10.14 μ . The results are shown in Fig. 4, in which are plotted absorbancies at various concentrations of soap in benzene. The absorbance furnishes a sensitive test for concentration of the aluminum soap, and would be useful in testing for uniformity in a gel.

The highly viscous character of gels of aluminum soaps in hydrocarbons has been attributed to the presence of large molecules, which are formed by bonding occurring between the aluminum carboxyl groups in the soap molecules. It has been found⁸ that the viscosity of aluminum soap-hydrocarbon gels of fixed soap concentration is lowered progressively when small amounts of *m*-cresol are added to the solvent, reaching a limiting value at a *m*-cresol to soap mole ratio of two. A series of gels, each containing 5% by weight (approximately 0.01 mole per cent.) of aluminum dilaurate, was prepared by dissolving the soap in benzene solutions containing varying amounts of *m*-cresol. After aging for 24 hours at 60° and cooling to 20°, the absorbance of each gel at 10.14 μ was measured. The absorbance was found to decrease rapidly as the ratio of *m*-cresol to soap increased, approaching a limiting value, as shown in Fig. 5. It thus appears that the bond in aluminum laurate associated with absorption at 10.14 μ is directly connected with the gelling power of the soap for benzene.

SOME PHYSICAL PROPERTIES OF THE POLYMORPHIC FORMS OF 1,2-DIACETO-3-STEARIN AND 1-ACETO-3-STEARIN¹

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Fatty products containing the triglyceride 1,2-diaceto-3-stearin and the diglyceride 1-aceto-3-stearin are unusual in that they are quite plastic and stretchable. In the present investigation each of the two glycerides was prepared, purified and examined dilatometrically over the temperature range of -17 to 60°. Expansibilities, melting dilations and temperatures at which polymorphic transitions occurred were determined from the dilatometric curves obtained. X-Ray data for all polymorphic forms of each glyceride were obtained and crystal spacings were calculated. Photomicrographs of two forms of each glyceride were made.

A review of the chemical literature reveals a dearth of information on the physical properties of di- and triglycerides containing one *n*-saturated fatty acid radical having 14 to 18 carbon atoms and either one or two *n*-saturated fatty acid radicals having two to six carbon atoms. The optical activity and refractive index of several compounds falling into this class have been reported⁸⁻⁵ and Jones, et al.,⁶ reported the melting point of 1,2-diaceto-3-palmitin. With the exception of information released recently by this Laboratory^{7,8} these few data comprise the only published information on compounds of this type.

It was discovered in this Laboratory that fatty products containing the triglyceride, 1,2-diaceto-3stearin and the diglyceride 1-aceto-3-stearin are unusual in that they are non-greasy solids possessing a relatively large amount of plasticity and stretchability. Because these fatty products appear to have practical use, additional information concerning the physical properties of the two acetoglycerides was deemed desirable.

(1) Presented at the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December 4-6, 1952.

(2) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

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Experimental

Preparation of Materials.—Both 1,2-diaceto-3-stearin and 1-aceto-3-stearin were prepared by the direct esterification of 1-monostearin with acetyl chloride, using a modification of the procedure of Malkin, *et al.*⁹ The 1-monostearin employed was prepared as described in a previous publication.¹⁰ Its purity analyzed 99.4% by the periodic acid oxidation method.¹¹

The 1,2-diaceto-3-stearin was prepared by the dropwise addition with stirring of 30.3 g. (0.39 mole) of acetyl chloride in 50 g. of chloroform to a solution of 53.8 g. (0.15 mole) of 1-monostearin in a mixture of 34.0 g. (0.43 mole) of pyridine and 200 g. of chloroform at room temperature. An excess of acetyl chloride was used to ensure complete esterification. The mixture was allowed to stand at room temperature (26°) for two days and then was taken up in 250 ml. of ethyl ether and washed successively with cold 0.25 N hydrochloric acid, 5% potassium bicarbonate solution and water. The solvents were removed by stripping with dry nitrogen under reduced pressure, and the product then was crystallized 7 times from acetone (1:8) at -18° and dried over phosphorus pentoxide.

Anal. Calcd. for C₂₅H₄₆O₆: C, 67.84; H, 10.48. Found: C, 67.99; H, 10.61; m.p. 48.6°.

The 1-aceto-3-stearin was prepared by the slow addition of 16.3 g. (0.21 mole) of acetyl chloride in 125 g. of chloro-

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form to a solution of 79.5 g. (0.22 mole) of 1-monostearin in a mixture of 49.2 g. (0.62 mole) of pyridine and 537 g. of chloroform. The mixture was refluxed on a steam-cone for 3 hours under anhydrous conditions, then was taken up in 1500 ml. of ethyl ether and washed successively with cold $0.5\ N$ sulfuric acid, 5% solution of sodium bicarbonate, and water. The solvents were removed by stripping with dry nitrogen under reduced pressure. A solution of the product in 1500 ml. of hexane was cooled to room temperature and filtered. The filtrate was further cooled to -15° , and the crystallized 1-aceto-3-stearin was recovered and purified by recrystallization from hexane and from acetone.

Anal. Caled. for $C_{23}H_{44}O_5$: C, 68.96; H, 11.20; hydroxyl value, 140. Found: C, 69.04; H, 11.19; hydroxyl value, 142; m.p. 50.3°.

Heating and cooling curves obtained by Smit's procedure¹² indicated that both of the final products were of high purity. **Expansibility.**—The expansibilities of the solid and liquid

states of 1,2-diaceto-3-stearin and 1-aceto-3-stearin were de-termined with gravimetric-type dilatometers. Melting dilations of the various polymorphic forms were calculated by the method reported in previous publications.¹³ Dilation measurements on all samples were begun at -17° , at which temperature only the solid state existed, and were con-

tinued until the samples were completely melted. Densities of the acetostearins were determined by the pycnometer method.

X-Ray Diffraction.-X-Ray diffraction patterns of the lower-melting polymorphic forms of the two glycerides were obtained by photographing the samples after solidification in capillary tubes. In each case the freshly prepared form was aligned on the camera mount while it was in a large cooler maintained at -10° , and the mounted sample was kept in an insulated box cooled to -10° with Dry Ice. This precaution was necessary to avoid exceeding the transition temperature of the lower-melting forms during the time they were exposed to radiation. For the higher-melting form of each glyceride the crystals were packed in a capil-lary tube and photographed at room temperature. The photographs were made with a General Electric X-Ray Diffraction Unit, Model XRD, using CuK α radiation with a nickel filter (0.0007 inch thick).

Photomicrographs.--A photomicrograph of the highmelting form of each of the glycerides was obtained by evaporating the solvent from a solution of the appropriate sample on a glass slide and photographing the crystals through a petrographic microscope with crossed nicol prisms. \mathbf{The} sample then was warmed to melt the crystals, and after solidification in the alpha form, another photograph was made.

Results and Discussion

1,2-Diaceto-3-stearin.-The calculated "d" spacings of the various forms of 1,2-diaceto-3-stearin are recorded in Table I. Three forms were distinguished, which have been designated as beta. alpha and subalpha, respectively, in accordance to their correspondence with the short spacings of 1-monostearin, a similar compound.¹⁴

The stable or high-melting form, beta, which was obtained by crystallization of the glyceride from solvent, or by tempering a previously melted sample, had a dilatometric melting point of 49.5°, and a capillary tube melting point of 48.6°. The transparency of the material makes it difficult to visually ascertain the exact melting point by the capillary tube method. Cooling the melted glyceride at a moderate rate produced the alpha or lower-melting polymorphic form. On slow heating this lowermelting form began melting at approximately 35°,

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22, 265 (1945).

(14) E. S. Lutton and F. L. Jackson, J. Am. Chem. Soc., 70, 2445 (1948).

but transformed to the beta form before the point of complete melting was reached. When held at a temperature just below 35°, the alpha form transformed into the beta form without melting. This transformation occurred slowly if the sample was allowed to stand at room temperature. The melting dilation of the alpha form had to be determined at a rapid rate in order to avoid transformation to the beta form. Therefore the exact melting point of the alpha form could not be determined dilatometrically. The capillary tube melting point of the alpha form was 36.4°.

TABLE I

INTERPLANAR SPACINGS OF 1,2-DIACETO-3-STEARIN AND 1-Aceto-3-stearin^a

| 1,2-Diaceto-3-stearin | | 1-Aceto-3-stearin | | |
|-----------------------|----------------------------------|---|--|---|
| Alpha | Sub- alpha | Beta prime | Alpha | Sub- alpha |
| 4.12 VS | 4.11 VS | 4.38 M | 4.18 S | $4.12\mathrm{VS}$ |
| | 3.68 S | $4.14 \mathrm{S}$ | 3.93 W | 3.68 S |
| | 2.95 W | $3.84 \mathrm{M}$ | | 2.96 M |
| | $2.48 \mathrm{W}$ | 3.55 M | | $2.49 \mathrm{M}$ |
| | 2.19 W | 2.92 W | | 2.20 M |
| | | $2.54 \mathrm{W}$ | | |
| | | 2.26 W | | |
| | | 2.17 W | | |
| | | $2.10 \mathrm{W}$ | | |
| | Diaceto-3-st Alpha 4.12 VS | Diaceto-3-stearin Sub- Alpha alpha 4.12 VS 4.11 VS 3.68 S 2.95 W 2.48 W 2.19 W | $\begin{array}{cccc} \text{Diaceto-3-stearin} & 1-4 \\ & \text{Sub-} & \text{Beta} \\ \text{Alpha} & \text{alpha} & \text{prime} \\ \hline 4.12 \text{ VS} & 4.11 \text{ VS} & 4.38 \text{ M} \\ & 3.68 \text{ S} & 4.14 \text{ S} \\ & 2.95 \text{ W} & 3.84 \text{ M} \\ & 2.48 \text{ W} & 3.55 \text{ M} \\ & 2.19 \text{ W} & 2.92 \text{ W} \\ & 2.54 \text{ W} \\ & 2.26 \text{ W} \\ & 2.17 \text{ W} \\ & 2.10 \text{ W} \end{array}$ | $\begin{array}{cccc} \text{Diaceto-3-stearin} & 1-\text{Aceto-3-stearin} \\ \text{Alpha} & \text{alpha} & \text{Beta} \\ \text{4.12 VS} & 4.11 VS & 4.38 M & 4.18 S \\ & 3.68 S & 4.14 S & 3.93 W \\ & 2.95 W & 3.84 M \\ & 2.48 W & 3.55 M \\ & 2.19 W & 2.92 W \\ & 2.54 W \\ & 2.26 W \\ & 2.17 W \\ & 2.10 W \end{array}$ |

^a Spacings reported in ångströms and relative intensity; W, weak; M, medium; S, strong; VS, very strong.

The third polymorphic form of 1,2-diaceto-3stearin, the subalpha form, was found to exist only below -4° . It did not melt on being heated but gave evidence of transformation to the alpha form between -4 and -2° .

Expansibilities of the solid state were determined to be 0.000301 ml./g./deg. for the beta form (up to be 0.000301 ml./g./deg. for the beta form (up to 14.7°) and 0.00115 ml./g./deg. for the alpha form (0 to 25°). Expansibility of the liquid state was 0.000960 ml./g./deg. The melting dilation of the beta form was 0.1118 ml./g., and of the alpha form, calculated at 36.4° , 0.0649 ml./g. The volume change accompanying the transformation of the gubelpha form into the alpha form 2000° the subalpha form into the alpha form was 0.0048 ml./g.

1-Aceto-3-stearin.—Three polymorphic forms of this compound have been distinguished on the basis of X-ray and dilatometric data. The calculated short spacings of these forms are included in Table I, the forms being designated beta prime, alpha and subalpha.

The dilatometric melting point of the beta prime form, obtained by crystallization from solvent, was 49.1°. The capillary tube melting point was 50.3°. The latter was difficult to observe accurately owing to the transparency of the material at temperatures near its melting point.

On being melted and resolidified, the 1-aceto-3stearin was found to have a capillary tube melting point of 47.5°. The melting point of this alpha form could not be determined dilatometrically because of an apparent transformation at some temperature below 47.5°. A very rapid determination of the expansibility of the alpha form gave evidence of its transformation to the beta prime form at about 36°.

The third polymorphic form, subalpha, occurred

upon cooling the melted acetostearin to below 0° . So cooled, an apparently irreversible transformation occurred between 0 and 4° , with a decrease in volume of 0.01 ml./g.

The expansibility of the beta prime form of 1aceto-3-stearin in the solid state (up to 15°) was 0.000352 ml./g./deg., and in the liquid state 0.000945 ml./g./deg. Melting dilation was 0.1185 ml./g.

Comparison of Density.—The densities of 1,2diaceto-3-stearin and 1-aceto-3-stearin at 50°, at which temperature both were liquid, were found to be 0.9423 and 0.9373 g./ml., respectively. The densities of these two glycerides in both the solid and liquid states were found to differ from the densities of ordinary fats such as lard, shortening and triglycerides of stearic through lauric acids¹³ by from 0.04 to 0.07 g./ml., a significant difference. Also, the densities of the glyceride series consisting of a monostearin,⁹ 1-aceto-3-stearin and 1,2-diaceto-3-stearin at comparative temperatures in the liquid state were found to increase as the number of ace-



Fig. 1.—Specific volumes of the polymorphic forms of the acetostearins as functions of temperature.

tyl radicals increased. With respect to melting dilation of this series, an increase in the number of acetyl radicals decreased the dilation.

From the density and expansibility data the absolute specific volume of each compound at various temperatures over its melting range was calculated. These results were plotted as functions of temperature and are reproduced in Fig. 1.

Effect of Polymorphic Form on Plasticity.— Photomicrographs were made of 1-aceto-3-stearin, 1,2-diaceto-3-stearin, and, for comparison, 1-monostearin. Crystals of the acetostearins obtained by crystallization from acetone are shaped quite differently from those of 1-monostearin obtained in a corresponding manner. The acetostearin crystals are long and narrow and seem to form a chain-like structure while the 1-monostearin crystals are block-like. Upon melting and resolidification, the 1-monostearin crystals merge into a pattern of rosettes, with distinct boundaries of the individual crystals being maintained. The acetostearins, however, form an unordered network of interlocked ribbon-like crystals.

The alpha forms of the acetostearin compounds exhibit the property of stretchability, which is unique among fatty materials. Ordinary fats can be stretched only about 2% of their original length, whereas the alpha forms of 1-aceto-3-stearin and 1,2-diaceto-3-stearin can be stretched 200 and 300 times as much, respectively, when tested under conditions described in a previous publication.⁷ The high melting forms of the acetostearins, obtained by tempering the alpha form, can be stretched only as much as an ordinary fat.

A photograph of a stretched sample of the alpha form of 1,2-diaceto-3-stearin gives the appearance of the crystalline network having become more ordered and aligned, possibly by the phenomenon of plastic flow. This phenomenon probably contributes to the stretching and flexing properties possessed by these compounds.

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