Additional Physical Properties of Diglyceride Esters of Succinic and Adipic Acids[1]

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FAT PRODUCTS are sometimes desired which are more viscous, higher melting, or harder than are products generally available. A potentially useful series of compounds which might meet these special requirements can be prepared by esterifying the diglycerides of the fat-forming acids with succinic, adipic, and other short-chain dibasic acids.

Prior to our investigation of these compounds practically no information concerning their properties was available. Blake (1) in a patent concerned with surface-active agents claimed that one of the products he prepared was bis(glycerol dioleate) malate. A number of compounds of this type have been prepared and examined in our laboratory, and their properties have been described (3, 10). One of the reports (3) was concerned with the 1,3-diolein and 1,3-distearin diesters of fumaric, succinic, and adipic acids; and the other report (10) was concerned largely with similar compounds made from unsymmetrical and diacid diglycerides.

Different systems of naming the compounds have been used in the references cited. In the preferred system of nomenclature the compound made by combining two molecules of 1,3-distearin and one of succinic acid is called bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] succinate. In the present report, which will be concerned only with the 1,3-distearin and 1,3-diolein diesters of short-chain dibasic acids, the above compound will be called distearin succinate for the sake of brevity and convenience. The other compounds to be discussed will be named accordingly.

The compounds which will be described probably are edible; however they have not yet been proven to be edible, hence cannot be recommended for food use at this time. Some information on the physiological behavior of related compounds has been obtained for us and will be published in another report.

The purpose of the present report is to describe some of the properties deemed most important in determining potential uses of the compounds. These properties include viscosity, hardness, thickening ability when mixed with a liquid oil, surface activity, and permeability to moisture.

Experimental

Materials. The 1,3-diolein and 1,3-distearin esters of succinic and adipic acids and the 1,3-diolein ester of fumaric acid employed in the current experimental work were the same compounds used in a previously described series of experiments (3). In the preparation of each compound, highly purified stearic acid or methyl oleate was converted into a mixture of mono-, di-, and triglycerides; and the 1,3-diglyceride fraction was isolated and carefully purified. The 1,3-diglyceride was dissolved in chloroform and treated with the acid chloride of the dibasic acid in the presence of a slight excess of pyridine or quinoline. When succinyl and fumaryl chlorides were used, quinoline and the acid chloride were added slowly and simultaneously so that the reaction mixture contained just enough quinoline to react with the hydrogen chloride which was liberated. The reaction product was purified by washing successively with dilute hydrochloric acid and water, then repeatedly crystallizing from *n*-hexane and from acetone. With the diolein compounds, the impurities rather than the compounds crystallized out of solution. The melting points and other data on the compounds are recorded in Table I.

Test Procedures. In making the solubility determinations, sealed glass tubes or ampules (10 × 60 mm.) containing known concentrations of binary mixtures of cottonseed oil and hard fat (distearin adipate, tristearin, or hydrogenated cottonseed oil) were tumbled end over end in a water bath, and the disappearance of the solid phase for each mixture was observed visually as the temperature of the bath was increased in a stepwise fashion (9).

Hardness was measured by a recently devised procedure (8). A steel sphere, ⅜ in. in diameter, was pressed onto the surface of the test specimen for a period of one minute with sufficient force to obtain a slight impression. From the area of the impression and the force, the hardness index was calculated in terms of kilograms per square centimeter. Consistency was measured with a micropenetrometer of the falling needle type. The instrument and technique used were those described in an earlier report from this laboratory (2).

Fat leakage tests were made by a previously described technique (4), which consisted of putting a 0.5-cm. cube of the test specimen on one end of a strip of filter paper measuring 0.4 × 4.0 cm., placing the entire assembly in a constant temperature oven, and measuring after different intervals of time the length of the filter paper wetted by the fat.

Permeability was measured by a modification (7) of the standard cup method. The permeability constant, P, was calculated by using the equation, $P = WX/Atp$, where W was the weight of water, in grams, diffusing through the fat film of thickness X, in centimeters, and area A, in square centimeters, during the time t, in seconds, when the vapor pressure difference p, was measured in millimeters of mercury.

Other data were obtained by conventional procedures. Thus surface and interfacial tensions were determined with an interfacial tensiometer of the ring type, and viscosities were determined with the aid of Ostwald-Cannon-Fenske microviscometers.

Results and Discussion

Solubility. A hard fat to be used in thickening an oil should, of course, be relatively insoluble in the oil. Because a compound like distearin adipate melts

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TABLE I

Diglyceride Esters Used in Tests

Compound		Melting point, °C.	Refractive index, $n^{95/D}$	Density, g./ml. at	
Short name	Exact name			30°C.	50°C.
Diolein fumarate	bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] fumarate	......	1.44900	0.9458	0.9346
Diolein succinate	bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] succinate	......	1.44709	0.9384	0.9281
Diolein adipate	bis[1-(oleoyloxymethyl)-2-(oleoyloxy)ethyl] adipate	......	1.44671	0.9397	0.9310
				94.6°C.	123°C.
Distearin succinate	bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] succinate	89.8	1.43861	0.8682	0.8583
Distearin adipate	bis[1-(stearoyloxymethyl)-2-(stearoyloxy)ethyl] adipate	82.1	1.43844	0.8910	0.8731

at a temperature well above that of ordinary fats and probably possesses a heat of fusion similar to that of such fats, it should be more insoluble in oils than are ordinary hard fats. This anticipation is borne out by the plotted data in Figure 1.

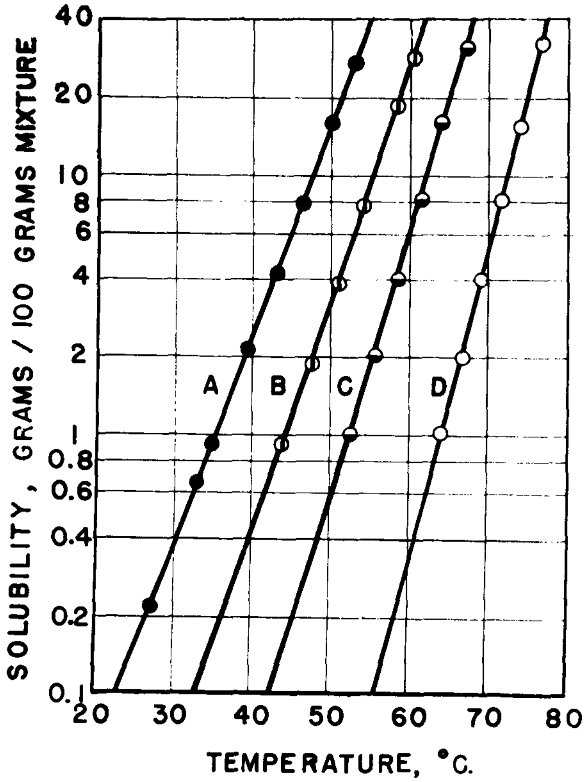

FIG. 1. Solubility in cottonseed oil: *A*, hydrogenated cottonseed oil, iodine value 29.3; *B*, hydrogenated cottonseed oil, iodine value 1.1.; *C*, tristearin; and *D*, distearin adipate.

At 55°C. the distearin adipate is soluble in cottonseed oil to the extent of less than 0.1% while tristearin and hydrogenated cottonseed oil of iodine value 1.1 are soluble to the extent of about 2 and 10%, respectively. Even at 70°C. the solubility of the distearin adipate in cottonseed oil is only about 5%. Obviously compounds like distearin adipate should be good stiffening agents from the standpoint of solubility characteristics.

The solubility of the 1,3-diolein esters of the short-chain dibasic acids lies at the other extreme of the range of solubilities of ordinary fats and oils. The diolein compounds are miscible with the natural oils in all proportions and apparently cannot be crystallized out of solution with a natural oil. Apparently the diolein compounds cannot even be crystallized from solvents by cooling with dry ice. The compounds themselves merely become more viscous on being cooled at a moderate rate. When stored at −20°C., some appeared to change partly to a crystalline form while others appeared to be highly viscous liquids, even after several weeks at −20°C. Thus compounds like diolein fumarate and diolein succinate should be useful in solubilizing the oleoyl group for utilization at low temperatures.

Hardness and Consistency. Distearin succinate and distearin adipate form glossy, white solids when their melts are rapidly cooled. Like rapidly solidified tristearin, these solids also are quite brittle. They differ from tristearin and other trisaturated fats in being much harder. The average hardness index obtained for each compound when the rapidly solidified test specimens were tempered at 40°C. for 20 hrs. prior to testing are recorded in Table II. Data for several common fats and waxes are also recorded.

TABLE II

Hardness Data

Product	Test temperature °C.	Hardness index
Distearin succinate	28	297
Distearin adipate	28	397
Carnauba wax	28	429
Rosin (8)	30	860
Tristearin (8)	30	170
Hydrog. cottonseed oil (I.V. 1.0) (8)	30	140
Beeswax (8)	30	17
Cocoa butter (aged) (8)	25	15

The distearin adipate was practically as hard as the carnauba wax, and the distearin succinate was approximately twice as hard as the highly hydrogenated cottonseed oil.

The distearin esters were more effective than either highly hydrogenated cottonseed oil or tristearin in their ability to form hard mixtures when mixed in large proportions with cottonseed oil. Some of the hardness indices obtained with such mixtures are recorded in Figure 2.

The consistency of cottonseed oil mixtures containing small proportions of the distearin esters and highly hydrogenated cottonseed oil apparently does not follow the order indicated for hardness in Figure 2. When the consistency was measured with a falling needle type of micropenetrometer, a cottonseed oil mixture containing 5% of distearin succinate was softer than a 5% mixture of highly hydrogenated cottonseed oil in cottonseed oil. At room temperature the micropenetration reading for the former was 218 mm./10 and that for the latter was 153 mm./10. Both mixtures were prepared by first melting all of the components and then rapidly cooling the solution. As the contents of solid material were increased, the micropenetration values for the two mixtures became more nearly alike until at a solids content of about 12% they were equal. As the solids content increased

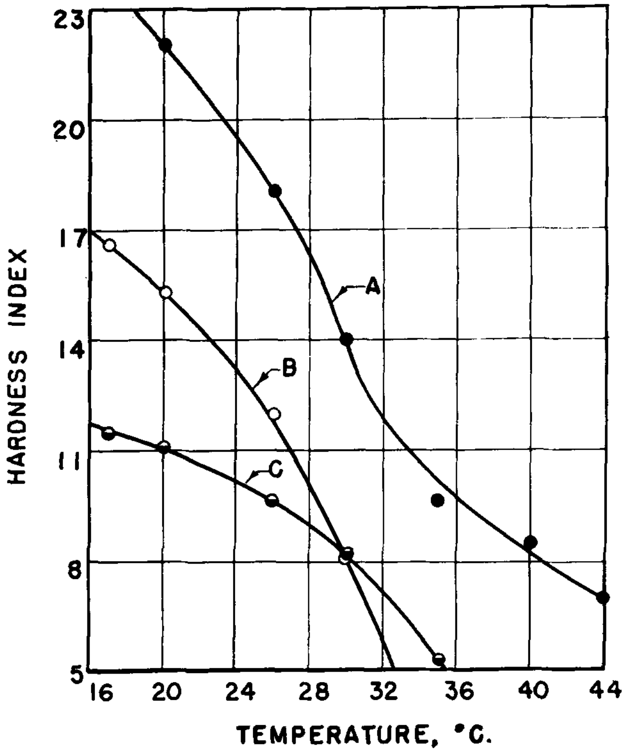

FIG. 2. Hardness curves for 1:1 mixtures by weight of cottonseed oil with *A*, distearin adipate; *B*, tristearin; and *C*, hydrogenated cottonseed oil, iodine value 1.0.

above 12%, the mixture containing the distearin succinate became progressively stiffer than that containing the hydrogenated cottonseed oil.

The relatively greater firmness of the hydrogenated cottonseed oil-cottonseed oil mixture at a low content of solids probably can be attributed to the fact that hydrogenated cottonseed oil crystallizes out of a cottonseed oil solution in the form of very minute and imperfect crystals while other hard fats having a composition quite different from that of hydrogenated cottonseed oil tend to form fewer, larger, and more isolated crystal masses and to produce a less rigid mixture (5).

Fat Leakage. The crystal habits of the distearin esters of the short-chain dibasic acids are such that the compounds should be suitable for use in fat products to retard fat leakage or bleeding. The distearin esters tend to crystallize out of solution as long, needle-like crystals. The tendency is particularly pronounced when the compounds have not been purified to a high degree. Some of the compounds have been obtained as masses of asbestos-like fibers. The extent to which fat leakage can be retarded by their use is indicated by the curves in Figure 3. In obtaining these curves the several mixtures were heated until liquid, then rapidly chilled. Cubes were cut from these masses and were held for 20 hrs. at 5°C. before the bleeding tests were made. The samples were tested simultaneously, using strips of filter paper cut from the same sheet.

Viscosity. At room temperature the diolein esters of the dibasic acids are more viscous than is cottonseed oil, a relationship which should be expected from the difference in molecular size. However they are not as viscous as castor oil. Thus, at 26°C., the viscosities of castor oil, diolein adipate, diolein fumarate, and cottonseed oil were found to be 560, 196, 155, and 69 centistokes, respectively (Figure 4). The distearin esters possess viscosities similar to those of the diolein esters (3). As the temperature increases, the viscosity of the diolein esters decreases in about the same manner as that of cottonseed oil while the viscosity of castor oil decreases at a proportionately faster rate. At 100°C. the diolein adipate and the castor oil possess approximately the same viscosity.

Surface and Interfacial Tensions. Several random tests confirmed the fact that the compounds under investigation resembled ordinary fats and oils with regard to surface and interfacial tensions. Diolein succinate had a surface tension of 25.35 dynes cm.$^{-1}$ at 70.2°C., and distearin succinate had a surface tension of 28.01 dynes cm.$^{-1}$ at 94.6°C. The interfacial tension against water for diolein succinate was found to be 21.88 dynes cm.$^{-1}$ at 70.2°C., and that for distearin succinate was 25.37 dynes cm.$^{-1}$ at 94.6°C.

Melting and Smoke Points. An earlier investigation (3) showed that distearin fumarate, succinate, and adipate can exist in at least two polymorphic forms. There is some evidence that each compound can exist in at least one additional form. The transition from one polymorph to the next apparently takes place without visible melting occurring. So far only one melting-point has been found for each compound.

Smoke points for two compounds were determined and found to be in the range usually associated with fats and oils. Specifically the following smoke points were found:

Distearin adipate	224°C.
Diolein adipate	231°C.
Cottonseed oil	234°C.
Paraffin oil	185°C.

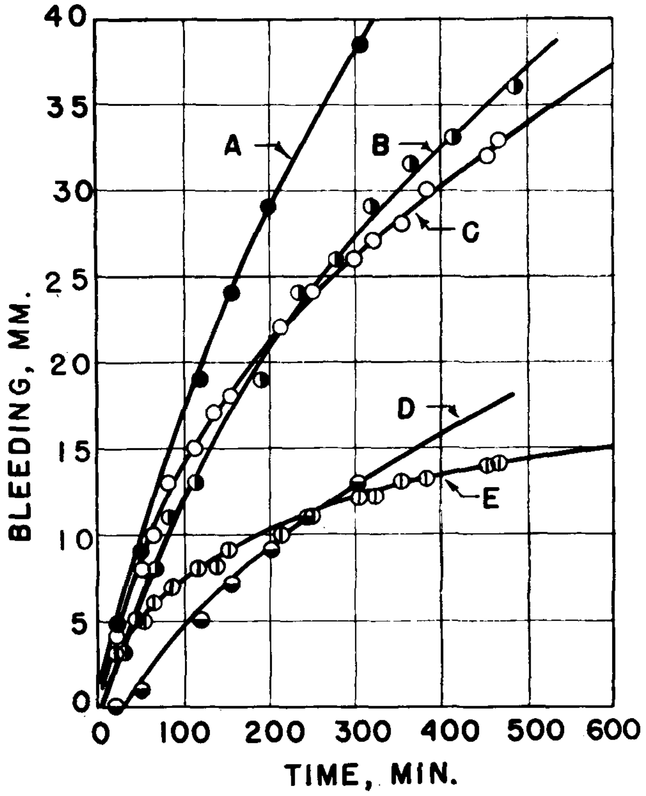

FIG. 3. Fat leakage rate at 40°C. for cottonseed oil mixtures contain *A*, 16% tristearin; *B*, 16% hydrogenated cottonseed oil, iodine value 1.0; *C*, 32% tristearin; *D*, 16% distearin adipate; and *E*, 32% distearin adipate. Percentages calculated on a total weight basis.

Permeability. The rate at which water vapor passes through distearin succinate, distearin adipate, carnauba wax, and highly hydrogenated cottonseed oil was determined in tests conducted simultaneously. The films used were formed, solidified, and heat-treated under similar conditions, that is, each compound or product was heated well above its melting point, poured into a mold, and quickly solidified with the aid of a brass block which previously had been chilled to about −16°C. All samples were warmed to and stored at room temperature before testing. The permeability data obtained, together with data obtained in a previous investigation (6), are recorded in Table III.

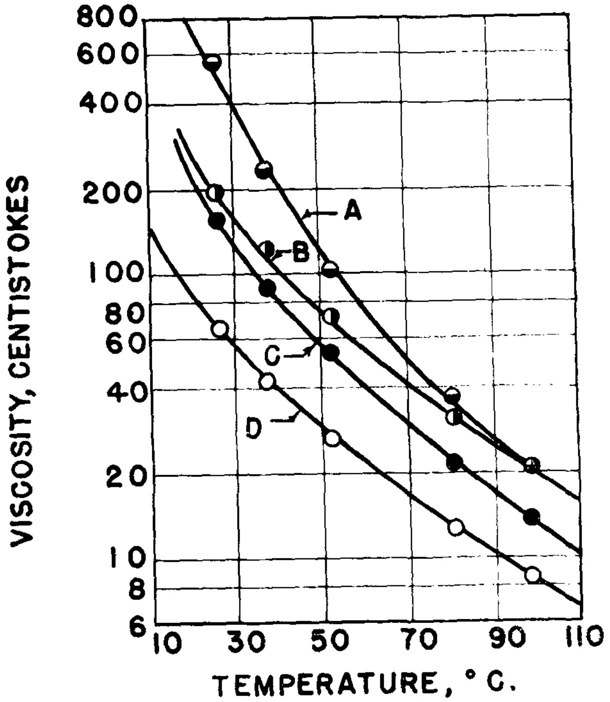

FIG. 4. Viscosity-temperature curves of *A*, castor oil; *B*, diolein adipate; *C*, diolein fumarate; and *D*, cottonseed oil.

By way of orientation, freshly solidified paraffin probably is the most impermeable of all organic compounds. The particular sample tested was found to have a permeability constant of zero, but other samples have been found to have permeability constants of about 0.2×10^{-12}.

TABLE III

Permeability to Water Vapor [a]

Product	Film thickness, mm.	Permeability constant $\times 10^{12}$	Moisture transferred, mg./hr./sq. cm.
Distearin succinate	3.00	82.5	0.0265
Distearin adipate	2.81	37.9	0.0130
Carnauba wax	2.15	2.2	0.0010
Hydrog. cottonseed oil (I.V. 1.0)	3.20	2.06	0.0018
Cocoa butter (6)	2.92	81.6	0.0263
Cocoa butter (6)	2.14	60.5	0.0269

[a] Tests made at room temperature with a relative humidity of 100% on one side of the film and 0% on the other.

The data obtained indicate that the distearin esters are about as impermeable to water vapor as is cocoa butter but not as impermeable as is carnauba wax. Actually the distearin esters when tested under other conditions may be even more impermeable than represented in Table III. As with many pure compounds, hairline cracks tended to develop in the films of distearin succinate and distearin adipate. While the films which were tested did not have visible cracks, the possibility of some very minute cracks cannot be excluded. An earlier investigation (6) has shown that the thermal history of a film of fat has a very marked effect on its permeability, and it might be possible to devise conditions of solidification which would result in less permeable films.

Summary

Diglycerides of the fat-forming acids yield, on esterification with succinic, adipic, and other short-chain dibasic acids, a potentially useful series of compounds ranging from hard, high-melting waxes to viscous oils which will not crystallize. A number of the properties of these compounds were determined in earlier investigations.

In the present investigation additional properties of the 1,3-diolein and 1,3-distearin esters of succinic and adipic acids were determined. Surface and interfacial tensions were measured and found to be similar to those of cottonseed oil. The smoke points also were found to be similar to that of cottonseed oil. The ability of the compounds to thicken cottonseed oil was measured and found to be somewhat better than that of highly hydrogenated cottonseed oil at levels above about 12%, and the mixtures were relatively resistant to fat leakage. In hardness the distearin esters of succinic and adipic acid were comparable to carnauba wax and were over twice as hard as highly hydrogenated cottonseed oil. Permeability to water vapor was found to be greater than that of highly hydrogenated cottonseed oil and carnauba wax and about equal to that of cocoa butter.

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