to weathering and some of the other qualities may be attributed in part to this factor. Similarly the polyvinyl esters are more readily gelled by heat treatment, or by being allowed to stand in partly filled containers with driers present, than are the corresponding glycerides. Gelation by the influence of heat alone occurs rapidly at temperatures above about 250°C. with polyvinyl soybean esters, and at considerably lower temperatures than this when the acid radicals of the esters include conjugated fatty acids. The partially hydrogenated sardine ester, B, Table I, gelled in 9 min. in a Browne heat test, in comparison with a very slightly shorter time for a sample of tung oil tested at the same time. High temperature cooking with varnish resins therefore is not appropriate for these polyvinyl esters. At room temperatures in filled containers the esters apparently will keep indefinitely without gelation. Solutions with added drier are susceptible to gelation when held in partly filled containers. Varnishes containing rosin esters appear to be less subject to this than solutions not containing the resin.

Summary

Mixed polyvinyl esters of acetic acid and higher fatty acids can be made by ester interchange between polyvinyl acetate and fatty esters. Their properties indicate that some of these products merit attention as materials for use in the drying oil industries. Because of their enhanced drying qualities and greater tolerance of the presence of saturated acid components, in comparison with the corresponding glycerides, they potentially broaden the range of fatty materials utilizable as drying oils.

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The Countercurrent Distribution of Pure Monoglycerides and Some Related Substances[1]

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THE COUNTERCURRENT distribution characteristics of several monoglycerides both of natural and synthetic origin have been determined and reported (1, 2). They were used to help identify the intermediate products formed during digestion of triglycerides by the rat (3) as well as to study the isolation and identification of monoglycerides in lard and breads (2) and from the intestinal contents of humans (4).

The present investigation was set up to determine the countercurrent distribution curves for a selection of pure monoglycerides, which served as a basis for a study of 2-monoglycerides (5) as well as for those mentioned above (2, 4). Nine monoglycerides were thus examined, from which certain effects due to the structural variations could be ascertained. Countercurrent distributions were also made for a diglyceride and for a diglycerol monoester.

Experimental

Procedure. The countercurrent distributions were carried out in a 50-tube, all-glass apparatus similar to that described by Craig (6). The apparatus was modified slightly in connection with the incorporation of an automatic drive (7). The procedure used to determine the distribution curves for the present study was essentially that reported in the previous publication. The solvent system employed consisted of Skellysolve B and an aqueous methanol solution containing 15% water by volume. The sample for distribution, about 120 mg., was weighed directly into a 12-ml. volumetric flask and dissolved in the petroleum solvent phase. A 10-ml. aliquot was transferred by pipette to the first tube of the apparatus. At the end of the distribution the entire contents of each tube was syphoned into tared cups. After complete removal of solvents, first by warm air and finally by vacuum, the net weight of each cup was determined. A plot of this weight against the tube number gave the distribution curve.

Materials. The 1-monoglycerides of myristic, palmitic, and stearic acids were synthesized from glycerin and the pure acid. The reaction mixture was molecularly distilled to isolate the monoglyceride component. This fraction was further purified by crystallization from methanol until the monoester content by periodic acid analysis reached 99% or better. Monobutyrin was an Eastman Organic Chemical (Cat. No. 4695). The 2-monostearin was prepared by hydrogenolysis of 1,3-benzylidene-glycerol-2-monostearate (8). The 2-mono-olein was isolated from the molecularly distilled mono-olein by solvent crystallization as explained in the following paper (5).

Distilled monoglycerides of lard fatty acids were prepared from the reaction of lard with glycerol. Using repeated molecular distillation as the sole method of purification, it was not possible to increase the monoester content above 92 to 94% as indicated by periodic acid analysis. This particular sample was once redistilled, and contained 92% monoglycerides.

Diglycerol monoesters of "cottonseed oil" were synthesized by reacting with diglycerol the acids obtained by saponification of the cottonseed oil. The monoester fraction was obtained by molecular distillation.

The diglyceride sample is essentially a mixture of

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[1] Communication No. 215 from the Laboratories of Distillation Products Industries.

the diglycerides of palmitic and stearic acids. It was prepared from hydrogenated lard and purified by molecular distillation.

Results and Discussion

The countercurrent distribution curves for the various glycerides studied are presented in Figures 1 to 5.

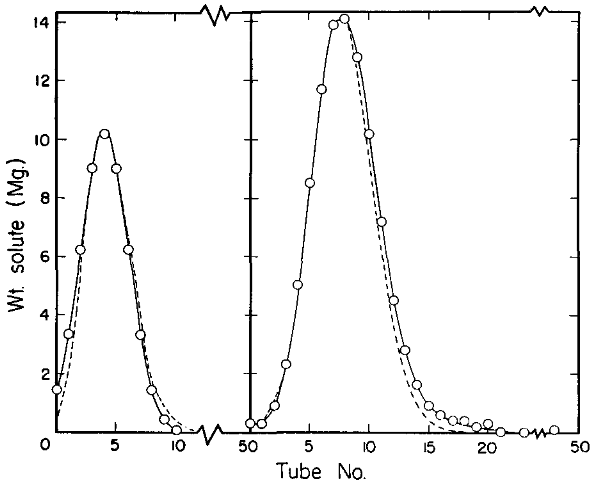

FIG. 1. Countercurrent distribution curves.
Left: 1-monomyristin.
Right: 1-monopalmitin.

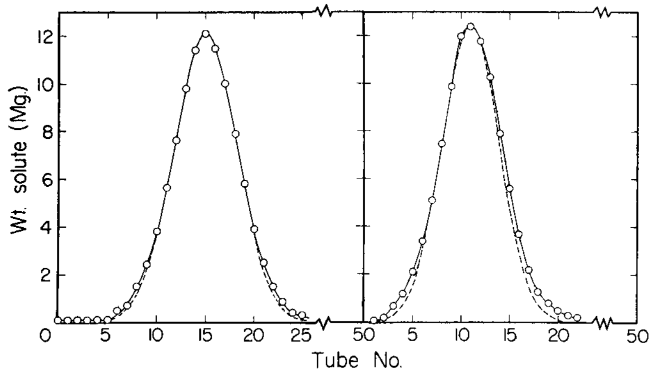

FIG. 2. Countercurrent distribution curves.
Left: 1-monostearin.
Right: 2-monostearin.

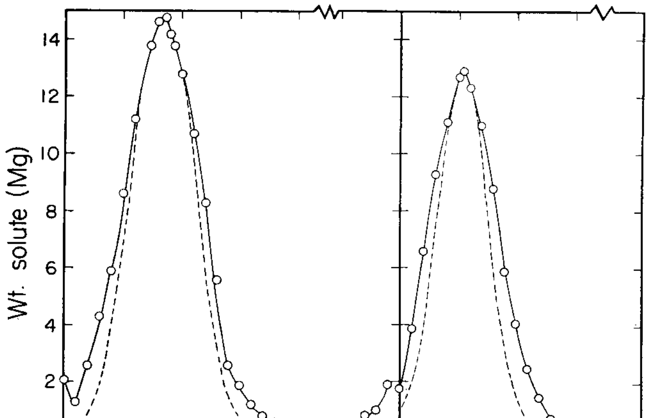

FIG. 3. Countercurrent distribution curves.
Left: 1-mono-olein.
Right: 2-mono-olein.

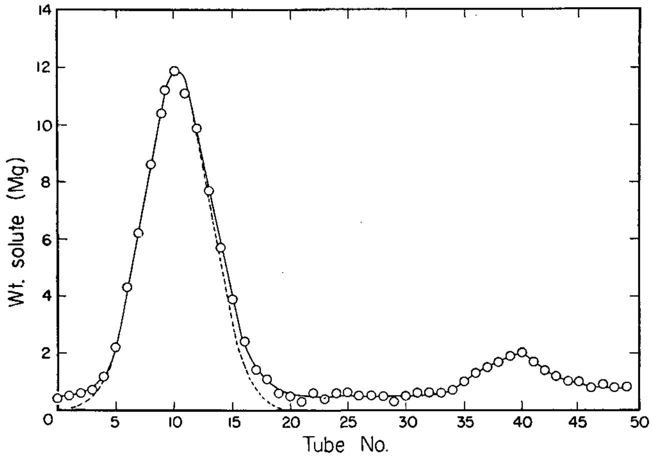

FIG. 4. Countercurrent distribution curve for oxidized 2-monostearin.

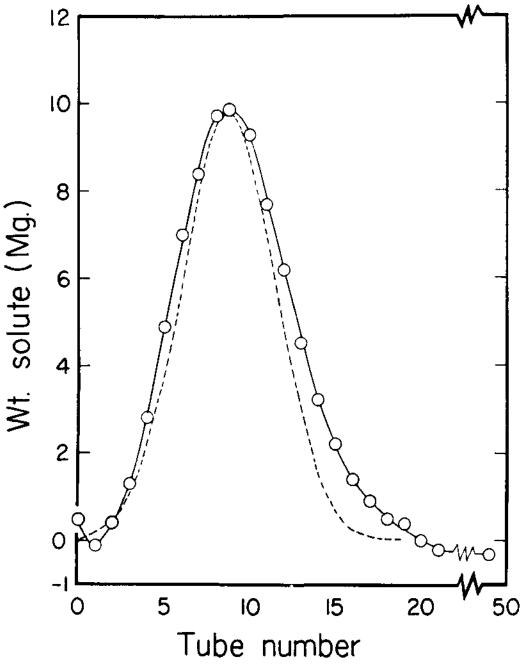

FIG. 5. Countercurrent distribution curve for distilled monoglycerides of lard.

The tube number of the peaks and the corresponding partition coefficient for each substance are given in Table I. Those substances of Table I which peak near or beyond the terminal tubes are not included in the graphs. The partition coefficients, K, were calculated from the experimental data by the following relationship derived from the binomial theorem (9):

$$K = \frac{T_r}{T_{r-1}} F \tag{1}$$

Each partition coefficient in Table I is the average of at least four pairs of tubes T_r and T_{r-1}, which were selected in the region of the peak.

Since the number of transfers applied in these distributions is relatively large, the theoretical curves were computed by the exponential equation (10)

$$y = \frac{1}{\sqrt{\frac{2\pi nK}{(K+1)^2}}} e^{-\frac{x^2}{\frac{2nK}{(K+1)^2}}} \qquad (2)$$

using the partition values of Table I. These theoretical curves are included in each figure as broken lines.

TABLE I

Distribution Data for Monoesters

No.	Substance	Peak tube for 49 transfers	Distribution coef. K
1	1-monobutyrin	>0	......
2	1-monomyristin	4	.101
3	1-monopalmitin	7.75	.194
4	1-monostearin	15.0	.452
5	2-monostearin	11.0	.299
6	2-monostearin (oxidized)	10.25	.270
7	1-mono-olein	8.3	.210
8	2-mono-olein	5.5	.128
9	diglyceride	~48	......
10	diglycerol monoesters from cottonseed oil acids	1.25	......
11	distilled monoglycerides of lard fatty acids	8.75	.222

The agreement between experimental and theoretical curves in almost every case is excellent. Most of the monoglycerides studied therefore were of reasonably high purity. The broad curve for 2-mono-olein however reveals a lesser degree of purity for this material. It will be remembered that this glyceride was isolated from 1-mono-olein by crystallization, and apparently the separation was not perfect. The sample was known to contain 6% 1-mono-olein (5) by periodic acid analysis. Good agreement was also obtained with the distilled monoglycerides from lard fatty acids.

The results disclose certain generalities between structure and partition values for the model monoglycerides studied. The value of the partition coefficient increases with the increasing chain length of the acid radical in the molecule. In other words, the polarity of the monoglyceride lessens as the number of carbon atoms in the acid radical becomes greater. The effect is observed for the series 1-monobutyrin, 1-monomyristin, 1-monopalmitin, and 1-monostearin in which the partition coefficients vary from about 0 to 0.452. A plot of these partition values *versus* the chain length is given in Figure 6. The curve rises sharply to a partition value of about 0.1 but then takes on a more gradual ascent to the value for stearic acid. This implies that the monoglycerides of the lower fatty acids will be more difficult to separate one from another than those composed of acids having 14 or more carbons.

The 2-mono-olein and 2-monostearin have lower partition coefficients than the corresponding 1-monoesters. The differences shown for each of these pairs should be sufficient to permit their separation in part, at least.

The increased polarity induced by unsaturation is exhibited in the values for the partition of oleates and stearates. The more polar oleates have partition coefficients which are considerably less than those for the stearates. The single double bond in 1-mono-olein is almost as effective in decreasing the partition coefficient as a reduction of two CH_2-groups in the acid part. The partition coefficient for 1-mono-olein is .210 compared to .194 for 1-monopalmitin.

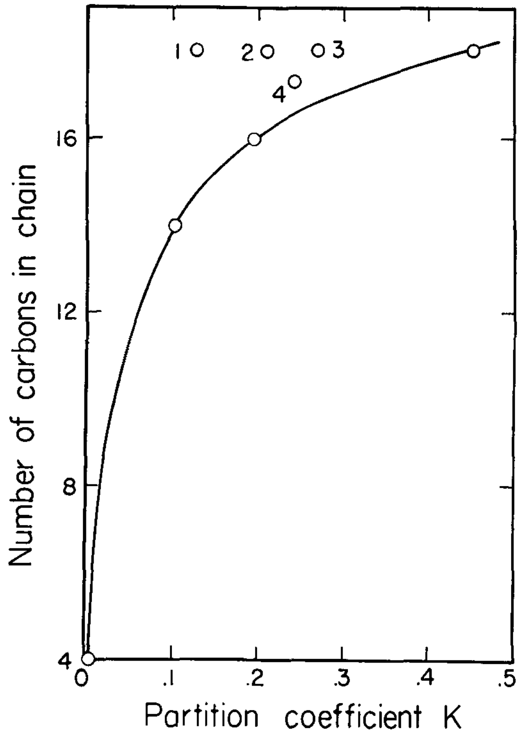

Fig. 6. Relationship between partition coefficients and chain length.

1. 2-mono-olein.
2. 1-mono-olein
3. 2-monostearin.
4. Distilled monoglycerides of lard.

For comparative purposes the partition values for 1-mono-olein, 2-mono-olein, and 2-monostearin are located in their proper places on Figure 6. The effect of structure on the partition coefficient is readily apparent for these 18-carbon acid monoglycerides. A value for distilled monoglycerides of lard is also included, which was obtained by computation on the basis that lard has approximately the following composition: 50% oleic acid, 35% palmitic acid, and 15% stearic acid. A partition value of 0.241 was thus obtained as compared to the 0.222 value resulting from the direct distribution of the lard monoglycerides. If a correction for the presence of 2-monoglycerides was included, the computed value would be smaller and in better agreement with the experimental one. This shows that in somewhat of a crude manner the partition coefficients can be deduced from the coefficients of pure monoglycerides and the approximate composition of monoglyceride mixtures.

The diglycerides of hydrogenated lard were found to be less polar than expected. The partition coefficient is comparable to that of a triglyceride, showing that the single hydroxyl group has little, if any, influence on the polarity of this type of molecule. This result has been found previously by others (1, 3). The diglycerol monoesters on the other hand are extremely polar. Under the conditions used, a well-developed maximum occurs in the curve with a peak at tube No. 1.25.

The second paper (5) of this series is concerned with the matter of establishing the presence of 2-monoglycerides in commercial monoglyceride mixtures as well as in pure synthetic monoglycerides. In one approach toward this end, use is made of the fact that periodic acid can oxidize preferentially 1-monoesters and not the 2-monoesters. Accordingly the countercurrent distribution curve for oxidized 1-monostearin, for example, is void of any monoglyceride peak. A poorly defined peak appears however at a higher tube number. This peak is due to the hydroxyacetaldehyde ester which is the reaction product of the oxidation.

Oxidation of 2-monostearin, on the other hand, survives the periodic acid treatment and comes through the distribution in its proper place. Figures 2 and 4 are distribution curves for 2-monostearin and oxidized 2-monostearin. It will be noticed that the peak for the oxidized sample shifted slightly to a lower tube number. This, in addition to the appearance of the hydroxyacetaldehyde peak in Figure 4, clearly suggests that the original 2-monostearin was contaminated with some 1-monostearin. This was indeed the case as periodic acid analysis indicated the presence of this contaminant. The partition coefficient for pure 2-monostearin therefore is judged to be the 0.270 value.

The possibility of separating the 1- and 2-monoester has been mentioned. Calculations with Equation 2 and the partition coefficients for the 1- and 2-monostearins indicated that 150 transfers should be sufficient to resolve these substances into two separate peaks from a mixture of equal weights of the two. In addition, a yield of about 20% of each isomer should result in the tubes on the extremities of the curve. The experimental verification of these calculations was not successful, owing to the great tendency of the 2-isomer to revert readily to the 1-form. Apparently the additional time involved to carry out 150 transfers, even with the automatic equipment, over a 49-transfer distribution was sufficient for the isomerization to take place. The experimental effort expended in this direction was quite limited however.

Conclusions

1. The countercurrent distribution curves have been determined for eight pure and one commercial monoglyceride, one diglyceride, and one diglycerol monoester.
2. Certain generalities exist between the partition coefficients and the structures of the acid radicals of the monoglyceride.
    a. An increase in the chain length of the acid produces an increase in the partition coefficient.
    b. The 2-monoesters have lower partition coefficients than the corresponding 1-isomers.
    c. Unsaturation in the acid decreases the value of the partition coefficient.
3. The direct separation of mixtures of 1- and 2-monoglycerides by countercurrent distribution is thwarted by the rapid isomerization of the 2-isomer to the 1-form.

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2-Monoglycerides[1,2]

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IN THE YEAR 1920 Emil Fischer (1) established that all attempted syntheses of 2-monoglycerides up to that time had resulted in 1-monoglycerides. He pointed out the greater stability of the 1-isomer and developed an isomerization mechanism to explain this result. It was 1931 before Bergmann and Carter (2) synthesized the first 2-monoglyceride of a fatty acid (2-monopalmitin). Feuge and Bailey (3) postulated the presence of 2-isomers in mono-diglyceride interesterification mixtures but rejected them as the source of small discrepancies between theory and their observations. Mattson *et al.* (4) demonstrated the presence of unsaturated 2-monoglycerides in intestinal contents but did not isolate them. In fact, unsaturated 2-monoglycerides were not prepared until 1953 when Martin (5) used a boric acid hydrolysis rather than the classic hydrogenolysis of the intermediate. He also proposed a perchloric acid isomerization to aid in direct determination of 2-monoglycerides since periodic acid (or lead tetra-acetate) oxidation will not detect the 2-isomer (5, 6). Very recently Borgstrom (7) isolated 1- and 2-monoglycerides from *in vitro* hydrolyzed fat, using silicic acid adsorption of periodic acid oxidized products.

In a variety of publications (for example, 3) it has been established that reactions of fats or fatty acids with glycerol normally result in a randomized reaction product, that is, the composition of the product can be calculated, based on the input molar ratios. In mono-diglycerides the monoglyceride analysis by periodic acid oxidation agrees rather closely with the calculated value for total monoglyceride, assuming equal participation of all three positions possible in glycerin. This suggests that the 2-isomer played an important part in determining the composition of that equilibrium mixture. This 2-monoglyceride has been transient since complete or partial isomerization to 1-monoglyceride has occurred in the final product. It was our purpose to determine whether the final product contains a detectable quantity of 2-monoglycerides.

The work to be described shows that 2-monoglycerides do exist in commercial monoglycerides; they have been isolated; and they apparently behave as do the 1-isomers in at least one application. A rapid

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[1] Communication No. 216 from the laboratories of Distillation Products Industries.

[2] Presented at the Minneapolis meeting of the American Oil Chemists' Society, Oct. 13, 1954.