Relative Hydrogenation Rates of Normal and Conjugated Linolenic and Linoleic Acid Glycerides

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IT has been a matter of common knowledge for many years that in triglyceride oils the linolenic and linoleic acids are more readily hydrogenated than the oleic acids. Bailey and Fisher (1) have described a mathematical treatment for expressing the relative reactivities toward hydrogen of these different unsaturated acids existing together in an oil at any given interval during the hydrogenation process. With this method they compared the reactivities of linolenic, linoleic, isolinoleic, oleic, and iso-oleic acids in different oils and under both selective and nonselective hydrogenation conditions. Later Bailey (2), using some of the same data, calculated relative reaction rates by a more complicated method and offered additional theoretical information concerning the hydrogenation process.

The present paper pertains to the determination of the relative reactivities toward hydrogen of normal and conjugated linolenic and linoleic acids, under a single set of conditions, by the Bailey and Fisher method. A mixture of 50% tung oil and 50% linseed oil was hardened at 150°C. with 0.1% electrolytic nickel catalyst in a laboratory converter, using 20 pounds' pressure of electrolytic hydrogen and good mechanical agitation. Samples withdrawn at approximately 10 I.V. intervals during the course of the reaction were analyzed for fatty acid composition.

Use of the above mixture and conditions were calculated to avoid such a complicating factor as the presence of diene-conjugated triene acids and to insure formation of sufficient conjugated linoleic acid to make its estimation practical.

Analytical Methods. Iodine values were determined by the Woburn Hanus method of Von Mikusch and Frazier (3) as well as the conventional Wijs procedure. Thiocyanogen values were determined with 0.1 N solution and a reaction time of 24 hours; the empirical values for linolenic, linoleic, and oleic acids determined by Riemenschneider, Swift, and Sando (4) were used in the calculations. Total eleostearic acid was determined by the spectrophotometric method of O'Connor, Heinzelman, McKinney, and Pack (5), which employs the absorption at 276.5 mµ where the alpha and beta curves coincide. Figures obtained by

the spectrophotometric procedure of the Rubber Reserve Company Laboratory Manual (method issued 4-16-45) were used as an indication of linolenic acid and of both normal and conjugated linoleic acid at some stages of the hydrogenation. Saturated acids were estimated by the A.O.C.S. lead-salt method, but results were arbitrarily increased by 1% because it has been our experience that in this range either the Bertram oxidation or iodine value-thiocyanogen value methods for saturated acid give values which are about that much higher and which are more nearly correct.

Original Tung Oil-Linseed Oil Mixture Composition. Both the tung and linseed oils were samples acquired on the open market. The tung-oil composition was calculated from the Woburn Hanus iodine value and the saturated acid figure to be 81.3% eleostearin, 14.2% olein, and 4.5% saturated acid glycerides. Incidentally, the spectrophotometric method of O'Connor, et al., gave a value of 80.4 for eleostearin, which checks quite well. The original linseed oil was estimated from its Wijs iodine value, thiocyanogen value, and saturated acid content to be 45.0% linolenin, 27.8% linolein, 14.9% olein, and 12.3% saturated acid glycerides. These analyses of the components were used as the basis for the composition of the 50-50 mixture used for hydrogenation.

Calculation of Composition as the Hydrogenation Progressed. The Woburn Hanus iodine value was used as the index of hydrogenation because it determines total unsaturation. Compositions were calculated on the glyceride rather than fatty acid basis as a matter of convenience. Table I data show how the eleostearin decreased as the reaction proceeded. There appears no reason to doubt the approximate validity of the spectrophotometric results. They follow a normal progression and give a nearly smooth curve when plotted. Figures taken from an arbitrarily improved curve (Figure 1) are listed in the last column. These corrected figures were used in calculation of other components of the mixture later.

Due to the large amounts of eleostearin present, the linolenin determined by the spectrophotometric method during the early stages of the hydrogenation

TABLE I
Change in Fatty Acid Composition During Hydrogenation of a Tung-Linseed Oil Mixture

| Sample	I.V.		T.V.	Composition of Glycerides										Saturated-% Lead Salt	Isolinolein-%	Olein-%
	Woburn Hanus	Wijs		Eleostearin-%		Linolenin-%		Linolein-%		Conj. Linolein-%						
				Spec.	Corrected	Spec.	Corrected	Spec.	Corrected	From I.V.	Spec.	Corrected				
Orig.	200.2	169.5	102.5	40.7	40.7	....	22.5	....	13.9	....	....	....	8.4	....	14.5
A	190.5	165.2	100.5	32.5	32.5	....	22.2	....	13.9	1.0	No Max.	5.8	8.5	....	17.0
B	180.4	158.0	98.2	26.0	25.5	....	21.9	....	13.9	3.6	No Max.	8.7	9.0	....	21.0
C	170.7	151.5	99.0	18.5	19.0	....	21.6	....	13.9	5.9	11.7	11.0	8.7	....	25.8
D	161.2	143.0	98.1	13.6	13.6	57.0	21.3	....	13.9	9.9	12.2	10.5	9.0	....	31.7
E	151.0	139.1	97.0	9.7	9.3	30.0	20.7	Neg.	13.9	5.6	11.1	9.8	9.1	....	37.2
F	139.6	130.2	96.1	4.8	5.0	18.3	20.0	Neg.	13.9	8.1	11.7	6.3	7.7	....	45.7
G	132.6	126.5	94.9	3.4	3.2	18.4	18.0	13.8	13.8	5.3	6.2	5.9	9.2	0.8	49.1
H	123.5	119.1	93.3	1.7	1.7	13.5	13.5	7.8	12.5	4.0	4.8	4.8	9.9	5.4	52.2
I	114.6	112.2	91.2	1.0	1.0	9.5	9.5	7.6	11.5	2.2	2.8	2.8	9.9	7.2	58.1
J	101.3	99.4	87.0	.7	.7	4.6	4.6	8.4	8.4	1.7	1.2	1.2	12.3	9.6	63.2
K	82.1	80.9	75.4	.5	.5	.9	.9	2.3	2.3	1.2	.8	.8	20.5	9.5	65.5
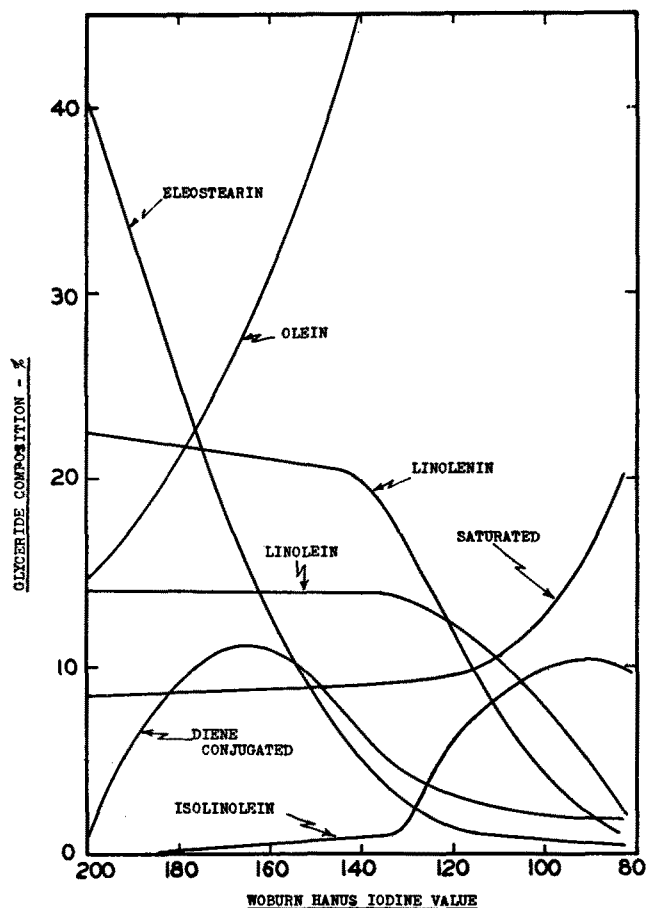
FIG. 1. Change in glyceride composition of a 50-50 tung-linseed oil mixture during hydrogenation.

is badly in error as illustrated by the Samples D and E values, Table I. Even in Sample E, after the iodine value has been dropped nearly 50 points and the eleostearin reduced to 9.3%, the linolenin was indicated to be considerably more than was initially present in the mixture. However at Sample G the eleostearin was down to 3.2%, and the linolenin assay gave a logical result.

Evidence of the validity of the spectrophotometric linolenin figure at Sample G can be obtained from the thiocyanogen value data. It is calculated from the T.V. of the original tung oil that eleostearin has a T.V. of 101. Our laboratories have also observed that conjugated linolein has practically the same T.V. as normal linolein, or about 90. The 37% eleostearin decrease up to Sample G therefore accounts for a 4.0 drop in T.V. while the remaining 3.6 T.V. decrease can be accounted for by the hydrogenation of the 4.1% linolenin. The figures in the second column under the linolenin heading of Table I were obtained as in the case of corrected eleostearin results from a smooth curve drawn from the plotted determined results.

The effect of large amounts of eleostearin on the spectrophotometric linolein determination was to produce negative calculated amounts, but here again when the eleostearin was reduced to a relatively low concentration as at Sample G, the determined linolein value became more logical. Acceptance of the Sample G result as correct means that hydrogenation of linolein has been balanced by its formation

from linolenin. The spectrophotometric linolein figures for Samples H and I are out of line with those for G and J. Unfortunately the samples had been destroyed before this was realized, and they could not be checked. The corrected figures, including those for Samples H and I, are based on a curve drawn with the assumption that the G, J, and K sample values are correct.

Figures for conjugated linolein were derived in three ways. The difference between the Hanus and Wijs I.V.'s furnishes an estimate of conjugation. In the original tung oil this difference corresponds to absorption by 2.13 of the three double bonds in the eleostearin. On the basis of this relationship the difference between Hanus and Wijs values becomes greater than is accounted for by the eleostearin as the hydrogenation progresses. The discrepancy has been calculated as conjugated linolein, formed from the eleostearin by assuming that the diene material absorbs Wijs reagent at only one bond. These are the first column of conjugated linolein figures in Table I. They are obviously erratic, perhaps partly because of variations in the excess of Wijs reagent used in that determination.

Another figure for diene conjugation is the spectrophotometric shown in the second column. The high amount of eleostearin apparently also interfered with this determination during the earlier stages of the hydrogenations, but from Sample C on the results are in a reasonable range.

Since the diene material is derived from the hydrogenation of eleostearin, the amount formed can also be calculated from the Woburn Hanus I.V. drop and the spectrophotometric eleostearin decrease with a small correction for the estimated slight hydrogenation of linolenin. Thus at Sample A the Hanus I.V. has decreased 9.7, but 0.6 I.V. are allotted to the linolenin change, leaving 9.1 I.V. available for the indicated 8.2% eleostearin decrease. As also shown in Table I, no saturated acid has been formed at this point so the only solution which fits the figures is the formation of 5.8% conjugated linolein with 2.4% eleostearin hydrogenated directly to olein. This method of calculation leads to the figures shown in the third conjugated linolein column for Samples A through F, and these have been assumed to be the most reliable of the three methods. From Sample G on, the first two methods described for the estimation of the diene material agree quite well. In this range the spectrophotometric figures were taken for the third column except that for the G sample the result was corrected slightly to make a smoother curve.

The estimates of saturated, oleic, and isolinoleic glycerides are listed in other Table I columns. The saturated acid figure is the lead-salt result plus 1% since, as previously mentioned, general experience with Bertram oxidation and I.V.-T.V. calculated results suggest that in this range the lead-salt figure is low by that amount. Note that no saturated acid was formed until the eleostearin and conjugated linolein had nearly disappeared and the linolenin and linolein were relatively low. The isolinolein and olein were simply calculated from the iodine value corrected for the results previously derived for the other components.

Curves illustrating change in fatty acid composition (glyceride basis) vs. decrease in Woburn Hanus iodine value during hydrogenation are shown in Figure 1.

Reactivity Ratios. The concept and method of calculating reactivity ratios as proposed by Bailey and Fisher are simple and briefly as follows:

Calculation of Reactivity Ratios

Let K_A = the reactivity of Compound A

K_B = the reactivity of Compound B

M_A = the % Compound A reacting in given interval

M_B = the % Compound B reacting in given interval

C_A = average concentration A during interval

C_B = average concentration B during interval

Then $M_A = K_A C_A$ and $M_B = K_B C_B$

or (1) $K_A = M_A/C_A$ and (2) $K_B = M_B/C_B$

Dividing (1) by (2) $K_A/K_B = M_A C_B/M_B C_A$

As previously pointed out, some of the eleostearin is converted directly to olein. In the first interval of hydrogenation this amounted to 29% of the eleostearin hydrogenated if it is assumed that none of the conjugated linolein formed was hydrogenated. Actually, of course, a small amount of the latter reacted. For purposes of calculating the reaction ratio of eleostearin to conjugated linolein the assumption has been made that one-fourth of the eleostearin went directly to olein.

If all three double bonds in the linolenic acid were equally reactive, two-thirds would be hydrogenated to conjugatable linolein and one-third to the 9-15 isomer. The work of Bailey and Fisher indicates the true proportion of isolinolein formed to be nearer one-half than one-third. However for the purpose of these reactivity ratio calculations the one-third figure has been used.

TABLE II
Reactivity Ratios

I. V. Interval	El/Ll	El/CL	CL/Ll	Cl/L	Ll/L
200-140	20.0	1.0	....	....	....
151-140	....	....	2.6	....	....
140-133	4.2	1.6	1.9	1.3	....
133-124	2.0	1.3	1.9	2.1	0.8
124-115	1.5	0.8	1.4	1.6	1.1

El = Eleostearin, Ll = Linolenin, CL = Conjugated Linolein, L = Linolein.

Reactivity ratios are shown in Table II. During the initial stages of the hydrogenation the eleostearin was 20 times more reactive than the normal linolenin but became proportionally less reactive as its concentration decreased until at the 1-2% level of the 124-115 I.V. interval, it was only 1.5 times as reactive as the normal linolenic glyceride. The conjugated linolein was about equally as reactive over the entire range of the experiment as the eleostearin and, therefore, also slowed down in relation to the normal linolenin and linolein in the later stages of the hydrogenation.

The reactivity ratio of eleostearin to conjugated linolein for the 200-140 I.V. interval was not calculated directly from the concentrations at those I.V. points, but is an average of the values derived for the several sampling intervals over that range. The ratio of eleostearin to linolenin for the 200-140 interval was calculated directly from the concentrations at those iodine values, however, because the change in linolenin was so small. The reactivity ratio of

linolenin to linolein, which approximates unity, is in the same range as found by Bailey and Fisher.

The reason for the very marked decrease in eleostearin and also conjugated linolein reactivity during the progress of hydrogenation may lie in glyceride structure. Many of the glyceride molecules in the original tung oil contain three eleostearic acid radicals, and these may be adsorbed on the catalyst much more readily than molecules containing one eleostearic acid with two oleic acids, the form of glyceride in which the eleostearic acid is likely to be present during the latter stages of the hydrogenation.

Indeed the results may be considered as evidence of selectivity among glycerides in the hydrogenation process. Total unsaturation in the glyceride as well as in the fatty acid may be an important factor in selectivity although, of course, the two are never entirely independent in practice. Such a possibility was suggested by Bushnell and Hilditch (6) some years ago when, in hydrogenating a mixture of alpha oleo palmitate and triolein, they found the latter to be preferentially hydrogenated.

Summary

A mixture of 50% tung oil and 50% linseed oil was hydrogenated and samples withdrawn at approximately 10 I.V. intervals during the course of the reaction were analyzed for fatty acid composition. Reactivity ratios for the various fatty acids were calculated.

Because of the limitations of the analytical methods, particularly the spectrophotometric methods used for linolein, conjugated linolein, and linolenin, and the arbitrary procedures of arriving at corrected values for these constituents, the composition data and reactivity ratios derived therefrom must be regarded as only approximations.

However it seems safe to conclude that during the initial stages of the hydrogenation the eleostearin was many times more reactive than normal linolenin for equivalent concentrations but as the eleostearin was reduced in concentration, its reactivity decreased until, at a 1% to 2% level, it was only slightly more reactive than the normal linolenin, again for equivalent concentration. Likewise the conjugated linolein formed from the eleostearin was many times as reactive as the normal linolein when present in considerable amounts, but the reactivity ratio of conjugated linolein to normal linolein dropped markedly in the latter stages of the process. Normal linolenin and normal linolein had similar reactivities.

It is suggested that the amount of conjugation and unsaturation in the glyceride rather than in the individual fatty acid may be the controlling factor in hydrogenation selectivity.

Acknowledgment

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