

THE CHEMICAL COMPOSITION OF THE FATTY OIL FROM KUKUI NUTS

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The oil¹ examined in this work was expressed from the nuts produced by the kukui tree, *Aleurites moluccana* (L.) Willd., which is indigenous to several of the Hawaiian Islands, India, and China. The kukui tree is small to medium in size, growing as high as sixty feet, and usually grows in the lower mountain zones. Each tree is capable of producing as many as one hundred pounds of the nuts in one season. The nuts have the general shape of an English walnut but possess a thick, hard, ebony-like shell. The average weight of the nuts examined was about twelve grams. The oil is also called lumbang and candle nut oil.

An anonymous writer in the "Oil, Paint, and Drug Reporter" of July 27, 1914, states that there is very little difference between the kukui nuts of Hawaii obtained from *Aleurites moluccana*, and the lumbang nuts of the Philippines obtained from *Aleurites triloba*. West and Montes² report an analysis of the oil from the nuts of *Aleurites moluccana* in which they found in part the following characteristics: saponification number, 214; iodine number, 140; linolenic acid 6.5%; linoleic acid 33.4%; oleic acid 56.9%; solid acids, 2.8%. Presumably their oil was obtained from nuts grown on the Philippine Islands. We obtained for the same characteristics of the Hawaiian oil: saponification number 191.3; iodine number 162; linolenic acid 5.2%; linoleic acid 61.6%; oleic acid 17.0%; and saturated acids 6.8%. Comparison of these results shows that the oil investigated by us was considerably different in properties from the Philippine oil.

So far as could be learned, no attempt has previously been made to identify and to determine the percentages of saturated acids in kukui nut oil.

Experimental Part

Some of the nuts (including shells) were ground and dried at 105°-110°. The moisture content was 3%. About 16% of the weight of the dried material was extractable with petroleum ether (b. p. 30°-60°). The extract was a slightly yellowish oil. This extracted oil possessed essentially the same physical and chemical characteristics as that which was expressed.

The physical and chemical characteristics of the expressed oil were determined by standard methods and are listed in Table I.

Unsaturated Acids

Preparation and Hydrogenation of Methyl Esters.—The oil was saponified with potassium hydroxide in alcohol solution, and the acids so obtained were separated into the saturated and unsaturated fractions by the lead salt-ether method. The methyl esters prepared from the unsaturated acids distilled from 175°-185° at a pressure of 3.5 mm.

¹Obtained from Hawaii through the courtesy of Mr. N. F. Ambrose, County Extension Agent, Wailuku Maui.

²Philippine Journal Science 18:619-635. 1921.

TABLE I. Physical and Chemical Characteristics of Kukui Nut Oil.

Specific gravity (20°/4°).....	0.922
Refractive index (Abbe 20°).....	1.4785
Iodine number oil (Hanus).....	162.0
Saponification value.....	191.3
Acetyl value.....	3.2
Acid value.....	17.4
Reichert-Meißl number.....	negligible
Mean molecular weight saturated acids.....	275.7
Mean molecular weight unsaturated acids.....	288.7
Iodine number saturated acids.....	15.6
Iodine number unsaturated acids.....	168.1
Unsaturated acids (basis of oil) (corrected %).	83.8
Saturated acids (basis of oil) (corrected %).	6.8
Unsaponifiable matter %.....	0.38

Five grams of these esters was reduced catalytically with hydrogen, and the resulting product was saponified and recrystallized from alcohol. The acid had a m. p. of 69°; a mixed m. p. with stearic acid showed no depression. This fact, together with the boiling range of the esters, and the neutral equivalent of the unsaturated acids, indicated that only eighteen carbon atom acids were in this fraction.

Bromination.—The unsaturated acids were brominated qualitatively by the method of Eiber and Muggenthaler.³ The bromination in ether produced a white precipitate melting at 177°-178°. This indicated the presence of linolenic acid. Removal of the ether and the addition of petroleum ether caused the separation of a precipitate, which after recrystallization from acetic acid melted at 112°. Further crystallization did not raise the melting point appreciably. This material, although not melting at 114° where tetrabromostearic acid should melt, was probably the slightly impure tetrabromo derivative of linoleic acid. Ozonolysis later proved the presence of this acid.

Ozonolysis.—Two hundred and sixty grams of the methyl esters was treated with ozone by the method of Riebsomer and Johnson.⁴

Unfortunately a small but undetermined amount of the material was lost in this process, so that calculations of theoretical yields cannot be made. The ozonized acids were converted to the methyl esters and fractionally distilled as follows, with the pressure at 14 mm.: fraction (1) b. p. 49°-54°, weight 13.5 g.; fraction (2) b. p. 54°-91°, weight 3.6 g.; fraction (3) b. p. 91°-94°, weight 9.1 g.; fraction (4) b. p. 94-143.5°, weight 6.7 g. With the remainder of the distillation at 2.5 mm. the following results were obtained: fraction (5) b. p. 115°-122°, weight 58.6 g.; fraction (6) b. p. 122°-143°, weight 25.7; fraction (7) b. p. 143°-155°, weight 0.7 g.; fraction (8) b. p. 155°-190°, weight 15.1 g.; undistillable 26.9 g.

Since fractions (2) and (4) were small and boiled over great ranges,

³Lewkowitsch, 1921. Chemical Technology and Analysis of Oils, Fats and Waxes, 6th Ed. Vol. 1, p. 585.

⁴Riebsomer, J. L. and Johnson, J. R., 1933. Jour. Amer. Chem. Soc. 55:3352.

they were considered to be intermediates and were not further investigated.

Fraction (1) was saponified and the acid redistilled. The most of this acid boiled at 101°-103° at a pressure of 14 mm., and it was shown to consist of caproic acid: neut. equiv. 116.9 (calcd. 116.1); N_D^{20} 1.4155 (reported 1.4138); D_4^{20} 0.927 (reported 0.929); anilide, m. p. 95°, mixed m. p. with known anilide (m. p. 96°) 95°.

Fraction (3) was saponified and proved to be pelargonic acid: neut. equiv. 157.2 (calcd. 158.1; N_D^{20} 1.430 (reported 1.433); D_4^{20} 0.9078 (reported 0.907); anilide m. p. 56° (reported 57°).

The refractive index and density of fraction (5) were determined: N_D^{20} 1.4360; D_4^{20} 1.0026. These same constants for dimethyl azelate are reported: N_D^{20} 1.436 and D_4^{20} 1.005. A part of this fraction was saponified and the acid recrystallized from hot water: m. p. 105.5° (mixed m. p. with azelaic acid gave no depression); neut. equiv. 94.3. The melting point of pure azelaic acid is 106.5°, and its neutral equivalent is 94.1. These data are sufficient to demonstrate the presence of azelaic acid.

Fraction (6) proved to be largely azelaic acid. Fraction (7) appeared to be impure palmitic acid, which had escaped the lead salt-ether separation process. Fraction (8) was largely unsaturated 18-carbon atom acids which were not decomposed by ozone.

Finding caproic and azelaic acids in the products of ozonolysis verifies the presence of linoleic acid.⁵

Likewise the finding of pelargonic and azelaic acids indicates the presence of oleic acid. Since linolenic acid was shown to be present by the bromination process, propionic acid should also have been found in the ozonized product, but it was apparently lost in the step for removing the acetic acid and water after hydrolysis of the ozonide. The separation of so small an amount of propionic acid from such a large quantity of acetic acid and water would be a difficult task.

In order to find the percentages of the three unsaturated acids, the thiocyanogen-iodine number⁶ of the unsaturated acids was determined. This number was 96.1. Using this figure and the iodine number of the unsaturated acids, the calculation of the percentages of oleic, linoleic, and linolenic acids was made.

	In Unsaturated Fraction %	In Oil % Acid	% Glyceride
Oleic acid	20.3	17.0	17.8
Linoleic acid	73.5	61.6	64.1
Linolenic Acid	6.2	5.2	5.4
	100.0	83.8	87.3

⁵Riebsomer, J. L. and Nesty, G. A., 1934. Jour. Amer. Chem. Soc. 56:1784.

⁶Jamieson, G., 1932. Vegetable Oils and Fats. Amer. Chem. Soc. Monograph 58, p. 345.

Saturated acids

About 25 grams of the saturated acids was fractionally crystallized from alcohol. From this process was obtained a less soluble acid with a m. p. of 68°, and its anilide melted at 93°. A mixed melting point with stearic acid (m. p. 69°) and the acid isolated was 68-69°. A mixed melting point of the anilide with known stearic anilide (m. p. 94°) showed no depression.

From the fractional crystallization was obtained a more soluble acid with a m. p. of 61.5°-62° (mixed m. p. with palmitic acid 61.5°-62°), and the anilide prepared from this acid melted at 88°. Palmitic anilide melts at 89°, and a mixed m. p. showed no depression. This evidence established the presence of palmitic and stearic acids in the saturated fraction.

Assuming no other acids present except palmitic and stearic and using the neutral equivalent (275.7), the percentages of these two acids may be calculated.

	In Saturated Fraction	In Oil	
		% Acid	% Glyceride
Palmitic acid.....	30.7	2.1	2.2
Stearic acid.....	69.3	4.7	4.9
	100.0	6.8	7.1

Glycerol was shown to be present by the preparation of the tribenzoate.

Summary

1. The physical and chemical characteristics of kukui nut oil have been determined.

2. The oil consists of the glycerides of oleic acid (17.0%), linoleic acid (61.6%), linolenic acid (5.2%), stearic acid (4.7%), and palmitic acid (2.1%), together with a small amount of unsaponifiable matter.