

WHEAT GERM OIL

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IN view of the use of wheat-germ oil in certain types of nutritional experiments, and the number of inquiries received concerning this product, it became desirable to make a study of the oil more comprehensive than that previously undertaken.

The oil content of the entire wheat kernel is about two per cent. The distribution of the oil in the kernel has been determined by Jacobs and Rask (*J. Ind. Eng. Chem.* 12, 899, 1920) with the following results: The germ contains 12.5 per cent of oil, the bran, 5.6 per cent, and the endosperm 0.75 per cent. Patent flour, therefore, should contain 0.75 per cent of oil, but it usually contains about one per cent, owing to the impossibility of completely separating those parts rich in oil.

Lewkowitsch [*Chemical Technology and Analysis of Oils, Fats and Waxes*, 6th Edition, 2, p. 180 (MacMillan & Company, 1922)] states that the oil content of the germ ranges from 12.5 to 17.5 per cent.

In the literature the oil from the germ has been designated as "wheat oil" and that from the flour as "wheat meal" or "wheat flour oil."

Both the wheat germ and flour oils have been the subjects of investigation at various times during the past seventy years, but the wheat bran oil has received less attention. C. D. Ball, Jr. (*Cereal Chem.* 3, 19, 1926) gives a summary of the investigations made on wheat oils between the years 1861 and 1924 inclusive.

The oils extracted from different parts of the wheat kernel are not identical. Wheat germ oil gives higher iodine numbers and saponification values than does wheat flour oil, and it contains larger quantities of unsaponifiable constituents. It also has a notably lower density than that of the flour oil.

The earlier workers apparently were interested chiefly in the lecithins and sterols of the germ oil. Consequently they determined but few of the characteristics. The quantity of lecithin was calculated by them from the phosphorus content of the oil but, of course, such a calculation would include any cephalins or other phosphatides, along with any other substances containing phosphorus that may be in the unrefined oil. The results obtained by these investigators regarding the character of the sterol fraction need not be given any consideration because later studies have definitely shown that this fraction, in the case of wheat and other fatty oils, consists of mixtures of unsaturated and saturated sterols. Those interested in the sterols from wheat should consult the following: Anderson and Nabenhauer, *J. Am. Chem. Soc.* 46, 1717, 1924 and 2113 (1924); Anderson, Shriner, and Burr *ibid.* 48, 2987 (1926). These investigators found that the sterols from wheat germ consist of a mixture that contains three isomeric sterols designated as alpha, beta and gamma sistosterol and the saturated di-hydrosistosterol.

Formerly it was believed that wheat germ oil had poor keeping qualities. Negri, for example (*Chem. Zeit.* 22, 976, 1898), reported that a sample of the oil which at first contained 5.65 per cent of free fatty acids after a year's storage had 43.8 per cent. Later investigators have found that, contrary to former reports, the oil has excellent keeping qualities as shown by the slight increase in the quantity of free fatty acids, even when the oil is held from one to three years after its extraction. We have found that wheat germ oil has good keeping qualities.

Power and Salway (*Pharm. J.* 91, 117, 1913) concluded from their investigation that the sat-

urated fraction of the fatty acids from wheat germ oil consists of approximately equal proportions of palmitic and stearic acids, and that the unsaturated fraction is chiefly linolic acid. Ball (loc. cit.) by means of the lead-salt-ether procedure found 15.3 per cent of saturated acids in the oil. From the unsaturated acid fraction he obtained by bromination in ether solution a hexabromide precipitate which was not pure, as shown by the melting point of 162° (the hexabromide of linolenic acid, when pure, melts at 180-1°). He attributed this low melting point to the presence of linolic acid tetrabromide (M. P. 113-114°). However, he believed that the oil contained some linolenic acid.

During the examination of the literature, it was found that the analysis of wheat germ oil, giving the percentages of the various fatty acids as glycerides, in Grün and Halden's "Analyse der Fette und Wachse," Band. 2, p. 27 (Julius Springer, Berlin, 1929), is an analysis of corn oil (J. Am. Chem. Soc. 43, 2696, 1922).

About a year ago this laboratory received from the Protein and Nutrition Division of this Bureau a sample of wheat germ oil which had been extracted with ether from an unusually fine sample of wheat germ in connection with the preparation of the material for a study of the proteins. After the removal of the solvent the oil remained in the form of amber-colored, limpid liquid. The more important chemical and physical characteristics of the oil which were determined are given in the following table:

TABLE I
Chemical and Physical Characteristics
of Wheat Germ Oil

Specific gravity 25°/25°.....	0.9268
Refractive index, 20°.....	1.4762
Acid value	7.6
Saponification value	186.5
Iodine number (Hanus).....	125.6
Thiocyanogen value	79.7
Hexabromide number	trace
Acetyl value	9.9
Reichert-Meissl value	0.2
Polenske number	0.35
Unsaponifiable matter (0/0).....	4.7
Iodine number of unsaponifiable matter	97.3

Thiocyanogen value of unsaponifiable matter	62.0
Saturated acids (corrected) 0/0....	13.3
Unsaturated acids (corrected) 0/0..	75.3
Iodine number of unsaturated acids.	160.7

The thiocyanogen numbers reported in Table I were determined by the Kaufmann method (Kaufmann and Keller, Z. Angew. Chem. 42, 20 and 73, 1929). The hexabromide method used was that of Steele and Washburn (Ind. Eng. Chem. 12, 52, 1920). Only a trace of linolenic acid hexabromide was obtained. The percentages of saturated and unsaturated acids were determined by the lead-salt-ether method. The percentage of saturated acids has been corrected for the small quantity of unsaturated acids that remain with this fraction, and this is added to the unsaturated acid fraction, after a correction has been made for the unsaponifiable matter. Through the use of the digitonin method, it was found that the unsaponifiable portion of the oil contained 73.5 per cent of sterols.

Unsaturated Acids

The percentages of oleic, linolic and linolenic acids in this sample of wheat germ oil were calculated from the iodine number and the thiocyanogen values of the oil. These results are given in Table II. As only a trace of ether insoluble hexabromide was separated it appears that most of the linolenic acid is of that form or forms which give ether-soluble hexabromides. In other kinds of oils examined the so-called alpha-linolenic acid, which gives the ether-insoluble hexabromide, has predominated over the other isomers.

TABLE II
Unsaturated Acids of Wheat Germ Oil

	Acids in Original Oil Per cent	Acids as Glycerides in Original Oil Per cent
Oleic acid	26.6	27.8
Linolic acid.....	39.1	40.9
Linolenic acid.....	9.6	10.0
	75.3	78.7

Saturated Acids

The saturated acids were separated from the oil (after saponification with alkali) in the usual manner by means of the lead-salt-ether method,

then esterified with absolute methyl alcohol with the aid of dry gaseous hydrogen chloride. The mixture of methyl esters, which amounted to 91 grams, was fractionally distilled under reduced pressure. A preliminary distillation from a 500-cc. Claissen flask gave five fractions and a

with alcoholic potash, and subjected to fractional crystallization from alcohol. The crystallized fatty acids were finally identified by their melting points and by observing whether or not they remained constant after being mixed with equal quantities of the respective acids, the

TABLE III
Saturated Acids of Wheat Germ Oil

Acids	Amount		Acids in	Glycerides in
	Grams	Per cent	Original Oil	Original Oil
Palmitic	76.6932	91.35	12.15	12.8
Stearic	5.2875	6.30	0.84	0.9
Lignoceric	1.9719	2.35	0.31	0.3
	83.9526	100.00	13.30	14.0

small undistilled residue. These, in the order collected, were subjected to refractionation from a 150-cc. Ladenburg fractionation distilling flask. After the six fractions were weighed, the iodine and saponification values were determined. With these results it was possible to make corrections for the presence of small quantities of esters of unsaturated acids and to calculate the mean molecular weight of the saturated acids in each fraction (cf. J. Am. Chem. Soc. 42, 152 and 1197, 1920). The mean molecular weights indicate in a measure what acids are present. In order to check the conclusions drawn from these data, the free fatty acids were recovered from the ester fractions, after saponification

purity of which had previously been determined by elementary analysis. In each case no change in the melting was observed, which confirmed the conclusions previously drawn from the mean molecular weights of the acids in each ester fraction. In various fractions, palmitic, stearic, and lignoceric acids were found; the last-mentioned acid being in fraction 6 and the small undistilled residue. The quantity of the saturated acid or acids in each ester fraction was calculated from the analytical data obtained, and the final results for the saturated acids in the oil are given in Table III.

The results of the investigation on wheat germ oil are summarized in Table IV.

TABLE IV
Composition of Wheat Germ Oil

	Per cent
(Linolenic acid.....)	10.0
(Linolic acid.....)	40.9
Glycerides of (Oleic acid.....)	27.8
(Palmitic acid.....)	12.8
(Stearic acid.....)	0.9
(Lignoceric acid.....)	0.3
Unsaponifiable matter	4.7