Acetin Fats. II. Preparation and Properties of Diacetin Fats from Some Common Vegetable Oils

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IN a preceding paper "acetin fats" or fats containing both the possible types of mixed acetyl glycerides, namely mono- and diacetyl triglycerides, besides the normal triglycerides have been discussed. For brevity, the terms "monoacetins" and "diacetins," respectively, are used throughout this paper for these acetyl group-containing triglycerides.

Saturated triglycerides containing two acetyl groups for each molecule, the "diacetins," have found considerable interest. They are unique in that they form waxy or non-greasy and highly flexible solids (1). These properties suggest utility for these fats as coatings, particularly for foodstuffs.

The preparation and properties of some diacetin fats, or acetostearins as they were called, have been reported by Feuge *et al.* of the Southern Regional Research Laboratory (2, 3). Their method of preparation involved the direct acetylation of monostearin. Variations in complete melting points and melting point ranges between 30° and 60°C. were obtained by variations in the purity of the monostearin and in the degree of acetylation. In the present report an alternate method of preparing diacetin fats together with the characterization of diacetin fats made from some common vegetable oils are described (4).

Preparation of Diacetin Fats

The diacetin fats described herein were prepared by the random interesterification of the selected normal fat with triacetin in the presence of a low-temperature interesterification catalyst. In this method, after removal or inactivation of the catalyst, the interesterified fat is subjected to molecular or vacuum steam distillation. Excess triacetin is removed first, and the next fraction is composed of diacetin fats.

In the selection of the normal fat to be used, the only requirements are that the fat be dry and relatively devoid of free acid or any other matter that may neutralize the catalyst. For most practical uses, a completely hydrogenated normal fat is selected as the starting material or the diacetins are hydrogenated after isolation.

The preparation of a diacetin fat is described below in more detail. First, the starting fatty material should be selected by considering the I.V., the high-molecular-weight fatty acids, and the total fatty acids desired in the final product. This fat or oil, refined and dried, is mixed with triacetin and about 0.3% of an interesterification catalyst. Usually sodium methoxide or sodium as a suspension in an inert solvent such as xylene is used. The mixture is kept at a temperature sufficiently high so that all components are liquid. This temperature is held for a period of about one-half hour, which is more than sufficient time for completion of random interesterification. Following this, the catalyst is inactivated with acid, water, or other means. Any excess acid is removed by refining or water-washing followed by drying. The neutral acetin fat is then vacuum steam-distilled under a pressure of 2 to 3 mm. Hg. Under these conditions any triacetin remaining from the water-washing or refining steps is removed at a distillation temperaature of about 130° to 140°C. Removal of triacetin is substantially complete at 160°C. The temperature is raised until the diacetins start to distill. The distillation temperature depends upon the component high-molecular-weight fatty acids of the diacetins. For an oil such as cottonseed oil, the initial diacetin distillation temperature is about 200°C.; for a lower-molecular-weight oil, such as coconut oil, the temperature is around 170° to 180°C. Table I shows the distillation data of diacetins from a number of common vegetable oils. Separation of the diacetins may also be accomplished by molecular distillation. The distillation cuts in either method are quite sharp, and the yield of diacetin fats is very close to theory. The desired yield is controlled therefore by the amount of triacetin used in the original random interesterification. The products from the distillation are usually colorless and frequently quite bland so that no further deodorization or any other processing techniques are required for edible usage.

TABLE I

Distillation and Analytical Data on Hydrogenated Diacetins from Some Common Vegetable Oils

Oil Source	Range of Head Distillation Temperature, °C. 1-3 mm. Hg. Pressure	Saponification Value	Iodine Value	Acid Value	Butyro Refractive Index at 48°C.
Cottonseed Oil	200-240	381.0(385.9)[a]	0.8	0.4	21.5
Soybean Oil	200-240	381.9(384.2)	0.6	0.9	22.0
Rapeseed Oil	210-270	367.0(365.0)	1.0	0.9	24.0
Coconut Oil	170-220	459.7(461.0)	0.1	0.8	15.1

[a] Values in parentheses are calculated values.

The analytical data on diacetin fats from some of the common oils, namely cottonseed, soybean, rapeseed, and coconut, are also shown in Table I. They are given for the completely hydrogenated diacetin fats. The data illustrate the extent to which the diacetin fats are freed from the triacetin, on one hand, and separated from the monoacetin fats or those triglycerides containing one acetic acid group per molecule, on the other hand. Separation of the monoacetins can be accomplished by further molecular distillation of the still residue. The distillation residue as well as the removed triacetin may be reused in the process.

Thermal Examination of the Diacetin Fats

The melting points of the hydrogenated as well as unhydrogenated diacetin fats from cottonseed, soybean, rapeseed, and coconut oils are given in Table II. The melting points are those of the alpha or sub-alpha polymorphic forms. The data on the hydrogenated diacetins illustrate how the melting point of this type of fat can be changed by varying the component high-molecular-weight fatty acids. This is also illustrated in Table III where the melting points of a number of the pure unsymmetrical diacetyl triglycerides are given. The data on the 1-palmitoyl

TABLE II

Thermal and X-Ray Data on Diacetins from Some Common Vegetable Oils

Oil Source	Cottonseed Oil	Soybean Oil	Rapeseed Oil	Coconut Oil
Melting Ranges, °C.				
Hydrogenated Diacetins	29.4 - 31.4	32.4 - 32.6	41.0 - 44.3	–19.0 - 2.5
Unhydrogenated Diacetins (Complete melting point)	4.6	–4.7	–7.5	–16.3
X-Ray Data: Long Spacings, Å.				
Hydrogenated Diacetins				
Sub-alpha-3[a]	35.8	37.3	36.8	37.5 & 28.5
Alpha-3[b]	35.5	37.2	36.9	—
Unhydrogenated Diacetins				
Sub-alpha-3	33.4	33.8	Too diffuse	27.7
Short Spacings, Å.				
Hydrogenated Diacetins				
Sub-alpha-3[c]	4.10S 3.66M	4.11S 3.66M	4.05S 3.63M	4.13S 3.74M
Alpha-3[d]	4.08S 2.37VVW	4.11S 2.35VVW	4.08S	—
Unhydrogenated Diacetins				
Sub-alpha-3	4.10S 3.66M	4.10S 3.67M	4.12S 3.66M	4.10S 3.73M

[a] Value for 1-stearoyl diacetin, 37.1 (5); for 1-palmitoyl diacetin, 34.7 (5); for 1-behenoyl diacetin, 41.1.

[b] Value for 1-stearoyl diacetin, 36.5 (5); for 1-palmitoyl diacetin, 34.1 (5); for 1-behenoyl diacetin, 40.3.

[c] Values for 1-stearoyl diacetin and 1-palmitoyl diacetin, 4.13VS and 3.65M (5); for 1-behenoyl diacetin, 4.11VS and 3.71M.

[d] Values for 1-stearoyl diacetin and 1-palmitoyl diacetin, 4.13VS and 2.41VW (5); for 1-behenoyl diacetin, 4.12VS.

and stearoyl diacetin are taken from Jackson and Lutton (5). The melting point of these diacetin fats can also be varied by the presence of other components, such as triacetin, monoacetins, or unhydrogenated diacetins. Data illustrating this are given in Table IV. Interestingly, the melting range of the diacetins is not significantly changed, but the presence of these various materials merely serves to change the complete melting point. When dealing solely with triglycerides, the melting point of the diacetin fats can be varied anywhere from about —20°C. up to about 53°C. For higher melting points it is necessary to go to incomplete or partial glyceride products, such as the acetostearins which have been reported by Feuge *et al.* (2, 3). However these products have the disadvantage of tending to decompose during deodorization.

Diacetin fats made from oils which show a very limited range in molecular weight of their fatty acid components have extremely sharp melting points. This is true, for example, of diacetins made from completely hydrogenated cottonseed and soybean oils which contain only C_{16} and C_{18} chain length fatty acids. As an illustration of the sharpness of melting of these diacetins, Figure 1 compares curves from dilatometric examination of hydrogenated soybean oil diacetins and cocoa butter. It is seen that the soybean diacetins melt quite sharply and, in doing so, have about the same melting properties as cocoa butter.

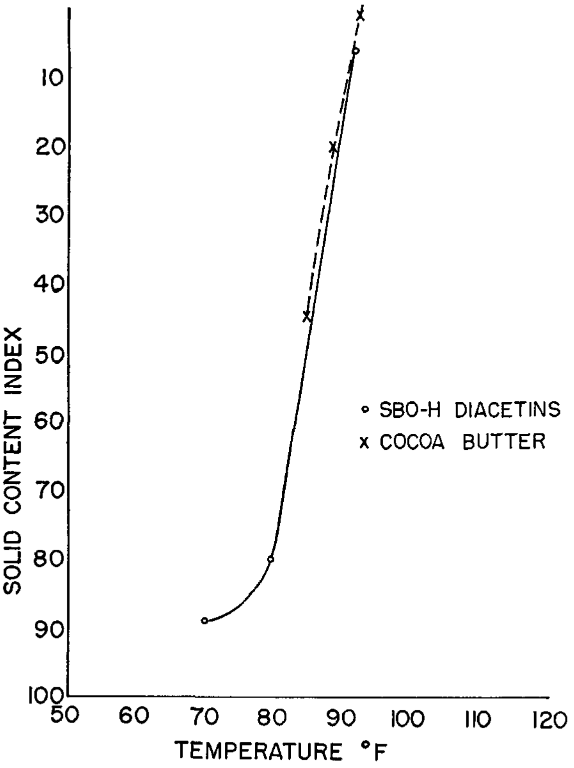


FIG. 1. Comparative dilatometer curves for hydrogenated soybean oil (SBO-H) diacetins and cocoa butter.

TABLE III

Melting Points of Alpha-3 Forms of Some Pure Diacetyl Triglycerides and Their Corresponding Monoglycerides

Glyceride	Complete Melting Point-Alpha-Polymorphic Form, °C.	Complete Melting Point of Stable Form of Corresponding Monoglyceride, °C.
1-Palmitoyl Diacetin	22.4(5)	76.0
1-Stearoyl Diacetin	34.1(5)	81.0
2-Stearoyl Diacetin	31.2	74.5(7)
1-Behenoyl Diacetin	53.1	87.2

TABLE IV

Variation in Melting Point Range of Hydrogenated Diacetins from Soybean and Cottonseed Oils Caused by the Presence of Some Miscellaneous Components

Oil Source of Diacetins	Constituent–%	Melting Point Range, °C
Soybean Oil	Triacetin–15	29.4-30.3
Soybean Oil	Hydrogenated Soybean Oil Monoacetins–30	34.0-35.6
Cottonseed Oil	Unhydrogenated Cottonseed Oil Diacetins–20	24.0-28.9
Cottonseed Oil	Hydrogenated Coconut Oil Diacetins–20	25.3-27.0
Cottonseed Oil	Hydrogenated Rapeseed Oil Diacetins–40	31.8-36.0
Cottonseed Oil	Hydrogenated Cottonseed Oil Monoacetins–25	32.4-33.3

Polymorphism of the Diacetins

The polymorphism of individual pure diacetyl triglycerides has been described by Jackson and Lutton (5) of these laboratories. The behavior of the diacetin fats discussed in this report is given in Table II. Shown are data on both hydrogenated and unhydrogenated diacetins of cottonseed, soybean, rapeseed, and coconut oils. The polymorphism was studied by the usual X-ray and melting point techniques used in these laboratories. A General Electric XRD unit with a 0.025″ pinhole system was used to obtain flat film patterns. Short-spacing determinations were made with a sample-to-film distance of 5 cm., while 10-cm. distance was used for long-spacing and detailed short-spacing determinations.

In general, the only forms observed for the diacetins are the alpha and sub-alpha forms. The sub-alpha form is in reversible solid-to-solid equilibrium with the alpha form at a transition temperature usually about 10° to 15°C. below the alpha m.p. and is stable at temperatures below this transition temperature. For the hydrogenated cottonseed, soybean, and rapeseed oil diacetins both forms were observed.

The alpha polymorphic form is obtained on cooling the liquid diacetins. To obtain the sub-alpha form it is necessary to chill quickly to about 0°C. Presence of triacetin, monoacetins, or other partial glycerides in these diacetins does not significantly affect the polymorphic behavior. For hydrogenated coconut oil only the sub-alpha form was observed. The long spacings which are shown in Table II for these diacetins are two in number, and correspond to 1-stearoyl diacetin and 1-lauroyl diacetin, respectively. Whether the diacetins exist in either the alpha or sub-alpha forms is of little practical importance since both forms show the waxy, translucent, highly flexible nature.

The unhydrogenated diacetins exist only in the sub-alpha form. Long-term storage of cottonseed oil diacetins for several months near the complete melting point failed to yield any alpha form. Mixtures of hydrogenated and unhydrogenated diacetins give the alpha form when the content of hydrogenated diacetins approaches 40 %. Mixtures of hydrogenated high-molecular-weight diacetins and hydrogenated coconut oil diacetins also give the alpha form when the content of high-molecular-weight hydrogenated diacetins approaches 40%.

Pure 1-stearoyl diacetin has a stability in the alpha polymorphic form of about three weeks at room temperature (5). The practical hydrogenated diacetins have been stored in the alpha form for as long as 3 to 4 years at room temperature with no transformation to a higher melting or more stable polymorphic form. One sample of cottonseed oil diacetins after storage for five years at room temperature was observed however to have a very small percentage of high melting material present. This particular material was opaque and brittle, reminiscent of normal, completely hydrogenated fat. X-ray diffraction characterization of it indicated that it was the beta form and composed primarily of 1-stearoyl diacetin. As the length of time required to produce the beta polymorphic form is so long, for all practical purposes, the mixed diacetins are stable in the waxy-translucent form. Not only is the solid-solid transformation of the alpha form to the higher melting beta form exceedingly slow, but it is also difficult to obtain the beta form from the melt. Liquid diacetins stored above the alpha melting point and below the beta melting point failed to show any crystallization after months of storage. Seeding with beta diacetins or with the beta form of 1-stearoyl diacetin did not hasten beta crystallization from the melt. No beta prime form has ever been observed for these materials.

Typical X-ray diffraction patterns on the sub-alpha, alpha, and beta forms of this type of fat are given in Plate I.

Discussion

There are five main characterizing features of the diacetin fats. These are: a) their waxy-translucency, b) their sharp melting point at relatively low temperatures, c) their flexibility, d) their oxidative stability, and e) their great stability in the alpha polymorphic form. The first three properties or features are related to and are an outgrowth of the last property, *i.e.,* the fact that the diacetin fats are almost indefinitely stable in the alpha polymorphic form.

The alpha polymorphic form of fats is noted for its translucency (6). The usual commercial fats show only fleeting existence in this form. At best it is only a matter of minutes or seconds before conversion to the more stable forms, beta prime or beta, takes place. Plate 2 pictures the translucency of diacetin fats as illustrated by 1-stearoyl diacetin.

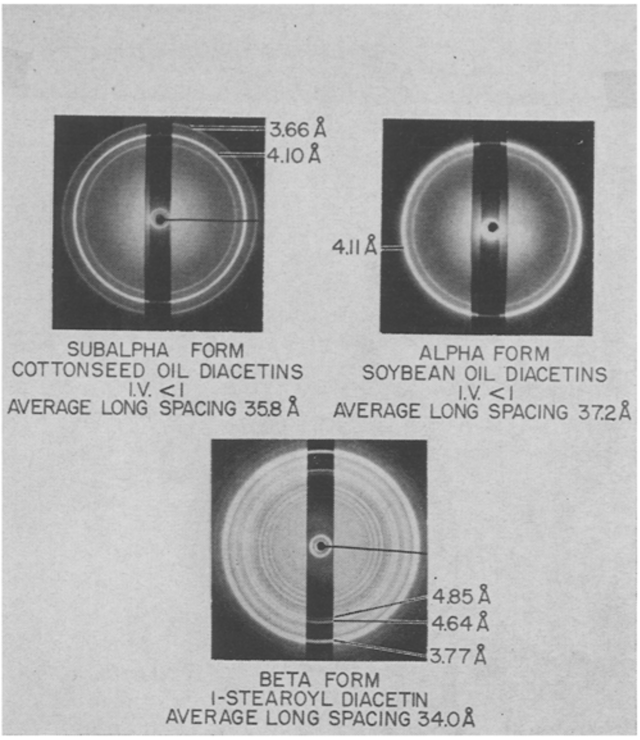
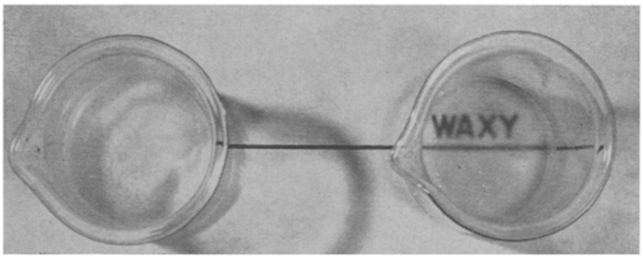


PLATE 1. X-ray diffraction patterns of typical hydrogenated diacetins.



Soybean oil, I.V. 8 1-Stearoyl diacetin

PLATE 2. Comparison of waxy, translucent hydrogenated diacetins (alpha form) and corresponding saturated high molecular weight hard fat.

The hydrogenated diacetin fats, by virtue of their lack of unsaturated material, are very stable to oxidation. This property is, of course, valuable when the material is used for coatings or similar applications. There has never been noticed any significant amount of hydrolytic rancidity encountered with these fats. Hydrolysis would, of course, give rise to acetic acid odors and flavors which would not be desirable in an edible use.

As the hydrogenated diacetins are completely saturated fats, they have fairly sharp melting points. This is particularly the case when the component high-molecular-weight acids vary little in chain length, such as diacetins made from soybean and cottonseed oils. The alpha melting point of a fat is considerably lower than the melting point of its most stable phase. Since the diacetins exist in the alpha polymorphic form, they have relatively low melting points. As derived from completely hydrogenated vegetable oils such as soybean, cottonseed, corn, peanut, and the like, the melting points are very close to body temperature.

The melting points of the diacetins can be changed by varying a number of factors. By altering the constituent high-molecular-weight saturated acids in a completely hydrogenated product, the melting point can be varied between about 0° and 50°C. If the high-molecular-weight acids are a mixture of unsaturated and saturated acids as in natural oils and fats, the melting point range can be varied between about —20°C. or below to 20°C. As the component high-molecular-weight acids are changed from a mixture as represented by a natural oil or hydrogenation product to a pure single fatty acid, the range in melting points obtainable is widened whereas the sharpness of melting of the product is narrowed. To obtain melting points higher than about 50°C., mixtures of glycerides including partial glycerides are used.

The alpha polymorphic stability and related properties of fats containing diacetins are a result of the component diacetyl triglycerides. The great phase stability of the diacetin fats as they are prepared is due to the simple fact that they are mixtures. It has been found that as one goes from 1-stearoyl diacetin to a mixture with 2-stearoyl diacetin, stability in the alpha form increases. If one further complicates the mixture by adding 1-palmitoyl diacetin, the stability is still greater. Interestingly, the compositions of the mixtures which give the greatest stability correspond with, roughly, the mixtures that one obtains in the particular process as described. Since this process involves random interesterification, it should give rise to ⅔ unsymmetrical diacetins (where the high-molecular-weight acid is in the 1-position) and ⅓ symmetrical diacetins (where the high-molecular-weight acid is in the middle or 2-position). Phase studies on synthetic mixtures of 1-stearoyl diacetin and 2-stearoyl diacetin have shown that compositions close to ⅓ symmetrical and ⅔ unsymmetrical have the greatest alpha stability.

The main use which has been suggested for the diacetins is for coatings. The great flexibility and translucency of the hydrogenated products make them promising for this purpose. The hydrogenated products may also be used as an icing fat, as a frozen dessert fat, as a filling fat, or any product requiring a fat which melts near body temperature. A high melting product such as can be made from rapeseed oil or incompletely acetylated superglycerinated C_{16}-C_{18} oils may be used as a chicle substitute,

The unhydrogenated diacetins or diacetins made from low-molecular-weight oils, such as coconut oil, could be utilized as salad oils. From coconut oil such a product would have exceptional oxidative stability. These oils could be compounded with hard fat or hydrogenated normal fats to yield shortenings of wide plastic range from 0° to 50°C. Additional compounding with various additives such as salt, coloring, and flavoring would give a margarine type product or spread.

Inedible uses other than coatings include carriers for medicinals, vehicles for drug products, and as plasticizers.

Summary

Mixed diacetyl triglycerides (diacetins) are unique in that they form waxy-translucent, non-greasy, and highly flexible solids.

Diacetin fats were prepared from a number of common vegetable oils by random interesterification with triacetin followed by removal of first the excess triacetin, then the diacetins by distillation. Both the hydrogenated or completely saturated diacetins and the unhydrogenated products were characterized by melting point behavior and X-ray diffraction patterns.

The waxiness and flexibility of diacetin fats is a result of their existence in the alpha polymorphic form. This polymorphic form and hence these properties are, for practical purposes, stable at room temperature or near their melting point. The stability is due to the fact that the diacetins are a mixture of ⅓ symmetrical and ⅔ unsymmetrical diacetyl triglycerides and contain more than one high-molecular-weight fatty acid.

The hydrogenated diacetin fats are very stable to oxidation. When made from C_{16}-C_{18} oils or fats, these materials have very sharp melting points, *i.e.*, a melting range of 2°C. or less, slightly below body temperature. Variation in melting behavior without loss in waxiness or flexibility can be obtained over a range of —20° to 60°C. by varying the constituent high-molecular-weight acids and/or the degree of esterification.

Diacetin fats, especially the completely saturated derivatives, are useful as coatings. Other edible fat uses include icing fats, filling fats, dessert fats, salad oils, and as base stocks for shortening or margarine formulation. Suggested inedible uses are as carriers or vehicles for medicinals or drug products and as plasticizers (8).

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