percent each of linoleic and saturated esters. It is believed that the Bertram value for saturated esters is essentially correct, and that the final product does not contain more than 0.1 percent of saturated or linoleic ester.

The product thus obtained was found to have the following physical properties:

| | 20°C | 25°C. |
|---|---|---|
| Refractive index, $n_d^{t°}$ | 1.4522 | 1.4502 |
| Density $\frac{t}{4°}$ (corr. to vacuo) | 0.8739 | 0.8704 |
| Melting Point (capillary) | -19.9° to | -19.6° C. |

Keffler and McLean (3) give 0.8738 and 0.8702 for densities at 20° and 25° respectively.

Oleic acid prepared from the ester in the usual manner and distilled in vacuo had the following constants:

| | |
|---|---|
| Iodine no. (Wijs ½ hr.) | 90.0 |
| Thiocyanogen no. (3 hr.) | 89.6 |
| Refractive index $n_d^{t°}$ | 1.4599 (20°), 1.4581 (25°) |
| Melting Point (capillary) | +13.0° to +13.2° C. and<br>+16.0° to +16.3° C. |

The refractive index shown is higher than that given by Brown (1) ($n_d^{20}$=1.4585) and lower than the value reported by Skellon (4) ($n_d^{20}$=1.4610). Others have reported similar values. The dimorphism observed has been previously reported, by Raymond (5) (m.p.'s 13° and 16° C.), Robinson (6) (m.p.'s 13° and "just above" 16° C.) and others.

### Summary

1. Methyl oleate of high purity has been prepared by fractional distillation and low temperature crystallization of the methyl esters of the acids of olive oil.

2. The steps involved in the purification have been followed by analysis of each fraction.

3. Some physical and chemical properties of the purified methyl oleate and of oleic acid obtained from it have been reported.

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# Solidification Point Curves of Binary Acid Mixtures

# I. Capric, Lauric, Myristic, Palmitic

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THE older conventional methods for separating the saturated acids of a fatty oil are essentially applications of fractional crystallization or precipitation techniques. A newer, more satisfactory, method of analysis rests upon the fractional distillation of the fatty acids as their lower alkyl esters. In both types of procedures the objective is reached when several fractions, each of different mean molecular weight, have been obtained. Given ample quantities of material, it is true that by laborious and painstaking effort these separations can occasionally be made to yield fractions corresponding, in molecular weight, to a pure, or nearly pure, fatty acid; but ordinary separations stop at a point at which each fraction contains a major proportion of a fatty acid and a lesser one of the next higher or lower homolog. For the purpose of arriving, then, at the composition of each fraction the mean molecular weight is determined from the saponification value and calculation is made of the composition represented by that value. Such a calculation is, of course, valid mathematically, yet it is nevertheless empirical in that it assumes the presence of the pair of acids selected, since, for example, a mixture of mean molecular weight between that of lauric and myristic acids does not necessarily indicate this pair, for it might just as well represent a mixture of lauric and palmitic acids, but in somewhat different proportion.

There exists an obvious need, therefore, for some means of corroborating calculations of this type, when they are pertinent to natural mixtures, insofar as they effect conclusions based upon the assumed presence of any given pair of acids in them. In this communication we suggest that the use of solidification point curves of binary fatty acid mixtures will meet that need.

Solidification point curves have long been a valuable analytical tool in the inorganic field; especially in that of metals and alloys has thermal analysis been very widely used and extensively developed. Although these principles have been applied by others to some extent to the long-chain fatty acids, yet there exist sufficient gaps in the homologous series of these compounds to warrant further study in this field. Herein recorded are the curves representing mixtures of capric-lauric, lauric-myristic, and myristic-palmitic acids.

The fatty acids used in this study were recovered from commercial products* of *ca* 90 per cent purity. The method of purification used varied somewhat with the acid but the general procedure followed was that of esterification, bromination, and fractional distillation. Methyl esters were prepared by the method

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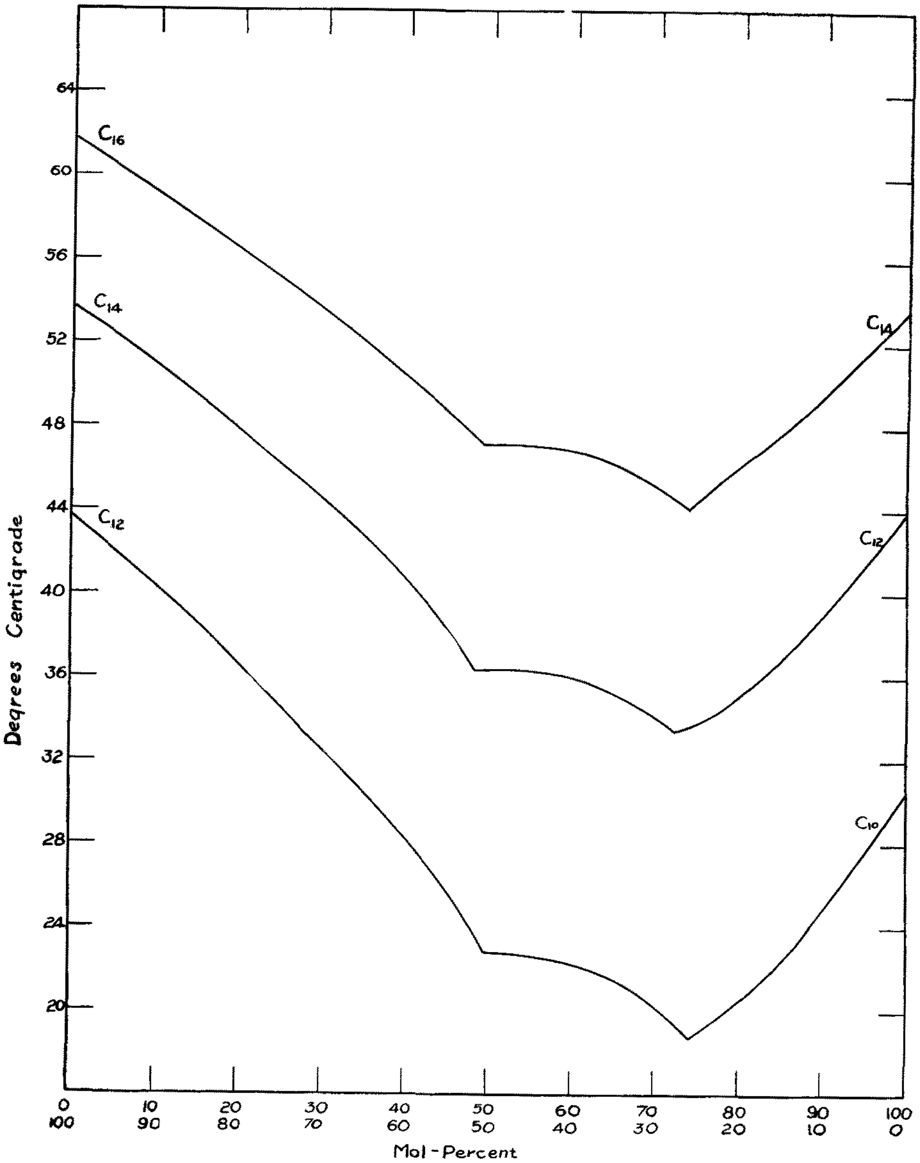
*Acknowledgement is made of the co-operation of Armour and Company, who generously furnished the fatty acids ("Neo-Fats") used in this investigation.



*Solidification Point Curves of Binary Acid Mixtures*

of Armstrong et al[1]. They were then brominated in chloroform solution by the procedure used by Grün and Janko[2], after which they were fractionally distilled at pressures of approximately 1 mm. Hg. The impure brominated methyl esters were refractionated until the material distilled over at a constant temperature. For each refractionation only the large middle fraction was taken, the first and last, containing, respectively, the fatty acids of lower and higher molecular weight than the fatty acid being purified, were discarded. After three refractionations the middle fraction distilled over at a constant temperature and had a mean molecular weight corresponding closely to that of the pure methyl ester desired.

Regeneration of the fatty acid from its pure ester by saponification with alcoholic potash solution and decomposition of the resulting soap presented some difficulties in that, because of re-esterification induced by the presence of mineral acid, the final product was invariably contaminated with *ca* one per cent of ester. After various attempts it was found that formation of the barium salts in petroleum ether, precipitation and very thorough washing with petroleum ether removed all of the contaminating ester.

The final step in purification was recrystallization from acetone; in the case of palmitic acid several recrystallizations from glacial acetic acid, followed by decolorization with Norite in ether solution and evaporation of the ether yielded the pure fatty acid in a very fine crystalline form.

The properties of the pure acids thus obtained were as follows:

Capric acid:
  mol. wt. 172.05 (theory 172.26)
  m.p. 31.60° C. (reported 31.4-31.5°)
  s.p. 30.62° C.
Lauric acid:
  mol. wt. 201.03 (theory 200.31)
  m.p. 44.2° C. (reported 43.35-44.1°)
  s.p. 43.68° C. (reported 43.75°)
Myristic acid:
  mol. wt. 228.99 (theory 228.37)
  m.p. 54.35° C. (reported 54.0-54.4°)
  s.p. 53.74° C. (reported 53.65-53.70°)
Palmitic acid:
  mol. wt. 256.8 (theory 256.42)
  m.p. 62.60° C. (reported 60.95-62.9°)
  s.p. 61.74° C. (reported 62.3-62.6°)

It will be noted that the only acid which appears not to be in close agreement in its properties with those reported in the literature is palmitic. Francis and Piper, et al. [3, 4, 5] have studied crystal spacings of fatty acids and succeeded in preparing a palmitic acid of m.p. 62.9° C. and s.p. of 62.6° C., both of these measurements being fully a degree above any of the best previously reported values. The palmitic acid prepared for this study was recrystallized according to their directions, but its m.p. and s.p. remained constant at 62.6° C. and 61.74° C., respectively. The latter value is almost a degree below the solidifying point reported by them.

Solidification points of the acids and their mixtures were obtained by melting them — in the case of the latter weighed amounts were used — in the reaction tube and then allowing them to cool slowly until solidification had set in. The apparatus used was a small three-inch test tube, surrounded by a water jacket made by cutting off five inches from an 8-inch test tube. Mixing and stirring to prevent excessive supercooling and uneven solidification were obtained by rotating the test tube itself, it being mounted into a stationary close-fitting piece of glass tubing. A rotary stirrer was fitted with a pulley, the belt passing around the test tube. In this way even rotation was obtained. Cooling was done by means of the comparatively colder atmosphere of the room decreasing the temperature of the

SOLIDIFICATION POINTS OF BINARY ACID MIXTURES

**Capric-Lauric Mixture**

| $C_{10}$ mol.-pct. | $C_{12}$ mol.-pct. | Sol. Pt. (corr.) |
|---|---|---|
| 0 | 100 | 43.68 |
| 10.37 | 89.63 | 40.10 |
| 21.20 | 78.80 | 36.00 |
| 28.00 | 72.00 | 33.20 |
| 35.15 | 64.85 | 30.30 |
| 41.62 | 58.38 | 27.50 |
| 47.53 | 52.47 | 24.05 |
| 48.47 | 51.53 | 23.50 |
| 49.37* | 50.63* | 22.80 |
| 50.38 | 49.62 | 22.83 |
| 52.03 | 47.97 | 22.75 |
| 53.45 | 46.55 | 22.70 |
| 59.49 | 40.51 | 22.25 |
| 65.79 | 34.21 | 21.25 |
| 71.80 | 28.20 | 19.55 |
| 73.04 | 26.96 | 19.10 |
| 74.02* | 25.98* | 18.80 |
| 75.25 | 24.75 | 19.15 |
| 77.28 | 22.72 | 19.65 |
| 81.82 | 18.18 | 21.30 |
| 85.23 | 14.77 | 22.65 |
| 87.48 | 12.52 | 23.70 |
| 88.60 | 11.40 | 24.15 |
| 93.04 | 6.96 | 26.70 |
| 95.33 | 4.67 | 27.90 |
| 100 | 0 | 30.62 |

**Lauric-Myristic Mixture**

| $C_{12}$ mol.-pct. | $C_{14}$ mol.-pct. | Sol. Pt. (corr.) |
|---|---|---|
| 0 | 100 | 53.74 |
| 9.70 | 90.30 | 51.05 |
| 16.53 | 83.47 | 48.97 |
| 17.13 | 82.87 | 48.87 |
| 26.56 | 73.44 | 45.55 |
| 29.45 | 70.55 | 44.64 |
| 36.44 | 63.56 | 42.07 |
| 39.25 | 60.75 | 41.11 |
| 43.35 | 56.65 | 39.09 |
| 47.23 | 52.77 | 36.90 |
| 48.50* | 51.50* | 36.23 |
| 50.79 | 49.21 | 36.21 |
| 51.84 | 48.16 | 36.22 |
| 53.42 | 46.58 | 36.20 |
| 54.32 | 45.68 | 36.21 |
| 55.52 | 44.48 | 36.20 |
| 60.60 | 39.40 | 35.76 |
| 65.19 | 34.81 | 35.15 |
| 71.15 | 28.85 | 33.74 |
| 71.90 | 28.10 | 33.46 |
| 73.12* | 26.88* | 33.43 |
| 73.69 | 26.31 | 33.44 |
| 74.82 | 25.18 | 33.59 |
| 76.99 | 23.01 | 34.10 |
| 82.61 | 17.39 | 35.80 |
| 86.90 | 13.10 | 37.48 |
| 94.45 | 5.55 | 40.90 |
| 100 | 0 | 43.68 |

**Myristic-Palmitic Mixture**

| $C_{14}$ mol.-pct. | $C_{16}$ mol.-pct. | Sol. Pt. (corr.) |
|---|---|---|
| 0 | 100 | 61.74 |
| 8.53 | 91.47 | 59.58 |
| 15.72 | 84.28 | 57.62 |
| 25.21 | 74.79 | 55.03 |
| 33.41 | 66.59 | 52.45 |
| 33.99 | 63.01 | 51.30 |
| 44.94 | 55.06 | 48.70 |
| 47.92 | 52.08 | 47.65 |
| 49.39* | 50.61* | 47.22 |
| 50.47 | 40.53 | 47.23 |
| 54.58 | 45.42 | 47.15 |
| 59.93 | 40.07 | 47.02 |
| 63.42 | 36.58 | 46.61 |
| 65.35 | 34.65 | 46.22 |
| 67.05 | 32.95 | 45.92 |
| 68.87 | 31.13 | 45.55 |
| 70.77 | 29.23 | 44.95 |
| 72.78 | 27.22 | 44.42 |
| 73.91* | 26.09* | 44.22 |
| 74.86 | 25.14 | 44.60 |
| 77.43 | 22.57 | 45.38 |
| 81.13 | 18.87 | 46.58 |
| 86.27 | 13.73 | 48.35 |
| 90.41 | 9.59 | 49.85 |
| 100 | 0 | 53.74 |

*Eutectic points

water jacket and of the melted mixture at a rate of about 0.2°C. per 15 seconds. For mixtures, such as capric-lauric acids, solidifying just above or below room temperature a beaker of cold water (10°C.) was placed around the water jacket.

Results obtained in the measurement of the behavior of the three pairs of acids involved in this study are recorded in two ways: complete data and graphic presentation by curves in which solidification temperature have been plotted against mol-per cent composition.

In discussing these curves much could be said concerning the theory of solid solutions as related to these binary mixtures. A matter of terminology should serve to introduce a discussion of the theoretical significance of these curves. Although the terms freezing point and solidification point have in the past been used interchangeably, yet adoption of the latter term is to be preferred when referring to mixtures. The reason for this becomes obvious when it is considered that in dealing with these mixtures of fatty acids we are dealing with a continuous series of solid solutions except at the eutectic points.

It is a well-known phenomenon in dealing with solidification point curves that, upon cooling down a "melt", there is a temperature at which component A of the mixture begins to crystallize out. Upon continued cooling the liquid remaining changes in composition, becoming relatively poorer in component A. Gradually a mixture containing also some of the second component, for convenience called component B, crystallizes. The solid mixture changes its composition continuously until the melt has all disappeared. At this point there is a completion of the process of solidification and, it is to be noted, that this is again a transition temperature at which the rate of cooling changes. Essentially this is what happens when these fatty acid mixtures solidify. There is no true freezing point, but there is obtained a constant temperature of solidification. This temperature is a constant one because the two temperatures of transition are so close together that by supercooling a slight amount, and supercooling is inevitable, cooling extends below the second transition temperature and when the supercooling is released the temperature rises to the point where total solidification takes place. A fuller explanation of the further theory involved here may be found in Findlay's "The Phase Rule"[6]; suffice it here to state that it is not true freezing points but constant temperatures of solidification of a melted mixture passing into a solid solution which are being observed.

The capric-lauric acid curve provided particular experimental difficulties from a composition of 74 mol-per cent capric to nearly pure capric acid. Here apparently the two temperatures of transition, the temperature at which crystallization begins and the temperature at which solidification is completed, do not lie very close together, being from about 0.3° to 2.0°C. apart. This being the case it was found that any temperature between these two extremes would serve as a constant temperature, the individual temperature obtained depending upon the rate of cooling. For this section of the curve the cooling was standardized by using cold water and regulating the cooling to a fairly constant rate of 0.2°C. per 15 seconds, which is the rate maintained on all other readings. This rate was controlled simply by varying the temperature of the water being used to cool the water-jacket.

Another subject which may prove a fertile one for discussion is that of the effect upon the curves of ascending in the homologous series. Such a discussion may very well be reserved for the future when similar curves for higher members of the series shall have been completed. It may be pointed out, however, that the break near the middle of each of these curves indicates the formation of an equimolecular compound between the two fatty acids and that its flatness indicates to some extent the strength of the bond between the two acids, i.e., the flatter the curve the less strength of union between them. From the curves it can be seen that with increasing molecular weight the tendency toward compound formation is becoming increasingly weaker. This is borne out also by the flatness of the break in the palmitic-stearic acid curve of Shriner[7].

Leaving the theoretical aspects, there now remains for discussion the practical value of these curves. It has been stated above that they would serve as a means of establishing the presence of two acids in a mixture of known molecular weight. Indeed, they constitute a relatively simple analytical aid since by locating on the proper curve the observed solidification temperature of the mixture of two fatty acids which have been isolated from a naturally occurring fatty oil there can be read off the mol-per cent composition. If it is suspected, for example, that myristic and palmitic acids are the components of an unknown mixture, as indicated by mean molecular weight, this suspicion can not only be verified but the calculated mol-per cent composition can also be checked, for the curves are capable of giving the composition of a synthetic mixture within one per cent, except, of course, in those instances in which the composition is such as to fall on a flat part of the curve where there is no temperature difference with difference in composition.

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# Sodium Bisulphite As A Stabilizer For Hydrogenated Cottonseed Oil Shortening

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## Abstract

Hydrogenated, deodorized cottonseed oil shortening, may be given increased keeping time and lowered peroxide values, if treated with small amounts of $NaHSO_3$ (either the dry powder or a saturated solution). The flavor of the treated shortening will be good if not too much bisulphite is used. The shortening so treated will contain a very small amount of $SO_2$.

A LARGE number of aldehydes, ketones and organic peroxides are known to react with sodium bisulphite. Since these compounds are responsible, or at least partially so, for rancidity in edible oils and fats, the present investigation was undertaken to determine whether or not an oil or fat which had been treated with sodium bisulphite would have a lowered peroxide value, and to determine whether or not the keeping time of such a fat would be prolonged.

An extensive search of the chemical literature revealed very little information regarding the effects or results obtained when edible oils or fats are treated with sodium bisulphite.

This material has been used in the preparation of phenylhydrazine, (1), to prevent the formation of dark resinous or tarry residues. It has also been used to prevent the oxidation of alkaloids and of adrenalin in aqueous solution.

Moureau and Dufraisse have published a number of papers on Autoxidation and Anti-oxidases (2) (3) (4) (5) (6). Several of these papers concerned themselves with the catalytic properties of sulphur and its compounds. Although they have investigated the autoxidation and anti-oxidative properties of a large number of both organic and inorganic sulphur compounds, they do not give data regarding the action of sodium bisulphite on oils or fats.

Simmons and Mitchel (7) mention the fact that sodium bisulphite, which possesses the property of combining with aldehydes, has been utilized in some cases for deodorizing oils and fats with good results.

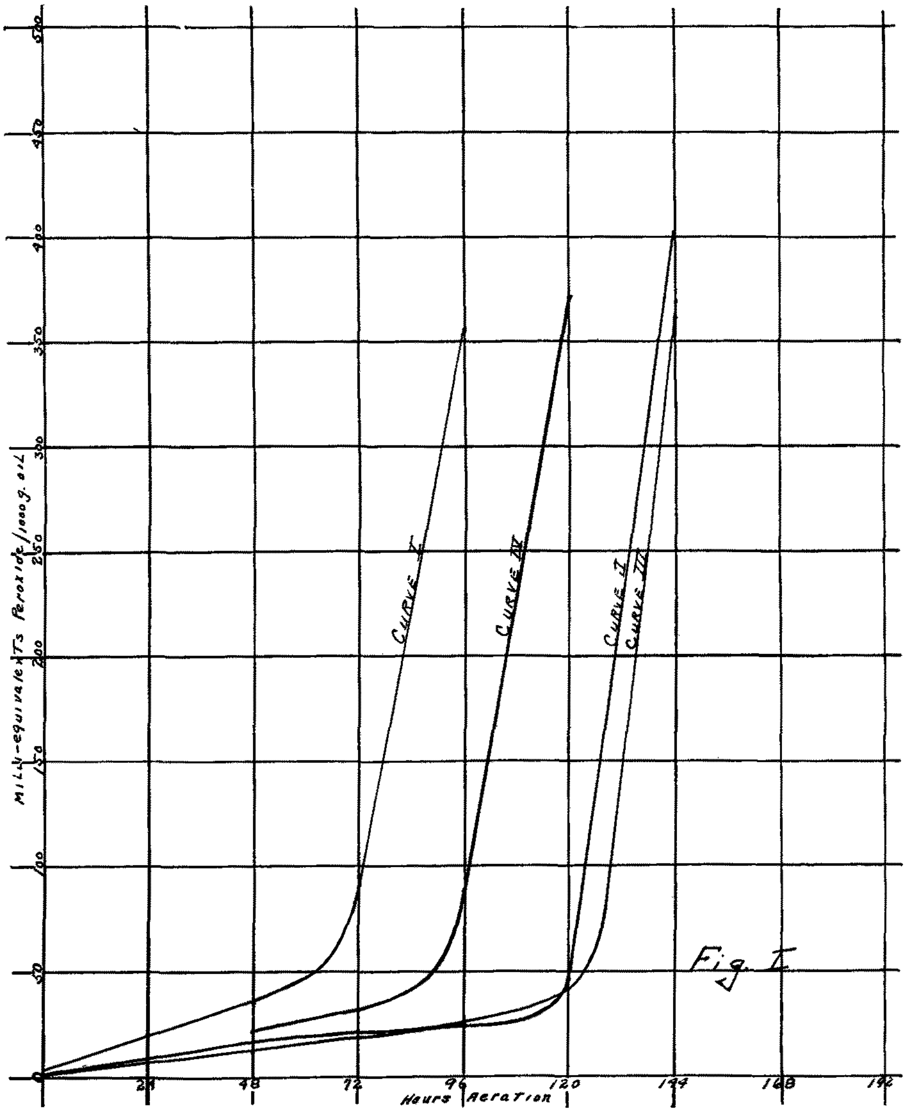

Fig. I

### Experimental

The fat used in these experiments was a fifty-pound can of hydrogenated deodorized cotton seed oil Shortening, which had the following chemical and physical characteristics:

| | |
|---|---|
| Iodine number | 65.8 |
| Melting Point (closed capillary) | 108° F. |
| Congealing Point | 31.0° C. |
| Saponification number | 197.8 |
| Peroxide value (Millequivalents per Kilo) | 1.8 |
| Lovibond Color | 20 yel.—1.45 red |
| Free Fatty Acid | 0.03% |
| Flavor | good |