strable alteration in the nutritional value of the flour protein (Frazer *et al.*—*J. Sci. Food & Agr. 7,* 375). Vitamin E is destroyed in this process, but this was not considered to be of a serious nutritional significance for flour provides only a small percentage of our needs for this factor.

Monoglycerides from super glycerinated fats were purified of flavor reverting materials by treatment with short chain ketones, cooled until two phases formed, one of which contained reverting material, the other nonreverting monoglycerides (Young & Black—*U. S. 2,740,799*). In an analysis of the odorous flavor-reverting materials distilled from peanut oil, hexanal, several long chain normal hydrocarbons, some hydrocarbons with terminal dimethyl groupings, and sitosterol were identified (Letort & Sorba—*Bull. soc. chim. France 1956,* 69). A coconut-like off-flavor of milk fat, dried whole milk, evaporated milk, and dried cream was attributed to the presence of the lactone of 5-hydroxydecanoic acid (Keeney & Patton—*J. Dairy Sci. 39,* 1104, 1114).

Maltschewsky (*Fette-Seifen-Anstrichmittel 58,* 331, 336) reviewed and recorded new experimental data on the microbiological spoilage of margarine. Two types of margarines were stored at +20, +15, +5, −5, and −25°, respectively and the amount and types of bacteria developed in the samples and the acidity through 90 days' storage were recorded.

Physical Properties of Aceto- and Butyro-Oleins, Mono-Olein, and Diolein[1]

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GLYCERIDES CONTAINING both long- and very short-chain fatty acids have been shown to exhibit unusual properties (10, 11, 13, 19), which are of potential value in a number of practical applications (3, 9, 16). The saturated glycerides like 1,2-diaceto-3-stearin and 1-aceto-3-palmitin possess the unique property of normally solidifying to a soft, waxy polymorphic form, the alpha form, which is quite stable for these compounds. Limited experiments with aceto-oleins (10) have indicated that these glycerides also solidify in a waxy polymorphic form though these modifications generally occur at temperatures far below 0°C. Such polymorphic modifications together with other physical properties are of interest because the unsaturated glycerides are potentially useful in applications requiring low-melting oils having good resistance to oxidation, polymerization, and deterioration.

Practically no data have been published on the physical properties of the aceto- and butyro-oleins. Data are meager even for 1-mono-olein and 1,3-diolein, glycerides whose characteristics should prove useful in correlating the characteristics of the aceto- and butyro-oleins. Carter and Malkin (5) have investigated the polymorphism of 1-mono-olein and have reported the existence of four forms including a vitreous form. The expansibility and melting dilation for the highest melting form and the expansibility in the liquid state have been determined for 1-mono-olein (18). The polymorphism of 1,3-diolein has been investigated by Carter and Malkin (5), who found two polymorphic forms, and by Daubert and Lutton (8), who found one polymorphic form.

In the present investigation physical measurements were made on the following six compounds: 1-aceto-3-olein, 1,2-diaceto-3-olein, 1-butyro-3-olein, 1,2-dibutyro-3-olein, 1-mono-olein, and 1,3-diolein. Refractive indices, densities, melting points, points of transition from one polymorphic form to another, expansibilities in the solid and liquid states, and melting dilations or volume changes accompanying transformations were measured or calculated. For 1-aceto-3-olein and 1-butyro-3-olein infrared spectra, which have heretofore not been reported, were obtained.

Experimental

Materials. The 1-mono-olein used in the measurements and in the preparation of the aceto- and butyro-oleins was prepared as described in a previous publication (10). Purified methyl oleate derived from pecan oil was interesterified with glycerol, the mixed glycerides were fractionated by molecular distillation, and the mono-olein fraction was further purified by crystallization from acetone. Purity of the final product was 98.6%, as analyzed by the periodic acid method of Handschumaker and Linteris (12).

The 1,3-diolein was prepared by repeatedly crystallizing from acetone the diolein fraction obtained as a by-product in the purification of the 1-mono-olein by molecular distillation.

The 1-aceto-3-olein, 1,2-diaceto-3-olein, 1-butyro-3-olein, and 1,2-dibutyro-3-olein were prepared by direct esterification of 1-mono-olein with either acetyl or butyryl chlorides, using a procedure essentially like that described by Malkin *et al.* (15). Briefly the monoglyceride and the required quantity of acid chloride, each in chloroform solution, were mixed and allowed to react at room temperature for two days. For the preparation of the diglycerides the mole ratio of acid chloride to monoglyceride was slightly less than 1:1 while for the preparation of the triglycerides this ratio was slightly greater than 2:1. After completion of the reaction the mixture was taken up in diethyl ether and washed successively with a dilute solution of hydrochloric acid, a dilute solution of sodium hydroxide, and water. The triglycerides were further purified by several crystallizations from acetone at low temperatures. The diglycerides were further purified by first removing unreacted monoglyceride and then crystallizing the diglycerides from hexane, a procedure which will be described more fully in a subsequent article.

As a check on purity all of the compounds were analyzed for monoglyceride content (12) and hydroxyl value. The latter analysis was made according to the procedure of West *et al.* (20) except that the weight ratio of the acetic anhydride to pyridine employed was 1:4.

Analytical data for the various products are recorded in Table I. Comparison of the data for monoglyceride contents and hydroxyl values reveals small discrepancies, which are believed to have no signifi-

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TABLE I

Analytical and Physical Data for the Oleoglycerides

Compound	Hydroxyl value		Content of monoglyceride [a] %	Refractive index n_D^{35}	Density, g./ml. at 35° C.	Melting or transition point [b] °C.			
	Experimental	Theoretical				Form I	Form II	Form III	Form IV
1,2-Diaceto-3-olein	0.0	0.0	1.04	1.45180	0.9623	—17.5	—26.0	—48.0	
1,2-Dibutyro-3-olein	0.0	0.0	0.97	1.45119	0.9438	—29.0	—37.0	—44.4	
1-Aceto-3-olein	137.6	140.8	1.38	1.45801	0.9536	7.8	6.0 [c]	—13.4	—28.2
1-Butyro-3-olein	129.4	131.4	1.19	1.45713	0.9416	—3.2	—6.4 [c]	—23.4	—36.0
1,3-Diolein	91.7	90.3	0.48	1.46419	0.9128	25.0	20.0 [c]	0	
1-Mono-olein	312.7	314.7	98.6	1.46384	0.9407	32.0	25.0 [c]	12.5	

[a] Calculated as mono-olein.
[b] Obtained by capillary tube method.
[c] Rapid chilling of melt to —70° C.

cance because they are approximately within the limits of accuracy of the methods employed.

Procedures. As a guide to the dilatometric treatment of the glycerides and as an aid in the interpretation of the dilatometric data, melting and transition points for each of the glycerides were obtained by the capillary tube method. A sample of each glyceride was sealed in a capillary tube. If not already at a temperature well above its melting point, the sample was heated to such a temperature. The sample was then allowed to cool slowly to —60°C. in a dry ice chest. The chilled sample was placed in a dry ice-acetone bath at —50°C., and the bath was warmed slowly. Temperatures at which melting or phase transformations occurred were noted; the phase transformations generally were detected by abrupt changes in translucence and other visual appearance. Each sample was further examined over short temperature intervals by the "thrust-in" technique, that is, each sample was solidified and tempered at various temperatures for various periods of time and then thrust into a constant temperature bath, maintained just above or below the temperature where melting or phase transformation was thought to occur. The recorded points of melting or phase transformation are the average of the lowest temperature where a change definitely was observed and the highest temperature where the change was not observed. The melting and transition points which were established are recorded in Table I.

In order to substantiate melting and transition point data, heating curves for each glyceride were obtained. The apparatus and procedure used was similar to that used by Daubert and Clarke (7) for investigation of the polymorphism of low-melting glycerides. The sample was placed in a small glass vial which was suspended inside a small, unsilvered vacuum flask containing acetone. The acetone, which previously had been cooled to a low temperature with dry ice, was stirred continuously by an air current and slowly heated by a 125-watt, knife-type of immersion heater operated through a rheostat so that the bath temperature increased uniformly at a rate of 0.5°C. or 1.0°C. per minute. As the bath temperature increased, sample temperatures were measured at 1-min. intervals with the aid of a potentiometer and an eight-junction copper-constantan thermopile.

The dilatometric examinations were carried out in dilatometers of the gravimetric type with mercury as the confining liquid. The construction of these dilatometers, their method of use, and methods employed in making the various calculations were in accordance with previously published descriptions (1, 2) except that the suggested precautions for the elimination of vacuole formation were not taken. Vacuole formation did not appear to be a factor in the determinations.

For one series of dilatometric measurements the liquid glycerides were chilled rapidly to about —60°C. by immersing the dilatometers in crushed dry ice, after which the dilatometers were warmed to the melting point of mercury (—38.7°C.). Then dilations with increasing temperature were recorded. For another series of determinations the dilatometers containing the samples were chilled slowly in steps of 5 Centigrade degrees. Dilations were measured during both the chilling cycle and the subsequent heating cycle.

The density of each glyceride at 35°C. was determined by the pycnometer method. The data obtained are recorded in Table I.

The refractive index of each glyceride was determined at 35°C. by use of a modified Abbé refractometer.

Infrared absorption spectra in the region 2 to 12 microns were measured for 1-aceto-3-olein and 1-butyro-3-olein with an automatic-recording infrared spectrophotometer at 25 ± 0.1°C. These data are compared with data for other diglycerides (17) and certain bands are examined. Heretofore no infrared data for these diglycerides have been published.

Results and Discussion

Densities. A comparison of the densities recorded in Table I reveals that the substitution of a short-chain acyl group for one or both of the hydroxyl groups in 1-mono-olein increases the density. The effect is more marked for two groups than for one group. The substitution of a long-chain acyl group, the oleoyl group, for one hydroxyl group in 1-mono-olein lowers the density.

Refractive Indices. Examination of Table I reveals that as the hydroxyl groups of 1-mono-olein are replaced by a short-chain group, such as the acetyl or butyryl group, the refractive index is decreased. The substitution of one acetyl group lowers the value of the refractive index of 1-mono-olein by 0.006 unit, and the substitution of two acetyl groups lowers the value by 0.012 unit. The effect is increased as the chain length increases; the effect is more marked for butyryl groups. However substitution of an oleoyl group for the hydroxyl group in 1-mono-olein actually increases the refractive index. This latter increase in refractive index is expected as a result of the introduction of an additional double bond in the molecule.

Infrared Spectral Data. The infrared absorption spectra were determined for 1-aceto-3-olein and 1-butyro-3-olein and are shown in Figure 1. These spectra were similar to those found by O'Connor *et al.*

(17) for other diglycerides. However the absorption band at 9.6 microns, tentatively assigned to a C-O stretching of an alpha substituted secondary alcohol (17), is much more profound for the two diglycerides mentioned above than it is for 1,3-diolein. The absorption for 1-aceto-3-olein is greater than it is for 1-butyro-3-olein. It has been shown that the band at 9.6 microns is almost three times more intense for 1-aceto-3-stearin than it is for 1,3-distearin (17).

A maximum at 9.1 microns was observed for each of the diglycerides but was much larger for the 1-butyro-3-olein than for the 1-aceto-3-olein. This maximum is characteristic of all glycerides and has been found to be unusually intense for butyro-containing compounds (17). No assignment has been given to this band.

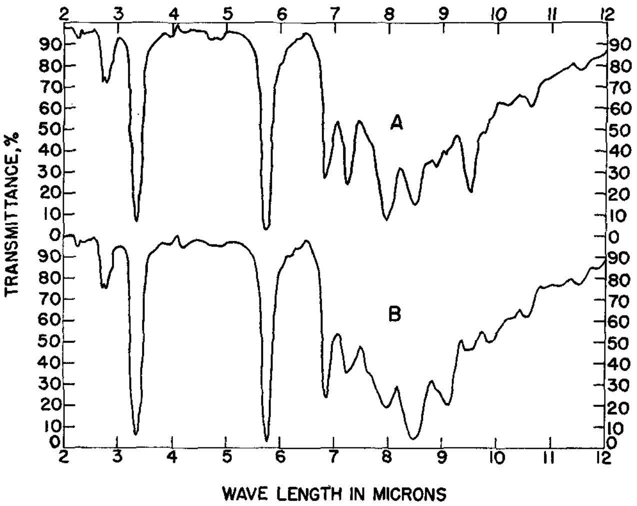

Fig. 1. Infrared absorption spectra of: *(A)* 1-aceto-3-olein in chloroform solution, 39.94 g./l., 0.4-mm. cell, and *(B)* 1-butyro-3-olein in chloroform solution, 41.77 g./l., 0.4-mm. cell.

Melting and Transition-Point Data. The data in Table I reveal that for the glyceride series consisting of 1-mono-olein, 1-aceto-3-olein, and 1,2-diaceto-3-olein, the melting points of the highest-melting forms decrease as the number of acetyl groups increases. This same effect is noted for the butyryl groups and is even more pronounced.

From capillary tube observations there appeared to be three solid forms for the 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein. For 1,2-diaceto-3-olein, Form I, the stable modification, melted at —17.5°C.; Form II changed in appearance at —26.0°C.; and Form III changed in appearance at —48.0°C. Form I was obtained by slow cooling. On rapid cooling, followed by slow warming, two transformation points were detected, Forms II and III. The transition from Form III to Form II at —48.0°C. appeared as a sudden increase in volume; the space between the solid sample and capillary walls disappeared abruptly. The change from Form II to I at —26.0°C. was characterized by the opaque, white solid becoming translucent. With 1,2-dibutyro-3-olein three similar forms were observed on similar heat treatment.

Wheeler *et al.* (21) have observed three polymorphic forms for triolein. However not all triglycerides containing the oleoyl group have three forms. Daubert and Clarke (7) have reported the existence of four distinct polymorphic forms for 1-oleo-2,3-dicaprin and 1-oleo-2,3-dilaurin. Hence the three forms found for 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein in the course of the present investigation may or may not include all of the possible polymorphic forms of the compounds. Characterizing the polymorphic behavior of the diaceto- and dibutyro-olein proved to be quite difficult. The compounds not only had low melting points, —17.5 and —29.0°C., but also had a great tendency to supercool. Rapid chilling to a low temperature (*ca.* —60°C.) to obtain unstable polymorphic forms gave supercooled liquids which were viscous and did not crystallize. The tendency of the compounds to crystallize in a translucent form was a further obstacle to visually observing polymorphic changes.

Even if all polymorphic changes could have been produced and observed with ease, establishment of the exact number of polymorphic forms might not have been possible. Baur *et al* (4) have found that some glycerides, like dilaurin, can exist in two forms which have identical melting points.

X-ray diffraction patterns, which would definitely establish differences in polymorphic form, were not obtained for the aceto- and butyro-oleins. The low melting points of these glycerides made it impossible to handle their solid forms in the X-ray diffraction equipment available to us. For the same reason the polymorphism of these glycerides could not be defined in the terms of accepted nomenclature for polymorphism (14).

The diglycerides, 1-aceto-3-olein and 1-butyro-3-olein, differ from the 1,3-diolein in regard to the number of polymorphic forms and the existence of seemingly non-crystalline forms of the first mentioned diglycerides. Slow chilling followed by slow warming of 1-aceto-3-olein produced a stable modification, Form I, which melted at 7.8°C. Form II was obtained by the "thrust-in" technique. It melted at 6.0°C. Rapid chilling, followed by slow wamring, produced Form IV, which changed from a crystalline to translucent appearance at —28.2°C. Another form, Form III, was observed at about —13.4°C. Four polymorphic modifications were found for 1-butyro-3-olein by the same techniques used for 1-aceto-3-olein. Form I, the most stable modification, melted at —3.2°C. Form II, obtained by the "thrust-in" technique, melted at —6.4°C. An unusual change in the appearance of 1-butyro-3-olein occurred at —36.0°C. At this temperature the crystalline material appeared to melt, transforming into a transparent form. The diglyceride remained in this seemingly non-crystalline form until a temperature of —23.4°C. was reached, where it changed to a crystalline form.

Carter and Malkin (5) found two polymorphic forms for 1,3-diolein. By X-ray examination these were shown to be alpha, m.p. 18°C., and beta, m.p. 25°C. Daubert and Lutton (8) found but a single melting point at 21.5°C. In the present investigation two forms which melted at 20.0°C. and 25.0°C. were found together with a transformation point at 0°C., where a volume change occurred.

For 1-mono-olein three polymorphic forms were observed by the capillary tube method. Form I, the stable modification, melted at 32.0°C. Form II melted at 25.0°C. A transformation of Form III was observed at 12.5°C. Carter and Malkin (5) described the form which transforms at 12.5°C. as the vitreous form.

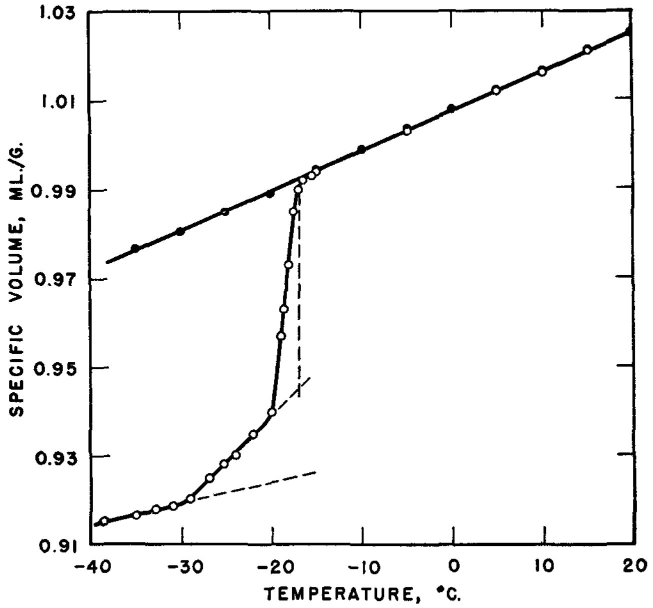

FIG. 2. Specific volume of 1,2-diaceto-3-olein as a function of temperature on cooling at a moderate rate (filled circles) and on warming after slow solidification (open circles).

The form which melts at 25.0°C. is called the alpha form, and that which melts at 32.0°C. is called the beta prime form. In addition, they report a fourth form, the beta form, which melts at 35.0°C. The transition beta prime to beta is said to be very slow, and it is usually necessary to hold the beta prime form near its melting point for some time in order to effect conversion into the stable beta form. Under the conditions employed in our investigation the beta form was not found.

In the absence of X-ray diffraction data the existence of transition points was substantiated by thermometric measurements. Phase transformations are accompanied by heat effects which are indicated by inflections in plots of temperature *vs.* time. Heating curves for the 1,2-diaceto-3-olein revealed inflections at approximately —18°C., —24°C., —42°C., and —48°C. Excepting the point at —42°C., these were the same as detected by the capillary tube method. The three forms detected for the 1,2-dibutyro-3-olein were verified by the heating curve. Also the points for 1-aceto-3-olein and 1-butyro-3-olein were the same as those determined by the capillary tube method. Three points corresponding to those obtained by the capillary tube method were found for the 1,3-diolein. For the 1-mono-olein however only one transition point, 32.0°C., corresponding to Form I was observed.

Dilatometric Behavior. Figure 2 illustrates the type of curves obtained on plotting volumetric expansion data for the two triglycerides, 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein. The coefficients of expansion in the solid and liquid states, the volume changes accompanying melting, and the dilatometric melting points were calculated from these curves. The calculated data are recorded in Table II.

Neither of the triglycerides could be crystallized by cooling the melt at a rapid rate. Even a moderate rate did not produce a completely crystalline state, at least not over the time interval used in the tests. Moderate or rapid cooling merely congealed the liquid and produced a glass-like solid. As as example, when liquid 1,2-diaceto-3-olein was cooled at a moderate rate, its volume-temperature relationship followed the upper, more horizontal portion of the curve in Figure 2. As the temperature was decreased below the normal melting point of —17.5°C., the volume of the melt simply contracted more and more. The volume-temperature relationship was represented by an extension of the upper, more horizontal line. At each of the plotted points below —17.5°C. the sample was held at the indicated temperature for 1 to 2 hrs. before a dilatometric reading was taken and the temperature lowered to the level represented by the next point. Readings were discontinued at —35°C., a limit imposed by the freezing point of mercury, the confining liquid.

TABLE II

Expansibility and Melting Dilation Data for the Oleoglycerides

Compound	Temperature interval,[a] °C.	Poly-morphic form	Coefficient of expansion ml./g./°C.	Melting dilation ml./g.	Dilatometric melting point, °C.
1,2-Diaceto-3-olein	—30 to —21	I	0.002065	0.0524	—17.2
	—38.6 to —30	II	0.000286	......	......
	—17.2 to 50	liquid	0.000912	......	......
1,2-Dibutyro-3-olein	—37 to —29	I	0.002300	0.0233	—28.3
	—28.3 to 50	liquid	0.000839	......	......
1-Aceto-3-olein	—38.6 to —15	I	0.000288	0.0825	8.3
	—13.0 to — 5	II[b]	0.001080	0.0523	6.8
	—29.0 to —13	III	0.000534	......	......
	—38.6 to —30	IV	0.000566	......	......
	8.3 to 50	liquid	0.000863	......	......
1-Butyro-3-olein	—38.6 to —25	I	0.000288	0.0596	—3.4
	—22.5 to —13	II[b]	0.001576	0.0312	—5.8
	—30.0 to —22.5	III	0.000553	......	......
	—38.6 to —31.0	IV	0.000288	......	......
	— 3.4 to 50	liquid	0.000852	......	......
1,3-Diolein	—38.6 to 11	I	0.000292	0.0884	25.0
	0.0 to 7	II	0.001100	0.0612	22.7
	—38.6 to — 5	III	0.000292	......	......
	25.0 to 50	liquid	0.000861	......	......
1-Mono-olein	11.0 to 20	I	0.000943	0.0600	32.0
	—38.6 to — 5	II	0.000344	......	......
	32.0 to 50	liquid	0.000812	......	......

[a] Temperature interval used to calculate coefficient of expansion and melting dilation was at lowest possible temperature level so as to minimize any effects of premelting.

[b] Expansibility and dilation values associated with this form are uncertain because of limitations of the dilatometric technique.

In other tests each of the triglycerides while in a dilatometer was chilled rapidly to —60°C., after which the sample and dilatometer were warmed carefully to about —35°C. and specific volumes were determined. The specific volumes indicated that the samples did not crystallize on being cooled rapidly to —60°C.

The lower portion of the curves represented in Figure 2 were obtained by cooling the sample of 1,2-diaecto-3-olein slowly to —60°C. over a period of about 24 hrs. The transition point for Form III, observed at —48.0°C. by the capillary tube method, occurs below the melting point of mercury (—38.7°C.) and thus could not be observed dilatometrically. Form II is the lowest form represented in Figure 2. At about —30°C. Form II changed into Form I without a change in volume, a second order transition. Form I is unusual in that its coefficient of expansion is greater than the coefficient for the liquid state.

The dilatometric behavior of triolein, which has been investigated by Craig *et al.* (6) and by Bailey and Singleton (2), might be mentioned for comparison with that of the diaceto- and dibutyro-olein. Values reported for the coefficient of expansion for the highest melting polymorphic form of triolein are

0.00038, 0.00071, and 0.00100 ml./g./°C., depending on the investigator and the specific sample of triolein examined. Values reported for the melting dilation are 0.0597 and 0.0830 ml./g. for the highest melting form. The coefficient of expansion for the liquid state was given as 0.00093 and 0.00082 ml./g./°C.

The melting dilations for the triolein and the diaceto- and dibutyro-olein are much smaller than those for the several forms of tristearin, which are 0.1671, 0.1316, and 0.1162 ml./g. for Forms I, II, and III, respectively (2).

The diglycerides, 1-aceto-3-olein and 1-butyro-3-olein, exhibited a tendency to supercool, but unlike the 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein this tendency was not strong enough to prevent obtaining lower melting forms by rapid chilling. Slow cooling readily produced the high-melting form. Dilatometrically the two diglycerides behaved in a similar manner.

The data on expansion and melting dilation are recorded in Table II.

Figure 3 illustrates the dilatometric behavior of 1-butyro-3-olein on rapid chilling, followed by slow heating, curve *A*, and on slow cooling, followed by slow heating, curve *B*. The latter curve represents the dilation and melting of Form I, which has a dilatometric melting point of —3.4°C. When the rapidly chilled sample was heated, curve *A*, Form IV underwent a first-order phase transformation (without visual melting) at about —30°C., which was accompanied by an increase in volume of 0.0037 ml./g. This same change was detected at —36.0°C. by the capillary tube method; the shift in temperature was attributed to tempering of the sample in the dilatometer. At about —22.5°C. the Form III in the dilatometer underwent a second-order phase transformation to Form II, which melted at —5.8°C.

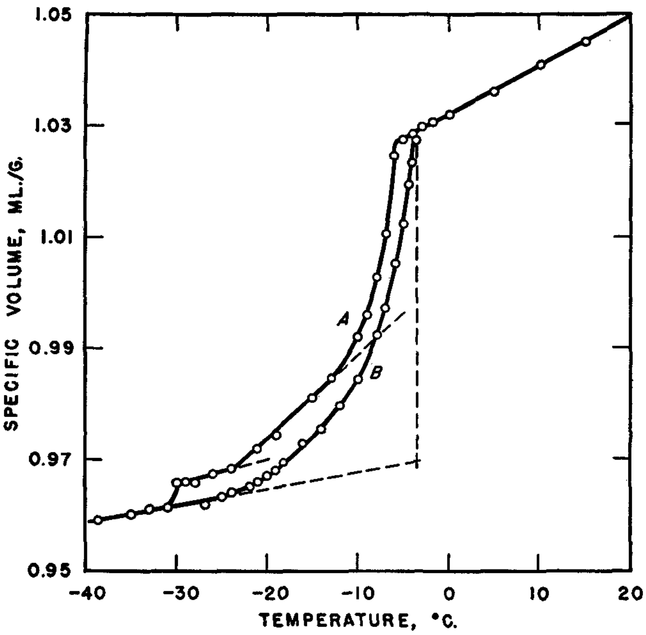

Fig. 3. Specific volume of the polymorphic forms of 1-butyro-3-olein as a function of temperature: *(A)* lower melting forms obtained by quick chilling of the melt followed by slow heating and *(B)* high-melting form obtained by slow cooling.

The behavior of 1-butyro-3-olein is in agreement with that of other unsaturated diglycerides in that the transition from Form III to Form II takes place readily, but the transition from Form II to Form I is relatively sluggish (4). Unlike unsaturated diglycerides examined heretofore, the 1-aceto-3-olein and 1-butyro-3-olein exhibited four polymorphic forms instead of the usual three.

Dilatometric examination of 1,3-diolein definitely showed the existence of three forms. Form III, obtained by quick chilling of the melt, transformed on slow heating to Form II at about —2°C. with a volume increase of about 0.0088 ml./g. Form II melted completely at 22.7°C. Form I was obtained by slow cooling of the melt. On heating, the latter form melted completely at 25.0°C.

Dilatometric measurements were made on 1-mono-olein after it had been cooled slowly to —60°C. and then warmed carefully to —38.5°C. Slight irregularities in the dilatometric curve were observed at temperatures just above the melting point of mercury. A slight discontinuity was also observed at 11.0°C. The 1-mono-olein melted completely at 32.0°C. The phase transformation detected at 25.0°C. by the capillary tube method could not be detected by the dilatometric technique. The values obtained for the coefficients of expansion of the solid and liquid states are in agreement with those reported previously (18). The beta form of 1-mono-olein, m.p. 35°C., reported by Carter and Malkin (5) was not obtained by the cooling technique employed in the current investigation. The rate of transformation to the beta form is claimed to be very slow.

Summary

1. A series of six oleoglycerides: 1,2-diaceto-3-olein, 1,2-dibutyro-3-olein, 1-aceto-3-olein, 1-butyro-3-olein, 1,3-diolein, and 1-mono-olein, was prepared and purified, and some of their physical properties were determined.

2. Data on densities and refractive indices of the compounds revealed that substitution of short-chain acyl groups for one or both of the hydroxyl groups in 1-mono-olein increases the density and decreases the refractive index. The effect is more pronounced for the aceto than the butyro groups.

3. By the capillary tube method, melting- and transition-point data were determined for each glyceride. For the triglycerides, 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein, one melting point and two transition points for each were found. For the diglycerides, 1-aceto-3-olein and 1-butyro-3-olein, two melting points and two transition points for each were found. Two melting points and one transition point each for 1,3-diolein and 1-mono-olein were found. These melting and transition points were substantiated by heating-curve data.

4. Where possible, dilatometric measurements were made for the various polymorphic forms of the glycerides. From the data were calculated expansibilities in the solid and liquid states, melting dilations or volume changes accompanying transformations, and dilatometric melting points.

Acknowledgment

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Reactions of Unsaturated Fatty Alcohols. II. Polymerization Of Vinyl Ethers and Film Properties of Polymers[1]

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IN A PREVIOUS PUBLICATION (6) we have described the preparation and properties of stearyl, soybean, and linseed vinyl ethers from the corresponding alcohols, using acetylene at atmospheric pressure. Preliminary experiments on the polymerization of these vinyl ethers with ionic catalysts were described, and the drying properties of the soybean and linseed polymers were observed. This paper reports the results of a more detailed study of the factors affecting polymerization and the preparation and properties of films from soybean and linseed polymers.

Preparation and Properties of Vinyl Ether Polymers

Soybean and linseed vinyl ethers were prepared from commercial samples of the respective alcohols (Unadol 40 and 90, Archer-Daniels-Midland Co.[2]). Stearyl vinyl ether was prepared from stearyl alcohol (Eastman Kodak white label).

A typical polymerization was carried out in the following manner. Three grams of vinyl ether monomer and 9 ml. of solvent were placed in a reactor fitted with a thermometer and stirrer. The flask was cooled in an ice bath or dry ice-ethanol bath to the temperature desired for polymerization. The catalyst was then added dropwise until a rapid temperature rise was noted. In most low temperature polymerizations the reaction was usually complete in less than 10 min. The catalyst was neutralized with ammonium hydroxide. The solution was washed with water, and the polymer was isolated by removing the solvent. In a few experiments polymerization was carried out at room temperature or above. Stearyl vinyl ether polymers were white to yellow waxy solids melting at 44° to 50°C. The polymers from linseed and soybean vinyl ethers were white to light yellow viscous oils. Molecular weights of the polymers were determined cryoscopically in cyclohexane solution (2).

Table I lists factors that influence the polymerization of fatty vinyl ethers. The first set of experiments shows the effect of solvents on the polymerization when boron trifluoride etherate was used as a catalyst at temperatures near 0°C. Methylene chloride, carbon tetrachloride, and pentane-hexane appeared to be the most useful solvents. A polymer of high molecular weight was obtained when carbon disufide was the solvent. Other solvents not shown in Table I were tried with boron trifluoride-etherate catalyst, *e.g.*, ethyl ether, acetone, tetrahydrofuran, and ethyl acetate, but little or no polymerization took place. Stearyl vinyl ether was not soluble in acetone or ethyl acetate at 0°C. Boron trifluoride-etherate was the only catalyst that worked well at 0°C. or below. It was particularly effective with soybean and linseed vinyl ethers since compatibility could be maintained at —30°C. Chloroform was a poor solvent in which to carry out polymerization with any of the catalysts studied.

TABLE I

Effect of Solvent and Catalysts on Polymerization of Stearyl Vinyl Eether

Catalyst	Temperature (°C.)	Solvent[a]	Molecular weight of polymer	Melting point
BF_3[b]	0	CH_2Cl_2	7,700	49.5
BF_3[b]	0	Pentane-hexane	6,000	49.5
BF_3[b]	0	$CHCl_3$	1,300	46.5–47
BF_3[b]	0	CCl_4	11,000	50–52
BF_3[b]	0	CS_2	14,000	48
$AL_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 7H_2O$	40	$CHCl_3$	<1,000	43–46
$AL_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 7H_2O$	40	CCl_4	<1,000	37–39
$AL_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 7H_2O$	0	CCl_4	<1,000	—
$AL_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 7H_2O$	0	Pentane-hexane	<1,000	36
$FeCl_3 \cdot 6H_2O$	0	$CHCl_3$	1,100	41
$FeCl_3 \cdot 6H_2O$	25	C_6H_6	8,600	49
None	<0	SO_2	<1,000	25

[a] 3 parts solvent to 1 part monomer.
[b] 6% by weight in dibutyl ether.

Aluminum hexahydrosulfate has been used as a polymerization catalyst at elevated temperatures (30°–120°C.) with the lower alkyl vinyl ethers (e.g., ethyl, n-butyl, isopropyl, and isobutyl) to produce polmers of high molecular weight (4). The use of this catalyst with the higher alkyl vinyl ethers at 40°C. gave polymers of low molecular weight as shown in Table I. A more suitable catalyst at room

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[2] Since the Department of Agriculture does not recommend the products of one company over those of another, these names are furnished for information only.