

The Formation of Isomers of Polyunsaturated Acids During the Hydrogenation of Soybean Oil

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IN the past three decades there have been numerous investigations of the various factors affecting the selectivity of hydrogenation of glyceride oils and fats. By selectivity is meant the preferential hydrogenation of the more unsaturated components.

The classical work of H. K. Moore, Richter, and van Arsdel (1), in 1917, established several general rules governing selective hydrogenation which have repeatedly been confirmed in principle since that time. They showed that in batch hydrogenations selectivity could be increased by increasing the temperature up to 200° C., and by decreasing the hydrogen pressure, the rate of agitation or the quantity of catalyst employed. During hydrogenation they found that the amount of linoleic acid present decreased, saturated acids increased, while the oleic acid passed through a maximum.

In 1919 C. W. Moore (2) discovered that the nature of the catalyst and the temperature employed in hydrogenation play an important part in the formation of "isoöleic" acid. Richardson, Knuth, and Milligan (3, 4) found selectivity to increase to about 200° C. but presented evidence that an increased amount of catalyst favored selectivity.

Professor Hilditch and his coworkers conducted an extended series of investigations concerning selective hydrogenation (5, 6, 7, 8, 9, 10). In general, their results confirmed the earlier work above. They extended the concept of selective hydrogenation of individual component fat acids to include the selective hydrogenation of triglycerides (7). Thus during the hydrogenation of a natural fat all triunsaturated glycerides are hydrogenated to diunsaturated-monosaturated before any other types are affected. For example, during the first half of the hydrogenation of cod-liver oil the production of trisaturated glycerides was negligible (9).

Essentially all of the above investigations were conducted at atmospheric pressure. Recently, Bailey, Feuge, and Smith (11) have studied hydrogenation of cottonseed and peanut oils at pressures similar to those used in commercial practice. Their calculations, based upon thiocyanogen numbers, iodine numbers, and saturated acid-isoöleic acid analyses, indicated that both selectivity and isoöleic acid production were favored by increasing the catalyst and by decreasing the pressure and/or agitation.

The present work was instituted in order to study the selectivity of hydrogenation under conditions similar to commercial operations, using the spectrometric method of analysis to determine the changes produced in the polyunsaturated fat acids. Samples of soybean oil were partially hydrogenated under varying conditions of hydrogen pressure, temperature, and catalyst concentration. Fractions of the oil were removed from the converter at intervals approximating drops of six iodine value units and the fat acid composition of each fraction was obtained by the customary methods. Linoleic and linolenic acids were determined

spectrometrically, and from these values and the iodine value the amounts of oleic acid were calculated. Saturated acids were obtained by difference.

From the analyses thus obtained no significant alteration of selectivity appeared to be effected by varying the conditions of hydrogenation within the usual limits of plant operation. However, selectivity of hydrogenation was observed although not to the extent that might be expected from the references cited above. Linolenic acid disappeared at a greater rate than did linoleic while the oleic acid concentration increased rapidly. These data looked reasonable until the saturated acids were obtained by difference. The calculated amounts of saturated acids present decreased during the progress of each hydrogenation. Obviously, such a condition is impossible.

At this stage of the work a similar investigation was reported by Lemon (12). He had observed the same phenomenon as above during the hydrogenation of linseed oil. His calculations by both the thiocyanogen and the spectrometric methods led to impossible answers. Lemon's explanation for this anomaly was "that hydrogenation of linolenic acid causes the formation of an isomeric linoleic acid that differs from natural linoleic acid in that the double bonds are so arranged that they will not form a conjugated system." In addition, his data would appear to indicate that the isomer does not react normally with the thiocyanogen reagent. The mechanism proposed by Lemon is that normal 9-, 12-, 15-linolenic acid hydrogenates preferentially at the 12:13 ethylenic linkage, yielding a 9-, 15-octadecadienoic acid whose double bonds are too far apart to form a conjugated system on treatment for spectrometric analysis.

IN the present work the above explanation appeared incomplete inasmuch as the loss of linolenic acid during the hydrogenation of soybean oil was insufficient to account for the amount of isolinoleic acid which must have been formed as deduced from our data. (Unfortunately, analyses for saturated, isoöleic, and iso-linoleic acids were impossible as the samples had been discarded before the calculations were made.)

An alternative hypothesis which occurred to us was that during hydrogenation there might be isomerization of all the unsaturated acids, caused by shifting of the double bonds. There has been considerable evidence in the literature favoring such a hypothesis. Moore (2) found 10- and 11-octadecenoic acids in the hydrogenation products of oleic acid. He stated that such a change did not occur in the absence of hydrogen. 10-octadecenoic acid has been isolated from the products of the hydrogenation of sunflower seed oil (13). Hilditch and Vidyarthi (14, 15) found 8- and 10-octadecenoic acids in the hydrogenation products of methyl oleate; 8-, 10-, 11-, and 12-octadecenoic acids from methyl linoleate. Bauer and Krallis (16, 17) indicated that not hydrogenation but heat alone

in the presence or absence of metallic catalyst caused the production of 8- and 10-octadecenoic acids from oleic acid. Lund (18) has reported that by selective hydrogenation of linseed oil there is formed a dienoic acid which added two moles of thiocyanogen reagent.

In an effort to establish the above hypothesis several samples of soybean oil containing nickel catalyst were heated for varying lengths of time under vacuum. On each sample analyses were made for iodine number, thiocyanogen number, and spectrometric linoleic, linolenic, diene conjugation and triene conjugation. In every case there was a decrease in the amounts of linoleic and linolenic acids, accompanied by a smaller increase in diene and triene conjugated acids. It is thus evident that under these conditions considerable shifting of the position of the double bonds had occurred. On the basis of Moore's work (2) it is probable that more extensive isomerization occurs in the presence of hydrogen.

Experimental

Analytical Methods: Iodine numbers were determined using Wijs reagent. Thiocyanogen numbers were run according to the A.O.A.C., using 0.2 N. reagent and 24-hour storage. Linoleic and linolenic acids were determined by a slight modification of the spectrometric method of Mitchell, Kraybill, and Zscheile (19). A 0.1 gram sample of fat is isomerized in 2 ml. of a 10% solution of KOH in ethylene glycol by heating at 185° C. for 30 minutes. The isomerized soaps were dissolved in double distilled water and diluted to suitable concentrations for spectrometric density readings at 2340Å and 2700Å, using a Gaertner quartz spectrograph (Model L 250-93).

The amounts of diene and triene conjugated acids were calculated from spectrometric measurements of the oil samples dissolved in purified cyclohexane, as described by Bradley and Richardson (20).

Hydrogenation of Soybean Oil. In all hydrogenations samples of commercial refined and bleached soybean oils were used. They were hydrogenated under the following conditions in a steam jacketed converter fitted with a paddle agitator and hydrogen circulating pump.

1. Forty-three pounds of oil and 16 grams of commercial nickel catalyst (reduced nickel formate supplying 25% nickel suspended on 75% hard fat) at 30-lb. pressure and 380-390° F. (193-199° C.).

2. Forty-three pounds of oil and 25 grams of catalyst at 30-lb. pressure and 300° F. (149° C.).

3. Forty-three pounds of oil and 25 grams of catalyst at one-pound pressure and 390° F. (199° C.).

During the progress of the hydrogenation samples were removed at intervals. The catalyst was removed

from each sample by filtration at 160-180° F. with filter-aid and bleaching earth. This treatment was kept as consistent as feasible. The filtered samples were then analyzed by the above methods. These data and the subsequent calculations of the fat acid compositions of the fractions are listed in Table I.

TABLE I
Analysis of Fractions Taken During Hydrogenation of Soybean Oils

Length of Hydrogenation (minutes)	Iodine Number	Spectrometric Analysis		Calculated Oleic Glycerides	Calculated Saturated Glycerides
		Linoleic Glycerides	Linolenic Glycerides		
(380-390° F., 30 lb. pressure, 16 gm. catalyst)					
0	132.3	56.3	8.1	15.7	19.9
8	123.0	47.9	6.2	27.6	18.2
13	121.4	46.2	5.6	31.0	17.2
20	117.5	41.3	5.1	37.9	15.7
32	111.8	33.0	4.1	51.0	11.9
50	107.7	30.6	3.0	54.4	12.0
(300° F., 30 lb. pressure, 25 gm. catalyst)					
0	132.3	56.3	8.1	15.7	19.9
7	127.2	47.7	7.1	30.2	15.0
14	124.1	47.5	5.8	30.9	15.8
40	111.7	35.6	3.8	46.6	14.0
54	108.0	33.3	3.0	49.3	14.4
(390° F., 1 lb. pressure, 25 gm. catalyst)					
0	130.5	50.5	7.5	27.1	14.9
13	122.8	47.7	5.3	30.5	16.5
28	114.6	39.5	4.4	40.3	15.8
48	109.0	33.8	2.8	50.1	13.2
68	104.0	29.6	2.2	54.6	13.6
98	100.5	24.2	1.7	62.9	11.3

Heat Treatment of Soybean Oil Containing Nickel Catalyst. Three samples of refined and bleached soybean oil were heated with nickel catalyst (same as above) under normal hydrogenation conditions with the exception that the sample was maintained under vacuum rather than hydrogen pressure. In one case samples were removed at intervals. As each portion of oil was taken from the converter the catalyst was removed by filtration with filter-aid and bleaching earth. The treatment of these samples and subsequent analyses are listed in Table II.

Discussion

From Table I it is evident that in all the hydrogenations a considerable degree of selectivity existed. Linolenic acid disappeared at about double the rate of linoleic acid in terms of the amounts originally present. The rates of hydrogenation of the polyunsaturated acids were sufficiently greater than that of oleic acid that the amount of the latter increased considerably. However, very little effect is noted due to variations of conditions although selectivity appears to be favored somewhat by the higher temperatures.

TABLE II
Changes in Characteristics of Soybean Oils Produced by Heating at 400° F. in the Presence of Nickel Catalyst

Time of Heating	Weight of Catalyst per Kg. of Oil	Iodine Number	Thiocyanogen Number	Spectrometric Analysis			
				Linoleic Acid	Linolenic Acid	Diene Conjugation	Triene Conjugation
				per cent	per cent	per cent	per cent
0	2	133.9	84.9	52	8.3	0.4	0.1
120	2	131.0	83.9	47	7.9	1.2	0.3
0	2	134.2	88.1	51	8.8	0.4	0.1
120	2	128.6	83.1	49	8.3	2.0	0.4
0	4	134.2	88.1	51	8.8	0.4	0.1
30	4	132.5	86.8	50	8.5	0.8	0.2
115	4	131.7	86.9	48	9.0	0.9	0.2
205	4	131.8	86.7	47	8.3	1.3	0.3
360	4	130.1	84.1	48	8.8	1.4	0.3

The anomalous results obtained in calculating the saturated acids present complications of the utmost significance. It has always been assumed for the purpose of analyses that the products of hydrogenation were, or reacted like normal fat acids. In natural, unhydrogenated fats one can obtain a reliable fat acid analysis from the iodine number and spectrometric data. Such an analysis is obviously impossible with hydrogenated fats. With our present knowledge and techniques it will be necessary that a direct analysis of saturated acids and isooleic acid contents be made in conjunction with the above analysis if a reasonably reliable composition is to be obtained.

In all three samples the heat-nickel treatment (Table II) caused a decrease in spectrometric linoleic acid and an increase in conjugated acids, evidently the result of induced isomerization. These changes, however, are not large enough to account for all the iso-linoleic acid produced in the hydrogenations, which leads to the suggestion that hydrogen may serve as an additional activator of the isomerization. In addition to the changes in spectrometric data there is a gradual decrease in both the iodine numbers and thiocyanogen numbers of the oils during the heat-nickel treatment. These changes might well have been anticipated from the isomerization of the polyunsaturated acids inasmuch as it is common knowledge that iodine and thiocyanogen reagents do not react normally with conjugated double bonds and, further, Lemon (12) has pointed out that his "isolinoic" acid does not absorb thiocyanogen in the expected manner.

The above observations lend a marked degree of confusion to the fat acid analysis of hydrogenated fats. It appears certain that the heat-nickel treatment caused changes within the fat molecules which result in lowered iodine numbers, thiocyanogen numbers, and spectrometric linoleic acid determinations but not in decreased total unsaturation (i.e. total

number of double bonds). Thus, at the moment it is difficult to conceive any reasonably simple and uncomplicated method for the analysis of hydrogenated fats which can lead to a true fat acid composition. The need for further intensive research in this direction is evident.

Summary

Spectrometric and iodometric analyses of hydrogenated fats and of heat-nickel treated oils indicate that during hydrogenation there are formed isomers of polyunsaturated acids which do not react normally upon analysis, making it impossible to obtain a valid fat acid composition by the usual methods.

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A Modified Kreis Test Suitable for Photocolorimetry

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Summary

A sensitive form of the Kreis test for rancidity in fats and oils is described, in which the reaction occurs in a one-phase system, which is suitable for direct photometric measurement. The procedure is convenient and rapid and yields reproducible results.

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BECAUSE of its sensitivity and simplicity, the Kreis test (1, 2) is extensively used to detect oxidative deterioration in fats and oils. While the results are not a definitive index of rancidity, the information obtained is a highly useful supplement to other evidence.

A number of techniques have been proposed for the more precise evaluation of the concentration of

active substances (3, 4, 5). Of these, the methods that involve distribution of the color-forming substance into two liquid phases and separation and also those involving removal of the active material in a stream of inert gas and absorption require considerable manipulation and do not always yield reproducible results. The procedure of Walters, Muers, and Anderson (5) offers the advantage that the reaction is carried out in a one-phase system, which requires no separation for photometric measurement.

Trials with this latter method were, however, disappointing. The acid reagent (1 gram of trichloroacetic acid per 0.382 ml. of amyl acetate) is unstable, produces large, variable blank values, and is unpleasant to use. It was not possible to reduce the blank values by purification of the reagents. It was learned, however, that the color could be developed equally as

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