THE COMPOSITION OF PILI-NUT OIL

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INTRODUCTION

Several species of the genus *Canarium* bear edible nuts which have a fine flavor and yield a valuable oil. According to Lewkowitsch,[1] Java almond oil is obtained from the seeds of *Canarium commune*, which is a tree indigenous to the Moluccas and Malabar. It is cultivated in tropical Asia, where the seeds serve as a foodstuff in place of sweet almonds.

Canarium oleosum and *Canarium polyphyllum* also yield seeds very similar to those obtained from *Canarium commune*.

Pastrovich[2] examined the oil obtained from the seeds of *Canarium commune*. When subjected to pressure the seeds yield 56.1 per cent of oil which is pale yellow and has a pleasant taste. On standing "stearine" separates out at 15° C. The percentage of unsaponifiable matter in the oil was found to be 0.44. The fatty acids separated by the lead-salt-ether method consist of 44.6 per cent saturated acids and 55.4 per cent unsaturated acids. The saturated acids contained palmitic and stearic acids. The unsaturated acids gave no hexabromides, showing the absence of linolenic acid. The fatty acids consist approximately of 44.6 per cent palmitic and stearic acids, 43 per cent oleic acid, and 12.5 per cent linolic acid.

In the Philippines, oil obtained from the seeds of *Canarium ovatum* is known as pili-nut oil. *Canarium ovatum* is a tree which reaches a height of about 20 meters and a diameter of

[1] Lewkowitsch, J., Chemical Technology and Analysis of Oils, Fats, and Waxes 2 (1913) 382.

[2] Pastrovich, P., Chem. Zeit. 31 (1907) 782.

40 centimeters. This species is very abundant in southern Luzon. The fruits are 6 to 7 centimeters in length and consist of hard, thick-shelled triangular nuts surrounded by a small amount of pulp. This pulp, which is edible when cooked, also contains an oil that is occasionally extracted locally and used for lighting and cooking.

Pili nuts are rich in oil and when roasted have a delicious flavor. They are used in making confections and, by many, are considered superior to almonds. Pili-nut oil is light yellow, has an agreeable odor and taste, and is suitable for culinary purposes. The keeping quality of the oil is very good, as shown by the fact that a sample stored for about six months had no rancid taste or odor and the acid value was only 1.42. It is said [3] that an average tree produces about 33 kilograms of pili nuts in one year.

Brill and Agcaoili [4] analyzed the kernels of pili nuts and determined the constants of the oil. Their results showed that the kernels contain about 74 per cent of fat and that the oil has an iodine value of about 59 to 61 and a saponification value of 186 to 192.

SAMPLE

The sample of pili-nut oil used in this investigation was obtained from pili nuts purchased in one of the markets in Manila. The hard shell of the nuts was broken with a hammer. The kernels were removed and ground into a meal, which was placed in a small press and the oil separated from the oil cake. When the oil was allowed to stand a few hours a small amount of "stearine" separated out. This was removed by filtration and the clear oil stored in glass-stoppered bottles. The constants of this sample of pili-nut oil are given in Table 1.

TABLE 1.—*Constants of pili-nut oil.*

Specific gravity $\frac{30°}{4°}$	0.9069
Refractive index at 30°	1.4646
Iodine value (Hübl)	55.9
Saponification value	197.4
Acid value	1.42
Unsaponifiable matter (per cent)	0.19

[3] West, A. P., and Brown, W. H., Bull. Philip. Bureau Forestry 20 (1920) 114.

[4] Brill, H. C., and Agcaoili, F., Philip. Journ. Sci. § A 10 (1915) 114.

In investigating the composition of pili-nut oil the saturated and unsaturated acids, which are present as glycerides in the oil, were separated by the lead-salt-ether method.[5] The unsaturated acids were determined by means of the bromo-derivative method.[6] The saturated acids were converted into their methyl esters [7] which were fractionally distilled. The composition of the saturated acids was estimated by calculating the data obtained from the methyl esters.

SEPARATION OF SATURATED AND UNSATURATED ACIDS

The lead-salt-ether method does not give a complete separation of saturated and unsaturated acids, since the saturated acids are always contaminated by a small quantity of unsaturated acids, as shown by the iodine value of the saturated acids. The unsaturated acids are also likely to be contaminated with a small quantity of saturated acids, but this error can usually be reduced to an unappreciable amount by not washing very thoroughly with ether the lead salts of the saturated acids.

In separating the saturated and unsaturated acids by the lead-salt method the unsaponifiable matter originally present in the oil goes with the unsaturated acids.[8] The percentage of impure unsaturated acids, as determined, must therefore be corrected, not only for the small amount of unsaturated acids present in the saturated acids, but also for the unsaponifiable matter which they contain. Since pili-nut oil contained only 0.19 per cent of unsaponifiable matter (Table 1), it was not considered necessary to correct the unsaturated acids for this small percentage of unsaponifiable as this slight correction may be applied directly to the unsaturated glycerides, thus giving the same result.

The percentage of impure saturated acids separated by the lead-salt method was 51.45, and the percentage of unsaturated acids, 43.87. The iodine value of the impure saturated acids was 23.32, and of the unsaturated acids, 89.92. The percentage

[5] Lewkowitsch, J., Chemical Technology and Analysis of Oils, Fats, and Waxes 1 (1921) 556.

[6] Ibid. 1 (1921) 585.

[7] Jamieson, G. S., and Baughman, W. F., Journ. Am. Chem. Soc. 42 (1920) 1200.

[8] Lewkowitsch, J., Chemical Technology and Analysis of Oils, Fats, and Waxes 1 (1921) 584; Baughman, W. F., and Jamieson, G. S., Journ. Am. Chem. Soc. 43 (1921) 2697.

of unsaturated acids present as contamination in the impure saturated acids [9] was 13.34.

$$\frac{51.45 \times 23.32}{89.92} = 13.34$$

The percentage of pure saturated acids was 51.45 — 13.34, or 38.11. The total percentage of unsaturated acids corrected for the unsaturated acids which were present as contamination in the impure saturated acids was 43.87 + 13.34, or 57.21.

The results of separating the saturated and unsaturated acids in pili-nut oil are given in Table 2.

TABLE 2.—*Separation of saturated and unsaturated acids in pili-nut oil by the lead-salt-ether method.*

	Per cent.
Impure saturated acids (determined)	51.45
Unsaturated acids and unsaponifiable matter (determined)	43.87
Total	95.32
Iodine value (Hübl) of unsaturated acids	89.92
Iodine value (Hübl) of impure saturated acids	23.32
Unsaturated acids present in the impure saturated acids (calculated)	13.34
Saturated acids corrected for unsaturated acids (calculated)	38.11
Unsaturated acids corrected for the unsaturated acids present in the saturated acids	57.21

UNSATURATED ACIDS

The iodine value of the unsaturated acids, separated by the lead-salt method, was found to be 89.92 (Table 2). Since the iodine value of oleic acid is 90.07, the result obtained indicates that the unsaturated acids consist entirely of oleic acid. To obtain confirmatory data the unsaturated acids were determined by means of the bromo-derivative method, which is used to separate and identify the unsaturated acids that may be present.

The bromine addition products of the unsaturated acids were prepared by dissolving a portion of the unsaturated acids (2.1368 grams) in ether; the ethereal solution was cooled to a

[9] Baughman, W. F., Brauns, D., and Jamieson, G. S., Journ. Am. Chem. Soc. 42 (1920) 2398.

temperature of —10° and bromine was added slowly, after which the solution was allowed to stand about three hours at —10°. No crystals of linolenic hexabromide, which is insoluble in ether, were obtained. This indicated that pili-nut oil contained no linolenic glyceride. The ethereal solution was then treated with 10 per cent sodium thiosulphate solution, to remove the excess of bromine. This treatment was repeated, to remove the last traces of bromine, after which the separated ethereal solution was dehydrated with anhydrous sodium sulphate, filtered, and distilled to eliminate the ether. The residue was then treated with petroleum ether (boiling point, 35° to 55°) and heated (reflux) for about a half hour. The petroleum ether solution was then cooled and allowed to stand several hours. No crystals of linolic tetrabromide were obtained. The solution was concentrated, by distilling, to a volume of about 200 cubic centimeters, cooled, and allowed to stand several hours, but still the tetrabromide did not crystallize. This indicated that, if the oil contained linolic glyceride, the percentage was probably small. The petroleum ether solution was concentrated to a volume of about 100 cubic centimeters, transferred to a small distilling flask, and the petroleum ether eliminated by distilling under diminished pressure. The dry residue (3.3540 grams) was weighed and the bromine content determined by boiling about 0.1 gram with about 0.5 gram of solid silver nitrate and 30 cubic centimeters of pure concentrated nitric acid. The precipitated silver bromide was then collected on a Gooch filter. The bromine content of the residue was found to be 36.03 per cent. Since oleic dibromide contains 36.18 per cent bromine the unsaturated acids consist entirely of oleic acid. The unsaturated acids separated by the lead-salt method and corrected for the unsaturated acids, which were present as impurity in the impure saturated acids, amounted to 57.21 per cent (Table 2). This is equivalent to 59.78 per cent of oleic glyceride which, according to the analysis, is the only unsaturated glyceride present in the oil.

Since the unsaponifiable matter (0.19 per cent, Table 1) present in the oil goes with the unsaturated acids in the lead-salt separation, the percentage of oleic glyceride corrected for unsaponifiable matter is 59.78 — 0.19, or 59.59.

The data obtained by analyzing the bromo-derivatives of the unsaturated acids are given in Table 3.

TABLE 3.—*Analysis of unsaturated acids.*

Sample of unsaturated acids (grams)	2.1368
Linolenic hexabromide insoluble in ether	.....
Linolic tetrabromide insoluble in petroleum ether	.....
Residue (grams)	3.3540
Bromine content of residue (determined) (per cent)	36.03
Oleic acid equivalent to dibromide (grams)	2.1400
Impure oleic glyceride in oil (per cent)	59.78
Oleic glyceride corrected for unsaponifiable matter (per cent)	59.59

SATURATED ACIDS

The impure saturated acids were converted into their methyl esters by dissolving the acids in methyl alcohol and saturating the solution with dry hydrogen chloride, which was prepared by treating fused ammonium chloride with sulphuric acid and passing the gas through sulphuric acid. The mixture was then heated on a water bath (reflux) for fifteen hours, after which it was treated with water and the ester layer separated. The esters were dissolved in ether and the ethereal solution washed with sodium carbonate solution and afterwards with water. The ethereal solution was then dehydrated with anhydrous sodium sulphate, filtered, and the ether removed by distilling. The impure esters (43.8832 grams), which were yellow, were distilled under diminished pressure. A preliminary distillation at about 15 millimeters pressure was made, to obtain the pure colorless esters and eliminate the dark impurities which were formed as by-products in the esterification process. The colorless esters (39.5476 grams) were then redistilled at 15 millimeters pressure. Data on the distillation of the esters are given in Table 4.

TABLE 4.—*Distillation of the impure methyl esters of the saturated acids; pressure, 15 millimeters.*

	Grams.
First distillation:	
Esters distilled, boiling point 195 ° to 210°C	43.8832
Distillate	39.5476
Residue	4.3356
Second distillation: Esters distilled	39.5476

Fraction.	Grams.	Saponification value.	Iodine value (Hübl).	Boiling point.
				°C.
I	19.1886	204.5	15.35	195.8–198.3
II	16.4020	201.5	21.53	198.3–209.7
Residue	3.9570			

The iodine values of the two fractions of methyl esters obtained in the second distillation (Table 4) show that these esters were contaminated with methyl oleate, since olein was found to be the only unsaturated glyceride in the oil. The percentage of unsaturated esters (methyl oleate) in each fraction of the impure esters was calculated from the iodine value. The saponification values and mean molecular weights of the esters of the saturated acids, uncontaminated with unsaturated esters, were then calculated, after which the composition of each fraction of the impure methyl esters was determined. The results are recorded in Table 5.

TABLE 5.—*Composition of methyl esters.*

Methyl esters of acids (second distillation).	Fractions.	
	I	II
	Per cent.	*Per cent.*
Oleic	17.89	25.09
Palmitic	82.11	67.45
Stearic	----------	7.46
Total	100.00	100.00

Acids, equivalent to esters.	Fractions.		Total.
	I	II	
	Grams.	*Grams.*	*Grams.*
Oleic	3.27	3.92	7.19
Palmitic	14.94	10.49	25.43
Stearic	----------	1.17	1.17

The saponification value of the saturated esters in the first fraction (Table 5) was 207.8, and the mean molecular weight, 270. Since the molecular weight of methyl palmitate is 270.3, the pure saturated esters in the first fraction consisted entirely of methyl palmitate. The saponification value of the saturated esters in the second fraction was 205.5, and the mean molecular weight, 273.1. Since the mean molecular weight is between the molecular weights of methyl palmitate (270.3) and methyl stearate (298.4), the saturated esters consist of a mixture of these two esters. Knowing the weights of the esters in each fraction (Table 4) and the composition of each fraction, the quantity of acids equivalent to the methyl esters was obtained (Table 5), after which the total percentage of saturated glycerides present in the original oil was calculated (Table 6). In making these various calculations the method adopted by Baughman and Jamieson in their investigation of Hubbard

squash-seed oil [10] was, in general, used and the following data were employed:

Molecular weight of potassium hydroxide	56.1
Iodine value of methyl oleate	85.81
Saponification value of methyl oleate	189.5

TABLE 6.—*Calculation of saturated acids to glycerides originally present in the oil.*

Acid.	Mixture of saturated acids.		Saturated acids calculated on basis of original oil.	Saturated glycerides in original oil.
	Grams.	*Per cent.*	*Per cent.*	*Per cent.*
Palmitic	25.43	95.60	36.43	38.25
Stearic	1.17	4.40	1.68	1.76
Total	26.60	100.00	38.11	40.01

As shown by the data given in Table 6, palmitin and stearin are the only saturated glycerides present in the oil.

In calculating the composition of the saturated acids the residues obtained in distilling the methyl esters were not considered. Since the esters seemed to decompose somewhat during the distillation, it was thought that the data obtained by analyzing the impure residues would not really represent the properties of the pure esters. There is, of course, a possibility that these residues contained other esters, in addition to those recorded. Considering the temperatures of the distillates and the experimental observations this would, however, appear to be unlikely.

SUMMARY

Pili-nut oil is an edible oil which has good keeping qualities and the following composition:

Constituent.	Per cent.
Oleic glyceride	59.6
Palmitic glyceride	38.2
Stearic glyceride	1.8
Unsaponifiable matter	0.2
Total	99.8

We wish to express our thanks and appreciation to Mr. Arthur F. Fischer, director of the Philippine Bureau of Forestry, for the material which he kindly supplied for this investigation and the assistance he has given.

[10] Baughman, W. F., and Jamieson, G. S., Journ. Am. Chem. Soc. 42 (1920) 156.