The results above indicate that the method of Robinson *et al.* (7) is useful in estimating both the total and the diglyceride contents of partial glycerides. The determination of diglycerides, of course, requires an independent analysis for monoglyceride.

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Tempering Triglycerides by Mechanical Working[1]

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Abstract

The tempering of fat products to convert their components to stable polymorphs is an important and a sometimes troublesome problem in the manufacture of these products, particularly chocolate and chocolate-type confections. It has been found that a solid-to-solid transformation to the stable polymorphs can be effected by mechanical working consisting of extrusion under pressure. With a fat of relatively few components, such as cocoa butter, evidence of the transformation can be obtained from X-ray diffraction patterns. For more complex fats, hardness and melting characteristics must be considered. There is evidence that mechanical working is also effective in the transformation of a cocoa butter-like fat made from hydrogenated cottonseed oil and olive oil, and in the transformation of highly hydrogenated cottonseed oil. Mechanical working to effect polymorphic transformation is also effective with products containing the fats mentioned.

Introduction

THE POLYMORPHISM of triglyceride products used in the solid or semi-solid state frequently poses practical problems. Among these is the tempering of chocolate and chocolate-type confections. The major components of cocoa fat in chocolate exhibit four distinct melting points (1). When chocolate is melted and resolidified, special precautions must be taken to ensure rapid transformation of the major components of the fat to their thermodynamically stable form. Failure to achieve this may result in the physical deterioration of the surface structure and may produce fat bloom, which is the appearance of grey spots on chocolate when the fat recrystallizes slowly into larger crystals. Confections containing cocoa butter-like fats also may bloom if proper precautions are not taken. Shortenings also are tempered and are said to perform best when their solid components are in the beta-prime state (2), the thermodynamically stable form of some of the components.

Customarily the transformation of a fat product to a more desirable polymorphic state is accomplished by one or more of three techniques: seeding of the solidifying melt, tempering of the solid or semisolid fat by holding it at a temperature just below its melting point, and aging of the solidified fat. In the manufacture of chocolate the first two techniques are employed. The melted chocolate is cooled to the point of partial solidification. Finely divided chocolate whose fatty components are largely in the most stable form is introduced. The mixture then is kneaded and mixed at a constant temperature until more seed crystals of the stable form appear. When such a mixture is solidified by passage through a cooling tunnel and subsequently warmed to room temperature, the greater portion of the fatty phase is converted into the stable polymorphic form within about 30 minutes (3).

The customary practice in the manufacture of shortenings is to temper the quickly solidified and plasticized products prior to shipment to the ultimate consumer (2). Tempering here consists of aging for a short time at a given temperature.

The present report is concerned with a rapid procedure for converting solid triglycerides to their thermodynamically stable polymorphic form; i.e., it is concerned with effecting a rapid solid-to-solid transformation. The procedure, which is more applicable to certain types of triglycerides than to others, consists simply of mechanical working by extrusion under pressure to extensively deform the triglyceride crystals.

Experimental

General Procedure. To demonstrate the effectiveness of mechanical working as a means of forcing polymorphic transformations, various fat products were heated to well above their melting points to destroy all traces of seed crystals, then the products were quickly solidified, and portions were worked at temperatures well below their melting points.

Mechanical working was accomplished by repeated extrusion through a sodium press, which consisted essentially of a plunger and a cylinder, the latter measuring 0.66 in. in diameter by 1.75 in. in length. The bottom of the cylinder was fitted with an orifice-containing plate through which the solid fat or fat product was extruded. For the cocoa butter and cocoa butter-containing products a plate having a cluster of three orifices, each measuring 0.0135 in. in diameter, was used. For the other fats and fat products a plate having an orifice measuring 0.25 in. by 0.02 in. was used. Both plates had a thickness of 0.074 in. Pressures up to about 1,000 psi were required for the extrusions. The first extrusions for each sample always required less force than did later extrusions.

X-ray diffraction patterns were obtained for the unworked and worked portions of the quickly solidified samples of the fats and for the same fats after thorough tempering by aging and holding them at

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temperatures a few degrees below their melting points.

In the case of the worked and unworked portions of the quickly solidified samples, the sample holders for the X-ray machine were filled by forcing in the solid fat with a spatula. The deformation and working required to fill the holder and form a film measuring 2 x 0.5625 x 0.0469 in. was not sufficient to cause any phase transformation and did not affect the X-ray patterns which were obtained.

The General Electric XRD-5 X-ray apparatus [4] which was used in the investigation was equipped with an argon-filled proportional counter tube. It had a copper target in the X-ray tube and a nickel filter. A one-degree slit was used in collimating the 2 θ angle between 10 and 40 degrees. The machine was operated at 45 KV and 15 MA. Approximately 20 min was required to obtain an X-ray diffraction pattern. To keep the fat samples well below their melting points and to help dissipate the heat created by the passage of the X-rays through the samples, a special cold stage was employed which maintained the temperature at approximately 0C for cocoa butter and cocoa butter-like fat.

X-ray diffraction patterns could not, of course, be obtained for chocolate and chocolate-type products. Instead, hardness values were determined by a modification of the Brinell hardness test for metals (4). In an earlier report it was shown that the hardness of a fat increases as the fat transforms into more stable polymorphs (5).

Cocoa Butter and Cocoa Butter-Like Fat. A sample of commercial cocoa butter was melted and heated to 70C to destroy all crystal nuclei. A thin layer of the melt was poured into a beaker, and the contents were cooled rapidly with dry ice. The beaker was then taken into a walk-in cooler kept at 4C. A portion of the cocoa butter was removed and extruded ten times through the sodium press. Sufficient time was allowed between extrusions so that the temperature of the extruded cocoa butter always remained below about 10C and no visible melting occurred. On about the fifth or sixth extrusion the fat became much harder. A total of ten extrusions was made. Then the samples were forced into separate molds and X-ray diffraction patterns were obtained. During the entire operation the temperature of the samples was always kept below about 10C.

A sample of the cocoa butter in the most stable polymorphic form was prepared by filling the sample holder with shavings from the cocoa butter as it had been received from the manufacturer and after it had been stored for several months at room temperature, or about 25C.

The three X-ray diffraction patterns for the cocoa butter are represented in Figure 1.

The cocoa butter-like fat, which was a fraction of the reaction product obtained by the random interesterification of three parts of almost completely hydrogenated cottonseed oil and one part olive oil (6), consisted essentially of oleo disaturated and linoleo disaturated glycerides in which the saturated fatty acids were essentially palmitic and stearic. The dilatometrically determined melting characteristics, which are recorded in Table I together with those of a typical cocoa butter, resembled the characteristics of cocoa butter reasonably well.

The three samples of cocoa butter-like fat used in

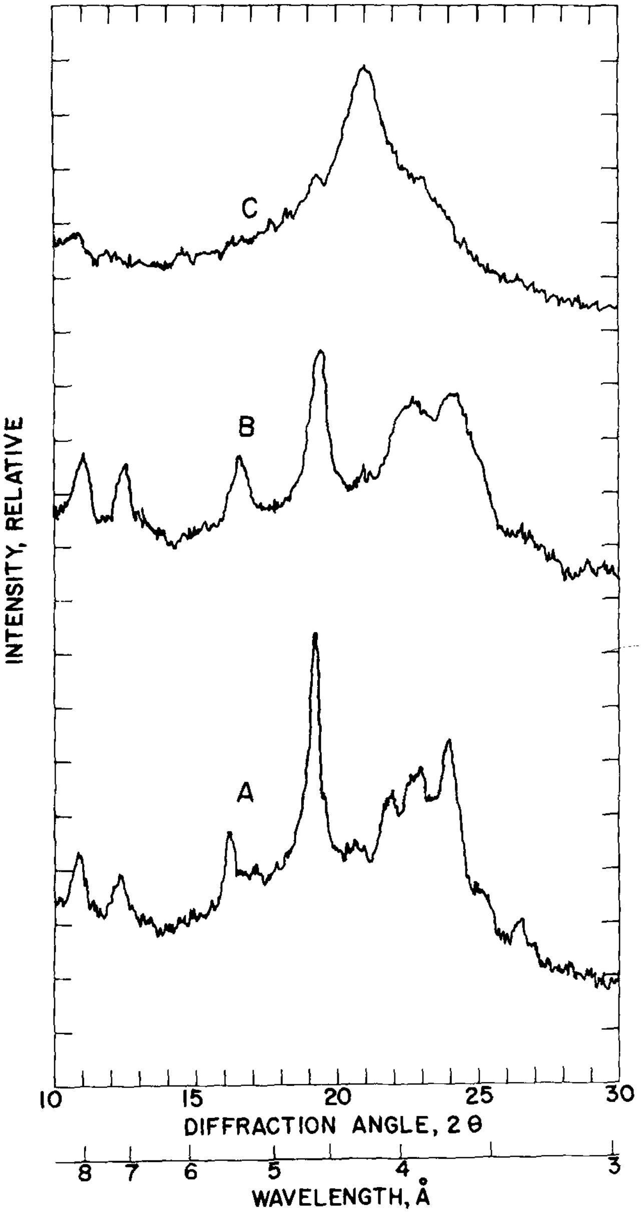

FIG. 1. X-ray diffraction patterns of cocoa butter: *A*, stabilized; *B*, quickly solidified and mechanically worked; and *C*, quickly solidified.

the X-ray analysis were prepared in the manner described for cocoa butter, except that the worked sample was extruded 25 times through the orifice measuring 0.25 x 0.02 in. The X-ray diffraction patterns obtained are represented in Figure 2.

Cottonseed Stearine. The almost completely hydrogenated cottonseed oil, iodine value 2, was a commercial product manufactured by the E. F. Drew Com-

TABLE I
Liquid Content of Cocoa Butter-Like Fat and Cocoa Butter after Tempering

Temperature, C	Liquid content, % [a]	
	Cocoa butter	Cocoa butter-like fat
0	0.6	......
5	1.9	......
10	4.1	......
15	6.8	0.7
20	10.8	8.1
25	16.7	21.7
30	36.1	46.7
35	100.0	96.3
40	......	96.9
45	......	98.5
50	......	100.0

[a] Determined dilatometrically (1).

[4] It is not the policy of the Department to recommend or endorse the products of one company over similar products manufactured by others. The manufacturer is named merely as part of the exact statement of the experimental conditions.

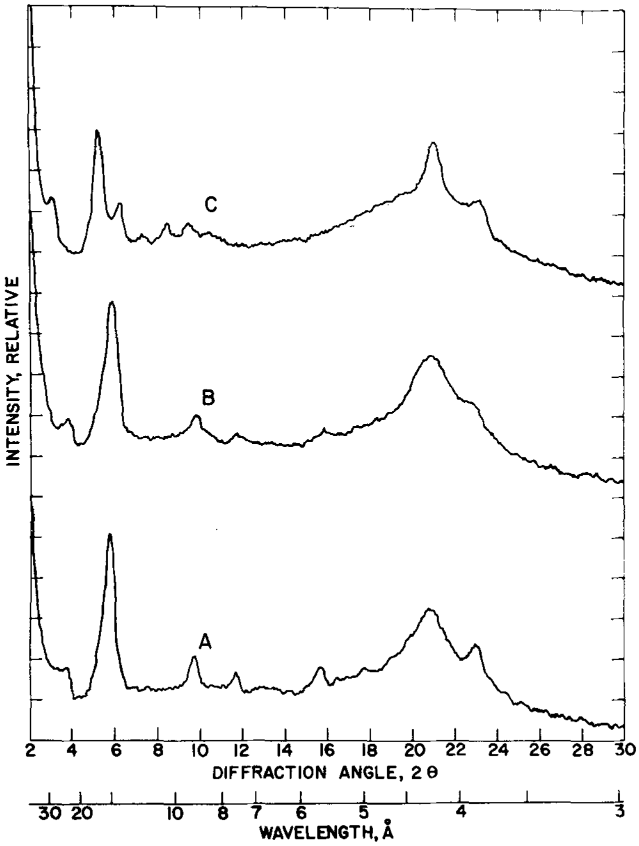

FIG. 2. X-ray diffraction patterns of cocoa butter-like fat No. 5: *A*, stabilized; *B*, quickly solidified and mechanically worked; and *C*, quickly solidified.

pany and was received in the form of flakes. A small quantity of the flakes was placed in a beaker, melted and heated to 80C to destroy all crystals, and then quickly solidified by placing the beaker in ice water. The sample and beaker were warmed to room temperature, about 25C, and a portion of the sample was removed and extruded ten times through the plate with the three orifices, each measuring 0.0135 in. in diameter. To prepare a sample of the flakes in which the components were stabilized insofar as conveniently possible, the flakes, which had been stored at room temperature for about a year, were held for an additional 12 days at 55C, which was just below the dilatometrically determined melting range of 56–63C. X-ray diffraction patterns for the worked and unworked portions of the quickly solidified sample and for the aged and tempered flakes are reproduced in Figure 3.

Chocolate Liquor, Chocolate, and Chocolate-Type Products. Chocolate liquor or cooking chocolate, which consists of roasted and ground cocoa beans, was melted and heated to 67C and then quickly solidified with the aid of ice water. The beaker and contents were transferred to the walk-in cooler kept at 4C, and a portion of the solidified chocolate liquor was removed from the beaker and extruded ten times through the small orifices. The worked and unworked portions were warmed to room temperature. Subsequently, both were heated to 34C, kept at this temperature for 30 min, and then poured into molds and solidified by storage in a refrigerator at 5C for 30 min. The temperature of the samples was allowed to increase stepwise and hardness determinations were made at each step. The data obtained are recorded in Table II.

Tests similar to those carried out with chocolate liquor were carried out with milk chocolate and a chocolate-type coating composition made with the cocoa butter-like fat.

Results and Discussion

Cocoa Butter and Cocoa Butter-Like Fat. About 80% of the triglycerides of cocoa butter consist of 2-oleopalmitostearin and 2-oleodistearin. Each of these triglycerides exhibits four distinct melting points (1). The lowest and highest melting polymorphs are generally recognized as the alpha and beta forms, respectively (7). When in the pure state, the solid-to-solid transformation of each triglyceride from the lowest melting form into the highest melting form requires several days of storage at a temperature just below the melting point (1). When the two glycerides are mixed, either with each other or with other triglycerides, the rate of transformation is decreased.

The X-ray diffraction pattern of the quickly solidified but unworked portion of cocoa butter, *C*, Figure 1, exhibits a single strong diffraction line at a 2 θ angle of about 21 degrees, which corresponds to a crystal spacing of 4.16Å, the characteristic short spacing of the alpha form (8). The diffraction pattern of the quickly solidified and worked cocoa butter, *B*, Figure 1, exhibits strong diffraction lines at 2 θ angles of about 19.4, 22.6, and 24 degrees which correspond to crystal spacings of 4.6, 3.85, and 3.7Å, respectively, which are the characteristic short spacings of the thermodynamically stable beta form (8). The diffraction pattern of the cocoa butter in the well-stabilized form, *A*, Figure 1, exhibits of course the same diffraction lines characteristic of the beta form. These diffraction patterns are evidence that the mechanical working of unstable cocoa butter can convert it into the thermodynamically stable polymorphic form.

The X-ray diffraction patterns of the worked and unworked portions of the quickly solidified sample of cocoa butter-like fat and the pattern of the fat after tempering by aging are practically identical between 2 θ angles of 18 and 30 degrees. Instead of sharp diffraction lines, the three patterns exhibit a diffused band centered at 20.5 degrees which corresponds to a crystal spacing of 4.3Å. One of the three patterns has a small band centered at 22.4 degrees, while the other two patterns show a hump at this angle. At angles below 18 degrees the pattern of the quickly solidified and worked sample resembles that of the aged and well-tempered sample, rather than that of the quickly solidified sample. Dilatometric data on this fat and others prepared in a similar manner (9) indicate that fats of this type do temper. On holding them at a temperature just below their

TABLE II
Hardness of Confectionery Products Made with Worked and Unworked Portions of Quickly Solidified Samples of the Products

Temp. C	Type of product	Hardness index $\times 10^{12}$ [a] Worked	Unworked
16.4	Chocolate liquor	64.0	26.9
20.3	Chocolate liquor	35.0	10.1
24.2	Chocolate liquor	20.5	6.3
28.1	Chocolate liquor	4.3	2.1
17.6	Milk chocolate	22.0	12.0
20.0	Milk chocolate	21.8	11.8
24.0	Milk chocolate	11.1	7.5
28.0	Milk chocolate	2.9	2.1
17.0	Chocolate-type product (made with cocoa butter-like fat)	18.1	15.2
20.0	Chocolate-type product (made with cocoa butter-like fat)	20.5	15.7
24.0	Chocolate-type product (made with cocoa butter-like fat)	15.7	13.0
28.0	Chocolate-type product (made with cocoa butter-like fat)	8.0	6.5

[a] Measured by Brinell type test (4).

melting point for a short time, the melting point and melting dilation are increased. As will be shown below, differences were found in worked and unworked coating compositions made with the cocoa butter-like fat.

The cocoa butter-like fat was composed mostly of the seven oleodisaturated glycerides of palmitic and stearic acids, but also contained several times this number of minor components. The characteristic short spacings are not identical for different triglycerides in the same polymorphic form. To further complicate the X-ray diffraction patterns, some of the triglycerides are thermodynamically stable in the beta prime form, while the others are unstable in this form and stable in the beta form. The formation of some solid solutions or mixed crystals undoubtedly produced new crystal spacings. Finally, the 1-oleodisaturated triglycerides, which comprise about two-thirds of this fat undergo relatively rapid polymorphic transformation (10) and probably transform to some extent even during rapid solidification. Hence, the latter triglycerides would tend to impart a sameness to the diffraction patterns.

Cottonseed Stearine. Most of the comments with reference to the diffraction patterns of the cocoa butter-like fat also apply to the diffraction patterns of the highly hydrogenated cottonseed oil, Figure 3. Between 2 θ angles of 18 and 30 degrees no significant differences are found. However, at the lower-angles, 1 to 18 degrees, the patterns of the unworked and worked portions of the quickly solidified sample of highly hydrogenated cottonseed oil differ. That of the worked portion resembles that of the sample which was tempered by aging and holding at a temperature slightly below the melting point. The diffraction lines at the low angles are a measure of the long spacings of the crystals. Presumably the similarity of the two diffraction patterns in this region indicates a similarity in the lengths of the repeating units of the crystals.

Chocolate Liquor, Chocolate, and Chocolate-Type Products. The melting and solidification of the confectionery products was carried out in a manner analogous to that employed in the manufacture of confections of this type. With such products it is customary to melt the fatty phase, which amounts to about 30% by weight, cool the mixture to solidify a portion of the fat, seed the fat with stable crystals, mold the product or use it to enrobe confections, and finally solidify the fat in the product by passage through a cooling tunnel held at about 15C. When the finished confections leave the cooling tunnel and are warmed to room temperature they will remain bright and glossy if the seeding and solidification process have been carried out properly.

When the worked and unworked portions of the quickly solidified chocolate liquor were warmed to room temperature, or 25C, partial melting of the unworked portion occurred; but the worked portion did not melt. Because stabilized cocoa butter melts at 34–35C and cocoa butter in unstable forms melts as low as 16–18C, the failure of the worked portion of the chocolate liquor to melt is good evidence that extensive stabilization occurred during the mechanical working.

Both the worked and unworked portions of the chocolate liquor were subsequently heated to 34C, molded, and resolidified as described above. Examination of the resolidified bars at room temperature revealed that those made from the worked chocolate

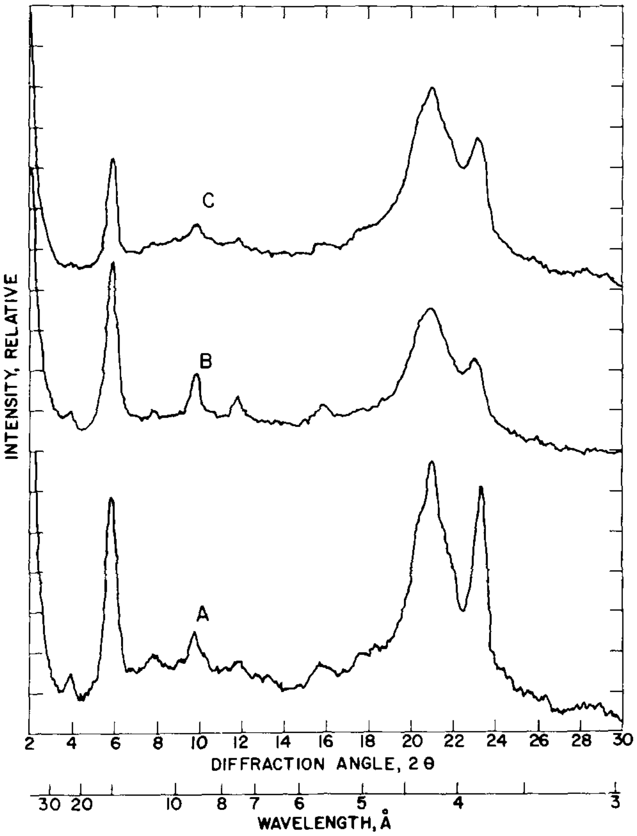

FIG. 3. X-ray diffraction patterns of cottonseed oil stearine: *A*, stabilized; *B*, quickly solidified and mechanically worked; and *C*, quickly solidified.

liquor possessed a good gloss and good contraction and could be demolded easily. In contrast, those made with the unworked chocolate liquor possessed poor gloss and poor contraction and could not be demolded. The bars made from the worked chocolate liquor behaved in every respect like bars made from chocolate liquor which had been seeded adequately with crystals of cocoa butter in the stable polymorphic form.

When tests similar to those carried out with the chocolate liquor were carried out with the sweet milk chocolate and a chocolate-type enrobing composition made with the cocoa butter-like fat, the behavior in each instance was similar to that observed with the chocolate liquor.

Independent evidence that the mechanical working of confectionery products containing cocoa butter and cocoa butter-like fats can be transformed into stable polymorphic forms is provided by the hardness data recorded in Table II. In each instance the bar made from the worked portion of the quickly solidified sample was harder than that made from the unworked portion. The hardness of the bars made from the worked portions was about equal to that of bars made with well seeded melts and described in other reports.

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