# Variables Affecting the Yield of Normal Oleic Acid Produced by the Catalytic Hydrogenation of Cottonseed and Peanut Oils[*]

A. E. BAILEY, R. O. FEUGE, and B. A. SMITH

Southern Regional Research Laboratory, Bureau of Agricultural Chemistry and Engineering,
U. S. Department of Agriculture, New Orleans, Louisiana

## Introduction

The fats and oils which contain glycerides of oleic and linoleic acids and only negligible quantities of other unsaturated acids comprise a large and industrially important group. They include, among others, cottonseed oil, peanut oil, palm oil, coconut oil, sesame oil, sunflower oil, corn oil, hog fat, and beef fat. When the oils of this group are subjected to catalytic hydrogenation, the initial tendency is largely for the hydrogen to enter into limited combination with the linoleic acid, with the formation of normal oleic acid. There is a lesser tendency for it to combine with oleic acid to form stearic acid, and for it to form solid or high melting oleic isomers, or so-called "iso-oleic" acid.

Early in the history of commercial hydrogenation it was recognized that the relative rates of formation of stearic, oleic, and iso-oleic acids were to some degree dependent upon the conditions under which the hydrogenation was conducted. The specific factors which may be independently varied in batch hydrogenation are the temperature, the hydrogen pressure, the degree of agitation of the catalyst-oil mass, the concentration of catalyst, and nature of the catalyst. The first workers to report an investigation of the effect of these variables were Moore, Richter, and Van Arsdel (8), who conducted a series of experiments with cottonseed oil and a nickel catalyst, and concluded that the conversion of linoleic acid preferentially to oleic acid ("selectivity") was favored by high temperature, low hydrogen pressure, a low degree of agitation, and a low concentration of catalyst. These workers made no attempt to estimate the content of iso-oleic acid formed in their reaction products. Richardson, Knuth, and Milligan (9) conducted a similar series of experiments using cottonseed, soybean, and peanut oils, with a nickel catalyst, and reported that selectivity was favored by high temperature and a high concentration of catalyst, and that the factors of pressure and agitation were relatively unimportant in determining the composition of the product. Richardson and co-workers determined the amount of iso-oleic acid formed in the hydrogenated products, and pointed out the error of Moore and co-workers in assuming that all of the solid acids in their products were saturated, but found no correlation between the formation of iso-oleic acid and operating conditions. In a later investigation, Richardson and Snoddy (10) used a platinum catalyst with cottonseed oil over a wide range of temperatures, and found that both selectivity and iso-oleic acid formation increased with increasing temperature. C. W. Moore (7) reported

that ethyl oleate when hydrogenated was converted partially into ethyl iso-oleate and that increased temperature favored this reaction. Mazume (6) observed that increased temperature favored the production of iso-oleic acid in the hydrogenation of soybean oil. Dhingra, Hilditch, and Rhead (3) found that an increase in either the temperature or the amount of catalyst made the hydrogenation of cottonseed oil with a nickel catalyst more selective and at the same time led to an increased production of iso-oleic acid. Gutman (5) found that the content of iso-oleic acid in hydrogenated sunflower oil increased with increase in temperature and decreased with a decrease in the rate of reaction. Etinburg, Sterlin, and Krushevskii (4), working with cottonseed and sunflower seed oils and a nickel catalyst, reported that selectivity was increased by increasing the temperature, but that the factors of catalyst and hydrogen concentration had to be correlated with each other for maximum selectivity.

It appears to be agreed that an increase in temperature simultaneously favors selectivity and iso-oleic acid formation. Evidence relative to the influence of the other factors, however, appears to be either conflicting, unsubstantiated, or entirely lacking. In connection with certain work in progress in the Southern Regional Research Laboratory, it became necessary to know the effects of all of the operating variables mentioned above, in order to be able to hydrogenate cottonseed and peanut oils with a maximum production of normal oleic acid, and a minimum loss of potential oleic acid through the formation of stearic or iso-oleic acids. The investigation reported here was consequently directed toward determining the effect of the different operating variables, establishing the optimum conditions for the laboratory treatment of cottonseed and peanut oils, and ascertaining the possible yields of normal oleic acid from these two oils.

## Experimental Procedure

The various hydrogenations were carried out in the apparatus illustrated in Figure 1, which consists essentially of a vertical, cylindrical steel vessel, designed for operation under moderate pressure, and provided with a motor-driven agitator of the paddle type. Hydrogen from an ordinary commercial cylinder was injected into the vessel at its bottom through an adjustable reducing valve, which served to maintain a constant pressure on the system. The temperature of the oil was measured by means of a potentiometer in conjunction with an iron-constantan thermocouple. Heat was supplied by a gas flame, and cooling was provided by a spray nozzle from which

water could be directed upon the sides of the vessel. Temperature control was entirely manual, but it was found to be easily possible to maintain the temperature within a range of one to two degrees Fahrenheit. The degree of agitation within the vessel was varied by simultaneously changing the speed of the
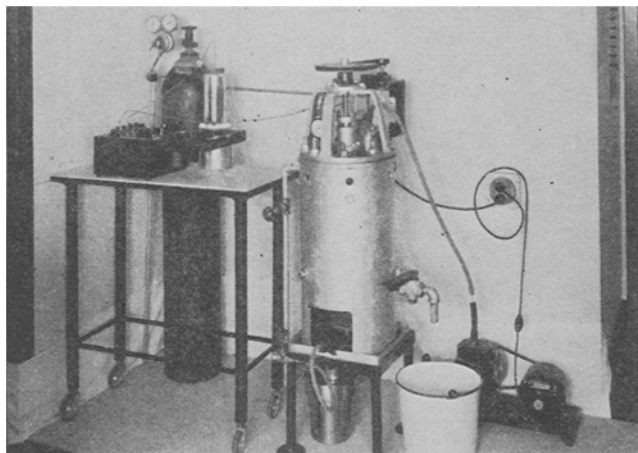


FIG. 1. Laboratory hydrogenation apparatus.

agitator and the size of the oil charge; a low speed and a large charge were used for low agitation, and a high speed and a small charge were used where high agitation was desired.

Three different nickel catalysts were used, which have been designated as Nos. 1, 2, and 3. Catalyst No. 1 was of the precipitated type, supported on kieselguhr and dry-reduced. It was of a type currently used for the production of all-hydrogenated vegetable shortening and was obtained from a commercial source in reduced form suspended in cottonseed oil. Catalyst No. 2 was prepared from nickel sulfate, by precipitation with sodium bicarbonate on kieselguhr, with subsequent dry reduction of the product at 900° F. Catalyst No. 3 was of the Raney, or nickel alloy type, and was prepared according to the directions given by the manufacturer, by treatment of the alloy with caustic soda. In all cases, the amount of catalyst used was calculated on the basis of its nickel content.

The official methods of the American Oil Chemists' Society (2) and the American Chemical Society (1) were used to determine the iodine and thiocyanogen values, content of solid acids, and the iodine values of the solid fatty acids of the hydrogenated oils. The composition of the oils in terms of saturated, oleic and linoleic acids was calculated from the iodine and thiocyanogen values. In making these calculations, however, the empirical thiocyanogen values suggested by Riemenschneider, Swift, and Sando (11) (89.4 for oleic; 96.8 for linoleic acid) were used, rather than the theoretical values of Kaufmann. The values thus found for total oleic acid were distributed to "normal" and "iso-" oleic acids on the basis of the yield and iodine number of the solid fatty acids by the modified Twitchell method. The methods of calculation used are summarized in the following equations and are those given in the official American

Oil Chemists' Society method, as modified by use of the empirical thiocyanogen values mentioned above:

I.V. = iodine value
T.V. = thiocyanogen value
M.A. = mixed fatty acids
S.N. = saponification number of oil
S.A. = solid fatty acids

$$\text{I.V. of M.A.} = \frac{(\text{I.V. of Oil})\,(100)}{100 - (0.02261)\,(\text{S.N.})} \tag{1}$$

$$\text{T.V. of M.A.} = \frac{(\text{T.V. of Oil})\,(100)}{100 - (0.02261)\,(\text{S.N.})} \tag{2}$$

Total oleic acid, per cent = (2.4185) (T.V. of M.A.) —(1.2931) (I.V. of M.A.)     (3)

Linoleic acid, per cent = (1.1943) (I.V. of M.A.)— (1.2006) (T.V. of M.A.)     (4)

Saturated acids, per cent = 100 — (percentage of total oleic acid + percentage of linoleic acid)     (5)

Iso-oleic acid, per cent = (0.011127) (percentage of S.A.) (I.V. of S.A.)     (6)

Normal oleic acid, per cent = (percentage of total oleic acid)—(percentage of iso-oleic acid)     (7)

In order to evaluate the effect of the different operating variables on the composition of the hydrogenated product, it was necessary to select some common basis for an intercomparison of the various hydrogenation experiments. It would appear logical for such a basis to be a specified degree of hydrogen absorption, or in other words, a specific iodine value of the hydrogenated oil. It was impracticable, with the apparatus used, to hydrogenate the charge of oil in each case precisely to a specific iodine number, but an equivalent result was achieved by withdrawing two or three samples at successively decreasing iodine numbers near the desired value and then determining the composition at this value graphically, by interpolation between the observed values. Actually, this method has a considerable advantage over that of examining a single sample, since it furnishes an additional check on the accuracy of the individual analyses. The hydrogenation curve is quite definite in form and any analysis inconsistent with it is likely to be erroneous. The method of making the interpolation, using triangular diagrams, is illustrated in Figure 2, for the three component system, saturated acids-total oleic acids-linoleic acid. The graphical representation of the system, solid acid-normal oleic acid—linoleic acid, is entirely similar, as illustrated in Figure 3.

As may be noted from an examination of Figure 2, the iodine values chosen for comparison of the cottonseed and peanut oil fatty acids, 65.7 and 72.6, respectively, are in each case critical in the sense that they are the minimum values at which the linoleic acid could have been wholly converted to oleic acid, and are the values which would have been found at 100 per cent linoleic acid disappearance, if the hydrogenation had been wholly selective.

In order to avoid any uncertainties arising from minor differences in the composition of the oil charges, and to make all results on a given type of oil strictly comparable, single lots of refined and

bleached cottonseed and peanut oil were set aside and used for all of the work. The analytical data on the two original oils are recorded in Table 1. The composition of the cottonseed oil is normal for oils from the East Texas area; the peanut oil is somewhat higher in iodine number and linoleic acid than is usual for American peanut oils.

### The Effects of the Operating Variables

The operating conditions under which the various experimental runs were made, and the analyses of the hydrogenated products are recorded in detail in Table 2.

The fatty acid composition of the hydrogenated cottonseed oils is recorded in Table 3 for each run at the critical iodine value of 65.7 for the acids, or 62.9 for the oil, and the results have been arranged so as to show the effect of each of the different independent operating variables. The results show quite definitely that selectivity, as evidenced by the repression of stearic acid formation and the elimination of

#### TABLE 1

Analysis of cottonseed and peanut oils used in laboratory hydrogenations

| | Cotton-seed oil | Peanut oil |
|---|---|---|
| Iodine value | 103.0 | 97.7 |
| Thiocyanogen value | 65.8 | 71.3 |
| Saponification number | 195.6 | 191.2 |
| Unsaponifiable matter, per cent | 0.58 | 0.38 |
| Solid acids, modified Twitchell method,per cent | 27.3 | 21.1 |
| Iodine value of solid fatty acids | 3.7 | 3.6 |
| Composition of fatty acids, per cent* | | |
| Saturated acids | 26.9 | 19.2 |
| Oleic acid | 27.1 | 48.3 |
| Linoleic acid | 46.0 | 32.5 |

\* Calculated from iodine and thiocyanogen values.

linoleic acid, is favored by increasing the temperature or the catalyst concentration, and by decreasing the pressure or the agitation. The formation of iso-oleic acid is favored by each of the conditions contributing to selectivity, being increased by raising the temperature or the catalyst concentration and by decreasing the pressure or agitation. The reactions leading to the formation of stearic and iso-oleic acid, therefore,
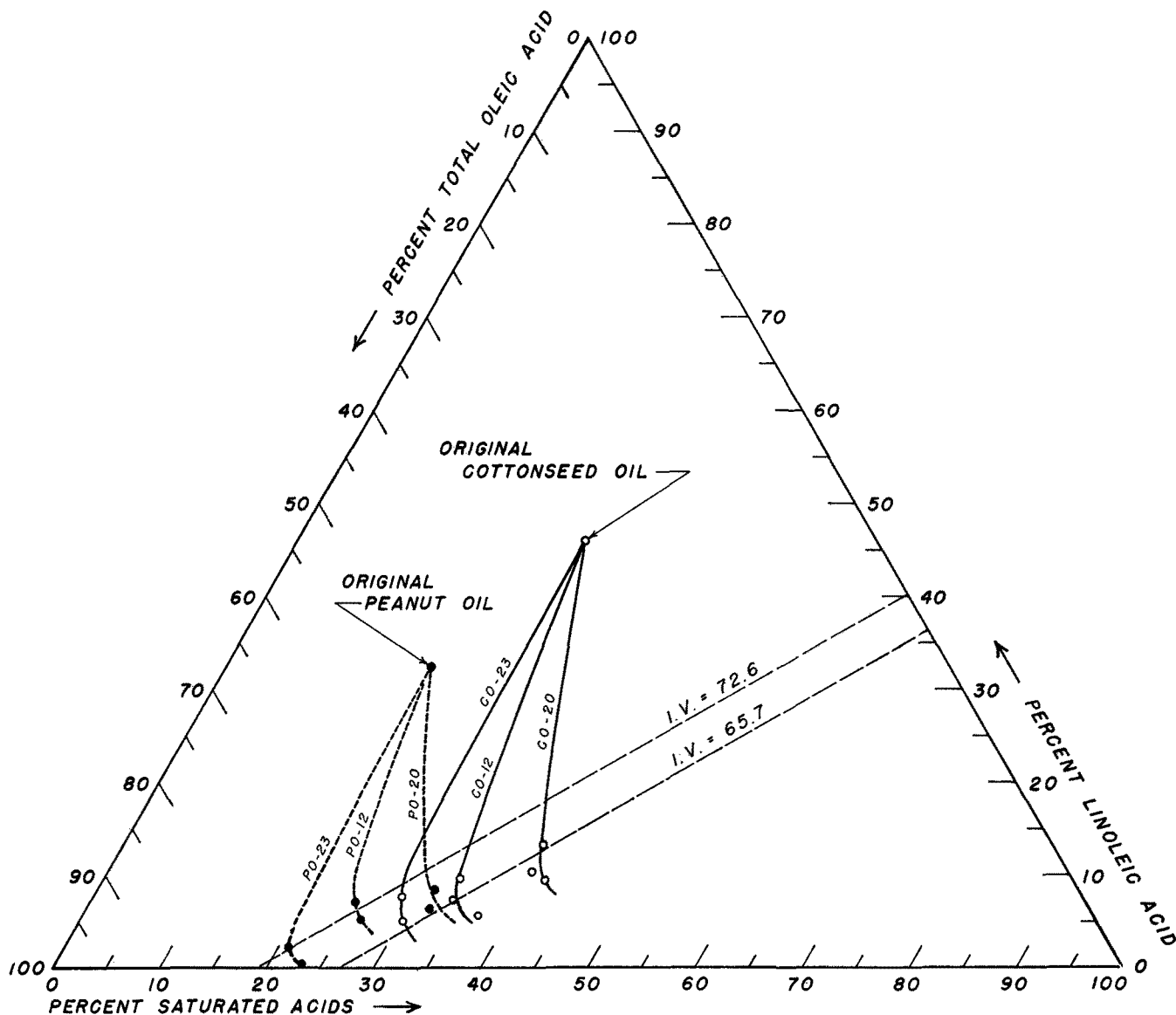


FIG. 2. Diagram used for estimating the composition of the various hydrogenated products at their critical iodine values.

tend to balance one another, so that the production of normal oleic acid remains relatively constant under a comparatively wide range of hydrogenation conditions. If conditions are such as to make either saturated or iso-oleic formation extreme, however, there is a decrease in the normal oleic acid produced. It should be noted that, in most of the experimental runs, extreme conditions did not obtain, as the factor investigated in each case was varied over a comparatively limited range. Run CO-20, however, represents a set of conditions under which the formation of stearic acid begins to become rather large and Run CO-23 illustrates the effect of conditions conducive to the production of large quantities of iso-oleic acid. It should be particularly noted that factors other than temperature may exhibit a marked effect on the formation of iso-oleic acid, which at a temperature of 300° F. was observed to vary from 10.2 per cent, in the case of Run CO-17, to 20.4 per cent in the case of Run CO-23. The rate of hydrogenation, *per se*, appears to be without effect on the composition of the product.

In attempting to determine whether the specific nature of the catalyst may have an effect on the composition of the hydrogenated products, no consideration was given to the use of metals other than nickel, since nickel is used almost, if not quite exclusively, in commercial operations. Certain difficulties arise in making comparisons between different catalysts, because of the wide variability of their activities. It has been shown by Taylor (12) and others that only a relatively small portion of the metal in a nickel catalyst is actually catalytically active, the remainder of the metal being quite inert. Consequently, comparisons of catalyst concentration cannot be made solely upon the basis of total nickel content where more than one catalyst is involved. If two hydrogenation experiments are conducted under identical conditions and with equal concentrations of metallic nickel, but with the use of different catalyst preparations, an observed difference in the hydrogenated products may not be due to a difference in the nature and consequent modes of action of the two catalysts, but rather to the fact that in one case
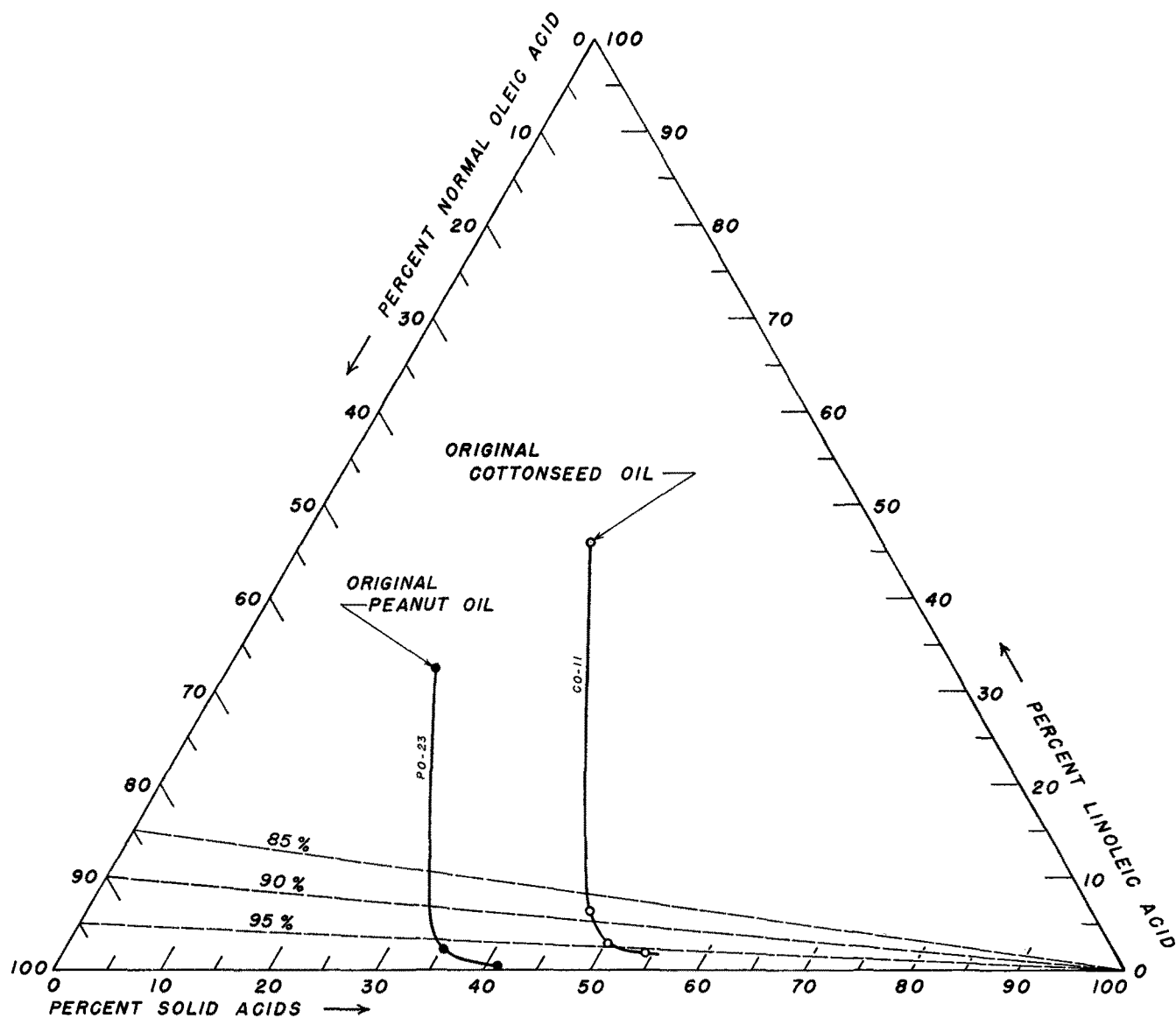


FIG. 3. Diagram for estimating yields of oleic acids of various degrees of purity.

TABLE 2

Details of operating conditions for the laboratory hydrogenation of cottonseed and peanut oils and analysis of the hydrogenated products

| Run and sample No. | Kind of oil | Temperature | Pressure lbs. per sq. in. | r.p.m. and lbs. of oil | Catalyst nickel | Cata-lyst No. | Hydro-genation time | Iodine value of oil | Thiocy-anogen value of oil | Solid acids | Iodine value of solid acids | Percentage composition of fatty acids | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | Satu-rated | Iso-oleic | Norm.-oleic | Lin-oleic |
| | | °F. | | | pct. | | min. | | | pct. | | | | | |
| CO-20-1 | Cotton | 250 | 27 | 408-12 | 0.050 | 1 | 70 | 63.7 | 52.8 | 43.3 | 18.2 | 39.3 | 8.8 | 38.6 | 13.3 |
| CO-20-2 | Cotton | 250 | 27 | 408-12 | 0.050 | 1 | 75 | 61.0 | 52.4 | 43.8 | 16.3 | 39.6 | 7.9 | 42.1 | 10.4 |
| CO-20-3 | Cotton | 250 | 27 | 408-12 | 0.050 | 1 | 80 | 58.6 | 50.8 | 44.8 | 17.0 | 41.3 | 8.5 | 40.7 | 9.5 |
| CO-12-1 | Cotton | 300 | 27 | 408-12 | 0.050 | 1 | 28 | 65.5 | 57.5 | 40.8 | 22.7 | 33.4 | 10.3 | 46.6 | 9.7 |
| CO-12-2 | Cotton | 300 | 27 | 408-12 | 0.050 | 1 | 30 | 63.3 | 57.1 | 42.0 | 23.7 | 33.8 | 11.1 | 47.7 | 7.4 |
| CO-12-4 | Cotton | 300 | 27 | 408-12 | 0.050 | 1 | 35 | 59.2 | 54.3 | 45.0 | 23.1 | 37.0 | 11.6 | 45.7 | 5.7 |
| CO-18-2 | Cotton | 350 | 27 | 408-12 | 0.050 | 1 | 17 | 65.9 | 59.2 | 42.8 | 28.8 | 31.4 | 13.7 | 46.9 | 8.0 |
| CO-18-3 | Cotton | 350 | 27 | 408-12 | 0.050 | 1 | 19 | 62.6 | 57.9 | 45.2 | 28.4 | 32.6 | 14.3 | 47.6 | 5.5 |
| CO-18-5 | Cotton | 350 | 27 | 408-12 | 0.050 | 1 | 23 | 58.5 | 54.9 | 48.5 | 28.1 | 36.2 | 15.2 | 44.4 | 4.2 |
| CO-19-2 | Cotton | 300 | 5 | 408-12 | 0.050 | 1 | 60 | 65.7 | 58.8 | 41.1 | 26.1 | 31.9 | 11.9 | 48.0 | 8.2 |
| CO-19-3 | Cotton | 300 | 5 | 408-12 | 0.050 | 1 | 66 | 63.1 | 58.0 | 43.3 | 27.3 | 32.6 | 13.2 | 48.3 | 5.9 |
| CO-19-5 | Cotton | 300 | 5 | 408-12 | 0.050 | 1 | 80 | 59.2 | 55.4 | 45.6 | 26.2 | 35.6 | 13.3 | 46.7 | 4.4 |
| CO-17-2 | Cotton | 300 | 50 | 408-12 | 0.050 | 1 | 18 | 66.6 | 57.3 | 40.0 | 21.6 | 33.9 | 9.6 | 45.2 | 11.3 |
| CO-17-3 | Cotton | 300 | 50 | 408-12 | 0.050 | 1 | 20 | 64.1 | 56.1 | 41.7 | 22.0 | 35.2 | 10.2 | 45.1 | 9.5 |
| CO-17-5 | Cotton | 300 | 50 | 408-12 | 0.050 | 1 | 24 | 59.7 | 53.4 | 43.6 | 20.4 | 38.1 | 9.9 | 44.6 | 7.4 |
| CO-11-2 | Cotton | 300 | 27 | 290-16 | 0.100 | 1 | 96 | 64.9 | 59.4 | 42.7 | 31.6 | 31.1 | 15.0 | 47.4 | 6.5 |
| CO-11-3 | Cotton | 300 | 27 | 290-16 | 0.100 | 1 | 108 | 60.1 | 57.5 | 47.5 | 31.4 | 33.0 | 16.5 | 47.5 | 3.0 |
| CO-11-4 | Cotton | 300 | 27 | 290-16 | 0.100 | 1 | 120 | 55.4 | 53.4 | 51.1 | 29.3 | 37.7 | 16.7 | 43.6 | 2.0 |
| CO-15-2 | Cotton | 300 | 27 | 408-12 | 0.100 | 1 | 22 | 64.5 | 58.4 | 41.3 | 27.1 | 32.2 | 12.5 | 48.0 | 7.3 |
| CO-15-3 | Cotton | 300 | 27 | 408-12 | 0.100 | 1 | 24 | 62.4 | 57.7 | 42.4 | 26.1 | 32.9 | 12.3 | 49.3 | 5.5 |
| CO-15-4 | Cotton | 300 | 27 | 408-12 | 0.100 | 1 | 26 | 59.6 | 55.5 | 44.1 | 25.3 | 35.3 | 12.4 | 47.6 | 4.7 |
| CO-9-2 | Cotton | 300 | 27 | 528-8 | 0.100 | 1 | 11 | 65.1 | 57.8 | 41.0 | 22.0 | 33.0 | 10.0 | 48.3 | 8.7 |
| CO-9-3 | Cotton | 300 | 27 | 528-8 | 0.100 | 1 | 12 | 62.1 | 56.4 | 42.2 | 22.9 | 34.6 | 10.8 | 47.8 | 6.8 |
| CO-9-4 | Cotton | 300 | 27 | 528-8 | 0.100 | 1 | 13 | 60.0 | 55.0 | 43.6 | 22.2 | 36.1 | 10.8 | 47.1 | 6.0 |
| CO-16-3 | Cotton | 300 | 27 | 408-12 | 0.025 | 1 | 82 | 66.1 | 56.6 | 41.0 | 22.0 | 34.7 | 10.0 | 43.8 | 11.5 |
| CO-16-4 | Cotton | 300 | 27 | 408-12 | 0.025 | 1 | 94 | 63.6 | 56.2 | 43.3 | 23.4 | 35.0 | 11.3 | 44.9 | 8.8 |
| CO-16-6 | Cotton | 300 | 27 | 408-12 | 0.025 | 1 | 115 | 59.8 | 53.8 | 44.8 | 21.5 | 37.6 | 10.7 | 44.5 | 7.2 |
| CO-23-3 | Cotton | 300 | 10 | 290-16 | 0.300 | 1 | 165 | 67.8 | 61.3 | 46.8 | 37.4 | 28.9 | 19.5 | 43.9 | 7.7 |
| CO-23-4 | Cotton | 300 | 10 | 290-16 | 0.300 | 1 | 180 | 64.3 | 59.9 | 48.4 | 37.5 | 30.3 | 20.2 | 44.4 | 5.1 |
| CO-22-2 | Cotton | 300 | 27 | 408-12 | 0.050 | 2 | 31 | 66.5 | 57.2 | 49.8 | 32.3 | 34.1 | 17.9 | 36.7 | 11.3 |
| CO-22-3 | Cotton | 300 | 27 | 408-12 | 0.050 | 2 | 34 | 63.8 | 56.1 | 51.5 | 32.4 | 35.1 | 18.6 | 37.1 | 9.2 |
| CO-22-4 | Cotton | 300 | 27 | 408-12 | 0.050 | 2 | 38 | 60.4 | 54.9 | 56.2 | 34.7 | 36.3 | 21.7 | 35.4 | 6.6 |
| CO-21-2 | Cotton | 300 | 27 | 408-12 | 0.100 | 3 | 70 | 66.7 | 58.2 | 43.3 | 22.2 | 33.8 | 10.7 | 46.3 | 10.2 |
| CO-21-4 | Cotton | 300 | 27 | 408-12 | 0.100 | 3 | 85 | 62.4 | 56.6 | 42.6 | 22.9 | 34.4 | 10.9 | 47.8 | 6.9 |
| CO-21-5 | Cotton | 300 | 27 | 408-12 | 0.100 | 3 | 95 | 61.2 | 55.6 | 41.0 | 22.5 | 35.4 | 10.3 | 47.7 | 6.6 |
| PO-20-4 | Peanut | 250 | 27 | 408-12 | 0.050 | 1 | 36 | 66.1 | 59.0 | 35.5 | 12.5 | 31.6 | 4.9 | 55.0 | 8.5 |
| PO-20-5 | Peanut | 250 | 27 | 408-12 | 0.050 | 1 | 39 | 64.0 | 58.5 | 35.6 | 12.0 | 32.1 | 4.8 | 56.7 | 6.4 |
| PO-12-2 | Peanut | 300 | 27 | 408-12 | 0.050 | 1 | 15 | 70.9 | 64.8 | 30.5 | 18.8 | 24.8 | 6.4 | 61.6 | 7.2 |
| PO-12-3 | Peanut | 300 | 27 | 408-12 | 0.050 | 1 | 17 | 68.0 | 63.4 | 32.8 | 21.1 | 26.3 | 7.7 | 60.7 | 5.3 |
| PO-23-2 | Peanut | 300 | 10 | 290-16 | 0.300 | 1 | 150 | 69.9 | 67.7 | 35.1 | 34.8 | 21.0 | 13.6 | 63.1 | 2.3 |
| PO-23-3 | Peanut | 300 | 10 | 290-16 | 0.300 | 1 | 165 | 66.5 | 65.8 | 39.6 | 39.3 | 23.1 | 17.3 | 59.1 | 0.5 |

TABLE 3

Influence of various operating variables on the composition of hydrogenated cottonseed oil

| Run No. | Variable | Value of variables | Hyd. time, min. to crit. I.V. | Percentage composition of fatty acids at their critical iodine value of 65.7 | | | |
|---------|----------|--------------------|-------------------------------|-----------------|-------------|----------------|-------------|
| | | | | Satu-rated | Iso-oleic | Normal oleic | Lin-oleic |
| CO-20 | Temperature | 250° F. | 72 | 39.6 | 8.5 | 39.3 | 12.6 |
| CO-12 | Temperature | 300° F. | 31 | 34.1 | 11.2 | 47.5 | 7.2 |
| CO-18 | Temperature | 350° F. | 19 | 32.5 | 14.3 | 47.6 | 5.6 |
| CO-19 | Pressure | 5 lbs./sq. in., gage | 67 | 32.8 | 13.2 | 48.1 | 5.9 |
| CO-12 | Pressure | 27 lbs./sq. in., gage | 31 | 34.1 | 11.2 | 47.5 | 7.2 |
| CO-17 | Pressure | 50 lbs./sq. in., gage | 21 | 35.2 | 10.2 | 46.2 | 8.4 |
| CO-11 | Agitation | 290 r.p.m.—16 lbs. oil | 101 | 31.7 | 15.8 | 47.7 | 4.8 |
| CO-15 | Agitation | 408 r.p.m.—12 lbs. oil | 24 | 32.8 | 12.4 | 48.9 | 5.9 |
| CO-9 | Agitation | 528 r.p.m.— 8 lbs. oil | 12 | 34.2 | 10.7 | 47.8 | 7.3 |
| CO-16 | Amount of catalyst | 0.025% Ni | 98 | 35.1 | 11.0 | 45.7 | 8.2 |
| CO-12 | Amount of catalyst | 0.050% Ni | 31 | 34.1 | 11.2 | 47.5 | 7.2 |
| CO-15 | Amount of catalyst | 0.100% Ni | 24 | 32.8 | 12.4 | 48.9 | 5.9 |
| CO-12 | Nature of catalyst | No. 1—0.050% Ni | 31 | 34.1 | 11.2 | 47.5 | 7.2 |
| CO-22 | Nature of catalyst | No. 2—0.050% Ni | 35 | 35.2 | 19.2 | 37.2 | 8.4 |
| CO-21 | Nature of catalyst | No. 3—0.100% Ni | 85 | 34.1 | 10.7 | 48.0 | 7.2 |
| CO-16 | Nature of catalyst | No. 1—0.025% Ni | 98 | 35.1 | 11.0 | 45.7 | 8.2 |
| CO-23 | Pressure; agitation; amount of catalyst | 10 lbs./sq. in.; 290 r.p.m.; 16 lbs., 0.300% Ni | 190 | 31.0 | 20.4 | 44.6 | 4.0 |

a greater concentration of *active nickel* is present than in the other. For this reason, the comparative results with the three different nickel catalysts, as recorded in Table 3, must be interpreted with some discretion. It is clearly evident, however, even after making allowances for differences in active metal, that the three catalysts are by no means equivalent in their action. There appears to be no significant difference between Catalysts No. 1 and No. 3, but No. 2 produces considerably more iso-oleic acid than either of the other two, and correspondingly less normal oleic acid. Its tendency to form excessive amounts of iso-oleic acid is unaccompanied by any unusual degree of selectivity. Obviously, Catalyst No. 2 is a very poor catalyst for the production of normal oleic acid. Catalyst No. 1 is presumably a relatively good catalyst for this purpose, since good selectivity combined with good iso-oleic acid suppression is required in the production of hydrogenated edible products. It is evident that the nature of the catalyst ranks in importance with the factors of temperature, pressure, agitation, and catalyst concentration in determining the composition of the hydrogenated product.

In attempting to interpret the experimental data, it should be borne in mind that whereas the three factors of temperature, catalyst concentration, and pressure can be easily measured and reproduced, the fourth factor, agitation, is capable neither of quantitative representation nor of easy reproduction. Consequently, products of the composition of those reported here can be expected under equivalent conditions of temperature, pressure, and catalyst concentration only if the hydrogenation equipment is of such construction as to give an equivalent degree of agitation. Actually, the agitation in two different laboratory vessels will seldom be the same at equal stirrer speeds, and the efficiency of agitation in a small laboratory vessel will invariably be much greater than can be obtained in large-size commercial equipment. Agitation in a batch hydrogenator is quite a different matter from agitation in the commonly employed sense of the term. In hydrogenation, *mixing* of the body of oil is relatively unimportant, agitation being useful mainly insofar as it serves to

extend the interface between oil and gas, and thereby promote solution of the hydrogen in the oil. This interface exists in two dimensions and its magnitude is, therefore, a function of the second power of a linear dimension of the apparatus. The size of the oil charge, on the other hand, is a function of the third power of this same linear dimension, so that it is impossible to maintain the same ratio between the two in large and small vessels. There appears to be no reason why similar products cannot be made in equipment of widely differing capacities, if proper adjustments are made in the other operating variables to compensate for the difference in agitation. In other words, with decreased efficiency of agitation; less catalyst, higher pressure, and lower temperature would be indicated. In practice, the concentration to which the catalyst can be reduced is limited by the necessity of providing a minimum amount to absorb traces of catalyst poisons in the oil. To obtain products similar to those reported here, the commercial operator would be expected to use lower temperatures or higher pressures, or both.

## Hydrogenated Cottonseed Oil
## vs.
## Hydrogenated Peanut Oil

Cottonseed oil contains a considerably greater percentage of linoleic acid than does peanut oil. Consequently, it was felt that it was a better material for the investigation of hydrogenation conditions, and most of the work was directed toward the hydrogenation of cottonseed oil rather than to that of peanut oil. However, in three different cases the experiments with cottonseed oil were repeated, using peanut oil. The conditions selected for duplication with peanut oil were those used in experiment No. CO-20, which led to poor selectivity and low iso-oleic acid formation; those of No. CO-23, which led to good selectivity and high iso-oleic acid formation; and those of No. CO-12, which gave moderate selectivity and moderate formation of iso-oleic acid. The data for these three peanut oil experiments, together with the data for the corresponding cottonseed oil experiments, are recorded in Table 4. It is apparent

that the hydrogenation of peanut oil follows a course comparable in every way to that of cottonseed oil, and that equivalent variations are obtained in the

| Run No. | Kind of oil | Degree of selectivity | Percentage composition of fatty acids at their critical iodine value * | | | |
|---------|-------------|-----------------------|--------|------|--------|------|
| | | | Saturated | Iso-oleic | Normal oleic | Linoleic |
| CO-23 | Cotton | High | 31.0 | 20.4 | 44.6 | 4.0 |
| PO-23 | Peanut | High | 21.1 | 14.0 | 63.7 | 2.2 |
| CO-12 | Cotton | Medium | 34.1 | 11.2 | 47.5 | 7.2 |
| PO-12 | Peanut | Medium | 25.3 | 7.1 | 61.3 | 6.3 |
| CO-20 | Cotton | Low | 39.6 | 8.5 | 39.3 | 12.6 |
| PO-20 | Peanut | Low | 30.3 | 4.8 | 53.7 | 11.2 |

* For cottonseed oil, 65.7; for peanut oil, 72.6.

composition of the hydrogenated products by changing the conditions of hydrogenation. The comparison between the hydrogenated cottonseed and peanut oil products is also shown graphically in Figure 2. The hydrogenated peanut oils, as compared with the corresponding hydrogenated cottonseed oils, are characterized by considerably lower proportions of saturated and iso-oleic acids, and correspondingly greater proportions of normal oleic acid. It is evident, however, that this result is due to the disparity in composition of the original oils, rather than to any difference in the manner in which hydrogenation occurs in the two cases.

### Possible Yields of Normal Oleic Acid

The preceding data provide an indication of the yields of normal oleic acid that could be obtained from cottonseed and peanut oils if it were possible to separate this acid quantitatively from the mixed fatty acids of the hydrogenated oils by fractional crystallization or other means. The maximum yields of oleic acid would appear to be about 48 per cent from a cottonseed oil of the particular composition used in these experiments, and about 63 per cent for the peanut oil. The degree of selectivity with which the hydrogenation reaction is carried out appears to be unimportant within comparatively wide limits, since any decrease in formation of saturated acids is compensated by an increase in formation of iso-oleic acid, and vice versa. In commercial practice, a quantitative or even approximately quantitative separation of oleic acid would probably be not only rather difficult, but possibly also unnecessary. Any practicable separation of oleic acid would probably leave all or most of the linoleic acid as an impurity in the normal oleic acid fraction. In this event, it would not be sufficient to merely hydrogenate the oil until its normal oleic acid content has reached a maximum; it would be necessary to carry the hydrogenation on until the linoleic acid has decreased to a point where it is no longer objectionable as an impurity in the oleic acid fraction. Under such circumstances, the important consideration would be not the possible yield of pure normal oleic acid, but the possible yield of an impure acid containing minor amounts of linoleic acid as an impurity.

As a means of estimating the possible yields of this hypothetical "impure oleic acid" the triangular co-ordinate chart illustrated in Figure 3 was prepared

and the yields of oleic acid of various degrees of impurity were determined from it graphically, for each of the various runs. The data thus obtained are recorded in Table 5. In the case of the less selective runs, the present experimental data cover an insufficient range to permit a close estimation of the yields of oleic acid of 90 and 95 per cent purity, but it is evident that these yields are quite low, and that reasonably high selectivity is required for the best yields of oleic acid of a high degree of purity. At the lowest level of purity (85 per cent oleic acid) there is no great difference between the moderately selective and moderately non-selective runs. In the case of cottonseed oil, neither extremely selective conditions (as in Run CO-23) nor extremely non-selective conditions (as in Run CO-20) gave the best yields of oleic acid at any degree of purity. With peanut oil, the best yields of oleic acid at all levels were obtained under the most selective conditions (PO-23). The maximum indicated yields were: for the cottonseed oil, 56 per cent of oleic acid of 85 per cent purity, 53 per cent of oleic acid of 90 per cent purity, and 48 per cent of oleic acid of 95 per cent purity; and for the peanut oil, 70 per cent of oleic acid of 85 per cent purity, 68 per cent of oleic acid of 90 per cent purity, and 66 per cent of oleic acid of 95 per cent purity.

### Summary

1. The effects of the following factors have been investigated in the hydrogenation of cottonseed and peanut oils: temperature, concentration of catalyst, pressure of the hydrogen, degree of agitation, and nature of the nickel catalyst.

2. The formation of stearic acid was found to be repressed and the formation of "iso-oleic" acid simultaneously favored by increasing the temperature, increasing the catalyst concentration, decreasing the pressure, and decreasing the agitation.

3. The nature of the nickel catalyst, as influenced by its method of preparation, may have a large effect on the composition of the hydrogenated product. One of the nickel catalysts investigated formed excessive amounts of iso-oleic acid without being correspondingly selective.

4. In the hydrogenation of cottonseed oil, within a comparatively wide range of conditions, the production of total solid acids with a given catalyst is relatively constant, since the conditions leading to the formation of stearic and iso-oleic acid are mutually exclusive. Extremes in either direction, however, lead to the production of excessive amounts of total solid acids.

5. Peanut oil is a more suitable raw material than cottonseed oil for the production of normal oleic acid, because of its initially greater content of this constituent and its lesser content of linoleic acid.

6. On the assumption that a quantitative separation could be made of the liquid acids from the solid acid fraction (saturated and iso-oleic) of the hydrogenated products, leaving minor amounts of unhydrogenated linoleic acid as an impurity in the separated normal oleic acid, the following maximum yields of "impure normal oleic acid" could be obtained: from cottonseed oil, 56 per cent of oleic acid of 85 per cent

TABLE 5

Calculated yields of normal oleic acid, of various degrees of purity, obtainable from cottonseed and peanut oil hydrogenated under different conditions. (On basis of complete separation of solid and liquid acids, impurity consisting of linoleic acid only.)

| Run No. | Kind of oil | Hyd. time, min. to crit. I.V. | Percentage composition of fatty acids at their critical I.V.* | | | | Per cent yield of normal oleic acid | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sat. | Iso-oleic | Normal oleic | Lin-oleic | 95% pure | 90% pure | 85% pure |
| CO-23 | Cotton | 190 | 31.0 | 20.4 | 44.6 | 4.0 | 45 | 48 | 50 |
| CO-11 | Cotton | 101 | 31.7 | 15.8 | 47.7 | 4.8 | 48 | 52 | 54 |
| CO-18 | Cotton | 19 | 32.5 | 14.3 | 47.6 | 5.6 | 40 | 52 | 54 |
| CO-19 | Cotton | 67 | 32.8 | 13.2 | 48.1 | 5.9 | 40 | 53 | 55 |
| CO-15 | Cotton | 24 | 32.8 | 12.4 | 48.9 | 5.9 | 40 | 53 | 56 |
| CO-12 | Cotton | 31 | 34.1 | 11.2 | 47.5 | 7.2 | <40 | 49 | 56 |
| CO-9 | Cotton | 12 | 34.2 | 10.7 | 47.8 | 7.3 | <40 | 47 | 55 |
| CO-16 | Cotton | 98 | 35.1 | 11.0 | 45.7 | 8.2 | <40 | 40 | 53 |
| CO-17 | Cotton | 21 | 35.2 | 10.2 | 46.2 | 8.4 | <40 | 40 | 53 |
| CO-20 | Cotton | 72 | 39.6 | 8.5 | 39.3 | 12.6 | <40 | <40 | <40 |
| PO-23 | Peanut | 135 | 21.4 | 14.0 | 62.9 | 1.7 | 66 | 68 | 70 |
| PO-12 | Peanut | 14 | 25.7 | 7.1 | 61.3 | 5.9 | 58 | 68 | 70 |
| PO-20 | Peanut | 30 | 30.0 | 4.8 | 55.0 | 10.2 | 45 | 59 | 64 |

* For cottonseed oil, 65.7; for peanut oil, 72.6.

purity, 53 per cent of oleic acid of 90 per cent purity, and 48 per cent of oleic acid of 95 per cent purity; and from peanut oil, 70 per cent of oleic acid of 85 per cent purity, 68 per cent of oleic acid of 90 per cent purity, and 66 per cent of oleic acid of 95 per cent purity.

## Acknowledgment

The authors wish to acknowledge the courtesy of Mr. A. R. Diehl, of the Cudahy Packing Company, Memphis, Tennessee, in furnishing the catalyst used for a large part of this work; they are indebted also to Messrs. G. E. Mann, W. G. Bickford, and C. L. Hoffpauir for valuable suggestions and assistance in carrying out the analytical phases of the investigation.

BIBLIOGRAPHY

1. American Chemical Society, Committee on Analysis of Commercial Fats and Oils. Ind. Eng. Chem., Anal. Ed. 8, 233-7 (1936).
2. American Oil Chemists' Society, Official and Tentative Methods, Revised to January 1, 1941. pp. 31-2, 44b-44f.
3. Dhingra, D. R., Hilditch, T. P., and Rhead, A. J. J. Soc. Chem. Ind., 51, 195-8 T (1932).
4. Etinburg, E., Sterlin, B., and Krushevskii, B. Masloboino Zhirovoe Delo. 11, 471-3 (1935).
5. Gutmann, R. Masloboino Zhirovoe Delo. 1931, No. 8-9, 32-6.
6. Mazume, T. J. Soc. Chem. Ind. Japan, 31, 467-9, Suppl. Bind. 111-2B (1928).
7. Moore, C. W. J. Soc. Chem. Ind., 38, 320-5T (1919).
8. Moore, Hugh K., Richter, G. A., and Van Arsdel, W. B. J. Ind. Eng. Chem., 9, 451-62 (1917).
9. Richardson, A. S., Knuth, C. A., and Milligan, C. H. Ind. Eng. Chem., 16, 519-22 (1924).
10. Richardson, A. S., and Snoddy, A. O. Ind. Eng. Chem., 18, 570-71 (1926).
11. Riemenschneider, R. W., Swift, C. E., and Sando, Chas. E. Oil & Soap, 18, 203-06 (1941).
12. Taylor, H. S. Proc. Roy. Soc. (London), 108A, 105-11 (1925).

# Factors Affecting the Stability of Cottonseed Oil. A Study of the Antioxygenic Activity of Alpha-Tocopherol[1]

C. E. SWIFT,[2] W. G. ROSE, Associate Chemist, and G. S. JAMIESON, Senior Chemist

Bureau of Agricultural Chemistry and Engineering, United States Department of Agriculture, Washington, D. C.

The report of the isolation of the tocopherols from vegetable oils (1) was followed closely by a description of their antioxygenic activity (2). Earlier studies of the sterol-free unsaponifiable fractions (inhibitols) of vegetable oils containing tocopherols formed a valuable background for the investigations of the antioxygenic activity of the tocopherols. The tocopherols are considered to contribute some if not most of the antioxygenic activity of the inhibitols, although it is recognized that other antioxidants may be isolated (3) (3a).

The mechanism by which the tocopherols inhibit oxidation is only partly understood; this is to be expected since the autoxidative reactions which they inhibit are complex and still obscure. In previous investigations of natural antioxidants several interesting observations have been made for which the antioxygenic activity of the tocopherols may be wholly or partly responsible. In an investigation of the inhibitols their effectiveness was found to be approximately proportional to the amounts used (4), but they were ineffective when added to the oils from which they were obtained (5). A completely satisfactory explanation of this phenomenon has not been advanced, but it has been suggested that the amounts of inhibitols added to the original oils were too small (6) and that other substances may have prevented the functioning of the inhibitols (3). In another investigation adequate explanations were lacking for the unusual behavior of a concentrate of the unsaponifiable substances of refined prime summer yellow cottonseed oil obtained in the most volatile fraction of molecularly distilled oil (7). The fraction was shown to contain the bulk of the protective substances of the oil, but it rapidly accumulated peroxides during air-blowing