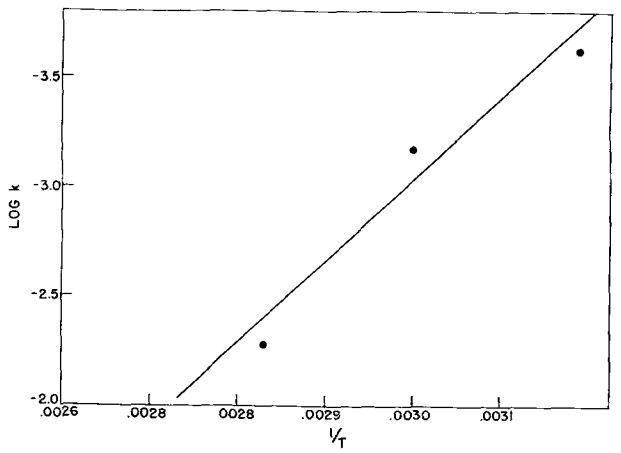

FIG. 4. Relationship between the reciprocal of the absolute temperature of storage and the specific reaction rate constant for the reaction of gossypol in cottonseed oil.

The reaction product is the same at each storage temperature, and there is no evidence of secondary or of consecutive reactions under the anaerobic conditions used. This suggestion is supported by the fact that the rate studies show the second-order equation to hold even when a large proportion of the gossypol has reacted. Further there is an absence of a drift with time or with temperature in the absorptivity of the reaction product, as may be seen from the data recorded in Tables I, II, and III. In addition, the van't Hoff relationship, $\log k = K/T + R$, where k is the specific reaction rate constant, T is the absolute temperature, and K and R are constants, holds reasonably well, as shown by the data plotted in Figure 4.

The temperature dependence of the specific reaction rate constant for the fixation of gossypol in cottonseed oil is indicated by the data plotted in Figure 4, where the logarithm to the base 10 of the specific reaction rate constant is plotted against the reciprocal of the absolute temperature. The energy of activation for this reaction was calculated to be 17,000 calories per mol.

Summary

It was shown in experiments carried out under anaerobic conditions that the fixation of gossypol in cottonseed oil is a reaction of the second order with respect to gossypol. In other words, the rate of fixation is proportional to the square of the gossypol concentration in the oil. The rate of fixation is temperature-dependent and increases 22-fold with an increase in temperature from 40° to 80°C.

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The Separation of Glycerides by Crystallization in a Thermal Gradient[1]

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FRACTIONAL CRYSTALLIZATION from solvents has been used for a long time to separate natural mixtures of glycerides and other lipides (1); however the separation achieved is generally much poorer than would be predicted on the basis of the relative solubilities of the lipides under the conditions of the separation. This has been attributed to mixed crystal formation, the mutual effects of the solutes on the other's solubility, and the difficulty of completely separating the crystals and mother liquor. These effects can be minimized and the separation improved by repeated crystallizations from dilute solutions, but this is a laborious and time-consuming operation. Recently Baker and Williams (2) designed an apparatus which automatically subjects a solute to repeated recrystallizations as the solution moves through a thermal gradient. They demonstrated the effectiveness of the apparatus in the separation of polystyrene into fractions of different molecular weights. Since the use of this apparatus appeared promising as a technique for separating glycerides and many other lipide mixtures, an apparatus similar to that of Baker and Williams was constructed. The present paper presents the results achieved in the separation of some synthetic triglycerides by using this apparatus.

Experimental

The apparatus is essentially a copy of that of Baker and Williams (2). The only major modification was the use of mechanical refrigeration instead of cold water to cool the bottom of the column. In these experiments acetone was the starting solvent, and the solvent reservoir was filled with 200 ml. of acetone. Skellysolve B was the eluting solvent, which was added continuously to the solvent reservoir as fractions were collected. The sample was 0.5 g. and was made up of equal weights of the two glycerides to be separated. Fractions of 10.5 ml. were collected by a fraction collector. The temperature at the bottom of

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the column was chosen so that the more soluble component came out in 10 to 12 fractions.

The Skellysolve B was distilled over potassium carbonate. The acetone was refluxed for three hours with potassium permanganate and sodium hydroxide, then distilled.

1-Oleo-2,3-dipalmitin was prepared as follows. Oleic acid was made according to the procedure of Knight *et al.* (3). 1,2-Isopropylidine glycerol was prepared according to the procedure of Malkin and Shurbagy (4). This was reacted with the oleic acid to form 1-mono-olein (4). Palmitic acid was prepared by converting commercial palmitic acid to its methyl ester and distilling it in an efficient column. The methyl ester was crystallized from methanol and analyzed. S.V. 208.2 (5), theory 207.4; $n^{20/D}$ 1.4409 (corrected), calculated value 1.4406 (6). This was saponified and converted to palmityl chloride (7). This was reacted with the 1-monopalmitin to form 1-oleo-2,3-dipalmitin (8). I.V. (9) 29.0, theory 30.5; $n^{40/D}$ 1.4552, reported 1.4556 (10).

Trimyristin was made by reacting methyl myristate with triacetin, using a sodium methoxide catalyst and reduced pressure. The resulting saturated glyceride was crystallized from Skellysolve B. The methyl myristate was prepared from commercial myristic acid and distilled. It had the following constants: S.V. 231.3 (5), theory 231.4; $n^{20/D}$ 1.4368, calculated 1.4368 (6). The trimyristin had the following constants: $n^{60/D}$ 1.4430, reported 1.44285 (11), S.V. (5) 232.6 calculated 233.1; m.p. 57.6°C., reported 57.0°C. (12).

The trilaurin was prepared by the same method as the trimyristin. The methyl laurate had the following constants: $n^{20/D}$ 1.4320 (corrected), theory 1.4320 (6), S.V. (5) 261.4, theory 261.7. The trilaurin had the following constants: $n^{60/D}$ 1.4401, reported 1.4404 (11); S.V. 260.4 (5), theory 263.5; m.p. 46.2°C., reported 46.4°C. (12).

The tripalmitin was prepared in the same way as the trimyristin and had the following constants: $n^{65/D}$ 1.4427; m.p. 65.8°C., reported 65.5°C. (12); S.V. (5) 206.8, theory 208.6.

The elution of the glycerides from the column was followed by taking a suitable aliquot of the eluate from each fraction, evaporating the solvent, and analyzing it for ester content by the procedure of Hack (13). A standard curve of the major glyceride in the fractions being tested was always made at the same time. The solvent was removed from the aliquots by heating them in warm water and drawing air over their surface. In the case of 1-oleo-2,3-dipalmitin nitrogen was drawn over the surface instead of air to prevent oxidation. The determinations were run in duplicate and the duplicates usually agreed within 3%.

For determination of traces of the higher-melting, more insoluble glyceride, in the presence of large amounts of the lower-melting, more soluble glyceride, determining the melting point of the mixture is a sensitive technique. Standard curves were prepared with mixtures of the various glyceride combinations. These contained 50, 25, 12.5, 6.25, 3.12, and 1.56 mol percentage of the higher-melting component. The melting points were taken by the official method of the American Oil Chemists' Society (14). The melting point of the unknown mixture was compared with the standard curve for that mixture to obtain the mol percentage of higher-melting component.

Theory of the Separation

The degree of separation possible by crystallization is limited by the ratio of the solubilities of the solutes in question in the solvent and the effect that they exert on each other's solubility. The ideal solution theory makes possible some prediction of how these factors will affect the separation. This theory was worked out by Hildebrand (15), and its application to fats has been discussed by Bailey (12). Solutions of glycerides in other glycerides follow the theory very closely. This has recently been confirmed by Lutton (16) for certain glyceride mixtures. Also the empirical relations of Kartha (17, 18) which were confirmed by Brooker and West (19) can be derived from the ideal solution theory by making certain approximations. In most organic solvents the solubility of triglycerides departs considerably from the ideal solubility; however one might assume that glycerides of similar structure would depart from ideality in the same direction and by the same relative amounts under any given conditions. If this is so, idea solution theory might still make valid predictions about the separation that can be achieved.

The theory states that:

$$\ln(1/S) = \triangle H(1/T - 1/T_m)/R \qquad (1)$$

where $\ln(1/S)$ is the natural logarithm of the reciprocal of the mol fraction of the solute, $\triangle H$ is the heat of fusion of the solute, R is the gas constant, T is the absolute temperature of the solution, and T_m is the melting point of the solute, and $T < T_m$. It has also been shown that for simple saturated glycerides in a particular crystal form that $\triangle H$ and $\triangle H/T_m$ may be calculated from additive constants (12). Thus

$$\triangle H = 3[(n-2)a + b] \qquad (2)$$

$$\triangle H/T_m = 3[(n-2)c + d] \qquad (3)$$

where n is the number of carbon atoms in one saturated fatty acid chain of the simple glyceride and "a" and "b" are constants. If two glycerides having fatty acids of chain lengths n_1 and n_2 are considered and the above equations are combined, it can be shown that:

$$\ln(S_2/S_1) = 3(n_1 - n_2)\,[(a/T) - c]/R \qquad (4)$$

where S_2/S_1 is the ratio of the solubilities of the glycerides corresponding to n_2 and n_1, respectively.

It can be seen from equation 4 that the ratio of the solubilities will be greater the greater the difference in chain length and the lower the temperature of the solution. Using the values $a = 1.06$ Kcal./mol and $c = 0.00269$ Kcal./mol°K. (12), it is possible to predict that simple glycerides with fatty acids differing in chain length by 2 carbons or more should be easily separated at 0 to 10°C. If it is assumed that the values for a and c are the same for mixed saturated glycerides, then it is found that glycerides differing by 4 in their carbon atom content should be separable at reasonable values of T. Glycerides differing by only two carbons however would not be separated very well at temperatures that are practically attainable (−70°C.). However the $\triangle H$ and $\triangle H/T_m$ of mixed glycerides is also affected by the relative chain lengths of the component fatty acids, and in specific cases the separation may be better or worse than these predictions. Unfortunately there are no data of the effect of double bonds on $\triangle H$ and $\triangle H/T_m$. The effect of one double bond on $\triangle H$ may be estimated from the data of Lut-

ton (16). If this is introduced into equation 4, it is found that glycerides containing one double bond ought to be separable from the corresponding saturated glyceride. In these calculations ratios of S_2/S_1 >19 were considered satisfactory.

However the assumptions made in using the above equations would also predict that a binary mixture of the glycerides corresponding to n_1 and n_2 would form an eutectic mixture. This has been found to be true experimentally. It has been found that the eutectic composition tends to be the limiting factor in separations in solution as well as from melts (12). Therefore the eutectic composition will probably be found to limit the separations obtainable by crystallization more than the relative solubilities. The eutectic composition cannot be predicted with accuracy. However the eutectic composition in glycerides usually melts within a few degrees of the melting point of the lower melting component. A rough estimate of the eutectic composition may be obtained by substituting the melting point of the lower melting component for T in equation 4. It is found that if the fatty acids in the glycerides to be separated differ in chain length by 4 or more carbons each, or if a double bond is introduced into one of the fatty acids, eutectic formation will not seriously interefere with the separation.

Results and Discussion

The elution curves for the glyceride mixtures are shown in Figures 1, 2, and 3. The peaks to the left of the figures represent the more soluble component only. After the more soluble component had emerged, the refrigeration was turned off, and about two fractions later the higher melting point component emerged quickly from the column. This is illustrated by the steeply rising line to the right of the figures.

Table I shows the melting points of the glyceride mixtures used to establish the standard curves.

TABLE I

Melting Points of the Triglyceride Mixtures at Various Compositions

Mole % of higher melting component	Tripalmitin and trilaurin	Tripalmitin and 1-oleo-2,3-dipalmitin	Trimyristin and trilaurin
100	65.8	65.8	57.6
50	62.2	61.8	53.2
25	58.5	57.9	49.6
15			46.0
12.5	54.0	53.9	44.6
10			45.2
8			45.4
6.25	51.2	49.0	45.3
3.12	47.7	37.1	45.6
1.56	45.8	33.2	45.9
0	46.2	31.6	46.2

The separation of the trilaurin and the tripalmitin is illustrated in Figure 1. The top of the column was at 35°C. and the bottom at 10°C. Three flow rates were used: 22, 60, and 110 min. per fraction of 10.5 ml. The flow rate of 22 min. per fraction was obviously too fast for the column to operate a equilibrium. This led to a tailing of the peak. There was not a great improvement in going from 60 to 110 min. per fraction, but in subsequent experiments the 110 min. rate was used.

In the separation of the trilaurin and tripalmitin, the trilaurin emerged in two peaks. This phenomenon was noted with the other mixtures studied to a greater or lesser extent. Its cause is not understood and will be discussed below.

At the 22, 60, and 110 min. flow rates the apparent

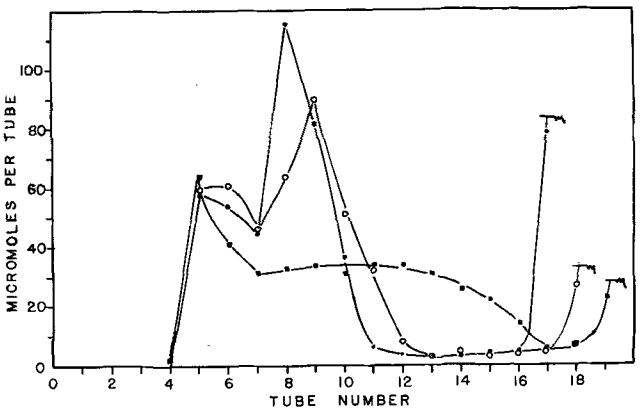

FIG. 1. Elution curves for the tripalmitin-trilaurin mixture, using a temperature gradient of 25°C. (10°–35°C.) and acetone-Skellysolve B as solvents. ■ Flow rate of 22 min. per tube, ○ flow rate of 60 min. per tube, • flow rate of 110 min. per tube.

recovery of ester determined by Hack's procedure (13) was 106, 108, and 105% for the trilaurin and 90, 85, and 98% for the tripalmitin, respectively. These are not very reliable for measuring the degree of separation because tripalmitin and trilaurin have different standard curves, and when the unknown analyzed is a mixture of the two, the choice of standard curves becomes arbitrary. Also most of the tripalmitin was collected in a few fractions. These had to be diluted for analysis, and small errors in the analysis were magnified in the calculation of total tripalmitin recovered.

The degree of contamination of the trilaurin with the tripalmitin can be estimated by extrapolating the tripalmitin curve under the trilaurin curve. The area under the extrapolated portion of the curve is proportional to the amount of tripalmitin contaminating the trilaurin. By this procedure the tripalmitin contamination of the trilaurin is 6, 2.5, and 2% for the 22, 60, and 110 min. flow rates, respectively. By melting-point analysis of selected fractions the contamination appears to be 8, 5 to 7, and 6 to 7% for the 22, 60, and 110 min. flow rates, respectively. Table I indicates that an eutictic mixture forms at about 1% tripalmitin, and this should limit the separation.

To investigate this further, tripalmitin was run alone through the column with 35° to 10° and 25° to 0°C. gradients. The results are shown in Figure 4. There are irregularities in the curve, but if tripalmitin is put through the column twice, these irregularities still persist. Therefore they do not seem to be caused by an impurity in the tripalmitin but rather to some irregularity in the operation of the column. The amount of ester present in fraction 4 to 11 is greater than would be anticipated from extrapolation of the curve plotted for fractions after 11; moreover the amount of material in these fractions agrees well with the amount found by the melting point method. Therefore it can be concluded that the melting-point method is the more reliable criterion for the separation actually achieved.

The fact that the actual separation is poorer than the eutectic composition will allow may result from the fact that the tripalmitin is more soluble than expected or the trilaurin is less soluble than expected. Comparison of the solubility of trilaurin in acetone (20) with the values found in fraction 4 or 5 and comparison of the solubility predicted for trilaurin and tripalmitin by the ideal solubility equation leads to

the conclusion that the solubility of trilaurin is of the correct order of magnitude while that of the tripalmitin is 20 to 25 times higher than the ideal theory predicts. Thus the separation of trilaurin and tripalmitin shown in Figure 1 does not come up to theoretical prediction because of an unexpectedly high solubility of tripalmitin.

Figure 2 shows the separation of a 1-oleo-2,3-dipalmitin and tripalmitin. A gradient of 25° to 0°C. was used. Again it appears that a flow rate of 110 min. per fraction is considerably superior to 22 min. per fraction. The apparent recovery of the 1-oleo-2,3-dipalmitin at the 22 and 110 min. flow rate was 105 and 92%, respectively. The apparent recovery of the tripalmitin was 101 and 99%, respectively. The amount of tripalmitin in the 1-oleo-2,3-dipalmitin determined by extrapolation was 5.5% and 4% at the 22 and 110 min. flow rates, respectively. By melting point the contamination was 12% and 5 to 6%, respectively. As with the previous separation, when tripalmitin is run alone, an amount comes out in the first 11 fractions which agrees with that found by melting-point determinations. Again the solubility of the tripalmitin seems to be higher than theory would predict, and this is the limiting factor in the separation.

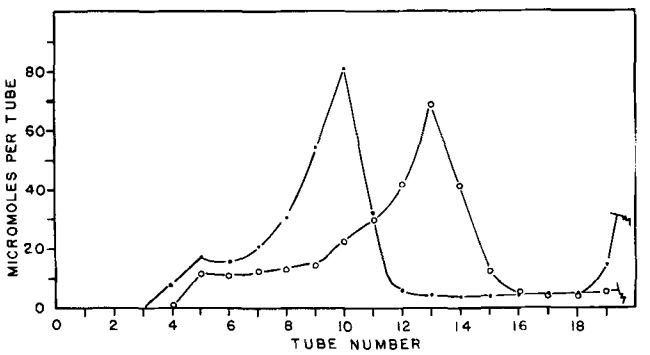

FIG. 2. Elution curves for the tripalmitin-1-oleo-2,3-dipalmitin mixture, using a temperature gradient of 25°C. (0°–25°C.) and acetone-Skellysolve B as solvents. ○ Flow rate of 22 min. per tube, • flow rate of 110 min. per tube.

Figure 3 shows the results of the separation of the trilaurin-trimyristin mixture. A 35° to 10°C. gradient was used and a flow rate of 115 min. per fraction. In this case the trimyristin came through so quickly that it was not possible to tell much about the separation by extrapolation. The melting points indicated that there was 12 to 14% of the trimyristin in the trilaurin. The data in Table I show that trilaurin and trimyristin form an eutectic mixture containing about 12% trimyristin. This was obviously the limiting factor in this separation. The apparent recovery of the trilaurin was 130% and of the trimyristin 92%.

All the elution curves show that the first component comes out in two peaks. The first peak comes out with approximately the volume of solvent required to move the solute from the top to the bottom of the column. There is a minimum solubility about fraction 7, and then the rest of the material comes out. This might be caused by running the solvent through the column too rapidly. Thus solute in solution at the warm top of the column might issue from the cold bottom of the column as a supersaturated solution because it did not have time to reach equilibrium on its way through the

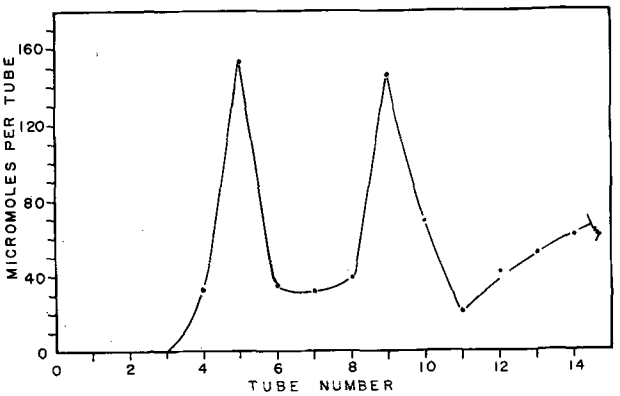

FIG. 3. Elution curve for the trimyristin-trilaurin mixture, using a temperature gradient of 25°C. (10°–35°C.), a flow rate of 115 min. per tube, and acetone-Skellysolve B as solvents.

column. This would explain the first large peak. On the other hand, material in a crystalline form in the colder portion of the column would not have time fully to saturate the solvent rapidly moving past it, and the solution would issue from the column undersaturated. This would explain the minimum between the peaks. Further change in the solvent composition might bring the remaining material out of the column to form the second peak. However slowing the rate from 22 to 110 min. per fraction did not reduce the amount of glyceride coming out in the first fraction. Another possibility is that the triglycerides are actually less soluble in mixtures of acetone and small amounts of Skellysolve B than they are in acetone alone. This was tested by using an apparatus similar to that of Privett *et al.* (20). Fraction 7 was estimated to contain about 15% Skellysolve in acetone by volume. It was found that 0.5 g. of trilaurin would dissolve in 100 g. of pure acetone at 11.1°C. With 15% Skellysolve in acetone, 0.5 g. dissolved in 100 g. of solvent at 9.0°C. With 10% Skellysolve in acetone the corresponding temperature was 9.75°C. Thus in the range of minimum elution of the trilaurin the solubility of trilaurin in Skellysolve-acetone was found to increase with the Skellysolve concentration. The splitting of the first peak was not caused by the presence of the high melting component for running trilaurin alone through the column gave a split peak, as shown in Figure 5.

Possibly the splitting of the peak of the first component to come out results from the formation of different polymorphic forms of its crystals under the

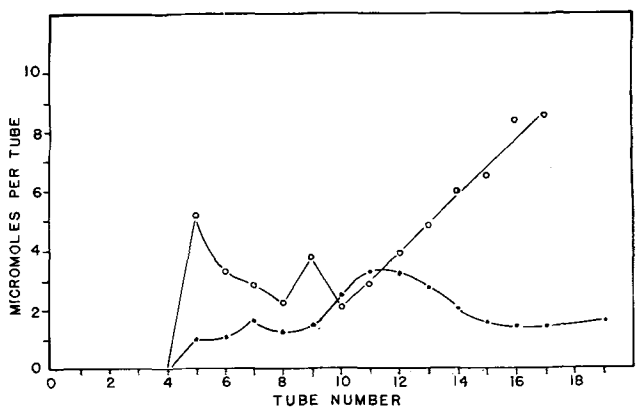

FIG. 4. Elution curve for tripalmitin alone, using a flow rate of 110 min. per tube and acetone-Skellysolve B as solvents. ○ Temperature gradient of 25°C. (10°–35°C.), • temperature gradient of 25°C. (0°–25°C.).

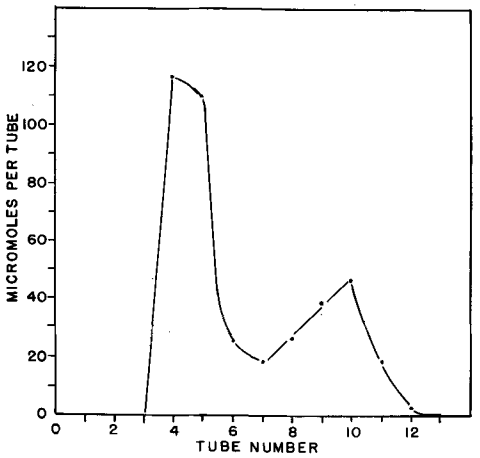

FIG. 5. Elution curve for trilaurin alone, using a temperature gradient of 25°C. (10°–35°C.), a flow rate of 110 min. per tube, and acetone-Skellysolve B as solvents.

conditions of the separation on the column. Further research will be necessary to explain this phenomenon.

Conclusions

The data presented indicate that fractional crystallization in a thermal gradient has definite possibilities as a tool in the separation of glycerides and other lipides. Even though the results were not as good as theoretically possible in some cases, the results indicated that the separation was as good as the actual solubilities under the conditions of the separation would allow.

In the present apparatus the separation is speeded by the use of gradient elution. This same effect could be achieved by raising the temperature of the bottom and top of the column at the same rate. By doing this, one solvent could be used, and the monitoring of the eluate as it came off the bottom of the column by some physical method might become more feasible.

This apparatus should be helpful in many separations of interest to lipide chemists. It should be of use in any of the separations where solvent crystallization has proved effective. For example, it might be used to study the glyceride structure of natural fats. It might be used to separate saturated and unsaturated fatty acids or acids differing considerably in chain length. It appears promising for the separation of waxes, phosphatides, and other complex lipides. It should be useful in separating branched- and normal-chain fatty acids and in the separation of *cis* and *trans* isomers. It is our hope that we may explore some of these applications in the future.

Summary

An apparatus designed to separate materials by automatic recrystallization in a thermal gradient has been tested for its ability to separate model glyceride mixtures. The theory of the separation has been discussed. The apparatus was able to separate the model mixtures efficiently; the separation was limited only by the actual relative solubilities of the components and the formation of eutectic mixtures. This apparatus should be useful in the separation of many lipide mixtures where crystallization is an appropriate technique.

Acknowledgments

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A Uniform Basis for Reporting Analytical Data on Fatty Materials[1]

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THE CHEMISTRY of the fatty acids and their derivatives is one of the oldest branches of organic chemistry, dating from Chevreul. The development of the field required some means of measuring purity and identity of pure compounds and of analyzing complex natural and industrial mixtures. The gradual evolution led to a variety of methods for analysis of the type and quantity of functional groups. In so doing, certain arbitrary units for these measurements were introduced and their use was perpetuated. Thus there are in existence the iodine number, saponification number, acetyl value, acid number, and so on (1). There is no doubt of their usefulness, but the existence of a variety of definitions and of the arbitrary units (grams of I_2/100 grams of sample, milligrams of KOH/gram of sample . . .) makes intercomparison difficult and their use a needless burden to the memory. In short, their use is a measure of historical impotence. Even the

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