Correlation of Stability with Fatty Acid Composition of Hydrogenated Vegetable Oil

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Introduction

IT is well known that the stability of an oil toward oxidative rancidity is determined by various factors among which are fatty acid composition, antioxidant content, and pro-oxidant content. Little data is available with respect to the quantitative effect on stability of changes in fatty acid composition. Stirton *et al.* (8) have reported work on the effect of the addition of antioxidants on the stabilities of various pure esters and known mixtures of them, but did not attempt to quantitatively correlate the stabilities and composition of the mixtures. Thompson (9) has recently presented data on the relationship between linolein content and stability in hydrogenated oils, but did not find any simple correlation between them. Bailey (1) has stated that "in the case of hydrogenated peanut, cottonseed, and soybean oils, hydrogenated with reasonably good selectivity, there is an approximately linear relationship between the iodine value of the oil and the logarithm of the keeping time, down to an iodine value of about 50 with the stability doubling each time that the iodine number is reduced 7-15 units."

In the present investigation efforts were made to correlate quantitatively the stability and fatty acid composition of several cottonseed, peanut, and linseed oils which were progressively hydrogenated and samples withdrawn periodically for determination of fatty acid composition, keeping quality, and other characteristics.

Experimental

The preparation and analyses of the fats used in this investigation are reported elsewhere (5). The keeping quality of each fat was determined by the active oxygen method (7) at 97.7° C. using a peroxide value of 100 milliequivalents per kilogram as the end point. The keeping time in hours designated as AOM, the reciprocal of the keeping time designated as 1/AOM, and the percentage concentration of the most highly unsaturated acid in each sample are given in Table 1, together with data on the congeal point for some of the samples.

The congeal points were determined by immersing a 200-ml. electrolytic beaker containing 70 g. of the melted fat (60° C.) in a water bath at the proper temperature and stirring the sample at the rate of 100 strokes per minute until the temperature of the sample became constant or began to rise at which time stirring was stopped and the beaker was transferred to an air bath surrounded by a water bath where it was allowed to stand until the temperature of the sample reached a maximum. This temperature was recorded as the congeal point unless the sample was obviously too hard or too soft to be worked. In the latter case, the bath temperature was raised or lowered 5° and the determination was repeated. In general, the bath temperatures used were 15° C. for samples having congeal points at 18° to 23° C.; 20° C. for congeal points of 23° to 28° C.; etc.

A modified Emmerie-Engel method was used to determine the tocopherol content of the samples.

Results

Hydrogenated cottonseed and peanut oils. Graphical examination of the data revealed no linear correlation between keeping time or the logarithm of the keeping time and the iodine value or the composition of the various series of oils.

Two series of selectively hydrogenated oils (PO-51 and CO-60) showed a linear correlation between the reciprocal of the keeping time (1/AOM) and the iodine value up to the point of disappearance of linoleic acid glycerides, but did not show a similar correlation in the case of the non-selectively hydrogenated oil (CO-61). It is thus apparent that hydrogenation occurred in the first two cases without increase in the amount of saturated acids formed while in the latter case (non-selective hydrogenation) variable amounts of saturated acid glycerides were formed, as hydrogenation progressed.

Correlation between keeping time and linolein content. A linear relationship was observed both for the selectively (PO-51 and CO-60) and for the non-selectively hydrogenated (CO-61) oils when the reciprocal of the keeping time (1/AOM) was plotted against the content of linoleic acid glycerides. As may be seen in Fig. 1, the hydrogenated cottonseed oils lie on one line and the hydrogenated peanut oils on a second line.

Quantitative evaluations of these linear relationships were made using the methods of correlation analysis for a small number of samples as described by Ezekiel (4). The constants for the regression equation

$$1/\text{AOM} = a + b\ (\%\ \text{linolein})$$

together with the adjusted coefficients of determination, standard errors of estimate, and "t" values are given in Table 2. The coefficient of determination indicates the fraction of the change in the dependent variable which results from the change in the independent variable. The standard error of estimate indicates the degree to which estimated values of the dependent variable may be expected to approximate the true values. The "t" value, together with the number of samples in the series, indicates the significance of the observed correlations. Values of "t" in excess of 10 for four or more samples or in excess of 3.4 for 10 or more samples indicates that there is less than one chance in a hundred that the observed correlation is a result of chance. In the present investigation the coefficients of determination are probably the most significant.

The results given in Table 2 indicate that when a peanut or cottonseed oil is hydrogenated, 99% of the

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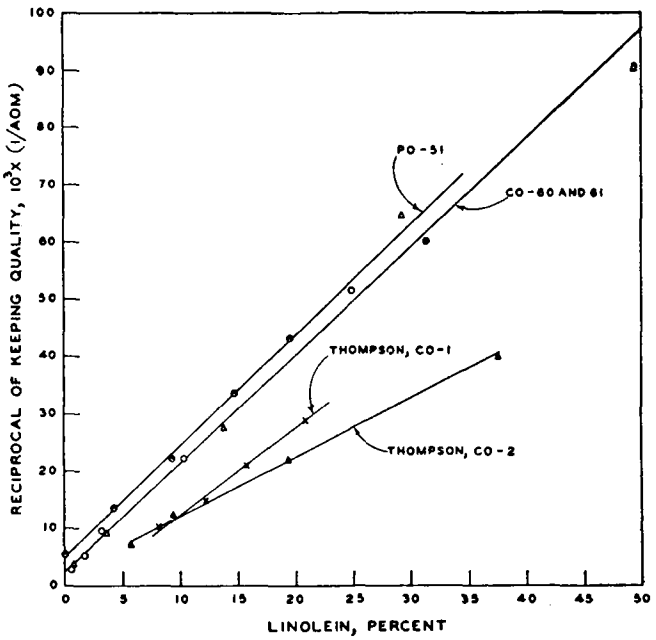

FIG. 1. Regression of reciprocal of keeping quality vs. linolein content of hydrogenated vegetable oils. △ refers to CO-60, ○ refers to CO-61.

change in stability is due to the change in linolein content and that the change in 1/AOM is proportional to the change in linolein content.

The same type of correlation applies to the two series of hydrogenated cottonseed oils reported by Thompson (9). Each series consisted of four samples prepared from the same refined and bleached oil by hydrogenating to different linolein contents. The reciprocal of the keeping time reported by Thompson has been plotted against the linolein content in Fig. 1 and the corresponding statistical data are included in Table 2. Here too, 99% of the variation in 1/AOM is attributable to the variations in linolein content.

The above results should not be interpreted to mean that 99% of the difference in stability of any two randomly selected samples of hydrogenated cottonseed or peanut oils is due to the difference in linolein content because the original oils may vary appreciably in composition, particularly with respect to content of anti- and pro-oxidants.

Bailey (1) has published graphical data for the stability of a number of hydrogenated cottonseed oils as a function of linolein content. These data apply to different original oils of unknown composition and no doubt varied in their contents of anti- and pro-oxidants. When these data were converted to plots of 1/AOM *vs.* linolein content a scattering of points was obtained which lay on or in the vicinity of a straight line corresponding to the constants indicated in Table 2.

The degree of correlation obtained with the oils reported by Bailey is lower than in those reported by the present authors and with the oils reported by Thompson but it is nevertheless highly significant. Approximately 70% of the variation in the stability of the series of oils reported by Bailey is due to the variation in linolein content while the remainder is

TABLE 1.

Characteristics of Hydrogenated Vegetable Oils.

Oil		Type of hydrogenation	Unsaturated constituent		AOM hours	1/AOM x 10^3	Congeal point °C.
Kind	No.		Type	%			
Cottonseed[1]	60-0	None	Linolein	48.4	11.0	90.9	.....
Cottonseed	60-1	Selective	Linolein	29.2	15.5	64.5	.....
Cottonseed	60-2	Selective	Linolein	13.9	36.0	27.6	21.6
Cottonseed	60-3	Selective	Linolein	8.6	110.0	9.09	27.3
Cottonseed[2]	60-4	Selective	Linolein	0.7	251	3.98	.....
Cottonseed	60-5	Selective	Olein	64.2	342	2.92	34.4
Cottonseed	60-6	Selective	Olein	58.0	395	2.53	.....
Cottonseed	60-7	Selective	Olein	49.5	470	2.13	.....
Cottonseed	60-8	Selective	Olein	40.3	646	1.55	.....
Cottonseed[1]	61-0	None	Linolein	48.4	11.0	90.9	.....
Cottonseed	61-1	Non-selective	Linolein	24.9	19.5	51.3	.....
Cottonseed	61-2	Non-selective	Linolein	10.3	45.0	22.2	25.7
Cottonseed	61-3	Non-selective	Linolein	3.1	104	9.62	30.6
Cottonseed	61-4	Non-selective	Linolein	1.6	197	5.08	35.0
Cottonseed	61-5	Non-selective	Linolein	0.5	342	2.92	.....
Cottonseed	61-6	Non-selective	Olein	52.6	452	2.21	.....
Cottonseed	61-7	Non-selective	Olein	42.8	593	1.69	.....
Cottonseed	61-8	Non-selective	Olein	31.1	705	1.42	.....
Peanut[3]	51-0	None	Linolein	32.8	16.5	60.6	.....
Peanut	51-1	Selective	Linolein	19.6	23.3	43.0	.....
Peanut	51-2	Selective	Linolein	14.6	30.0	33.3	.....
Peanut	51-3	Selective	Linolein	9.3	45.5	22.0	.....
Peanut	51-4	Selective	Linolein	4.6	75	13.3	.....
Peanut	51-5	Selective	Linolein	0.0	190	5.26	25.5
Peanut	51-6	Selective	Olein	72.1	365	2.74	28.4
Peanut	51-7	Selective	Olein	66.9	480	2.08	.....
Peanut	51-8	Selective	Olein	56.1	700	1.43	.....
Peanut	51-9	Selective	Olein	46.6	975	1.03	.....
Peanut	51-10	Selective	Olein	32.8	1125	0.89	.....
Linseed[4]	1-0	None	Linolenin	52.0	3.0	333.3	.....
Linseed	1-1	Non-selective	Linolenin	34.7	5.3	189.0	.....
Linseed	1-2	Non-selective	Linolenin	20.6	10.8	93.0	.....
Linseed	1-3	Non-selective	Linolenin	8.8	21.0	47.6	.....
Linseed	1-4	Non-selective	Linolenin	1.9	56.0	17.9	12.6
Linseed	1-5	Non-selective	Linolenin	0.1	151	6.6	30.4
Linseed	1-6	Non-selective	Isolinolein	7.0	740	1.35	42.7
Linseed	1-8	Non-selective	Olein	25.8	1800	0.56	.....
Linseed[4]	2-0	None	Linolenin	52.0	3.0	333.3	.....
Linseed	2-1	Selective	Linolenin	35.3	4.3	235.0	.....
Linseed	2-2	Selective	Linolenin	22.7	7.0	143.0	.....
Linseed	2-3	Selective	Linolenin	9.9	17.0	58.8	.....
Linseed	2-4	Selective	Linolenin	0.9	50.5	19.8	14.2
Linseed	2-5	Selective	Linolenin	0.2	174	5.75	29.3
Linseed	2-6	Selective	Isolinolein	7.6	386	2.59	41.0
Linseed	2-7	Selective	Isolinolein	2.8	1400	0.71	.....
Linseed	2-8	Selective	Olein	33.1	1575	0.65	.....

[1] Tocopherol content, $\alpha = 0.072\%$, $\gamma = 0.026\%$.
[2] Tocopherol content, $\alpha = 0.071\%$, $\gamma = 0.029\%$.
[3] Tocopherol content, $\alpha = 0.023\%$, $\gamma = 0.023\%$.
[4] Tocopherol content, $\alpha = 0.002\%$, $\gamma = 0.058\%$.

TABLE 2.

Statistical Correlation of Reciprocal of Keeping Quality With Composition of Hydrogenated Vegetable Oils.

Oil		Unsaturated constituent							
Type	Series No.	Type	Range %	a	b	$\overline{r^2}$[b]	$\overline{S}$[c] 1/hrs.	t	n[g]
Cottonseed[a]	CO—60 & 61	Linolein	0.50-48.4	0.002902	0.001897	0.993	0.00254	43	10
Peanut[a]	PO-51	Linolein	0.04-32.8	0.0063	0.001725	0.992	0.00203	18	6
Cottonseed[a]	Thompson, CO-1	Linolein	8.3 -20.8	−0.00202	0.001455	0.991	0.00074	14	4
Cottonseed[a]	Thompson, CO-2	Linolein	5.7 -37.6	0.00228	0.00101	0.991	0.0138	14	4
Cottonseed[a]	Bailey	Linolein	1.1 - 8.8	0.00263	0.00169	0.713	0.00232	13	19
Cottonseed[d]	CO—60 & 61	Olein	31.1 -64.2	1072	−11.51	0.954	28.7[f]	10	7
Peanut[d]	PO-51	Olein	32.8 -72.1	1827	−20.0	0.958	65.8[f]	8	5
Linseed[e]	LO-2	Linolenin	0.2 -52.0	0.0050	0.0063	0.995	0.0097	28	6

[a] Regression equation, 1/AOM = a + b (% linolein).
[b] Coefficient of determination, adjusted for number of samples.
[c] Standard error of estimate, adjusted for number of samples.
[d] Regression equation, AOM = a + b (% olein).
[e] Regression equation, 1/AOM = a + b (% linolenin).
[f] Standard error of estimate in hours.
[g] Number of samples in series.

due to some other and unknown variable or variables.

Correlation between stability and olein content. For samples containing no polyunsaturated acids, the best linear correlation which has been found is between keeping quality and olein content.

In Fig. 2, the keeping quality (AOM) in hours is plotted against percentage of olein for those cottonseed and peanut oils which have been hydrogenated to the point of complete disappearance of linolein. The statistical constants for these curves corresponding to the equation

$$AOM = a + b\ (\%\ olein)$$

are also given in Table 2. Although the degree of correlation is not as high as in the case of the linolein content *vs.* the reciprocal of the keeping time, it is highly significant.

Hydrogenated linseed oil. The fatty acid composition of linseed oil and particularly of hydrogenated linseed oil is much more variable than that of either peanut or cottonseed oil. It has been shown by Bailey and Fisher (2) that during the hydrogenation of linseed oil under relatively highly selective conditions linolenic, linoleic, and oleic acids are hydrogenated in the ratio of 40:20:1. As might be expected, therefore, a fairly linear correlation of linolenin or linolein content with the reciprocal of the stability was observed in the case of the selectively hydrogenated linseed oils, but not in the non-selectively hydrogenated oils, and in fact, no linear correlation of any type was found for the latter series. In the case of the selectively hydrogenated linseed oils the correlation between the reciprocal of the keeping quality and the linolenin content was better than with the linolein content The plot of the data relating the percentage of linolenin with reciprocal of the keeping quality is shown in Fig. 3. The statistical constants for the equation

$$1/AOM = a + b\ (\%\ linolenin),$$

corresponding to the data in Fig. 3, are given in Table 2. The number of samples of hydrogenated linseed oils which did not contain linolenin was too small for application of correlation methods of analysis and their graphical treatment is, therefore, omitted here.

General Discussion

It is known that peanut oil of any given iodine value, linolein or olein content is more stable than cottonseed oil having the same characteristics which is contrary to expectancy on the basis of the respective tocopherol contents of these two oils. The data reported here do not provide a complete explanation for this difference in the relative stabilities of the two oils. Peanut oil may contain unidentified antioxidants in addition to the tocopherols, as suggested by Bailey *et al.* (3), or cottonseed oil may contain pro-oxidants in greater amounts than does peanut oil, or the glyceride configuration and fatty acid composition may affect the stability of the oil in some obscure manner.

However, it is probable that some combination of the first two factors is responsible for the observed difference.

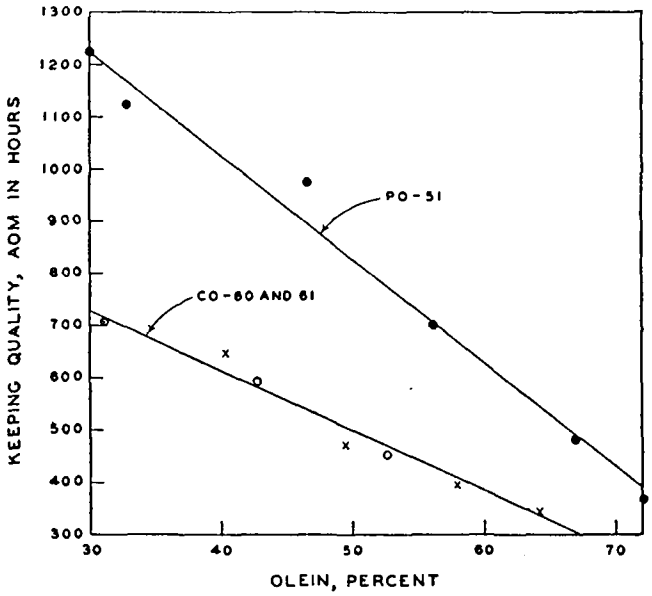

FIG. 2. Regression of keeping quality vs. olein content of hydrogenated vegetable oils. × refers to CO-60, ○ refers to CO-61.

When hydrogenated to the same iodine value linseed oil is more resistant to oxidative rancidity than are cottonseed and peanut oils. This is probably the result of the presence in hydrogenated linseed oil of a large amount of isolinoleic acid in which the double bonds are separated by two or more methylene groups. Isolinoleic acid should be more stable than normal linoleic acid but hydrogenated linseed oil containing this acid apparently undergoes a deterioration in flavor which is not associated with oxidative rancidity and which Lemon (6) attributed to the isolinoleic acid.

Summary

Cottonseed, peanut, and linseed oils were hydrogenated under selective and non-selective conditions and samples were withdrawn periodically for determination of their fatty acid composition, keeping quality,

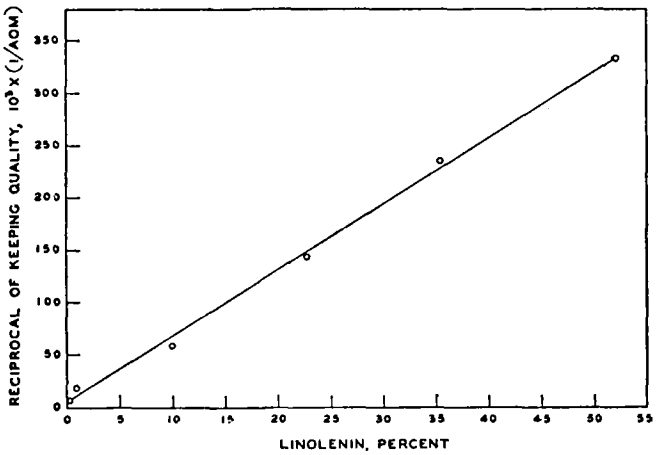

FIG. 3. Regression of reciprocal of keeping quality vs. linolenin content of hydrogenated linseed oil.

and other characteristics. The results were submitted to graphical and statistical analysis from which the following conclusions were drawn.

(1) When cottonseed or peanut oil is hydrogenated either under selective or non-selective conditions, the change in the reciprocal of the keeping quality, as measured by the active oxygen method, is proportional to the change in linolein content up to the point of disappearance of linolein.

(2) After all linoleic acid has disappeared, the change in keeping quality is proportional to the change in olein content.

(3) When linseed oil is hydrogenated under selective conditions, the change in the reciprocal of the keeping quality is proportional to the change in the linolenin content up to the point of disappearance of the linolenin.

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Fatty Acid Composition of Hydrogenated Vegetable Oils

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Introduction

SINCE development of the thiocyanogen method by Kaufmann (7), many workers have estimated the content of oleic and linoleic acids in fats which do not contain linolenic acid by means of simultaneous equations involving iodine and thiocyanogen values and have estimated the content of saturated acids as the difference between the contents of total and unsaturated acids. When linolenic acid is present as a constituent of the fat, the saturated acids are generally determined by the Twitchell lead salt-alcohol (14) or Bertram oxidation method (15) and the result applied with another set of simultaneous equations involving iodine and thiocyanogen values in estimating the contents of oleic, linoleic, and linolenic acids. More recently Mitchell, Kraybill, and Zscheile (11) developed a method for estimating the contents of linoleic and linolenic acids in fats on the basis of the ultraviolet absorption spectra of the fat or fatty acid mixture after alkali isomerization.

This method, or a modification (3, 4) thereof, has been used by a number of investigators who have reported data on the fatty acid composition of vegetable oils. In some cases reasonably satisfactory comparisons of the two methods have been made, but in others they have given results differing by more than the probable experimental errors of the individual methods. For example, Reimenschneider (17) found 3-5% more linoleic acid in tobacco seed oil by the spectrophotometric than by the iodine-thiocyanogen method. Lemon (9) investigated the composition of hydrogenated linseed oil using both methods and found that the iodine-thiocyanogen method was unsatisfactory because of the presence of an octadecadienoic (isolinoleic) acid which absorbs more thiocyanogen than normal linoleic acid. This acid does not undergo conjugation upon treatment with alkali under conditions which produce isomerization in normal linoleic acid, therefore Lemon applied the spectrophotometric and iodine-saturated acid value methods to estimate the amount of isolinoleic acid which was present in hydrogenated linseed oils. Subsequently Mattil (10) reported the results of work which indicated the presence of isolinoleic acid in hydrogenated soybean oil, a fact which was confirmed by Daubert and Filer (5) who concentrated the acid by the lead salt-alcohol method but did not determine the actual extent of its presence in this fat. Lemon assumed that the isolinoleic (9,15-octadecadienoic) acid was produced solely by the selective hydrogenation of the central double bond of linolenic acid, but Daubert claimed that a similar and perhaps identical acid is produced by isomerization of linoleic acid when its methyl ester is hydrogenated at room temperature and atmospheric pressure with palladium black as catalyst. If the phenomenon reported by Daubert occurs during hydrogenation of fats at super-atmospheric temperatures and pressures with a nickel catalyst, it might also be expected that isolino-

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