Kinetics of Linolenate Hydrogenation

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INVESTIGATIONS on the hydrogenation of linolenate have largely been prompted by the need for a conclusive solution to the flavor problem of soybean oil. For the successful answer to this problem, linolenate must be selectively hydrogenated over linoleate and oleate groups; in addition, to obtain a liquid cooking oil of highest nutritional value, the residual double bonds must be unisomerized, i.e., they must remain in the naturally occurring positions and configurations. The fundamental investigations aimed at solving the flavor problem further illustrate serendipity, in that this basic information developed with food uses in mind may find important applications to problems of fatty acid modification for industrial uses.

Literature dealing specifically with the hydrogenation of linolenate is limited. Lemon (17) hydrogenated linseed oil until no alkali-isomerizable acids were present and isolated an isolinoleic acid having at least one double bond in *trans*-configuration; Rebello and Daubert (20) isolated a mixture of at least three isomers, the 8,14- 9,15-, and 10,14-isolinoleic acids. Willard and Martinez (28) analyzed partially hydrogenated methyl linolenate by alkali isomerization and ultraviolet spectrophotometry and concluded that the initial reaction of hydrogenation strongly favors the 12 position. Equations describing the rate of hydrogenation of linolenate were formulated by Bailey (3) and evidence for direct reduction of linolenate to oleate was thus obtained. This listing brings the researches on linolenate hydrogenations up to date, except for the series of papers coming from the Northern Laboratory which are covered in this review.

Like kinetics generally, kinetics of hydrogenation are concerned with (a) the kinds and the amounts of reactants, intermediates, and products and (b) the rate at which these transformations take place. The complexity of products formed by the heterogeneous catalytic reduction of linolenate has defied fractionation and characterization procedures in the past and challenges the resolving power of the best modern techniques. In our researches such tools as countercurrent distribution with and without the addition of silver-ion complexing agents, capillary chromatographic columns, radioactively labeled intermediates, highly developed procedures for oxidative cleavage and double bond locations, mass spectrometry, alkali and lipoxidase isomerization, and ultraviolet and infrared spectrometry have been employed. Studies of the rates of reactions have employed radioactive tracers and digital computers. These physical procedures and new techniques will be cited throughout this review in discussing knowledge gained by their use.

Heterogeneously catalyzed hydrogenation has occupied most of the attention of research workers to date; however, other types of reductions exist, e.g., heterogeneous radiation activation. Still another type is homogeneous reduction which is also treated in the the present review.

Heterogeneous Catalysis. A mixture of reaction products formed by the addition of one mole of hydrogen/mole of linolenate has frequently been the starting material for isolation studies. The reaction

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TABLE I

Analysis of Hydrogenated Methyl Linolenate

Method of analysis	Monoene	Diene	Triene
	%	%	%
Alkali conjunction-spectro	......	7.1	18.5
Gas liquid chromatography	......	......	16.4
Countercurrent distribution	36.9	43.5	20.6

has been conducted at atmospheric hydrogen pressure, 140C and with an electrolytic nickel catalyst. It results in the formation of saturates, monoenes, and dienes in the proportions shown in Table I (25). Application of conventional gas chromatography with polyester columns reveals a broadening of monoene, diene, and triene peaks which will be subsequently shown to be caused by the formation of incompletely resolved geometric and positional isomers. In fact, only on the residual triene fraction is alkali isomerization, gas chromatography, and countercurrent distribution in agreement and its percentage able to be calculated.

Countercurrent distribution for a hydrogenation mixture between petroleum ether and acetonitrile solvents is shown in Figure 1. This solvent system has the distinct advantage in resolving monoene, diene, and triene esters, but not resolving the geometric and positional isomers within the group. By judicious combinations of fractions, as shown in Figure 1, multigram amounts of the individual isologues may be recovered for subsequent fractionation of their positional and geometric isomers and double bond location.

The complexity of the monoene fraction so obtained is illustrated in Figure 2, which gives a chromatogram from a 200-ft Apiezon capillary column. No less than nine individual components can be identified from the peak on these curves. Conventional fractional crystallization from aqueous methanol is surprisingly effective, as shown in the other two curves of Figure 2 in yielding the *cis* oleic acid component (B) principally in the filtrate fraction and restricting the *trans* elaidic acid (C) to the crystal fraction. Unfortunately, the resolution of other positional and geometric isomers is not clear-
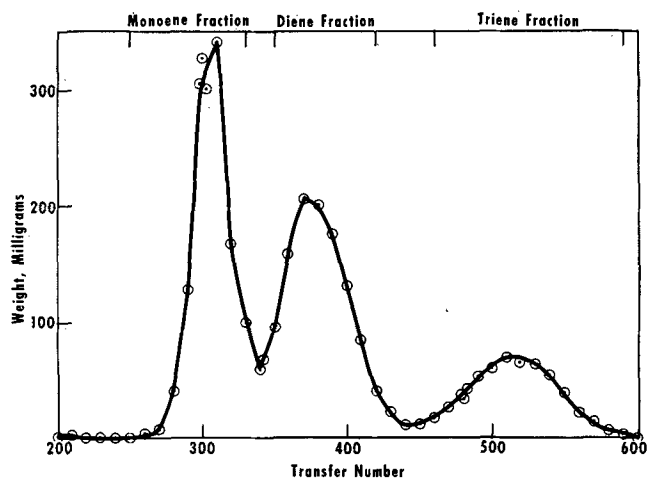

FIG. 1. Countercurrent distribution of hydrogenated methyl linolenate in a 200-tube instrument, with 40 ml acetonitrile for lower layer and 10 ml of pentane-hexane for upper layer.
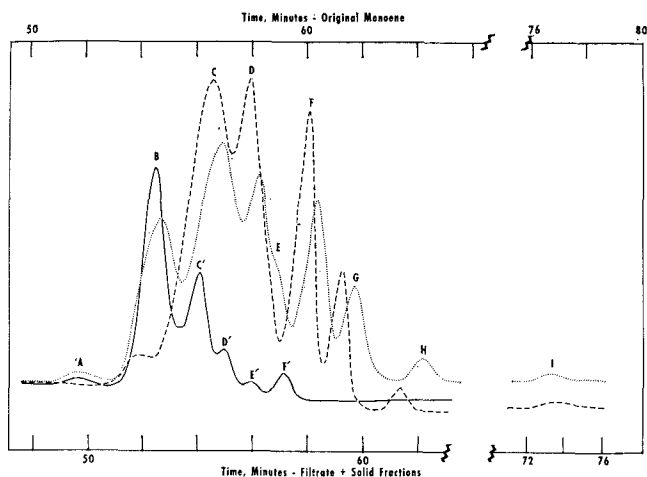
FIG. 2. Gas chromatogram of monoene portion of hydrogenated methyl linolenate and its liquid and crystal fractions from methanol at −35C from a 200-ft capillary column coated with Apiezon L and operated at 215C. Dotted line, monoene; dash line, crystal; solid line, filtrate.

cut among these monoenes. While multiple systematic fractional crystallization of monoene fractions has been carried out and shown to be effective in resolving this mixture (27), the labor involved in making the separations and performing analyses and the excessive losses of components into intermediate fractions have discouraged further use of this procedure. Fortunately, the needed tool for the resolution of geometric isomers has been provided by exploiting the tendency of silver ion to complex preferentially with cis bonds over trans bonds in countercurrent distribution solvent systems (12,22). Cis and trans monoenes are well-resolved and in high yield by countercurrent distribution between hexane and 0.2 N methanolic silver nitrate. Dibasic acids recovered after oxidative cleavage of the trans monoene fractions show that the double bonds are widely distributed except for a minimum at the 12 carbon atom and are in nearly a statistical pattern between the 6th and 17th carbon atom. Cis monoenes have their double bonds largely in the original 9, 12, and 15 positions.
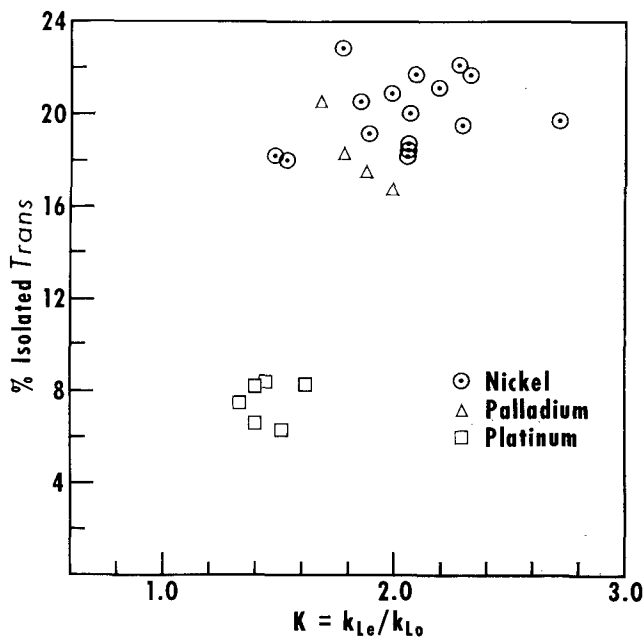

FIG. 3. A plot of selectivity ratio, K, to the percentage isolated trans in methyl esters for various hydrogenation catalysts.

Only the catalytic hydrogenation of methyl esters of linolenate has been discussed so far; however, trilinolenin has been hydrogenated under conditions nearly identical with those described (23). The isologues and isomers isolated were comparable in kind and amount to those found for methyl linolenate. This result was not anticipated because it was believed that restrictions imposed by the triglyceride structure over the monoester structure would make the 15,16 bond relatively more available for adsorption in the triglyceride form.

The second aspect of our kinetic problem is determining the rates by which the complex intermediates and the legion of products are formed. For practical application to the flavor stability problem, the ratio of reaction rates for linolenate to linoleate is most significant. The added objective, as pointed out earlier, is that the residual double bonds must also be unchanged with regard to their position of geometric configuration.

A procedure for evaluating catalysts for their selectivity and trans formation has been described (10). It consists in hydrogenating an equimixture of linoleate and linolenate with 0.5 mole of hydrogen/mole ester. Dienes, trienes, and monoenes are determined on the hydrogenated mixture by gas chromatography, and the value of the ratio for the reaction rate constants—linolenate to linoleate—is calculated after determining the percentage of remaining linolenate.

When this procedure was applied to a number of commercially available catalysts (14), wide differences in their isomerization characteristics were observed (6.3–22.8% trans). The ratio of reaction rate constants for linolenate to linoleate varied from 1.48–2.71 (Fig. 3). It was concluded that these ratios of reaction rates, however, were insufficiently high to eliminate linolenic acid effectively from soybean oil by hydrogenation alone.

In an extension of this research, the catalyst that demonstrated the highest linolenate selectivity and moderate isomerization tendency was selected for further intensive study to learn how the parameters of the hydrogenation reaction might influence the characteristics of the products (15). Temp of the reaction was varied from 70–230C and nickel concentration of the catalyst was varied from 0.005–10%. The results for the trans content of the ester over these experimentally practicable ranges are presented in Figure 4 as an isomeric drawing. The isomerization tendency of the catalyst is seen to be essentially a function of temp and is only slightly influenced by the concentration of catalysts. Selectivity with respect to attack on linolenic acid was shown to be little
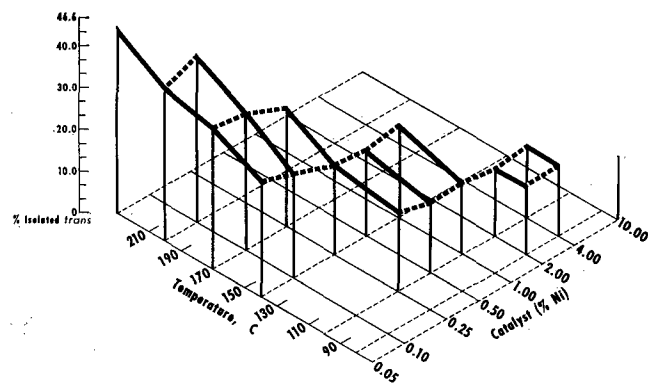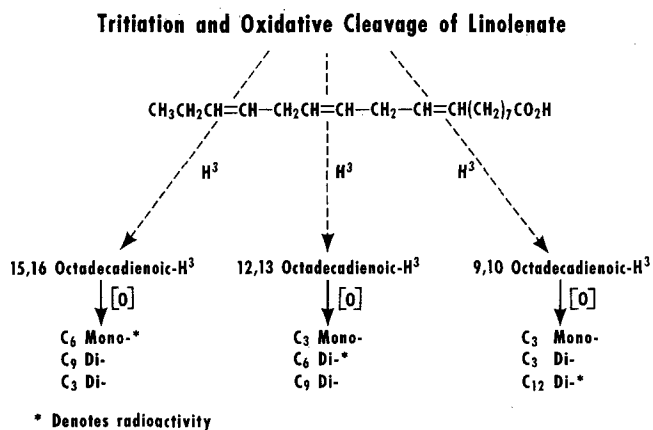

FIG. 4. Plot of isolated trans (vertical) versus temp and log of nickel concentration (horizontal axes).

affected by these two parameters. As would be expected from prior literature, the rate of hydrogenation depends strongly upon the temp and catalyst concentration. The implication of these results is that even smaller amounts of *trans* acids may be formed if one can lower the temp of hydrogenation.

Apparently there is a need for intensive research on catalyst preparations, particularly concerning the specificity of reduction of double bonds. There is also a great need for basic research and for new and novel approaches. For example, it is known that activation of hydrogen by an electric discharge will cause reduction of double bonds; reduction with hydrazine, to be discussed in a subsequent section on homogeneous catalysis, does provide one method of reducing double bonds without isomerization of those remaining.

A novel way of heterogeneously reducing double bonds without catalysts is to activate the fatty acids by beta radiation (16,19). Experimentally, 1–5 curies of high purity tritium gas is placed over methyl linolenate (11). This tritium serves both as a source of activating radiation and of the inserted radioactive label. The diene reduction product obviously is highly radioactive and has interest primarily for basic research purposes. Indications are, however, that this form of heterogeneous reduction by radiation is not specific with regard to its attack on any of the three double bonds of linolenate, and it has no tendency to isomerize the *cis* configuration of the residual bonds. The various paths of reduction of methyl linolenate, as indicated below, are supported by evidence from gas chromatography and dibasic analysis after oxidative cleavage:

Tritiation and Oxidative Cleavage of Linolenate

$$CH_3CH_2CH=CH-CH_2CH=CH-CH_2-CH=CH(CH_2)_7CO_2H$$

15,16 Octadecadienoic-H³	12,13 Octadecadienoic-H³	9,10 Octadecadienoic-H³
↓[O]	↓[O]	↓[O]
C₆ Mono-*	C₃ Mono-	C₃ Mono-
C₉ Di-	C₆ Di-*	C₃ Di-
C₃ Di-	C₉ Di-	C₁₂ Di-*

* Denotes radioactivity

The tritiated products have particular interest to further research on the mechanism of catalytic hydrogenation in that they present a source of dienes which occur during hydrogenation with the residual bonds in naturally occurring 9, 12, and 15 positions and are already labeled with tritium.

Recent researches with tritium-labeled intermediates, i.e., 9,10-octadecenoate-9,10-H³, have demonstrated that tritium is exchanged for hydrogen and appears in part in gas phase on saturation of the double bonds (6). In a similar manner when a catalytic deuteration is monitored by a mass spectrometer, the carbon-bonded hydrogen appears in gas phase diluting the deuterium. Both methyl oleate and methyl stearate isolated from the reaction mixture show extensive exchange of deuterium for carbon-bonded hydrogen (21). These observations of exchange and those of bond migration, isomerization, and saturation are collated by mechanisms currently accepted

in the field of petroleum and catalyst chemistry and involve half-hydrogenation (1) and alternation of mono- and diadsorbed alkanes (7).

Homogeneous Reduction. Two types of reduction of unsaturated fatty acids by homogeneous procedures have been recently published. deVries (9) has described the reduction of sorbic acid (2,4-hexadienoic acid) using pentacyanocobaltate II as catalyst. His reported selectivity with respect to reduction of the 4,5 bond has been confirmed in part by Mabrouk et al. (18), whose gas chromatographic analysis of products indicates 80, 19, and 1% yields of the 2-, 3-, and 4-hexanoic acids, respectively. Although this work does not confirm the absolute specificity of the attack on the 4,5 double bond of sorbic acid, the high degree of selectivity does encourage further study of homogeneous catalysts on higher fatty acids.

The utility of hydrazine for the homogeneous reduction of double bonds in organic materials has long been known, but it was only recently that Aylward and Rao (2) observed that hydrazine is effective for reducing a number of unsaturated fatty acids. This reaction was observed to proceed without isomerization of the residual bonds. By means of countercurrent distribution it was possible to separate the monoene from the diene, triene, and saturate and to determine the isomeric contents of the individual isologue (24). Oxidation of the separated monoene fraction by permanganate periodate mixture and by gas chromatography of the resultant dibasic acid shows that the double bonds were in the original 9, 12, and 15 positions and that the double bonds farthest from the carboxyl were reduced at a slightly faster rate than those closer. The gas chromatogram on a capillary column for the monoene fraction (Fig. 5) indicated three peaks, which were identified in order of their elution as the 9, 12, and 15 monoenes. In the diene fraction three components were identified in order of elution as the 9,12, 9,15, and 12,15 dienes. On alkali isomerization of this diene fraction only the 9,12 and 12,15 isomers were conjugated. These materials were then reacted with a maleic anhydride, and the unconjugated 9,15 isomer was separated by distillation.
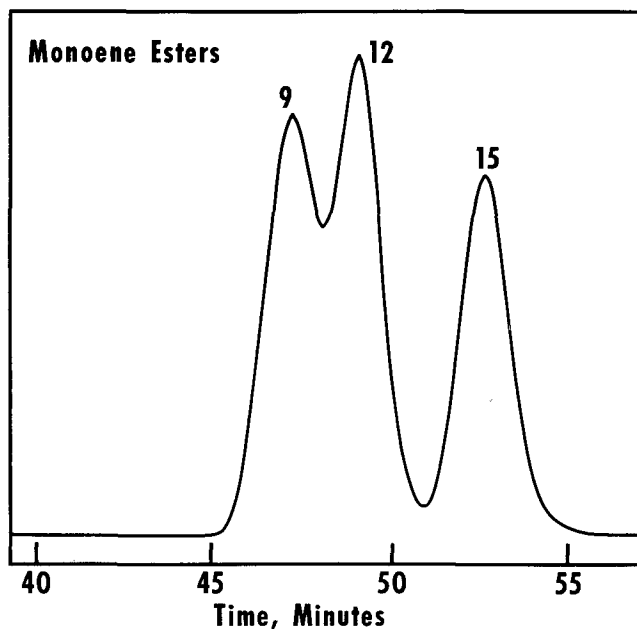

FIG. 5. Gas chromatogram of monoene fraction (200-ft capillary column).

At this time, it seems doubtful that hydrazine reduction has practical applications to the flavor problem of soybean oil because of the high toxicity of hydrazine and because of the reaction of hydrazine with the ester oxygen of glycerides to form hydrazides. Further, the reaction is essentially nonselective with regard to the attack on the 15 versus the 9 and 12 double bonds; however, as pointed out early and explained more in detail later, this basic research to solve a problem in the food use of soybean oil may result in important new industrial outlets for soybean oil.

Mathematical Description of Catalytic and Homogeneous Chemical Reduction. The discussion thus far about the reduction of linolenic acid has had little reference to the rates at which intermediates and products are formed. In 1949, Bailey (3) summarized the formation available on the catalytic reduction of triglyceride oils containing linolenic acid. He adapted first order equations for estimating rate constants for oleic, isolinoleic, linoleic, and linolenic acids according to the following scheme:
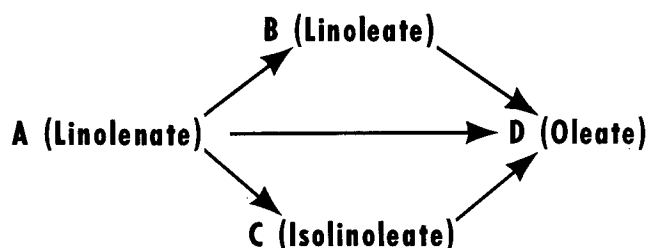
By empirical variations in reaction rate constants, so that the theoretical calculation would match the
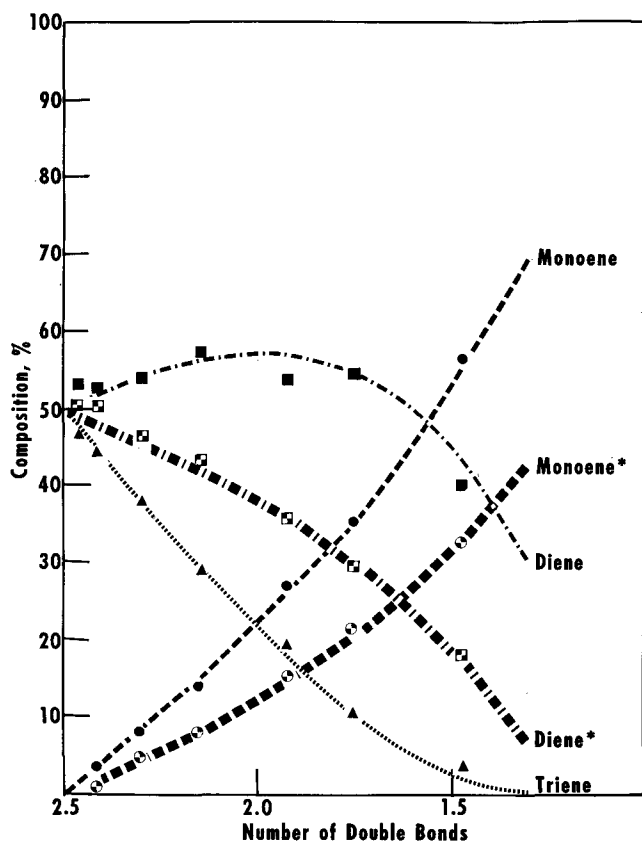
FIG. 6. Catalytic hydrogenation of a linolenate-linoleate mixture with C¹⁴-labeled linoleate calculated on basis that isolinoleate is formed and an oleate shunt occurs. Asterisks denote curves for radioactivity.

experimental data, he was led to conclude that a large proportion of linolenic acid was directly reduced to oleate not stopping at the linoleate stage. With the availability of C^{14}-labeled fatty acid methyl esters and of equipment for monitoring gas chromatographic effluents for these labeled compounds, it has been possible to confirm experimentally Bailey's suggestion in the case of catalytic reduction and to demonstrate the absence of the "oleate shunt" in homogeneous chemical reduction (26). Figure 6 shows the course of a catalytic hydrogenation for equal linolenate-linoleate mixtures to which C^{14}-labeled linoleate has been added. The good fit observed for gas chromatographic data of the inactive ester and particularly the agreement of the data for the radioactive content are possible only by consideration of the scheme involving isolinoleate and the oleate shunt, the specific rate constants for the reactions indicated, and the relative proportions of fatty acids that are reduced by various paths. In this experiment 29% of the linolenate reduced goes directly to the monoene level by the so-called oleate shunt.

By contrast, the hydrazine reduction of a similar mixture went by the simple mechanism—Linolenate→ Diene→Monoene→Saturate, according to simple first order reaction kinetics. The ratios for the reaction rate constants were approx the ratios of the number of double bonds present.

C_9, C_{12}, and C_{15} *Dibasic Acids from Hydrazine-Reduced Linolenic Acid.* Although the chief significance of the hydrazine reduction reaction is probably that of providing a simple straightforward reduction reaction with a minimal number of intermediates and of providing fundamental information and new compounds valuable to basic research, some very practical applications are apparent. Linolenic acid by virtue of its unsaturation at the 9, 12, and 15 carbon atoms potentially constitutes a unique commercial source of C_{12} and C_{15} dibasic acids. The required processing steps are (a) the reduction and separation of monoenoic acids, (b) oxidative cleavage at the double bond, and (c) separation of the resultant dibasic acids. It is apparent from Table II that if one isolates the monoenes from hydrazine-reduced linolenic acid, that one will have an approx equal mixture of the 9, 12, and 15 octadecenoic acids. On oxidative cleavage, approx equal molar amounts of the 9, 12, and 15 dibasic acids should be obtained.

The kinetics for the hydrazine reduction of linolenic acid, presented in Figure 7, are those calculated using the specific reaction rate constants determined as mentioned above. This kinetic pattern is also readily obtained with the use of analog computers (8). It is apparent that the large experimental reduction indicated by the data points on the curve was near

TABLE II

Approximate Yields for Fatty Acid Isomers and Derived Dibasic Acids.

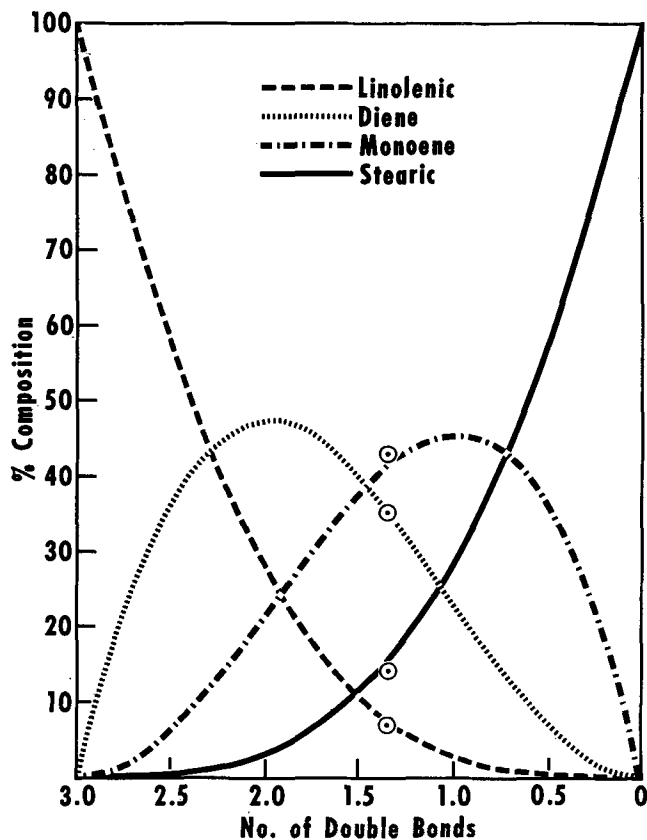| Yield of dibasic acids	Fatty acids	Yields of isomeric fatty acids
1 C₉ ←—O₃—	9,12,15 Octadecatrienoic	1
	↓	
2/3 C₉ ←—O₃—	9,12 Octadecadienoic	1/3
1/3 C₁₂ ←———	9,15 Octadecadienoic	1/3
	12,15 Octadecadienoic	1/3
	↓	
1/3 C₉ ←—O₃—	9 Octadecenoic	1/3
1/3 C₁₂ ←———	12 Octadecenoic	1/3
1/3 C̲₁₅	15 Octadecenoic	1/3
	↓	
	Octadecanoic	

FIG. 7. Kinetics for hydrazine reduction of linolenic acid calculated with ratios $k_{triene} :: k_{diene} :: k_{monoene}$ of $3.41 :: 2 :: 1$, respectively. Circles represent the composition of the laboratory-scale reduction.

an optimal point, i.e., near where maximal monoene content was obtained with minimal saturates and dienes. Although the desired C_9, C_{12}, and C_{15} dibasic acids may be obtained by direct ozonization of the reaction mixture, it is apparent that by first separating the monoenoic fatty acids from the reaction, one can recover the diene and triene for further reduction and can also have the advantage of oxidatively cleaving only the monoene fraction. Furthermore this procedure gives efficient use of raw materials and chemicals and gives a higher yield of the unusual and desired C_{12} and C_{15} dibasic acids. In large laboratory-scale experiments involving countercurrent extraction for the separation of the monoenoic fatty acids and the spinning band column for separation of dibasic acid methyl esters obtained by oxidative cleavage, the C_9 acids have been isolated in 92% purity, the C_{12} acids in 87% purity, and the C_{15} acids in 90% purity (13).

Anticipated reduction in cost resulting from its production as a rocket fuel suggests the need for reconsideration of hydrazine as an industrial chemical reactant. Estimates indicate that hydrazine produced by neutron irradiation of ammonia may result in prices as low as 15–25 cents/lb depending upon rate of production. At this price the chemical cost for reduction of a double bond/lb of linolenic acid is 2½ cents. Depending upon yield, efficiency of the reaction, and value of the product, conceivably hydrazine reduction may become an economically feasible reaction.

Whereas the outlet for the C_{15} dibasic acid has yet to be established, there is an immediate demand for C_{12} dibasic acid, for example, in the production of nylon 6,12. If production of a C_{12} dibasic acid was

the major objective, then reduction of linoleic acid would present a relatively straightforward method of making 12-octadecanoic acid resulting in the C_{12} dibasic acid. Pilot-plant procedures for the production of linolenic (5) and linoleic (4) acids in 90% or higher purity have been worked out. Further pilot-plant work may be justified to produce the C_{12} and C_{15} dibasic acids in amounts sufficient to evaluate their properties and determine the demand for them in commercial products such as polymers, plasticizers, and fibers.

In looking to the future then, one is inclined to end upon a philosophical note. The basic research that we initiated to solve the flavor problem in soybean oil now stands a good chance of turning up a practical process for the production of dibasic acids. On the other hand, it may very well be that a search for improved heterogeneous catalysts, which will yield the desired monoenoic acids at lower cost, may hold the answer to a solution of the soybean reversion problem. It is this serendipity and unpredictability which the research chemist experiences in his search for new information that give the endless excitement and fascination to his profession.

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