The Application of Liquid-Liquid Extraction to the Fractionation of Coconut Oil[1,2]

WILLIAM R. FISH,[3] M. H. MENAKER, P. M. ALTHOUSE and H. O. TRIEBOLD
Department of Agricultural and Biological Chemistry, The Pennsylvania State College
State College, Pennsylvania

BECAUSE of the complex composition of fats and oils and the difficulties which their analysis presents, comparatively little is known with respect to their glyceride structure. The methods available to chemists for investigations of the component glyceride composition of fats and oils have been limited. Prior to 1927 fractional crystallization was the only method available; by means of this technic small yields of certain individual higher-melting simple and mixed triglycerides were obtained from various sources. A discussion of this earlier work will be found in the review of Hilditch (1). In recent years interest in fractional crystallization as a method of fractionating glycerides has been revived (2). In 1927 Hilditch and Lea (3) introduced the permanganate oxidation method, by means of which Hilditch and his collaborators have been able to investigate quantitatively the glycerides of fats and oils in terms of their saturation and unsaturation (1). During the past several years, molecular distillation has been applied to the fractionation of glyceride mixtures, but the results have not been encouraging as far as the elucidation of glyceride structure is concerned. The literature in this field was summarized and reviewed by Detwiler (4) and by Embree (5).

The success which attended the use of liquid-liquid extraction in the petroleum and other fields suggested its application to fat and oil problems. Thus far the method has been utilized to prepare from vegetable oils fractions more highly unsaturated than the original oils (6, 7); to extract fatty acids from tall oil (8, 9); and to separate known mixtures of pure glycerides, fatty acids, and natural fats (10, 11). Consequently it seemed reasonable to believe that liquid-liquid extraction might be of value in the fractionation of fats and oils with the view of elucidating their component glyceride composition. This communication describes the fractionation of coconut oil by the batch method and by means of a continuous counter-current extractor using 95% ethanol as solvent. During the progress of these studies Oyler (12) investigated the fractionation of olive oil by means of continuous counter-current extraction.

Material and Methods

The coconut oil used in this work was edible oil which had the following physical and chemical constants: neutral equivalent, 661.5; iodine number, 8.5; $n_D^{45°}$, 1.4471.

The batch extractions were carried out in a series of six conical, glass extraction vessels, in which the coconut oil and 95% ethanol were intimately mixed at room temperature by electrically driven spiral glass stirrers. After phase separation by gravity settling the extract layer was withdrawn by siphoning, and fresh solvent added to re-extract the raffinate. In this manner 2.1 kilograms of coconut oil were separated into 43 fractions, including the final raffinate. Preliminary experiments showed that four hours of stirring were necessary to obtain equilibrium between the oil and solvent. Phase separation was allowed to proceed until the extract layer was entirely free of cloudiness. The quantities of solvent used for the first 15 extractions were equal to the estimated weight of raffinate extracted. During the remaining extractions the solvent weight was maintained constant at 1,200 gms., i.e., the weight of the raffinate during the fifteenth extraction.

TABLE I.

Fractionation Data for Methyl Esters of Fatty Acids from Glyceride Fraction No. 3.

Cut	Boiling range °C.	Pressure mm.	Weight gms.	$n_D^{45°}$	Neutral equivalent	Iodine value
1	132-141	40	3.17	1.4068	164.8	
2	141-162	40	5.81	1.4103	172.5	
3	165-167	40	5.33	1.4179	196.8	
4	167-174	40	8.57	1.4208	210.3	
5	179-179	40	11.80	1.4217	215.6	
6	179-182	40	10.36	1.4220	214.8	
7	128-132	2	6.53	1.4228	221.1	
8	132-140	2	7.55	1.4256	233.8	
9	140-142	2	5.99	1.4273	242.4	0.0
10	144-179	2	8.21	1.4331	268.8	25.1
Residue			0.0			
Holdup			1.20			
Cold Trap			1.20			
Loss			0.35			

The continuous counter-current extraction was performed in a slightly modified reflux extraction unit of the type described by Cannon and Fenske (13). The contacting, tower, and disengaging sections were fitted with electric heating coils of chromel ribbon and lagged with asbestos to prevent extreme heat losses. The heat input to the tower and contacting sections was adjusted to maintain their temperature at 40°C. while that of the disengaging section was adjusted so that ethanol distilled over at the rate of three to four milliliters per minute. During the entire period of operation a fine stream of nitrogen gas was injected into the disengaging section. The coconut oil and solvent were allowed to reach equilibrium for 48 hours before a fraction was withdrawn and solvent added. Thus 700 gm. of oil were separated into 32 fractions, including the final raffinate.

Each extract layer was subjected to distillation under reduced pressure to recover the solvent and obtain the extracted glycerides. After measuring the refractive index (at 45°C.) of each glyceride fraction, it was hydrolyzed to separate the free fatty acids. The latter were then converted to the methyl esters and fractionally distilled in a packed column. Typical fractionation data are presented in Table I. The compositions of the fractions obtained by distillation were determined by means of refractive indices, neutral equivalents, and iodine numbers.

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[3] Present address: Research Laboratories, Swift and Company, Chicago, Illinois.

Results and Discussion

Inasmuch as results obtained by the two methods of extraction were similar in all essential aspects, only those obtained by the batch method are presented.

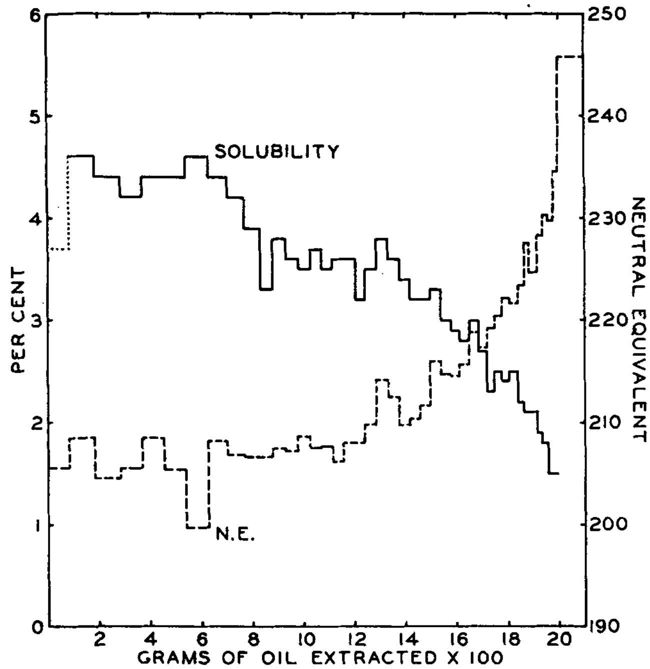

FIG. 1. Variation of solubility of glyceride fractions and neutral equivalents calculated from fatty acid composition of glyceride fractions from coconut oil in relation to weight of material extracted.

The approximate solubilities of the glyceride fractions obtained by the liquid-liquid extraction are presented graphically in Figure 1. The solubility values were calculated by dividing the weight of each glyceride fraction by the weight of solvent used plus the weight of the glyceride fraction. They clearly show that the solubility of the fractions decreased as fractionation progressed. From an initial value of about 4.5% the solubility dropped to about one-third of that at the termination. The low value obtained for the first fraction (dotted line) is due to the fact that much of the ethanol remained dissolved in the fat layer and, after phase separation, did not contribute to the volume of the extract layer. Consequently, the weight of that glyceride fraction was low relative to the quantity of solvent used in the extraction.

Concomitant with the decrease in solubility was an increase in the neutral equivalents [4] (Fig. 1), refractive indices (Fig. 2), and iodine numbers [5] (Fig. 2) of the extraction fractions. All these factors are indicative of a separation of the coconut oil into fractions containing glycerides of progressively larger molecular structure and of increasing unsaturation. The trend of the refractive indices follows very closely that of the iodine numbers, which is in agreement with the fact that in general the introduction of unsaturated linkages into a molecule causes an increase in its index of refraction. It should be noted, however, that the trends of these physical and chemical properties did not commence to change until approximately one-half of the coconut oil had been extracted.

Inasmuch as the solubility of glycerides containing fatty acids of the acetic acid series is known to decrease with increasing chain length of the acids, it would be expected that the earlier, more soluble glyceride fractions would contain more short-chain acids than the later, less soluble ones; and that the converse would be true with respect to glycerides containing longer-chain acids. In general, this expectation was borne out by the results obtained as will be apparent from an examination of Figure 3. The proportions of the shorter-chain acids (caproic to lauric) in the glyceride fractions decreased as extraction progressed whereas the proportions of longer-chain acids increased.

It is interesting to note from Figure 3 that the glycerides containing oleic acid are found in greater proportions in the later glyceride fractions. This fact would seem to indicate that the solubility of triolein is of the magnitude of the solubility of glycerides containing longer-chain saturated acids. However, no data are available on the solubility of triolein relative to the saturated glycerides; and it cannot be concluded from observations made in the present study whether the solubility of triolein is comparable to that of the longer-chain saturated glycerides or whether triolein compares in solubility with the shorter-chain saturated glycerides but appears in increasing proportions in the later extraction fractions because it is more soluble in the higher glycerides than in the solvent employed.

Although extraction effected a separation of the coconut oil into fractions different in composition from the original oil, all the glyceride fractions contained at least six and in most cases all of the eight fatty acids present in coconut oil. It is possible that this is due, in part at least, to the fact that the component fatty acids of coconut oil may be distributed among the glyceride molecules to a very large degree, in accordance with Hilditch's rule of even distribution. If this were the case, the oil might contain

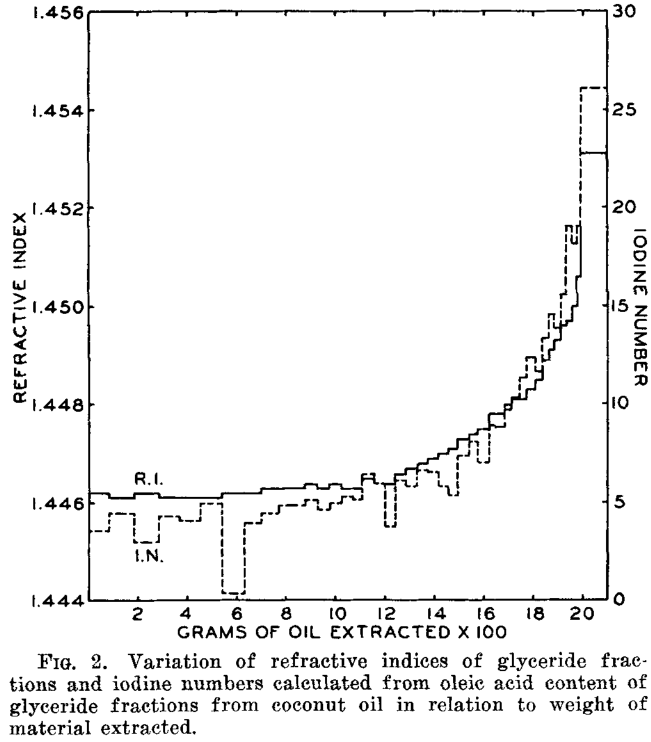

FIG. 2. Variation of refractive indices of glyceride fractions and iodine numbers calculated from oleic acid content of glyceride fractions from coconut oil in relation to weight of material extracted.

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[4] Calculated from fatty acid composition of glyceride fractions.
[5] Calculated from oleic acid content of glyceride fractions.