The Question of Differences Between Iodine Numbers of Coconut Oil and of the Corresponding Soapstock Fatty Acids

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THE DIFFERENCES BETWEEN the chemical properties of coconut oil and those of the corresponding soapstock fatty acids have been known for many years, but the reasons for these differences have not been well explained until recently. F. W. Wittka (1, 3) appears to have been the first investigator to publish an explanation for these phenomena. He attributed the differences entirely to the presence of oil from the rind of the coconut. Oil from the rind, or testa, of the coconut, always has a higher iodine value than does oil from the meat, or endosperm, and at the same time a higher free fatty acid content. E. F. Armstrong *et al.* (4) investigated the two different oils, testa and endosperm, of copra, and verified the differences in their chemical composition. J. Jacobsen (5) has attributed them to the presence of oil from dust and small particles of copra. This is essentially the same explanation as that of Wittka since it is claimed that the dust comes principally from the testa of the coconut.

S. R. Kuber and Wales Newby (6), in a study of commercial crude coconut oils, have shown that a relation exists between the degree of hydrolysis, which a crude oil has undergone, and the chemical characteristics of the soapstock fatty acids. They suggested that preferential hydrolysis of the long chain fatty acid glycerides, in this case also the unsaturated glycerides, may be responsible.

In a previous communication (7), the present author noted that some of his work, done in Europe before the war, appeared to support the theory of preferential hydrolysis. Unfortunately this work was interrupted by the hostilities, and no supporting data were available.

Recently an additional study has been completed which indicates that the presence of testa oil, although unquestionably a factor, is not the only reason for the relatively high iodine value of the fatty acids from coconut oil soapstock. In several cases it has been possible to show that another factor is involved, which appears to be preferential hydrolysis. This agrees with the findings of Kuber and Newby. Since no similar data have appeared previously, it is felt that the results will be of general interest to both science and industry.

TABLE I

Analytical Data

Crude Coconut Oil Extracted from Endosperm and Testa Separately

Identification Fraction Copra	Oil Extracted %	Oil Extracted %FFA[a]	Oil Extracted I.V.[b]	Ratio Copra Endosperm	Ratio Copra : Testa	Ratio Oil Endosperm	Ratio Oil : Testa
Endosperm A	68.2	0.72	6.5	93.1	6.9	96.3	3.7
Endosperm B	70.1	0.79	6.3	92.7	7.3	96.1	3.9
Endosperm C	69.5	1.32	6.2	92.9	7.1	96.2	3.8
Testa A	34.4	3.32	36.2				
Testa B	36.1	4.65	37.1				
Testa C	35.2		35.8				
Endosperm	71.0	0.17[c]	6.4	92.0	8.0	94.0	6.0 (1)
Testa	47.0	2.68	38.8				
Endosperm	60.0	—	6.0	95.0	5.0	97.3	2.7 (4)
Testa	32.0	—	39.9				

[a] % FFA expressed as Lauric.
[b] Hanuš Method.
[c] Calculated from Acid Value.

Experimental

In order to determine the relative role of testa oil in commercial coconut oil, three samples of copra were carefully separated into endosperm and testa. These samples will be referred to hereafter as samples A, B, and C. Part of A and B were also reserved in their whole, unseparated form. The oil was then extracted from all these fractions, with Skellysolve F, and iodine value and free fatty acids determined. Portions of the whole crude oil, obtained by extracting unseparated copra, were also refined; their soapstock was acidulated, and the iodine values were determined. Results appear in Tables I and II.

TABLE II

Analytical Data

Crude Coconut Oil Extracted from Whole Copra
Iodine Value[a]

Copra	% Oil	% FFA Oil	Oil	Soapstock Fatty Acids
A	66.1	0.80	7.8	16.0
B	67.9	1.05	7.7	15.6

[a] Hanuš Method.

In addition to the present data two sets of quotations from the literature are included in Table I. These, being of the same order of magnitude, tend to confirm the present analyses.

The data in Table I can be used to calculate the free fatty acid, such as lauric, to be expected in whole crude oil extracted from copra A as follows: $(.963 \times .72) + (.037 \times 3.32) = 0.82\%$, and the value actually found in Table II is 0.80%. By a similar calculation it can be shown that an iodine value of 7.6 would be expected on the whole crude oil whereas 7.8 was found. On copra B similar comparisons give 0.97% FFA calculated, 1.05% found; 7.5 iodine value predicted, 7.7 found. In all cases the predicted values agree very well with those actually found.

If the iodine values of the fatty acids, which will end up in the soapstocks from these oils, are predicted from these same data and compared to those actually found in Table II, the results are somewhat different, as follows: 100 g. of crude oil from copra A should contain 96.3 g. of endosperm oil and 3.7 g. of testa oil. At a free acid content of 0.72%, 96.3 g. of endosperm oil should contribute 0.693 g. of free fatty acid while 3.7 g. of testa oil at 3.32% should contribute 0.123 g. This is a total of 0.816 g. of free fatty acids which should appear in the 100 g. of crude oil. Of this 0.816 g. the endosperm oil contributed 84.9% while the testa oil contributed 15.1%. If the free fatty acid fraction of these oils corresponds with that of the whole oil, the iodine value of the free fatty acids can be found thus: $[(.849 \times 6.5) + (.151 \times 36.2)] \times 1.08 = 11.9$ iodine value. A similar calculation on oil from copra B will yield a figure of 13.3, but the respective values actually found on fatty acids from the two soapstocks were 16.0 and 15.6. From this it appears that the free fatty acids in either the endosperm oil, the testa oil, or both, were of higher iodine value than were the fatty acids combined in the neutral glycerides.

Put another way, the presence of testa oil in crude oil from copra A raised the iodine value of its soapstock acids from 8.4 to 11.9, but some other factor was responsible for the further increase to 16.0. Similarly, on crude oil B, testa oil raised the iodine value from 8.3 to 13.3, but some other factor caused a further increase to 15.6.

Following these results, it was decided to approach the problem from a different angle. A portion of 80-100 g. each of the pure endosperm oils, containing no testa oil, was added to 50 ml. of 95% ethanol, and the free acids present were neutralized with normal potassium hydroxide, using a small excess. Water to the extent of 40 ml. was then added, and the mixture was extracted three times with Skellysolve F. The Skellysolve solutions of neutral fat were each washed three times with 50% ethanol, and the Skellysolve was then evaporated.

The alcoholic solutions of soap from each oil were combined, the alcohol was evaporated off, and the soaps were hydrolyzed with dilute hydrochloric acid. The released free acids were extracted with ethyl ether, dried over sodium sulfate, and filtered directly into an iodine value flask. Most of the ethyl ether was evaporated on a water bath, with final constant weight being accomplished under a stream of nitrogen at room temperature. The results of these experiments are shown in Table III.

TABLE III

Analytical Constants of Pure Coconut Endosperm Oil

Separated Into Free Fatty Acid and Neutral Oil Fractions

	Copra A	Copra B	Copra C
% Free Fatty Acid of Crude Coconut Oil as Lauric	0.72	0.82	1.37
Iodine Value[a] of Crude Oil	6.5	6.3	6.2
Iodine Value[a] of Neutral Oil Fraction of Crude	6.5	6.3	6.2
Iodine Value[a] of Total Fatty Acids from Neutral Oil Fraction	7.0	6.8	6.7
Iodine Value[a] of Free Fatty Acid Fraction of Crude Coconut Oil	10.9	9.4	7.9

[a] Hanuš Method.

From a study of Table III it is clear that the free fatty acid fraction of all three crude oils was appreciably higher in iodine value than were the fatty acids combined in the neutral oils. Furthermore there was an inverse correlation between the free fatty acid content, *i.e.*, the degree of hydrolysis, of the crude oils, and the spread in iodine values between the combined and the free fatty acids. This is made clearer in Table IV.

This is exactly the same sort of relation which has been reported previously (6), on commercial oils, except that the spreads are smaller. This is probably due to the fact that the testa oil was eliminated. It is possibly significant that the spreads on samples A and B, found here, are approximately equal to the difference which could not be accounted for by testa oil influence in the preceding experiments.

TABLE IV

Copra Oil Source	% Free Acid	Spread in I. V. Free to Combined F.A.	Iodine Value[a]	
			Neut. Oil F.A.	Free F.A.
A	0.72	3.9	7.0	10.9
B	0.82	2.6	6.8	9.4
C	1.37	1.2	6.7	7.9

[a] Hanuš Method.

It is difficult to explain the relations found in Table IV on any other basis except by preferential hydrolysis. And the high iodine value of the acids from coconut oil soapstocks now appears to be due to a combination of preferential hydrolysis and the presence of testa oil. The testa oil itself is possibly disproportionally unsaturated in its free fatty acid fraction due to preferential hydrolysis.

Further Theoretical Consideration. Regarding the evidence in support of the unsaturated acids in crude coconut oil, there are several references in the European literature. Papers by Kaufmann (8) and Nizamuddin and Kulkarni (9) are particularly applicable.

In the latter, data are presented on the partial hydrolysis of peanut, safflower, and linseed oils by lipase. The ratios of the iodine values of the free fatty acids resulting, to those of the combined fatty acids remaining, were 119.7 : 75.0, 171.8 : 121.0, and 203.2 : 135.0, respectively. From these data it appears that the rate of hydrolysis of the more unsaturated acids was much greater than that of the less unsaturated acids. In view of these results it would be surprising if there were not some preferential character to any hydrolysis taking place in coconut oil where there are not only differences in the degree of unsaturation but also a rather wide difference in the chain length of the acids involved.

There is, of course, one other factor which may favor higher iodine values in the hydrolized portion of coconut oil; that is the greater ease with which the shorter chain acids, in this case also the saturated acids, are converted to the corresponding ketones. Several publications (10, 11, 12, 13) have shown that such molds as Aspergillus, Penicillium, etc., can effect this conversion, and moist copra is often covered by these molds. This would be a factor only with poorly dried or stored copra however.

Summary

Experiments have been made on coconut oil from pure endosperm, pure testa, and normal mixtures of the two. These experiments have shown that the spread in iodine value between refined coconut oil and the fatty acids found on the corresponding soapstock are greater than can be accounted for by the proportion of testa oil present in extracted whole crude oils. Furthermore the iodine value of the free fatty acid fraction of pure endosperm oils was found to be higher than that of the combined fatty acids in the same oils by an amount which varied inversely as the degree of hydrolysis which had occurred in the oil. From this it appears that preferential hydrolysis plays an important part in the production of coconut oil soapstock having higher iodine values than those of the corresponding refined oils.

Attention is also called to some European publications which deal with this question and to the possibility that molds may be involved through their ability to decompose short chain acids to ketones.

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Consistency of Mixtures of Cottonseed and Paraguayan Palm Kernel Oils[1]

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MBOCAYA OIL, the kernel oil from the Paraguayan palm, *Acrocomia Totai Mart (Fam. Palmae)*, is used for edible purposes and in the preparation of high-grade soaps. Production of the oil could be increased greatly if it were economically advantageous. However the physical characteristics of the oil are such that in the unmodified state it is not suitable for use either as salad oil or shortening.

Mbocaya oil resembles that from the kernel of the more generally known oil palm, *Elaeis guineenis Jacq*, but there are some differences. It has been reported (6) that the iodine value of mbocaya oil ranges between 28.0 and 30.2, about twice that for the usual palm kernel oil; and the melting point is correspondingly low, 20.0 to 23.0°C. The saponification value lies between 239 and 246, slightly less than the value of 244 to 254 for the usual palm kernel oil but still indicating the presence of a considerable proportion of glycerides of short chain fatty acids.

As in all palm kernel oils, the proportion of linoleic acid and other polyunsaturated fatty acids among the component fatty acids of mbocaya oil is very low. The composition of the component fatty acids has been reported (7) to range as follows: saturated acids, 67–68%; oleic acid, 29–31%; and linoleic acid, 2–4%. The content of unsaponifiables in the oil (6) is low, 0.25 to 0.40%. Also in common with ordinary palm kernel and coconut oils, the oil in the crude state contains practically no coloring matter, and the flavor is mild and nut-like. Refining, bleaching, and deodorization produce a bland, water-white product.

The above-described properties indicate that mbocaya oil should be suitable for use in a blended or compound-type of shortening in which the other component is hydrogenated cottonseed oil. Because of the apparently relatively high content of oleins, mbocaya oil should yield a compound-type of shortening superior to that obtained with coconut oil. On the other hand, the shortening should be substantially free of linoleins and hence more resistant to oxidation than are the ordinary compound-type of shortenings. It might also be possible to produce mixtures having suitable consistencies by interesterifying hydrogenated cottonseed oil and mbocaya oil or by blending hydrogenated mbocaya oil with cottonseed oil. To evaluate these possibilities various mixtures and products were prepared and subjected to consistency measurements. The results which were obtained will be presented and interpreted.

Materials and Procedures

The cottonseed oil, C-1, used in the tests was a refined and bleached oil of good quality obtained from a commercial source. It had an iodine value of 108.3. A portion of this oil was hydrogenated in the laboratory to obtain a product, C-2, having an iodine value of 9.8 and a capillary melting point of 61.4°C., determined according to the official methods of the American Oil Chemists' Society.

The hydrogenated cottonseed oil identified as C-3 was also prepared from a commercially refined and bleached oil and possessed an iodine value of 1.8.

The mbocaya oil identified as M-1 was a refined and bleached product possessing an iodine value of 29.5, a melting point of 22.4°C., and a saponification value of 242.8. It was prepared from a crude oil received

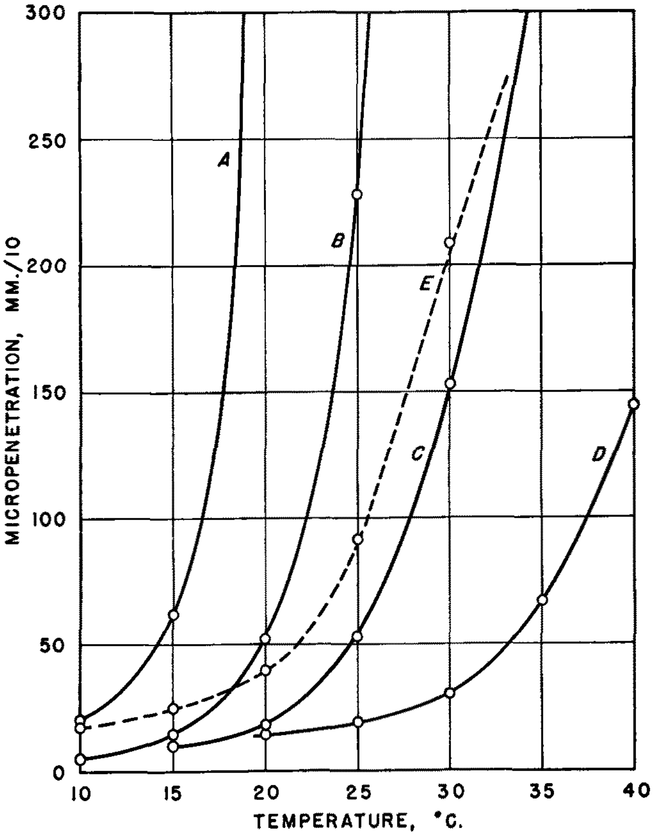

FIG. 1. Effect of hydrogenation on the consistency of mbocaya oil M-1: (A) original oil, iodine value, 29.5, (B) hydrogenated to an iodine value of 19.2, (C) hydrogenated to an iodine value of 11.2, and (D) hydrogenated to an iodine value of 0.2. Curve E represents a shortening of the all-hydrogenated type.

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