

Summary

Data on the products obtained on polymerizing styrene in the presence of various methyl esters of fatty acid have been presented. These data show that no copolymerization between the esters and styrene occurs and that homogeneity of some of the reaction products cannot be considered as proof for interpolymerization.

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Modification of Vegetable Oils. XII. Plasticity of Some Aceto Derivatives of Monostearin^{1,2}

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A RELATIVELY stable fat which solidifies to a non-greasy yet flexible solid should have many potential uses. So far as the authors are aware, a fat which is non-greasy and highly flexible at the same temperature has never been prepared heretofore. Normally non-greasiness and flexibility in fats are mutually exclusive properties. The authors have found that fats composed of certain mixtures of acetostearins are extremely flexible solids at and below room temperature. The preparation and some of the properties of these acetostearins are described here.

Preparation of Acetostearins

Acetostearins were prepared by reacting acetic anhydride with monostearin. A temperature of 110°C. and a reaction time of one hour were used in most instances. The reactants were stirred and kept under dry hydrogen to prevent reaction of the acetic anhydride with atmospheric moisture. The reaction was interrupted as desired by adding hot water to the reaction mixture and stirring for 10 minutes to hydrolyze the unreacted acetic anhydride. After washing the reaction product with distilled water it was dried by warming it under reduced pressure and stripping with hydrogen.

Three monostearins, referred to as A, B, and C, were used to prepare the acetostearins. Monostearin A, prepared from pure stearic acid, contained 99.2% monostearin by analysis (1) and had a hydroxyl value of 306.5 according to the acetylation method of West *et al.* (2), modified by using one part of acetic anhydride to three parts of pyridine. Monostearin B was a commercial, molecularly distilled product. It had a hydroxyl value of 335.5 and

a monoglyceride content of 91.5%. The average molecular weight of the combined fatty acids in this product was 270.5, which corresponds to a 1:1 ratio of stearic and palmitic acids. Of the three monostearins only monostearin B contained free glycerol, about 2%. Monostearin C was a technical grade product made from completely hydrogenated cottonseed oil. Its hydroxyl value was 236.9, and it contained 61.0% monoglycerides of fatty acids, having an average molecular weight of 280.0.

Physical properties of the acetostearins formed by reaction of monostearin with acetic anhydride could be controlled to a considerable extent by manipulating the reaction time, temperature, and proportion of acetic anhydride employed. None of the reactions was carried to 100% completion, as evidenced by the hydroxyl value of the finished products. A plot of the hydroxyl value *vs.* reaction time at 110°C. between one hydroxyl-equivalent of monostearin B and one mole of acetic anhydride is reproduced in Figure 1. A similar curve was obtained when different proportions of acetic anhydride were reacted for one hour at 110°C.

The ratios of monostearin to acetic anhydride used in making the products subjected to elongation and bending tests were such that one equivalent of hydroxyl in the monostearin was mixed with 0.5, 1.0, and 2.0 moles of acetic anhydride, respectively. The reactions were stopped after one hour at 110°C.

Since the acetostearins were used solely for making physical measurements, no precautions were taken to assure that they were entirely free of odor and taste.

Composition of the Products

The free fatty acid content of the acetostearins was nearly always between 1.0 and 1.5%, which is quite low in view of the fact that two of the monostearins used to prepare the products contained several tenths of a per cent of free fatty acids. Therefore it must

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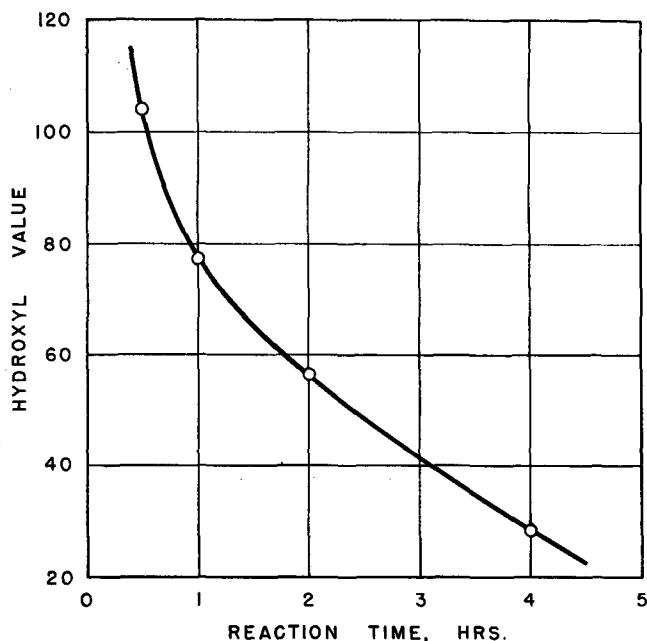


FIG. 1. Rate of reduction of hydroxyl value for one hydroxyl equivalent of monostearin B and one mole of acetic anhydride reacted at 110°C.

be concluded that reaction occurred by direct acetylation, uncomplicated by acid substitution. The short melting range of the products prepared with monostearins A and B, which in one case was less than a degree, and the fact that monostearin is relatively stable when heated to 110°C. in glacial acetic acid substantiate the validity of this conclusion.

Since the reaction consisted of uncomplicated acetylation, the approximate composition of each of the products subjected to elongation and bending tests can be calculated from the data which will be presented. For example, one product (No. 3, Table I)

TABLE I
Elongation at Break Point and Resistance to Stretching of Acetostearins, Monostearin, and Paraffin

Product No.	Monostearin used ^b	Mole (CH ₃ CO) ₂ O/OH equivalent ^a	Maximum load, lbs.	Load at break, lbs.	Elongation, %
1.....	A	0.5	1.7	> 800
2.....	A	1.0	0.71	> 800
3.....	A	2.0	0.49	> 800
4.....	B	0.5	1.6	0	467
5.....	B	1.0	0.43	0	513
6.....	B	2.0	0.32	> 800
7.....	C	0.5	9.8	9.1	31
8.....	C	1.0	6.7	0.3	241
9.....	C	2.0	1.6	> 800
Monostearin B.....	3.7	3.7	4
Paraffin.....	8.0	8.0	5

^aRatios are moles of acetic anhydride used per OH equivalent in the preparation of the acetostearins.

^bMonostearin used in preparing the acetostearins.

which was prepared from monostearin A contained about 19% of 1-aceto-3-stearin, 80% of 1,2-diaceto-3-stearin, and 0.3% of 1-monostearin. The other acetostearin products prepared from monostearin A differed from the given composition only in the relative proportion of the different glycerides.

Mixtures resulting from the reaction between commercial and technical grade monostearins and acetic anhydride are, of course, quite complex. However for

the sake of simplicity of discussion these mixtures will be termed *acetostearins*.

Physical Properties

Flexibility. The flexibilities of the acetostearins were measured by stretching test samples of each product. This was accomplished by heating the acetostearins to 60°C., pouring them into a mold at the same temperature, and solidifying them by cooling to room temperature (26°C.). After being removed from the mold, the samples were held overnight at 22°C. and tested at the same temperature.

The test samples were formed by casting the melted product in a mold consisting of three plates of 1/8-inch sheet aluminum separated by aluminum foil. The center plate, or mold proper, was cut out to form a ribbon-shaped opening. The other two plates were confining faces of the mold.

Each molded test sample measured five inches in length and 1/8 inch in thickness. The center portion of the sample was 3/4 inch in width, but one inch from each end the width increased gradually so that the enlarged end-sections of the sample were covered with fine sand paper and clamped in the jaws of the testing machine. The central section of the sample measuring 3 x 3/4 x 1/8 inches was subjected to stretching.

An Instron Tensile Tester was used to stretch the samples. In this machine one of the jaws is pulled away from the other at a constant rate while the machine automatically records the load or pull necessary to maintain the rate of elongation and synchronizes this value with a recording of the amount of elongation or stretch of the test sample.

A typical load-elongation curve obtained with the Instron Tensile Tester is shown in Figure 2. In this

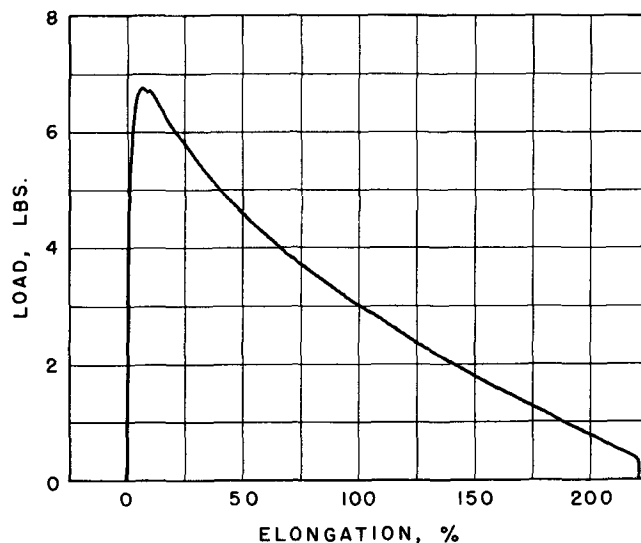


FIG. 2. Typical load elongation curve obtained by stretching a standard test piece of an acetostearin at a constant rate of one inch per minute.

test the sample was stretched at a constant rate of one inch per minute. The load increased to a maximum of 6.7 lbs. almost immediately. As the sample stretched and its effective cross-sectional area decreased, the required load decreased. When the sample had been stretched 220% of its original length, it broke. At the breaking point the cross-sectional area of the cen-

tral section of the sample was so small that the load was only 0.3 pound.

The results of the tests made by applying a stretching rate of 1.0 inch per minute are recorded in Table I. Data for tests made with monostearin B and a paraffin (m.p., 50-52°C.) are also included in the table.

Each acetostearin shown in Table I stretches far more than either monostearin B or the paraffin. More than half of the acetostearins stretched over 800%, which was the limit of the testing machine. The lowest value observed for any of the acetostearins was six times greater than was obtained with paraffin. From the data for the acetostearins prepared from monostearins B and C, it is apparent that the stretchability increased as the proportion of acetic anhydride used to prepare a given product increased.

The relative tenacity or resistance to stretching, which is indicated by the maximum load values in Table I, varied greatly, depending on the type of monostearin and proportion of acetic anhydride employed in the preparation of the products. The higher proportions of acetic anhydride gave products with the least tenacity because they acetylated greater proportions of the monostearins and transformed them into lower melting compounds.

Products made with monostearin B were not as tenacious as the corresponding products made with monostearin A, probably because the former contained monoglycerides of palmitic and possibly other fatty acids. The use of monostearin C resulted in the toughest products because it contained a large proportion of diglycerides.

The maximum loads shown in Table I are numerically equal to about 1/11 of the stress in pounds per square inch which must be applied to the molded product to start stretching at a rate of 33.3% per minute. A force of 73.7 pounds per square inch had to be applied, for example, to product No. 8 to start it stretching at a rate of 33.3% per minute.

Several of the acetostearins were subjected to stretching at rates other than one inch per minute. The results of these tests are shown in Table II.

TABLE II

Elongation at Break Point and Resistance to Stretching of Acetostearins Under Different Rates of Elongation

Product No.	Rate of elongation, in./min.	Maximum load, lbs.	Load at break, lbs.	Elongation, %
1	1	1.7	> 800
	5	3.2	0	> 800
	20	4.4	0	547
2	1	0.71	> 800
	20	2.2	0	630
3	1	0.49	> 800
	20	1.6	> 800
4	1	1.6	0	467
	10	3.2	0	350
9	1	1.6	> 800
	5	3.0	0.3	613
	10	4.2	0.8	360
	20	5.4	2.2	173

From the data in Table II it can be seen that even at greatly increased rates of elongation the products flowed like liquids. A 20-fold increase in the rate of elongation resulted in about a 3-fold increase in the load or force necessary to overcome the resistance to stretching. Increased rates of elongation decreased the amount of elongation before the sample ruptured.

In order to obtain data on the flexibility of the acetostearins at a temperature other than that of the testing laboratory (22°C.) in which the Instron Tensile Tester was located, bending tests were made at 4°C. on several of the products listed in Table I. For these tests a 5 x 3/4 x 1/8-inch ribbon of acetostearin was molded on a strip of high-strength filter paper by using a molding technique similar to that described, except that a sheet of filter paper was substituted for one of the sheets of aluminum foil. The molded product was maintained at 4°C. overnight before testing.

The bending test consisted of fastening one end of the ribbon of acetostearin and filter paper to a brass cylinder one inch in diameter and rotating the cylinder at a rate of 33° per minute while pulling at the other end of the ribbon with a force of two pounds.

Paraffin and monostearin B cracked when tested in this manner. Acetostearins Nos. 7 and 8 also cracked; but products Nos. 2, 3, 4, 5, and 6 did not crack. Acetostearins Nos. 1 and 9 cracked only slightly.

The acetostearins made with monostearin B were also tested in another way, which consisted of placing strips of the products in the freezing compartment of a domestic refrigerator. The products, especially Nos. 5 and 6, remained pliable at freezing temperatures.

Melting Range. The melting range of a coating fat is an important physical property. This property of the acetostearins is about as important as flexibility, especially if the products are to be used as edible coatings.

The nine acetostearins listed in Table I were non-greasy solids at room temperature (26°C.), but their melting ranges, determined by the capillary tube method, differed appreciably. The melting ranges, hydroxyl values, and monoglyceride contents of the products are recorded in Table III.

TABLE III
Melting Range, Hydroxyl Value, and Monoglyceride Content of Acetostearins

Product No.	Melting range, °C.	Hydroxyl value	Monoglyceride content, %
1.....	45.0-48.0	153	17.8
2.....	39.5-42.0	78	2.7
3.....	38.0-39.0	36	0.3
4.....	41.0-44.0	166	11.4
5.....	32.0-35.5	78	2.8
6.....	29.0-31.0	56	0.9
7.....	44.0-54.0	122	14.1
8.....	38.0-54.0	84	4.9
9.....	35.0-54.0	38	0.4

The lower temperature recorded for each product is the temperature at which melting was first observed; the higher temperature is the one at which the product was completely liquid.

Product No. 6 began melting at 29°C. and product No. 1 began melting at 45°C. All of the products except those made with monostearin C have relatively short melting ranges. The shortest melting range observed (product No. 3) was less than one degree.

When a monostearin like product B, which was composed almost entirely of monoglycerides, was converted into acetostearins, the melting points of the products were found to be roughly proportional to their hydroxyl values. From the plot of melting point vs. hydroxyl value for the products prepared with monostearin B (Figure 3) it may be seen that there

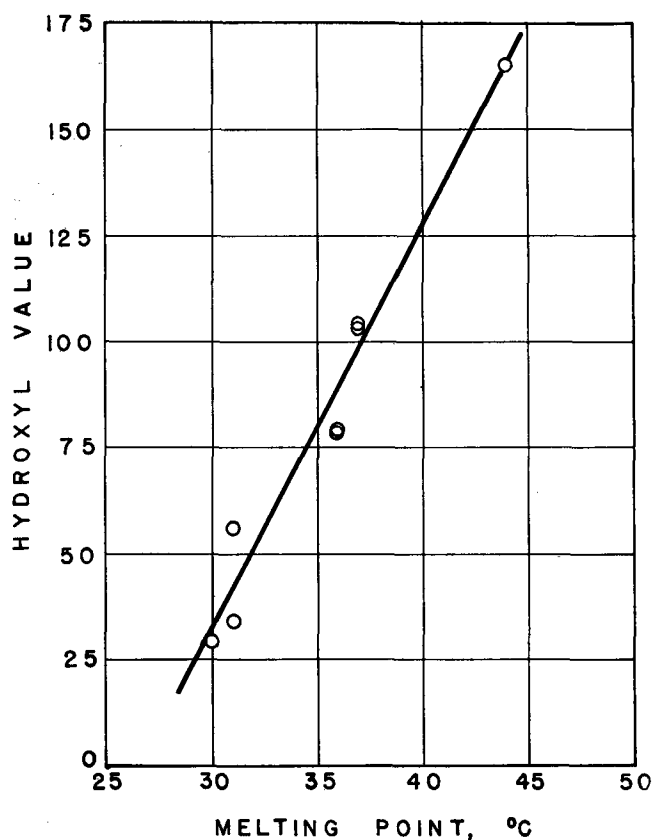


FIG. 3. Relationship between melting point and hydroxyl value of acetostearin made by acetylating monostearin B.

is a relationship between the melting point and hydroxyl value.

A number of acetostearins other than those given in Table III and Figure 3 were found to have melting points higher and lower than those shown. Some products were liquid at room temperature and others

melted as high as 60°C. It is evident that, within limits, acetostearins can be prepared with any desired melting range by the proper choice of monostearin and proportion of acetic anhydride.

Summary

1. Acetostearins were prepared by reacting various proportions of acetic anhydride with a monostearin of 99.2% purity, a commercially available monostearin containing 91.5% monoglycerides, and a technical grade monostearin containing 61% monoglycerides. The last mentioned product was prepared from a completely hydrogenated cottonseed oil. After the removal of unreacted acetic anhydride and acetic acid from the reaction products, the flexibility and melting characteristics were determined.

2. All of the acetostearins tested were non-greasy solids at room temperature yet were highly flexible. At a temperature of 22°C. most of them could be stretched more than 800% under the test conditions. Bending tests revealed that some of the products possessed good flexibility even at 4°C.

3. The melting characteristics of the products were dependent on the purity of the monostearin used and the degree of acylation. Some products melted completely below body temperature (37°C.), and others melted at temperatures up to 60°C. The temperature interval over which melting occurred was usually very short (1-3°); however products made from technical grade monostearin melted over a temperature range of 10-20°C.

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Effect of Winterization on the Composition and Stability of Cottonseed Oil

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DESPITE the fact that winterization of cottonseed oil has been practiced on an industrial scale for nearly half a century, no information could be found in the literature with respect to the effect of this process on the composition and autoxidative stability of the products. The two most important factors affecting the autoxidative stability of cottonseed oil are its content of unsaturation and tocopherols. It is known that the saturated components of the glycerides are decreased when cottonseed oil is winterized (1), but no data are available regarding the effect of this practice on the tocopherols. Consequently no correlation of tocopherol content and composition of the

glycerides with autoxidative stability has been made.

In order to investigate the relationship of the three factors mentioned above, a series of oils consisting of refined and bleached cottonseed oil, the same oil after winterization, and the stearine press cake remaining after winterization was analyzed with respect to the compositions of the glycerides, total tocopherol contents, autoxidative stability, and color. The samples were obtained from three refineries located in different cotton-producing states, namely, Tennessee, Louisiana, and South Texas. Before being analyzed, the samples were freed of soaps, when necessary, and deodorized in a laboratory deodorizer (2).

Methods of Analysis and Calculations

Iodine values were determined by the American Oil Chemists' Society modification of the Wijs method

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