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

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IGHER 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 LowOil corn inbreds and their F<sub>1</sub> and F<sub>2</sub> 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

TABLE I Identification of Corn Oil Samples

Identification of corn	Oil content of corn (% d.b.)	Kernel portions used	Method of oil recovery		
Commercial hybrid yellow corn, wet-milled	4.75	Germ	Combined expelled and extracted crude oil		
Commercial hybrid vellow corn wet-milled	4.75	Germ	Above crude refined (Mazola oil)		
High-oil hybrid from Iowa Agr. Eypt. Station	0.91	Germ	Soxhlet: hexane		
High-oil strain from III. Agr. Expt. Station.	11.5	Entire	Soxhlet: CHCla		
Low-oil strain from III. Agr. Expt. Station	1.63	Entire	Soxhlet; CHCl <sub>3</sub>		
Mixture of high-oil hybrid corns	7.10	Germ	Wet-milled; soxhlet; hexane		
3-way yellow dent hybrid cross A	6.16	Entire	Waring Blendora; hexane, then CCl4		
3-way yellow dent hybrid cross B	6,24	Entire	Waring Blendora; hexane, then CCl4		
3-way yellow dent hybrid cross C	6.91	Entire	Waring Blendora; hexane, then CCl4		
3-way vellow dent hybrid cross D	7.00	Entire	Waring Blendora; hexane, then CCl4		
3-way yellow dent hybrid cross E	7.05	Entire	Waring Blendora; hexane, then CCl4		
3-way yellow dent hybrid cross f'	7.15	Entire	Waring Blendora; hexane, then CCL		
3-way yellow dent hybrid cross G	7.21	Entire	Waring Blendora; hexane, then COl4		

<sup>\*</sup>Essentially the method of Pinto and Enas (16).

TABLE II Characteristics and Calculated Compositions of Fractions of Distilled Methyl Esters of Oil from High-Oil Burr White Variety Corn

Fraction Refract index 45°	Refractive Saponifica-	Iodine	Weight	Saturated esters (g.)				Unsaturated esters (g.)		
		equivalent value	value	(g.)	C14	C16	C <sub>18</sub>	C <sub>20</sub>	Mono- C <sub>18</sub>	Di- C <sub>18</sub>
1	1.4317	269.4	4.72	2.44	0.16	2.19			0.04	0.05
2	1.4315	273.6	11.74	4.83		4.20	0.20		0.19	0.24
}	1.4466	291.3	125.7	14.24		0.29	0.77		5.57	7.61
1	1.4477	294.7	134.1	15.74		0.03	0.20		6.51	9.00
5	1.4472	294.5	132,6	12.65	*****	0.04	0.21		5.32	7.08
3	1.4471	294.1	128.4	14.98		0.04	0.24		7.05	7.65
7	1.4459	295.8	116.8	6.48		0.06	0.52		3.01	2.89
Residue	1.4559	301.4	79.59	3.31			0.84	0.10	1.68	0.69
. Total as esters				74.67	0.16	6.85	2.98	0.10	29.37	35.21
Total as acids				71.04	0.15	6.50	2.84	0.10	27.95	33.50
% as fatty acids					0.2	9.2	4.0	0.1	39.3	47.2

TABLE III Chemical Characteristics and Fatty Acid Compositions of Corn Oils

Corn	Oil content (% d.b.)	Unsaponifi- ables (%)	Refractive index (45°C.)	Iodine value (Wijs, ½ hr.)	Fatty acids (% by weight)			
					(Unsa	Total		
					Diethenoid	Monoethenoid	saturated	
Commercial Yellow (Crude oil)	4.8	2.9	1.4650	126.0	56.2ª	30.6a	13.2ª	
Commercial Yellow (Refined oil Mazola oil)	4.8	1.5	1.4652	126.0	56.3	32.9	10.8	
Iowa Agr. Expt. Station	9.2	1.7	1.4640	113.2	45.8	39.3	14.9	
High-oil Burr White	11.5	3.9	1.4691	115.5	47.5a	38.6a	13.9a	
		1		1	(47.2)	(39.3)	(13.5)	
Low-oil Burr White	1.6	8.0b	1.4712	130.6°	66.1	23.0	10.9	
High-oil content, hybrid mixture	7.1	3.3	1.4658	118.0	50.3a	34.8a	14.9a	
Hybrid Cross A	6.2	2.8	1.4664	125.7	56.7	32.1	11.2	
Hybrid Cross B	6.2	2.7	1.4665	125.0	56.2	32.1	11.7	
Hybrid Cross C	6.9	2.9	1.4652	118.0	48.1	40.3	11.6	
Hybrid Cross D	7.0	2.7	1.4660	122.7	52.4	37.1	10.5	
Hybrid Cross E	7.1	2.8	1.4662	123.8	55.0	33.2	11.8	
Hybrid Cross F	7.2	2.6	1.4662	123.4	53.7	35.3	11.0	
Hybrid Cross G	7.2	2.8	1.4657	121.0	52.1	35.7	12.2	

 <sup>&</sup>lt;sup>a</sup> Analysis by methyl ester distillation; other analyses by A.O.C.S. method CD 7-48.
 <sup>b</sup> Also contained 5.5% phospholipids as compared to 3.05% for oil from high-oil Burr White.
 <sup>c</sup> I.V. of methyl esters freed of unsaponifiables was 134.1; fatty acid analysis of esters.

procedures (13, 14, 15). Characteristics of fatty acid compositions of each fraction and the complete fatty acid composition of one of the oils are shown as an example in Table II. Analyses of crude and refined (Mazola oil) commercial corn oils were made similarly. Data on the crude oil were presented previously (7). After extraction of the whole grain by a modification of the method of Pinto and Enas (16), the other nine oils and oil from the High-Oil Burr White inbred were analyzed by the A.O.C.S. method (10). For simplification the very small amounts of conjugated dienoic acids calculated according to the above method were included in the total dienoic acids. Data on all the oils are summarized in Table III. A comparison of results obtained by the two methods of fatty acid analysis can be noted in the two sets of data for the High-Oil Burr White sample. Agreement was considered sufficiently satisfactory to justify the use of the shorter A.O.C.S. method on the small samples of oil obtained from eight of the corn samples.

## Statistical Analysis of the Data

The fatty acid analyses of all the samples were examined statistically by determination of the equation of the line, the correlation coefficient, the standard error of estimate, and the significance levels of the correlation coefficients (17, 18), for the relationships of iodine value to oil content and to fatty acid composition and for the relationships of oil content to the iodine value and the fatty acid composition. Equations and data are graphically represented in Figures 1 and 2. Significance levels of the relationships as shown in Table IV were found to be high. i.e., at above the 1% level, except for that of saturated acids and percentage of oil in the kernel which was barely significant at the 5% level and for that of saturated acids and iodine value which was significant at the 2% level.

The data obtained and the statistical evaluations indicate that linear relationships apparently exist between a) iodine value and fatty acid composition,

TABLE IV

Statistical Relationships Among Characteristics of Oils from Corns with Various Oil Contents (Range of oil contents studied was 1.63 to 11.5%; number of samples was 13)

Equation of the line $(y = a + bx)$	Correla- tion coef- ficient	Signifi- cance levels (%)	Standard error of estimate	
% Linoleic acid = $0.94 (I.V.) - 61.1$	0.98	0.1	$\begin{array}{c} \pm 1.0 \\ \pm 2.1 \\ \pm 1.2 \\ \pm 1.1 \\ \pm 2.7 \\ \pm 2.6 \\ \pm 2.6 \\ \pm 1.4 \end{array}$	
% Oleic acid = $124.4 - 0.73 (I.V.)$	0.90	0.1		
% Saturated acids = $35.4 - 0.19 (I.V.)$	0.68	2.0		
% Oil in kernel = $52.0 - 0.87 (I.V.)$	0.88	0.1		
Iodine value = $136.5 - 2.10 (\% \text{ oil})$	0.88	0.1		
% Linoleic acid = $67.0 - 2.01 (\% \text{ oil})$	0.88	0.1		
% Oleic acid = $23.4 + 1.63 (\% \text{ oil})$	0.84	0.1		
% Saturated acids = $9.80 + 0.36 (\% \text{ oil})$	0.54	5.0		

b) amount of oil in the kernel and iodine value, and c) amount of oil in the kernel and fatty acid composition. These relationships should be useful for approximation of fatty acid compositions from iodine values and of iodine values and fatty acid compositions from oil contents of corn kernels.

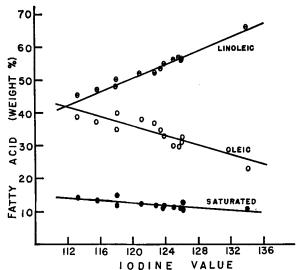


Fig. 1. Relationship between iodine values and fatty acid compositions of corn oils.

Relationships in the corn oils are similar to those found in oils from soybeans and cottonseed. An increase in oil content of the seed is accompanied by a decrease in iodine value, a decrease in linoleic acid content of the oil, and an increase in the oleic acid and saturated acid contents.

Although the increase in oil content of the corn is accompanied by an increase in saturation of the oil, the change is relatively small over the range of 5 to 8% oil in corn. The trend however would appear to be favorable for livestock feeding and to have little or no effect on the processing of corn oil. After the work reported here was completed, a larger sample of oil has been recovered from 9.7% oil corn and refined in the laboratory. No unusual winterization or other processing problems were noted.

## Summary

The fatty acid compositions of 13 oils from corns having oil contents over the range of 1.6 to 11.5% oil, d.b., were determined either by a spectrophotometric technique applied to the whole oil or by the methyl ester fractional distillation technique. Linear relationships between iodine values and fatty acid compositions, between oil contents of the corns and iodine

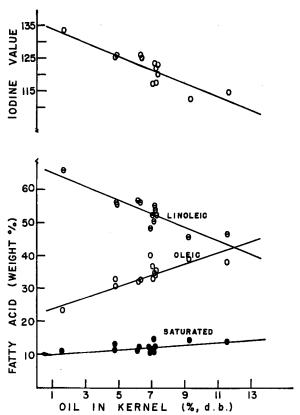


Fig. 2. Relationships between oil contents of corns and iodine values and fatty acid compositions of the oils.

values, and between oil contents and fatty acid compositions were determined. An increase in oil content of the corn is accompanied by a decrease in iodine value and linoleic acid content of the oil and by an increase in oleic acid and saturated acids.

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