rivatives tested were effective antioxidants for carotene in alfalfa meal. Insufficient data are available to permit conclusions regarding relationships between changes in antioxidant activity and minor structural variations.

Acknowledgment

The authors gratefully acknowledge the analytical assistance of I. V. Ford of this laboratory.

REFERENCES

1. Morris, S. G., and Riemenschneider, R. W., J. Am. Oil Chem. Soc., *26*, 638 (1949).
2. Bickoff, E. M., J. Am. Oil Chem. Soc., *28*, 65 (1951).
3. Campbell, T. W., and Coppinger, G. M., J. Am. Oil Chem. Soc., *73*, 2708 (1951).
4. Williams, K. T., Bickoff, E., and Lowrimore, B., Oil and Soap, *21*, 161 (1944).
5. Thompson, C. Ray, Ind. Eng. Chem., *42*, 922 (1950).

[Received August 22, 1951]

Relation Between Fatty Acid Composition and Iodine Value of Cottonseed Oil[1,2]

MACK F. STANSBURY and CARROLL L. HOFFPAUIR, Southern Regional Research Laboratory,[3] New Orleans, Louisiana

THOUGH it is well known that the iodine value of a vegetable oil of a given species of a plant is influenced by the genetical characteristics of the variety and the environment under which the oil is elaborated and that the iodine value is related to the amounts of the several unsaturated fatty acids present, no systematic investigation of this relationship for cottonseed oils has been found in the literature. Such relationships have been investigated for soybean oils (8) and linseed oils (6). Grindley (4) reported data on the fatty acid composition and the iodine value for a few cottonseed oils obtained from seed taken at various stages of maturity. Bailey (2) cited that the fatty acid composition of cottonseed oils will seldom fall outside the limits of 44 to 53% linoleic, 22 to 28% oleic, and 23 to 28% saturated acids.

The purpose of this paper is to report compositional data on 48 cottonseed oils, varying more widely in iodine value than oils heretofore available in one laboratory for investigation, and to correlate the percentages of the fatty acids present with the iodine values, providing a basis for approximating the fatty acid composition of a cottonseed oil from its iodine value.

The oils investigated were obtained from 48 lots of cottonseed selected from 312 samples whose oils had previously been analyzed for iodine value. They were selected to give an even distribution in iodine values between limits of 89.8 and 117.0 and, as shown in Table I, represent a random distribution of samples with respect to 8 varieties, 13 stations, and 3 years. The seed were from experimental growths of the Division of Cotton and Other Fiber Crops and Diseases of the Bureau of Plant Industry, Soils, and Agricultural Engineering. The seed cottons were picked from freshly opened bolls and dried. Hence the seed were subjected to little if any field damage as is shown by the analyses of the oils for free fatty acids. On receipt of the ginned seed they were stored in sealed containers at 0°F. Storage at this temperature and at less than 8% moisture has been shown previously to preserve cottonseed with no significant change in chemical composition (10).

The oils were extracted from approximately 140 g. of freshly separated and ground meats (2 mm. mesh) in large Butt-type tubes by cold percolation with successive 125, 50, 50, and 50 ml. portions of commercial pentane (Skellysolve F[4]). The solvent was removed under an atmosphere of nitrogen by heating on a steam bath and subsequently under vacuum in an oven at a low temperature. The solvent-free oils were stored under nitrogen in stoppered bottles in a refrigerator.

The oils were analyzed for iodine and thiocyanogen values by the American Oil Chemists' Society method Cd 1-25 (1) and the Lambou and Dollear method (5), respectively. Unsaponifiable matter was determined by the method of the Society of Public Analysts (9) and free fatty acids by a procedure originally designed for small cottonseed samples (10). The percentages of the fatty acids present in the oils were calculated by substituting the iodine and thiocyanogen values found in the equations specified in the American Oil Chemists' Society method Cd 2-38 (1). The results are expressed in Table I as hypothetical pure triglycerides of linoleic, oleic, and saturated acids. Average results of closely agreeing duplicates are reported in each instance.

Results

The free fatty acid contents of the oils, expressed as oleic acid were low, averaging 0.22% and ranging from 0.10 to 1.88%. This indicates that the seed had been collected and preserved with little or no deterioration.

The unsaponifiable matter averaged 0.65%, varying from 0.57 to 0.77%. The values are within the range of those found for authentic samples of commercial cottonseed oils reported in A.O.C.S. Table I 2-46 (1).

The iodine and thiocyanogen values ranged from 89.8 to 117.0 and from 62.2 to 71.1, respectively. The oils were uniformly distributed between the limits of these absorption values.

[1]Report of a study made under the Research and Marketing Act of 1946.
[2]Presented at the spring meeting of the American Oil Chemists' Society, New Orleans, La., May 1-3, 1951.
[3]One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[4]The mention of firms' names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

TABLE I

Analysis of Cottonseed Oils

Sample No.	Variety of Seed	Station	Year	Free Fatty Acids (as oleic)	Unsaponifiable Matter	Iodine Value	Thiocyanogen Value	Glycerides		
								Linoleic	Oleic	Saturated
				%	%	Wijs		%	%	%
1	..................[1]	....	....	0.17	0.77	89.8	62.2	34.0	36.0	29.2
2	Coker Wilds	Greenville, Texas	1947	0.12	0.76	90.6	62.6	34.4	35.9	28.9
3	Coker Wilds	Greenville, Texas	1948	0.14	0.71	91.1	62.5	35.2	35.0	29.1
4	Acala 4-42	Greenville, Texas	1947	0.13	0.67	93.7	62.3	38.7	31.0	29.6
5	..................[2]	....	....	0.16	0.65	94.6	62.8	39.2	31.0	29.1
6	Rowden 41B	College Station, Texas	1948	0.31	0.64	95.0	63.5	38.8	32.3	28.3
7	Rowden 41B	Greenville, Texas	1947	0.28	0.61	95.9	63.1	40.4	30.1	28.9
8	Coker Wilds	Stoneville, Miss.	1947	0.12	0.64	96.4	63.6	40.4	30.6	28.4
9	Coker Wilds	Sacaton, Ariz.	1948	0.11	0.66	96.7	63.3	41.2	29.5	28.6
10	Rowden 41B	Chickasha, Okla.	1947	0.23	0.62	97.4	64.0	41.2	30.3	27.9
11	Acala 1517W	Sacaton, Ariz.	1948	0.11	0.60	98.7	63.2	43.8	26.5	29.1
12	Coker Wilds	Jackson, Miss.	1947	0.13	0.63	98.7	64.3	42.4	29.3	27.7
13	Mebane (Watson's)	Chickasha, Okla.	1947	0.17	0.64	98.8	65.0	41.7	30.9	26.8
14	Coker Wilds	St. Joseph, La.	1947	0.13	0.60	100.2	64.5	44.0	27.8	27.6
15	Coker Wilds	Chickasha, Okla.	1948	0.10	0.66	100.5	64.1	44.9	26.4	28.0
16	Deltapine	Sacaton, Ariz.	1947	0.13	0.62	100.8	63.8	45.7	25.2	28.5
17	Rowden 41B	Sacaton, Ariz.	1947	0.19	0.63	100.9	63.5	46.2	24.3	28.9
18	Acala 4-42	Stoneville, Miss.	1947	0.11	0.64	100.9	63.6	46.0	24.6	28.8
19	Acala 4-42	Sacaton, Ariz.	1949	0.16	0.68	101.0	64.5	45.0	26.7	27.6
20	Acala 4-42	Greenville, Texas	1949	0.17	0.65	101.3	64.4	45.5	26.1	27.7
21	Rowden 41B	Jackson, Miss.	1947	0.19	0.62	101.7	65.0	45.3	27.0	27.1
22	Rowden 41B	Sacaton, Ariz.	1949	0.32	0.63	102.2	64.9	46.0	26.1	27.3
23	Deltapine	Statesville, N. C.	1947	0.18	0.71	102.7	65.6	45.8	27.2	26.3
24	Mebane (Watson's)	Jackson, Miss.	1947	0.12	0.62	104.8	66.9	46.8	27.7	24.9
25	Mebane (Watson's)	Chickasha, Okla.	1948	0.15	0.61	105.1	66.3	47.9	25.7	25.8
26	Acala 1517W	Statesville, N. C.	1947	0.11	0.65	105.5	66.0	48.8	24.4	26.1
27	Acala 4-42	Auburn, Ala.	1947	0.19	0.62	105.7	65.7	49.4	23.4	26.6
28	Deltapine	Florence, S. C.	1949	1.88	0.64	105.8	66.4	48.6	25.0	25.8
29	Coker 100W	Tifton, Ga.	1948	0.47	0.64	106.9	67.8	48.2	27.1	24.1
30	Coker 100W	Statesville, N. C.	1947	0.20	0.68	107.3	66.8	50.0	24.0	25.3
31	Stoneville 2B	Jackson, Miss.	1947	0.18	0.61	108.1	68.5	48.9	27.2	23.3
32	Coker 100W	Auburn, Ala.	1949	0.24	0.64	108.2	67.0	50.9	23.3	25.2
33	Stoneville 2B	Chickasha, Okla.	1948	0.17	0.66	109.2	68.5	50.2	25.8	23.3
34	Coker 100W	Florence, S. C.	1947	0.28	0.61	109.8	68.2	51.4	24.2	23.8
35	Acala 1517W	Chickasha, Okla.	1949	0.13	0.72	110.5	67.8	52.7	22.2	24.4
36	Acala 1517W	Shafter, Calif.	1948	0.15	0.67	110.6	67.7	53.0	21.9	24.4
37	Stoneville 2B	Auburn, Ala.	1947	0.14	0.61	110.8	68.7	52.0	24.1	23.3
38	Stoneville 2B	Tifton, Ga.	1948	0.19	0.59	111.1	70.5	50.1	28.2	21.1
39	Stoneville 2B	Stoneville, Miss.	1949	0.19	0.59	111.9	69.2	52.7	23.9	22.8
40	Stoneville 2B	St. Joseph, La.	1949	0.15	0.57	112.2	68.6	53.8	22.0	23.6
41	Rowden 41B	State College, N. M.	1949	0.25	0.71	113.0	69.8	53.3	23.9	22.1
42	Stoneville 2B	Florence, S. C.	1949	0.94	0.61	113.2	69.7	53.7	23.4	22.3
43	Mebane (Watson's)	State College, N. M.	1947	0.10	0.68	113.7	70.1	53.8	23.7	21.8
44	Coker 100W	Statesville, N. C.	1949	0.17	0.70	114.6	69.9	55.2	22.0	22.1
45	Stoneville 2B	Chickasha, Okla.	1949	0.11	0.71	116.0	71.1	55.4	23.2	20.7
46	Stoneville 2B	State College, N. M.	1949	0.13	0.65	116.2	71.1	55.7	22.9	20.7
47	Stoneville 2B	Shafter, Calif.	1948	0.11	0.65	116.8	71.1	56.4	22.1	20.8
48	Stoneville 2B	Statesville, N. C.	1949	0.16	0.63	117.0	71.1	56.7	21.8	20.9
Highest value				1.88	0.77	117.0	71.1	56.7	36.0	29.6
Lowest value				0.10	0.57	89.8	62.2	34.0	21.8	20.7
Range				1.78	0.20	27.2	8.9	22.7	14.2	8.9
Average				0.22	0.65	104.5	66.3	47.1	26.5	25.7

[1] Mixture of samples of similar iodine values of Coker Wilds grown at College Station, Texas, in 1948 and at Chickasha, Oklahoma, in 1947.

[2] Mixture of samples of similar iodine values of Deltapine and Mebane grown at College Station, Texas, in 1948 and of Deltapine grown at Chickasha, Oklahoma, in 1947.

The calculated values for linoleic glycerides ranged from 34.0 to 56.7%. Those for oleic and saturated glycerides varied from 21.8 to 36% and 20.7 to 29.6%, respectively. The values for saturated glycerides are corrected for the unsaponifiable matter found in the oils.

The scatter diagrams of the relations between the percentage of each fatty acid glyceride present and the iodine value are shown in Figure 1. A high degree of correlation is indicated. This was proven by calculation of the regression of each glyceride on the iodine value by the method of least squares (3) and of the correlation coefficients (r_{xy}) and the standard errors of estimate (S_{yx}). In making the calculations, the iodine value was taken as the independent variable. The equations found are as follows:

$$\% \text{ linoleic glyceride} = 0.791 \text{ (I.V.)} - 35.5$$
$$r_{xy} = +0.99 \qquad S_{yx} = \pm 0.7$$

$$\% \text{ oleic glyceride} = 71.7 - 0.432 \text{ (I.V.)}$$
$$r_{xy} = -0.88 \qquad S_{yx} = \pm 1.8$$

$$\% \text{ saturated glycerides} + \% \text{ unsaponifiable matter} = 63.9 - 0.359 \text{ (I.V.)}$$
$$r_{xy} = -0.95 \qquad S_{yx} = \pm 0.9$$

$$\% \text{ saturated glycerides} = 63.1 - 0.358 \text{ (I.V.)}$$
$$r_{xy} = -0.94 \qquad S_{yx} = \pm 1.0$$

These regression equations are shown graphically in Figure 1. It is seen that as the iodine value increases there is an increase in the linoleic and a decrease in oleic and saturated glycerides. The similarity in the values for oleic acid and the saturated acids is striking. It would appear that at the lower limit of iodine value the percentages of linoleic, oleic, and saturated acids approximate each other.

The relation between fatty acid composition and iodine value for the cottonseed oils is compared with those for soybean and linseed oils in Figure 2. The regressions for soybean oil are those reported by Scholfield and Bull (8), and the ones for linseed oil are

TABLE II

Regression Coefficients for the Regression of the Percentages of Glycerides on the Iodine Value of Cottonseed, Soybean, and Linseed Oils

Glyceride	Oil		
	Cottonseed	Soybean	Linseed
Linolenic	....	+0.170	+0.552
Linoleic	+0.791	+0.669	−0.067
Oleic	−0.432	−0.792	−0.382
Saturated	−0.358	−0.045	−0.103

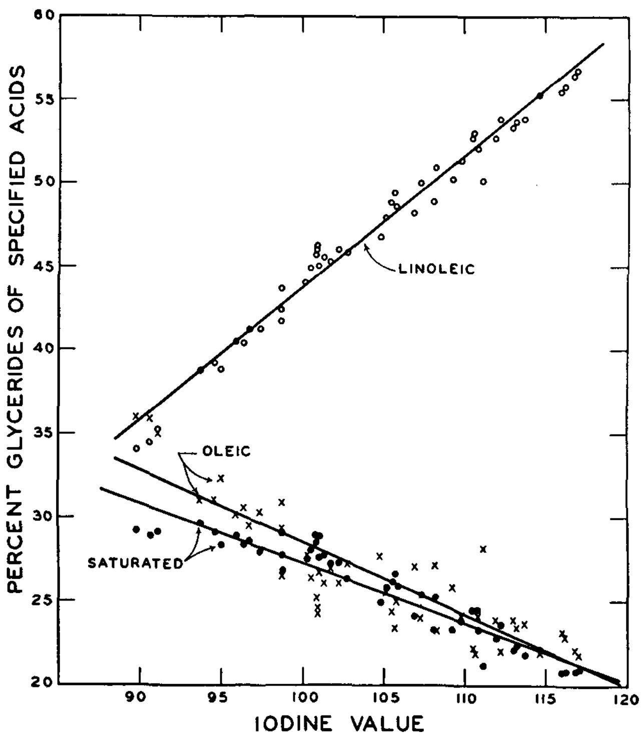

FIG. 1. Relations between percentages of fatty acid glycerides and iodine values of cottonseed oils.

taken from the reports of Painter (6) and Powers (7). The characteristic changes in fatty acid composition with increasing iodine value for each oil are shown by the direction and amount of the slope of the regressions. It is of interest to note the comparatively large decrease in saturated acids in cottonseed oil with an increase in the iodine value. The regression coefficients of the regression equations for the three oils are given in Table II. They represent the amount of change of each glyceride in each oil per one unit increase in iodine value and whether this change is an increase or a decrease.

Summary

The regularity in the increase in linoleic, and in the decrease in oleic and saturated acids with increase in iodine value of cottonseed oils has been shown by obtaining the regression equation for the glyceride of each acid on the iodine value by use of the compositional data on 48 samples of oil ranging from 89.8 to 117.0 in iodine value. These equations offer a ready means of approximating the fatty acid composition of cottonseed oils from their iodine values. Such approximations may prove useful in the segregation of oils for different end uses.

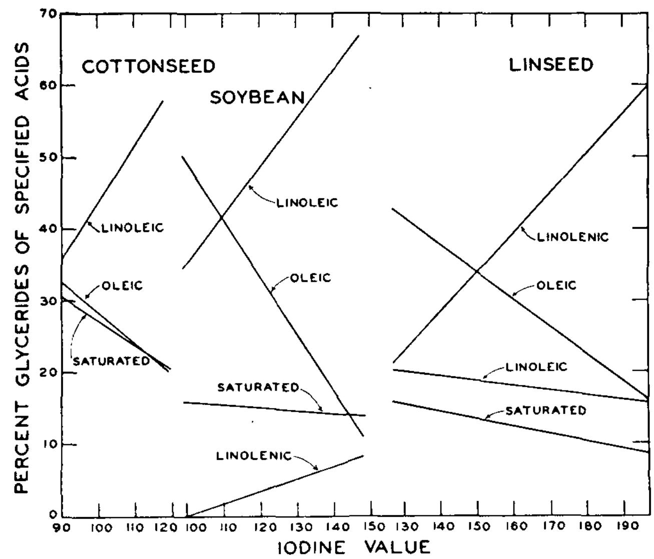

FIG. 2. Relations between percentages of fatty acid glycerides and iodine values of cottonseed, soybean, and linseed oils.

The compositional pattern of cottonseed oils is compared with those reported in the literature for soybean and linseed oils.

Acknowledgment

The assistance of H. D. Barker of the Division of Cotton and Other Fiber Crops and Diseases of the Bureau of Plant Industry, Soils, and Agricultural Engineering, in connection with work from which the cottonseed samples were made available, is acknowledged. Thanks are due to S. M. Stark Jr., Alva F. Cucullu, and L. E. Brown for performing some of the analyses. The authors also acknowledge with thanks the encouragement and suggestions of T. H. Hopper and F. G. Dollear.

REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods, 2nd Ed., edited by V. C. Mehlenbacher, Chicago, 1946, rev. to 1950.

2. Bailey, A. E., "Cottonseed and Cottonseed Products," New York, Interscience Publishers Inc., 1948, p. 374.

3. Ezekiel, M., "Methods of Correlation Analysis," New York, John Wiley and Sons, 2nd Ed., 1941.

4. Grindley, D. N., J. Soc. Food and Agriculture, May 1950, 147-151.

5. Lambou, M. G., and Dollear, F. G., Oil and Soap, *22*, 226-232 (1945).

6. Painter, Edgar P., Oil and Soap, *21*, 343-346 (1944).

7. Powers, P. O., Oil and Soap, *22*, 52 (1945).

8. Scholfield, C. R., and Bull, W. C., Oil and Soap, *21*, 87-89 (1944).

9. Society of Public Analysts, Report of the Subcommittee on Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps to the Standing Committee on Uniformity of Analytical Methods, Analyst, *58*, 203-210 (1933).

10. Stansbury, Mack F., and Guthrie, John D., J. Agr. Research, *75*, 49-61 (1947).

[Received August 24, 1951]