

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.

#### REFERENCES

1. Bailey, A. E., *Industrial Oil and Fat Products*, Interscience Publishers, Inc., New York, 1945, especially pp. 243 and 610.
2. Bailey, A. E., and Fisher, G. S., *Oil & Soap*, 23, 14-18 (1946).
3. Bailey, A. E., Oliver, G. D., Singleton, W. S., and Fisher, G. S., *Oil & Soap*, 20, 251-255 (1943).
4. Ezekiel, M., *Methods of Correlation Analysis*, John Wiley and Sons, Inc., New York, 1941, especially pp. 146-162 and 318.
5. Fisher, G. S., O'Connor, R. T., and Dollear, F. G., *J. Am. Oil Chemists' Society*, 24, 382-387 (1947).
6. Lemon, H. W., *Can. J. Research*, 22F, 191-198 (1944).
7. "Report of the Committee on Analysis of Commercial Fats and Oils," *Oil & Soap* 22, 101-107 (1945).
8. Stirton, A. J., Turer, J., and Riemenschneider, R. W., *Oil & Soap*, 22, 81-83 (1945).
9. Thompson, S., Committee on Food Research of the Office of the Quartermaster General, Conference on Deterioration of Fats and Oils, Quartermaster Corps Manual, QMC 17-7 55-59 (1945).

## Fatty Acid Composition of Hydrogenated Vegetable Oils

G. S. FISHER, R. T. O'CONNOR and F. G. DOLLEAR

Southern Regional Research Laboratory<sup>1</sup>  
New Orleans, Louisiana

### 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 (isolinoic) 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 isolinoic acid which was present in hydrogenated linseed oils. Subsequently Mattil (10) reported the results of work which indicated the presence of isolinoic 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 isolinoic (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-

<sup>1</sup>One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

leic acid would be produced under such conditions in partially hydrogenated cottonseed and peanut oils.

The present investigation is concerned with a comparison of the results obtained by the application of the iodine-thiocyanogen, spectrophotometric, and modified Bertram oxidation method to unhydrogenated and hydrogenated oils, and the possible production of isolinoleic acid during hydrogenation of oils which do not contain appreciable quantities of linolenic acid.

#### Description of Material

The fats used in this investigation were prepared in connection with work reported (2, 6) elsewhere and consisted of one series of peanut oils (PO-51), three series of cottonseed oils (CO-60, CO-61, and CO), one series of soybean oils (SO), and two series of linseed oils (LO-1 and LO-2). Each series represents successive samplings of a given oil undergoing progressive hydrogenation. Hydrogenations were carried out on a laboratory scale (1) using 0.1% of electrolytically precipitated, dry-reduced nickel as catalyst. The oils represented by series PO-51, CO-60, CO, and SO were hydrogenated at 350° F. and 15 p.s.i. pressure of hydrogen (selective conditions). The oils represented by series LO-2 were also hydrogenated under selective conditions at 15 p.s.i. and 375° F. The oils represented by series CO-61 and LO-1 were hydrogenated at 250° F. and 60 p.s.i. pressure of hydrogen (non-selective conditions).

#### Methods of Analysis and Calculations of Results

Iodine values were determined with 100-150% excess of 0.2 N Wijs reagent and a 30-minute reaction time. Thiocyanogen values were determined by the modified method and reagent described by Lambou and Dollear (8), and the results were calculated by means of the equations recommended by the American Oil Chemists' Society (16). The results are expressed as percentages of the hypothetical pure glycerides, *e.g.*, percentage of linolenin in the fat.

Normal linoleic and linolenic acids were determined by a modification of the spectrophotometric method of Mitchell *et al.* (11), standardized with highly purified acids (12). The samples were isomerized with potassium hydroxide in ethylene glycol solution over which a stream of purified nitrogen was passed continuously (13). Isomerization of these acids indicated that the values for the content of linolenic acid require correction for the absorption at 268  $\mu$  resulting from the presence of linoleic acid. The specific extinctions for the isomerized acids are as follows: Linoleic  $a_{234} = 85.4$ ,  $a_{268} = 0.77$ , linolenic  $a_{234} = 61.5$ ,  $a_{268} = 50.9$ . In calculating the values for the content of linoleic and linolenic acid the absorption values for the original fat were subtracted from those for the isomerized fat by application of the following equations:

$$\% \text{ linoleic} = 1.19 (a'_{234} - a_{234}) - 1.43 (a'_{268} - a_{268}) \quad (1)$$

$$\% \text{ linolenic} = 1.99 (a'_{268} - a_{268}) - 0.019 (a'_{234} - a_{234}) \quad (2)$$

where  $a$  and  $a'$  are the extinction coefficients before and after isomerization at the indicated wavelengths. The correction, recommended by Brice *et al.* (4), for background absorption was not applied because the magnitude of this correction was found to be negligible and in some cases negative for most of the fats investigated.

Saturated acids were determined by the Pelikan and von Mikusch (15) modification of the Bertram

oxidation method using sintered-glass filter sticks instead of cotton for the filtration of the magnesium soaps except for series CO and SO with which cotton was used for the filtration.

The results of the determination of linolenic, linoleic, and saturated acids obtained by application of the above-mentioned methods were converted to percentages of the corresponding triglycerides by multiplying each value by the constant 1.045.

The values for isolinolein were calculated from the iodine value, and the values for linolenin, linolein, and saturated glycerides obtained by the spectrophotometric and Bertram oxidation methods by means of the following equations:

$$IV = 2.618 \times LL + 1.733 \times L + 0.860 \times O + 1.733 \times IL \quad (3)$$

$$100 = LL + L + O + S + IL \quad (4)$$

from which,

$$IL = 1.145IV - 2.013LL - 1.000L - 98.5 + 0.985S \quad (5)$$

where LL and L are the percentages of linolenin and linolein, respectively, S the percentage of saturated glycerides, IL the percentage of isolinolein, and O the percentage of olein. The values for olein were obtained by difference.

Isoleic acid, as well as saturated acids, were determined by the Twitchell lead salt-alcohol method (14) and are expressed in Tables 1 and 2 as respective percentages of the total acids. These values do not differ appreciably from those calculated for the fat itself.

#### Results

*Peanut Oils.* The results of the analyses of the hydrogenated oils in series PO-51 are given in Table 1. From these data it is apparent that the values for fatty acid composition obtained by the iodine-thiocyanogen method and the spectrophotometric method agree very well, and the calculated content of saturated acids obtained by these methods agrees with that obtained by the modified Bertram oxidation method. The content of saturated acid obtained by the Twitchell lead salt-alcohol method is also in agreement except in the unhydrogenated and slightly hydrogenated oils.

*Cottonseed Oils.* The results obtained for the fatty acid composition of the cottonseed oils are also given in Table 1. As in the case of the peanut oils, the values for the content of saturated fatty acids calculated from iodine-thiocyanogen determinations are in good agreement with those determined by the modified Bertram oxidation method. The spectrophotometric method, however, gave values for the content of linoleic acid of the unhydrogenated and slightly hydrogenated oils which are appreciably higher than those obtained by the iodine-thiocyanogen method. The Twitchell lead salt-alcohol method gave values for the content of saturated acid which were consistently lower than those obtained by the modified Bertram oxidation method. The ultraviolet absorption spectra for the isomerized oils in series CO-60 are given in Fig. 1.

*Soybean and Linseed Oils.* The fatty acid composition of the soybean and linseed oils calculated from equations 1, 2, and 5 is given in Table 2 together with the content of saturated acids determined by the modified Bertram oxidation and Twitchell lead salt-alcohol methods. Here too the Twitchell lead

TABLE 1.  
 Composition of Unhydrogenated and Hydrogenated Peanut and Cottonseed Oils.

Sample	Iodine value	SCN value	Percentage composition of glycerides								
			Linoleic		Oleic			Saturated			
			A <sup>1</sup>	B <sup>2</sup>	Total		Iso <sup>4</sup>	A <sup>1</sup>	B <sup>2</sup>	C <sup>5</sup>	D <sup>4</sup>
					A <sup>1</sup>	B <sup>2</sup>					
PO-51-0.....	95.9	70.3	32.8	32.4	45.5	46.2	1.3	21.8	21.4	21.9	20.1
PO-51-1.....	84.3	69.4	19.6	18.6	58.6	60.5	4.3	21.8	20.9	22.0	20.7
PO-51-2.....	79.9	68.7	14.6	14.8	63.5	63.1	6.0	21.9	22.1	22.3	21.2
PO-51-3.....	75.2	68.2	9.3	9.6	68.8	68.1	8.0	21.9	22.3	22.4	22.6
PO-51-4.....	71.1	67.9	4.6	4.3	73.3	74.0	11.4	22.1	21.7	22.6	22.8
PO-51-5.....	65.9	65.9	0.0	0.8	76.6	75.0	16.7	23.4	24.2	24.2	24.0
PO-51-6.....	62.0	62.5	.....	0.0	.....	72.1	20.8	.....	27.9	27.8	27.2
PO-51-7.....	57.5	57.9	.....	0.0	.....	66.9	24.6	.....	33.1	33.1	33.7
PO-51-8.....	48.2	48.6	.....	0.0	.....	58.1	26.3	.....	43.9	43.3	42.5
PO-51-9.....	40.1	40.7	.....	0.0	.....	46.6	21.1	.....	53.4	52.1	53.1
PO-51-10.....	28.2	28.7	.....	0.0	.....	32.8	12.7	.....	67.2	66.1	66.4
CO-0.....	101.7	65.8	44.7	47.1	29.1	23.3	.....	26.2	29.6	26.2 <sup>5</sup>	.....
CO-1.....	76.6	63.3	16.1	18.2	56.6	52.4	.....	27.2	29.4	27.5 <sup>5</sup>	.....
CO-2.....	71.9	62.8	10.9	13.2	61.6	57.0	.....	27.5	29.1	28.6 <sup>5</sup>	.....
CO-3.....	67.0	61.2	6.8	6.9	64.2	64.0	.....	29.0	29.1	28.3 <sup>5</sup>	.....
CO-4.....	62.6	59.1	3.9	3.3	64.8	66.1	.....	31.1	30.0	30.6 <sup>5</sup>	.....
CO-5.....	57.8	56.6	1.1	1.0	65.0	65.2	.....	33.9	33.7	32.6 <sup>5</sup>	.....
CO-6.....	52.8	52.8	.....	0.3	61.4	60.8	.....	38.6	38.9	34.6 <sup>5</sup>	.....
CO-7.....	46.7	46.8	.....	0.0	.....	54.3	.....	.....	45.7	43.2 <sup>5</sup>	.....
CO-8.....	40.7	40.8	.....	0.0	.....	47.3	.....	.....	52.7	50.2 <sup>5</sup>	.....
CO-9.....	31.4	31.2	.....	0.0	.....	36.5	.....	.....	63.5	60.6 <sup>5</sup>	.....
CO-60&61-0.....	104.0	64.4	48.4	52.4	23.4	15.3	0.8	28.2	32.3	28.3	26.7
CO-60-1.....	87.5	63.0	29.2	31.9	42.9	37.5	6.1	27.9	30.6	28.6	27.4
CO-60-2.....	73.6	62.1	13.9	13.8	57.6	57.8	11.3	28.5	28.4	28.5	27.3
CO-60-3.....	64.1	60.9	3.6	3.5	67.4	67.4	16.8	29.0	29.1	30.1	28.8
CO-60-4.....	59.7	58.8	0.7	0.2	68.0	69.0	21.0	31.3	30.8	30.9	30.0
CO-60-5.....	55.2	55.2	.....	0.0	.....	64.2	22.7	.....	35.8	35.3	33.9
CO-60-6.....	49.9	50.4	.....	0.0	.....	58.0	21.1	.....	42.0	41.9	38.5
CO-60-7.....	42.7	42.4	.....	0.0	.....	49.5	19.0	.....	50.4	50.2	47.5
CO-60-8.....	34.7	34.5	.....	0.0	.....	40.3	15.8	.....	59.7	58.8	57.0
CO-61-1.....	82.2	61.6	24.9	27.7	45.5	39.8	5.5	29.2	32.5	29.1	28.1
CO-61-2.....	67.9	59.3	10.3	11.3	58.2	56.0	9.8	31.5	32.7	31.7	29.6
CO-61-3.....	58.5	55.7	3.1	3.6	61.8	60.8	11.5	35.1	35.6	34.7	33.5
CO-61-4.....	54.3	52.7	1.6	1.5	59.9	60.1	10.9	38.5	38.4	38.6	35.7
CO-61-5.....	50.0	49.3	0.5	0.2	57.1	57.7	10.4	42.4	42.1	.....	40.0
CO-61-6.....	45.3	45.0	.....	0.0	.....	52.6	11.2	.....	47.4	46.8	44.8
CO-61-7.....	37.0	36.7	.....	0.0	.....	42.8	10.0	.....	57.2	55.8	54.2
CO-61-8.....	27.9	27.6	.....	0.0	.....	31.1	8.5	.....	67.9	66.7	64.3

<sup>1</sup> Iodine-thiocyanogen method; saturated acids by difference.

<sup>2</sup> Spectrophotometric method; oleic acid calculated from iodine value; saturated acids calculated by difference.

<sup>3</sup> Modified Bertram oxidation method.

<sup>4</sup> Twitchell lead salt-alcohol method.

<sup>5</sup> Pelikan and von Mikusch modification of Bertram oxidation method.

salt-alcohol method gave lower values than did the modified Bertram oxidation method. The ultraviolet absorption spectra for the isomerized linseed oils (series LO-2) are given in Fig. 2.

### Discussion

**Saturated Fatty Acids.** The results obtained in this investigation indicate that the modified Bertram oxidation method was more accurate for determining the content of higher saturated acids of unhydrogenated or hydrogenated oils than any of the other methods employed. When cotton was used for filtering the magnesium soaps, low results were obtained with samples whose content of saturated acids exceeded about 30% (see CO-5 to CO-9 in Table 1). Use of sintered-glass filter sticks for the filtrations led to satisfactory results even with a content of saturated acids as high as 60% (see CO-60 and 61-6 to 8 in Table 1). Unfortunately, even the modified Bertram method is quite time consuming and this reduces its utility in routine analyses. For such analyses in the absence of polyunsaturated acids other than linoleic, it is satisfactory to calculate the saturated acids by difference between total fatty acids and unsaturated fatty acids (oleic and linoleic) determined by the iodine-thiocyanogen method. Use of the Twitchell lead salt-alcohol method, which generally gives low results, may be justified when it is necessary to determine by a direct method the approximate value of saturated acids on a large number of samples in a relatively short time.

**Oleic Acid.** The content of oleic acid of the fats or oils can only be determined directly in the absence of other unsaturated acids, in which case it can be calculated from the iodine number. In other cases it must be calculated either by methods of difference or from a set of simultaneous equations. Hence, the value for oleic acid must carry the algebraic sum of the errors in the determinations of all the other constituents. Since this work was completed a method of selective oxidation has been proposed for the independent determination of oleic acid (6a).

**Linoleic Acid.** The results reported in Table 1 for the fatty acid composition of the unhydrogenated and slightly hydrogenated cottonseed oils indicate that the iodine-thiocyanogen method yields more accurate results than does the spectrophotometric method which was used. Recalculation of the results to include the background corrections recommended by Brice *et al.* (4), made no significant difference in the final results, from which it might be inferred that such correction is necessary only when the samples are exposed to air during isomerization or when they contain only very small amounts of polyunsaturated acids.

The reason for the high values for the content of linoleic acid of the cottonseed oil samples which were obtained by the spectrophotometric method is not apparent, unless cottonseed oil contains an isomer of normal linoleic acid which adds thiocyanogen normally but which differs from both normal and previously described isolinoleic acids in its behavior during alkali isomerization. Such an isomer would have

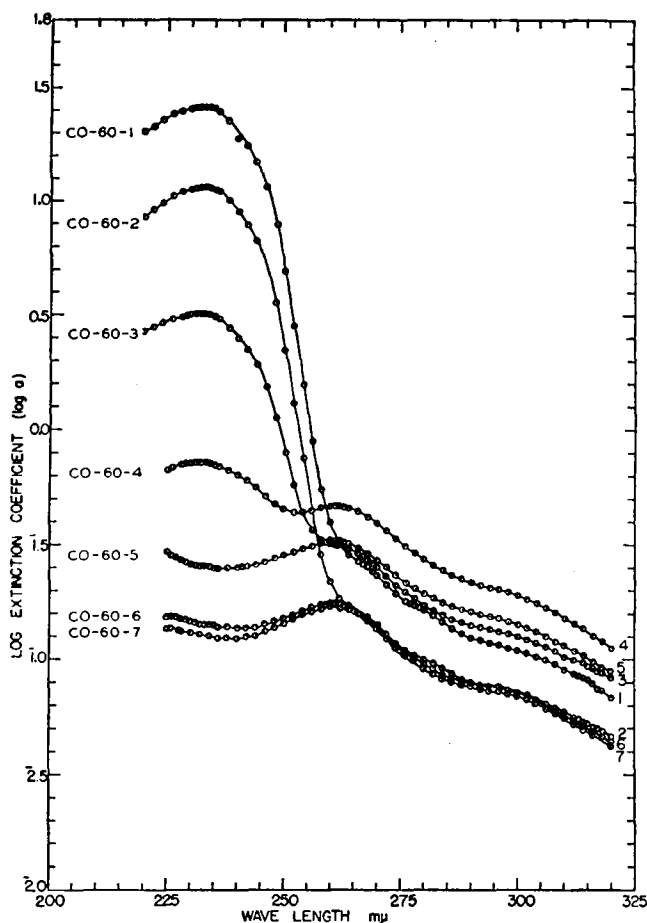


FIG. 1. Ultraviolet absorption spectra of hydrogenated cottonseed oils after alkali isomerization.

to undergo a greater degree of conjugation when treated with alkali at high temperatures than does the linoleic acid obtained from corn oil fatty acids

by debromination of tetrabromostearic acid (m.p. 115.5-115.8° C.). It is apparent from the data in series CO-60 that this isomer is hydrogenated quite readily since there is no evidence of its presence in sample CO-60-2 which still contains 14% of normal linoleic acid. Selective conditions seem to favor its hydrogenation since in the non-selectively hydrogenated series, CO-61, there is still evidence of its presence in sample CO-61-2 which contains only 10% of normal linoleic acid.

**Isolinoleic Acid.** Calculation of the content of isolinoleic acid requires the use of the equations given above. The accuracy of the values obtained will be influenced by any errors which might occur in the determinations of the iodine value, the content of linoleic and linolenic acids by the spectrophotometric method, and the content of the saturated acids. Some verification of the accuracy of the results obtained by this method can, however, be obtained from the thiocyanogen values. The close agreement between the iodine and thiocyanogen values in samples LO-2-5, 6, and 7, in which isolinoleic acid is the only polyunsaturated acid occurring in appreciable quantities, indicates that thiocyanogen adds nearly quantitatively to both double bonds in this isolinoleic acid. Assuming the same degree of addition to each bond as is observed for the double bond in oleic acid, the thiocyanogen value for isolinolein would be 172.3. In Table 2 the observed thiocyanogen values for the linseed and soybean oils are compared with those calculated from the composition using 172.3 for the thiocyanogen value of the isolinolein and the accepted empirical values (16) for olein, linolein, and linolenin. The relatively good agreement between the calculated and observed values (maximum difference five parts per hundred) indicates that the methods used in this investigation give relatively correct values for the composition of hydrogenated linseed and soybean oils.

In the case of the hydrogenated peanut and cottonseed oils there was no evidence of the presence of an

TABLE 2.  
Composition of Unhydrogenated and Hydrogenated Soybean and Linseed Oils.

Sample	Iodine value	Percentage composition of glycerides							SCN value	
		Lino- lenic <sup>1</sup>	Linoleic		Oleic		Saturated		Obs.	Calc. <sup>6</sup>
			Normal <sup>2</sup>	Iso <sup>2</sup>	Total <sup>3</sup>	Iso <sup>4</sup>	A <sup>5</sup>	B <sup>5</sup>		
SO-0.....	129.6	6.6	52.5	.....	26.4	.....	14.5	.....	81.8	81.7
SO-1.....	116.2	8.9	41.0	.....	40.7	.....	14.4	.....	80.3	79.0
SO-2.....	108.5	2.6	33.4	1.7	47.9	.....	14.5	.....	80.0	78.9
SO-3.....	98.0	1.2	23.4	2.3	58.5	.....	14.6	.....	78.6	77.5
SO-4.....	90.4	0.5	14.8	3.8	66.1	.....	14.8	.....	77.1	77.6
SO-5.....	81.1	0.2	5.7	3.9	74.5	.....	15.7	.....	75.3	75.0
SO-6.....	71.2	0.1	0.9	2.2	76.3	.....	20.5	.....	70.1	70.0
SO-7.....	60.2	0.0	0.0	0.9	68.2	.....	30.9	.....	60.2	59.8
SO-8.....	51.2	0.0	0.0	0.0	59.5 <sup>†</sup>	.....	39.8	.....	51.3	50.9
LO-1&2-0.....	188.9	52.0	17.1	5.0	17.0	0.7	8.9	6.0	122.7	122.2
LO-1-1.....	163.4	34.7	17.6	10.6	27.7	2.6	9.4	7.4	116.1	113.7
LO-1-2.....	141.8	20.6	15.6	17.0	36.5	5.6	10.3	8.0	108.9	107.8
LO-1-3.....	119.7	8.8	11.7	22.3	44.0	7.4	13.2	10.9	99.5	100.9
LO-1-4.....	96.3	1.9	5.5	21.1	52.7	11.6	18.8	16.0	88.5	89.5
LO-1-5.....	75.8	0.1	1.3	14.9	55.1	15.8	28.6	26.8	72.9	74.1
LO-1-6.....	54.6	0.0	0.1	7.0	49.3	13.3	43.6	41.5	52.7	54.4
LO-1-7.....	31.3	0.0	0.0	1.0	34.3	9.9	64.7	62.8	29.5	31.0
LO-1-8.....	22.2	0.0	0.0	0.0	25.8	6.8	74.2	70.2	20.1	22.1
LO-2-1.....	162.9	35.3	15.6	11.1	28.4	2.6	9.6	6.0	118.8	113.2
LO-2-2.....	143.6	22.7	13.2	16.8	37.5	5.9	9.8	7.0	112.5	109.5
LO-2-3.....	124.4	9.9	8.4	25.6	46.1	12.1	10.0	7.5	106.7	107.1
LO-2-4.....	104.5	0.9	4.8	25.5	57.7	18.5	11.1	8.6	97.6	99.1
LO-2-5.....	85.7	0.2	0.0	16.7	65.4	27.3	17.7	14.9	85.9	85.0
LO-2-6.....	66.0	0.1	0.0	7.6	61.3	29.0	31.0	29.1	65.1	65.7
LO-2-7.....	47.1	0.0	0.0	2.8	49.1	22.5	48.1	46.3	46.9	46.8
LO-2-8.....	29.3	0.0	0.0	0.5	33.1	10.7	66.4	63.1	26.9	29.2

<sup>1</sup> Spectrophotometric method.

<sup>2</sup> % isolinoleic = 1.145 × IV - 98.47 - 2.013 × % linolenic - 1.00 × % linoleic + 0.985 × % saturated.

<sup>3</sup> By difference.

<sup>4</sup> Twitchell lead salt-alcohol method.

<sup>5</sup> Modified Bertram oxidation used on the linseed oils (LO); Pelikan and von Mikusch modification use on soybean oils (SO).

<sup>6</sup> Assuming thiocyanogen value of isolinolein as 172.3.

<sup>†</sup> IV/86.0.

isolinoic acid which failed to conjugate during alkali isomerization, *i.e.*, of an isolinoic acid of the type observed by Lemon (9) on hydrogenation of linseed oil and by Daubert (5) on hydrogenation of methyl linoleate with palladium black. It would appear, therefore, that linoleic acid does not isomerize during hydrogenation under the described conditions to give an isolinoic acid of the type which has been previously reported to be produced during hydrogenation of other products and under other conditions. The data on the hydrogenated soybean oils gives further evidence of this fact. During the hydrogenation of this oil the content of isolinoic acid increased to a maximum value coincident with the disappearance of the linolenic acid and then decreased to zero. The maximum concentration of isolinoic acid corresponded to about 60% conversion of the linolenic acid to isolinoic acid, thus indicating that the isolinoic acid was formed only by the hydrogenation of linolenic acid.

*Linolenic Acid.* Inasmuch as isolinoic acid was found in all but one of the samples containing linolenic acid, only the spectrophotometric method could be used for the determination of the content of linolenic acid. As previously mentioned, the agreement between the observed and calculated thiocyanogen values provides some support for the validity of the results obtained by the application of this latter method.

Calculation of the content of linolenic acid in the highly hydrogenated oils by means of equation 2 indicates that during hydrogenation linolenic acid to the extent of 0.9% is formed and subsequently disappears. However, the ultraviolet absorption curves for the isomerized samples of oil do not exhibit the characteristic structure associated with triene conjugation,<sup>2</sup> but show, instead, a broad absorption in the wavelength region of 260-265  $m\mu$ . This is best illustrated by the absorption spectra for series CO-60 which are reproduced in Fig. 1. As may be seen from this figure, (CO-60-2 and CO-60-5), the concentration of the substance responsible for this absorption actually increases during the hydrogenation. The difference between this absorption and the characteristic absorption due to triene conjugation is well illustrated by the spectra for the isomerized oils in series LO-2 (Fig. 2). In this series the fine structure characteristic of triene conjugation decreases as the degree of hydrogenation increases and is eventually replaced by a broad absorption band having a maximum in the region of 260-265  $m\mu$ . At present the nature of the absorbing material and its precursor is not known, but the recognition of its presence is important since it indicates the necessity for checking the characteristic structure of the spectrum before reporting absorption at 268  $m\mu$  as triene conjugation.

### Summary

The fatty acid compositions of a number of unhydrogenated and hydrogenated peanut, cottonseed, soybean, and linseed oils have been calculated from the iodine number, thiocyanogen number, ultraviolet absorption after alkali-isomerization, and the content of saturated acids determined by a modified Bertram

<sup>2</sup> Brice and Swain (a) have also reported an absorption band in this spectral region which does not possess the structure characteristic of triene conjugation.

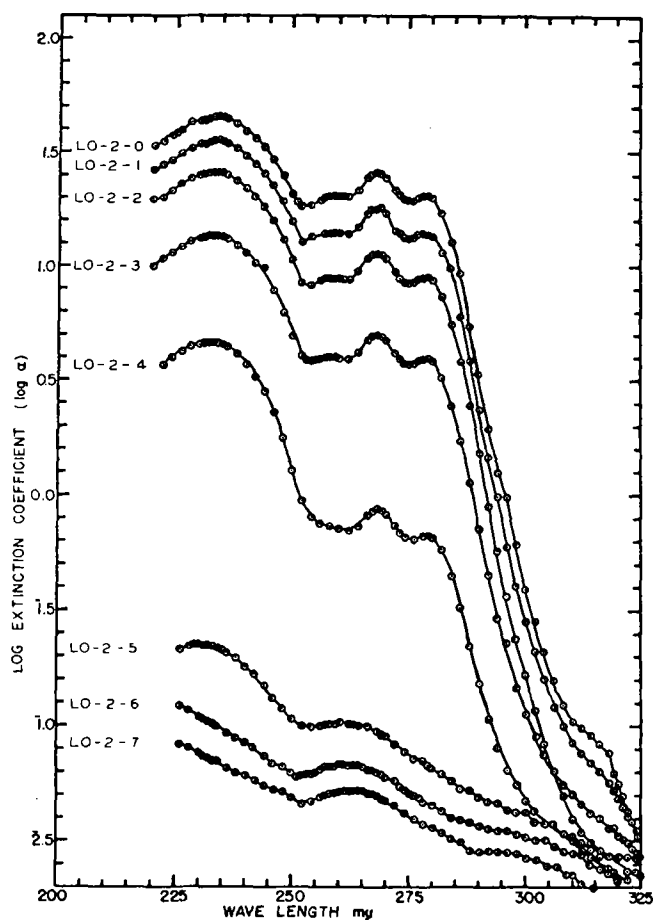


FIG. 2. Ultraviolet absorption spectra of hydrogenated linseed oils after alkali isomerization.

oxidation method. Analysis of these results indicates:

1. All of the methods applied give values for fatty acid composition which are in good agreement for the various samples of peanut oil.
2. The iodine-thiocyanogen method and the modified Bertram oxidation method give values for fatty acid composition which are in good accord in case of cottonseed oils, but the values for linoleic acid obtained by the spectrophotometric method are too high in the unhydrogenated and slightly hydrogenated cottonseed oils.
3. Isolinoic acid is not produced during hydrogenation of cottonseed and peanut oils under the conditions used in this investigation.
4. The production of isolinoic acid during the hydrogenation of soybean oil can be accounted for by hydrogenation of the linolenic acid which is present in this oil.
5. Isolinoic acid absorbs about two moles of thiocyanogen per mole of acid.
6. In applying the spectrophotometric method for the determination of linolenic acid, the characteristic structure of the ultraviolet absorption band in the region of 250-275  $m\mu$  requires examination before such absorption is attributed to the isomerization of linolenic acid.

### Acknowledgment

The authors acknowledge with thanks the assistance of Miss Dorothy Heinzelman in obtaining the spectrophotometric data, and the assistance of B. Ashby

Smith for some of the chemical analyses reported here.

## REFERENCES

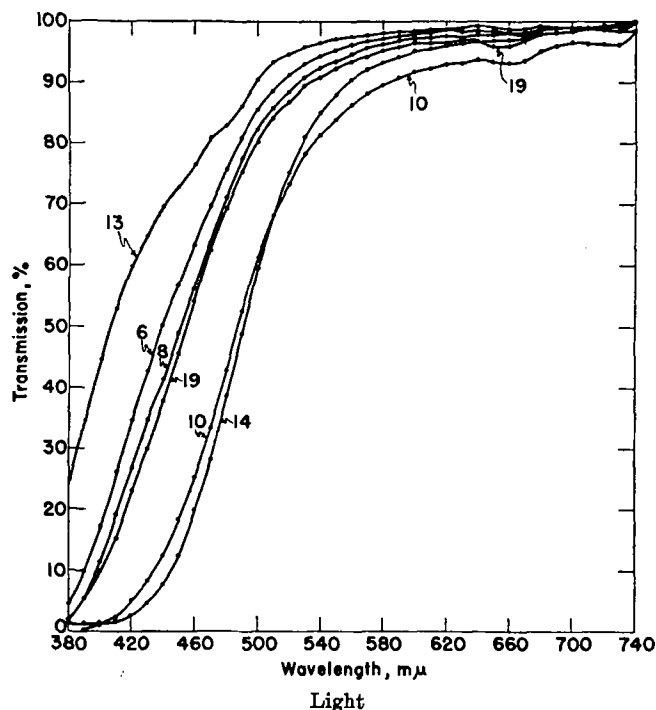
1. Bailey, A. E., Feuge, R. O., and Smith, B. A., *Oil & Soap*, **19**, 169-176 (1942).
2. Bailey, A. E., and Fisher, G. S., *Oil & Soap*, **23**, 14-18 (1946).
3. Baldwin, A. R., and Longenecker, H. E., *Oil & Soap*, **22**, 151-153 (1945).
- 3a. Brice, B. A., and Swain, M. L., *J. Opt. Soc. Am.*, **35**, 532-544 (1945).
4. Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C., *Oil & Soap*, **22**, 219-224 (1945).
5. Daubert, B. F., and Filer, Jr., L. J., *Oil & Soap*, **22**, 299-302 (1945).
6. Fisher, G. S., Bickford, W. G., and Dollear, F. G., *J. Am. Oil Chem. Soc.*, **24**, 379-382 (1947).
- 6a. Iselin, E., *Mitt. Lebensmitt. Hyg.*, **36**, 377-386 (1945).
7. Kaufmann, H. P., *Studien auf dem Fettgebiet*, Verlag Chemie, G.M.B.H., Berlin, 1935.
8. Lambou, M. G., and Dollear, F. G., *Oil & Soap*, **22**, 226-232 (1945).
9. Lemon, H. W., *Can. J. Research*, **22F**, 191-198 (1944).
10. Mattil, K. F., *Oil & Soap*, **22**, 213-215 (1945).
11. Mitchell, Jr., J. H., Kraybill, H. R., and Zscheile, F. P., *Ind. Eng. Chem., Anal. Ed.*, **15**, 1-3 (1943).
12. O'Connor, R. T., Heinzelman, D. C., Caravella, M., and Bauer, S. T., *Oil & Soap*, **23**, 5-9 (1946).
13. O'Connor, R. T., Heinzelman, D. C., and Dollear, F. G., *Oil & Soap*, **22**, 257-263 (1945).
14. American Oil Chemists' Society, *Official and Tentative Methods*, ed. V. C. Mehlenbacher, Chicago, 1946.
15. Pelikan, K. A., and von Mikusch, J. D., *Oil & Soap*, **15**, 149-150 (1938).
16. Progress Report of the Committee on Analysis of Commercial Fats and Oils, *Oil & Soap*, **21**, 143-145 (1944).
17. Riemenschneider, R. W., Speck, R. M., and Beinhardt, E. G., *Oil & Soap*, **22**, 120-122 (1945).

## Methods of Reading Color Without Lovibond Glasses

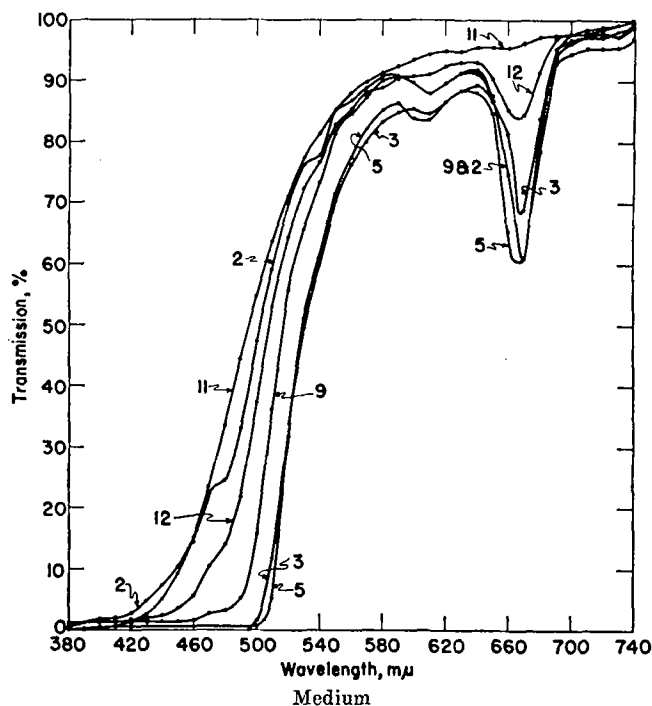
MANY of the producers of soybean oil do not have Lovibond type and cannot secure them. Tintometer, Limited, will not sell loose glasses except to replace breakage. They will sell complete instruments fitted with their new small glasses. Since they insist that their glasses are not susceptible to spectrophotometric calibration, there are some misgivings about their use. A subcommittee of the Color Committee has been working on the development of a filter-photocell instrument to yield values comparable to Lovibond red colors. Good progress has been made, but no filter-photocell instrument now on the market will do the work.

On account of the unsatisfactory situation in color determination, G. W. Agee called a meeting of a "task force" of the Color Committee for Saturday before the Chicago meeting. At that time it was brought out that recently three different companies started, inde-

Spectral transmission of oils. (Light)  
5 cm. cell



Spectral transmission of oils. (Medium)  
5 cm. cell



pendently, to use for color evaluation, the same model of a small photoelectric spectrophotometer.

At Procter and Gamble our selection of wave length was based on the 19 oils studied by the Color Committee in 1943, the characteristics of which are shown herewith.

As the dark oils do not transmit below 500 and the first chlorophyll dip starts about 580, a choice between these was indicated. 550 was picked as representing about the peak of the visibility curve. The rank order correlation between 550 transmission and Lovibond red is .965. A fairly good fit is shown by the curve Lovibond red = (10 cm. density at 550 mμ) 11.2 + .4. Our readings were made on a 25-mm. tube and calculated to 10 cm.

Archer-Daniels-Midland have used the small spectrophotometer to keep track of the color of soybean oil. Because they are concerned with light oils, they