Kylander, R. L., and Garwin, L., Chem. Eng. Progress, 41, 186 9. Kylander, M. 2., 201
 (1951).
 10. Mayfield, F. D., and Church, W. L. Jr., Ind. Eng. Chem., 44, 2253 (1952).

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Distribution of Fatty Acids in Corn Oil^{1,2}

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T has been known for many years that oil content of corn grain is a variable character (10) and that the percentage of oil varies among strains and among individual ears within a strain. In the hands of the breeder it has proved to be a very plastic character, and some strains with much higher oil content and others with much lower oil content than previously known have been produced through the use of suitable breeding techniques (10).

Grindley (5) and Stansbury and Hoffpauir (9) showed the fatty acid composition of cottonseed oil to be closely related to the iodine value of the oil, and similar findings were reported for linseed oils by Painter (7) and for soybean oils by Scholfield and Bull (8). However corn oil has not been investigated so completely as other vegetable oils. A recent report (6) showed a close relationship between the iodine value and refractive index of corn oils. The purpose of this paper is to present relationships between percentage of oil, iodine value, and fatty acid composition of corn oils.

Experimental Methods

Oil Extraction. Full-length rows of kernels (20 g. minimum) from an individual ear of dry field-grown corn was ground, and a 5-g. sample was extracted with ether in a Goldfisch apparatus for 15 hours. The solvent was removed under vacuum at 50°C., and, after weighing, the oils were stored in stoppered glass tubes at 20°C. The oils were brought to room temperature, mixed thoroughly, and centrifuged before the analyses were made.

Iodine Value. The iodine value was determined by the Wijs method (1) modified for a 50-mg sample of the oil. Since many of the low-oil samples of corn yielded only small quantities of oil, it was necessary to use 50-mg. samples for both the iodine value and fatty acid determinations.

Fatty Acid Distribution. The fatty acid composition of the oils was determined by the Brice et al. (3) modification of the spectrophotometric method. The analytical procedure and the calculation of the results were performed as recommended except that 5.5 gm. of the glycerol-KOH reagent, instead of 11.0

gm., was used for the 50-mg. sample of oil. The optical density of the isomerized mixture was determined with a Beckman Model DU spectrophotometer. The percentage of oleic acid was calculated from the percentage of linoleic acid and the iodine value, by the method of Beadle (2), and the percentage of saturated acids was determined by difference. No evidence was obtained for the presence of linolenic acid in any of the samples.

Corn Samples. From percentage oil and refractive index data which were available on several thousand samples of corn grown during a four-year period, 392 selections were chosen to give the widest available range in iodine value, and the fatty acid composition of these samples was determined. Typical data are shown for some of these samples from the 1950 crop (Table I) since space does not permit publication of the entire series of analyses. However regression equations and correlation coefficients were derived by statistical analysis of the entire group of 392 samples of corn.

TABLE I Some Typical Results of Corn Oil Analyses^a

Sample number	Oil content	Refrac- tive index (40°C.)	Iodine value (Wijs)	Fatty acids		
				Linoleic	Oleic	Saturated
	%			%	%	%
4	2.57	1.4687	139.5	67.6	25.8	6.6
5	2.66	1.4681	137.6	58.8	41.2	0.0 5
7	2.58	1.4688	131.4	65.9	19.8	14.3
55	5.83	1.4672	130.2	56.4	37.6	6.0
67	5.45	1.4679	131.2	61.8	27.8	10.4
72	5.63	1.4662	122.4	51.4	38.6	10.0
17	9.38	1.4628	88.4	16.2	70.1	13.7
23	9.84	1.4644	103.7	38.4	43.1	18.5
73	9.89	1.4632	98.7	19.2	75.9	4.9
69	13.80	1.4658	114.8	44.0	44.7	11.3
75	13.10	1.4639	104.5	29.3	62.3	8.4
87	12.54	1.4649	105.0	30.6	60.3	9.1

Representative samples chosen from the 1950 crop. ^b See page 413.

Results and Discussion

Iodine Value and Percentage Oil. The oil content of the samples from individual ears ranged from 1.13% to 13.80% and the iodine values from 88.4 to 147.4. A negative correlation between oil content and iodine value (r = -.700) significant at the 1% level compared favorably with correlations of -.405 to -.571 reported by Brimhall and Sprague (4). The standard error of estimate was $7.5\overline{\%}$. Although the correlation is highly significant, there appears to be sufficient variability in degree of unsaturation among

Othmer, D. F., White, R. E., and Trueger, E., Ind. Eng. Chem., 33, 1241 (1941).
 Scheibel, E. G., Chem. Eng. Progress, 44, 771 (1948).
 Treybal, R. E., "Liquid Extraction," p. 20, New York, McGraw-Hill Book Company (1951).

^{14.} Ibid., p. 13.

^{15.} Ibid., p. 21.

^{16.} *Ibid.*, p. 24. 17. *Ibid.*, p. 159.

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samples with fairly high oil content to provide a basis for selection of strains of either high or low unsaturation. A calculated regression line of iodine value on oil content is shown with the scatter diagram (Figure 1).



FIG. 1. Regression of iodine value on percent oil.

Relation of Fatty Acids to Iodine Value and Oil Content. The ranges in the degree of unsaturation and in percentages of individual fatty acids in these corn selections were considerably greater than any encountered in the literature for corn oils. The linoleic acid content ranged from 15.7% to 67.6%, oleic acid from 16.5% to 75.9%, and saturated acid from zero to 21.3%. No significance is attached to the fact that a few samples appeared to contain no saturated acids since the saturated acids were not determined directly. It seems clear however that samples which



FIG. 2. Relationship of iodine value to the fatty acid composition of corn oil. L, linoleic; O, oleic; S, saturated. Regression equations and correlation coefficients:

% linoleic	= 51.7 + .874 (I.V 124.8); r = .9)51,
% oleic	= 40.8600 (I.V 124.8); r =7	(11,
% saturated	= 7.56263 (I.V. $- 124.8$); $r =6$	680.

are high in linoleic acid contain very little saturated acids.

Linoleic acid percentage increased sharply with iodine value, and a high positive correlation was observed (Figure 2). Thus, using the regression equation, it is possible to predict the linoleic acid content of corn oil, from the iodine value, with good accuracy. Both oleic acid and the saturated acids decreased with increasing iodine value; however the degree of correlation between these acids and the iodine values was not so high as that for linoleic acid. (Standard error of estimate: linoleic, 3.0; oleic, 6.25; saturated, 12.5). It should be borne in mind that since oleic and saturated acids were calculated from the percentage of linoleic acid and the iodine value, the degree of correlation in each case may be distorted due to cumulative errors. The observed relationships between iodine value and fatty acid percentages in corn oil agree well with those reported by Stansbury and Hoffpauir (9) for cottonseed oil which is derived from the same fatty acids.

The different fatty acids showed a relationship not only to the degree of unsaturation but also to the total amount of oil in the corn (Figure 3). Although



FIG. 3. Relationship of percent oil to the fatty acid composition of corn oil. L, linoleic; O, oleic; S, saturated. Regression equations and correlation coefficients:

% linoleic	= 51.7 - 2.47 (% oil $- 5.72$); r = -	691,
% saturated	= 7.56 + .624 (% oil $- 5.72$); r =	.415.
% oleic	=27.56 + .624 (% oil $- 5.72$); r $=$.415.

the correlation coefficients can hardly be considered high, the relationship seems to be definite. Again, linoleic acid showed the best correlations. Linoleic acid, like iodine value, decreased with increasing oil content while oleic and saturated acids increased with increasing oil.

Summary

The oil content of 392 samples of corn ranged from 1.13% to 13.80%. As the percentage oil in the corn increased, the degree of unsaturation decreased. Iodine values ranged from 88.4 to 147.4, a range in degree of unsaturation greater than any previously reported for corn oils.

The percentage of linoleic acid in the oils ranged from 15.7% to 67.6% and varied inversely with oil content (r = -.691). Oleic acid ranged from 16.5%to 75.9% and saturated acids from zero to 21.3%.

The iodine value of the oil showed a high degree of correlation with the percentage of linoleic acid (r =-.951) and can be used as a basis for the accurate prediction of linoleic acid content.

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REFERENCES

- Asso. Official Agr. Chemists, Official Methods of Analysis, 7th ed.,
 433 (1950).
 Beadle, B. W., Oil and Soap, 23, 140-145 (1946).
 Brice, B. A., Swain, M. L., Schaeffer, B. B., and Ault, W. C.,
 Oil and Soap, 22, 219-224 (1945).
 Brimhall, B., and Sprague, G. F., Cereal Chemistry, 28, 225-231 (1951).
- (1951). 5. Grindley, D. N., J. Soc. Food and Agriculture, 147-151, May,
- Lofland, H. B., and Quackenbush, F. W. (paper submitted to this
- 6. Lofland, H. B., and Quackenbush, F. W. (paper submitted to this Journal).
 7. Painter, E. P., Oil and Soap, 21, 343-346 (1944).
 8. Schofield, C. R., and Bull, W. C., Oil and Soap, 21, 37-89 (1944).
 9. Stansbury, M. F., and Hoffpauir, C. L., J. Am. Oil Chemists' Soc., 29, 53-55 (1952).
 10. Woodworth, C. M., Leng, E. R., and Jugenheimer, R. W., Agron. Jour., 44, 60-65 (1952).

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Fatty Acid Compositions of Corn Oils in Relation to Oil Contents of the Kernels

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TIGHER oil content is of economic interest to most users of corn. Livestock feeders view the extra oil as a dividend in calories which furnish added energy to the ration; for each 1% increase in oil content, approximately 1,150 kilocalories of potential energy are added per bushel of corn. An increase in oil content usually is accompanied by an increase in germ protein which is highly desirable, especially from the feeders' standpoint. Feeding tests (1) indicate that higher oil corn does not cause "soft pork" and that it may effect substantial savings in high cost mixed supplement feeds. Wet millers and dry millers of corn are interested in the oil content because it is an economically significant constituent of the grain. These aspects of the commercial development of higher oil corns and the great potentialities of hybrid corn breeding programs, which are moving toward such a goal, make it desirable to study the effects upon corn oil itself.

The annual corn crop in the United States contains more oil than does any other domestic crop. In 1953 the corn grown contained more than 7,000,000,000 lbs. of oil as compared with a little over 4,000,000,000 lbs. of butterfat, 3,000,000,000 lbs. of soybean oil, 2,000,-000,000 lbs. of cottonseed oil, and 1,000,000,000 lbs. of peanut oil. Although most of the corn oil is fed in situ to livestock, approximately 250,000,000 lbs. per year is recovered from germ obtained in the wet and dry corn milling industries. A 2% increase in oil content of corn would increase the total oil in corn to over 10,000,000,000 lbs. and the recovered corn oil to around 375,000,000 lbs. It is not inconceivable that some day corn might be considered an oilseed crop. A 75-bu. yield of 8% oil corn contains about the same amount of oil as a 25-bu. yield of 21% oil soybeans. Such yields of higher oil corn are already feasible, and this may be just a start. An understanding of the relationships between oil composition and oil content of corn therefore is important in hybrid corn breeding programs and in corn oil processing studies.

Brimhall and Sprague (2) have reported a linear correlation between the oil contents of the germ and of the kernel and the total unsaturation as measured by iodine values of the oils from High-Oil and Low-

Oil corn inbreds and their F_1 and F_2 backcross populations. However iodine values alone do not tell a complete story of the changes which take place in fatty acid compositions of oils as the oil content of the corn is varied. It has been shown that variations in fatty acid compositions accompany changes in iodine values of oils from different varieties of soybeans (3), cottonseed (4), and flaxseed (5, 6). Therefore it well might be expected that similar alterations in the fatty acid relationships in corn oil accompany changes in the iodine value. Since these compositional changes might be very significant to the end-uses of corn oils, a study has been made of their trends in several inbred and hybrid corns.

Experimental

Sources of 13 samples of oil which were analyzed for their fatty acid compositions are given in Table I. Germ oil was recovered from only the larger samples of corn. However previous fatty acid analyses (7)of oils from corn germ and corn gluten indicate that oil extracted from whole grain should have a fatty acid composition within the probable experimental error of that for oil from the germ.

Four of the oils were analyzed by the methyl ester fractional distillation technique. The methyl esters of the fatty acids were prepared from the fatty acids liberated from the saponified oil by reacting the acids with anhydrous methanol, using concentrated sulfuric acid as catalyst.

The crude esters, in ethyl ether, were washed with 5% aqueous sodium carbonate and then with water to remove inorganic salts. After drying with anhydrous sodium sulfate and removal of solvent, 100 g. of the esters were distilled through a single-turn, glass-helices-packed fractionating column (8), having a calculated efficiency of about 17 theoretical plates (9) and a total condensation partial take-off distilling head (10). The collected fractions were characterized by determination of the weight, refractive index, iodine value, saponification equivalent, and polyunsaturated acid content by the A.O.C.S. modification (11) of the spectrophotometric method of Mitchell, Kraybill, and Zscheile (12). Compositions of the fractions were then calculated according to recognized