Avocado Oil

The Composition and Constants of a Little-Known Pericarp Oil

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AVOCADO growing[1] is one of the minor industries of California and Florida. One of the problems of this industry is to find use for the large quantities of cull fruit which at present go to waste. Incidentally, large quantities of this fruit are produced in certain regions of the West Indies, Central America, and tropical South America, from which it is not feasible to ship the fruit in fresh condition to northern markets. With this in view, the authors have made an investigation of the fatty oil contained in the pulp of the fruit.

The edible portion or pulp of the different varieties of avocado grown in California constitutes from about 68 per cent to 85 per cent of the fruit at maturity.[2] This pulp is rich in fat, some varieties containing, on a water-free basis, at least 70 per cent of this constituent. The large seed of the fruit contains very little oil, an air-dried crushed sample of seed contained only 2.2 per cent of oil.

Extracted by Ether

The oil has been extracted with ether from several samples of dehydrated avocado pulp and expressed from several other dehydrated samples by E. M. Nelson of the Protein Investigation Laboratory. Previous attempts to express the oil from the fleshy portion of the avocado gave only a stable emulsion of oil and juice, consequently it it necessary to dehydrate the pulp before it is pressed. In all cases the oil was dark green by transmitted light and red by reflected light, but the expressed oil was lighter in color than the extracted oil. The expressed oil had but little odor and a pleasant fruity flavor and probably could be used as a commercial edible oil if it were not for its color. A sample of the ether-extracted oil was refined by the caustic soda process and bleached with 6 per cent fuller's earth. The resulting product was considerably lighter in color, but it still had too dark a greenish hue to be used as a commercial edible oil. A boiled settled soap made from the crude oil by R. S. McKinney of this laboratory was of moderate hardness. It had a pale green color but on exposure to sunlight for three or four days the surface of the soap bleached to a cream color. This experiment shows that the oil could be used in combination with other fats for the manufacture of hard soap.

Kept for Year

The oil has good keeping qualities. Several samples of the crude oil were kept in partly filled bottles on a laboratory table for a year. They were low in acidity

[1] C. G. Church and E. M. Chace, "Some Changes in the Composition of California Avocados During Growth," U. S. Dept. of Agri. Bull. No. 1073; Wilson Popenoe, "The Avocado in Guatemala," U. S. Dept. of Agri. Bull. No. 743.

[2] C. G. Church and E. M. Chace, ibid.

when first extracted (7), being around 1.0 in acid value (1 mg. of KOH was required to neutralize the free fatty acids in 1 gm. of oil), and their acidity did not increase much. The acid value of one sample at present is 3.0, having increased two units, but the acid values of the other samples increased only 0.2 or 0.3 of a unit. They show no symptoms of rancidity.

Chemical Composition

The chemical composition of a sample of the oil extracted with ether from the dehydrated pulp of the Fuertes variety of avocado has been determined, and is reported below. The more important chemical and physical characteristics of this oil are recorded in Table I. The percentages of saturated and unsaturated acids were determined by the lead salt-ether method,[3] and corrections were made for the small quantity of unsaturated acids that separates with the saturated acids fraction. It was also taken into account that the unsaponifiable matter separates with the unsaturated acids fraction.

The iodine number of the unsaturated acids fraction is 101.2, indicating that this fraction consists of oleic acid (iodine number 90.1) and linolic acid (iodine number 181.4). The following percentage composition of the unsaturated acids fraction was calculated from these figures.

	Per cent.	In original oil Per cent	Glycerides in original oil Per cent
Oleic acid, ..	87.8	74.0	77.3
Linolic acid,.	12.2	10.3	10.8
	100.0	84.3	88.1

The saturated acids were separated from the oil by the lead salt-ether method and esterified with methyl alcohol. This mixture of methyl esters, which weighed 102.2 gm., was fractionally distilled under diminished pressure. The data for the distillation are given in Table II. The preliminary distillation was made from a 1-liter Claissen flask and divided the mixture into five fractions and a residue. These were redistilled from a 250-cc. Ladenburg flask according to the manner indicated in the table. Five final fractions were obtained.

The iodine numbers and the saponification values of these five final fractions were determined and are recorded in Columns 2 and 3, Table III. The small final residue consisted of decomposition products and was disregarded. The iodine numbers are measures of the contaminating unsaturated acids, and from these values the percentage of unsaturated acid esters in each fraction was calculated. From these percentages and the saponification values the mean molecular weights of the saturated acid esters in the different fractions were calculated as recorded in Column 6.[4]

Results Indicate Esters

The results in Column 6 indicate what saturated acid esters may be present in each fraction. Thus, the mean molecular weight of the saturated acid esters in fraction 1 lies between the molecular weights of methyl myristate (242.3) and methyl palmitate (270.3), and suggests therefore that this fraction contains these two esters. The results for fractions 2, 3 and 4 suggest that these

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

[4] J. Am. Chem. Soc., 42, 152, 1197 (1920).

fractions are composed mostly of methyl palmitate, but contain also small portions of methyl sterate (298.4). The indicated saturated acid esters in fraction 5 are methyl stearate and a small amount, less than 1 per cent, of methyl arachidate (326.4).

Recover Fatty Acids

In order to test the correctness of these deductions, the free fatty acids were recovered from some of these fractions by saponifying with alcoholic potash and decomposing the soap solution obtained with hydrochloric acid. The constituent saturated acids were isolated by fractional crystallization from ethyl alcohol. Their identities were established by determining the melting points and by observing whether or not these melting points were lowered when the substances were mixed with equal quantites of the respective acids which they were suspected of being, the purity of which had been established previously by elementary analyses.

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 fraction 5. Portions of stearic acid, $C_{18}H_{36}O_2$, identified by the melting point 68-69°, were obtained from fractions 5 and 4. As was to be expected, it was not difficult to obtain pure palmitic acid, $C_{16}H_{32}O_2$, melting at 63°, from fractions 4 and 1. On account of the solubility of myristic acid, $C_{14}H_{28}O_2$, in alcohol and the large quantity of palmitic acid present, it is not surprising that it was not possible to separate this acid in a pure condition from fraction 1. Seven crops of crystals were obtained from the alcoholic solution of fraction 1 by gradually evaporating the alcohol and adding water. The melting point of the small seventh crop was 56-57°, and since the melting point of pure myristic acid is 54-55° it was considered to be a mixture of myristic and palmitic acids.

The quantities of saturated acids in the various fractions were calculated from the mean molecular weights of their esters (Columns 6, Table III) and the theoretical molecular weights of the two esters in each fraction. The results are given in Column 7-14, Table III.

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 recorded in Column 3. In Column 4 are the equivalent percentages of glycerides.

Summary

It may be possible to utilize the cull avocado fruit, which at present goes to waste, by making use of the fatty oil contained in it. This oil probably would not find a market as an edible oil on account of its color, but experiments have shown that it would be valuable for the manufacture of soap. The composition of this oil has been determined and is recorded below.

	Per cent
Glycerides of:	
Oleic acid	77.3
Linolic acid	10.8
Myristic acid	trace
Palmitic acid	6.9
Stearic acid	0.6
Arachidic acid	trace
Unsaponifiable matter	1.6

TABLE I

Avocado Oil

Chemical and Physical Characteristics

Specific gravity $\frac{25°}{25°}$	0.9132
Refractive index 20°	1.4700
Acid value	2.8
Saponification value	192.6
Unsaponifiable matter (per cent)	1.6
Iodine number (Hanus)	94.4
Acetyl value	9.2
Reichert-Meissl number	1.7
Polenske number	0.2
Saturated acids (corrected) (per cent)	7.2
Unsaturated acids (corrected) (per cent)	84.3
Iodine number of unsaturated acids	101.2

TABLE II

Avocado Oil

Fractional Distillation of Methyl Esters of Saturated Acids

(102.2 g. subjected to distillation)

	Fraction	Temperature °C.	Weight Grams
(Preliminary distillation under 15 mm. pressure)	A	192	20.0
	B	192–3	24.0
	C	193–4	23.52
	D	195–9	23.20
	E	200–15	7.44
	Residue		3.84
(Final distillation under 2 mm. pressure)			
Fractions A and B added	1	154–5	11.00
Fractions C and D added	2	155	46.80
Fraction E added	3	156–7	24.00
	4	157–164	12.50
Residue added	5	178–205	7.27
	Residue		0.34

TABLE III

Avocado Oil

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

Fraction	Iodine Number	Saponification value	Mean molecular weight	Esters of unsaturated acids	Mean Molecular weight of esters of saturated acids	Myristic Acid		Palmitic Acid		Stearic Acid		Arachidic Acid	
				Per cent		Per cent	G	Per cent	G	Per cent	G	Per cent	G
1	3.7	208.2	269.4	3.84	268.5	5.82	0.64	85.32	9.39	....	....	....	....
2	6.2	205.9	272.5	6.43	271.0	....	....	86.51	40.49	2.22	1.04	....	....
3	10.2	205.0	273.6	10.58	271.1	....	....	82.37	19.77	2.43	0.58	....	....
4	22.4	202.7	276.8	23.24	271.4	....	....	69.94	8.74	2.86	0.36	....	....
5	36.8	188.5	297.6	38.17	298.6	....	....	.....	.....	58.51	4.25	0.42	0.03
							0.64		78.39		6.23		0.03

TABLE IV

Avocado Oil

Saturated Acids

Acids	Acids in saturated acid fraction		Acids in original oil	Glycerides in original oil
	Grams	Per cent	Per cent	Per cent
Myristic	0.64	0.75	.05	trace
Palmitic	78.39	91.91	6.62	6.9
Stearic	6.23	7.30	0.53	0.6
Arachidic	0.03	0.04	trace	trace
	85.29	100.00	7.20	7.5

Recommends Benzoate Test for Olive Oil

The Olive Oil committee of the American Oil Chemists' Society, headed by Louis M. Roeg, chief chemist for Brewer & Company, Worcester, Mass., recommended to the recent convention of the Society the use of the silver benzoate method for testing olive oil extracted by carbon disulphide. During the year the committee members tried other methods, but came to the conclusion that the silver benzoate one shows the best reaction. Extracts from the committee's report follow:

Problem Stated

"On October 25, 1927, the chairman of the committee sent to its members a statement of the problem, saying that it was necessary to detect in edible olive oil the small quantities of extracted olive oil containing sulphur from the carbon disulphide solvent, and that his own laboratory had tried the three methods for doing this that were outlined by Mr. F. Lauro in the September, 1927, issue of OIL AND FAT INDUSTRIES.

"These three methods are the coin test, the acetic-anhydride test (Italian test of Pachini or Bracci), and the silver benzoate test. The following results were noted:

"*Coin Test:* With 100 per cent extracted olive oil, a shiny new dime was very definitely blackened. With ten per cent extracted oil and ninety per cent edible olive oil by volume, the dime was not blackened to an appreciable extent.

Acetic Test

"*Acetic-Anhydride Test*: With 100 per cent extracted olive oil, a definite, rosy-red coloration was secured. With ten per cent extracted oil and ninety per cent edible olive oil, a slight pink coloration was noticed. This shows a better reaction than under the coin test.

"*Silver Benzoate Test:* For this test we make the silver benzoate from silver nitrate and sodium benzoate by precipitation from hot aqueous solutions. After cooling, washing with cold water and drying, twenty milligrams of silver benzoate were added to five cc. of mixed olive oils and the mixture heated to 150 degrees C. in an oil bath. With ten per cent extracted oil and ninety per cent edible oil, a dark brown coloration was obtained. With five per cent extracted oil and ninety-five per cent edible oil, a brown coloration about half as dark as the first was

secured. With one per cent extracted oil and ninety-nine per cent edible oil, a definite brown coloration, distinctly different from 100 per cent edible olive oil, was produced.

"These results were secured in the laboratory of the chairman of the committee. The results were sent to all members of the committee with instructions to make similar tests on samples of extracted and edible oils mailed to them. On October 31, G. S. Jamieson stated that he supposed that the sample marked 'extracted oil' had subsequently been refined, basing his opinion on its light color. Others including the chairman are of the same opinion. This is an important point, for it shows that a light colored (and probably refined) olive oil extracted by carbon disulphide makes a definite brown coloration with silver benzoate, even with one-half of one per cent extracted oil and ninety-nine and one-half per cent edible oil.

"W. H. Dickhart in his letter of December 29, 1927, stressed that the above three tests when applied to olive oils extracted by carbon disulphide show that silver benzoate is a more definite reagent than the Italian acetic-anhydride test, but that the latter test will act positive with oils extracted by other solvents, whereas silver benzoate fails with oils extracted by solvents other than silver benzoate. However, since the majority of commercial oils are extracted by carbon disulphide, we shall continue this report as per our original problem.

"On January 31, M. L. Sheeley sent his results from the use of the three tests, and since they also agreed with the conclusions of the others, the committee recommends that the silver benzoate test be adopted for testing olive oil extracted by carbon disulphide."

Jackson Becomes Sales Manager for "Purit"

THE Purit Company, Amsterdam, Holland, manufacturers of "Purit" activated carbons, and the Glidden Food Products Company, United States Depository Agents for "Purit," announce the appointment of A. A. Jackson as General Sales Manager. Mr. Jackson's headquarters are at 82 Wall Street, New York, with the Glidden Food Products Company.

Mr. Jackson has been closely identified with the activated carbon business for the past several years and enjoys a wide personal acquaintance with the consuming trades in this line throughout the country. He has returned recently from an extensive visit with his principals in Holland, during which arrangements were completed for carrying in stock at convenient American distributing points a new grade of decolorizing carbon in addition to the regular grades heretofore handled.

Society Gains 55 New Members

GROWTH of the American Oil Chemists' Society is shown by the report of the Membership Committee at the recent convention held at New Orleans. During the past year fifty-five new applicants were submitted to the Society by the Committee, which is composed of Miss Rosalind U. Norris and Messrs. W. G. McLeod, P. W. Tompkins, L. C. Howe, W. A. Peterson, and A. W. Putland. That this growth was due to "recognition and approval of the Society's work and activities" rather than to the efforts of the Committee was expressed.