heating compared with 1.0 percent for the same oil heated in air. A significant difference was observed in the final iodine values of these two samples and it is evident that, if it were feasible to blanket the oil chamber of the tinning bath with an inert atmosphere, the life and utility of tinning oils would be increased appreciably.

Summary and Conclusions

An investigation has been made of the relative effects of added metallic compounds, normally found as contaminants in the tin bath, upon the formation of free fatty acids and the rate of increase in the viscosity of heated palm and hydrogenated cottonseed oils.

It was found that when palm and hydrogenated cottonseed oils were heated in the presence of tin to temperatures comparable with those obtaining in the tin pot during the hot dipping of tin, palm oil showed a slightly lower rate of increase in viscosity compared to hydrogenated cottonseed oil. On the other hand, when zinc and ferric salts were added to the otherwise similarly treated oils, hydrogenated cottonseed oil was found to be more stable than palm oil.

Metallic contaminants such as ferric oxide, which had a marked effect on the rate of viscosity increase of palm oil, produced no change in the rate of increase in viscosity in the case of hydrogenated cottonseed oil.

The addition of zinc stearate, of zinc chloride alone, or of zinc chloride and ferric salt, had the effect of retarding polymerization of both oils, as measured by the rate of increase in viscosity. The addition of either ferric oxide or ferric stearate resulted in acceleration of the rate of viscosity increase of the heated oils. It may, therefore, be assumed that the inorganic salts are partly converted to ferric and zinc soaps *in situ* by reaction with free fatty acids already present or formed in the heated oils.

It was observed that when palm oil was heated with various metallic compounds, it lost free fatty acids rapidly during the early stages of heating until the concentration attained a definite value, at which it remained during further heating. The concentration at which the free fatty acids in the palm oil became constant was directly affected by the specific nature of the added metallic compound. Also, when hydrogenated cottonseed oil, having a lower initial content of free fatty acids than the palm oil was treated in the same manner, there was an accumulation of free fatty acids during heating until the concentration attained a definite value, after which it remained constant on further heating. The concentration at which the free fatty acids of any sample of oil became constant was found to be dependent on the specific nature of the added metallic compound.

Acknowledgments

The authors wish to express their appreciation of the assistance rendered by Miss M. Caravella, Mr. R. O. Feuge, and Mr. E. A. Kraemer in this investigation.

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Unsaturated Synthetic Glycerides*

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The complexity of the glyceride composition of animal and vegetable fats and the inherent difficulties of isolating single components with definite and known configuration are facts well known to investigators in the field of fat chemistry. While considerable progress has been made in the analysis of the fatty acid composition of individual fats, the determination of the glyceride composition has not been nearly so precise.

The isolation of individual glycerides from naturally occurring fats has been reported by many investigators but the assignment of specific configurations to them has been accompanied with some degree of uncertainty. Greater assurance of the structure and configuration of those glycerides isolated from natural sources can be, and in a few instances has been, obtained by comparing their physical and chemical properties with those prepared by reliable synthetic methods. Certainly complete information relative to the properties of synthetic glycerides would be of considerable value in planning methods of isolating and identifying individual glycerides in anticipated mixtures. As a case in point, solubility studies should be of inestimable value when solvent partition and crystallization methods are used for isolation purposes. A fact much more important than the actual isolation of components in glyceride mixtures is the determination of the glyceride composition of a fat without, necessarily, an accompanying isolation. This latter, while seemingly impossible at the moment, may be accomplished through the correlation of properties of glycerides of proved configuration obtained by synthetic methods.

Since methods for the synthesis of glycerides of a high degree of purity containing primarily saturated fatty acids have been discussed recently in other reviews (1, 2, 3), this report will be concerned mainly with the adaptability of those methods to the synthesis of glycerides composed of both saturated and unsaturated fatty acids and to a discussion of some of the physical properties of such unsaturated glycerides. As most naturally occurring fats are composed of glycerides containing some unsaturation, this group of synthetic glycerides assumes increasing importance in the study of glyceride mixtures.

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* Support for this program has been generously provided by the Buhl Foundation Research Project and Swift and Company.

Contribution No. 509 from the Department of Chemistry, University of Pittsburgh.

The preparation, with a high degree of purity, of mixed triglycerides containing unsaturated acids must of necessity be dependent on the purity of the acids and other intermediates. Prolific investigation of oleic acid has resulted in the development of methods for obtaining an acid of a high degree of purity, the more recent of which have been those of Brown et al. (4, 5, 6, 7, 8), (9, 10, 11, 12, 13). With sufficient care in experimental procedure an oleic acid can be obtained repeatedly from olive oil fatty acids, and subsequently used in the synthesis of unsaturated glycerides.

While linoleic and linolenic acids of satisfactory purity can be obtained by debromination of the tetra- and hexabromostearic acids, respectively, by the method of Rollet (14) it is doubtful, on the basis of recent investigation, that the debromination acids are identical with those naturally occurring. Until further progress is made in the isolation of both linoleic and linolenic acids by the low temperature crystallization techniques so excellently developed by Brown and associates (4, 5, 6, 7, 8), synthetic glycerides containing these two acids may or may not be identical with those present in natural glyceride compositions.

Review of Earlier Work

The major emphasis in the past has been centered on the development of methods of synthesis for glycerides containing saturated acids, while only minor attention has been given to the synthesis of those containing unsaturated acids. Much of the earlier work in the latter field, however, must be looked upon as questionable, particularly in view of the uncertainties regarding the purity of intermediates and the fact that possible rearrangements during the reactions were obviously not taken into account. The synthesis of saturated glycerides was in a state of confusion until it was clearly recognized that acyl migration was a factor in assigning a configuration to the synthetic product. Fisher (15) and later King and coworkers (16, 17, 18, 19, 20, 21, 22) contributed much to emphasize the necessity of observing the conditions conducive to rearrangement.

The preparation of 1-monoölein † was reported by Guth (23) on heating 1-chloropropylene glycol with sodium oleate for four hours and by Kraft (24) using essentially the same procedure. The same monoglyceride was synthesized by Berthelot (25) by heating glycerol with oleic acid at 200°, by Pottevin (26) from glycerol and oleic acid in the presence of pancreatic lipase and by Amberger and Bromig (27) from oleyl chloride and acetone-glycerol. Guth (23), likewise, reported the preparation of 1,2-diolein and 1,3-diolein on treating 2,3-dibromopropanol and 1,3-dichloropropanol with sodium oleate respectively. The symmetrical diglyceride was also prepared by Berthelot (25) by heating 1-monoölein with excess oleic acid at 250°, and also by heating triolein with glycerol at 200°. All of these methods involved the use of high temperature and intermediates of questionable purity. Certainly, on the basis of present information, based on extensive studies of saturated synthetic glycerides as mentioned above, acyl migration must have occurred in the supposed preparation of the reported 1,2-diolein. The use of a 1,2-diglyceride as an intermediate for the synthesis of unsymmetrical mixed triglycerides is of doubtful value because of the risk of rearrangement. In fact, unsymmetrical mixed triglycerides prepared from supposed 1,2-diglycerides have been mistakenly identified in the past by many investigators.

Kreis and Hafner (28) reported the synthesis of 1-oleyl-2,3-distearin from oleic acid and 1,2-distearin. It is doubtful whether either intermediate was sufficiently pure for proper characterization of the triglyceride. The same triglyceride was prepared by Amerger and Bromig (27) from 1-monoölein and stearyl chloride. The symmetrical isomer was prepared by Hafner (29) from oleic acid and 1,3-distearin by heating for 10 hours under diminished pressure in an atmosphere of carbon dioxide and by Grün and Schacht (30) by heating 1,3-distearin with oleic anhydride for six hours at 170° and 20-25 mm. pressure. Abderhalden and Eichwald (31) reported the preparation of 1-oleyl-2,3-dibutyrin from oleyl chloride and 1,2-dibutyrin.

The simple glyceride, triolein, has been reportedly prepared by a variety of methods. Guth (23) reported its preparation from tribromopropanol and sodium oleate, Berthelot (32) and Bellucci (33, 34) by direct esterification of glycerol and Pottevin (35) from oleic acid, 1-monoölein and pancreatic lipase. The most satisfactory recent preparation of triolein is undoubtedly that of Wheeler, Riemenschneider and Sando (36). Their method consisted of esterifying glycerol directly with an oleic acid of a high purity in an atmosphere of purified nitrogen with p-toluenesulfonic acid as a catalyst. Molecular distillation yielded a triolein with physical constants of a highly purified product. Warming and cooling curves established the existence of three crystalline forms, 4.3° being the melting point of the form most stable.

Izar (37) and Grün and associates (38) have contributed largely to the synthesis of glycerides containing linoleic acid as the unsaturated component. Izar (37) reported the preparation of 1-monolinolein by heating dry potassium linoleate with 1-monochlorhydrin at 160° in an atmosphere of carbon dioxide for one hour. No constants were reported other than that the monoglyceride was an oily liquid. Black and Overley (39) recently prepared this monoglyceride by the debromination of 1-(9,10,12,13-tetrabromo)-stearin, which had been synthesized from 9,10,12,13-tetrabromostearyl chloride and acetone-glycerol. Physical and chemical constants agreed well with theoretical values.

The symmetrical diglyceride, 1,3-dilinolein was reportedly prepared both by Izar (37) and Grün (38) by heating 1,3-dichlorohydrin and potassium linoleate at 120-160° in an atmosphere of carbon dioxide. These same investigators reported the preparation of a series of mixed triglycerides containing linoleic acid, in most instances using mono- or dilinolein or potassium linoleate and the appropriate chlorhydrin intermediates. Grün (38) also resorted to the use of linoleic anhydride and the mono- or diglycerides.

Although the synthesis of trilinolein was reported by Izar (37) from potassium linoleate and trichlorhydrin, Black and Overley (39) and later Wheeler,

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† Since the nomenclature of synthetic glycerides has been inconsistent in the recorded literature, we have elected to use numbers exclusively, in place of Greek letters, to indicate the position of the ester group in the glycerol molecule.

Riemenschneider and Sando (36), prepared the glyceride by independent and more satisfactory methods. The latter investigators directly esterified glycerol with linoleic acid in an atmosphere of purified nitrogen and p-toluenesulfonic acid as catalyst, while the former made the acid chloride of tetrabromostearic acid and from it prepared the triglyceride, which they debrominated to obtain trilinolein. The physical constants of the independently prepared trilinoleins agreed well with theoretical values.

Since many of the earlier investigators of synthetic glycerides did not, in most instances, adequately characterize the products they prepared, it has been difficult to evaluate their purity. As a consequence of the lack of sufficient data for unsaturated mixed triglycerides and the evident need for such data for this important group, the program in our laboratory is at present directed to the complete study of this type of glyceride. This program includes (1) the synthesis of both symmetrical and unsymmetrical mixed triglycerides containing one and two moles of unsaturated fatty acid, (2) the establishment of the purity and (3) a study of their physical and chemical properties, e.g. solubilities, X-ray diffraction data, polymorphism, film formation, rates of oxidation and hydrolysis with lipases.

Methods of synthesis well established for the preparation of mixed triglycerides containing saturated fatty acids are easily adaptable, with some modification, to those containing unsaturated acids. These methods have been used, with satisfactory results, in all investigations in our laboratory. In order to use several of the methods for the ultimate preparation of the triglyceride, unsaturated acid chlorides of a high degree of purity are a necessity.

We have found oxalyl chloride to be a satisfactory acylating agent for the preparation of oleyl, linoleyl, linolenyl and elaidyl chlorides. The oleic acid used in the preparation of oleyl chloride was obtained by the methods of both Brown (7, 8) and Wheeler and Riemenschneider (13) and the more highly unsaturated acids by the debromination procedures of Rollet (14). Elaidic acid, subsequently used in the preparation of elaidyl chloride, was obtained by the elaidinization of highly purified oleic acid. Recent work (40) has indicated there is a negligible increase in diene conjugation during the preparation of linoleyl and linolenyl chlorides. We are fully cognizant of the fact, however, that manipulation of these two unsaturated acids may result in isomerizing effects and glycerides prepared from them may not be identical with those naturally occurring. However, a 1-monolinolein (41) prepared from linoleyl chloride and acetone-glycerol and subsequent hydrolysis of the intermediate compound, yielded a product identical with the 1-monolinolein prepared by Black and Overley (39) from a 1-(9,10,12,13-tetrabromo)-stearin.

Unsymmetrical Monoöleyl-disaturated Triglycerides

A series of unsymmetrical monoöleyl-disaturated triglycerides (42) was prepared from 1-monoölein and the appropriate saturated acyl chloride. To prevent the possible formation of mixed diglycerides, it was found necessary to maintain the reaction mixture at temperatures of 40-50° for several days. Low-temperature fractional crystallization procedures yielded products of a high degree of purity. Hydrogenation to the completely saturated analogues was utilized to prove further the unsymmetrical configuration. Iodine values, refractive indices and molecular weight determinations were used in preference to combustion data as criteria for purity. Molecular weight determinations permitted the recovery of triglyceride, although in some instances saponification equivalents were determined. The molecular weights, determined by the method of Menzies and Wright (43) as modified by Hanson and Bowman (44) presented an interesting anomaly. Negative slopes were obtained which made extrapolation to zero concentration necessary in order to obtain a true molecular weight. Each addition of triglyceride to solvent (benzene) resulted in a decrease in the calculated apparent molecular weight, i.e. the apparent molecular weight decreased with increasing concentration. The best straight line for each series of molecular weights was determined by the method of least squares and the true molecular weight taken at zero concentration. This anomaly was further observed in the determination of the molecular weights of the symmetrical monoöleyl-disaturated triglycerides and the unsymmetrical dioleyl-monosaturated triglycerides. Since this phenomena has been observed with all synthetic unsaturated glycerides, it is being further studied for a possible explanation. Figure 1, taken from the molecular weight determination of 1-oleyl-2,3-distearin, represents results typical of the glyceride series.

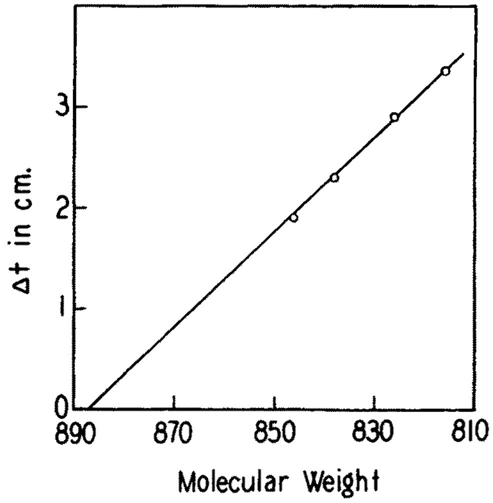

FIG. 1. Molecular Weight of 1-Oleyl-2,3-distearin.

Melting point and refractive index data for the series of unsymmetrical monoöleyl-disaturated triglycerides are summarized in Figure 2. It is observed that both the melting points and refractive indices increase with increasing length of the carbon chain of the saturated fatty acid. For comparison, the melting point relationship of the products obtained on hydrogenation are given. It can be seen that the presence of an oleyl radical in the triglycerides results in an approximate decrease of 30° in melting point. From the data obtained to date for the corresponding triglycerides containing elaidic acid in place of oleic acid, the melting points are 15-20° higher for the elaidins.

Symmetrical Monoöleyl-disaturated Triglycerides

The symmetrical monoöleyl-disaturated triglycerides (45), isomeric with the triglycerides just discussed, were prepared from symmetrical saturated diglycerides and oleyl chloride. With this series, it was found expedient to allow reaction to proceed at the temperature of a steam bath for periods of from three to five hours. The refractive index and melting point data are summarized in Figure 3. The melting points of the products obtained on hydrogenation are plotted for comparison. It will be seen that, as in the preceding series, the melting points and refractive indices increase with increasing length of the carbon chain of the saturated fatty acid. Here again, the presence of a single oleyl group in place of a stearyl group results in an approximate decrease of 30° in melting point. It is further observed that the melting points are from 2 to 5° higher than those of the corresponding unsymmetrical isomers. This general relationship was evident in other series of mixed triglycerides containing only saturated acids.

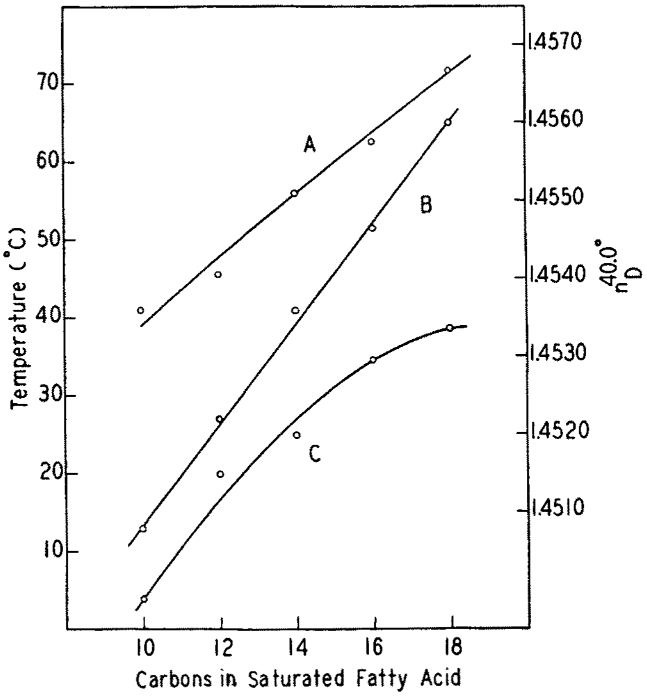

FIG. 2. Unsymmetrical Monoöleyl-disaturated Triglycerides.

A—Melting point of hydrogenated compound; B—Refractive index at 40.0°; C—Melting point of unsaturated compound.

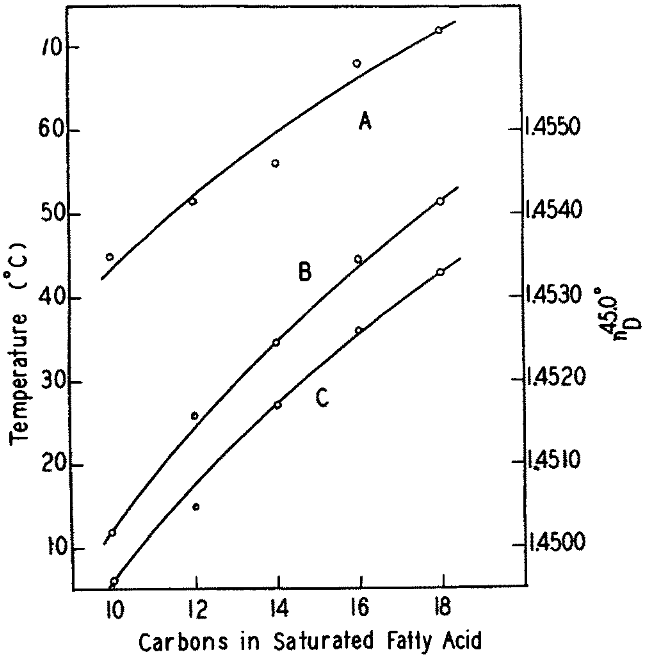

FIG. 3. Symmetrical Monoöleyl-disaturated Triglycerides.

A—Melting point of hydrogenated compound; B—Refractive index at 45.0°; C—Melting point of unsaturated compound.

Unsymmetrical Dioleyl-monosaturated Triglycerides

In the preparation of this series (46) of unsaturated triglycerides from saturated 1-monoglycerides and oleyl chloride, reaction temperatures of 70-85° were necessary. Temperatures of 25 to 35° for several days invariably produced mixed symmetrical diglycerides, which were in several instances isolated and purified. Melting point and refractive index data for the triglycerides are given in Figure 4. In contrast to the refractive index relationship of the monoöleyl-disaturated triglycerides, this series shows a peculiar refractive index anomaly. As the chain length of the saturated fatty acid increased from C_6 to C_{12}, a decrease in refractive index was observed, followed by an increase in value from C_{12} to C_{18}. Molar refractivities, calculated from density measurements, did not adequately explain the anomaly. Since these data are so unusual with respect to other series of triglycerides, investigation for a possible explanation is being continued. It is also interesting to observe that the melting point difference between these triglycerides with two oleyl groups and their saturated analogues

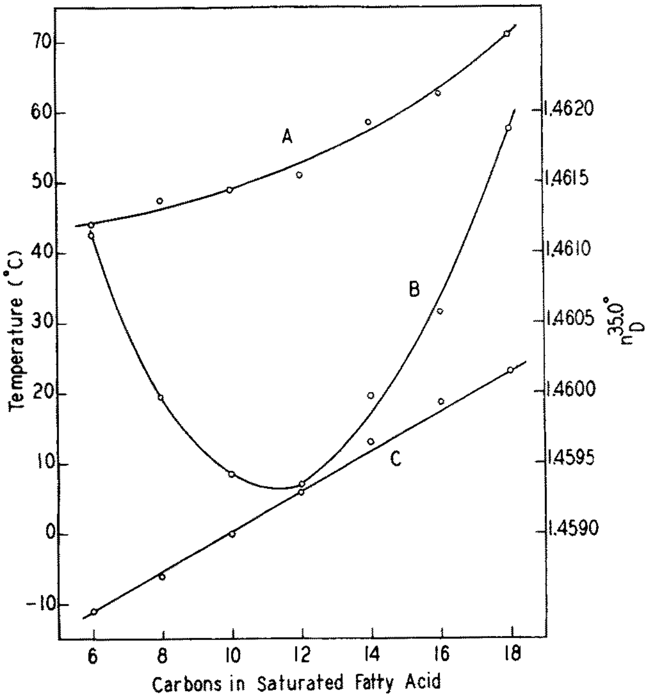

FIG. 4. Unsymmetrical Dioleyl-monosaturated Triglycerides.

A—Melting point of hydrogenated compound; B—Refractive index at 35.0°; C—Melting point of unsaturated compound.

is of greater magnitude than those containing but one unsaturated (oleyl) group.

Unsaturated Symmetrical Mixed Diglycerides

Esterification of 1-acyl-3-trityl glycerols with oleyl chloride and subsequent removal of the trityl group by acid hydrolysis produces symmetrical diglycerides containing both saturated and unsaturated acids (47). This method is essentially that described by Verkade (48) for the preparation of mixed diglycerides containing only saturated acids. If the acyl group present is the C_{18} saturated acyl radical, the resulting diglyceride contains a saturated and unsaturated acid of the same chain length. On the other hand, if an acyl group containing fewer carbon atoms is originally part of the glycerol molecule, esterification with oleyl chloride produces a symmetrical diglyceride containing two different acids of unequal chain length. Thus, these mixed diglycerides may be used as intermediates for the preparation of mixed triglycerides composed of three different fatty acids one of which is unsaturated. Since such triglycerides are theoretically possible in a complex glyceride mixture, characterization of their physical properties should be of considerable ultimate value.

Hydrogenation of the unsaturated symmetrical mixed diglycerides to known saturated analogues gives added support to their structure and identity. In Figure 5, melting point and refractive index relationships are plotted together with those of the symmetrical diglycerides obtained by hydrogenation. There is evidence that the melting points of the hydrogenated products are approximately 25 to 30° higher than the unsaturated diglycerides. The same relationship, as was previously indicated, held for the series of monoöleyl-disaturated triglycerides and their hydrogenated derivatives. While we are aware of the fact that a single melting point determination does not indicate the existence of other polymorphic forms, we are reasonably sure that under the experimental conditions of the melting point determinations the melting points reported are those of the most stable crystal form.

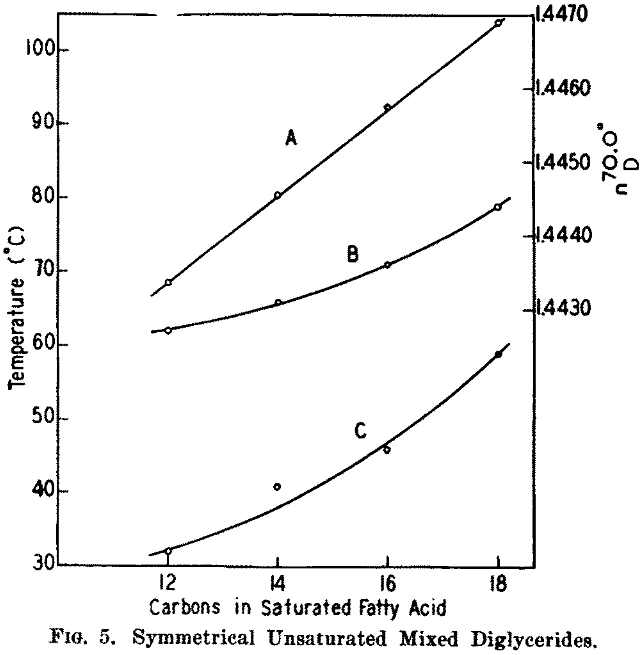

FIG. 5. Symmetrical Unsaturated Mixed Diglycerides.

A—Refractive index at 35.0°; B—Melting point of hydrogenated compound; C—Melting point of unsaturated compound.

It is our opinion that polymorphism in synthetic glycerides is of sufficient importance to warrant a series of separate investigations. These studies together with complete X-ray analyses are now in progress in our laboratory. Although Malkin (49, 50, 51, 52) has accomplished much regarding the structure of both symmetrical and unsymmetrical saturated triglycerides through X-ray diffraction patterns, it is obvious that for identification purposes the available information is relatively incomplete. Complete X-ray powder diffraction data, not only of the synthetic glycerides containing unsaturated acids but also of mono-, di- and triglycerides of saturated acids, are being included in our investigations.

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