to these ratings. As before, the use of a bar in Table V to bracket several mean values indicates no experimental evidence of a significant difference within the group. Statistical values for whiteness retention are given in Table VI.

TABLE V

Summary of Whiteness Retention Rankings with Four Detergency Test Fabrics as Soil Load

Fabric No. 1		Fabric No. 2		Fabric No. 3		Fabric No. 4	
Detergent	Reflectance	Detergent	Reflectance	Detergent	Reflectance	Detergent	Reflectance
E	87.5	E	87.8 |	E	84.8 |	A	88.2 |
D	86.8 |	D	87.5 |	A	84.2 |	E	88.0 |
C	86.5 |	C	87.2 |	D	82.0	C	87.8 |
A	86.5 |	A	87.0 |	C	77.8	B	87.2 ||
B	85.3	B	85.8	B	74.5	D	87.0 ||
(Yardstick)	(0.7)		(0.9)		(0.8)		(0.6)

TABLE VI

Precision of Whiteness Retention Data

	Standard error of mean	Confidence limits for means
Fabric 1	0.18	$\bar{X} \pm 0.4$
Fabric 2	0.24	$\bar{X} \pm 0.5$
Fabric 3	0.20	$\bar{X} \pm 0.4$
Fabric 4	0.16	$\bar{X} \pm 0.3$

Summary and Conclusions

Four types of artificially-soiled cloths are compared in their ability to evaluate cleaning of representative detergent products. Three of these cloths are commercially available while the fourth is from a private laboratory. These are compared in their ability to rate detergents in the same order as naturally-soiled clothes rate detergents. Sensitivity and reproducibility of the various soiled cloths in measurement of soil removal and whiteness retention are studied.

Results show that artificially-soiled cloths must be used advisedly. There is no substitute for actual performance tests of detergent products under practical conditions. At best, artificially-soiled cloths are useful for "screening" purposes where positive test results are confirmed by practical tests.

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[Received December 29, 1952]

Fractionation of Castor Oil Methyl Esters by Liquid-Liquid Extraction

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METHYLATION of castor oil produces a mixture of methyl esters useful in reactions involving ricinoleic acid. The composition of castor oil, as given by Dean (5), ricinoleic 87.0%, oleic 7.0%, linoleic 3.0%, dihydroxystearic 0.5%, saturated 2.5%, and Bolley (2) shows the nature of this ester mixture. While the methyl esters, other than methyl ricinoleate, do not interfere particularly with the ricinoleic acid reactions, it is nevertheless desirable to remove them so as to have the purest possible starting material.

Since it is well known that compounds are most soluble in solvents which they resemble structurally, it is reasonable to suppose that the hydroxylated compounds, methyl ricinoleate and the methyl ester of dihydroxystearic acid, would be preferentially distributed in the alcohol phase in an alcohol-castor oil methyl ester-hydrocarbon system and that the non-hydroxylated compounds, methyl oleate, etc., would appear chiefly in the hydrocarbon phase.

Consideration of the possibility of separating castor oil methyl esters by liquid-liquid extraction is not entirely new. Cannon (4) discussed the separation of methyl ricinoleate and methyl 12-hydroxystearate in the hydrocarbon (pentane-hexane)-nitroparaffin (20% nitromethane-80% nitroethane) system. Methanol, of all of the alcohols, is the most like water and the least like a hydrocarbon. It is therefore the least soluble of the mono-hydroxy alcohols in hydrocarbons. The castor oil methyl esters are completely soluble in methanol and are produced in this solvent. Methyl alcohol is then preferred over other alcohols as one of the solvents in any liquid-liquid extraction system. There are a great many theoretical possibilities for a hydrocarbon solvent in such a system, but availability, ease of removal from castor oil methyl esters, and cost make pentane, hexane, and heptane the three practical solvents. Preliminary experiments showed that these three solvents were about equal in solubility in methanol and in selectivity for the non-hydroxylated methyl esters. Since this was the case, heptane was selected as the hydrocarbon solvent. It is being used for the extraction of castor oil from the press cake, and its use in fractionation would not involve handling a new solvent in the plant.

The first experimental work in this investigation was the determination of the solubility relations in the system methanol-castor oil methyl esters-heptane.

It is recognized that castor oil methyl esters are not a single component and hence that this is not truly a three-component system. It is however convenient to consider this system as one of three components, and, as this study will show, it is useful to do so.

The equilibrium solubility data were obtained as described by Treybal (13) and Othmer (11) for 8.4°C. and 24°C. and are given in Figure 1. These data show that the system is the Type 1 discussed by Treybal (14). The two-phase region is not large in the temperature range studied, and so it is preferable to present the data on a right triangle following Brown (3) instead of on the usual equilateral triangle. Since the greatest concentration of castor oil methyl esters plotted was less than 16 weight %, the homogeneous region representing higher ester compositions was omitted so that the part of the diagram which is pertinent to this study might be enlarged. The hypoteneuse of the triangle, representing mixtures of methanol and castor oil methyl esters, therefore appears as a line from 100 weight % methanol to 84 weight % methanol, 16 weight % castor oil methyl esters on the right side of Figure 1. The solubility data were complete for methanol-esters-heptane at 24° C.; it was incomplete for methanol-esters-heptane at 8.4°C. above 11 weight % castor oil methyl esters. The upper part of the curve for the lower temperature is therefore shown as a dotted line.

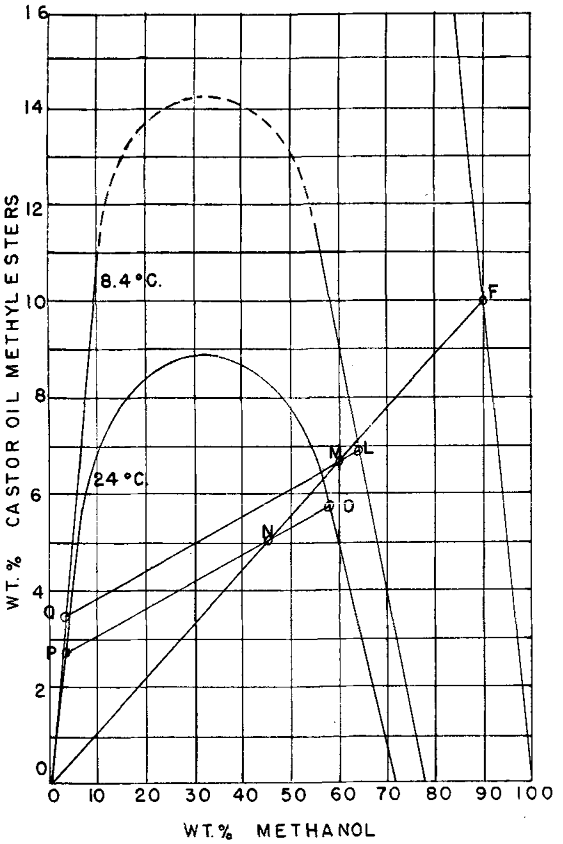

FIG. 1

The next experimental work was a determination of the distribution of castor oil methyl esters between methanol-heptane and heptane methanol. This was done in the usual manner (15). The ester composition of the equilibrium layers was determined by evaporation of most of the solvent from a weighed sample of the layer, followed by sparging with carbon dioxide at 110°C. to constant weight. The resulting data are presented in Table I and in Figure 2.

TABLE I

Distribution of Castor Oil Methyl Esters Between Methanol and Heptane

Temp., °C.	Esters in methanol phase, %	Esters in heptane phase, %	Optical activity of esters in methanol phase	Optical activity of esters in heptane phase
1.4	14.8	9.0	6.33[a]	2.33[a]
8.4	5.7	2.6	5.74[b]	......
8.4	8.0	3.8	......	......
8.4	10.5	5.0	5.04[b]	......
8.4	13.5	9.2	4.69[b]	......
24.0	2.7	1.4	......	......
24.0	6.5	3.0	......	......
24.0	8.6	3.8	......	......

[a] Specific rotation determined in methanol; [b] determined in acetone.

The equilibrium tie-lines are presented as a selectivity diagram (16) rather than as lines in Figure 1 so as not to make the solubility curves confusing. Figure 1 and Figure 2 are used together to read the composition of the equilibrium layers in this system. A 45-degree line is drawn in Figure 2 to show that the castor oil methyl esters are preferentially distributed in the methanol phase. This line represents equal distribution between the two phases. There was so little change in selectivity with respect to temperature that only one curve, applying to all the determinations given in Table I, is shown in Figure 2.

The following examples illustrate some of the extraction calculations which can be made with Figures 1 and 2. Elgin and Wynkoop (6) explain these calculations in detail.

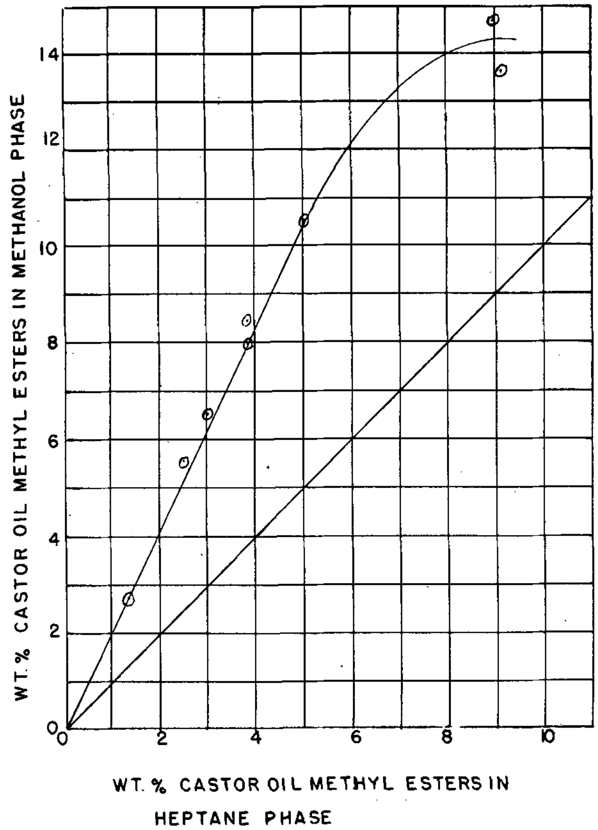

FIG. 2. Selectivity diagram.

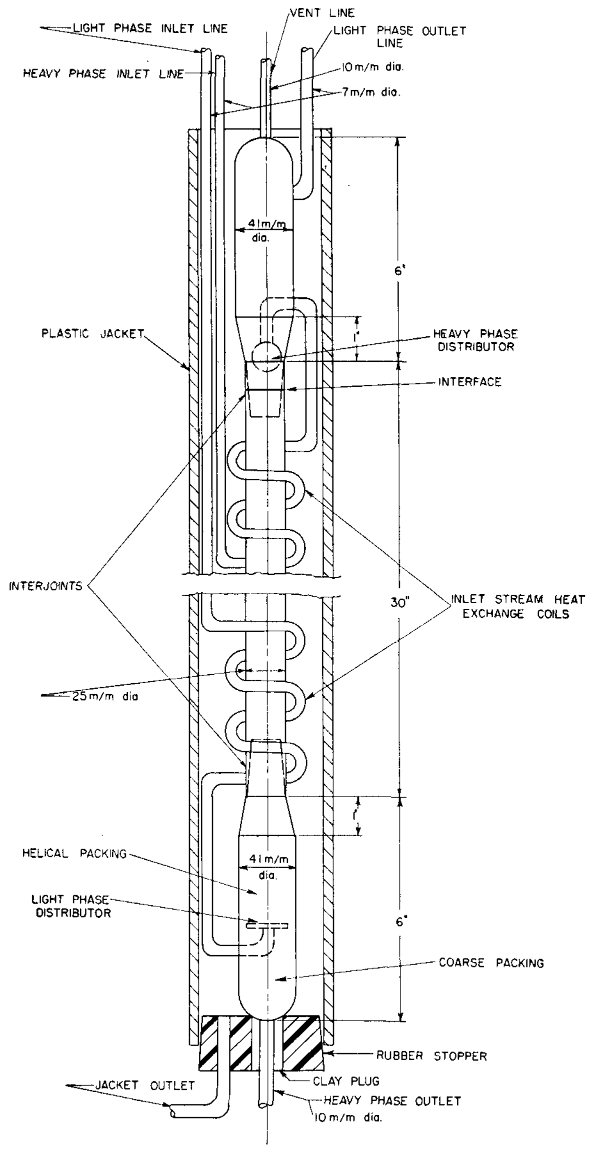

FIG. 3. Extraction column.

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1. What result would be expected on extracting 100 lb. of a mixture of 10% castor oil methyl esters, 90% methanol, with 50 lb. of heptane at 24°C.?

   The feed mixture is represented by point F in Figure 1. It is mixed with heptane so that the resulting mixture, M, lies on the line FM extended to 0% methanol, 0% castor oil methyl esters (100% heptane). The length of this line represents 150 lb. of feed-solvent mixture, and M divides it so that FM equals one-third of its total length. Since the point M lies outside the two-phase region for this temperature, the resulting feed-solvent mixture is a homogeneous solution and there can be no extraction.

   Suppose however that the extraction temperature is changed to 8.4°C., M is the two-phase region for this temperature, and the mixture represented by M will separate into the layers Q and L. Q and L are the intersections of the tie-line, Figure 2, passing through M with the solubility curve, Figure 1. The percentage of castor oil methyl esters in Q is 3.5 and in L, 6.9. From material balances (or from the properties of triangular diagrams) L is calculated to be 140 lb. and Q, 10 lb. Q, the heptane phase, contains 0.35 lb. castor oil methyl esters, or 3.5% of the ester feed. L, the methanol phase, contains 9.65 lb. castor oil methyl esters, or 96.5% of the ester feed.

2. What result would be expected on extracting 100 lb. of a mixture of 10% castor oil methyl esters, 90% methanol, with 100 lb. of heptane at 24°C.?

   F is the same as in example 1. N, the composition of the 200 lb. of feed-solvent mixture, divides the feed-solvent line in equal segments. N lies within the two-phase region and separates into the layers O and P. The compositions of O and P were selected from Figure 2 (5.8% castor oil methyl esters in the methanol phase, 2.8% esters in the heptane phase) so that OP passes through N. As before, example 1, O is calculated to be 146.6 lb. and P, 53.4 lb. The heptane phase, P, contains 1.5 lb. esters, and the methanol phase, O, contains 8.5 lb. This amounts to separating the ester feed into 85% of a methyl ricinoleate fraction and 15% of a residue fraction.

Methyl ricinoleate (as well as methyl dihydroxy stearate) is optically active while the other castor oil methyl esters are not. The change in optical activity from that of the original esters to that of the esters in the methanol layer, or to that of the esters in the heptane layer, was a measure of the distribution of the optically active constituents between the two phases. Table 1 shows that the optical activity of the esters in the methanol phase was usually greater than that of the original esters while that of the esters in the hydrocarbon phase was less. The optical activity reported in this table is the specific rotation determined, using the sodium line. The optical activity of the original castor oil methyl esters was 4.68, with the esters dissolved in acetone.

This experimental work showed that fractionation of the esters should be possible and that more concentrated solutions could be produced by operating at lower than room temperature, also established the concentration and temperature range in which separations were possible.

Liquid-Extraction Apparatus

A small glass liquid extraction column as shown in Figure 3 was set up with the required auxiliary equipment (Figure 4). The end-design of this column was that developed by Blanding (1) and Elgin (7)

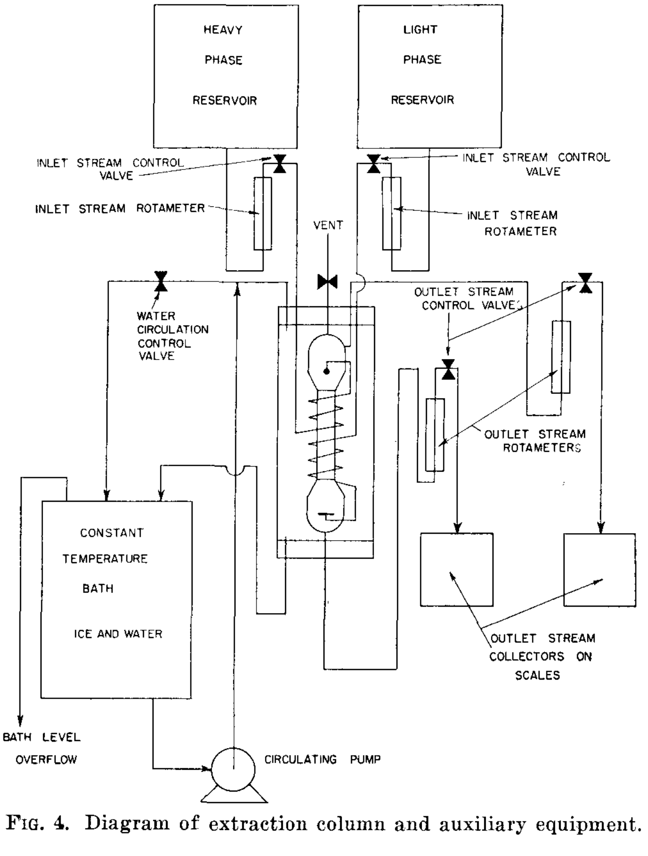

FIG. 4. Diagram of extraction column and auxiliary equipment.

TABLE II

Countercurrent Fractionation of Castor Oil Methyl Esters

Feed composition, % ester	9.9	10.0	10.1	10.3	10.0	2.9	7.2	7.4
Temp., °C.	6	6	6	6	6	3	3	3
Solvent-feed ratio, lb./lb.	1.03	0.96	1.21	1.16	0.70	0.52	0.49	0.55
Flow rate, lb. per hour								
Feed	1.56	1.65	2.18	2.25	1.20	2.76	2.48	1.94
Solvent	1.49	1.72	1.81	1.93	1.70	1.40	1.20	1.07
Composition, % ester								
Outlet methanol phase	6.6	6.5	6.6	7.7	7.6	2.1	5.3	5.6
Outlet heptane phase	3.5	3.6	3.6	3.6	4.0	1.4	3.5	2.4
Methyl ricinoleate fraction								
Yield, % of feed	61	63	62	62	74	80	82	84
Hydroxyl value	207	209	206	203	204	193	204	194
Optical activity	6.0	5.6	5.8	6.1	5.7	6.3	5.8	5.9
Residue fraction								
Yield, % of feed	39	37	40	38	26	20	18	16
Hydroxyl value	142	136	146	142	134	71	99	89
Optical activity	3.8	4.5	4.9	4.7	4.5	......	4.4	......

and used by Johnson (8) and Kylander (9). The distributor for the light phase (heptane) was a Pyrex No. 3935 Immersion Tube with a 30-mm. diameter fritted disc, medium porosity. The lower enlarged section, heavy phase separation section, was packed with ¾ in. long sections of 10 mm. O. D. glass tubing to the level of the fritted disc. The column was packed above this to the upper ground joint with ⅛ in. I. D. glass helices. The entire unit was jacketed with a 3⅛ in. I. D. Plexiglas tube. The inlet steams were led into the column through glass coils around the column and within the jacket so that material entered the column at constant temperature. The jacket was connected through insulated copper lines to an insulated 35-gal. reservoir and a circulating pump. This reservoir was maintained at the constant temperature of an ice and water mixture. The temperature of the inlet water to the jacket was 1.1°C. and of the exit water from the jacket, 4.7°C. The operating temperature was taken as 3°C.

The extraction column was evaluated in terms of theoretical stages by the method of Varteressian and Fenske, described by Treybal (17), and used by Schiebel (12) and Mayfield (10). The column contained an average of four theoretical stages using the system water-acetic acid-isopropyl ether, extracting acid from 10.3% water-acid and from 23.5% water-acid at 3°C. and 24°C.

Countercurrent Fractionation of Castor Oil Methyl Esters

Castor oil methyl esters were fed to the extraction column dissolved in methanol saturated with heptane at 3°C. and extracted with heptane similarly saturated with methanol. Methanol-heptane and heptane-methanol were used to reduce the phase-volume changes which occur in a column using methanol and heptane and to avoid the necessity of fractionation of methanol-heptane mixtures in solvent recovery.

The flow rates were controlled by reference to the inlet stream rotameters, the outlet flows were checked by reading the outlet stream rotameters. The interface between the two phases in the column was maintained at a fixed position just below the heavy phase inlet by controlling the heavy phase outflow. The outflow streams were collected in tared bottles on scales. Samples of all oil containing streams were analyzed by evaporation of solvent to constant weight at 105°C. The ester fractions were prepared from the column outlet phases by distillation of solvent, followed by removal of traces of solvent by passing a stream of CO_2 through the oil heated to 110°C. These fractions were evaluated in terms of hydroxyl value and optical activity with the results in Table II.

The figures for hydroxyl value and optical activity in this table are compared with the hydroxyl value of 178 and optical activity of 5.5 for the mixed castor oil methyl esters and the hydroxyl value of 185 and optical activity of 5.8 for methyl ricinoleate.

The optical activities given in this table are specific rotations determined on the undiluted ester fraction indicated, using the mercury line.

The solvent distilled passed from the still condenser through a jacketed phase separator with the jacket filled with ice and water so as to produce methanol-heptane and heptane-methanol at essentially the extraction temperature.

Summary and Conclusions

A solubility diagram has been constructed for methanol-castor oil methyl esters-heptane at 8.4°C. and 24°C.

A selectivity diagram has been prepared for methanol-castor oil methyl esters-heptane at 8.4°C. and 24°C.

Castor oil methyl esters have been fractionated by continuous countercurrent liquid-liquid extraction at 3°C. and at 6°C. with methanol-heptane and heptane-methanol as solvents, using an extraction column containing four equilibrium stages. The methyl ricinoleate fraction produced compared favorably with pure methyl ricinoleate with respect to hydroxyl value and optical activity. It should be noted that there were undoubtedly some mono- and diglycerides in the castor oil methyl esters used in this study. These go along with the methyl ricinoleate and cause discrepancies between hydroxyl value and optical activity (2).

The column feeds ranged from 2.9 to 10.3% methyl esters by weight in methanol-heptane. Solvent-feed ratios were from 0.49 to 1.21 lb. per pound. The flow rates were from 706 to 1,020 lb. per hour per square foot of column cross section (based on the cross section of the empty column).

Acknowledgment

This work was sponsored by the Baker Castor Oil Company at the University of Detroit. The samples were evaluated by the Baker Castor Oil Research Laboratories. Appreciation is hereby expressed to the Baker Castor Oil Company for permission to publish the results and to A. J. Paquette for preparing the drawings.

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[Received January 21, 1954]

Distribution of Fatty Acids in Corn Oil[1,2]

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IT 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	Refractive 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[b]
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

[a] 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%. Although the correlation is highly significant, there appears to be sufficient variability in degree of unsaturation among

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[1] Contribution from the Departments of Biochemistry and Botany and Plant Pathology, Purdue University Agricultural Experiment Station and the Division of Cereal Crops and Diseases, Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, U.S.D.A., cooperating.

[2] Journal Paper No. 641 of the Purdue University Agricultural Experiment Station, Lafayette, Ind.

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