

REFERENCES

1. de Vries, B., Chem. Ind. 1049 (1962).
2. Scholfield, C. R., E. P. Jones, R. O. Butterfield and H. J. Dutton, Ann. Chem. 35, 1588 (1963).
3. Nichols, P. L., Jr., J. Am. Chem. Soc. 74, 1901 (1952).
4. de Vries, B., JAOCS 41, 403 (1964).
5. Morris, L. J., Chem. Ind. (London) 1238 (1962).
6. Barrett, C. B., M. S. J. Dallas and F. B. Padley, JAOCS 40, 580 (1963).
7. Privett, O. S., and M. L. Blank, *Ibid.* 40, 70 (1963).
8. Litchfield, C., M. Farquhar and R. Reiser, *Ibid.* 41, 588-592 (1964).
9. Subbaram, M. R., and C. G. Youngs, *Ibid.* 41, 445 (1964).
10. Kaufmann, H. P., and H. Wessels, Fette, Seifen, Anstrichmittel 66, 81 (1964).
11. Kaufmann, H. P., and H. Wessels, *Ibid.* 66, 13 (1964).
12. Litchfield, C., and R. Reiser, "Analysis of Triglycerides by Multiple Chromatographic Techniques," presented at The World Fat Congress, Hamburg (1964).
13. McCarthy, M. J., and A. Kuksis, JAOCS 41, 527-530 (1964).
14. Mattson, F. H., and R. A. Volpenheim, J. Lipid Res. 2, 58 (1961).
15. Privett, O. S., M. L. Blank and W. O. Lundberg, JAOCS 38, 312 (1961).
16. Privett, O. S., and M. L. Blank, J. Lipid Res. 2, 37 (1961).
17. Blank, M. L., and O. S. Privett, J. Dairy Sci. 47, 481 (1964).
18. Jurriens, G., B. de Vries and L. Schouten, J. Lipid Res. 5, 267 (1964).
19. VanderWal, R. J., H. J. Ast, E. G. Perkins and G. H. Chacko, "Specific Orientation in Fat Molecules," JAOCS in press.
20. VanderWal, R. J., *Ibid.* 37, 18 (1960).

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Composition of Corn Oil

J. B. BEADLE, D. E. JUST, R. E. MORGAN and R. A. REINERS,
Moffett Technical Center, Corn Products Company, Argo, Illinois

Abstract

The composition of commercial corn oil from USA corn is remarkably constant. A total of 103 samples of refined corn oil produced over a period of 2.5 years were analyzed by the alkali isomerization procedure. Nearly 86% of the samples had an iodine value (I.V.) within one unit of the average value, 123.6. Linoleic content on a fatty acid basis, averaged 55.5%; 93% of the values were within two units of this value. All samples contained small amounts of linolenic acid. This uniformity undoubtedly results from the system of corn marketing and buying which brings grain from the entire corn belt to the processing plants.

A number of corn oils were analyzed by GLC. The average linoleic acid content by this method was ca. 2.5 units higher than that found by the isomerization method. This difference may occur because GLC responds to all C-18 dienes equally while the alkali isomerization method responds only to conjugatable dienes. Possible sources of error in both methods of fatty acid analysis are discussed.

Corn oil samples taken over a 16-month period were analyzed by GLC. Average values were:

I.V. (Wijs)	Constituent fatty acids (% , fatty acid basis)					
	C-16:0	C-18:0	C-18:1	C-18:2	C-18:3	C-20:0
124.4	11.5	2.2	26.6	58.7	0.8	0.2

Although much of our experience has been with the alkali isomerization method, the GLC technique is preferred because it is simpler and yields more information on fatty acid composition. Another important advantage is that determination of the I.V. of the oil serves as a check on GLC results. The I.V. calculated from the GLC results, making allowance for 1.25% unsaponifiables in the case of corn oil, should be within a few units of the Wijs value.

Oils derived commercially from corns grown in other countries are generally more saturated than those from USA corn. The I.V. of the samples examined varied from 107-125, the linoleic acid contents from 42-56%. The relationship between I.V. and linoleic acid content established by others from hybrid corns holds fairly well for these samples.

Introduction

THE DEGREE OF UNSATURATION of oil from corn germ varies considerably. AOCS tabulation of "Physical and Chemical Characteristics of Oils, Fats and Waxes" shows a spread of 110-128 in I.V. (1). A much greater spread was found by Lofland et al. (2) on examination of strains of corn used in breeding programs. I.V. of the oils extracted from these corns varied from 88-147 and the linoleic acid content from ca. 20-70%. I.V. of the oils from the most common inbreds used by midwestern corn breeders ranged from 111-151 (3). This difference is reflected in the I.V. of the oils from 25 commercial midwestern hybrid corns which have been found to vary from 115-130 (4).

Despite this wide variation in the degree of unsaturation of corn oil from the individual hybrids, commercially available corn oil from midwestern corn (the pre-eminent USA source) is of relatively uniform composition. The purpose of this paper is to offer evidence to support this statement, to discuss methods of fatty acid analysis and possible sources of error, and to show that corn oils derived from corn grown in other parts of the world may differ greatly in composition from that grown in the Midwest.

Considerable information has been published on the composition of commercially available domestic corn oil. These data were reviewed and a number of analyses, including some extreme values, are cited in Table I. Some values are from work in which the sources of the corn oil are not clearly identified but were most likely domestic.

While these literature values will be discussed later, several observations are at once evident. The bulk of the results by all three of the analytical methods (methyl ester distillation, alkali isomerization and GLC) are quite similar for the principal fatty acids. Palmitoleic acid, almost invariably found by methyl ester distillation, was reported by only one of these investigators using GLC. Linolenic acid is almost always reported in results obtained in GLC and alkali isomerization. Results by the last two methods are in fair agreement.

Analytical Methods

Alkali Isomerization. Extreme care is required in carrying out the isomerization technique in order to obtain reproducible results. The method used in this laboratory is essentially that of Brice and Swain

TABLE I
Fatty Acid Composition of Corn Oil from USA Corn—Various References

Method of analysis	I.V.		Constituent fatty acids (% , fatty acid basis)										Reference
	Wijs	Calc.	C-12:0	C-14:0	C-16:0	C-18:0	C-20:0	Total saturates	C-16:1	C-18:1	C-18:2	C-18:3	
Me ester distillation.....				1.4	10.2	3.0		14.6	1.5	49.6	34.4		5
Me ester distillation.....				0.5	9.7	3.6		13.8	0.2	30.4	55.6		6
Me ester distillation.....	126			0.2	9.9	2.9	0.2	13.2	0.5	30.1	56.2	0.0	7
Me ester distillation.....				0.1	8.1	2.5		10.7	1.2	30.1	56.3		8
Isomerization.....	123.5							14.7 ^a		35.9	47.7	1.7	9
Isomerization.....	113										52	0	10
Isomerization.....	125.9							9.0		36.1	54.9		12
Isomerization.....	126.1							12.5		27.1	55.0	0.5	13
Isomerization.....	126.8							8.8		35.5	55.7		12
Isomerization.....											55.9	0.7	11
Isomerization.....	125.4							13.5		28.9	56.8	0.6	14
Isomerization.....	126.0							10.8		32.9	56.3		15
Isomerization ^b											56.8	0.7	16
Isomerization.....											57.2	0.4	17
GLC.....	126	117.4	0.1	0.3	12.7	2.7		15.8		30.7	53.5		19
GLC.....		118.5			13	2		15		31	54		20
GLC.....	126	117.3	0.4	0.2	13.0	2.3		15.9		28.8	54.4		21
GLC.....		125.3			10.7	3.2		13.9		28.4	54.7	3.0	22
GLC.....	123.5	121.9						14.3 ^a		29.7	54.8	1.2	9
GLC.....		120.8			13.3	1.6		14.9		28.7	56.2	0.2	23
GLC.....		123.4			11.7	1.7		13.4	0.3	28.6	57.0	0.7	16
GLC.....		125.0		0.0	10.7	2.0		12.7	0.0	29.1	57.2	1.0	24
GLC.....		123.6			12.4	1.7		14.1		27.7	57.4	0.8	25
GLC.....		125.3		0.2	12.2	0.7		13.1		26.9	60.0		26
GLC.....	126.3	126.4			10.0	2.7		12.7		26.7	60.3	0.3	27
GLC.....		135.7			8.3	1.3		9.6		23.3	66.5	0.9	18

^a Calculated from this author's results.
^b Isomerized, using potassium tertiary butoxide reagent.

(28,29,30) in which isomerization is conducted at 180 ± 0.5C for 45 min in an 11% solution of potassium hydroxide in glycerol. The equations used to determine fatty acid composition are those given in the 1952 article.

Several precautions are necessary for reproducible results. Time and temp of isomerization must be closely controlled as well as sample size and mixing of sample and reagent. Isomerization time (45 min) is controlled in our laboratory to within ±0.5 min. The alkaline glycerol solution is held at 180C for 20 ± 1 min prior to sample introduction. A 100 ± 1-mg sample is used for corn oil. The oil is stirred into

the alkaline glycerol solution by removing the tube from the bath 60 sec after the sample has been introduced, placing it in a tube mixer for 60 sec, then replacing the tube in the bath for 60 sec. This procedure is then repeated and the sample tube reintroduced into the bath. By the end of the second mixing the sample should be clear, indicating that saponification is underway. The bath temp must be controlled within ±0.5C. A high temp thermistor in conjunction with an electronic controller has proven satisfactory. Good agitation of the bath is essential. These precautions are probably useful in the analysis of all polyunsaturated vegetable oils.

TABLE II
Fatty Acid Composition of Refined Corn Oil by Alkali Isomerization and by GLC

Date oil processed	I.V.		Alkali isomerization ^a				GLC ^a						
	Wijs	Calc.	Total saturates	C-18:1	C-18:2	C-18:3	C-16:0	C-18:0	C-20:0	Total saturates	C-18:1	C-18:2	C-18:3
5-61.....		124.2					11.5	2.3	0.4	14.2	26.8	57.6	1.2
4-62.....	123.7	125.4	14.4	29.0	55.8	0.7	11.4	1.9	0.3	13.6	27.2	58.7	0.8
		125.0					11.4	2.3	0.2	13.9	27.1	58.5	0.8
6-62.....	124.0	125.4	14.2	29.0	55.8	0.8	11.3	1.9	13.2	27.3	58.8	0.7
			13.5	30.3	55.3	0.8							
			13.0	31.0	55.4	0.5							
8-62.....	124.3	125.6	13.9	29.1	56.3	0.7	11.4	1.8	13.2	27.1	59.2	0.6
			13.6	29.6	56.2	0.6							
8-62.....	123.7	125.2	14.3	29.1	55.8	0.7	11.2	2.1	13.3	27.4	58.5	0.8
			14.5	28.7	56.1	0.7							
8-62.....	124.0	125.2	13.8	29.7	55.8	0.7	11.1	1.8	12.9	27.6	58.4	0.8
			14.2	28.8	56.3	0.6							
8-62.....	123.9	124.7	14.2	29.1	55.9	0.7	11.6	1.8	13.4	27.5	58.3	0.7
			14.8	27.8	56.7	0.6							
8-62.....	123.7	124.6	14.4	28.9	56.0	0.7	11.5	2.3	13.8	27.4	58.0	0.9
			14.8	28.0	56.5	0.6							
8-62.....	124.2	126.0	14.2	28.6	56.5	0.7	11.1	1.9	13.0	27.3	59.0	0.8
			14.1	28.8	56.4	0.6							
8-62.....	124.5	126.1	13.4	29.9	56.0	0.7	11.2	1.6	12.8	27.5	58.8	0.9
			13.5	29.8	56.1	0.7							
8-62.....	124.0	125.6	14.4	28.6	56.0	0.9	11.4	1.8	13.2	27.1	58.9	0.8
			14.3	28.8	56.1	0.8							
8-62.....	124.1	125.4	14.3	28.8	56.0	0.8	11.6	1.7	13.3	27.2	58.7	0.8
			13.9	29.5	55.8	0.8							
8-62.....	124.0	126.0	14.1	29.2	55.8	0.8	11.4	1.6	13.0	27.3	59.0	0.8
			13.8	29.9	55.5	0.8							
			13.8	29.9	55.5	0.8							
10-62.....	123.7	124.6	14.5	28.8	56.0	0.7	11.4	2.2	0.2	13.8	26.9	58.7	0.6
		124.2					11.6	2.4	0.2	14.2	26.5	58.5	0.7
2-63.....	124.1	124.6	14.2	28.8	56.3	0.7	11.6	2.3	0.2	14.1	26.5	58.6	0.8
		124.7					11.5	2.2	0.2	13.9	26.7	58.7	0.7
3-63.....	124.4	125.5	14.5	27.9	56.9	0.7	11.4	2.1	0.2	13.7	26.4	59.2	0.7
		126.3					11.5	2.3	0.2	14.0	26.6	59.7	0.7
3-63.....	124.5	126.5					11.7	2.2	0.2	14.1	26.1	59.6	1.0
4-63.....	124.5	125.1					11.8	2.2	0.2	14.2	26.4	58.9	0.8
4-63.....	125.0	125.7					11.4	1.9	0.3	13.6	26.1	59.4	0.8
5-63.....	125.0	125.9					11.5	2.3	0.2	14.0	26.2	59.2	1.0
6-63.....	124.0	125.2					11.7	2.3	0.2	14.2	26.0	59.0	0.9

^a Results expressed as %, fatty acid basis.

Under these conditions and, of course, otherwise adhering strictly to the published procedure, excellent reproducibility was obtained. Results of replicate determinations on 11 finished corn oil samples are shown in Table II. Although most of these samples were taken during Aug. 1962, no two samples were taken on the same day. The max difference in linoleic acid content between replicate determinations is 0.8%.

Gas-Liquid Chromatography. GLC has been widely applied to determine the fatty acid composition of corn oil. Much of the popularity of this method is due to its apparent simplicity. However, our experience indicates that many pitfalls await even the skilled analyst.

All GLC analyses reported here were carried out on a Beckman Gas Chromatograph, Model GC-2A, equipped with a mechanical integrator (Disc Instruments, Inc.) and a flame ionization detector. The copper column (0.25 in x 7.5 ft) was packed with diethylene glycol succinate (20%) on 60/80-mesh, acid washed Chromosorb W and was operated at 194C with a helium flow rate of 106 ml/min measured at 194C. A 0.8-mg sample was used. These operating parameters permitted complete resolution of all components of interest so that all peak areas could be measured with the integrator. The instrument was standardized with a known mixture of pure methyl esters simulating the composition of corn oil. The pure compounds were purchased either from Lachat Chemicals, Inc. or from Applied Science Laboratories.

Two major problems were encountered in applying the GLC method to corn oil: the preparation of the methyl esters for injection into the column, and column carry-over. Although sodium methoxide catalyzed methyl transesterification has been widely used to prepare glycerides for GLC (31), application to corn oil led to incomplete reaction. Reaction under

rigorously anhydrous conditions gave 93% yields of methyl esters from corn oil. The method finally adopted was one in which ca. 0.8 g of corn oil is saponified with alcoholic potassium hydroxide solution and evaporated as described by Benedict (32) except that no benzene is added. The soaps are dissolved in water, acidified with 1.0 N HCl and the fatty acids extracted with petroleum ether. After removal of the solvent under a stream of nitrogen, the fatty acids are esterified with boron trifluoride-methanol reagent using a 15-min reaction time and the esters then recovered by petroleum ether extraction (33). The solvent is again evaporated under nitrogen and the methyl esters are dissolved in xylene to form ca. an 8% solution.

Analysis of pure triglyceride mixtures by this method showed that methyl esterification was ca. 97% complete. The recovered methyl esters were found to have the same fatty acid composition as the original triglycerides. Similarly high yields of methyl esters were attained on application of this method to corn oil.

Possibly the most serious source of error in GLC work is carry-over (34). This is a poorly understood phenomenon in which components from a previous analysis remain on the column and appear as constituents in subsequent analyses. Carry-over presents a particularly difficult problem in the analysis of fatty acids present in only small quantities. For example, on one occasion a polyester column was standardized using a methyl ester mixture containing 33% methyl arachidate. The undiluted esters were injected into the instrument. A sample of corn oil was analyzed next and found to contain 3.1% arachidic acid. Repeated analyses after this anomalous result showed the arachidic acid content of this sample to be only 0.4%.

By standardizing daily with a methyl ester mixture of composition similar to that of corn oil, column carry-over is minimized or at least recognized. The known mixture is injected into the column as an 8% solution in xylene. Injection of undiluted methyl esters increased carry-over. Although our experience is largely with corn oil, the same precautions undoubtedly are desirable in the analysis of other oils.

All fatty acids analyses are expressed on a fatty acid basis. In calculating the I.V. of the oil from GLC fatty acid analysis, a factor of 0.9435 was used which accounts for the conversion of the fatty acids to glycerides and the presence of 1.25% unsaponifiables in corn oil.

The results of a number of GLC analyses of corn oil are given in Table II and are in fair agreement with results obtained by the alkali isomerization method.

Phosphorus. AOCS Official Method Ca 12-55 is used with the following exception: The phosphomolybdate is reduced in H₂SO₄ with ascorbic acid.

Color-Spectrophotometric. Crude corn oil is diluted 1:10 (v/v) with carbon tetrachloride and the difference between the absorbance at 450 m μ and 600 m μ /cm, multiplied by 1000, is reported as the color.

Refining-Chromatographic. AOCS Official Method Ca 9f-57.

Iodine Value. AOCS Official Method Cd 1-25.

Free Fatty Acids. AOCS Official Method Ca 5a-40.

Unsaponifiable. AOCS Official Method Ca 6a-40.

Oil. Corn, ground through a 1-mm screen (Wiley mill), is dried at 100C in a vacuum oven for one hr, than a 5-g sample extracted with carbon tetrachloride for 24 hr in a modified Butt extractor.

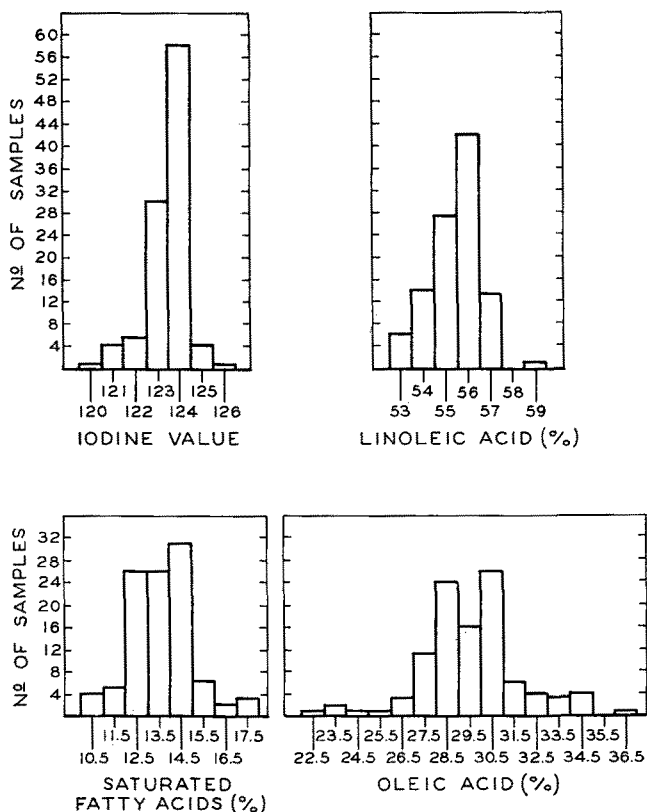


Fig. 1. The composition of 103 corn oil samples as determined by the alkali isomerization method.

Results and Discussion

USA Oil. Over a period of about 2.5 years, 103 samples of finished corn oil were taken at irregular intervals and their fatty acid composition determined by the alkali isomerization method. Most of these samples were of oil processed at the Argo plant of the Corn Products Co.; some were of oil processed at the Bayonne or San Francisco plants. Results are shown in Figure 1.

The composition of corn oil over this period was quite constant. The I.V. averaged 123.6 ranging from 120.2–126.3 with 85% of the values falling between 122.6–124.5. The same narrow distribution is evident in the linoleic acid contents. The average is 55.5 and the range from 53.1–58.6%, but 93% of the samples fell within the 53.6–57.5% range. The values for saturated fatty acids and for oleic acid show considerable spread around their averages of 14.1 and 29.7%, respectively. This is to be expected as these values reflect errors both in the determination of I.V. and linoleic acid content. Linolenic acid was found in all samples. The average value is 0.6%; the range is from 0.1–0.9%. Approx 0.1% conjugated triene is present in all samples.

The true ranges of the fatty acid composition of these oils are probably narrower than indicated by these data since some of the early samples were analyzed before the need for the precautions discussed earlier was appreciated. The values obtained over this 2.5-year period by alkali isomerization are in good agreement with those reported in the literature (Table I) determined by the same method. Only two of the linoleic acid and two of the linolenic acid values cited are outside the range of those reported here.

As must be expected of natural products, some variations in the I.V. of corn oil may occur over a period of several years. The average I.V. of 72 samples taken over 18 months during 1957 and 1958 was 125.4. This is not too different from 123.6, the value obtained more recently.

Although the GLC data are in fair agreement with the results obtained by alkali isomerization, significant differences are apparent on close examination. Fifteen of the corn oil samples shown in Table II were analyzed by both methods and the average results are shown below:

	I.V.		Constituent fatty acids (% , fatty acid basis)			
	Wijs	Calc.	Total Saturates	Oleic	Linoleic	Linolenic
Alkali isom.	124.0	14.2	29.1	56.1	0.7
GLC	125.7	13.4	27.2	58.7	0.8

Most important is the difference in linoleic acid content. Ca. 2.5% (based on oil wt) more linoleic acid is found in corn oil by GLC analysis than by alkali isomerization. Both the content of oleic acid and that of total saturated fatty acids are lower by GLC than by alkali isomerization. Linolenic acid contents are the same by both methods. Although the I.V. calculated from the GLC data are consistently higher than those obtained by the Wijs method, the difference is small and of doubtful significance.

The differences found in the linoleic acid content of corn oil by these two methods are not in accord with the experience of some other investigators analyzing similar oils. Kauffman et al. (35) found good agreement between the results by these methods when determining the linoleic acid content of cottonseed and soybean oils (oils similar to corn in linoleic content). Excellent agreement between the two methods was obtained by Herb et al. (36) on analysis of sesame oil and safflower oil. French (9) applied the two methods to a variety of oils and showed generally good agreement between the two. Corn oil was one of the exceptions. The reported linoleic acid content was 54.8% by GLC and 47.7% by alkali isomerization. However, the I.V. by the AOCS method agreed well with that calculated from the GLC data. After examining soybean, sunflower and corn oil, Craig and Murty (37) concluded that there was fair agreement between I.V. as determined by the Wijs method and that calculated from GLC data. There were, however, very significant differences in fatty acid composition by the two methods. The data of Wolff from the analysis of 10 samples of corn oil by both methods show good agreement for linoleic acid contents (39).

Recently, Sreenivasan et al. (16) showed that not all the C-18 dienes in corn oil were the 9,12-isomers. These authors show that 3.9% of the linoleic acid in corn oil was not conjugated after heating at 180C for 25 min in the ethylene glycol-potassium hydroxide reagent. Some evidence is presented to indicate that a diene with the first double bond at C-11 position is present.

TABLE III
Properties of Various Commercial Corn Samples and of the Crude Oils Derived Therefrom

Origin of corn	Color	Type	Oil in kernel (% d.b.)	Oil properties				
				I.V.	Color ^a	FFA (% as oleic)	Unsaponifiable (%)	Phosphorus (%)
Rhodesia.....	White	Dent	4.9	107.6	97
Rhodesia.....	White	Dent	4.9	107.6	117
Kenya.....	White	Dent	4.9	108.4	139	1.56	1.39	0.067
Tanganyika.....	White	Dent	5.2	111.6	86	1.60	1.42	0.056
So. Africa.....	White	Dent	4.2	111.8	96	1.58	1.47	0.047
No. America.....	White	Dent	5.7	114.5	108	1.86	1.21
USA.....	White	Dent	4.8	119.1	128	1.48	0.031
No. America.....	White	Dent	4.2	122.9	144	2.07	1.44	0.057
Angola.....	White	Flint	5.2	110.4	111
Congo.....	White	Flint	4.3	110.5	117	2.40	1.48	0.031
Angola.....	White	Flint	4.8	111.5	145	1.46	1.05	0.068
Turkey.....	White	Flint	5.5	114.1	96	2.00	1.61	0.046
Angola.....	White	Flint	5.1	114.5	130
Kenya.....	Yellow	Flint	4.8	110.4	202
Morocco.....	Yellow	Flint	5.0	113.3	208	1.96	1.43	0.049
Argentina.....	Yellow	Flint	5.2	124.2	208
Yugoslavia.....	Yellow	Dent	4.9	114.5	260
Yugoslavia.....	Yellow	Dent	4.9	123.4	266
France.....	Yellow	Dent	4.7	123.7	234	1.83	1.33	0.045
USA (corn belt) ^b	Yellow	Dent	4.8	125.4	2.71	1.25	0.054
Mexico (Jalisco).....	White	Dent	110.4	144	1.82	1.22	0.032
Brazil.....	112.5	416	2.20	1.86	0.026
Colombia.....	113.4	210	2.70
Brazil.....	113.6	304	2.69	1.46	0.032
Brazil.....	113.9	323	2.09	2.07	0.031
Colombia.....	115.4	220	5.12	1.38	0.042
USA.....	White	121.6	99	1.10	1.26	0.053

^a Spectrophotometric.

^b Average of oil produced in 1957 and 1958 at Argo, Ill. plant, Corn Products Co. as judged by the analysis of 72 samples taken over this period.

TABLE IV
 Fatty Acid Composition of Some Foreign Corn Oils

Origin	Kernel properties		Oil ^b	Oil properties			
				I.V.	Constituent fatty acid (% fatty acid basis) ^a		
	Color	Type			Total saturates	C-18:1	C-18:2
Mexico.....	White	Dent	Crude	110.4	14.1	43.9	42.0
			Refined	110.4	15.3	41.5	43.2
Angola.....	White	Flint	Crude	111.5	15.8	39.3	44.9
			Refined	112.6	15.7	38.2	46.1
So. Africa.....	White	Dent	Crude	111.8	14.7	41.1	44.2
			Refined	112.6	15.1	39.5	45.4
Brazil.....	Crude	113.6	16.0	36.5	47.5
			Refined	113.6	15.2	38.1	46.7
No. America.....	White	Dent	Crude	114.5	16.1	35.3	48.6
			Refined	115.0	14.7	37.4	47.9
Colombia.....	Crude	115.4	16.1	34.2	49.7
			Refined	116.4	14.9	35.5	49.6
France.....	Yellow	Dent	Crude	123.7	12.8	31.3	55.9
			Refined	123.9	12.9	30.8	56.3

^a Determined by alkali isomerization.

^b Refined oil prepared from crude by chromatography on alumina column (Official Method Ca 9f-57).

The occurrence of such dienes presents a ready explanation for our findings. The GLC linoleic acid values include all the C-18 dienes since these are not separated on packed polyester columns of this length (7.5 ft). On the other hand, the isomerization method has been standardized using *cis*, *cis*-9,12-octadecadienoic acid and, although other spatial and positional isomers may conjugate under the influence of alkali, the degree of conjugation is not the same as that of the *cis*, *cis*-9,12 compound. Thus the alkali isomerization results correspond approx to the content of *cis*, *cis*-9,12-octadecadienoic acid.

It seems likely that the same situation exists with regard to the analysis of oils other than corn oil. Sreenivasan et al. found 3.2% nonconjugatable C-18 diene in cottonseed oil and 2.5% in safflower oil.

The GLC conditions generally used in this laboratory are such that the minor constituents are not observed. However, by decreasing the attenuation at the appropriate times, the fatty acids present in only small amt can be quantitatively determined. Lauric, myristic, palmitoleic and arachidic acids have been found when the appropriate GLC operating conditions have been used. Typical results for the first three of these acids are shown below:

Sample	Fatty acids (% , fatty acid basis)		
	C-12:0	C-14:0	C-16:1
A	0.015	0.016	0.06
B	0.006	0.055	0.1
C	0.013	0.014	0.1

Values for arachidic are shown in Table II. They range from 0.2-0.4%. Baldwin and Sniegowski (7) using the distillation technique found 0.2% arachidic acid in corn oil.

Lauric, myristic, palmitoleic and arachidic acids were present in all corn oils examined. Analysis by the methyl ester distillation technique regularly showed the presence of palmitoleic acid (Table I). Our results confirm this earlier work.

There is little doubt that linolenic acid is a constituent of corn oil. Crespo (38) has isolated a hexabromostearic acid from Argentine corn oil after appropriate manipulation.

From December, 1962 until March, 1964 samples of corn oil were obtained every three months and analyzed by GLC. A total of 42 samples were examined. The average results are shown below:

I.V. (Wijs)	Constituent fatty acids (% , fatty acid basis)					
	C-16:0	C-18:0	C-18:1	C-18:2	C-18:3	C-20:0
124.4	11.5	2.2	26.6	58.7	0.8	0.2

As in the case of the samples analyzed by the alkali isomerization procedure, these also showed remarkably little variation; for example the I.V. ranged from 123.7-125.5, the dienoic acids from 57.8-60.1%.

With few exceptions, our results agree fairly well with those reported in the literature (Table I) for USA corn oil. The linoleic acid values reported by Longenecker (5) and French (9) seem low as judged by our experience. The value for this acid reported by Fleischman et al. (18) appears too high.

Imported Corn Oil. While oil prepared from commercially available midwestern corn is of relatively constant composition, that derived from corn grown in other parts of the world varies considerably. To determine the degree of this variation, samples of crude oil were obtained from corn wet milling plants throughout the world. These plants separate corn into its components by the same process used in this country. Many varieties of corn are processed. Some plants purchase corn on the world market, other process only locally grown corn. Since we hope to relate corn oil properties to the type of corn and the country of origin, samples of corn and of the crude oil derived from them were obtained from plants outside the USA. The samples were taken only when the plant had been running on a single kind of corn for some time. In all cases the oil was expressed from the dried wet milled corn germ by mechanical screw presses. This group of samples, then, is representative of commercially produced oils from corns which are grown on a large scale in various parts of the world.

Surprisingly, the ranges of protein and oil contents of these kernels (9.1-10.8% and 4.2-5.7%, respectively) were well within those of USA grown corns. The most significant variation was found in crude oil properties, particularly in iodine value. The latter ranged from 107.6-124.2 (Table III). This variation may result from genetic characteristics or climatic conditions which exert a considerable influence on I.V. (2,15,40,41).

As might be anticipated, crude oil from yellow corn is appreciably darker colored than that from white

 TABLE V
 Relationship Between I.V. and Linoleic Acid Content of Corn Oils—Regression Equation Constants

Source of data	Constants ^a		Standard deviation (σ)
	a	b	
This report, crude oils	-66.4	1.00	1.1
Sniegowski and Baldwin (15)	-61.1	0.94	1.0
Lofland, Quackenbush and Brunson (2) ..	-57.4	0.87	3.0
This report, refined oils	-61.8	0.95	0.32

^a For equation $y = a + bx$ where y = percentage linoleic acid on fatty acid basis and x = I.V.

TABLE VI
 Fatty Acid Composition of Imported Corn Oils

Origin of oil	I.V.		Method of analysis	Constituent fatty acids (% fatty acid basis)								
	Wijs	Calc.		C-12:0	C-14:0	C-16:0	C-18:0	C-20:0	Total saturates	C-18:1	C-18:2	C-18:3
Germany		125.9	GLC	0.006	0.064	11.3	2.3	0.4	14.1	26.9	56.3	2.7
Germany	124.8		Isomerization						13.4	30.3	54.8	1.4
Germany		125.2	GLC	0.009	0.028	11.1	2.1	0.4	13.6	26.6	57.7	1.6
Germany	125.0		Isomerization						14.7	27.5	56.3	1.4
Germany		125.5	GLC	0.011	0.014	11.2	2.1	0.4	13.7	26.7	57.2	2.0
Germany	124.8		Isomerization						14.1	29.0	55.6	1.4
Germany		126.4	GLC	0.015	0.016	11.1	2.1	0.3	13.5	26.7	58.2	1.7
Germany	125.3		Isomerization						14.7	27.3	55.5	1.5
Germany		125.1	GLC			11.0	2.1	0.3	13.4	27.4	58.0	1.1
Germany	123.9		Isomerization						13.1	31.5	54.5	0.9
Brazil	113	114.4	GLC	0.023	0.042	13.7	2.4	0.5	16.7	32.4	49.1	1.2
Mexico	109	110.1	GLC	0.024	0.042	12.6	3.9	0.6	17.1	37.2	44.3	1.1
Colombia	114.9	113.6	GLC			14.9	1.2	0.2	16.3	34.3	48.6	0.6

corn despite the effect of oil recovery methods (Table III). The free fatty acid content of these oils is within normal limits except for one sample from Colombia which was unusually high (5.1%). Again with one or two exceptions both unsaponifiable and phosphorus contents were in the usual range.

Imported oils are of ca. the same phosphorus content as USA oils but of slightly higher unsaponifiable content. Seventy-two samples of crude USA corn oil were analyzed in 1957 and 1958 (Table III). Unsaponifiables averaged 1.25%, ranging from 1.00–1.47%. Corresponding values for phosphorus content are 0.054% and 0.038–0.070%.

Evidence in the literature indicates that as the I.V. of corn oil declines, its linoleic acid content likewise declines. This relationship is based on the analysis of various hybrids of widely different oil content (2,15). The fatty acid compositions of seven samples of imported corn oil as determined by the alkali isomerization method are given in Table IV. In spite of the divergent genetic background and climatic conditions under which these samples were grown, about the same relationship between linoleic acid content and I.V. holds for these samples as for those where genetic characteristics were the chief variable (Table V). Possibly this is an indication that the genetic factor is dominant.

The isomerization method for analysis of fatty acid composition may be applied with more confidence to refined oils than to crude oils. In Table IV the results of analysis of the refined oils prepared from the crude oils are also shown. The chromatographic method for determining neutral oil was used to prepare the refined oil. The standard error of estimate of the regression equation based on the analyses of the refined oils is much lower than that from the analyses made on the crude oils (Table V).

More recently a number of imported corns oils have been analyzed by GLC and by the alkali isomerization method. The results are shown in Table VI. The five German samples were obtained from Deutsche Maizena Werke G.m.b.H. and were produced early in 1962 when sizable amounts of yellow USA corn were being processed. Comparing the results by the isomerization and GLC procedures, the differences are the same magnitude as found previously. The linoleic acid values are higher and the oleic and total saturates lower by the GLC analysis. These samples are unusual chiefly in their high linolenic acid content compared to typical USA oils. Kaufmann and Mankel (42) also found high linolenic acid values on examining a German corn oil.

The results of the GLC analysis of the Brazilian, Mexican and Colombian oils (Table VI) agree fairly well with the values reported in Table IV for oils from

these countries. An exception is the value for linolenic acid where results of the GLC analyses were in the expected range. Both the Brazilian and Mexican oils contained more lauric and arachidic acids than found in USA oils.

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REFERENCES

1. Official and Tentative Methods of the AOCS second ed., "Additions and Revisions to 1962 Inclusive," Table I I-46, Chicago.
2. Lofland, H. B., F. W. Quackenbush and A. M. Brunson, *JAOCS* 31, 412–14 (1954).
3. Quackenbush, F. W., Jean G. Fitch, A. M. Brunson and L. R. House, *Cereal Chem.* 40, 250–59 (1963).
4. Watson, S. A., Personal Communication.
5. Longenecker, H. E., *J. Biol. Chem.* 129, 13–22 (1939).
6. Kummerow, F. A., *Oil & Soap* 23, 167–70 (1946).
7. Baldwin, A. R., and M. S. Sniogowski, *JAOCS* 28, 24–27 (1951).
8. Baur, F. J., and J. B. Brown, *J. Am. Chem. Soc.* 67, 1899–1900 (1955).
9. French, R. B., *JAOCS* 39, 176–8 (1962).
10. Okey, Ruth, M. M. Lyman, Anne G. Harris, Betty Einset and W. Hain, *Metab. Clin. Exp.* 8, 241–255 (1959).
11. Firestone, D., *J. Assoc. Offic. Agr. Chem.* 38, 657–63 (1955).
12. Ahrens, E. H., Jr., J. Hirsch, W. Insull, Jr., T. T. Tsaltas, R. Blomstrand and M. L. Peterson, *Lancet* 1957, I, 943–53.
13. Chang, Irene C. L., L. I. Y. Tchen and Betty M. Watts, *JAOCS* 29, 373–9 (1952).
14. Firestone, D., *J. Assoc. Offic. Agr. Chem.* 40, 487–91 (1957).
15. Sniogowski, M. S., and A. R. Baldwin, *JAOCS* 31, 414–16 (1954).
16. Sreenivasan, B., J. B. Brown, E. J. Jones, V. L. Davison and Janina Nowakowska, *Ibid.* 39, 255–59 (1962).
17. Swain, Margaret L., and B. A. Brice, *Ibid.* 26, 272–7 (1949).
18. Fleischman, A. I., A. Florin, J. Fitzgerald, Anne B. Caldwell and Gertrude Bastwood, *J. Am. Dietet. Assoc.* 42, 394–8 (1963).
19. Ahrens, E. H., Jr., W. Insull, Jr., J. Hirsch, W. Stoffel, M. L. Peterson, J. W. Farquhar, T. Miller and H. J. Thomasson, *Lancet* 1959, I, 115–19.
20. Wissler, R. W., L. E. Frazier, R. H. Hughes and R. A. Rasmussen, *Arch. Pathol.* 74, 312–22 (1962).
21. Perkins, E. G., J. G. Endres and F. A. Kummerow, *Proc. Soc. Exp. Biol. Med.* 106, 370–72 (1961).
22. Wheeler, Priscilla, D. W. Peterson and G. D. Michaels, *J. Nutr.* 69, 253–60 (1959).
23. Bernfeld, P., F. Homburger and T. F. Kelly, *Am. J. Clinical Nutr.* 11, 554–8 (1962).
24. Marion, J. E., and H. W. Edwards, Jr., *Poultry Sci.* 42, 825–8 (1963).
25. Swell, L., P. E. Schools, Jr. and C. R. Treadwell, *Am. J. Clinical Nutr.* 11, 102–107 (1962).
26. Bhalerao, V. R., M. Inoue and F. A. Kummerow, *J. Dairy Sci.* 46, 176–80 (1963).
27. Scholfield, C. R., Janina Nowakowska and H. J. Dutton, *JAOCS* 38, 175–177 (1961).
28. Brice, B. A., and Margaret L. Swain, *J. Opt. Soc. Am.* 35, 532–44 (1945).
29. Brice, B. A., Margaret L. Swain, B. B. Schaeffer and W. C. Ault, *Oil & Soap* 22, 219–24 (1945).
30. Brice, B. A., Margaret L. Swain, S. F. Herb, P. L. Nichols, Jr. and R. W. Riemenschneider, *JAOCS* 29, 279–87 (1952).
31. Luddy, F. E., R. A. Barford and R. W. Riemenschneider, *Ibid.* 37, 447–51 (1960).
32. Benedict, J. H., *Ibid.* 37, 415–18 (1960).
33. Metcalf, L. D., and A. A. Schmitz, *Anal. Chem.* 33, 362–64 (1961).
34. Smith, E. D., and A. B. Gosnell, *Ibid.* 34, 438–9 (1962).
35. Kauffman, F. L., T. J. Weiss, G. D. Lee and B. N. Rockwood, *JAOCS* 38, 495–97 (1961).
36. Herb, S. F., P. Magidman and R. W. Riemenschneider, *Ibid.* 37, 127–29 (1960).
37. Craig, B. M., and N. L. Murty, *Ibid.* 36, 549–52 (1959).
38. Crespo, F., *Anales Asoc. Quim. Arg.* 47, 143–7 (1959).
39. Wolf, J. P., *Rev. Franc. Corps Gras* 8, 68–84 (1961).
40. Brimhall, B., and G. F. Sprague, *Cereal Chem.* 28, 227–31 (1951).
41. Hilditch, T. P., "The Chemical Constitution of Natural Fats." 3rd ed., John Wiley and Sons, New York, 1956, p. 444.
42. Kaufmann, H. P., and G. Mankel, *Fette-Seifen Anstrichmittel* 65, 179–84 (1963).