Cocoa Butter-Like Fats from Fractionated Cottonseed Oil: I. Preparation

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ABSTRACT

The manufacture of salad oil from cottonseed oil can produce a byproduct stearine fraction consisting essentially of 1-palmito and 1,3-dipalmito triglycerides of oleic and linoleic acids and having an iodine value of ca. 72. Hydrogenation of this fraction to an iodine value of ca. 28-42, under conditions simultaneously selective and conducive to a low rate of *trans*-isomer formation, yielded a product that could readily be fractionated to produce over 60% of a cocoa butter-like fat. The conditions of fractionation influenced the yield and properties. Fractionation was most easily accomplished by tempering the solidified hydrogenation product and leaching with a petroleum naphtha or acetone.

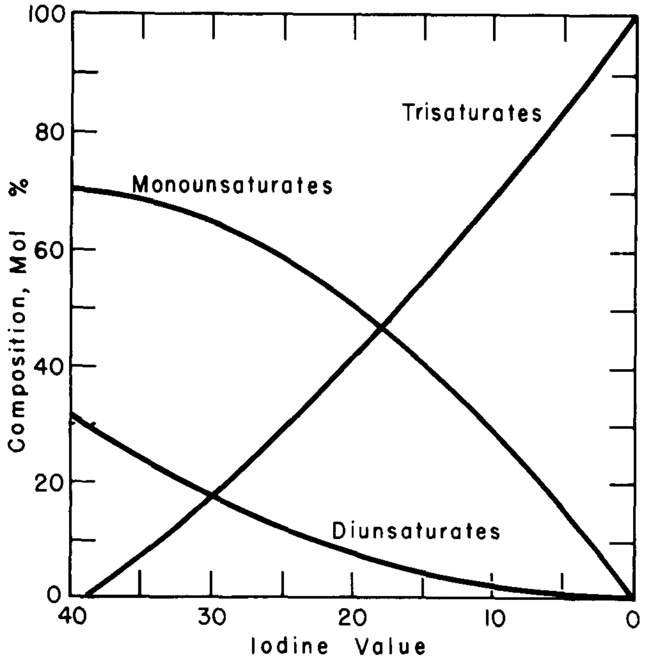

FIG. 1. Composition of triglycerides resulting from the completely selective hydrogenation of cottonseed oil stearine A.

INTRODUCTION

The volume of cocoa butter-like fats, the so-called "hard butters," probably amounts to over half of the more than 50 million pounds of fats and oils used annually by the domestic confectionery industry. Mostly these cocoa butter-like fats are prepared from lauric acid oils, but a few are prepared from oleic-linoleic acid oils. These fats have a price advantage over cocoa butter, but their physical properties usually are not ideal for the intended uses. If a really excellent cocoa butter-like fat could be manufactured at a competitive price, better confections would be produced and the market for such fats would expand.

The prized characteristics of cocoa butter include a very short melting range, a melting point of ca. 35 C, marked

TABLE I

Characteristics of Byproduct Stearine from Solvent Winterization of Cottonseed Oil

Characteristic	Stearine A	Stearine B
Iodine value	72.4	71.5
Fatty acids, wt %[a]		
Myristic	0.2	0.4
Palmitic	52.4	49.9
Stearic	2.1	2.1
Oleic	9.6	10.8
Linoleic	35.8	36.8
Liquid content, wt %[b]		
10 C	0.0	0.0
15 C	5.4	5.1
20 C	25.7	26.0
25 C	73.5	78.4
30 C	96.6	97.4
35 C	99.6	99.3

[a] Calculated from gas liquid chromatographic data on methyl esters derived from the stearine.

[b] Determined by dilatometric examination of well tempered samples.

TABLE II

Hydrogenated Products from Cottonseed Oil Stearine A and Cocoa Butter-like Fractions Prepared by Fractional Crystallization

			Composition of derived methyl esters, wt %[c]				Cocoa butter-like fraction			
Product[a]	Iodine value	*Trans* isomers, wt %[b]	Palmitate	Stearate	Oleate	Linoleate	Number	Yield, %[d]	Iodine value	*Trans* isomers, wt %[b]
Original stearine	72.4	0.0	52.4	2.1	9.6	35.8	—	—	—	—
HP-1	40.9	10.6	50.2	8.0	35.2	6.4	HP-1F	84.4	45.8	10.2
HP-2	36.2	10.2	51.4	10.3	35.2	2.9	HP-2F	76.1	41.4	10.7
HP-3	29.3	10.7	50.0	14.1	34.8	0.8	HP-3F	68.6	37.9	11.6
HP-4	42.9	4.2	50.1	16.2	16.8	16.7	HP-4F	60.4	53.4	4.3
HP-5	33.8	4.4	50.1	21.3	17.2	11.2	HP-5F	55.0	53.6	5.4

[a] Products HP-1 through -3 obtained with zirconium-promoted nickel catalyst. Products HP-4 and HP-5 obtained with Raney nickel.

[b] Calculated as trielaidin.

[c] Only those esters present at levels above 1% are listed.

[d] Calculated on the basis of complete separation of liquid and solid phases.

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[1] ARS, USDA.

TABLE III

Triglyceride Compositions of Products HP-3 and HP-6

Type of triglyceride	Product HP-3, %	Product HP-6, %
Trisaturated	21	22
Monounsaturated	66	63
Diunsaturated	12	13
Triunsaturated	1	3

contraction after solidification of a partially melted and tempered sample, and brittleness at room temperature. These characteristics reflect the structure and properties of its components: ca. 57% 2-olelpalmitostearin and 22% 2-oleodistearin, plus lesser amounts of palmitodiolein, stearodiolein and oleodipalmitin (1,2).

Cottonseed oil contains ca. 13% monounsaturated and ca. 58% diunsaturated triglycerides of oleic and linoleic acids (3), the saturated acid being essentially palmitic. The higher melting members of these triglycerides are concentrated in the byproduct stearine obtained in the commercial winterization of cottonseed oil to produce salad oil. This concentration is particularly marked in solvent winterization employing a hexane solution (4). Obviously, hydrogenating the linoleoyl groups in cottonseed oil stearines yields mixtures containing sizable proportions of triglycerides, the properties of which resemble those of the major components of cocoa butter. The preparation of cocoa butter-like fats from these stearines reduces essentially to hydrogenation and fractionation.

COMPOSITION AND PROPERTIES OF COTTONSEED OIL STEARINE PRODUCED BY SOLVENT WINTERIZATION

A drum of cottonseed oil stearine produced as a byproduct in solvent winterization was obtained from a commercial processor at two different times. Representative samples from each drum were analyzed. The results obtained are recorded in Table I.

The two stearines were quite similar in composition and melting characteristics. Both samples exhibited a very short melting range, but the point of essentially complete melting was ca. 5 C below that of a typical cocoa butter. An analysis was made of the types and proportions of the fatty acid groups in the 2 and 1,3 positions using the pancreatic lipase hydrolysis technique of Mattson and Volpenhein (5). Slightly over 90% of the fatty acid groups found in the 2 position was unsaturated. This is within a unit of the percentages found by Mattson and Lutton (6) for cocoa butter and for unfractionated cottonseed oil. Thin layer chromatographic analyses indicated the presence of less than 0.3% trisaturated glycerides. Calculations based on the data in Table I reveal that stearine A consisted of 70% mono- and 30% diunsaturated triglycerides, while stearine B consisted of 64% mono- and 36% diunsaturated triglycerides. For all practical purposes the stearines consisted of two-thirds 1,3-dipalmito and one-third 1-palmito triglycerides of oleic and linoleic acids. The presence of a high proportion of 1,3-disaturated triglycerides in cocoa butter-like fats is highly desirable, because it ensures a polymorphic behavior similar to that of cocoa butter.

TABLE V

Effect of Leaching Temperature on Melting Characteristics of Cocoa Butter-like Fats from Hydrogenated Product HP-7[a]

	Liquid content, %[b]			
		Cocoa butter-like fat obtained by leaching at		
Temperature, C	Cocoa butter	15 C	20 C	25 C
10	—	—	1	1
15	7	4	4	4
20	11	14	12	11
25	17	26	18	17
30	36	51	30	29
35	100	99	79	63
40	—	—	100	91

[a] Cocoa butter-like fats nos. HP-7-3 through HP-7-5, Table IV. Product HP-7 leached in each case with an equal weight of hexane for 60 min.

[b] Liquid content determined dilatometrically on well tempered samples.

HYDROGENATION

Ideally the preparation of a cocoa butter-like fat from a cottonseed oil stearine obtained by solvent winterization would consist of hydrogenating the linoleoyl groups to oleoyl groups and possibly removing by fractional crystallization a small portion of dioleopalmitin to adjust the melting point. In practice, iso-oleic acid groups and stearoyl groups are formed during the hydrogenation of linoleoyl groups. However a reasonably selective hydrogenation of linoleoyl groups will produce a relatively low proportion of stearoyl groups. In Figure 1 are plotted the triglyceride compositions attainable on hydrogenation of stearine A if the reaction could be conducted in a completely selective manner.

Two catalysts were used in the laboratory hydrogenations. One was dry-reduced, zirconium-promoted nickel on kieselguhr (No. 70 manufactured by the Catalysts Div., Chemetron Corp.), used at a level of 0.25% nickel, based on the weight of the oil; and the other was highly active Raney nickel (7), used at a level of 3.6% nickel. Before hydrogen-

TABLE IV

Cocoa Butter-like Fats Obtained by Leaching Hydrogenated Product HP-7[a]

Fat no.	Solvent used[b]	Leaching temperature, C	Yield, %[c]	Iodine value	Melting point, C
HP-7-1	Pentane	20	83.5	40.7	40.0
HP-7-2[d]	Hexane	15	50.8	43.5	36.0
HP-7-3	Hexane	15	63.8	42.3	35.0
HP-7-4	Hexane	20	71.3	40.7	35.0
HP-7-5	Hexane	25	78.2	39.7	43.0
HP-7-6	Heptane	20	66.9	41.7	37.5
HP-7-7	Acetone	20	65.7	42.7	32.0
HP-7-8	Acetone	25	66.9	41.4	37.5

[a] Product HP-7 obtained by hydrogenating stearine B to an iodine value of 31.7 and a *trans*-isomer content of 10.9%, employing zirconium-promoted nickel catalyst.

[b] Ratio of solvent (commercial grade) to product HP-7 was 1:1 w/w.

[c] Calculated on basis of complete separation of liquid and solid phases.

[d] Untempered fat used.

ation, the stearine was bleached with a neutral, activated clay to remove any catalyst poisons. To minimize the formation of isomers, the hydrogenations were conducted at a hydrogen pressure of 22 psig, and the lowest practical temperature, 84 C with the nickel-on-kieselguhr catalyst and 43 C with the Raney nickel catalyst. Unless indicated otherwise, the reaction was conducted in a stainless steel, laboratory hydrogenation apparatus (Pressure Reaction Apparatus, Series 4500, Parr Instrument Co.) using 560 g stearine per batch.

The hydrogenations reported in Table II were conducted with the stearine dissolved in heptane 1:1 w/w. The *trans*-isomer contents found in the hydrogenated products are well below the levels usually encountered in ordinary hydrogenations. The objective of relatively low proportions of *trans*-isomer was achieved. However the Raney nickel catalyst was quite unselective, and the end products contained unacceptably high levels of linoleoyl groups.

Other hydrogenations were conducted in hexane solution and in the absence of a solvent. Subsequent analyses revealed that the presence or absence of petroleum naphtha had no significant effect on the reaction rate, the formation of *trans*-isomers or the fatty acid composition of the reaction product.

To establish the reproducibility of the hydrogenations, a reaction equivalent to that employed to obtain product no. 3 was conducted using equipment of small pilot plant size (8) and substituting cottonseed oil stearine B for A. Product RP-6, obtained with the larger equipment, and product HP-3 were analyzed for triglyceride composition, using a silicic acid-silver nitrate column; the results are shown in Table III.

FRACTIONATION

The five hydrogenated products listed in Table II were fractionated. Each product was dissolved in commercial pentane 1:1 w/w, the solution cooled to ca. 20 C over a period of 16 hr, held at 20 C for an additional 6 hr, and then filtered. Results from previous tests indicated these conditions were about correct for obtaining cocoa butter-like fats in the filtrate fraction. Yields and other data obtained on the cocoa butter-like fractions are recorded in Table II.

While crystallization from solvents—the classical technique for fractionating fats—can be employed for making cocoa butter-like fats, a better technique consists of tempering the solid fat and then leaching out the cocoa butter-like fraction with petroleum ether or acetone. Fractional crystallizations conducted as described above approached equilibrium after ca. 8 hr but did not reach it, according to crystallizations conducted in a large dilatometer. Leaching was a more rapid process, which could be accomplished in ca. 30 min when the solid, tempered fat was ground or extruded through an orifice into the leaching solvent. Tempering the fat to be leached tended to unscramble any mixed crystals and to convert each triglyceride into a single polymorphic form, simplifying the structure of the fat mixture and reducing the number of phases involved in the fractionation. Of course the type of solvent and leaching temperature affected the yield and properties of the cocoa butter-like fractions. These effects are indicated in Tables IV and V. On comparing the samples represented in Table V, it is evident that changes in the leaching temperature were an effective means of changing the melting characteristics of the fat. Considering the ease and efficiency with which solid fats can be fractionated by leaching, it is surprising that the technique has not attained prominence.

Obviously the byproduct stearines from the winterization of cottonseed oil, which meet the important requirement of being rich in 1,3-disaturated triglycerides, are suitable starting materials for the preparation of cocoa butter-like fats. A fairly selective hydrogenation to reduce the proportion of linoleoyl groups resulted in products that could be readily fractionated to obtain high yields of fats possessing melting points and melting characteristics similar to those of cocoa butter. A more extensive examination of the properties of such fats is presented in the following report.

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[Received May 18, 1972]