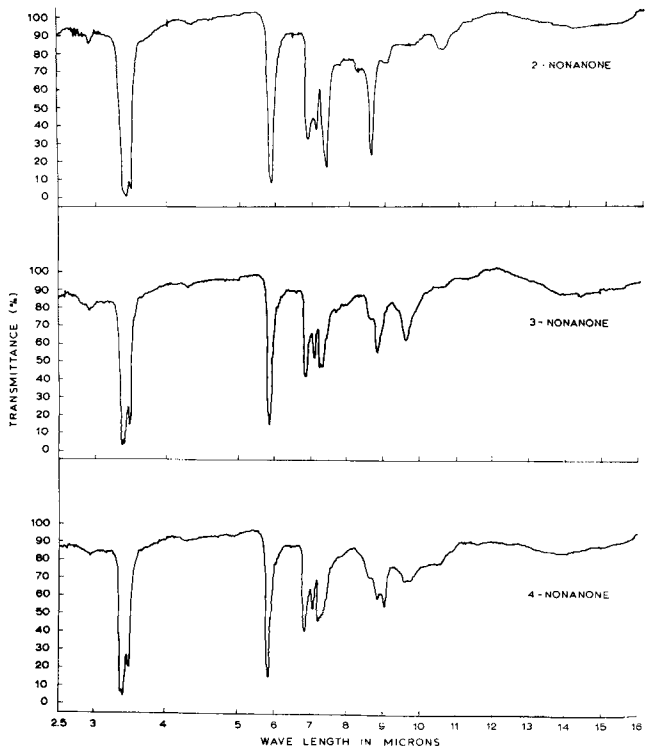


FIG. 2. Infrared spectra of 2-nonanone, 3-nonanone, and 4-nonanone.

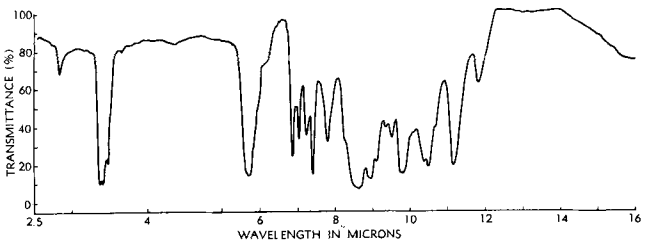


FIG. 3. Infrared spectrum of the fraction 45-A identified as γ-hexalactone.

hexanoate which was only of negligible size. However, if the oil used for hydrogenation was not previously deodorized to remove the volatile compounds in the crude oil, considerable amounts of fatty acids were observed. It seems, therefore, that no significant amount of free fatty acids was produced during catalytic hydrogenation using nickel as catalyst.

Gas chromatography of the nonacidic volatile by-products developed during hydrogenation yielded 45 peaks, of which peak No. 2 was the solvent ethyl ether (Fig. 1). This gas chromatogram was significantly different from that of the volatile decomposition products developed during hydrogenation of a slightly autoxidized soybean oil which was not deodorized previous to the hydrogenation in order to remove any volatile compounds already present (2).

A total of 37 compounds was identified as shown in Table I. Nine were a homologous series of normal saturated hydrocarbons from C_6 to C_{17} with the exception of C_7, C_{13} and C_{15}. Five other small gas chromatographic peaks were identified as unsaturated hydrocarbons. The position of the double bond could not be exactly located by the use of infrared and mass spectrometry. It is interesting to note that all of them except one were *trans* isomers.

A complete homologous series of normal saturated primary alcohols from C_3 to C_{10} were identified. Three of these alcohols were the largest peaks of the gas chromatograms. A total of 12 carbonyl compounds was identified, four of which were normal saturated aldehydes, three methyl ketones, three ethyl ketones and two propyl ketones. The infrared spectra of these ketones showed significant differences (Fig. 2). The characteristic absorption band of methyl ketone at 7.39 μ shifted to 7.25 and 7.3 μ and became broader and less intense in ethyl and propyl ketones. The strong absorption of methyl ketone at 8.6 μ was shifted to higher wavelengths with decreased intensity for the ethyl and propyl ketones.

Two γ-lactones of C_6 and C_9 were identified. The infrared spectrum of the rechromatographed fraction 45A (Fig. 3) showed a carbonyl absorption band and a broad band at 8.5 μ, which suggested that it

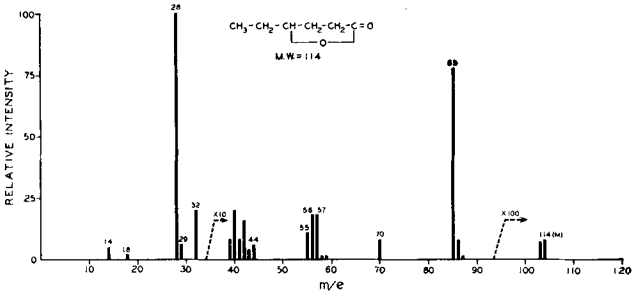


FIG. 4. Mass spectrum of the fraction 45-A identified as γ-hexalactone.

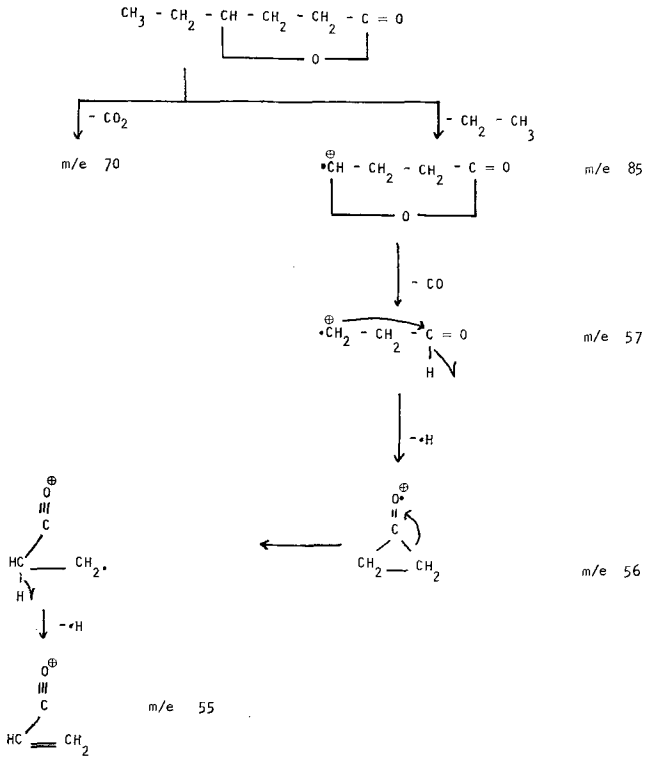
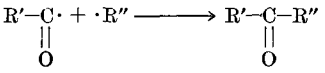


FIG. 5. Interpretation of the mass spectrum of the gas chromatographic fraction identified as γ-hexalactone.

was an ester. The location of the carbonyl band at 5.70 μ indicated the possibility of a saturated γ-lactone. The mass spectrum of this gas chromatographic fraction had a molecular ion of m/e 114 (Fig. 4). A loss of carbon dioxide yielded the peak m/e 70. A loss of ethyl group could produce the peak m/e 85. The latter may then lose a CO to yield the peak m/e 57, which may then undergo rearrangement to produce peaks m/e 56 and 55 (Fig. 5). It was therefore concluded that this fraction was γ-hexalactone. This conclusion was then confirmed by comparison of the retention times of this fraction with those of the authentic compound with the use of two different stationary phases, Ucon Polar and methyl silicone gum.

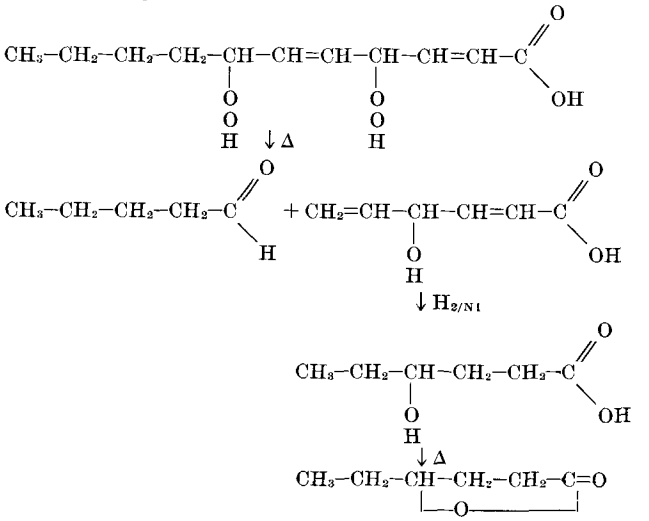
The odor and flavor characteristics of the compounds identified indicated that the characteristic flavor developed during the catalytic hydrogenation is unlikely to be due to one or two compounds. Chang et al. (1) reported that saturated aldehydes and ketones may contribute to the hydrogenation flavor. The present results appear to substantiate their observations. The higher members of the aldehydes and ketones, as well as the higher alcohols and the lactones had flavor notes all of which could contribute to the total characteristic flavor developed during hydrogenation.

The mechanisms for the formation of hydrocarbons, alcohols, aldehydes, and ketones through the decomposition of the precursors of the volatile by-products of hydrogenation, that is hydroperoxides, have been discussed in a previous paper (2). In addition, the 2-alkanones, 3-alkanones, and 4-alkanones may be produced through the coupling of alkyl free radical with methyl, ethyl, and propyl free radicals, respectively (8).

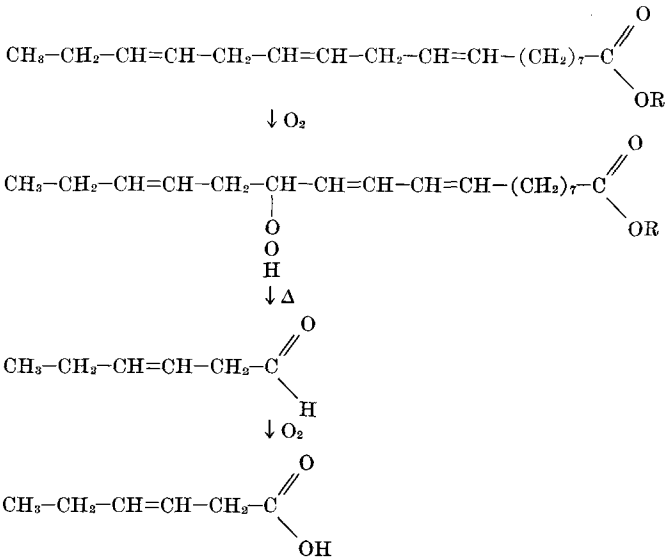


Under the conditions of catalytic hydrogenation, alcohols may also be formed through the reduction of carbonyl compounds with the simultaneous formation of a small amount of hydrocarbon through carbonylation. Studies with model systems indicated that, under the conditions used in this experiment for catalytic hydrogenation of soybean oil, n-nonanal was reduced to 85% n-nonanol, and 5% octane with 7% remained unchanged. The octane was evidently produced through decarbonylation. Under the hydrogenation conditions, 2-pentanone was reduced to only 26% of 2-pentanol with 73% remained unchanged. This explains why relatively large amounts of alcohols and ketones and relatively small amounts of aldehydes were identified.

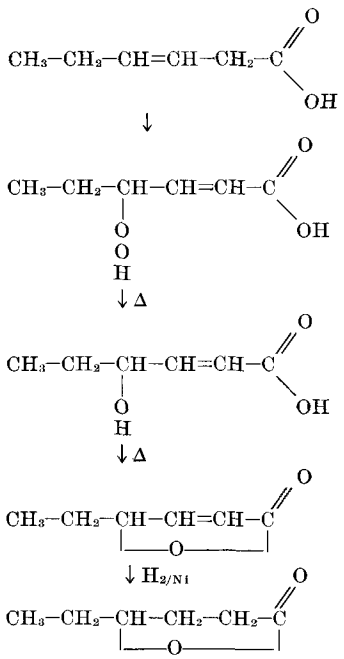
The lactones could only be formed through hydroxy acids. A mechanism for the formation of γ-hexalactone from the dihydroperoxide of a free fatty acid which may originate from linoleate is postulated as following:



The dihydroperoxide has a high boiling point and may therefore remain in the oil during the deodorization which precedes hydrogenation A second mechanism involves the secondary autoxidation of 3-*cis*-hexenoic acid is also possible. This acid may be produced by the autoxidation of linolenate as follows:



This acid may form a hydroperoxide which is relatively nonvolatile and may remain in the oil during the deodorization previous to hydrogenation.



It should be noted that there were significant qualitative as well as quantitative differences between the volatile decomposition products of hydroperoxides produced under autoxidative and under hydrogenation conditions. Lea and Swoboda (9) distilled autoxidized sunflower oil at 75 and 210C and identified 16 aldehydes, 3 hydrocarbons, 2 ketones, and 1 alcohol. The present investigation, on the other hand, identified 4 aldehydes, 14 hydrocarbons, 8 ketones, 8 alcohols, and 2 lactones. Furthermore, the three largest gas chromatographic peaks were all normal saturated alcohols, and the next five largest peaks were two alcohols, two hydrocarbons and one methyl ketone.

ACKNOWLEDGMENT

Study of hydrogenation of n-nonanal and 2-heptanone by Kosaku Yasuda; assistance in determining and interpreting mass spectra by P. E. Funk and A. K. Bose, Department of Chemistry, Stevens Institute of Technology; soybean oil supplied by K. F. Mattil, Swift and Company.

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[Received October 15, 1965]