TABLE IV

Comparison of Tentative A.O.C.S. and Modified Method for the Determination of Acetone Insolubles

Sample No.	Official Tentative A.O.C.S. Method		Modified Method No Pet. Ether, A.I. Sat. Acetone Direct Weighing
	Direct Weighing	Indirect Weighing	
	%	%	%
A	62.56 62.71 63.12	62.66 62.85 62.83	63.93 64.09 64.33
B	64.15 63.87 63.98	64.43 64.04 63.64	65.32 65.24 65.24
C	65.03 64.83 65.14	65.46 65.22 65.04	66.31 66.62 66.62

Attempts were made to recombine dry acetone insolubles, soybean oil, and soybean fatty acids to produce synthetic commercial lecithins of known composition. Difficulty was encountered in reblending these materials and the final products did not truly resemble normal commercial lecithins. When these synthetic mixtures were analyzed by the above methods, differences between the calculated and found values for acetone solubles and acetone insolubles varied from 1.72 to 2.64%. It is unfortunate that synthetic mixtures could not be prepared to test the accuracy of the two procedures. Drying and heating of the acetone insoluble residue apparently causes changes in solubility through resinification and structural changes.

Summary

Data are presented from numerous analyses of commercial lecithins for the comparison of values obtained from the determination of acetone insolubles by a direct weighing method against those by the A.O.C.S. Tentative Method Ja 4-46. Discrepancies introduced into these methods by the use of petroleum ether as a solvent and those due to the solubility of acetone insoluble compounds in the acetone extract and wash solution are evaluated. A proposal is made for the consideration of a direct weighing procedure for the acetone insolubles content of commercial lecithins whereby petroleum ether is eliminated, the acetone extract solution saturated with pure phosphatides before use, and the insoluble residue dried and weighed.

REFERENCES

1. Official and Tentative Methods of the American Oil Chemists' Society, 2nd ed., Chicago, 1946.
2. Report of Committee on Analysis of Commercial Fats and Oils, October 1946, J. Am. Oil Chem. Soc., *24*, 76-79 (1947).
3. Scholfield, C. R., *et al.*, J. Am. Oil Chem. Soc., *25*, 368-372 (1948).
4. Stanley, J., "Soybeans and Soybean Products," Vol. II, Chap. XVI, Interscience Publishers, New York, 1950.

[Received May 20, 1953]

Formation of Trans Isomers During the Hydrogenation of Glyceride Oils

REX J. SIMS and LEE HILFMAN, Swift and Company, Chicago, Illinois

WITH the development of the infrared spectrophotometric method for the determination of trans isomers in fats (1, 2), workers in the field have shown renewed interest in the natural occurrence and synthesis of these high-melting glycerides (3, 4, 5, 6, 7). Lemon (8) developed curves showing the formation and disappearance of trans double bonds during the hydrogenation of vegetable oils. The present paper is in part an extension of this study to the animal fats.

TABLE I–

Hydrogenation—Soybean Oil

200°C.

PSI H_2	% Ni. Cat.	Time Min.	I No.	FAC M.P.	Soft. Pt.	% Linoleic	% Linolenic	% Trans isomers
10	1	240	78	96	93	1.28	0.00	54
225	0.05	38	76	118	98	5.37	0.13	44
700	0.05	3	79	122	109	12.30	0.64	30

Conditions which favor selective hydrogenation of glyceride oils also favor the development of trans isomers. For example, Table I shows the effect of using high hydrogen pressure for the partial hydrogenation of soybean oil (9). Although all three of these samples were hardened to approximately the same iodine number, the first contains the largest percentage of trans double bonds.[1] It also has the least number of polyunsaturated chains, the lowest melting point, and the shortest spread between melting and softening points. The third sample was very firm, as the result of its relatively high content of fully saturated fatty acid chains.

TABLE II

Hydrogenation—Soybean Oil

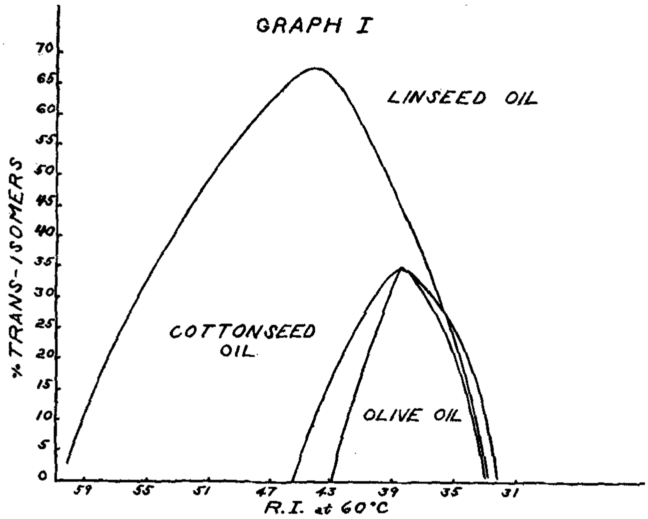
200°C.

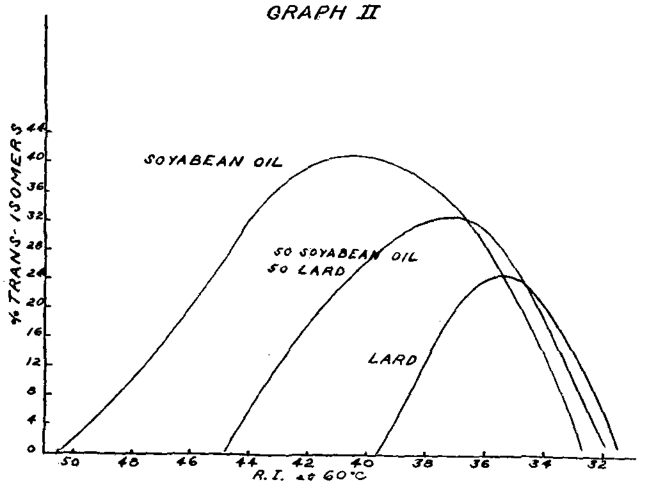
PSI H_2	% Ni. Cat.	Time	I No.	FAC M.P.	Soft. Pt.	% Linoleic	% Linolenic	% Trans isomers
1100	0.05	30 sec.	100	135	115	28.4	3.5	18
550	0.05	45 sec.	100	130	111	27.8	3.2	19
225	0.05	80 sec.	100	123	106	25.3	2.8	25
30	0.05	8 min.	99	....	....	23.5	1.2	32
0	0.05	57 min.	99	83	....	21.3	1.0	39

Table II illustrates further the direct relationship which exists between selectivity of hydrogenation and formation of trans isomers (9). As the hydrogen gas pressure is increased, the content of polyunsaturates at a given iodine number increases, but the percentage of trans linkages formed decreases. The last sample of this series was hardened by bubbling hydrogen through the oil while maintaining a vacuum of 28 inches. Notice that it actually melts higher than the sample hardened at 30 PSI, which was too soft to be

---

[1] The contents of trans isomers in these samples and in all others described in this paper were determined by measuring absorptions in chloroform at 10.3 microns in the infrared (1). These absorptions were compared with that of pure elaidic acid, prepared by the isomerization of oleic acid with selenium (10, 11).





Legend—Graphs I through VII

Horizontal Axes. Refractive indices at 60°C. on butyro scale, each curve drawn from data on 12-15 samples taken during course of hydrogenations.

Vertical Axes

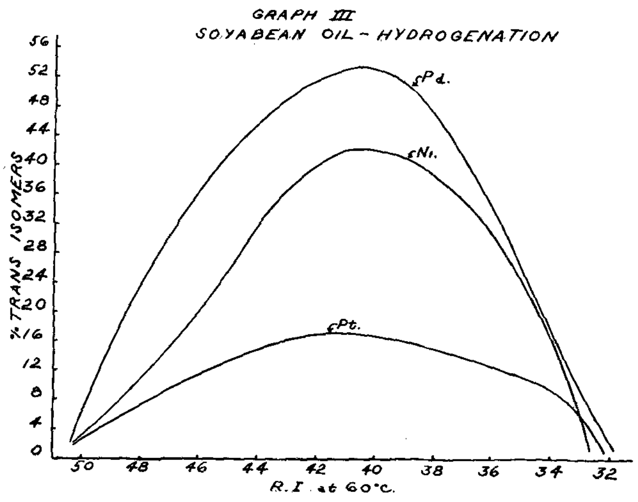
% trans isomers (1)
% linoleic (9)
FAC melting and softening points[2]
A.S.T.M. cloud point (°F.)

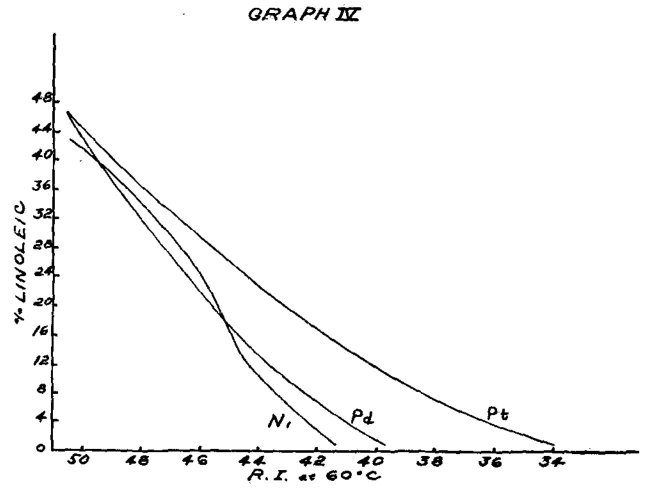
Conditions of Hydrogenation

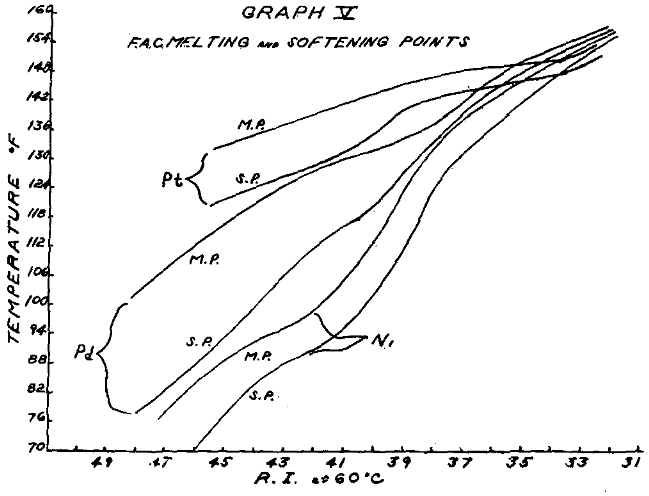
GRAPHS I AND II
200°C.
30 PSI hydrogen
0.2% by weight of a commercial reduced catalyst containing about 25% Ni

GRAPHS III THROUGH VI
Pd (5% on carbon)—0.03% by weight
200°C.
30 PSI hydrogen
Pt (5% on carbon)—0.1% by weight
100°C.
500 PSI hydrogen
Ni (25%)—0.2% by weight
200°C.
30 PSI hydrogen

GRAPH VII
Ni (25%)—0.2% by weight
200°C.
30 PSI hydrogen

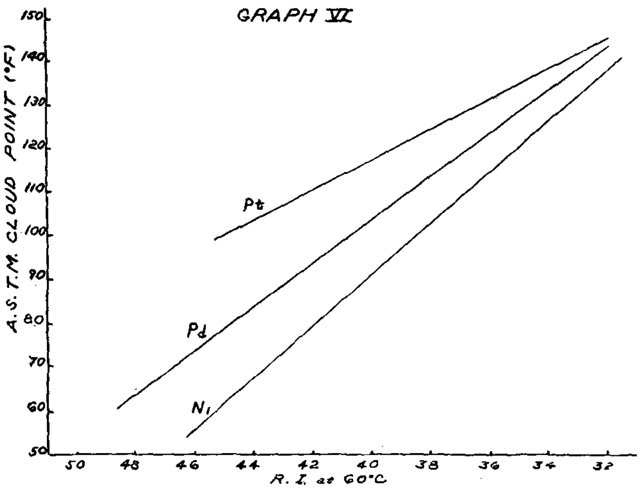


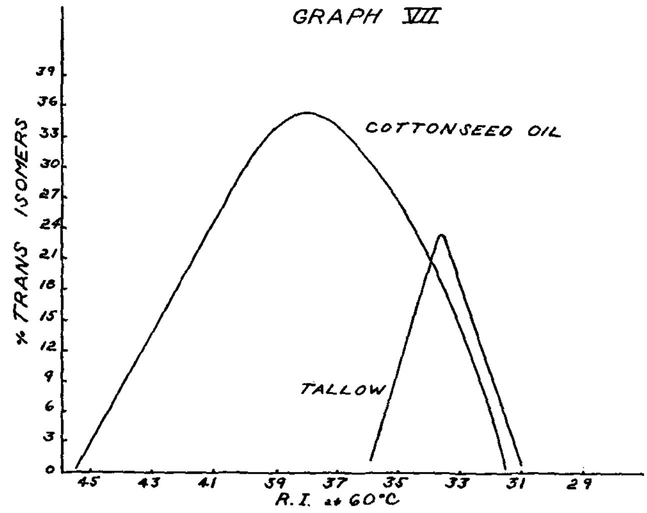




measured by the FAC method.[2] This is an example in which the content of trans glycerides is an important factor in determining melting point and consistency. Trans isomer formation and good selectivity are both promoted by elevating the temperature of hydrogenation, by decreasing the amount of agitation of the charge, and by increasing the catalyst concentration (12).

In Table III are shown the comparative results of hardening soybean oil with nickel, palladium, and





platinum catalysts at various temperatures. Palladium (5% on carbon) is remarkably selective in its action, even at 40°C. In fact, it is as selective at this low temperature as is nickel (commercial reduced catalyst containing about 25% Ni) at 200°C. Use of temperatures above 40°C. with palladium does not increase its selective action appreciably but does considerably increase its tendency to form trans isomers. On the basis of an iodine number of 82 the sample hardened with palladium catalyst at 200°C. has 76% of its double bonds in the trans form.[3] Note the high melting and softening points of this sample as compared with the corresponding sample hardened at 40°C.

Platinum catalyst (5% on carbon) is much less active and much less selective in its action than palladium, especially at the lower temperatures. Products with relatively high melting and softening points invariably result when platinum catalyst is used.

In Graph I the percentages of trans isomers formed during the hydrogenation of linseed, cottonseed, and olive oils are plotted against refractive indices.[4] These three oils represent typical linolenic, linoleic, and oleic acid oils, respectively. Notice that in each case the percentage increases as hydrogenation proceeds until the rate of disappearance exceeds the rate of formation and that it rapidly falls off as the fat approaches complete saturation. The unusually high peak obtained with olive oil is probably due to the fact that it contains such a large initial proportion of oleic acid which can isomerize to elaidic acid without taking up hydrogen. All three of the oils were hardened at 200°C. and 30 PSI of hydrogen with 0.2% by weight of nickel catalyst. Small samples were removed periodically from the converter for analysis, and the hydrogenations were continued until the fats in each case were near complete saturation.

TABLE III

Hydrogenation—Soybean Oil

Catalyst	Ni (0.1%)	Pd (0.01%)	Pd (0.1%)	Pt (0.1%)	Pt (0.2%)
Temp. °C.	200	40	200	100	200
PSI H_2	30	30	30	30	30
Time	33 min.	2.5 hr.	3 hr.	3 hr.	36 min.
I. No.	82	81	82	81	79
FAC M.P.	96	97	123	136	130
Soft. Pt.	86	87	106	128	119
% Linoleic	9.9	9.8	8.4	21.5	7.2
% Linolenic	0.34	0.08	0.41	1.2	0.35
% Trans isomers	41	35	72	18	42

Graph II illustrates the effect of mixing two fats. Here soybean oil, PS lard, and a 50-50 mixture of soybean oil and PS lard were hardened, removing small samples from time to time in order to plot the complete curves. In general, the higher the initial iodine number of the oil being hardened, the higher the percentage of trans isomers reached before they begin to disappear through further hydrogen absorption. Thus animal fats of a given consistency will usually contain much less of these high-melting trans glycerides than vegetable oils hardened to the same consistency. The conditions of hydrogenation used here were the same as those described for Graph I.

Graph III shows complete curves for the hydrogenation of soybean oil with reduced nickel and palladium at 30 PSI and platinum at 500 PSI of hydrogen. The catalyst concentrations were 0.2, 0.03, and 0.1% by weight of the oil for the nickel, palladium, and platinum runs, respectively. The run with platinum was made at 100°C. whereas the other two were at 200°C. Notice that, with the same oil, all the way from 16 to 53% of trans isomers can be formed as a maximum, depending upon the catalyst and conditions used.

In Graph IV are plotted the percentages of linoleic acid *versus* refractive indices for the three hydrogenations mentioned above. Notice that palladium and nickel show comparable selectivity whereas platinum is relatively non-selective at 100°C. and 500 PSI.

Graph V is a plot of melting and softening points *versus* refractive indices for these same three hydrogenations. Even near the top of the refractive index range, the sample hardened with platinum catalyst was quite firm. In spite of the comparable selectivity obtained with nickel and palladium, the samples prepared with the latter catalyst were firmer than the former over the entire range, probably due to their higher content of trans glycerides. Note the unusually large spread between melting and softening points on the palladium curve.

Graph VI shows the A.S.T.M. cloud points run on samples taken during these three hydrogenations. They follow the same pattern as the melting and softening points.

---

[2] A.O.C.S. Official Methods Cc 1-25 and Cc 3-25.

[3] This calculation is based upon 86 as the iodine number of triolein and assumes 100% of the fatty acids are C_{18}.

[4] Refractive indices were measured with a Zeiss Butyro refractometer at 60°C.

In Graph VII are plotted the complete curves for formation and disappearance of trans isomers during the hydrogenation of cottonseed oil and edible beef tallow. Again these oils were hardened at 200°C. and 30 PSI of hydrogen, with 0.2% by weight of reduced nickel catalyst.

It is obvious that the slope of the curve for tallow is unusually steep, considering its low initial iodine number and the short range through which it can be hardened. In Table IV are shown data on samples taken at the peaks in trans isomer content for the various hydrogenations described in this paper. The percentage of the total number of double bonds in the trans form was estimated for each sample on the basis of its iodine number.[2] The figure for tallow (74%) is considerably higher than that for any of the other fats.

TABLE IV
Maximum Percentage of Trans Isomers Formed

Fat	Catalyst	No.	% Trans isomers	% Total double bonds in trans form
Linseed	Ni	91	68	64
Soybean	Ni	66	42	55
Soybean	Pd	65	53	65
Soybean	Pt	75	16	19
Cottonseed	Ni	58	36	53
Olive	Ni	58	36	54
Lard	Ni	42	26	53
Tallow	Ni	28	24	74

This observation is especially interesting in view of the published method of Swern *et al.* for the preparation of oleic acid from partially hydrogenated tallow (13, 14). Using the conditions described by Swern for the selective hydrogenation of tallow, we obtained a product which contained almost half of its double bonds in the trans form. Furthermore, after the glycerides had been split with water, the resulting fatty acids were not readily separable into cis and trans forms by low temperature crystallization from acetone. In fact, with a change in the conditions of hydrogenation to favor the formation of trans isomers, preliminary experiments showed promise of providing a new method for the synthesis of elaidic acid.

Summary

Conditions which favor the selective hydrogenation of glyceride oils also favor the development of trans isomers. Complete curves are presented showing the formation and disappearance of trans isomers during the hydrogenation of linseed oil, soybean oil, cottonseed oil, olive oil, lard, and edible tallow, as determined by the infrared spectrophotometric method. An unusually high percentage of trans linkages develops during the hydrogenation of tallow.

REFERENCES

1. Swern, D., Knight, H. B., Shreve, O. D., and Heether, M. R., J. Am. Oil Chem. Soc., *27*, 17-21 (1950).
2. Jackson, F. L., and Callen, J. E., J. Am. Oil Chem. Soc., *28*, 61-65 (1951).
3. Swern, D., Knight, H. B., and Eddy, R. C., J. Am. Oil Chem. Soc., *29*, 44-46 (1952).
4. Knight, H. B., Eddy, R. C., and Swern, D., J. Am. Oil Chem. Soc., *28*, 188-192 (1951).
5. Feuge, R. O., Pepper, M. B., O'Connor, R. T., and Field, E. T., J. Am. Oil Chem. Soc., *28*, 420-426 (1951).
6. Jackson, J. E., Paschke, R. F., Tolberg, W., Boyd, H. M., and Wheeler, D. H., J. Am. Oil Chem. Soc., *29*, 229-234 (1952).
7. Paschke, R. F., Tolberg, W., and Wheeler, D. H., J. Am. Oil Chem. Soc., *30*, 97-99 (1953).
8. Lemon, H. W., Report of Fifth Symposium on Flavor Stability of Soybean Oil. National Soybean Processors' Association. October 31, 1949.
9. Sims, R. J., J. Am. Oil Chem. Soc., *29*, 347-350 (1952).
10. Griffiths, H. N., and Hilditch, T. P., J. Chem. Soc., *1932*, 2315-2324; J. Soc. Chem. Ind., *53*, 75-81 T (1934).
11. Kass, J. P., and Burr, G. O., J. Am. Chem. Soc., *61*, 1062-1066 (1939).
12. Bailey, A. E., Feuge, R. O., and Smith, B. A., Oil & Soap, *19*, 169-176 (1942).
13. Swern, D., Knight, H. B., Scanlan, J. T., and Ault, W. C., J. Am. Oil Chem. Soc., *22*, 302-304 (1945).
14. Swern, D., Scanlan, J. T., and Roe, E. T., J. Am. Oil Chem. Soc., *23*, 128-131 (1946).

[Received May 27, 1953]

The Flavor Problem of Soybean Oil. XIII. Sulfur Coordination Compounds Effective in Edible Oil Stabilization[1]

A. W. SCHWAB, HELEN A. MOSER, ROSEMARY S. GURLEY, and C. D. EVANS,
Northern Regional Research Laboratory,[2] Peoria, Illinois

SOYBEAN oil is subject to deterioration by the catalytic effects of pro-oxidant metals, such as iron and copper. The catalytic effect is destroyed by the formation of a metal chelate, and the efficiency of the chelate varies with the coordinating atom. A theoretical study has been made in which the coordinating atom of model compounds was varied and an order of effectiveness was established. The effectiveness of some nitrogen chelates was shown in a previous publication (22). A similar investigation of a number of sulfur compounds capable of metal chelation is presented in this communication.

The use of coordination compounds finds application in many industries where oxidation is promoted by trace metal contamination (4, 5, 15, 18, 25, 27). The most common pro-oxidant metal encountered in soybean oil is iron, which occurs naturally in the oil in concentrations of about 0.8 part per million (10). Processing steps to which the oil is subjected may increase the iron concentration 4- to 8-fold. This increased iron content is associated with and is a cause for a greatly decreased flavor stability. Iron accumulated during processing has a much greater catalytic activity than iron native to the oil, and although improved processing conditions and the use of stainless and corrosion-resistant equipment offer a measure of control, damaging concentrations of iron still may persist. It is the role of the metal scavenger to inactivate the remaining traces of pro-oxidant metal.

Early work has emphasized that many acidic compounds capable of forming chelation complexes were effective stabilizers for edible oils (9, 22) and a systematized study with model compounds was undertaken. Model compounds of the general formula

$$HOOC-(CH_2)_m-X-(CH_2)_n-COOH$$

---

[1] This paper is based on work submitted by A. W. Schwab in partial fulfillment of the requirements for the Ph.D. degree at Bradley University, Peoria, Ill. Presented at fall meeting of American Oil Chemists' Society, Oct. 20-22, 1952, in Cincinnati, O.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.