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To the Graduate Council:

I am submitting herewith a thesis written by Mary Ann Harvey entitled "The Effect of Re-Use of Two Frying Fats on the Fatty Acid Content of French-Fried Potatoes." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Foods.

Ada Marie Campbell
Major Professor

We have read this thesis and
recommend its acceptance:

Francis Schofield
Bernadine Meyer

Accepted for the Council:

Dean of the Graduate School

42
33

THE EFFECT OF RE-USE OF TWO FRYING FATS ON THE FATTY
ACID CONTENT OF FRENCH-FRIED POTATOES

A Thesis
Presented to
the Graduate Council of
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In Partial Fulfillment
of the Requirements for the Degree
Master of Science

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CHAPTER I

INTRODUCTION

In spite of the almost universal acceptance of foods fried in deep fat, a problem exists due to the susceptibility of frying fats to deteriorative changes and the transfer of undesirable flavors to the food cooked in degraded fat. Several studies relating to changes in fats have been reported and these have been reviewed by Bennion and Hanning (1956). The studies involving problems of deep fat frying were carried out mostly on a commercial scale since fats are used repeatedly in this operation. Holding fats at frying temperatures for relatively long periods has been found to induce simultaneously three chemical changes: hydrolysis, polymerization and oxidation (Carlin et al., 1954).

Several studies have been carried out in which thermally treated fats were fed to experimental animals (Johnson et al., 1956, 1957; Kaunitz et al., 1953; Crompton, 1953). Thermally oxidized fats produced a growth-depressing effect, but the effect was not a permanent one; when animals were changed to a normal diet, they quickly recovered and grew to maturity. In Johnson's studies the effect was found to be multiple in nature; in addition to the characteristic growth depression, an irritant or diarrhea effect was noted as well as a possible enzyme-inhibiting or vitamin-destroying effect. It appeared that products formed during thermal treatment were related to unsaturated

portions of oil since the animals on a thermally treated saturated fat did not exhibit the characteristic effects. This indicated that triglycerides containing short chain fatty acids and relatively small percentages of polyunsaturated fatty acids are more stable to thermal oxidation than are corn oil and hydrogenated fats. According to Johnson, a high degree of unsaturation is assumed also to produce thermal polymers. Whether the polymers formed are strictly thermal is not known.

The problem of deteriorative changes in fried foods and thermally treated fats is currently of great concern to nutritionists. On the one hand, evidence such as that cited above indicates a possible need for caution in the use of unsaturated fats, at least when heating is involved. On the other hand, evidence implicating saturated fats in the incidence of hypercholesterolemia has led to considerable interest in the use of highly unsaturated oils (Brown et al., 1962). Consideration of these factors, plus the recent application of gas liquid chromatography to food lipid analyses, led to the present research. The purpose of this study was to determine the changes occurring in the kinds and amounts of fatty acids present in potatoes cooked in a polyunsaturated fat (cottonseed oil) and in a more highly saturated fat (hydrogenated cottonseed oil) when these fats were used repeatedly in the frying of potatoes. Since there is an increasing interest in the possible role of phospholipids in the deteriorative changes that occur in foods, fractionation of the fats into glyceride-sterol and phospholipid fractions seemed desirable.

CHAPTER II

REVIEW OF LITERATURE

The question of changes occurring during the re-use of frying fats in both the fat and the foods fried therein is by no means a new one. As early as 1919 Woodruff et al. reported a study on changes in fats absorbed by fried foods. At about the same time Morgan et al. carried out a related study to find changes in physical and chemical constants of fats used for frying standard doughs. The results of these early studies do not shed a great deal of light on the data needed today, for we are living in an era of controversy concerning the advisability of emphasizing polyunsaturated fats in the diet.

Through the years many other workers have conducted studies concerned with changes occurring in heated fats. The studies will be reviewed in chronological order.

Carlin and Lantz (1938) found that rapid hydrolysis occurred when fats were held at a temperature of 380° F. in the presence of a constant flow of steam. Hydrolysis was slow after free fatty acid levels of 0.5 to 1.0 per cent were reached. According to these workers, this is in accord with actual production experiences of manufacturers of fried foods from which large volumes of water must be evaporated. Carlin and Lantz also reported that highly saturated fats developed free fatty acids more rapidly than did less saturated fats.

In 1939 Thiessen et al. reported work to determine the frying

life of four different fats--lard, corn oil, hydrogenated fat and cottonseed oil--used under household conditions. They found evidence that free fatty acids develop in all of these fats on re-use for a total of 18 hours. Lard and hydrogenated fat showed the greatest amount of hydrolysis. Chemical tests indicated decreased iodine number and lowered smoke point with continued re-use. Thiessen et al. concluded also that reheating and re-use of fat up to 12 hours did not seem to affect quality or flavor of products fried in these fats.

Robinson et al. (1940) found that various fats had tendencies to develop foam when used for frying purposes after preheating periods at 375° F. Thermal decomposition was evidenced by increased refractive indices, lowered active oxygen values and increased viscosity.

Carlin and Lannerud (1941) found a rapid drop in oxidative stability of fats subjected to deep fat frying temperature and subsequent reduction in keeping quality of potato chips cooked in the fats. They noted foaming tendencies in the fat, a decrease in the iodine number, an increase in saponification number and an increased refractive index.

Vail et al. in 1943 reported work which had as its purpose the determination of certain characteristics of fats and oils which might relate to their suitability for deep fat frying. Smoke points and per cent free fatty acids were determined for seventeen fats and oils. The smoke point of "Snowdrift" was found to be 236-237° C. and that of "Wesson Oil," 235-237° C. Both of the fats are composed of cottonseed oil, the difference being that "Snowdrift" is hydrogenated. The

percentages of free fatty acids (as oleic) found by Vail's group for these two fats are given below:

Sample	Before heating	After heating	
		6 hours	12 hours
"Snowdrift"	0.009	0.108	0.116
"Wesson Oil"	0.028	0.109	0.165

All the fats studied were found to produce a gum formation at the surface of the fat, close to the sides of the container, after being heated for 12 hours.

Arenson and Heyl (1943) found that physical structure of doughnuts fried in various fats was modified by addition of fatty acids and by the presence of substances thermally developed in the normal process of frying. They concluded also that the stability of shortening as measured by resistance to peroxide formation is without significance in the measurement of frying quality. They used frying conditions in which free fatty acid content of the fats did not reach levels above 0.6 per cent.

A similar study was conducted by Fisher (1949) in which a correlation was shown between thermally developed free fatty acids of frying fat and physical characteristics of doughnuts. The fats used did not develop free fatty acids above the level of 0.4 per cent, but possible influence of other heat formed constituents in frying fat was recognized.

Chang et al. (1952) studied fatty acid changes in commercial fats (lard, butter and vegetable oils) when used in baked products,

hard candy and as a medium for deep fat frying. The changes occurring during deep fat frying included an initial increase in the peroxide number when fat was heated to 180° C. and kept at that temperature for 10 minutes, followed by a decrease in the peroxide number to a negligible value after 40 minutes of additional heating. The changes occurring with prolonged heating at 180° C. indicated that peroxides were decomposed as fast as they formed.

Conjugated dienes increased significantly in the corn oil with the additional heating period. Total unsaturation as measured by iodine number showed a gradual decrease with heating, resulting in an increase in the calculated value of saturated fatty acids. Among unsaturated acids the changes in oleic were small, while linoleic definitely decreased and linolenic decreased slightly at first and then increased to a higher value than the original. According to Chang et al., the increased percentage of linolenate and decreased percentage of linoleate probably could be explained by slight oxidation of the large amount of linoleic acid present. The fatty acid determinations were made by saponification with potassium hydroxide followed by spectrophotometric analyses to determine linoleic, linolenic, arachidonic and conjugated diene acids.

A summary of the work on problems encountered in commercial use of frying fats was compiled by Goodman and Black (1952). The changes reported in composition of fat used in frying were a decrease in iodine value, an increase in refractive index, an increase in free fatty acids, an increase in acetyl value, a drop in smoke point, a

lowering of the melting point, the appearance of foaming in frying and flavor deterioration. Fat absorption increased in foods fried in fats used repeatedly.

Carlin et al. (1954) studied factors affecting decomposition of frying fats. Hydrolysis, polymerization and oxidation were found to take place simultaneously at elevated temperatures. These workers concluded that oxidation of the frying fat is a much more important aspect than recognized previously and that hydrolysis is thus of only secondary importance.

Since changes taking place in frying fats and problems involved in deep fat frying had been studied mostly on a commercial scale, Bennion and Hanning (1956) investigated changes in lard produced by frying potatoes and fritter batters under home conditions. They found very little change in free fatty acids. The peroxide values remained low at first but increased with prolonged heating, reaching a higher level with potatoes than with batter samples. Iodine and saponification numbers were little affected. The smoke point was affected only slightly.

Lowe et al., (1958) in an attempt to bring up to date the information on smoke points and free fatty acid content of fats then marketed, carried out a series of experiments with hydrogenated shortenings, oils and lard. They found that the initial free fatty acid content was lowest in oils, slightly higher in shortenings and highest in lards, although there was some variation. The free fatty acid content of all fats increased during heating, the final content in some cases

being as much as fifteen times greater than the initial concentration. The final free fatty acid content of lard did not increase as much as did that of oils. The smoke points of all fats were lowered with use.

Rust and Harrison (1960) studied the effect of method of care on frying life of fat. This work revealed that filtering and refrigerating fats and cleaning the fryer between frying periods did prolong the frying life of the fat. Regardless of the method of care, there was a significant negative correlation between acid number of the fat and acceptability of French-fried potatoes.

All of the studies reviewed have been concerned with changes occurring during thermal treatment and re-use of fat, but the kind and amount of information obtained from the studies changed very little over a period of approximately twenty years. Information concerning possible changes in specific fatty acids still is lacking, largely because of inadequate methods of analysis. The minute quantities of fat extracted from many food samples are too small for macro-analysis.

About ten years ago James and Martin (1952) published the first practical details of the technique known as gas liquid chromatography. Since the development of this apparatus, analysis of small quantities of mixtures of volatile liquids has been possible. The apparatus has been found useful in most aspects of research and chemical industry and recently has come into use for analysis of changes occurring in food lipids.

Of the work reported thus far in which gas chromatography has been applied to the study of food lipids, some has been concerned with

the lipids of vegetables. The method was used to study the influence of prior treatment upon alteration in vegetable lipids during freezer storage (Lee and Mattick, 1961; Mattick and Lee, 1961). Samples of raw and blanched peas and spinach were frozen and analyzed after one year of storage. Decreases in several fatty acids in the phospholipid fraction from the raw vegetables were large in comparison to changes in the blanched samples. Blanching was found to attenuate lipolytic enzyme systems of the vegetables, and this seemed to account for the difference in response between the blanched and unblanched samples. These workers feel that changes in fatty acids in foods could be involved in development of the off-flavors that sometimes occur in frozen foods during storage, and certainly it is known that blanching vegetables prior to freezing prolongs their storage life. Other changes in vegetables noted by Lee and Mattick were that the fatty acids in neutral fat and the free fatty acids of the raw material showed a net gain in total quantity of palmitic acid. They believed it possible that this increase came from unsaturated 18-carbon fatty acids.

CHAPTER III

PROCEDURE

Materials

Idaho potatoes purchased in one lot were stored in the refrigerator until 24 hours prior to use, at which time they were removed and held at room temperature. The entire lot of each cooking fat (polyunsaturated--"Wesson Oil" and more highly saturated--"Snowdrift") was mixed thoroughly before use in order to obtain a homogeneous sample. Each time potatoes were fried an additional supply of fat was heated under identical conditions to replace any fat that had been absorbed by the potatoes and thus maintain a constant level of cooking medium in the fryer.

The equipment used for frying the samples was a Presto deep-fat fryer having thermostatic heat control and a capacity of 5 pints. A wire basket was used to hold the potatoes during cooking. The same deep-fat fryer was used to heat the reserve fat. A thermometer was suspended from a ring-stand into the fryer for observing the actual temperature of the fat.

Preparation of Potato Samples

The potatoes were pared with a vegetable parer and sliced uniformly with a French-fry cutter. They were then washed and allowed to stand in cold water for a few minutes. They were drained on paper towels and cooked for 5 minutes in a deep-fat bath held at $176^{\circ} \pm 10^{\circ} \text{C}$.

The temperature of the bath was always 176° when the potatoes were placed in it, but the temperature did drop at first and then gradually rise during the cooking operation. A sample of approximately 150 g was cooked each time.

After the potatoes were cooked for 5 minutes, they were drained for 5 minutes on six thicknesses of paper toweling and immediately wrapped in heavy weight aluminum foil, frozen and held at -20° C. until time for analysis. Although only one lot of potatoes was fried each time, the fat was held at frying temperature for an hour.

The frying procedure was carried out on twelve consecutive days for each fat. Although only samples from fryings 1, 3, 6, 9 and 12 were to be analyzed, potato samples from all twelve fryings were saved for possible future use. After each use, the frying fat was strained and refrigerated. Portions of the two cooking fats were taken before the first frying and after the sixth and final fryings. These were stored under nitrogen in 10-ml Erlenmeyer flasks at -12° C. until they were analyzed.

Extraction of Lipids

The method of Bligh and Dyer (1959) was used for extraction. The samples of French-fried potatoes were thawed in the wrap, and a 20-g portion of each was accurately weighed and extracted with 400 ml of a 2:1 chloroform-methanol mixture. The thawed potato was broken slightly in the Waring Blendor and then blended for 2 1/2 minutes with 80 ml of the solvent mixture. Lipid extract was separated from potato solids on a fine sintered funnel in a suction flask. Solids

were returned to the Blendor and re-extracted with 80 ml of solvent. This re-extraction process was repeated three times and the remaining 80 ml of solvent were used for final rinsing of the Blendor and funnel. To the combined filtrates 175 ml of distilled water were added and the extraction mixture was allowed to stand overnight in the refrigerator.

Since phase separation was not clean cut, the extraction mixture had to be centrifuged after standing. In order to reduce the volume to be centrifuged, the water-methanol layer was drawn off by suction to a point well above the emulsified layer. The remaining mixture was quantitatively transferred into 250-ml centrifuge bottles and centrifuged at 1500 rpm for 30 minutes. The mixture then was transferred into a 250-ml graduated cylinder in such a way that the emulsion was not re-formed. The volume of the lower phase (chloroform and lipid) was recorded, the upper phase was siphoned off and discarded and 2 10-ml aliquots of the extract were removed by pipette and evaporated under nitrogen for determination of total lipids in the samples. The remaining chloroform extract was washed with chloroform into a 500-ml evaporating flask and the solvent was removed on a rotary evaporator under vacuum.

Fractionation of Lipids

The small amount of lipid in the evaporating flask was dissolved in chloroform and transferred quantitatively into a 500-ml Erlenmeyer flask. The procedure used for fractionation with silicic acid was the one described by Murty et al. (1960). The sample was mixed with 100 ml of chloroform and stirred with 25 g of silicic acid (100 mesh)

for 10 minutes on a magnetic stirrer. The solution was decanted from the silicic acid into a fine sintered funnel and filtered under reduced pressure. The silicic acid was washed twice with a total of 100 ml chloroform. The combined filtrate and washings, containing glycerides and sterols, were transferred to a 250-ml graduated cylinder; the volume was recorded and 2 10-ml aliquots were taken. After the solvent was removed in a stream of nitrogen and the sample was weighed, it was ready for methylation.

The chloroform-washed silicic acid was shaken with 100 ml of redistilled methanol to remove adsorbed phospholipids and filtered through a fine sintered glass funnel. After washing the silicic acid with 2 25-ml portions of methanol, the combined methanol extracts were pooled, the volume was recorded, and 2 10-ml aliquots were taken in tared 100-ml evaporator flasks. The aliquots then were evaporated on the rotary evaporator, weighed accurately and methylated.

Methylation of Total Lipids and Fractions

The total lipid and the fractions obtained as described above were methylated by a modification of the method described by James (1960). Approximately 40 mg of lipid were placed in a 15-ml stoppered centrifuge tube. To the sample were added 3 ml of a 1 per cent sulfuric acid-methanol solution. This mixture was refluxed for 4 hours in a sand bath held at 70° C. The sample was stirred at frequent intervals until the lipid was dispersed.

At the end of the reflux period, 5 ml of redistilled pentane and 2 ml of distilled water were added to each tube. Separation of

two phases occurred immediately and the lower phase, containing the methanol, sulfuric acid and water, was removed and discarded with a pipette. The pentane, containing the methyl esters, was washed once more with water; after removal of the aqueous layer, anhydrous sodium sulfate was added to remove the remaining traces of the water. If samples were to be chromatographed on the same day, the methyl esters were allowed to stand on the sodium sulfate for at least 1 hour. If the methyl esters were to be stored overnight, they were stored on the sodium sulfate.

Gas Liquid Chromatographic Analysis

The pentane-lipid mixture was decanted into another conical 15-ml tube and the pentane was evaporated from the methyl esters under nitrogen. When all the solvent was removed, the fatty acid methyl esters remaining were diluted with acetone and injected into a Barber-Colman Model 61C gas chromatograph having a radium ionization detector. The most satisfactory sample size was obtained by diluting 2.5 μ l of methyl esters with 10 μ l of acetone and charging the column with 2 μ l of the dilution. An 8 ft. coiled copper column (1/4-in. inside diameter) packed with diethylene glycol succinate polyester (15.4 per cent by weight on 80-100 mesh chromosorb W) was used. The column, with argon flowing through, was preconditioned by heating for approximately 30 hours at an operating temperature of 190° C. before it was connected to the detector.

The following operating conditions were used for gas chromatographic analyses:

Column Temperature 185° C.
 Detector Cell Temperature. .218° C.
 Flash Heater 225° C.
 Split Heater 235° C.
 Voltage. 900
 Argon Pressure 25 psi
 Sensitivity. 10
 Attenuation. 16*

Peaks were identified by comparing their retention times (number of minutes elapsing between charging of the column and reaching of maximum peak height) with those of the components of a standard mixture of fatty acid methyl esters (Appendix).

Peak "areas" were calculated by the equation:

Area = Height of peak x Width of peak at 1/2-height x Attenuation factor.**

The areas of the peaks for each sample were added to give the total area under all peaks and the percentages were calculated:

$$\% \text{ Fatty acid in sample} = 100 \times \frac{\text{Area of peak}}{\text{Total area under all peaks}}$$

The percentages thus obtained are on a molar basis. Weight percentages were not calculated because the molecular weights of the major components in the samples analyzed varied so little that weight percentages would have been almost identical to molar percentages.

* Attenuation setting was 16 except when it was necessary to reduce sensitivity for large sample components.

** Attenuation factor is used only if attenuation is changed during a tracing.

CHAPTER IV

RESULTS AND DISCUSSION

Attempts to extract and fractionate the lipids quantitatively were not successful, as evidenced by the fact that the amounts of glyceride-sterol plus phospholipid did not equal the amount of total extracted lipid for each sample. Several factors may have contributed to the problem: the necessity of centrifuging and the large number of transfers required possibly resulted in some loss. The equipment available was not always appropriate--e.g. the use of a smaller Blendor, operated through a rheostat, would have been helpful. Some evidence was obtained late in the study that the time of day at which weighings were made affected weights, although weighing was done in a constant temperature room. Insufficient mixing of lipid extracts prior to removal of aliquots is another possible factor. Because of these difficulties, it is impossible to report the results on a weight basis. This does not make the findings useless since data on the fatty acid composition of foods usually are reported on a percentage basis.

Because there is little information concerning fatty acid content of foods, some preliminary comparisons of fatty acid distribution in the unheated fats are of interest. Gas liquid chromatographic analysis of the two types of fat studied revealed two completely different fatty acid patterns (Table I, Figure 1). The major fatty acid component of the cottonseed oil was linoleate while the major

TABLE I
DISTRIBUTION OF FATTY ACIDS IN COTTONSEED OIL
AND HYDROGENATED COTTONSEED OIL
(UNFRACTIONATED, UNHEATED)

Fatty acid	Per cent of total	
	Cottonseed oil	Hydrogenated cottonseed oil
Myristic (C ₁₄)	0.4	Tr
Palmitic (C ₁₆)	24.9	12.4
Stearic (C ₁₈)	1.0	5.2
Oleic (C _{18:1})	10.0	70.7
Linoleic (C _{18:2})	63.7	11.7

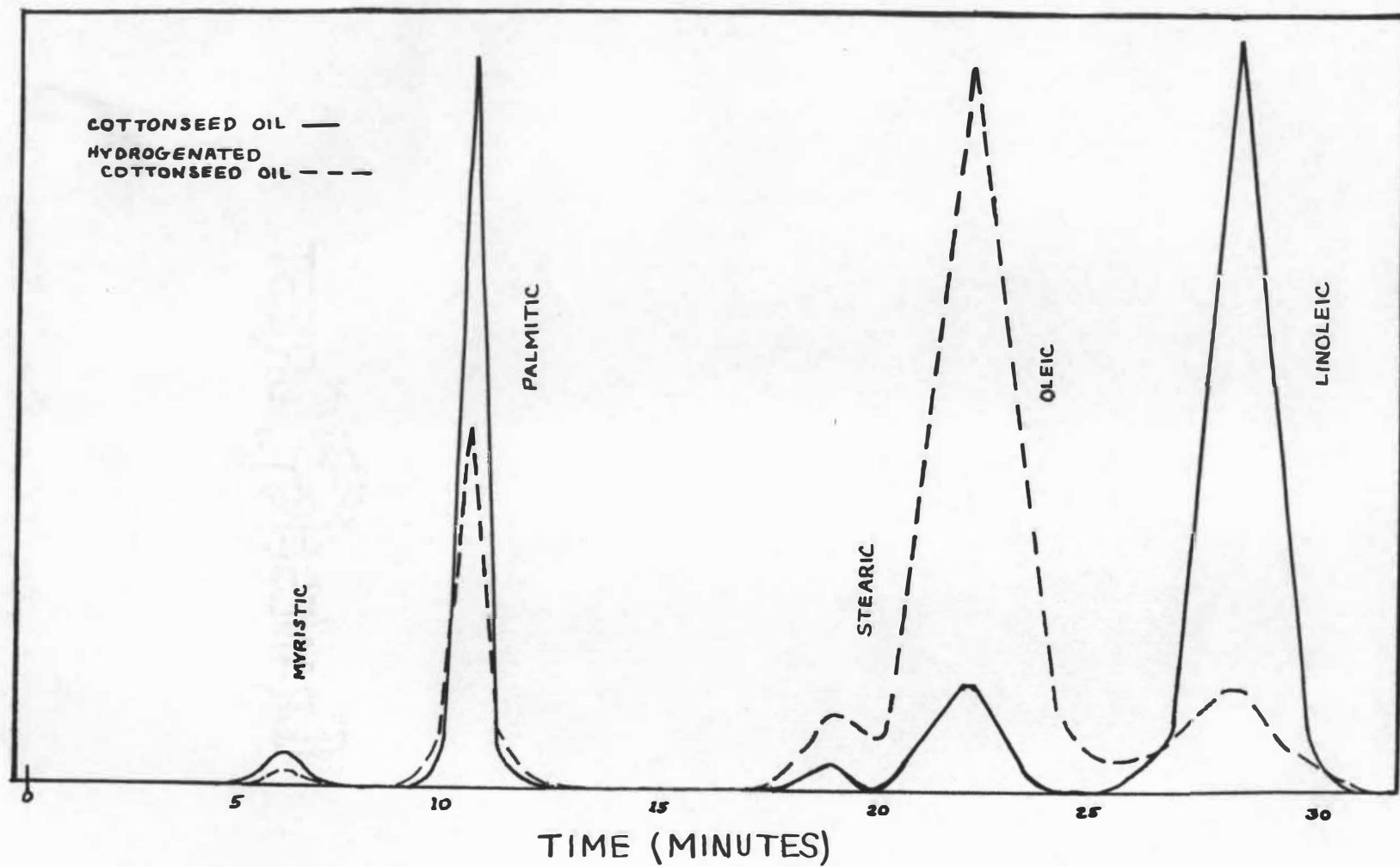


Figure 1. Comparison of fatty acid pattern for cottonseed oil and hydrogenated cottonseed oil.

component of the hydrogenated cottonseed oil was oleate.

Few data are available for comparison with the values obtained in this study. In the USDA tables (1959) percentages for the saturated fatty acids are combined. The values for the two fats in this study have been tabulated similarly and compared with those presented in the USDA publication (Table II). The USDA figures were obtained from a review of the literature and thus represent results of various methods of fatty acid analysis; probably few of the data were obtained by gas chromatography.

In Table III the percentages of fatty acids in the total lipid and glyceride-sterol and phospholipid fractions of the unheated fats are compared. It should be noted that the data from Table I are repeated in Table III for the purpose of comparing values for the lipid fractions with those for the total lipids. As shown in Table III, the fatty acid pattern of the glyceride-sterol fraction tended to be very similar to that of the total lipid for the cottonseed oil. The phospholipid fraction of the cottonseed oil differed from the total lipid in being much higher in oleic and lower in linoleic acids. In the hydrogenated fat the greatest difference between total lipid and the glyceride-sterol fraction was in the oleic-linoleic ratio. The greatest difference between total and phospholipid was in the relative amounts of palmitic and oleic acids. Traces of palmitoleic and linolenic acid were detected in the phospholipid fractions of the two fats but usually were not measurable.

Table IV gives a comparison of fatty acid distributions in the

TABLE II

A COMPARISON OF THE FATTY ACID DISTRIBUTION IN COTTONSEED OIL
AND HYDROGENATED COTTONSEED OIL WITH VALUES FROM
THE USDA TABLES (PER CENT OF TOTAL)

Fatty acid	Cottonseed oil		Hydrogenated cottonseed oil	
	Expt'l values	USDA values	Expt'l values	USDA values
Total saturated (C ₁₄ , C ₁₆ , C ₁₈)	26.3	25.8	17.6	38.0
Oleic	10.0	22.3	70.7	54.9
Linoleic	63.7	51.9	11.7	7.1

TABLE III

DISTRIBUTION OF FATTY ACIDS IN UNHEATED SAMPLES OF
COTTONSEED OIL AND HYDROGENATED COTTONSEED OIL
AND IN LIPID FRACTIONS (PER CENT OF TOTAL)

Fatty acids	Cottonseed oil			Hydrogenated cottonseed oil		
	Total lipid	Glyceride-sterol	Phospho-lipid	Total lipid	Glyceride-sterol	Phospho-lipid
Myristic	0.4	0.5	0.5	Tr	Tr	0.2
Palmitic	24.9	24.1	26.7	12.4	11.0	20.0
Stearic	1.0	1.4	1.3	5.2	5.5	4.2
Oleic	10.0	11.6	22.1	70.7	76.2	64.2
Linoleic	63.7	62.5	49.5	11.7	6.8	11.4

TABLE IV

COMPARISON OF FATTY ACID DISTRIBUTIONS IN THE FRYING FATS
WITH THOSE OF FAT EXTRACTED FROM FRENCH-FRIED
POTATOES (PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Cottonseed oil</u>					
After 6th frying					
Frying fat	0.7	24.3	0.9	16.3	57.8
Extracted fat	0.6	25.6	1.2	14.0	58.7
After 12th frying					
Frying fat	0.4	29.9	1.0	10.5	58.2
Extracted fat	0.4	30.1	1.0	11.7	56.8
<u>Hydrogenated cottonseed oil</u>					
After 6th frying					
Frying fat	0.1	11.4	5.3	76.3	7.0
Extracted fat	0.1	12.5	5.3	74.4	7.7
After 12th frying					
Frying fat	0.2	12.3	5.7	74.8	7.0
Extracted fat	Tr	13.5	7.2	71.7	7.7

frying fats with those of the fat extracted from potatoes fried in each of the fats. Fatty acid patterns of the frying fat and of the fat extracted from the potatoes are very similar, as would be expected since practically all fat in French-fried potatoes is derived from the fat in which they are fried. Only the total lipid values are presented though the fractions also showed a close similarity between frying fat and extracted fat.

In Table V are shown the fatty acid distribution in cottonseed oil and in fat extracted from potatoes fried in the oil. The most important change in both cases is the decrease in linoleate, most of which had occurred after six fryings. During the first six fryings the percentages of other fatty acids, except that of oleate, remained fairly constant. Oleate increased as linoleate decreased. With continued re-use through the final frying, palmitate increased and oleate decreased. The data suggest that the first change occurring with re-use of cottonseed oil was autoxidation of linoleate and that further re-use of the oil resulted in β -oxidation. This explanation might be possible for the extracted fat if the potatoes provide the enzymes needed for β -oxidation, but it does not seem reasonable in the case of oil heated alone for several hours.

Similar, though somewhat smaller, changes apparently occurred in the hydrogenated cottonseed oil extracted from potatoes. Values are shown in Table VI for samples from the first, sixth and twelfth fryings. The frying fat showed the first change mentioned above but not the simultaneous decrease in oleate and increase in palmitate with

TABLE V

FATTY ACID DISTRIBUTION IN COTTONSEED OIL USED FOR FRYING
AND IN FAT EXTRACTED FROM POTATOES FRIED IN THE OIL
(PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Cottonseed oil</u>					
0	0.4	24.9	1.0	10.0	63.7
6	0.7	24.3	0.9	16.3	57.8
12	0.4	29.9	1.0	10.5	58.2
<u>Oil extracted from potatoes</u>					
1	0.3	25.0	0.8	9.0	64.9
3	0.5	25.8	0.8	10.2	62.7
6	0.6	25.6	1.2	14.0	58.7
9	0.6	28.6	1.2	12.2	57.4
12	0.4	30.1	1.0	11.7	56.8

TABLE VI

FATTY ACID DISTRIBUTION IN HYDROGENATED COTTONSEED OIL
USED FOR FRYING AND IN FAT EXTRACTED FROM POTATOES
FRIED IN THE FAT (PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Hydrogenated cottonseed oil</u>					
0	--	12.4	5.2	70.7	11.7
6	0.1	11.4	5.3	76.3	7.0
12	0.2	12.3	5.7	74.8	7.0
<u>Fat extracted from potatoes</u>					
1	Tr	11.0	7.2	71.7	10.1
6	0.1	12.5	5.3	74.4	7.7
12	Tr	13.5	7.2	71.7	7.7

continued use (Table VI).

With the lipid fractions for extracted and frying fat of both types, changes are similar to those discussed above in some respects but are less clear-cut. The additional handling required for preparation of the fractions might possibly be responsible for apparent discrepancies. The values obtained for the fractions are included in the appendix as a matter of record.

Considering the manner in which the fat was cared for between fryings, the total treatment given the fat probably cannot be considered severe. Whether effects would have been more pronounced and clear-cut with further re-use of the fats is not known. Future work should involve more extreme heat treatment of the fat. Analysis of samples of fried foods and fats obtained from commercial eating establishments might show the effect of fat re-use more dramatically.

In the frying of potatoes some hydrolysis of fat undoubtedly occurs. Hornstein (1960) developed a method of separating unesterified fatty acids from other lipid material by adsorption on a strong anion base resin. The fatty acids were converted to their methyl esters without prior elution from the adsorbent and the esters were analyzed by gas chromatography. Original plans for this study included Hornstein's procedure but lack of equipment prevented the carrying out of that work. It would be of interest in the future to separate the unesterified fatty acids and analyze their methyl esters.

The need for further work on quantitative extraction and fractionation also seems apparent from the results of this study.

CHAPTER V

SUMMARY

The effect of re-use of two frying fats--cottonseed oil and hydrogenated cottonseed oil--on the fatty acid content of French-fried potatoes was studied. The fatty acids in both the extracted and the frying fat and in fractions of each fat were analyzed by gas chromatography. The major fatty acids present in both fats were myristic, palmitic, stearic, oleic and linoleic. Cottonseed oil was highest in linoleic acid and hydrogenated cottonseed oil was highest in oleic acid.

A comparison of the fatty acid distribution in the fats used in this study with values from the USDA tables showed some differences which probably are due partially to the use of different methods of analysis.

The fatty acid distribution in the total lipid and in the glyceride-sterol fraction of cottonseed oil were similar, while the phospholipid fraction contained more oleate and less linoleate. In the hydrogenated cottonseed oil both fractions differed from the total lipid in relative amounts of palmitate, oleate and linoleate.

Changes occurring in the fatty acid distribution of the two fats with re-use were mainly a decrease in linoleate with subsequent increases first in oleate and later in palmitate. Evidence concerning the possibility of autoxidation followed by β -oxidation is inconclusive.

Recommendations for further work include: more severe heat treatment of the fats, separation and analysis of unesterified fatty acids and development of more quantitative procedures for extraction and fractionation of food lipids.

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APPENDIX

TABLE VII
RETENTION TIMES OF FATTY ACIDS DETERMINED FROM
A STANDARD MIXTURE OF METHYL ESTERS

Fatty acids	Time
	min.
Myristic	6.5
Palmitic	11.0
Palmitoleic	13.0
Stearic	19.2
Oleic	22.4
Linoleic	28.0
Linolenic	37.4

TABLE VIII

FATTY ACID DISTRIBUTION IN GLYCERIDE-STEROL FRACTION OF
COTTONSEED OIL USED FOR FRYING AND OF FAT
EXTRACTED FROM POTATOES FRIED IN
THE OIL (PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Cottonseed oil</u>					
0	0.5	24.1	1.4	11.6	62.5
6	0.6	25.1	1.7	12.9	59.7
12	0.4	28.1	1.0	11.2	59.2
<u>Fat extracted from potatoes</u>					
1	0.8	23.7	1.2	10.8	63.5
3	0.6	25.7	1.1	12.2	60.5
6	0.5	26.0	1.0	11.4	61.1
9	0.7	23.4	0.9	11.9	63.1
12	1.1	23.5	1.9	14.5	59.1

TABLE IX
FATTY ACID DISTRIBUTION IN GLYCERIDE-STEROL FRACTION OF
HYDROGENATED COTTONSEED OIL USED FOR FRYING AND
OF FAT EXTRACTED FROM POTATOES FRIED
IN THE FAT (PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Hydrogenated cottonseed oil</u>					
0	Tr	11.0	5.2	70.7	11.7
6	Tr	13.1	6.9	70.8	9.2
12	Tr	13.7	7.6	70.5	8.1
<u>Fat extracted from potatoes</u>					
1	Tr	12.0	6.9	70.9	10.2
3	Tr	11.4	5.5	75.3	7.9
6	Tr	13.5	6.6	71.7	8.2
9	Tr	13.3	6.8	71.9	7.9
12	Tr	13.7	5.7	73.8	6.8

TABLE X

FATTY ACID DISTRIBUTION IN PHOSPHOLIPID FRACTION OF COTTONSEED
OIL USED FOR FRYING AND OF FAT EXTRACTED FROM POTATOES
FRIED IN THE OIL (PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Cottonseed oil</u>					
0	0.5	26.7	1.3	22.1	49.5
6	0.5	30.7	0.8	16.5	51.4
12	0.5	33.6	0.8	13.7	51.3
<u>Fat extracted from potatoes</u>					
1	0.4	29.3	1.2	10.8	58.3
3	0.3	29.2	1.2	10.4	58.9
6	0.8	27.6	1.9	13.6	56.1
9	0.6	28.0	1.6	12.0	57.6
12	0.8	25.7	2.5	15.3	55.7

TABLE XI
FATTY ACID DISTRIBUTION IN PHOSPHOLIPID FRACTION OF
HYDROGENATED COTTONSEED OIL USED FOR FRYING AND
OF FAT EXTRACTED FROM POTATOES FRIED
IN THE FAT (PER CENT OF TOTAL)

Frying	Fatty acids				
	14	16	18	18:1	18:2
<u>Hydrogenated cottonseed oil</u>					
0	0.2	20.0	4.2	64.2	11.4
6	0.3	21.6	4.8	67.7	5.5
12	0.2	19.8	4.1	70.8	5.1
<u>Fat extracted from potatoes</u>					
1	Tr	16.9	4.8	61.9	16.3
3	Tr	16.2	7.5	61.3	15.1
6	0.2	15.5	5.8	64.0	14.5
9	Tr	15.3	6.9	63.8	14.0
12	0.3	17.2	6.1	56.1	18.9