OURICURY PALM KERNEL OIL

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Abstract

A small sample of ouricury palm fruits from Florida, as well as the oil expressed from the kernels imported from Brazil have been investigated. The fruits consisted of 47.5 per cent of pulp and 52.5 per cent of palm nut, of which the kernel amounted to 23.8 per cent. On the basis of the whole fruit, the oil in the pulp only amounted to 0.9 per cent. The kernels from Brazil contained 69.7 per cent of oil, some of the characteristics of which were as follows: Saponification value, 256.9, iodine number (Hanus), 14.69, thiocyanogen value, 12.78, Reichert-Meissl value, 5.93, Polenske number, 18.38, and unsaponifiable matter, 0.27 per cent. The percentages of fatty acids found in the oil were as follows: Caproic 1.66, caprylic 9.10, capric 7.64, lauric 42.7, myristic 8.43, palmitic 7.15, stearic 2.15, arachidic 0.96, oleic 12.18, and linoleic acid 2.04 per cent.

Attention has been called to the importance of not assuming the presence in distilled ester fractions of the lower homologues of oleic acid from deductions made only from calculations using the iodine number and saponification value of the fraction without confirmation by other evidence. The present investigation has shown the danger of such assumptions.

OURICURY oil is obtained from the kernels of the Brazilian palm Syagrus (or Cocos) coronata. Although for 10 years or more the kernels have been exported from Brazil to Marseilles, France, only in very recent years have they been shipped to this country for the manufacture of oil and meal. It is understood that here the oil is chiefly used as an ingredient in margarine and it is said to be particularly suitable for that purpose.

In view of the number of requests received for information on the composition of the oil, and the lack of such data in the literature, it was decided to make an investigation of it.

At about this time, six pounds of ouricury fruits from Lakeworth, Florida, which were sent to Mr. R. A. Young of the Foreign Plant Introduction Division, were given to us. The thin-skin, fibrous fruits, which had the general appearance of small yellow plums, averaged 6.5 grams in weight. They contained 47.5 per cent of pulp which is filled with long, slender, strap-like fibers and the so-called palm "nut" accounted for the remaining 52.5 per cent. The pulp was found to contain 3 per cent of red oil which, on the basis of the whole fruit, amounts to 1.43 per cent. As this small quantity of palm oil is of no commercial interest, no investigation of it was attempted. The palm nuts consist of 23.8 per cent of kernel and 76.2 per cent of shells.

The present investigation of the kernel oil was made possible through the kindness of the Franklin Baker Company, Hoboken, N. J., which sent about 25 pounds of the kernels received from Brazil. These kernels, which averaged 0.8 grams in weight, were found to contain 69.7 per cent of oil and 2.4 per cent of moisture. The oil which was expressed in the laboratory was slightly yellow, and as known for a long time in France, it has a distinctly lower solidification point than any other commercial palm kernel oil. The sample at hand, when standing at a temperature of about 18° C., was observed to deposit only a small quantity of "stearine."

The chemical and physical characteristics, which were determined on the expressed oil, are given in Table I.

TABLE I
CHEMICAL AND PHYSICAL CHARACTERISTICS OF OURICURY PALM KERNEL OIL

Specific gravity, 25°/25	0.9221
Refractive index at 25°	1.4543
Saponification value	256.9
Iodine number (Hanus)	14.69
Thiocyanogen value	12.78
Acid value	11.2
Reichert-Meissl value	5.93
Polenske number	18.38
Unsaponifiable matter, %	0.27
Saturated acids, %	78.9
Unsaturated acids, %	14.2

The percentages of oleic and linoleic acids were calculated in the customary manner, using the iodine number and the thiocyanogen value. This calculation indicated that the oil contained 12.2 per cent of oleic and 2 per cent of linoleic acid. Afterwards, by bromination, the tetrabromide of linoleic acid was isolated and identified.

The percentage (78.9) of the saturated acids present in the oil was determined from the total quantity of these acids found by the analysis of the distilled ester fractions and residues, originally obtained from a known weight of oil.

For the determination of the quantity of the individual fatty acids, 200 grams of the oil were directly esterified with 100 grams of anhydrous ethyl alcohol in the presence of dry hydrochloric acid (J. Amer Chem. Soc. 42, p. 1200, 1920). The esters freed from solvents and moisture were fractionally distilled, using a specially-constructed, electrically-heated, fractionation column. The size, wire packing and heating jacket of this column resembled that described by Riemenschneider and Ellis (Biol. Chem. 113, p. 222, 1936). Standard glass joints connected the round-bottom distillation flask and the thermometer to the column. A condenser for refluxing was attached above the column and another in between the column and delivery tube. At the entrance of the delivery tube was a stop-cock which permitted the control of the collection of the distillate. By means of this stop-cock, it was possible to interrupt the collection of the distillate at any time in order to allow the system to reach a satisfactory condition for the continuation of the ester fractionation. The condenser above the column was connected by a tube which entered the delivery tube beyond the stop-cock, so that when the latter was closed, the same pressure of both sides of the equipment would be maintained. An excellent control of the temperature of the air between the glass jacket tube, which was heated by a coil of nichrome wire, and the fractionation tube was maintained by means of a variable rheostat and a "Variac" (transformer type) having a range from 0 to 135 volts, which were placed in series with the heating element.

Before undertaking the distillation, the round-bottom flask containing the esters was insulated by surrounding it with rock wool, which was supported by an asbestos paper tube. This arrangement greatly facilitated the proper distillation of the esters, which were heated with an electric unit of the transformer type known as "Ful-Kontrol," which permitted close control of the temperature. It should be mentioned that during the removal of the last of the ether from the esters while being heated in a boiling water bath at ordinary atmospheric pressure, a volatile portion (see Table II) was obtained which weigh 1.95 grams. This was reserved for later examination. Meanwhile the rest of the esters were fractionally distilled under diminished pressure. During the distillation, the heating of the esters in the flask, as well as the jacketed air about the distillation column, was so regulated that the coiled wire (packing) was all kept moist with condensing esters at the same

time avoiding the flooding of the distillation column. Twenty-two fractions and a small residue were obtained. After setting aside the residue for analysis, each fraction in turn was refractioned from a 100 cc. distillation flask. Eighteen fractions were collected and there remained, as usual, a small residue of undistilled esters. The fractions and residue, as well as the volatile portion previously mentioned and the ester residue from the first distillation, were weighed. Then their iodine numbers and saponification values were determined. As the first 13 fractions were found to give no iodine number, the proportions of the individual saturated acids were calculated directly from their molecular weights. After determining the thiocyanogen values of the following fractions, this data, together with the iodine numbers, served to give an approximate estimate of the proportions of oleic and linoleic acids present in each of these fractions. On account of the possibility that the esters might contain some of the more volatile unsaponifiable constituents of the original oil from which the esters were directly prepared, as well as small quantities of decomposition products, it was decided to determine by the Bertram procedure the quantity of both the unsaponifiable matter and the saturated acids present. Each fraction, as suspected, was found to contain some unsaponifiable constituents. Using the neutralization equivalents found for the isolated saturated acids, the proportions of each acid in the fractions were calculated. As was expected, these results were somewhat different from those previously calculated by using the iodine numbers, thiocyanogen and saponification values of the ester fractions.

The quantity of saturated acid esters in those fractions containing unsaturated acid esters was also determined by the acetone-permanganate procedure of Armstrong and Hilditch (J. Soc. Chem. Ind. 44, 43T, 1925). The saponification values of the separated saturated esters were determined and from them were calculated the corresponding mean molecular weights of the acids themselves. These were found in good agreement with those previously found for the saturated acids obtained by means of the Bertram method. However, it was found that the calculation of the saponification equivalents of the unsaturated acid esters from the appropriate analytical data gave incorrect results, as shown by the following example: Fraction 15, which contained 0.31 per cent of unsaponifiable constituents, was found to have a saponification equivalent of 270.9. The acetone-permanganate oxidation procedure indicated that the fraction contained 64.9 per cent of saturated acid esters, having a saponification equivalent of 277.7. From the analytical data obtained, it was calculated that the neutralization equivalent of the unsaturated acids present in the fraction was 232.2 (that for tetradecenoic acid being 226.2). However, by subjecting a weighed portion of the acids from the fraction to the Lapworth-Mottram alkaline permanganate oxidation method, nearly all of the unsaturated acid present was recovered in the form of dihydroxy-stearic acid, which showed that the major portion of the unsaturated acids in the fraction was oleic acid and not tetradecenoic acid.

Several years ago in this laboratory similar misleading results (unpublished) were obtained with distilled esters prepared from the fatty acids of yellow mustard seed oil. The fractions of the lower boiling esters gave iodine numbers and saponification values which indicated the presence of unsaturated acid, or acids, of low molecular weight of the oleic acid series, but in this case only dihydroxystearic acid was obtained by the use of the Lapworth-Mottram method, which definitely showed that the lower homologues of oleic acid were not present in these ester fractions. It appears that during the distillation, in cases where the esters contain relatively large quantities of esters of oleic and linoleic acids, some volatile, saponifiable, low molecular weight degradation products from these acids are formed. Obviously, the presence of small quantities of such products in an ester fraction would invalidate the results calculated from the analytical data customarily used for this purpose.

To return to the present investigation, it should be mentioned that the acids were recovered in the usual manner from the residues remaining from the distillation of the esters and subjected to exhaustive fractional crystallization from alcohol. Not only were the saturated acids in each residue identified, but their weights were obtained. Also, the saturated acids from the ester fractions were fractionally crystallized and identified in the usual manner. These identifications confirmed in all cases the deductions

TABLE II
FRACTIONAL DISTILLATION OF THE ETHYL ESTERS

Ester Fraction	Volatile	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	R1*	R2**
Pressure in m.m.	760	9	9	9	9	9	9	9	9	9	9	9	9	9	6	6	6	6	6	....	....
Temperature °C.	100	75-81	81-3	84-108	108-14	114-17	117-39	117-39	139	141	141	141-66	166-9	169-71	151-68	168-80	180-2	182-4	181	....	....
Weight in grams	1.95	2.15	14.56	5.0	4.9	3.7	9.6	5.0	16.3	22.9	21.7	24.4	4.8	13.0	4.85	6.8	11.7	21.7	4.4	4.4	2.2
Saponification value	339.4	332.1	322.0	288.0	282.5	256.0	267.0	249.7	246.2	244.8	243.0	227.2	224.4	221.6	207.1	203.5	196.0	206.2	219.0	229.0	
Iodine number	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.8	22.4	38.7	53.5	56.1	53.0	38.4
Thiocyanogen value	....	....	....	....	....	....	....	....	....	....	....	....	....	....	3.8	21.3	36.9	51.7	56.1	31.4	36.8
Neut. Equiv. of Acids	116	137.3	141.0	146.2	166.8	170.6	191.1	182.0	196.5	199.8	201.2	203.0	218.9	221.9	225.1	242.9	247.6	257.2	244.0	227.4	217.0
Per cent Sat. Acids	67	....	....	....	....	....	....	....	....	....	....	....	....	....	....	53.9	41.6	26.6	22.0	19.8	18.6
Neut. Equiv. of Sat. Acids	116	....	....	....	....	....	....	....	....	....	....	....	....	....	....	251.2	256.9	265.0	285	....	....

*Residue from preliminary fractionation of the esters.
**Residue from the refractionation of the esters.

TABLE III

Percentages of Acids and Glycerides in Ouricury Oil.

	Acids	As Glycerides
Caproic	1.66	1.8
Caprylic	9.10	9.9
Capric	7.64	8.2
Lauric	42.70	45.3
Myristic	8.43	8.9
Palmitic	7.15	7.5
Stearic	2.15	2.3
Arachidic	.096	.1
Oleic	12.18	12.7
Linoleic	2.04	2.1

previously made from the mean molecular weights of the saturated acids.

The distillation data for the fractionation of the esters, and the results of their analysis, are given in Table II. Table III contains the percentages in the oil of the saturated and unsaturated acids and their glycerides.

New Applications for Referee Certificates

Robert H. Acock, of The Oil Mill Laboratory, Austin, Texas, has applied for appointment as Referee Chemist of the American Oil Chemists' Society on cottonseed cake, meal, oil and soap stock. John T. Boyd, Jr., of Barrow-Agee Laboratories, Inc., Cairo, Illinois, has applied for appointment as Referee Chemist on cottonseed, cake, and meal. Information concerning the qualifications of either of these applicants will be gladly received by the Referee Board from any member of the society. Address A. S. Richardson, Ivorydale, Ohio.

REPORT OF 1937-38 ACTIVITIES—REFINING COMMITTEE—AMERICAN OIL CHEMISTS' SOCIETY

THE activities of the Refining Committee for the past year have been characterized by the same very excellent cooperative spirit which has prevailed for many years past in this very important work. As chairman of this year's committee, I wish to thank every member for the prompt attention given to the cooperative samples and also for the many helpful suggestions made. Much credit is again due Mr. H. L. Kevern of the Swift & Company Laboratory for his work leading to what appears to be a satisfactory method for handling Extracted Soybean Oil.

The program carried out this year and the recommendations resulting from the several studies were as follows:

Crude Soybean Tentative Refining Method—A.O.C.S. Methods—Pages 16D-16E

The tentative methods adopted last year for Expeller and Hydraulic Soybean Oils have been used rather extensively in many laboratories of the committee members. No serious difficulties have been reported.

Two cooperative samples (Numbers 1 and 3), both of the Expeller type, were sent out to committee members. The tabulations of results on both samples are attached.

The oil selected for the first cooperative study contained a rather large amount of extraneous material. This selection was made deliberately in order to develop possible improvements in the method. It will be noted that the results reported on this sample were quite widely variant. Two possible causes for the discrepancies were suggested by our own experience and confirmed by a number of the committee members:

(1) Oils of this type must be heated in the original container before mixing. The lecithin, together with other extraneous material, settles to the bottom of the container and cannot be thoroughly mixed with the same treatment that is satisfactory in the handling of cottonseed oil samples. It will be necessary to incorporate in the method a provision that any sample which has been allowed to settle should be heated to 30° C. before mixing. This applies particularly to expeller and hydraulic oils. Care must be exercised that the settlings be thoroughly incorporated with the rest of the sample.

(2) Some difficulty with soft foots was encountered in the regular refinings in the Swift Laboratory, using the tentative methods for Expeller and Hydraulic oils. A number of committee members also had similar trouble. A rather extensive study of the oil used for cooperative sample No. 1 indicated that the sloppy condition of the foots very probably influenced the results reported. Chilling to a temperature of 12-15° C. was found to eliminate this difficulty.

Another sample of Expeller Oil was sent out for cooperative study, which was designated as Cooperative Sample No. 3, 1937-38. The method suggested for handling this sample called for heating the sample to 30°C. followed by sufficient mixing to thoroughly incorporate the settlings with the rest of the sample. Another change in the tentative method provided for the cooling of the oil-foots mixture after the one-hour settling period at 65° at the end of the slow agitation period for an additional hour at 12-15° C. The mixture was again chilled to 12-15° C. for 30 minutes after standing overnight, unless this temperature had been maintained within that range. The soap stock was hardened by chilling in water at 12-15° C. to permit satisfactory draining of the oil.

The results reported by the committee on the second sample of Expeller Oil using the modified tentative method were satisfactory and led to the suggested recommendation for changes in the tentative methods adopted last year, as given at the end of this report.

Extracted Soybean Oil

The refining method development work in the Swift Laboratory this year has been pointed toward the development of a satisfactory method for extracted oil. Some work was also carried out on clarified extracted oil. Detailed tabulations covering these studies, as well as summaries of these tabulations, were submitted to the committee as a matter of record and these are attached to this report. A satisfactory method for the extracted oil was indicated by this work, and a cooperative sample (No. 2) was submitted to the committee to be handled in accordance with the proposed procedure. The results on this sample were reported to the committee and are given in the attached tabulation. These results, together with the development work carried on in Swift's Laboratory on a number of samples of this type of oil, indicate to your chairman that the proposed method used is satisfactory for recommendation for adoption as an addition to the present tentative methods for soybean oil.