

The Composition of California Walnut Oil

Contribution from Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, Department of Agriculture

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THE manufacture of walnut oil is one of the minor industries of California which utilizes the broken and imperfect kernels of the walnut, *Juglans regia*, separated at the shelling plants. The average oil content of this material is about fifty percent. The oil is obtained by expression and the press cake in mixture with other materials is used for feeding cattle and poultry. At the present time the annual production of oil is about two hundred and fifty tons but in view of the increasing acreage of walnut trees which are beginning to bear it is estimated that the production of oil within five years will be doubled.

The crude walnut oil produced in California is largely used in making soap, but some is used in the manufacture of paints, particularly of the enamel type for which it appears to be well adapted. When refined the oil is suitable for edible purposes.

Walnut oil is a good drying oil and paint films containing it are less liable to crack than those of linseed oil paints. It has been used for centuries in Europe as a paint oil, especially in the preparation of artists' colors.

For the present investigation, a gallon of the crude oil was received at our request from the Pacific Nut Company of Los Angeles, California. The sample was clear and had a deep yellow color when observed in a 6-oz. sample bottle.

The chemical and physical characteristics are given in Table I. The high iodine value of this oil should be observed. Bolton (Oils, Fats, and Fatty Foods, 1928, p. 182) gives the usual limits by the Wijs method as 138 to 148. H. A. Gardner (Pt. and Var. Mfrs.' Assoc. Circ. 189) in 1923 examined a sample of California walnut oil which gave an iodine number of 154.1 by the Hanus method. This result, together with ours, would indicate that the California oil is characterized by having an iodine number much higher than that commonly reported for the European oil. The percentages of saturated and unsaturated acids were determined by the lead-salt-ether method, and corrections were made for the small quantity of unsaturated acids that is precipitated and weighed with the saturated acid fraction ** (J.

Amer. Chem. Soc. 1920, 42, 2398. Cotton Oil Press 1922, 6, 41). The percentage of unsaturated acids has also been corrected for the unsaponifiable matter that remains with the unsaturated acid fraction.

TABLE I
WALNUT OIL

Chemical and Physical Characteristics	
Specific gravity 25/25°.....	.9235
Refractive index at 25°.....	1.4751
Acid Value	5.11
Iodine number (Hanus).....	158.5
Iodine number (Wijs).....	161.7
Saponification Value	194.5
Acetyl Value	6.09
Reichert-Meißl value	0.11
Polenske No.	0.19
Hexabromide	8.88
Unsaponifiable matter51
Saturated Acids (corrected) %.....	5.34
Unsaturated Acid (corrected) %.....	89.74
Iodine number of Unsat. acids.....	156.7

Unsaturated Acids.—The linolenic acid was separated and weighed as hexabromide according to the Washburn and Steele procedure ** (Ind. Eng. Chem. 1920, 12, 521). The average of two determinations in close agreement was 8.88 percent of hexabromide, which is equivalent to 3.08 percent of linolenic acid in the original oil. After the percentage of linolenic acid has been determined it is possible to calculate the percentages of oleic and linolic acids from the iodine number of the unsaturated fraction, 166.7 and the theoretical iodine number of the three acids; 274.1 for linolenic acid, 181.4 for linolic acid, and 90.1 for oleic acid. In this way the percentage composition of the unsaturated acids tabulated below was calculated.

	Unsaturated Acid Fraction %	Unsaturated Acids in Oil %	Glycerides of Unsaturated Acids %
Linolenic Acid	3.44	3.08	3.2
Linolic Acid	11.74	69.75	72.8
Oleic Acid	18.82	16.91	17.6
	100.00	89.74	93.6

Saturated Acids.—The saturated acids which were separated from the oil by the lead-salt-ether method were esterified with absolute methyl alcohol (J. Amer. Chem. Soc. 1920, 42, 1200), and the resulting esters were fraction-

ally distilled under diminished pressure. The data for the distillation are given in Table II. The preliminary distillation was made from a 500 cc. Claissen flask, which divided the mixture of esters into four fractions and a residue. These were redistilled from a 150 cc. Ladenburg flask according to the manner indicated in the table. Six final fractions and a small residue were obtained.

TABLE II
WALNUT OIL
Fractional Distillation of Methyl Esters of Saturated Acids.
(88.65 g. subjected to distillation)

	Fraction	Temperature °C	Wt. Grs.
Preliminary distillation under 3mm. pressure.	A	171-3	18.7
	B	174-5	21.7
	C	176-8	23.1
	D	185-195	21.0
	Residue		4.0
Final distillation under 2 mm. pressure. Fractions A and B added	1	164-6	8.50
	2	167-171	24.25
	3	172	23.70
	4	172-5	19.43
	5	175-180	7.80
	6	184-194	4.60
	Residue		.22

The iodine numbers and the saponification values of these six final fractions were determined and are recorded in Table III. The small final residue was saponified with alcoholic potash, and the fatty acids were liberated with hydrochloric acid, collected, dried, and crystallized from 10 cc. of alcohol. The crystalline fatty acid (.150 g.), which melted at 74 to 75°, was recrystallized. Then it melted at 77°. Another recrystallization did not change the melting point. Equal quantities of this acid and arachidic acid of known purity were mixed, and the melting point of the mixture was 77°. No other acid could be isolated from the residue. The iodine numbers of the various fractions are the measures of the contaminating unsaturated acids, and from these values the percentage of unsaturated acid esters were calculated. From these percentages and the saponification values the mean molecular weights of the saturated acid esters in the different frac-

tions were calculated. The mean molecular weights indicate what saturated acids may be present in each fraction. For example, the mean molecular weight of the saturated acids esters in fraction 1 (column 5, Table 3) is between methyl myristate (242.3) and methyl palmitate (270.3) and indicates that this fraction contains both of these esters. The result for fraction 2 indicates that it contains only methyl palmitate, whereas the results for fractions 3, 4, 5 and 6 suggest that they contain various proportions of methyl palmitate and stearate (298.4).

In order to test the correctness of these deductions, the free fatty acids were recovered from several of the fractions by saponifying with alcoholic potash, removing the alcohol, dissolving the soaps in water and decomposing them with hydrochloric acid. The constituent saturated acids entirely freed from mineral acid were isolated by fractional crystallization from ethyl alcohol. Their identity was established by determining the melting points and by observing whether or not they were lowered when the substances were mixed with equal quantities of the respective acids which they were suspected of being, the purity of which had been established by analysis.

The deductions drawn from the mean molecular weights were confirmed as follows: Arachidic acid, $C_{20}H_{40}O_2$, melting at 77° was isolated from the residue; Stearic acid, $C_{18}H_{36}O_2$, melting at 69 to 70° was obtained from fractions 5 and 6; Palmitic acid, melting at 63° was obtained from fractions 1, 2 and 3. Twelve crops of crystals were obtained from the alcoholic solution of fraction 1 by gradually reducing the volume of alcohol and finally adding small quantities of water. The melting point of the final very small crop of crystals was about 55°, indicating that it was myristic acid, $C_{14}H_{28}O_2$, which melts at 54 to 55°.

The quantities of saturated acids in the fractions were calculated from the mean molecular weight of their esters and the theoretical molecular weights of the two esters in each fraction. The results are given in Table III:

TABLE III
Results of Analyses of Fractions from Distillation of the Methyl Esters.

Fractions	Iodine Nos.	Sapon. Values	Esters of Unsat. Acids	Mean Molec. Wt. of Esters of Sat. Acids	Myristic Acid		Palmitic A.		Stearic Acid		Arachidic Acid-G
					%	G	%	G	%	G	
1	3.1	207.7	1.94	269.7	2.01	.171	90.99	7.734			
2	4.6	206.3	2.85	270.3			94.61	22.431			
3	8.6	204.3	5.26	273.2			84.96	19.536	7.43	1.763	
4	11.1	200.1	6.64	279.3			60.12	11.682	28.44	5.526	
5	26.1	197.3	14.21	282.6			45.68	3.563	35.75	2.788	
6	27.8	189.0	15.13	297.2			3.44	.158	77.41	3.561	
Residue											.150
							.171	65.104	13.638		.150

TABLE IV
Walnut Oil
Saturated Acids
Acids in Sat.
Acid Fraction

Acids	Grams	Per Cent	Acids in Oil Per Cent	Glycerides in Oil Per Cent
Myristic	0.171	.22	.01	trace
Palmitic	65.104	82.34	4.40	4.60
Stearic	13.638	17.25	.92	.95
Arachidic (Residue)150	.19	.01	trace
		100.00	5.34	5.56

In Table IV the percentage composition of the saturated acids is given in column 2. These values have been calculated to the basis of the original oil and are given in column 3. Column 4 gives the equivalent percentages of glycerides.

Summary

The chemical and physical characteristics of a sample of oil expressed from California walnuts have been determined. With the exception of the iodine number, the characteristics are similar to those reported for European walnut oil. The unusually high iodine number (161.7) of this sample of oil is noteworthy; the usual limits by the Wijs method are given as 138 to 148. This oil was found to contain 89.7 per cent of unsaturated and 5.3 of satu-

rated acids. Contrary to the repeated statements in the literature, walnut oil does not contain lauric acid and only a trace of myristic acid, which is in accordance with the saponification value (192 to 197) of the oil. The percentages of the fatty acids as glycerides are given below:

The composition of this oil has been determined, with the following results:

Glycerides of:	Per cent
Oleic acid	17.6
Linolic acid	72.8
Linolenic acid	3.2
Myristic acid	trace
Palmitic acid	4.6
Stearic acid9
Arachidic acid	trace
Unsaponifiable matter5

Mayonnaise Standard Interpreted

In reply to a letter addressed to the United States Department of Agriculture by Mr. Frank Honicker, Executive Secretary of the Mayonnaise Products Manufacturers' Association, the Assistant Chief of the Food, Drug and Insecticide Administration has given an interpretation of the mayonnaise standard and definition recently published by the Department. The letter as received by Mr. Honicker follows:

UNITED STATES DEPT. OF AGRICULTURE
FOOD, DRUG AND INSECTICIDE ADMINISTRATION
Washington, D. C.

January 22, 1929.

Mr. Frank Honicker,
Executive Secretary,
Mayonnaise Products Mfrs. Assn. of America,
505 Bulletin Building,
Philadelphia, Penna.

Dear Sir:

This will acknowledge receipt of your letter of January 7 in which you submit certain inquiries on behalf of your association with reference to the definition and standard for mayonnaise. You inquire what is meant by the term "semi-solid."

The term "semi-solid" may be given its ordinary, or dictionary, meaning, e.g., half solid, part solid, partially solid, almost solid, or incompletely solid, so viscous as to be nearly solid. Obviously, it is not possible to fix hard

and fast limits for the variations in consistency or firmness of emulsions which a consumer is entitled to expect in a product sold as mayonnaise.

Mayonnaise should have a consistency such that it will not flow readily from a bottle and that it will retain its shape to a degree when removed from the package and for a time sufficiently long to admit of its use for the purpose to which this type of salad dressing is commonly applied.

The definition has been adopted and was published in the form of a press notice on November 15, 1928. It contains no provisions for the use of fillers or so-called stabilizers. Substances, such as starch, may be added to mayonnaise, provided they are wholesome food products and their use does not conceal damage or inferiority, and, provided further, the principal label carries a plain and conspicuous declaration of the presence of the added substance printed in connection with the name of the product. Products which fail to meet the requirements of the standard should not be sold as mayonnaise.

The definition and standard became effective upon its publication and no date has been specified after which it will be put in force. Manufacturers are expected to conform to its requirements as promptly as possible.

Very truly yours,

(Signed) P. B. DUNBAR,
Assistant Chief.