Puerto Rican Fatty Oils

1. The Composition of the Liquid Fraction of Expressed Avocado Pulp Oil*

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The pulp of the avocado pear (*Persea Persea* Cockerell) is very rich in oil. This oil is finding increasing use in cosmetic and pharmaceutical preparations (1).

The only complete investigation on whole avocado oil, so far reported in the literature, is that of Jamieson, Baughman, and Hann (2). The oil examined by these investigators was extracted with ether from the dehydrated pulp of the Fuertes variety of avocado, cultivated in California. They reported the range of the characteristic constants as well as composition of the oil, finding tangible amounts of glycerides of oleic, linoleic, palmitic, and stearic acids, but only traces of myristic and arachidic. Other than the work of these investigators, the data on avocado oil, found in the literature, is all very fragmentary, consisting principally of reports of the characteristics of the oil and of its vitamin content (1, 3, 4, 5, 6).

The present work was undertaken to supply information relative to the liquid fraction obtained from Puerto Rican avocado oil. The sample of oil investigated was kindly supplied to us by the Division of Investigation and Industrial Development of the Department of Agriculture of Puerto Rico. The oil was expressed by them from ripe and over-ripe fruits belonging to the wild variety of avocados, locally sold for edible purposes, and was nearly a year old at the time we started our investigation. Each fruit averaged 0.5 pound in weight and was made up of 60 per cent pulp, 31 per cent seed, and 9 per cent rind. The yield of oil per fruit averaged 6 per cent and the yield of oil per weight of wet pulp was 10 per cent. The whole oil was partly refined with NaOH and Darco, which removed some of its original deep green color. The product obtained had a light yellow-green color.

It was observed that, on standing, a solid, white, fat-like substance separated out of this oil. This substance, which amounted to nearly 8 per cent by weight of the original whole oil, was completely removed by successively freezing the oil and filtering off the solid deposit. This substance remained solid at room temperature, 28°C. The composition of this solid, fat-like substance will be the subject of a separate communication.

Experimental

Characteristics of the liquid fraction of avocado pulp oil. By using the methods of analysis of the Association of Official Agricultural Chemists (7), unless otherwise indicated, the following characteristics of the oil were determined, as shown in Table I.

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Unsaturated acids. The unsaturated acids were separated from the saturated acids by the lead salt ether method. These acids were in turn brominated at a temperature of —10°C. Twenty-two and nine-tenths (22.9) gms. of unsaturated acids yielded 0.05 gms. of linolenic acid hexabromide (insoluble in diethyl-ether, observed m.p. 177°; reported m.p. 180-182°); 2.10 gms. of linoleic acid tetrabromide (insoluble in petroleum ether, observed m.p. 114°; reported m.p. 114°), and 34.43 gms. of oleic acid dibromide. The oleic acid was characterized by oxidizing it at room temperature with alkaline $KMnO_4$ to the dihydroxy stearic acid (observed m.p. 125°-126°C.; reported m.p. 131°C.). Dihydroxy stearic acid, prepared from Kodak Tech. oleic acid, gave also a m.p. 125°-126° after several crystallizations. On mixing the two compounds, no depression was observed in the melting point.

TABLE I

Characteristics of the Liquid Fraction of Puerto Rican Avocado Pulp Oil

Sp. gr. 25°/25°	0.9159
Refractive index 20°	1.4692
Iodine no. (Hanus)	70.9
Saponification no.	197.4
Acid value	7.4
Acetyl value	7.7
Reichert-Meissl no.	3.0
Polenske no.	0.3
Unsaponifiable matter per cent	1.1
Soluble acids per cent	3.4
Insoluble acids per cent	87.7
Saturated acids (corrected) per cent	26.7
Unsaturated acids (corrected) per cent	65.6
Iodine no. of unsaturated acids	97.9
Saponification no. of unsaturated acids	201.3
Peroxide no. CC. 0.02N $Na_2S_2O_3$ / gm. of liquid fraction (1½ years old at time of determination) (8)	4.8

Using the yields of bromine derivatives obtained, the per cent of acids in the oil were calculated (Table II).

TABLE II

Per Cent of Unsaturated Acids in the Liquid Fraction of Avocado Pulp Oil, Calculated From the Yield of Bromine Derivatives

Acid	Acids %	Acids in Oil %	(Glycerides In Oil %)
Linolenic	0.08	0.05	0.05
Linolic	4.27	2.81	2.95
Oleic	95.98	62.99	65.82

Considering that the amount of linolenic acid in the unsaturated acid fraction is just a trace, it can be safely assumed that only two acids are present. The per cent of each of these acids can be calculated then by using the iodine number of the unsaturated acid fraction (Table III).

The percentages of linolic and oleic acids, when calculated from the iodine number of the fraction of unsaturated acids (Table III), agree quite closely with those calculated from the yield of bromine derivatives (Table II).

Saturated acids. The saturated acids were refluxed with anhydrous methyl alcohol for 12 hours in a flask through which a current of dry HCl continuously

TABLE III

Per Cent of Linolic and Oleic Acids in the Liquid Fraction of Avocado Pulp Oil, Calculated From the Iodine Number

Acid	Acids %	Acids in Oil %	(Glycerides In Oil %)
Linolic	8.77	5.75	5.98
Oleic	91.23	59.85	62.64

passed. One hundred (100) gms. of saturated acids yielded about 94 gms. of methyl-esters.* The esters were distilled under diminished pressure (2 mm.), obtaining a small residue R I and a large distillate. The distillate was, in turn, fractionated at 1-2 mm. pressure into 5 fractions and a residue R II.

Using the iodine and saponification numbers of the fractions and the method of calculation of Baughman and Jamieson (9), the percentage of the various saturated acids, present in the mixtures, was calculated. The results are given in Table IV.

The next step in this investigation was the isolation of the acids from the various ester fractions and their characterization by melting point determina-

TABLE V

Melting Points of Saturated Acids and Derivatives

Acids	Melting Point of Acid °C.	Melting Point of Anilide °C.
Myristic (Shriner & Fuson) (10)	53.8	83.4
Myristic from fractions 1-5	57.9	80.9
Palmitic (Shriner & Fuson) (10)	62.0	89.5
Palmitic from fractions 1-R II	63.2	89.5
Stearic (Shriner & Fuson) (10)	69.2	92.6
Stearic from fraction R II	69.3	92.1

tions, as well as by preparing their corresponding anilide derivatives. The free fatty acids were recovered after saponifying the esters and decomposing the potassium soaps. These acids were fractionally crystallized from 95 per cent ethyl alcohol. The results of these fractionations are summarized in Table V, together with the melting point of the anilide derivatives, prepared from each one of the acids isolated. For the purpose of comparison, the melting point, reported in the literature for each one of these substances, are also tabulated.

* Three gms. of a fatty substance, insoluble in petroleum ether, were separated at this stage. This substance formed a layer just below that of the soluble methyl esters. A preliminary examination revealed this substance to be somewhat soluble in ethyl acetate but completely insoluble in all the other common fat solvents. This substance was saponified and an acid, melting at 60-61°C., was recovered. The anilide prepared from this acid melted at 88-89°C. These melting points agree quite closely with those of palmitic acid and of its corresponding anilide.

Considering the large quantity of palmitic acid present in fractions 1-5 and the high solubility of myristic acid in alcohol, it is not surprising that it was not possible to obtain this acid in a purer form. After four recrystallizations from alcohol and water, the melting point remained at 57.9°C. This melting point corresponded to a mixture of palmitic and myristic acids, in which the former predominated. The anilide, prepared from this mixture, gave a melting point, after crystallizing it twice from alcohol of 80.9°C., a value which came close to that of myristic acid anilide.

The percentage composition of the saturated acid fraction of the liquid fraction of avocado oil is given in Table VI.

TABLE VI

Percentage of Saturated Acids and Corresponding Glycerides in the Liquid Fraction of Avocado Oil

Acid	Acid %	Acid in Oil %	Glycerides in Oil %
Myristic	7.55	2.02	2.13
Palmitic	90.38	24.13	25.31
Stearic	2.07	0.55	0.57

Summary

The liquid fraction of Puerto Rican avocado pulp oil is decidedly a non-drying oil, iodine number 70.9. Its composition, according to our findings, is as follows:

Glyceride of	Per cent in the oil
Linolenic acid	Trace
Linolic acid	6.0*
Oleic acid	62.6*
Myristic acid	2.1
Palmitic acid	25.3
Stearic acid	0.6
Unsaponifiable matter	1.1

* Values calculated from the iodine number of the unsaturated acid fraction.

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TABLE IV

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids

Fraction	Weight of fraction in grams	Iodine number	Saponification value	Esters of unsaturated acids %	Mean molecular weight of esters of saturated acids	Myristic acid		Palmitic acid		Stearic acid	
						Per cent	Gm.	Per cent	Gm.	Per cent	Gm.
1.	12.55	2.72	209.4	2.81	267.2	13.47	1.69	78.65	9.87	.....	.....
2.	19.87	2.51	208.6	2.60	268.3	6.54	1.30	85.76	17.04	.....	.....
3.	20.87	2.78	208.8	3.01	268.0	7.47	1.56	84.43	17.62	.....	.....
4.	16.11	7.78	206.5	8.43	269.8	1.49	0.24	85.29	13.74	.....	.....
5.	10.41	11.58	207.5	12.54	267.3	8.74	0.91	74.06	7.71	.....	.....
R II.	4.13	46.43	199.6	50.29	269.8	0.91	0.04	46.25	1.91	.....	.....
R I.	5.08	48.76	192.7	50.54	289.0	.....	.....	15.67	0.80	30.96	1.57