ORIGINAL CONTRIBUTIONS

THE CHEMICAL COMPOSITION OF CALIFORNIA OLIVE OIL

By George S. Jamieson and Walter F. Baughman

Hazura and Grüssner[1] report that the unsaturated acids of olive oil consist of approximately 93% oleic acid and 7% linolic acid. Hehner and Mitchell[2] were unable to detect stearic acid in the saturated acid portion. Holde,[3] while endeavoring to resolve the saturated acids into their components, obtained a small quantity of an acid with a molecular weight of 368.7 and a melting point of 72–72.8°C. In regard to this Lewkowitsch[4] says, "it is left open to doubt whether this acid is lignoceric acid (m. p. 80.5, mol. weight 368)." It is his opinion that the saturated acids consist of palmitic acid and a minute proportion of arachidic acid.

The oil used in this investigation was expressed in a commercial plant from Mission olives (crop of 1923) grown in Butte County, California. It was washed with water and filtered at the plant. It had a greenish color and a fine flavor.

Chemical and Physical Characteristics.—The more important characteristics of olive oil are recorded in Table I. 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

Table I

Olive Oil

Physical and Chemical Characteristics

Specific gravity $\frac{25°}{25°}$	0.9119
Refractive index 20°	1.4690
Acid value	1.5
Iodine number (Hanus)	85.1
Saponification value	190.6
Unsaponifiable matter (%) (iodine number 170.6)	1.0
Acetyl value	11.2
Saturated acids (determined) (%) (iodine number 7.5)	9.7
Unsaturated acids plus unsaponifiable matter (determined) (%)	85.6
Iodine number of unsaturated acids plus unsaponifiable matter	95.7
Iodine number of unsaturated acids	94.8
Saturated acids (corrected) (%)	8.9
Unsaturated acids (corrected) (%)	85.2

[1] *Monatsh.*, **9**, 944 (1888).

[2] *Analyst*, **21**, 328 (1896).

[3] *Ber.*, **38**, 1250 (1905).

[4] "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan & Co., 6th ed., **2**, 362 (1922).

that contaminated the saturated acid fraction.[5] The percentage of unsaturated acids was also corrected for the unsaponifiable matter, all of which separates with the unsaturated acids fraction. The iodine number of the fraction containing the unsaturated acids and the unsaponifiable matter is 95.7 and the iodine number of the unsaponifiable matter is 170.6. The iodine number of the pure unsaturated acids, therefore, is 94.8.

Unsaturated Acids.—The iodine number of the unsaturated acids fraction (94.8) indicates that it consists of oleic acid (iodine number 90.1) and linolic acid (iodine number 181.4). Using the iodine numbers, the percentages have been calculated as follows:

	%	Original oil %	Glycerides %
Oleic Acid	94.85	80.81	84.4
Linolic Acid	5.15	4.39	4.6
	100.00	85.20	89.0

Saturated Acids.—A quantity of the saturated acids prepared by the lead salt-ether method was esterified with methyl alcohol (*J. Am. Chem. Soc.*, **42**, 1200 (1920)). This mixture of methyl esters was fractionally distilled under diminished pressure. The data for this distillation are given in Table II. A preliminary distillation was made from a 1-liter Claissen flask; seven fractions (A, B, C, D, E, F, G) and a residue were obtained. The preliminary fractions were redistilled from a 250 cc.

TABLE II

FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS

(126.3 g. subjected to distillation)

Distillation at 6 mm. pressure.

	Fraction	Temperature °C.	Weight G.
	A	172	22.95
	B	173	22.39
	C	173–174	22.60
	D	175–178	22.30
	E	179–184	22.72
	F	185–192	10.13
	G	192–203	2.60
	Residue		0.25
Fractions A and B redistilled	1	165–170	4.80
	2	171–172	24.20
Fractions C and D added	3	172–174	23.40
	4	175–178	24.00
Fraction E added	5	179–184	18.80
Fraction F added	6	185–194	21.60
Fraction G added	7	195–205	6.00
Residue added	8	205–215	3.10
	Residue		0.23

[5] *J. Am. Chem. Soc.*, **42**, 2398 (1920); *Cotton Oil Press*, **6**, 1, 41 (1922).

Ladenburg flask according to the manner indicated in the table; eight fractions and a residue were obtained.

The iodine numbers, which are measures of the contaminating unsaturated acids, and the saponification values of Fractions 1 to 8 are given in Columns 2 and 3 of Table III. Using these data, the mean molecular weights of the saturated acid esters in each fraction were calculated as recorded in Column 6 (*J. Am. Chem. Soc.*, **42**, 152, 1197 (1920)).

The results in Column 6 indicate what saturated acids may be present in the fractions. The mean molecular weight of the saturated acid esters in Fraction 1 is slightly less than that of methyl palmitate (270.3) and indicates that this fraction contains principally methyl palmitate and a little methyl myristate. The results for Fractions 2–7 lie between the molecular weights of methyl palmitate and methyl stearate (298.4), which indicates that the fractions contain these esters in various proportions. The probable constituents of Fraction 8 are methyl stearate and methyl arachidate (326.4).

The free mixed acids were recovered from some one of these fractions by saponifying with alcoholic potash and acidifying the soap solution with hydrochloric acid. The constituent acids were then isolated by fractional crystallization from alcohol. Their identity was established by the melting points and by whether or not these melting points were lowered when the substances were mixed with equal quantities of the respective acids which they were suspected of being and the purity of which had been established previously by elementary analysis.

In all cases the melting points of the isolated acids confirmed the deductions drawn from the mean molecular weights of the fractions.

Arachidic acid ($C_{20}H_{40}O_2$), which melted at 77°C., was isolated from Fraction 8. No acid with a higher molecular weight could be detected in this fraction. Stearic acid ($C_{18}H_{36}O_2$), which melted at 69°C., was isolated from Fractions 6 and 7. Palmitic acid ($C_{16}H_{32}O_2$), melting at 63°C., was crystallized from Fraction 1. By reducing the volume of the mother liquor from Fraction 1, several crops of pure palmitic acid crystals were obtained. Finally a very small crop of crystals with a melting point of 56–57°C. was obtained. The crop was too small to recrystallize. It is believed that this crop consisted of palmitic and myristic acids. The melting point of pure myristic acid is 54°C. and the formula is $C_{14}H_{28}O_2$.

This establishes the identity of the saturated acids in the various fractions. The quantities were calculated from the mean molecular weights of the saturated acid esters (Column 6, Table III) and the theoretical molecular weights of the two esters in each fraction. The results are given in Columns 7–14, Table III. The small residue contained only decomposition products.

TABLE III

OLIVE OIL

FRACTIONAL DISTILLATION OF METHYL ESTERS OF SATURATED ACIDS

Fraction	Iodine number	Saponification value	Mean molecular weight	Esters of unsaturated acids %	Mean molecular weight of esters saturated acids of	Myristic Acid %	Myristic Acid G.	Palmitic Acid %	Palmitic Acid G.	Stearic Acid %	Stearic Acid G.	Arachidic Acid %	Arachidic Acid G.
1	2.7	207.7	270.1	2.99	269.3	3.26	0.16	88.70	4.26				
2	3.2	206.2	272.1	3.54	271.3			88.21	21.35	3.27	0.79		
3	5.5	205.7	272.7	6.09	271.3			85.88	20.10	3.18	.74		
4	6.6	204.4	274.5	7.31	272.9			79.76	19.14	8.17	1.96		
5	12.2	196.3	285.8	13.51	283.9			42.32	7.96	39.90	7.50		
6	17.8	193.6	289.8	19.71	287.8			28.72	6.20	47.66	10.30		
7	18.1	188.4	297.8	20.04	297.6			2.16	0.13	74.04	4.44		
8	12.2	178.9	313.6	13.51	316.1					30.33	0.94	52.32	1.62
							0.16		79.14		26.67		1.62

In Table IV the percentage composition of the saturated acids is given in Column 2, the percentages of saturated acids in the original oil in Column 3, and the equivalent percentages of glycerides in Column 4.

TABLE IV

OLIVE OIL

SATURATED ACIDS

Acid	Acids in saturated acid fraction G	Acids in saturated acid fraction %	Acids in original oil %	Glycerides in original oil %
Myristic	0.16	0.15	0.01	trace
Palmitic	79.14	73.56	6.55	6.9
Stearic	26.67	24.79	2.21	2.3
Arachidic	1.62	1.50	0.13	0.1
	107.59	100.00	8.90	9.3

Summary

The chemical composition of olive oil from Mission olives has been determined, with the following results:

	Acid	%
	Oleic	84.4
	Linolic	4.6
	Myristic	trace
Glycerides of	Palmitic	6.9
	Stearic	2.3
	Arachidic	0.1
Unsaponifiable matter		1.0

Stearic acid constituted approximately 25% of the saturated acids. It is believed that the much discussed question regarding the presence or absence of stearic acid in olive oil has been definitely settled by this investigation.

MACADAMIA NUT AND ITS OIL

BY C. A. LATHROP

The Macadamia or Queensland Nut (Macadamia ternifolia F. v. M.) is a native of the coast district of Queensland and the north coast district of New South Wales, Australia, where it is also known as the "Bush Nut" and "Possum Nut." Seeds of this tree were introduced into Hawaii about 1883 and a considerable growth has since been developed, and it is one of the most promising of nuts for commercial cultivation within the tropics and sub-tropics.

The tree is very ornamental, has a dense foliage, attains a height of about 35 feet, and the nuts occur singly or in clusters up to as many as eight. The nuts have leathery husks which often open on the tree; the chocolate colored spherical shell is about 3 mm. thick and very hard