SYNTHESIS AND PROPERTIES OF MINOR CRYPTO-ACTIVE TRIGLYCERIDES OF COCOA BUTTER

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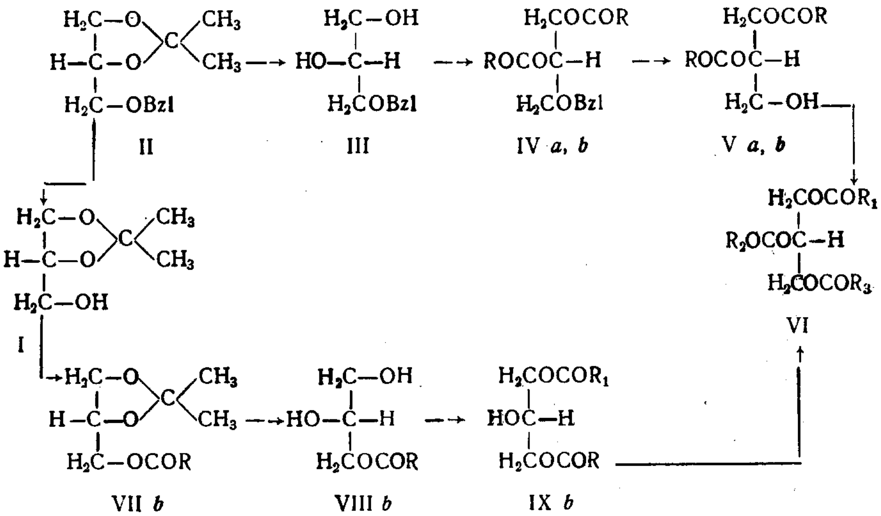
Cocoa butter stands out among plant oils and fats by its special properties. Under ordinary conditions it is solid and brittle with a melting point of about 35°C. These properties of the butter, which are very important for the production of high-quality chocolate, are determined mainly by its glyceride composition. As investigations have shown [1-4], the main components of cocoa butter are triglycerides containing residues of saturated acids (palmitic and stearic) and of the monounsaturated oleic acid (POS, SOS, POP). More unsaturated triglycerides (POO, SOO, etc.) are present in considerably smaller amounts.

In recent years, crypto-active triglycerides (sn-PPO, sn-SSO, sn-OSS, etc.) have been found in cocoa butter in small amounts [3].

In searches for synthetic cocoa butter substitutes, the properties of mixtures of the main racemic triglycerides have been studied [1]. However, they differ in their acid composition and melting point from natural butter. In view of this, it appears of interest to study the influence of the minor components on the properties of a mixture of main triglycerides of cocoa butter.

Continuing investigations on obtaining the triglycerides of cocoa butter [2, 5], we have performed the synthesis of minor crypto-active triglycerides.

Synthesis of crypto-active triglycerides



a) $R_1=R_2=C_{15}H_{31}$; $R_3=C_{17}H_{33}$; *b*) $R_1=R_2=C_{17}H_{35}$; $R_3=C_{17}H_{33}$; *c*) $R_1=C_{17}H_{33}$ $R_2=R_3=C_{17}H_{35}$.

a) $R=C_{15}H_{31}$; *b*) $R=C_{17}H_{35}$; $R_1=C_{17}H_{33}$ (IV, V, VII, VIII, IX); $Bzl=CH_2C_6H_5$.

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TABLE 1. Glyceride and Acid Compositions and Melting Points of Mixtures of Triglycerides

Mixture No.	Glyceride composition (in parts by weight)										Acid composition, %				Melting point of the mixture after		
	POS	SOS	POP	SOO	POO	SLL	OOL	snPPO	snSSO	snOSS	S	P	O	L	1 day (18-20°C)	10 days (25°C)	1 month (25°)
1	32,8	24,2	12,1								39,8	26,1	34,1		30,3	36,7	36,8
2	32,8	24,2	12,1	6,0	10,0	5,0					34,6	23,5	38,2	3,7	33,4	35,2	36,1
3	32,8	24,2	12.1	6,0	10,0	5,0	1,0				34,3	23,2	38,5	4,0	32,8	34,8	35,5
4	32,8	24,2	12,1					1,1	0,8	0,7	39,8	26,1	34,1		30,3	36,7	36,9
5	32,8	24 2	12,1	6,0	10,0	5,0		1,1	0,8	0,7	34,7	23,6	38,1	3,6	29,6	35,7	36,0
6	32,8	24,2	12,1	6,0	10,0	5,0	1,0	1,1	0,8	0,7	34,4	23,3	38,4	3,9	32,9	34,3	36,6
7*	32,8 - 57,0	18,4 - 27,0	3,7 - 15,4	3,5 - 12	2,6 - 8,4			1,1	0,8	0,7	31,8 - 37,3	22,0 - 28,7	32,0 - 38,9	2,0 - 4,0	28,0	34,8	35,1

*Cocoa butter.

The main glyceride components of cocoa butter in the racemic form, which contain residues of stearic, palmitic, oleic and linoleic acids in various combinations (POS, SOS, POP, SOO, POO, SLL, LOO), were obtained by known methods via 1,2-isopropylideneglycerol using the chlorides of the higher fatty acids [2, 5, 6]. The crypto-active triglycerides sn-PPO (VIa), sn-SSO (VIb), and sn-OSS (VIc) were synthesized by a method based on 1,2-isopropylidene-sn-glycerol (I), obtained, in its turn, from D-mannitol.

For the synthesis of the triglycerides (VIa) and (VIb), containing oleic acid in the 3rd position, 1,2-isopropylidene-sn-glycerol (I) [7] was converted by benzylation into 3-O-benzyl-1,2-isopropylidene-sn-glycerol (II) [8, 9]. Removal of the isopropylidene protection led to 3-O-benzyl-sn-glycerol (III) [8, 10]. The acylation of (III) with palmitoyl or stearoyl chloride yielded compound (IVa) or (IVb), respectively [6, 11]. After elimination of the benzyl protection by hydrogenolysis in the presence of a palladium catalyst, the diglyceride (Va) or (Vb) was isolated [11, 12], and by means of oleoyl chloride it was converted into 3-oleoyl-1,2-dipalmitoyl-sn-glycerol (VIa) or 3-oleoyl-1,2-distearoyl-sn-glycerol (VIb) [6, 13, 14].

To synthesize a triglyceride containing oleic acid in position 1, 1,2-isopropylidene-sn-glycerol (I) was acylated with stearoyl chloride to give 1,2-isopropylidene-3-stearoyl-sn-glycerol (VIIb) [6, 7]. After the removal of the isopropylidene protection [7], 3-stearoyl-sn-glycerol (VIIIb) was obtained. When mixtures of the antipode (VIIIb, mp 77.5°C) with the racemic monostearate (mp 83°C) were melted, a clear eutectic was observed at a 1:1 ratio at 76°C. The successive action of oleoyl and stearoyl chlorides converted (VIIIc) first into 1-oleoyl-3-stearoyl-sn-glycerol (IXb) and then into 1-oleoyl-2,3-distearoyl-sn-glycerol (VIc) [6, 13, 14].

The enantiomeric triglycerides (VIb) and (VIc) had the same melting points, and their mixtures in equal amounts gave a eutectic:

Triglycerides, %	SSO	100	90	80	70	60	50	0
	OSS	0	10	20	30	40	50	100
Melting point of the mixture, °C		46.8	45.4	44.6	43.7	43.4	43.3	46.7

From the triglycerides synthesized, mixtures were made up approximating to cocoa butter in glyceride and acid compositions. The results obtained (Table 1) showed that after a month a mixture consisting of three components (No. 1) had a melting point (36.8°C) exceeding that of cocoa butter (No. 7, 35.1°C). A lowering of the melting point of the mixture

(36.1°C, 35.5°C) was achieved by the introduction of more unsaturated triglycerides (Nos. 2 and 3). The addition to these mixtures of optically active triglycerides (Nos. 4, 5, and 6) scarcely affected the melting points (36.9°C, 36.0°C, 35.6°C).

EXPERIMENTAL

The individuality of the compounds synthesized was checked by chromatography in a thin layer of type KSK silica gel (200 mesh) fixed with gypsum and impregnated with boric acid (5-10%) in various systems depending on the polarities of the glycerides: 1) chloroform—acetone (96:4; 99.5:0.5), and 2) chloroform—acetone—methanol—acetic acid (72.5:25:2:0.5); the chromatograms were revealed by spraying with a 10% solution of sulfuric acid followed by calcining at 300-350°C.

The melting points of the mixtures of triglycerides were determined by the method used for natural cocoa butter [15]. To allow for the phenomonon of polymorphism, the determination of the melting point was performed after a day (20°C), after 10 days (25°C), and after a month (25°C).

1,2-Isopropylidene-sn-glycerol (I). This was obtained by a published method [7]. bp 83-84°C (12 mm); $[\alpha]_D^{20}$ + 13.83 (no solvent); d_4^{20} 1.0700: n_D^{20} 1.4340.

3-O-Benzyl-1,2-isopropylidene-sn-glycerol (II). Obtained by a published method [8, 9]. bp 150°C (12 mm); $[\alpha]_D^{20}$ + 19.33 (undiluted substance); d_4^{20} 1.0509; n_D^{20} 1.4955.

3-O-Benzyl-sn-glycerol (III). Obtained by a published method [8, 10]. bp 135°C (0.6 mm); $[\alpha]_D^{20}$ + 6.42 (no solvent); d_4^{20} 1.1416; n_D^{20} 1.5322.

3-O-Benzyl-1,2-dipalmitoyl- and -1,2-distearoyl-sn-glycerols (IVa, IVb). Obtained by a published method [6, 11]. mps, respectively, 45.5°C (def. 44.2°C) and 52.5°C (def. 51.5°C).

1-2-Dipalmitoyl- and -1,2-Distearoyl-sn-glycerols (Va and Vb). Obtained by a published method [11, 12]. For (Va): mp 69°C, def. 68.5°C, $[\alpha]_{589}^{20}$ − 2.82; $[\alpha]_{546}^{20}$ − 3.39; $[\alpha]_{404}^{20}$ − 6.94; $[\alpha]_{302}^{20}$ − 15.44 (c 7.5; chloroform), and for (Vb): mp 77°C, def. 76°C; $[\alpha]_{589}^{20}$ − 2.24; $[\alpha]_{546}^{20}$ − 2.68; $[\alpha]_{404}^{20}$ − 5.42; $[\alpha]_{302}^{20}$ − 11.83 (c 8; chloroform).

3-Stearoyl-sn-glycerol (VIIIb). Obtained by a published method [6, 7]. mp 77.5°C, def. 76°C; $[\alpha]_{589}^{20}$ − 3.45; $[\alpha]_{427}^{20}$ − 7.17; $[\alpha]_{373}^{20}$ − 10.2; $[\alpha]_{354}^{20}$ − 11.61 (c 9; pyridine).

1-Oleoyl-3-stearoyl-sn-glycerol (IXb). Obtained by a published method [6]. bp 49°C, def. 48.3°C.

General Method for Obtaining the Triglycerides (VIa, b, c). To a solution of 0.0026 mole of a diglyceride in 40 ml of anhydrous chloroform and 0.0039 mole of pyridine was added 0.0039 mole of an acid chloride in a current of nitrogen with stirring at 0°C. The mixture was left at 18-20°C for 48 h [in the preparation of (VIa and b)] or for 72 h [for (VIc)]. The solvent was driven off in vacuum. The residue was treated three times with a 15-fold amount of a mixture of ethanol and acetone (9:1) with stirring. The precipitate was filtered off, washed with the same mixture, and dried in vacuum (0.1 mm, 25°C). The triglyceride isolated, containing small amounts of diglycerides and fatty acids, was dissolved in a 10-fold amount of a mixture of petroleum ether and diethyl ether (98:2) and was purified on a column containing 2-3 g of alumina (activity grade II). After elimination of the solvent and "drying" in vacuum (0.1 mm), the chromatographically pure triglycerides were obtained with yields of 70-80%.

3-Oleoyl-1,2-dipalmitoyl-sn-glycerol (VIa). mp 37.8°C, def. 37°C (after a day at 20°C); mp 37.8°C, def. 37.3°C (after a month at 25°C).

3-Oleoyl-1,2-distearoyl-sn-glycerol (VIc). mp 47.1°C, def. 45.9°C (after a day at 20°C); mp 46.8°C, def. 46.2°C (after a month at 25°C).

1-Oleoyl-2,3-distearoyl-sn-glycerol (VIc). mp 46.7°C, def. 45.3°C (after a day at 20°C); mp 46.7°C, def. 45.8°C (after a month at 25°C).

SUMMARY

1. The crypto-active triglycerides sn-PPO, sn-SSO, and sn-OSS have been synthesized.

2. It has been shown that the melting points of mixtures of the main racemic triglyceride components of cocoa butter are affected by more unsaturated triglycerides. Cryptoactive triglycerides scarcely affect the melting points of the mixtures.

LITERATURE CITED

1. R. L. Wille and E. S. Lutton, J. Amer. Oil Chemists' Soc., 43, 491 (1966).
2. I. K. Sarycheva, G. A. Serebrennikova, E. N. Zvonkova, T. K. Mitrofanova, M. E. Maurit, O. V. Utkina, and N. A. Preobrazhenskii, Dokl. Akad. Nauk SSSR, 135, 617 (1960).
3. J. Sampugna and R. G. Jensen, Lipids, 4, 444 (1969).
4. H. J. Dutton, C. R. Scholfield, and T. L. Mounts, J. Amer. Oil Chemists' Soc., 38, 96 (1961).
5. G. G. Zapesochnaya, E. N. Zvonkova, T. K. Mitrofanova, G. A. Serebrennikova, I. K. Sarycheva, and N. A. Preobrazhenskii, Zh. Obshch. Khim., 32, 3906 (1962).
6. J. G. Quinn, J. Sampugna, and R. G. Jensen, J. Amer. Oil Chemists' Soc., 44, 439 (1967).
7. E. Baer and N.-H. Flehmig, Canad. J. Biochem., 47, No. 2, 79 (1969).
8. E. Baer and H. O. L. Fischer, Chem. Rev., 29, 287 (1941).
9. N. E. Frank and R. Montgomery, Carbohydrate Research, 6, No. 3, 286 (1968).
10. W. E. M. Lands and A. Zschoke, J. Lipid Res., 6, 324 (1965).
11. W. E. M. Lands, R. A. Pieringer, S. P. M. Slakey, and A. Zschoke, Lipids, 1, 444 (1966).
12. E. Baer and Kates, J. Amer. Chem. Soc., 72, 942 (1950).
13. J. Sampugna and R. G. Jensen, Lipids, 3, 519 (1968).
14. H. Brockerhoff, J. Lipid Res., 6, 10 (1965).
15. T. P. Ermakova and R. D. Normanova, Solid Fats in the Confectionery Industry [in Russian], TsINTIpishcheprom, Moscow (1965).