Modification of Vegetable Oils. XIII. Some Additional Properties of Acetostearin Products '

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FATS prepared by the acetylation of monostearin are unique in that they can exist simultaneously as non grossy and bighly florible solids (6) As as non-greasy and highly flexible solids (6). As such they usually resemble household paraffin wax in feel and appearance but differ in this respect: whereas a film of refined paraffin wax (melting point 50°-52°C.) can be stretched only about 5% before breaking, similar films of acetostearin product when tested under the same conditions may stretch over 800%. The latter are stretchable at both room temperature and temperatures encountered in the freezing chamber of domestic refrigerators. The properties of the products can be varied within limits; that is, the melting range, point of complete melting, and stretchability can be varied by changing the degree of acetylation and the grade or purity of monostearin used in the preparation.

A number of possible uses for acetostearin products are being investigated in this and other laboratories. Preliminary results indicate that the products melting between 30° and 60° C. may have application as coatings for. meats which are to be stored at freezing temperatures and for processed meats, such as frankfurters, where thin, almost-invisible coatings have been found to produce beneficial effects; and also as coatings for cheese. In certain applications acetostearin products of this melting range appear to act as desirable plasticizers for hard fats and other materials. Products melting below 30° C. also have potential uses, particularly where a low-melting oil of high resistance to oxidative rancidity is needed. For example, acetostearin products which are liquid at the temperature of a warm room appear to perform satisfactorily as "slab oils" in the manufacture of candy. Use of the products in foods must await the outcome of feeding tests now under way.

All uses of acetostearin, even those not involving edibility, must take into account properties not investigated and described heretofore. The object of the present investigation was to examine some of these properties. They include ease of purification; such physical properties as changes in flexibility on storage, consistency of temperatures below the melting point, viscosity, and permeability to moisture; and such chemical changes as resistance to oxidation, stability at elevated temperatures, and resistance to hydrolysis.

Preparation and Analysis

Preparation. Two samples of monostearin were used in the preparation of nine acetostearins of different degrees of acetylation. Five of the products were prepared from commercial, molecularly distilled monostearin made from triple-pressed stearic acid which had an average molecular weight of 270.9. This monostearin contained 91.5% of mono-esters and

had a hydroxyl value of 332.7. A small percentage of free glycerol, glycerides of oleic acid, and free fatty acids were present as impurities. The other four acetostearins were prepared from technical grade monostearin made from hydrogenated cottonseed oil having an iodine value of $1.1\,(5)$. The monostearin contained no free glycerol and had the composition indicated in the third column of Table I.

TABLE ^I Changes in Properties on Converting Highly Hydrogenated
Cottonseed Oil Into Acetostearin Products

Property	Hydro- genated cotton- seed oil ^a	Mono- glycerides from hydrogen- ated cot- tonseed oil	Acetostearin product, $[$ mole (CH_3CO) $_3\text{O}$: OH equivalent ^b]		
			No.1 (0.5:1)	No. 2 (1:1)	No. 3 (2:1)
Lovibond color, yellow/red Free fatty acids, as oleic, % Monoglycerides, % Hydroxyl value	10/1.4 0.18 	20/3.0 1.41 59.0 231	20/3.4 1.07 15.0 122	20/2.9 0.84 1.7 55.6	15/2.6 1.06 0.2 27.7
Viscosity.centistokes	62.8 24.13 16.14	64.0 44.61 24.57	50.8 20.51 12.84	51.8 15.22 9.99	35.6 22.05 13.58 9.04

aIodine value, 1.1. bRatio is moles of **acetic anhydride** per OH equivalent of monog!yee~'- ide used in the preparation of the acetostearin.

The monostearins were converted to acetostearins as described previously (6). A predetermined number of moles or mole fraction of acetic anhydride was allowed to react with one hydroxyl equivalent of monostearin for 1 hour at 110° C. while the reactants were stirred under an inert atmosphere of dry hydrogen. The reaction was stopped by the addition of water, which hydrolyzed any unreacted acetic anhydride; acetic acid was removed by washing with water; and the product was dried by warming it under reduced pressure and stripping with hydrogen.

Table I shows the typical changes in color, content of free fatty acids, and other properties on converting highly hydrogenated cottonseed oil into acetostearins of three different degrees of acetylation. Table II shows properties of the fourth acetostearin made from the technical grade sample, together with properties of the acetostearins made from the distilled sample. The acetostearins listed in Table II, except product No. 5, were bleached and rendered tasteless by deodorization (see discussion below).

Methods of Analysis. Measurements of color, content of free fatty acids, and melting point were made according to the methods of the American Oil Chemists' Society (1). Hydroxyl values were determined according to the acetylation method of West *et al.* (10), modified by using I part of acetic anhydride to 3 parts of pyridine. The method of Handschumaker and Linteris (7) was used to determine the content of monoglycerides. Resistance of a number of acetostearin products to oxidation was determined by the active oxygen method (8). Viscosity measure-

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ments were made with a Cannon-Fenske-Ostwald type viseometer (3).

Purification

Acetostearin products when prepared from monostearin of good quality possess only a slight taste and odor. Their color is about equal to that of the monostearin used as starting material, and their content of free fatty acids is approximately 1%. Although the color of acetostearin products, as well as their content of free fatty acids, can be reduced by the alkali refining process used with vegetable oils, their color is most easily reduced by bleaching with clay or carbon. For example, a product having a Lovibond color of 10 yellow and 1.7 red was bleached to a color of 2 yellow and 0.7 red by treating it at 80~ with 1% of activated carbon.

TABLE II Preparation and Properties of Acetostearin Products

Product No. ²	Mono- stearin used	Mole $(CH_3CO)_2O$ per OH equivalent ^b	Mono- glyceride content	Hydroxyl value	Melting point
			%		$^{\circ}C$.
4	Technical	1.0 :1	2.5	49.4	49.7
	grade	(approx.)			
5	Distilled	0.4 :1	21.3	167.0	46.0
6	Distilled	0.5:1	20.6	156.5	47.5
	Distilled	0.5:1	14.2	136.1	410
8	Distilled	0.75:1	6.4	84.7	40.0
9	Distilled	2.0:1	0.5	33.0	31.7

a All products except No. 5 were bleached with 4% of neutral, **acti-vated** clay for 10 minutes at 80~ and deodorized for 1 hour at 175 ~ C. and a pressure of 1 mm. of mercury. bRatio is moles of acetic anhydride used per OH equivalent of mono-

glyceride.

It was found that steam deodorization, as commonly practiced in the processing of vegetable oils, can be employed to produce tasteless and odorless acetostearin products. Table III records the changes which occurred when product No. 2 (see Table I) was deodorized in an all-glass deodorizer (2) at a pressure of approximately 1 mm. of mercury for various lengths of time at 175[°] and 230[°]C. All samples rep**resented in this table were odorless and tasteless after deodorization. Adverse changes in the product at the lower temperature were minor, but the fatty acids were removed at a relatively slow rate. At the higher temperature the increase in color, by 1.2 to 2.6 Lovibond red units, was the most undesirable effect. Some difficulty was experienced in raising the temperature** in the deodorization flask to 230°C. because of the heavy reflux which occurred under 1 mm. of pressure. **The material involved in the refluxing may have been a minor fraction of the total material in the flask, and its loss by distillation may or may not be reflected in the increased viscosities shown in the last three columns of Table III. The hydroxyl value, which is a measure of mono- and diglyceride content, did not change greatly from its original value of 55.6 during** the deodorization at 230°C. In contrast, when prod**uct No. 8 (Table II), made from commercial, molecularly distilled monostearin and having originally a hydroxyl value of 102.3, was deodorized for 1 hour** at a temperature of 175°C. and a pressure of about **1 ram. of mercury, its hydroxyl value decreased to 84.7. Thus it appears that the higher the mono- and diglyceride content of an acetostearin product, the more susceptible it is to changes during deodorization.**

TABLE III Effect of Deodorization on Acetostearin Product No. 2

Property	After deodorization at 175° C. and 1 mm. of mercury for			After deodorization at 230° C. and 1 mm. of mercury for a		
	0.5 _{hr}	1 hr.	2 hr.	0.5 _{hr}	1 hr.	2 hr.
Lovibond color. yellow/red	15/2.7	20/3.1	20/3.8	20/4.1	20/4.8	35/5.5
Free fatty acids, as						
	0.64	0.50	0.30	0.17	0.10	0.11
Monoglycerides. %	1.60	1.56	1.51	1.54	1.43	1.35
Hydroxyl value					53.2	52.3
Melting point, °C	50.3	50.3	50.3	51.0	51.9	54.4
Viscosity, centistokes						
65°C	15.33	15.32	15.47	15.51	16.03	17.02
80°C	10.06	10.07	10.15	10.26	10.54	11.19
95° C	7.13	7.12	7.17	7.22	7.43	7.92
^a Heavy reflux occurred and the maximum temperature was 221°C.						

aHeavy reflux occurred and the maximum temperature was 221~ during the first 0.5 hour and 224~ during the first hour.

Whereas vegetable oils generally become lighter in color as deodorization proceeds, acetostearin products become darker. The mono- and diglycerides in the products tend to decompose during deodorization and thereby change the melting point and other physical properties. Losses of acetostearins by distillation during deodorization are greater than for vegetable oils treated under the same conditions. Nevertheless aeetostearin products can be deodorized readily without appreciably changing their properties.

Physical Properties

Flexibility. It is generally recognized that monostearin or other pure monoglycerides are quite waxy immediately after solidification ; however much of this waxiness disappears within 24 hours. Also recognized is a tendency for the physical properties of solidified cocoa butter and other fats composed of relatively simple mixtures of triglyceride molecules to change with the passage of time. Acetostearin products, which consist in large part of 1,2-diaceto-3-stearin³ and 1-aceto-3-stearin, were investigated to determine whether they undergo physical changes with the passage of time which would affect their flexibility.

A sample of 1,2-diaceto-3-stearin, which was of high purity according to its melting point curve (9), was prepared by a standard method of synthesizing fats of special structure. When crystallized from an acetone solution, the 1,2-diaceto-3-stearin was a brittle, granular solid with a melting point of 48.9° C. However when the melt of the sample was cooled, it was a flexible, wax-like solid with a melting point of 37.8° C. Tempering of this solid for 12 hours at 34° C. did not change its melting point. It must be concluded that under these conditions the lower melting, flexible form did not show a tendency to return to the higher melting polymorphic form.

To obtain an indication of the relative degree of flexibility possessed by various acetostearin products, stretching tests were made on molded films of the products. These tests were made in preference to flexing tests because stretchability is more easily determined and suitable equipment for making the tests was available.

All the normally solid acetostearin products tested to date were still stretchable after aging for various periods of time. A product aged at room temperature for over two years was still highly stretchable. All

³ Since the present article was prepared for publication, some of the properties of 1,2-diaceto-3-stearin have been described in an article by F. L. Jackson and E. S. Lutton, J. Am. Chem. Soc., 74, 4827-4829 (1952).

of the acetostearin products described in the earlier publication (6) were still stretchable after approximately one year at room temperature. However those which were made from pure monostearin and commercial, molecularly distiiled monostearin by a low degree of aeetylation (0.5 mole of acetic anhydride per hydroxyl equivalent) became harder and lost a good proportion of their original stretchability. The more highly acetylated products appeared to have lost little or none of their stretchability after one year.

Quantitative measurements of the amount of stretchability retained on aging were made with product No. 5. This product was. chosen because it contained a relatively high proportion of monostearin, which is known to become brittle on aging, and it was thought that any changes in stretchability would be more apparent in such a sample. Product No. 5 was formed into ribbons by pouring it in liquefied form into previously heated molds and allowing them to cool to room temperature (26°C.). The ribbons were stored for various lengths of time at temperatures varying between 22.2° and 32.2°C. before being tested for stretchability with an Instron Tensile Tester⁴ at 22° C. Each ribbon was maintained at this temperature for 16 hours just prior to testing. The test itself consisted of stretching lengthwise at a rate of 1 inch per minute a section of ribbon measuring $\frac{1}{8}$ inch in thickness, $\frac{3}{4}$ inch in width, and 3 inches in length. The amount of stretching and the force or load required to maintain a constant rate of stretching were reeorded automatically. The results obtained are shown in Table IV.

TABLE IV Effect of Aging on the Elongation at Break Point and Resistance
to Stretching of Acetostearin Product No. 5^a

Age	Maximum load	Elonga- tion	Age	Maximum load	Elonga- tion
days	lb.	%	days	lb.	$\%$
0.75	2.6	298	112	5.8	80
14	7.8	69	133	6.2	98
28	6.9	83	154	6.5	113
35	6.0	125	175	6.7	90
49	6.0	95	266	6.5	83
70	5.6	100			
34	5.6	93			

^a Aged at room temperatures of $22.2^{\circ} \cdot 32.2^{\circ}$ C, and tested at a temper-
ature of 22° .

It is apparent that a marked change in the stretchability of the product occurred in the first 14 days, after which no significant change occurred. Variations in the results obtained after 14 days were due mainly to the fact that the test pieces often did not stretch evenly. Any slight flaw in a test piece resulted in an early break by causing most of the stretching to occur in one area.

Stretching tests were made on products Nos. 5, 7, and 8, in which both aging and testing were conducted at 22° C. The results obtained, which are recorded in Table V, show that the stretchability of product No. 5 again changed appreciably over a period of 14 days. Stretchabilities for the other products did not change significantly.

Any changes in flexibility of acetostearin products should be reflected by changes in melting point since flexibility is associated with polymorphic form. Therefore a further cheek of the effect of aging on flexibil-

TABLE V Effect of Aging on the Elongation at the Break Point and Resistance to Stretching of Acetostearin Products a

	Product No. 5			Product No. 7	Product No. 8		
Age	Maxi- mum load	Elonga- tion	Maxi- mum load	Elonga- tion	Maxi- mum load	Elonga- tion	
daus	lb.	%	lb.	%	Lb.	$\%$	
0.75	2.6	298	1,1	680	$_{0.8}$	> 800	
			0.9	774	0.8	800	
4	2.1	181					
			1.1	650	0.8	790	
14	3.0	101					

ity was made by determining the melting points after various periods of time. Products Nos. 3, 4, 8, and 9 were stored in capillary tubes at room temperature and their melting points determined after aging for 0, 7, 14, 21, 28, and 35 days. No change of melting point with age was detected.

Just why solidified acetostearin products are highly flexible is not fully understood. It has been observed however that slow cooling of their liquid form produces a dense, felt-like matrix of needle- shaped crystals. Possibly the sliding of these crystals along each other produces the unusual flexibility. The minor amounts of aceto-oleins and other liquid impurities present in most of the products probably serve to enhance their flexibility.

Consistency. In the utilization of acetostearin products, such as flexible coatings or films, consistency is an important factor. Films whose consistency remains relatively unaffected by changes in temperature below their melting points are preferred. This means, in practice, that the films must melt sharply. The curves in Figure 1 show how 1,2-diaceto-3-stearin and

acetostearin product $No₆$ changed in consistency as the temperature changed, the consistency being measured in terms of micropenetration, *i:e.,* the depth in mm./10 to which a falling needle penetrated the sample when dropped under certain specified conditions (4) . It is evident from the curves that the consistency

⁴This instrument or product is named as pa⁺t of the specification of the exact experimental conditions and does not imply that it is particularly endorsed or recommended by the Department of Agriculture over those of

of neither the 1,2-diaceto-3-stearin nor product No. 6 changed appreciably with temperature below their melting points; and both products melted sharply.

Viscosity. In the liquid state the acetostearin products resemble ordinary vegetable oils in oiliness. Their viscosities vary according to the degree of acetylation and the grade of monostearin used in the preparation. Those made from technical grade monostearin (Table I) we less viscous than those made from technical-grade monoglycerides from highly hydrogenated cottonseed oil; however one of them (No. 1) was of only slightly lower viscosity. Several of the products prepared from the commercial, molecularly distilled monostearin had a viscosity higher than that of normal cottonseed oil. For example, product No. 8 had a viscosity of 25.2 centistokes at 50° C. as compared to about 20 centistokes for cottonseed oil. Product No. 9, which was the least viscous of the products made from the distilled monostearin, had a viscosity of 18.2 centistokes at 50° C. The relative values of the viscosities of acetostearin products and cottonseed oils do not change much when the comparison is made on the basis of centipoises instead of centistokes. At 50° C. the density of product No. 9 was 0.944 g./ml. whereas that for cottonseed oil is approximately 0.90.

Permeability to Moisture. The ability of films of solidified acetostearin products to resist the passage of moisture was investigated in two similar series of experiments. In one series 2-ounce bottles were filled approximately one-fourth full with warm water, and melted acetostearin products were poured on the water surfaces to form films about 1 mm. thick. After the bottles had cooled to room temperature and the films had solidified, the space above the films was dried, about 1 g. of an indicator-containing desiccant (Drierite³) was added to each bottle, and the bottles were sealed. The time required for the desiccant to absorb enough moisture to change color was recorded. In a second series of experiments the desiccant was placed in small glass cups, and the cups were sealed with preformed fihns of product. Increases in the weights of the cups were determined after they had been stored at room temperature and 100% relative humidity for given lengths of time.

The results obtained in the two tests indicated that the permeability of acetostearin films to moisture varied about 3-fold. The greater the degree of acetylation the more impermeable was the film. Products made from the molecularly distilled monostearin were more permeable than those made from the technical grade monostearin. Films of the latter products were comparable to films of peanut oil which had been hydrogenated to a shortening-like consistency.

Chemical Properties

Resistance to Oxidation. The aeetostearin products would be expected to be quite resistant to oxidation because they are highly saturated. For example, products Nos. 8 and 9 had iodine values of 0.6 and 1.5, respectively, while No. 4 had an iodine value of 0.9. When product No. 4 was aerated by the active oxygen method (8) at 97.7 $^{\circ}$ C., no peroxides developed up to 1,000 hours of aeration time. The other two products, which had been prepared from molecularly distilled monostearin and hence contained no natural antioxidants, developed peroxides at a rate normal for fats of such a composition. Both absorbed oxygen at a

fairly constant rate, 1.4 milliequivalents per kilogram per hour during the aeration period of 0-70 hours. When a small amount of antioxidant (0.05% of butylated hydroxyanisole) was added to these two products, they could be aerated for 1,000 hours without developing peroxides and developed only a mild offflavor during the test.

Stability at Elevated Temperatures. Changes in color, viscosity, and content of free fatty acids during heating of acetostearin products for extended periods of time in the presence of air were measured at two temperatures, 97.7° and 200° C. For tests at 97.7°, 35-g. samples of the selected products (Nos. 4 and 9) were placed in test tubes $(25 \text{ mm}, \text{ x } 200 \text{ mm}$. and these were placed in the stability apparatus and heated for 500 hours without bubbling air through the samples. Under these conditions the Lovibond color of product No. 4 changed from 15 yellow and 1.9 red to 15 yellow and 4.5 red. The content of free fatty acids, measured as oleic, increased by 0.13%, and the viscosity at 50° C. increased by 0.09 centistoke. The color of product No. 9 was reduced slightly (0.2 Lovibond red unit) during the 500 hours, but its content of free fatty acids rose from 1.58% to 2.26%, and its viscosity increased by 0.68 centistoke at 50° C When 0.05% of butylated hydroxyanisole was added to product No. 9 before heating, a lesser increase in free fatty acids and viscosity resulted, but there was an increase in color.

For tests at 200° C., 35-g. samples of products Nos. 3, 8, and 9 were heated in open test tubes (25 mm. x 200 mm.) partially immersed in a constant temperature oil bath. The changes observed after various lengths of time are recorded in Table VI.

From the data shown in the table and from a knowledge of the behavior of ordinary fats it may be concluded that acetostearin products are about as stable at a high temperature as are most hydrogenated vegetable oils:

As might be expected, a taste and an odor resembling those of charred organic matter developed in all of the samples after a few hours at 200° C.

Resistance to Hydrolysis. The resistance to hydrolysis of acetostearin products and of refined and bleached peanut and cottonseed oils was determined under various conditions by a series of tests on each. For each series 10 g. of sample and 5 g. of water were

placed in each of a number of glass-stoppered Erlenmeyer flasks of 125-ml. capacity. The flasks were sealed and placed upright in a constant temperature oven. At regular intervals a flask for each series was withdrawn; its contents were diluted with 75 ml. of neutralized ethanol and titrated with a standardized solution of sodium hydroxide to determine the content of free fatty acids. The results obtained for testa made at a temperature of 40° C. are recorded in Table VII.

These data on acetostearin products prepared from the commercial, molecularly distilled monostearin show that the content of free fatty acids (calculated as oleic, on the basis of the weight of the fatty portion) increased at an average rate of 0.025% per day. The addition of an antioxidant to these products did not affect the rate of hydrolysis. A distinct odor of acetic acid developed toward the end of the storage period.

During the first 35 days the refined and bleached cottonseed and peanut oils hydrolyzed at a much slower rate than did the aeetostearin products; but at some time prior to 49 days of storage the cottonseed and peanut oils developed an unpleasant odor, and their acidity increased rapidly. After 63 days both were definitely rancid and had a higher acidity than did any of the acetostearin products. These same phenomena occurred during storage tests at 30° C.; however at the latter temperature the rapid increase in acidity commenced after 112 days, and rancidity developed after 143 days, at which time the acidity of the cottonseed oil was 8.35%.

The addition of a small amount of acetic acid to the cottonseed oil before storage at 40° C. decreased the rate of hydrolysis slightly; undoubtedly the fact that acetic acid did not remain in the oil phase when it was brought into contact with water influenced the results. On the other hand, the addition of cottonseed oil fatty acids doubled the rate of hydrolysis during the first 49 days so that it was equal to approximately one-third that observed with the acetostearin products.

In interpreting the results of the hydrolysis tests, it should be remembered that in each case a completely liquid layer of acetostearin product was in contact with water and that the temperature of the system was 40° C. When acetostearin products are used in the form of solid films, the rate of hydrolysisis undoubtedly much lower and possibly ceases to be a factor in their use.

Summary

Acetostearin products were prepared by interacting various proportions of acetic anhydride with a commercially available, molecularly distilled monostearin (monoester content, 91.5%) and with a technical grade monostearin (monoester content, 59.0%). After water washing and drying of the products a number of properties were determined.

The products, which possessed only a small amount of odor and flavor, could be bleached with activated clay or carbon and rendered odorless and flavorless by ordinary steam deodorization. The latter process had to be conducted under relatively mild conditions (approximately 1 hour at 175° C. and 1 mm. of mercury pressure) to prevent the products from darkening unduly or being degraded.

Evidence was obtained which indicated that the unusual degree of flexibility of acetostearin products was associated with a lower melting polymorphic form, or forms, of 1,2-diaceto-3-stearin, which was quite stable at room temperature. Products stored at room temperature for periods of time up to two years remained flexible, but some products, those of a relatively low degree of acetylation, lost a portion of their flexibility.

The viscosity of liquefied products varied with the degree of acetylation and grade of monostearin used in their preparation, but for most products it was similar to that of cottonseed oil.

The impermeability to moisture of solidified films of the products increased with the degree of acetylation, and those prepared from the technical grade monostearin were more impermeable than corresponding ones prepared from the distilled monostearin. Some products were equivalent in moisture resistance to peanut oil hydrogenated to a shortening-like consistency.

Resistance to oxidation and stability at elevated temperatures were as good as expected on the basis of the low degree of unsaturation of the products. One made from the technical grade monostearin developed no peroxides and only mild off-odor and flavor during aeration for $1,000$ hours at 97.7° C.

In the liquid state at 40° C. and in contact with water the acetostearin products at first hydrolyzed about three times as rapidly as did cottonseed oil containing the same percentage of free fatty acids. After about the first 50 days of the test the acidity of the latter increased at a much greater rate.

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