Some Relationships Between Fat Acid Composition and the Iodine Number of Linseed Oil[1,2]

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THE drying oil industries prefer linseed oil of high iodine number. The iodine number, which has been used as a criterion of quality, may vary over a wide range. Those factors which are known to influence the iodine number of linseed oil are variety and weather conditions during the growth of the flax plant (1, 2, 3). In their efforts to improve flax varieties plant breeders consider important the iodine number of the oil produced. Now that the analyses of oils such as linseed are far more dependable than they were a few years ago, it may be desirable to attempt to define quality more specifically, namely, in terms of fat acid composition. The object of this report is to point out some of the relationships of fat acid composition to the iodine number and the limitations of the iodine number alone as an estimate of composition of linseed oils.

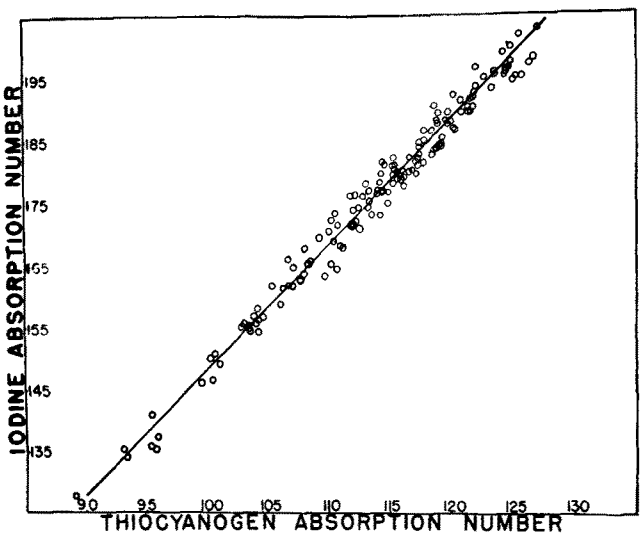

FIG. 1. Linear relationship between the iodine and thiocyanogen number of linseed oils.

All of the oils upon which this study is based have been analyzed in this laboratory by the thiocyanometric technique. Constants used in the equations were those determined on purified acids prepared in this laboratory (4). The oils were from several varieties of flaxseed (5) grown at many widely separated locations in the United States and Canada. The majority of the oils were pressed from ground meal at approximately 60°C.; a few from immature seed (6, 7) were obtained by petroleum ether extraction.

When the thiocyanogen numbers of the 148 oils are plotted against the iodine numbers (Fig. 1) it is evident, from the equations used to calculate composition, that there are some relationships between composition and the iodine number. The equation of the regression line is:

Thiocyanogen number = 0.496 Iodine number + 26.7.

Saturated, oleic and linolenic acid glycerides are plotted against the iodine number in Figures 2, 3 and 4. The best fitting lines were calculated by the method of least squares.

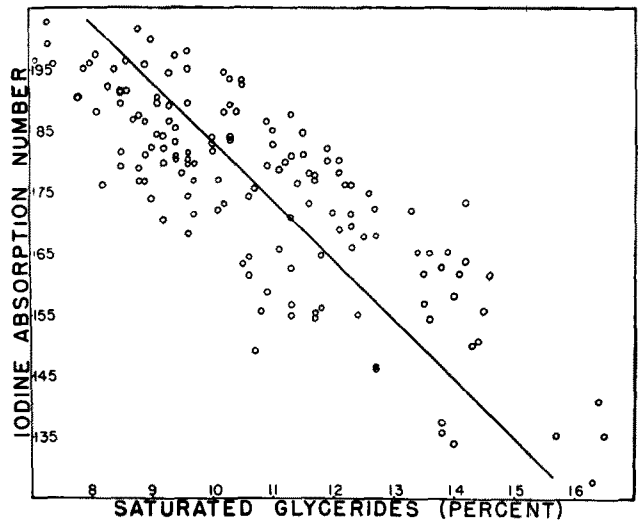

FIG. 2. Relationship of the saturated acids to the iodine number of linseed oils.

In the case of linoleic acid, unlike the other three acids, no relationship was evident from plotted values. Correlation coefficients between the iodine number (Y values), and the thiocyanogen number and acid glycerides (X values) were calculated. The values based on 148 samples are as follows:

	r_{xy}
Thiocyanogen number	+.99
Saturated glycerides	—.80
Oleic glycerides	—.94
Linoleic glycerides	—.27
Linolenic glycerides	+.97

The correlation coefficients, except those for linoleic, are highly significant. That linoleic acid shows little relationship to the iodine number and the negative sign of the correlationship coefficient is surprising. In the case of saturated acids, which are determined directly, the relationship to the iodine number is slightly less than for oleic and linolenic acids.

The group of oils includes those from eight varieties of flaxseed. Since the fat acid composition of linseed oil is related to variety (5), correlation coefficients were calculated for oils from each of four varieties.

ALTHOUGH the number of oil samples from two of the varieties is small for statistical analysis, most of the correlation coefficients are close to those for all samples. Saturated acids in Rio and Linota

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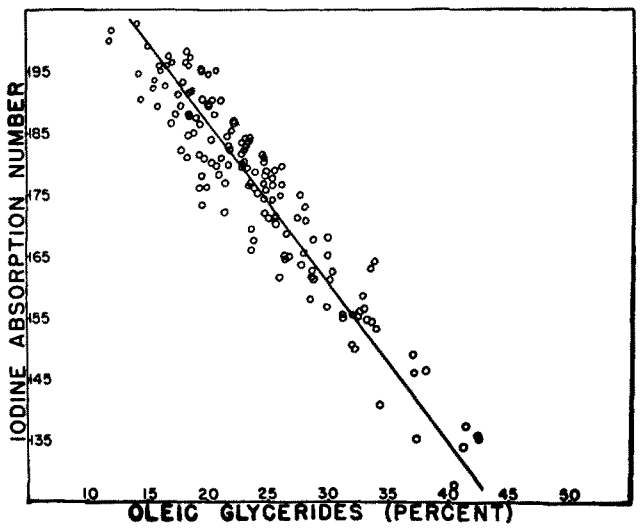

FIG. 3. Relationship of oleic acid to the iodine number of linseed oils.

oils show a closer relationship to the iodine number than do saturated acids in oils from all varieties. In the case of Redwing oils the relationship of saturated acids is not as high. All of the correlation coefficients for linoleic acid, with the possible exception of Linota oils, are of little significance. There appears to be no explanation for the change in sign with Rio oils. Linolenic acid follows the iodine number closely in all oils.

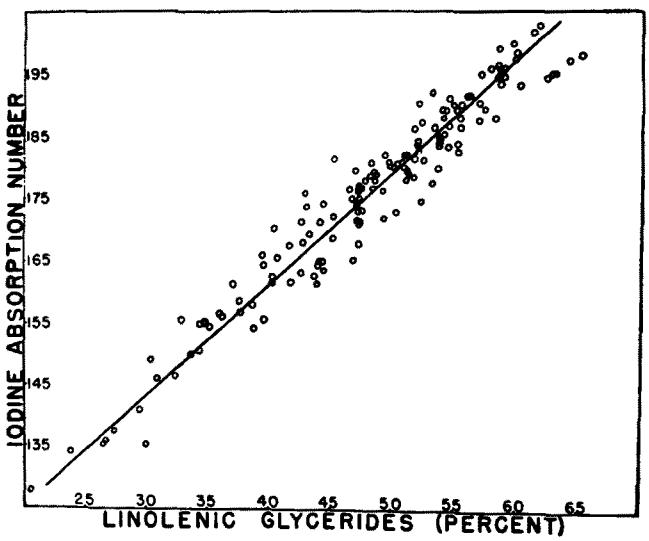

FIG. 4. Relationship of linolenic acid to the iodine number of linseed oils.

Before giving further consideration to the results shown in the figures we should inquire into the method of analysis to learn something of the precision to be expected in the results. The amount of unsaponifiable matter, even though the error in its determination may be high, changes the fat acid composition of the glyceride fraction by insignificant amounts. The values used in modified Kaufmann equations, namely the iodine number, thiocyanogen number and percent saturated acids, determine the calculated unsaturated acids composition of the oil. Data are available to show the precision which can be expected from determinations of each. Before

TABLE 1.

Correlation Between Iodine Number and Fat Acid Glycerides in Oils From Single Varieties.

Variety	Number of samples	Correlation coefficients			
		Saturated glycerides	Oleic glycerides	Linoleic glycerides	Linolenic glycerides
		r_{xy}	r_{xy}	r_{xy}	r_{xy}
Bison	48	—.80	—.96	—.25	+.97
Redwing	38	—.70	—.87	—.36	+.96
Rio	16	—.93	—.94	+.38	+.94
Linota	15	—.90	—.91	—.56	+.97

freshly prepared Wijs iodine and thiocyanogen solutions were used for analyses of oils, the iodine number and thiocyanogen number of one or two "reference" oil samples was determined. These oil samples were preserved to check new solutions so many determinations were made on the same sample. The maximum and average deviations from the mean, without excluding a single determination of several of these "reference" samples, are as follows:

	Number of determinations	Average deviation from mean	Maximum deviation from mean
Iodine number	64	0.5	1.4
Thiocyanogen number	38	0.8	2.3

A series of determinations of the saturated acids in a single oil sample has not been made, but the saturated acids have been determined in oil samples and in the fat acids of the same oil samples (4) after saponification. The maximum difference was 0.5 percentage points, the average 0.3. These values probably represent the sum of plus and minus deviations, so, true deviations from the mean are likely near one-half the values given. They will, however, be used as maximum and minimum deviations to illustrate how the saturated acid content changes the calculated unsaturated acid composition.

A table has been prepared to show how deviations in the analytical results will alter the calculated fatty acid composition. For the purpose of illustration we assume the following analytical values were found in a linseed oil sample: Iodine number, 180; thiocyanogen number, 116; and saturated acids, 10%. It is assumed that these are "true" values. In Table 2 glyceride composition was calculated, using the above analytical results as average and maximum deviations from the mean found by studies of the precision of the methods. The equations (4) are as follows:

$$\% \text{ oleic glyceride} = 1.724\,TN - 1.303\,IN - 0.638\,S + 63.8$$

$$\% \text{ linoleic glyceride} = -3.426\,TN + 1.457\,IN - 1.693\,S + 169.3$$

$$\% \text{ linolenic glyceride} = 1.701\,TN - 0.154\,IN + 1.330\,S - 133.0$$

where TN = thiocyanogen absorption number, IN = iodine absorption number, and S = percent saturated acids.

The analytical values in Table 2 are not arranged in all possible combinations, but enough are given to show how the calculated composition may be modified when the analytical values differ by amounts expected from the precision of the analysis.

WE will assume that the values in example 1 give the correct composition of the oil. In examples 2, 3 and 4 the iodine number, thiocyanogen number and saturated acids are increased (separately) by amounts equal to the average deviation from the

mean. The probable deviation of the iodine number (0.5 points) changes oleic acid 0.6 percentage points, linoleic acid 0.7 percentage points, and linolenic acid only 0.1 percentage points. When the thiocyanogen number is changed by 0.8 points, oleic changes by 1.4 percentage points, linoleic by 2.8 percentage points, and linolenic by 1.4 percentage points. When the saturated acids are changed by 0.3 percentage points, linoleic is changed most, 0.5 percentage points, and linolenic next, 0.4 percentage points. Each value has been increased in the examples cited. Had the values deviated in the opposite direction (a minus is just as probable as a plus), the calculated composition would be changed by an amount approximately those shown, but in the opposite direction.

When an analysis is carried out, the probability of plus or minus deviations is equal. In example 5 all are increased. In example 6 the values are changed so that the calculated linoleic and linolenic acids differ by the maximum possible from mean deviations. In the latter example the calculated composition is altered much more than when each analytical value is changed separately or when all are changed by the same sign.

In examples 7, 8 and 9 differences in composition, when the analytical results deviate by the maximum from the mean, are shown. If the values are arranged with both plus and minus deviations, it is possible to change the linoleic content as much as ± 10 percentage points from the value in example 1.

We can see that an error in the precision of each of the three analyses will change the calculated linoleic acid more than oleic or linolenic acid and that, of the three determinations, the thiocyanogen number reduces the precision by the greatest amount.

Although the unsaturated fat acid composition is not greatly changed by results within the probable precision of the analyses, the composition is changed so greatly by maximum deviations that there may be some question regarding the significance of the figures and the correlation coefficients. The probable errors due to the precision obtained in the analyses are those to be considered in the values obtained by statistical calculation. It is possible to estimate the probable error for the calculated value of each fat acid. Since the composition is calculated from n determinations ($n = 3$, Table 2), and each determination will deviate plus or minus by the amounts of the average deviation from the mean, the number of combinations (each is equally probable) is given by 2^n, or 8. Two of these combinations are examples 5 and 6, Table 2. The composition has been calculated from each of the eight combinations. The Σ d/8 [where d = calculated—"true value" (Example 1, Table 2)] for each fat acid glyceride is: Saturated, ± .35%; oleic, ± 1.39%; linoleic, ± 2.74%; linolenic, ± 1.35%. These values, as well as those in Table 2, apply to an oil giving the analytical values shown in example 1, Table 2. Had the composition of an oil of much different iodine number, thiocyanogen number and saturated acids been calculated by varying the analytical results by the amounts shown, the deviations from the accepted "true" composition would not be identical to those of the illustration shown. The difference from the values shown would, however, be very small.

IN actual practice the analyses are much better than Table 2, or the probable error in the determination of each fat acid, would indicate. It was realized early in the work that the thiocyanogen number should be determined with greater precision than obtained by a single determination. Nearly all of the composition reported from this laboratory was calculated from thiocyanogen numbers determined with two or more thiocyanogen solutions. When a plot of the iodine and thiocyanogen number gave a point several units from a straight line, the iodine number determination was also repeated. Two iodine number determinations were adopted as the routine practice during the later analyses. Two determinations of the thiocyanogen number should reduce its probable error to 0.4 point. Had this value, and a smaller mean deviation of the iodine number and saturated acids, been used in Table 2, as well as in the calculations of probable errors, deviations from the "true" values would have been much smaller. The maximum deviation from the mean would remain the same when two sets of determinations are made, but it is indeed improbable that two determinations on the same sample would deviate by the maximum in the same direction.

From the dispersion of the points along the best fitting lines (Figs. 2, 3 and 4) it should be possible to predict, within limits, the saturated, oleic and linolenic acids from the iodine number alone. The standard error of estimates is a measure of the dispersion along the regression line. It is the standard deviation (σxy) in linear correlation. The standard deviation on the regression line for each fat acid glyceride is: Saturated, 1.25; oleic, 2.12; linolenic, 2.16. This means that, knowing the iodine number, the chances are approximately 2 to 1 that each fat acid will fall ± within the units given. The composition of the three acids can be obtained approximately within the limits given from equations of the regression lines.

$$\% \text{ saturated glycerides} = -.103 \text{ iodine number} + 28.9$$
$$\% \text{ oleic glycerides} = -.382 \text{ iodine number} + 91.4$$
$$\% \text{ linolenic glycerides} = .552 \text{ iodine number} - 49.1$$

TABLE 2.

Changes in Fat Acid Composition When Analytical Results Vary by Amounts Expected From Single Determinations *

Example No.	Iodine No.	Thiocyanogen No.	Saturated acids	Composition of glycerides			
				Saturated	Oleic	Linoleic	Linolenic
			Pct.	*Pct.*	*Pct.*	*Pct.*	*Pct.*
1	180	116	10	10.5	22.5	16.4	50.6
2	180.5	116	10	10.5	21.9	17.1	50.5
3	180	116.8	10	10.5	23.9	13.6	52.0
4	180	116	10.3	10.8	22.3	15.9	51.0
5	180.5	116.8	10.3	10.8	23.1	13.9	52.2
6	180.5	115.2	9.7	10.1	20.8	20.5	48.6
7	181.4	116	10	10.5	20.7	18.4	50.4
8	180	118.3	10	10.5	26.5	8.5	54.5
9	180	116	10.5	11.0	22.2	15.5	51.3

* One determination with duplicates.

In the case of linoleic acid the standard deviation along the regression line is 3.74, while the standard deviation from the mean is 3.89. It is thus obvious that the linear correlation between this acid and the iodine number is of little significance.

It should also be noted that the standard deviation along the regression line is in each case much larger than the probable error of the analysis. It appears probable that, especially in the case of linoleic acid, part of the dispersion is due to errors of precision It is also evident that values of r_{xy} would not show perfect correlation in any case if the precision errors were reduced to zero. This means that oils of the same iodine number may have differences in composition of such character as to affect their technological use. This also suggests that satisfactory technological evaluation should no longer rest solely upon iodine numbers.

The composition of linseed oil found in this laboratory agrees well with that reported by Rose and Jamieson (8). The results on a single sample by Mitchell, Kraybill and Zscheile (9), who proposed a new independent method for the determination of linoleic and linolenic acids (9), support the more recent data obtained by the thiocyanometric technique. The following table gives a summary of the results obtained in this laboratory.

TABLE 3.

Composition of Glycerides of 148 Linseed Oil Samples.

	Average	Highest	Lowest
Iodine number	175.9	202.8	127.8
Saturated glycerides	10.8	16.5	6.8
Oleic glycerides	24.2	42.5	11.9
Linoleic glycerides	17.0	26.8	6.9
Linolenic glycerides	48.0	65.2	20.5

. Fat acid glycerides may vary over a wide range in linseed oils. The range of each fat acid when expressed as percentage is far greater than is that of the iodine number. Analyses of the oils showing a fat acid unusually high or low have been repeated so the extremes can hardly be due to precision. In connection with varietal differences in composition (5) it may be of interest that the highest linolenic acid and lowest linoleic acids have been found in oils from B. Golden (6). These were high iodine number oils but not the highest analyzed. When plotted, the unsaturated acids of these oils fall several units from the regression lines so approximate values found by applying equations of the regression lines would differ greatly from the values determined by analysis.

The value of the iodine number as a criterion of quality of linseed oil depends upon what fat acids determine the drying properties of the oil. High iodine numbers indicate low oleic acid and low saturated acids (varietal differences are large) and these acids are not wanted in drying oils. Presumably linolenic acid is by far the most valuable constituent of linseed oils. A high linoleic acid content may, however, be desirable. Some of our vegetable oils which are high in linoleic and low in linolenic give good drying fractions after removal of glycerides high in saturated and oleic acids. The iodine number may be used as an excellent prediction value in estimating the linolenic acid but, for all practical purposes, the iodine number is of no value in predicting the linoleic content of linseed oil.

Summary

RESULTS of analysis of 148 linseed oil samples are summarized. When the constituent fat acid glycerides are plotted against the iodine number the points fall close to a straight line in the cases of saturated acids, oleic acid and linolenic acid. In the case of linoleic acid, however, the points were so dispersed that no significant relationship to the iodine number was apparent. Correlation coefficients between iodine number and the fat acids were: Linolenic, +.97; oleic, —.94; saturated, —.80; and linoleic, —.27.

It is possible to estimate within limits the amount of linolenic, oleic and saturated acids in linseed oil by applying equations where the iodine number is the only variable. In the case of linoleic acid, however, the standard deviation along the regression line is almost equal to the standard deviation from the mean.

Real differences in composition which are independent of the iodine number exist, however, because the dispersion of the points along the regression lines is greater than would result from errors of precision in the analyses.

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