Positional and Geometrical Isomerization During Partial Hydrogenation of Trilinolein: A Comparison of Copper and Nickel Catalysts

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Abstract

We have compared a nickel with a copper catalyst in the formation of some geometrical and positional isomers during the partial hydrogenation of trilinolein. The copper catalyst was found to produce fewer diene isomers than the nickel catalyst at a comparable iodine value. The copper catalyst produced more monoene isomers however, than did the nickel, particularly *trans* monoenes. The distribution of the monoene isomers appeared to obey an equilibrium relationship with each other, independent of both iodine value and reaction conditions. We have presented additional evidence to postulate that copper catalysts hydrogenate polyenoic acids by first conjugating the acids. The selectivity of copper catalysts for triene over diene is probably due to the greater ease of conjugation of the triene.

Introduction

During the hydrogenation of linoleic acid ($\Delta^{9,12}$ *cis,cis*-octadecadienoic acid) to a monoene, the products formed are a mixture of geometrical and positional isomers, which may be formed by saturation of either of the double bonds in the chain, and also by migration of the bonds during the hydrogenation reaction (1,2).

In recent years, new techniques for analysis of methyl esters of fatty acids have been discovered and older ones improved. A few examples would be infrared analysis (3) ultraviolet spectrophotometric measurements of conjugation (4,5), countercurrent distribution (6), gas chromatography (7), thin layer chromatography (TLC) (8) and oxidative cleavage for the determination of the position of the double bonds (9).

The development of these techniques led to several studies on the hydrogenation of oleic acid (10–12) including the study of the effect of operating conditions on the migration of double bonds in hydrogenated samples (10).

Some work has been done with higher unsaturated, e.g., linoleic, linolenic acids (13–15), but practically no detailed study of the effects of the operating conditions on the formation of positional and geometrical isomers has been carried out yet because of the staggering amount of analytical effort involved in such a venture.

As a result of recent development in TLC (8) and capillary gas chromatography (7) a simplified procedure was developed which allows a relatively quick determination of several positional and geometrical isomers of a C_{18} fatty acid containing up to two double bonds.

In the present investigation, the effect of operating conditions on the positional and geometrical isomerizations during the hydrogenation of trilinolein with copper chromite catalyst was studied, using some of the analytical procedures mentioned. The data from the copper catalyst study were compared with data from a similar study using nickel catalyst. This paper covers a comparison of the catalysts.

Experimental Procedures

Materials

Trilinolein was prepared from ethyl linoleate (98%), obtained by the purification of ethyl esters of safflower oil, which was then transesterified with glycerol using an alkaline catalyst. The excess ethyl linoleate and the partial glycerides were removed by crystallization four times from 4 to 6 vol of acetone at −75 C. The solid was taken in petroleum ether and water washed. The trilinolein thus obtained had 0.3% $C_{16:0}$; 1.3% $C_{18:1}$; 97.8% $C_{18:2}$ and 0.2% $C_{18:3}$.

Refined and bleached commercial soybean oil was also used in some of this investigation.

Analytical Procedure

The analytical procedure used was a modification of the Chapman and Kuemmel (16) technique.

Methylated samples of the partially hydrogenated trilinolein were fractionated on a preparative scale via TLC, on silver nitrate impregnated silica-gel thin layer plates (51 mg; 17 spots; 3 mg/spot). This procedure is known to separate unsaturated fatty methyl esters according to the number of double bonds and the geometrical configuration of the double bonds. The best development solvent was found to be a mixture of 92% petroleum ether and 8% acetone. Six fractions were found to contain mainly: (a) traces of triene; (b) *cis,cis* diene; (c) *cis-trans* and *trans-cis* diene; (d) *cis* monoene and *trans,trans* diene; (e) *trans* monoene; (f) saturates. Each of these fractions was extracted with chloroform and then fractionated by capillary gas chromatography.

All gas chromatographic analyses were performed on 150 ft × 0.01 in. capillary column coated with polyphenyl ether (OS-138, Perkin Elmer Corp.), under programmed temperature conditions at 140 C to 180 C and at 0.5 C/min at 35 psig inlet pressure of helium.

Equipment and Operating Procedures

Trilinolein was hydrogenated in a stainless steel, baffled and agitated batch reactor through which hydrogen was continuously passed. Trilinolein (250 g) and the desired amount of catalyst were added to the reactor and were heated under N_2 flow to the desired operating temperature. The start of each run was considered to be when agitation was started, after hydrogen was introduced. A high degree of agitation was provided with a high speed agitator.

Five to seven glyceride samples were collected at intervals during each run. Methyl esters of the samples were analyzed via the procedure mentioned

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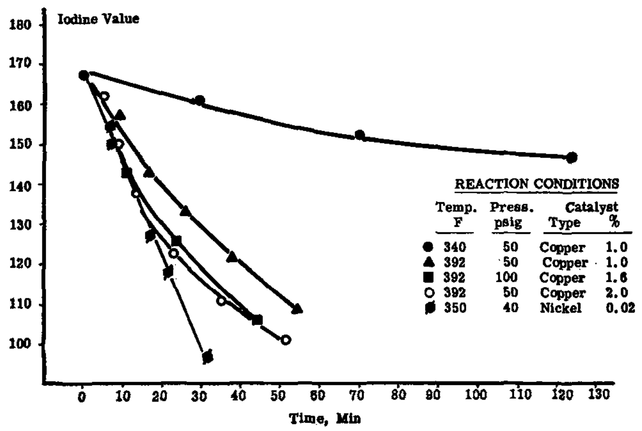


FIG. 1. Iodine value vs. reaction time trilinolein hydrogenation of copper nickel catalysts.

earlier. Iodine values (IV) were calculated from the sample compositions. *Trans* levels were determined by the IR technique (5) and from the composition. Conjugation levels were determined by UV spectroscopy (4). Catalysts used were as follows:

(a) a nickel catalyst promoted with zirconium and (b) a copper chromite catalyst promoted with manganese from the Girdler Catalyst Department of Chemetron Chemicals (T970). Both were slurry type catalysts.

Results and Discussion

Reaction Rates—Copper Catalyst

Increasing pressure, temperature and catalyst concentration produced the expected effect of increasing rate of reaction as shown in Figure 1. Temperature has a pronounced effect on rate of reaction since increasing temperature from 340 F to 397 F increased the rate from 0.23 IV/min to 1.11 IV/min. Figure 1 also shows a comparison of a nickel catalyst hydrogenation under similar pressure and temperature conditions. We see from this comparison that the copper catalyst is considerably less active than the nickel as 1% of the copper catalyst gave a slower rate of reaction than did 0.02% nickel catalyst. These weights of catalyst are based on total copper catalyst weight and nickel catalyst as per cent nickel.

Product Distributions

Dienes. Both copper and nickel catalysts at similar reaction conditions give the same total diene levels during the hydrogenation as shown by Figure 2. The nickel catalyst produces more diene isomers, however, as shown by Figure 2 where higher levels of $\Delta^{10,13}$*cis,cis* $\Delta^{9,12}$*cis,trans* and $\Delta^{9,12}$*trans,cis* dienes are formed during the course of the hydrogenation. There was little evidence of $\Delta^{9,12}$*trans,trans* diene being formed with the copper catalyst whereas the nickel catalyst did produce levels up to about 1%. The ratio of $\Delta^{9,12}$*cis,trans* diene to $\Delta^{9,12}$*trans,cis* diene formed with the copper catalyst remained constant during the run at 1.0 whereas this ratio increased above 1.0 with the nickel catalyst as shown in Figure 3. It can be surmised from this observation that nickel catalyst isomerization activity with dienes varies depending on the position of the double bond whereas copper catalyst is less selective as far as position is concerned.

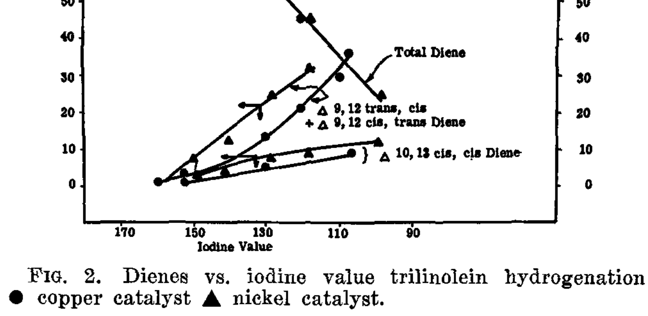


FIG. 2. Dienes vs. iodine value trilinolein hydrogenation ● copper catalyst ▲ nickel catalyst.

Monoenes. Trans monoene formation with copper catalyst is a constant 70% of total monoene formed throughout most of the hydrogenation run. With nickel catalyst, the initial percentage of *trans* monoene formed is low and increases towards 70% during the reaction. This is shown in Figure 4. The constant monoene valuve of 70% *trans* in the case of copper catalyst is seen regardless of reaction conditions and corresponds favorably with literature values of the equilibrium *trans,cis* isomer ratio.

Distribution of the various monoene isomers differs with copper and nickel catalysts. This is shown in Table I. The distribution of the various monoene isomers is insensitive to reaction conditions or to actual level and appears to be an equilibrium situation. Allen and Kiess (13) found a similar situation in their study on linoleic acid and methyl linoleate.

As shown by Table I, the percentage of Δ^9 and $\Delta^{11} + \Delta^{12}$ *cis* monoene formed with copper catalyst is less than that with nickel indicating along with the greater total *trans* monoene content with copper, that either isomerization of monoenes is greater with copper than with nickel catalyst or that in the process of hydrogenating diene to monoene, isomerization is more likely to simultaneously occur with copper catalyst than with nickel catalyst. This is in contrast with what was observed with diene where nickel catalyst gave more isomerization. The distribution of the various *trans* monoene isomers is fairly comparable, however, with both catalysts. Why this should be so is not obvious.

Saturates. Copper catalyst produces essentially no saturates during normal hydrogenation whereas nickel catalyst does. This is illustrated in Figure 4. The lack of saturate formation with copper catalyst agrees with a mechanism of hydrogenation that will be presented next.

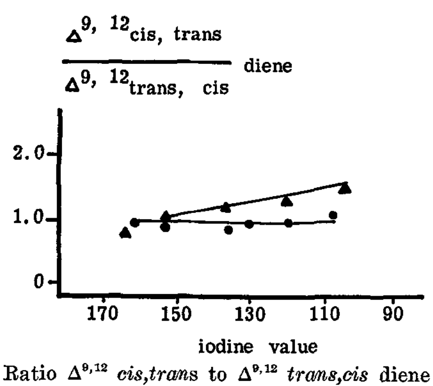


FIG. 3. Ratio $\Delta^{9,12}$ *cis,trans* to $\Delta^{9,12}$ *trans,cis* diene vs. iodine value trilinolein hydrogenation ● copper catalyst ▲ nickel catalyst.

TABLE I

Equilibrium Distribution Values Monoene Isomers

Isomer	Trilinolein hydrogenation	
	cis as percent of total *cis*,*trans* as percent of total *trans* monoenes	
	Copper catalyst, %	Nickel catalyst, %
Δ^9 *Cis*	46	54
Δ^{10} *Cis*	18	5½
$\Delta^{11} + \Delta^{12}$ *Cis*	28	38
Δ^{13} *Cis*	8	2½
Total	100	100
Δ^9 *Trans*	53	57
Δ^{10} *Trans*	23	24
Δ^{11} *Trans*	12	11
Δ^{12} *Trans*	10	6½
Δ^{13} *Trans*	2	1½
Total	100	100

Reactor Mechanism

In addition to the trilinolein study, soybean oil was hydrogenated with the copper catalyst. The results of this study plus that of the trilinolein work were used to arrive at the following postulated mechanism for copper catalyzed hydrogenation. The mechanism postulated here, is the one believed to account for more of the products in the reaction mixture. This mechanism has been proposed by others (20). Our data provide additional support.

The experimental results have lead to the following observations: (a) No stearate was formed during the reaction under the conditions studied. (b) In all the hydrogenation runs of trilinolein with copper catalyst, levels of conjugation (up to 4%) were formed, exhibiting a characteristic pattern which depended on the reaction conditions. (Fig. 5). It was not possible in this study to determine the identity of the conjugated species. (c) The rate of reaction, as expressed by $\Delta IV/_{\Delta t}$ for soybean oil has been found to be proportional to the conjugated diene level in the system (Fig. 6).

There have been several studies in the past relating conjugation to the mechanism of hydrogenation of polyenoic acids. In particular are the studies of Feuge et. al. (2), Allen and Kiess (13), Coenen and Boerma (19), and Koritala et al. (20). These studies were mostly done with nickel catalysts and for the most part concerned hydrogenation of linoleic acid and methyl linoleate although some work with cottonseed and safflower oils was reported. The latter reference covers work with copper catalysts.

Previous study by Mounts and Dutton (17) who studied the kinetics of the hydrogenation of soybean oil with the Cu/Cr type of catalyst via the radioactivity-chromatography technique, suggested that the reaction involved can be represented by the following scheme:

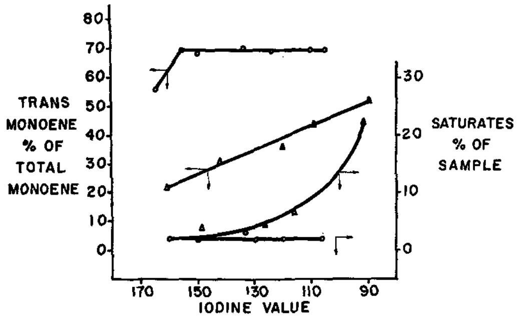


FIG. 4. Total *trans* monoene and saturates iodine value trilinolein hydrogenation ● copper catalyst ▲ nickel catalyst.

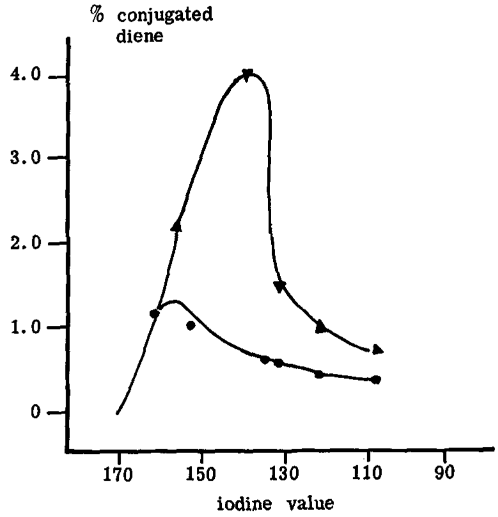
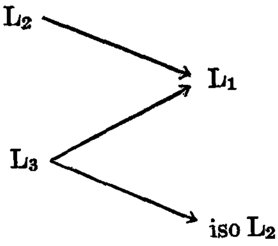


FIG. 5. Conjugated diene vs. iodine value trilinolein hydrogenation copper catalyst ● 340 F, 50 psig, 1% catalyst ▲ 392 F, 50 psig 1% catalyst.



where: L_3, triene; L_2, diene; iso L_2, nonconjugatable diene (more than one methylene interrupted); L_1, monoene.

The implication from their experimental data was that the Cu/Cr catalyst converts linolenate to nonconjugatable dienes almost exclusively, which requires that the middle double bond is selectively attacked.

Mounts' scheme agrees well with the results obtained during the present study, where stearic acid was not formed and a significant level of isolinoleate was found. However, our results indicate that additional steps should be included.

The fact that the conjugated diene concentration was proportional to the rate of the reaction, reaching a maximum when the maximum rate of reaction was

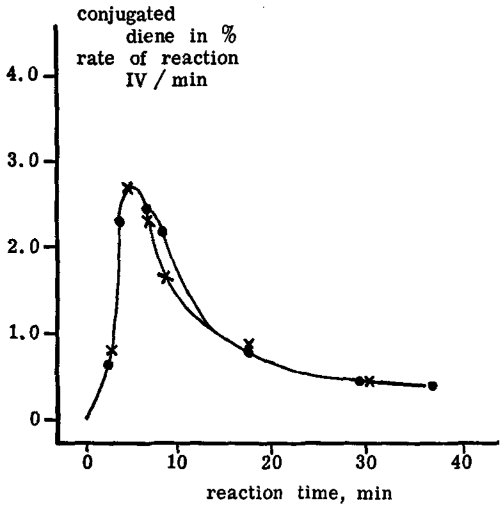


FIG. 6. Conjugated diene and rate of reaction vs. reaction time soybean oil hydrogenation copper catalyst 392 F, 50 psig, 0.28% catalyst ● conjugated diene, X rate of reaction.

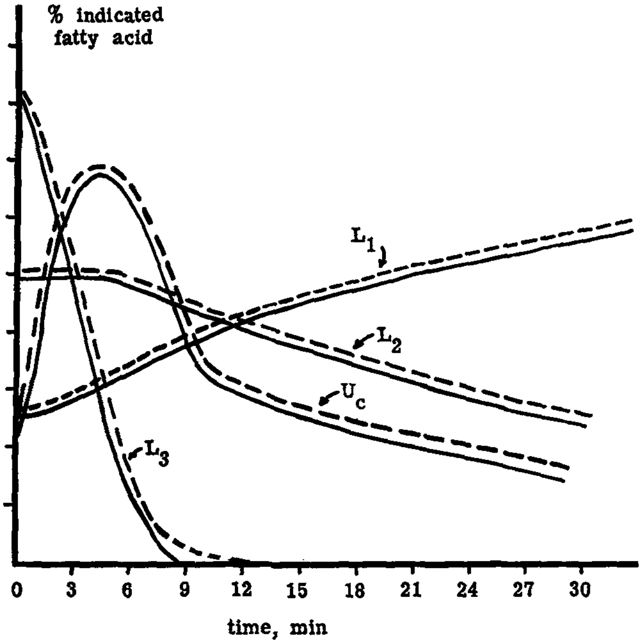


FIG. 7. Computer simulation of hydrogenation of soybean oil with copper catalyst – – – experimental values; —— simulation values 392 F, 75 psig, 0.28% catalyst L_3 triene (1% divisions) diene, (10% divisions) L_1 monoene (10% divisions) U_c total conjugated diene (0.5% divisions).

reached (Fig. 6), strongly suggests that the conjugated dienes are important intermediates in the hydrogenation process. Also, since no hydrogenation of monoene occurred in the soybean oil and trilinolein, the hydrogenation mechanism requires an intermediate system consisting of two double bonds at least. The most probable candidates are conjugated or conjugatable (methylene interrupted) diene.

Our analytical data clearly showed that the triene, if conjugated, will contain only one conjugated system. Also, it was observed that, as the reaction progressed, the difference between gas chromatography fatty acid composition and UV fatty acid composition determinations for diene increased considerably, e.g., at IV 85, UV diene was a considerably smaller value, 8.9%, than the gas chromatography value of 13.4%. This difference is probably the nonconjugatable material, and supports the observation that considerable fraction of the triene was hydrogenated to nonconjugatable diene.

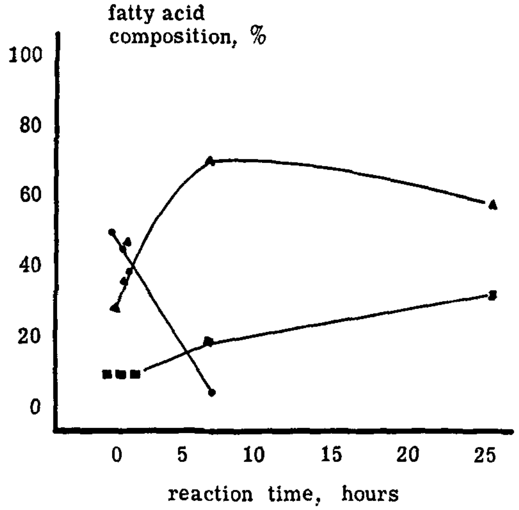


FIG. 8. Fatty acid composition vs. reaction time soybean oil hydrogenation copper catalyst 392 F, 50 psig, 0.28% catalyst ● diene, ▲ monoene, ■ saturates.

TABLE II

Simulation Values for a

Pressure, psig	a
0	0.16
25	0.2
50	4.93
75	28.56
100	39.29
125	12.74

Thompson (18) found eleosteric acid to be more rapidly hydrogenated with nickel catalyst than was linolenic acid. Feuge et al. (2) reported much more rapid hydrogenation of conjugated than nonconjugated linoleic acid. Others have speculated that the induction period was a period of conjugation.

Based on the present study and previous studies (17,18,20), the following scheme is proposed to account for the main features of the hydrogenation, with the Cu/Cr type of catalysts:

$$\begin{tikzcd}
L_3 \arrow[r] & L_{3_C} \arrow[r] \arrow[dr] & \text{iso } L_2 \\
L_2 \arrow[r] & L_{2_C} \arrow[r] & L_1
\end{tikzcd}$$

where: L_{3_C}, triene with one conjugated system; L_{2_C}, diene with one conjugated system.

With the above scheme, a kinetic model has been developed in which the following assumptions were made: (a) All active sites on the catalyst surface are identical; (b) Hydrogen molecules are chemisorbed, and split into atoms on pairs of active sites; (c) Fatty acids are not chemisorbed but probably form a complex with the H-atoms on the surface; (d) The chemical reaction is the rate controlling step.

The resulting rate equations are as follows:

$$r_{L_1} = [A/(1 + C_2/aC_3) + B/(1 + aC_3/C_2)]C_c$$

$$r_{L_2} = [E/(1 + C_2/aC_3) - G/(1 + aC_3/C_2)]C_c + (FC_2 - HC_1)$$

$$-r_{L_3} = MC_c/(1 + C_2/aC_3) - NC_2 - RC_1$$

where: $L_{2_C} + L_{3_C} = L_c$ and a is defined by: $C_{3_c}/C_c^2 = a\,(C_3/C^2)$; r_{L_1}, rate of monoene formation; r_{L_2}, rate of diene change; r_{L_3}, rate of triene consumption; C_1, concentration of monoene; C_2, concentration of diene; C_3, concentration of triene; C_c, total conjugation; C_{3_c}, conjugated triene (one conjugated system); C_{2_c}, conjugated diene; A, B, E, F, G, H, M, N, R, constants.

An analog computer EAI 680 was used to simulate the kinetic data using this model. A typical analog simulation and the experimental value is shown in Figure 7 for 75 psig. The agreement between the two is remarkable. Agreement in other pressures was essentially the same in pressures of 50 to 125 psig range.

The simulation values for a at different pressure are summarized in Table II.

The values of a indicate that above about 50 psig the high selectivity of Cu catalyst might be due to the selective conjugation of linolenate thus making the effective concentration of triene much higher than its relative proportion in the oil. The small a values for 0 and 25 psig are believed to be due to diffusion resistance which might be considerable under these conditions and which may cause the assumption that the chemical reaction is rate controlling invalid. The selective conjugation concept raises another question. If a considerable fraction of the conjugated diene is actually triene with one conjugated system, this will cause the UV determination of triene to be very unreliable, especially with high levels of conjugation. For example, at 392 F, 0 psig and 0.28% catalyst concentration (T-970), UV analysis showed 4.2% triene and 4.0% conjugated diene. This may mean that actually about 8.0% triene is still in the system although 4% is shown as conjugated diene.

Since process conditions affected both conjugation and rate in the trilinolein study but had relatively little effect on composition, it supports the conjugation mechanism. This, however, does not necessarily mean that these are the only steps involved. For example, in one particular run with T-970 catalyst, 0.28% by weight, 50 psig of H_2 and 392 F, the reaction was continued for 25 hr. The results are presented in Figure 8. As time progressed, monoene began to hydrogenate to stearate and after 25 hr the stearate content changed from 4.7% to 31.5%. This indicates that although the steps proposed in this study are much faster than steps which do not require a conjugated intermediate, given enough time the latter will have a significant effect.

REFERENCES

1. Boelhouwer, C., J. Gerckens, L. E. Ong. Tian and H. I. Waterman, JAOCS *30*, 59 (1953).
2. Feuge, R. D., E. R. Cousins, S. P. Fore, E. F. DuPre and R. T. O'Connor, Ibid. *30*, 454 (1953).
3. Shreve, O. D., M. R. Heether, H. B. Knight and D. Swern, Anal. Chem. *22*, 1261,1264 (1950).
4. American Oil Chemists' Society "Official and Tentative Methods," 2nd Edition, Col. 7–58, Revised to 1959, Chicago 1949–59.
5. Brice, B. A., M. L. Swain, S. F. Herle, P. L. Nichols, Jr. and R. W. Reimenschneider, JAOCS *29*, 279–287 (1952).
6. Scholfield, C. R., Janina Nowakowska and H. J. Dutton, Ibid. *37*, 27–80 (1960).
7. Kuemmel, D. F., and L. R. Chapman, Anal. Chem. *38*, 1611 (1966).
8. Lees, Ann M., and E. D. Korn, Biochem. Biophys. Acta *116*, 403–6, (1966).
9. Jones, E. P., and J. A. Stolp, JAOCS *35*, 71–76 (1958).
10. Feuge, R. O., and E. R. Cousins, Ibid. *37*, 267 (1960).
11. Allen, R. R., and A. A. Kiess, Ibid. *32*, 400 (1955).
12. Vandenheuvel, F. A., Ibid. *33*, 347 (1956).
13. Allen, R. R., and A. A. Kiess, Ibid. *33*, 356 (1956).
14. Scholfield, C. R., E. P. Jones, Janina Nowakowska, E. Solke, B. Sreenivasan and H. J. Cutton, JAOCS *37*, 579 (1960).
15. Rebello, D., and B. F. Daubert, Ibid. *28*, 177 (1951).
16. Chapman, L. R., and D. F. Kuemmel, Anal. Chem. *37*, 1598–1600 (1965).
17. Mounts, T. L., and H. J. Dutton, JAOCS *44*, 67 (1967).
18. Thompson, W., Ibid. *28*, 339–41 (1951).
19. Coenen, J. W. E., and H. Boerma, Fette Seifen Anstrichm. *70*, 8–14 (1968).
20. Koritala, S., R. O. Butterfield and H. J. Dutton, Oral presentation at AOCS Meeting, New York, October 1968.

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