Confectionery Fats. II. Characterization of Products Prepared by Interesterification and Fractionation

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Several cocoa butter-like fats, which had been prepared by fractional crystallization of the reaction product obtained on interesterifying highly-hydrogenated cottonseed oil and a triolein product or olive oil, were characterized and compared with cocoa butter.

The fats, as obtained by fractional crystallization from acetone solutions, contained varying amounts of glycerides melting above 37°C, an undesirable feature which caused the fats to thicken too much when used in chocolate type compositions under the same conditions employed with cocoa butter. The higher-melting glycerides could be removed by filtration, or their proportions could be decreased by changing the fractionation temperatures. The fats melted mostly over the same temperature range associated with cocoa butter, and the best of the fats resembled cocoa butter closely over the temperature range 0°C to 30°C.

The cocoa butter-like fats resembled cocoa butter in hardness at all test temperatures. The fats were reasonably compatible with cocoa butter, that is, in mixtures of the two, one did not cause extensive premelting of the other.

According to their cooling curves, the cocoa butter-like fats did not supercool as cocoa butter does. The former contained not only the 2-oleodisaturated glycerides of cocoa butter but also positional isomers of these glycerides. When the fats were molded under the same conditions employed with cocoa butter, linear shrinkage was only about one-third that of cocoa butter.

In a preceding article (9) the preparation of cocoa butter-like fats on a pilot-plant scale was described. In these preparations highly-hydrogenated cottonseed oil (iodine value, 1.8) was randomly interesterified with a triolein product or olive oil, and a cocoa butter-like fraction consisting mostly of oleodisaturated glycerides was obtained by fractional crystallization from acetone. The unwanted by-products could be reused in succeeding runs. The process employed was relatively simple and should be suitable for large-scale commercial use. Some of the characteristics of the products which were obtained are recorded in Table I. The fats, as obtained by fractional crystallization from acetone, were characterized and compared with cocoa butter.

The purpose of the present article is to present a further evaluation of the cocoa butter-like fats, particularly with respect to those characteristics which affect performance in confections.

Dilatometric Examination

One of the prized characteristics of cocoa butter is a very short melting-range lying almost entirely between room temperature and body temperature, 37°C, which makes it possible for the cocoa butter to be hard and brittle at room temperature yet melt abruptly in the mouth when eaten. This characteristic is attributable to the fact that approximately 80% consists of two closely related glycerides, 2-oleopalmitostearin and 2-oleostearin. To define quantitatively and compare the melting characteristics of the cocoa butter-like fats and cocoa butter, dilatometric data were obtained. Dilatometers of the gravimetric type with mercury as the confining liquid were used. Previously-described techniques and methods of making the calculations were followed (2,3). Usually the dilatometer was kept at each test temperature for 20 min. before a weighing was made. To obtain data on untempered samples, a "thrust-in" technique was employed (7), that is, whenever necessary, the sample in the dilatometer was melted, resolidified by rapid chilling, and thrust directly into the dilatometer bath at the test temperature. The mercury reservoir on the dilatometer was placed so that mercury was forced into the reservoir as expansion of the sample occurred but could not return as tempering occurred.

The dilatometric curves for the tempered samples of the three fats, Figure 1, indicate that the greater

### Table I

<table>
<thead>
<tr>
<th>Fat No.</th>
<th>Yield, %</th>
<th>Iodine value</th>
<th>Free fatty acid, as oleic</th>
<th>Softening point, °C</th>
<th>Melting point, °C</th>
<th>Trans isomers, %</th>
<th>Linoleate, %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>27.2</td>
<td>0.22</td>
<td>50.0</td>
<td>57.1</td>
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<td>49.0</td>
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</table>

Analytical methods of American Oil Chemists' Society (1) were used, unless noted otherwise.

1. Calculated as trielaidin (4).
2. Approximately value.
3. Obtained by warming Fat No. 1 to 37°C and filtering out solid glycerides.
4. After tempering for 4 days at 20°C.
5. Olive oil used in the preparation of this fat. Triolein product used in the preparation of Fats No. 1 and 2.

Portion of each sample melted over a relatively short temperature-interval. Fat No. 3 possessed the most desirable melting characteristics while those of Fat No. 1 were least desirable. All three contained small amounts of high-melting glycerides, which explains the high melting-points recorded in Table I. The presence of 1% of completely hydrogenated cottonseed oil can raise the melting point of a fat by about 10°C. Cocoa butter, Curve B, Figure 2, contains no high-melting glycerides. The cocoa butter was a sample produced by a large manufacturer of chocolate.

Percentages of solids at various temperatures were calculated and are recorded in Table II. From these
data it is evident that 61% of Fat No. 1 melted between 20° and 35°C. Over this range the per-
centages of melting of Fat No. 2, Fat No. 3, and cocoa 
butter were 70, 77, and 89%, respectively.

The differences among the three cocoa butter-like 
fats can be attributed primarily to differences in 
the temperature ranges over which the three fats were 
collected and their contents of iso-oleic acid-containing 
glycerides. Fat No. 3 was collected over the narrow-
est range, 17° to 1°C. It also contained the lowest 
content of \textit{trans} isomers.

Under the conditions of fractionation which were 
employed, some high-melting glycerides remained dis-
solved in the solutions of acetone and oleodisaturated 
glycerides. However, after the acetone was removed, 
these glycerides did not dissolve readily in the main 
body of the cocoa butter-like fats. The high-melting 
glycerides could be removed by filtering at 37°C.

Table II

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Cocoa butter</th>
<th>Fat No. 1</th>
<th>Fat No. 2</th>
<th>Fat No. 3</th>
<th>1 to 1 mixture of cocoa butter and Fat No. 3, temp'd</th>
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</thead>
<tbody>
<tr>
<td>°C</td>
<td>Tempered</td>
<td>Untempered</td>
<td>Tempered</td>
<td>Untempered</td>
<td>Tempered</td>
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<tr>
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<td>22.3</td>
<td>22.3</td>
<td>22.3</td>
<td>24.2</td>
</tr>
</tbody>
</table>

though this was a relatively slow process. Fat No. 1a 
is such a product.

When quickly solidified, the cocoa butter-like fats 
exhibited a tendency to crystallize to some extent in 
unstable polymorphic forms. Curves A for Fats No. 2 
and 3, Figure 1, show that quick chilling produced 
mixtures which started to melt at lower temperatures 
than do the same mixtures after tempering. In this 
respect they resembled cocoa butter (Curve A, Fig-
ure 2). However there was a difference. The lower-
melting polymorphs of the components of cocoa butter 
were much more stable. Curve A for cocoa butter, 
Figure 2, was obtained without the use of the “thrust-
in” technique. Several weeks of tempering at 26°C.