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PHYSICAL AND CHEMICAL PROPERTES OF SOME COCOA BUTTER SUBSTITUTES

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ABSTRACT: Cocoa butter substitutes (CBS) are lauric fats normally derived from palm kernal oil, are good stability shelf life and very good texture. This study compared between Croklaan Special 555/E (CLSP 555/E), kerme and two blends from CLSP 555/E and kerme at ratio of 3:1 and 1:1 (w/w). Cocoa butter substitutes and their blends were examined for some physical and chemical characteristics. The obtained results revealed slight differences in the refractive index of CLSP 555/E, kerme and their blends 3:1 and 1:1 being 1.44205, 1.44324, 1.44238 and 1.44264, respecteively. The melting point of CLSP 555/E was 37 – 38°C, kerme 34 – 35.1°C, blend (3:1) 35 – 36.5°C and blend (1:1) was 34.8 – 35 °C. Free fatty acids for CLSP 555/E, kerme, blend (3:1), and blend (1:1) were 0.036%, 0.054%, 0.042% and 0.05%, respectively. Iodine values of CLSP 555/E, kerme, blend (3:1) and blend (1:1) were 1.05, 9.75, 2.13 and 4.47, respectively. Peroxide values recorded 0.106, 0.183, 0.120, and 0.143 for CLSP555/E, kerme, blend (3:1) and blend (1:1), respectively. Saponification values of both cocoa butter substitute and blends was ranged from 248 to 250. The unsaponifiable matter of CLSP555/E, kerme, blend (3:1) and blend (1:1) were 0.57%, 1.24%, 0.72% and 0.83%, respectively. Solid fat contents of both CLSP555/E and blend (3:1) were higher than that of kerme and blend (1:1) at tempreature of 20°and 30° C.

Key Words: Physical and chemical properties, cocoa butter substitutes, unsaponifiable matter, fattey acid composition, solid fat content.

INTRODUCTION

Cocoa butter substitute (CLSP 555 and Coberine) produced by Loders Croklaan Company) have been enjoyed reputation for quality and consisteny that appreciated by confectionery manufacturers over the world since 1950. Lauric cocoa butter replacers did not need to tempered. They offered a very good balance between cost and quality in terms of melting behaviour (Anon, 1995).

Nalur (1999) reported that oil blends are based on palm kernel oil and its derivatives. Hydrogenated palm kernel oil, palm kernel stearin and hydrogenated palm kernel stearin are used in food products including confectionery and chocolate products. Cocoa butter substitutes (CBS) are lauric fats normally derived from palm kernel oil. Through a sophisticated manufacturing process they are behaved into products with melting properties similar to cocoa butter (Lidefelt, 2002). Cocoa butter substitutes are produced from palm kernel and ground nut oils be fractionation and hydrogenation. The constitution of these fats and oils differs from cocoa butter. The use of these fats in chocolate is forbidden by law in many countries, that is, if the product is described as chocolate. But such fats may by used in products very closely resembling chocolate for coating biscuits confectionery bars and ice cream. This attitude was resulted from some draw backes attached to such fats as described by Abd-El-Hady (1987). Shukla (1995) showed that palm kernel stearin is used in the manufacture of lauric cocoa butter substitutes (lauric CBS). Loders croklaan special 555/E (CLSP 555/E) and Loders croklaan special 499 (CLSP 499) represent the top in this segment in terms of quality. CBS lauric have good stability and shelf life, texture and flavor release. They did not need tempring as does in case of cocoa butter, they contract and mould well, and not to be over looked, they are much cheaper than cocoa butter (Minifie *et al.*, 1989). Palm kernel stearine is used in the manufacture of lauric cocoa butter substitutes (lauric CBS). The present study aims to evaluate some physical and chemical characteristics of two type of lauric cocoa butter substitutes (lauric CBS) and their blends.

MATERIALS AND METHODS

Materials

Cocoa butter substitutes

Two substitutes were used, the first bearing a commercial brand

Croklaan Special 555/E (CLSP555/E), and the second brand was Kerme as a lauric and tempering cocoa butter substitutes produced by Loders Croklaan Company and they were obtained from Arma Industry of Fats and Oils Co., 10th of Ramadan City, Egypt.

Prepration of Cocoa Butter Substitutes Blends

Both of lauric cocoa butter substitutes were melt at 50°C in water bath until completely melted and prepared blends from CLSP555/E and Kerme at ratio of 3:1 and 1:1 (w/w) at Department of Food Science, Faculty of Agriculture, Zagazig University, Egypt.

Methods of Analysis

Physical properties

Refractive index, melting point and solid fat content were determined according to A.O.A.C. (1990). Color was measured by Lovibond Tintometer (5.25 cell) at Arma Industry for Fats and Oils Co., 10th of Ramadan City, Egypt.

Chemical analysis

Free fatty acids (FFA) content as percentage of lauric acid, iodine value (IV), peroxide value (PV), saponification value and unsaponifiable matter were determined according to A.O.C.S (1998) at Arma Industry for Fats and Oils Co., 10th of Ramadan City, Egypt.

Gas Liquid Chromatography of Fatty Acids Composition

Fatty acids were transesterified into methyl esters (FAME) using N-trimethylsulfoniumhydroxide (Macherey - Nagel, Duren, Germany) according to procedure reported by Arens *et al.* (1994). FAME were identified on a Shimadzu GC-14A equipped with flame ionization detector (FID) and C-R4AX chromatopac integrator (Kyoto, Japan). The flow rate of the carrier gas helium was 0.6 mL/min and the split value with a ratio of 1: 40. A sample of 1 uL was injected into a 30 m x 0.25mm x 0.2 um film thickness Supelco SP™-2380 (Bellefonte, PA, USA) capillary column. The injector and FID temperature was set at 250°C. The initial column temperature was 100°C programmed by 5°C/min until 175 °C and kept 10 min at 175 °C, then 8°C/min until 220 °C and kept 10 min at 220 °C. A comparison between the retention times of the samples with those of authentic standard mixture (Sigma, St. Louis, MO, USA; 99% purity) specific for (GLC), run on the same column

under the same conditions, was made to facilitate identification.

Gas Liquid Chromatography of Unsaponifiable Matter

The unsaponifiable matters were injected into a Perkin-Elmer Sigma 3B gas chromatograph with a stainless steel column (1.5 m x 4 mm) and equipped with dual flam ionization detectors under the following conditions:

- Stationary phase: Supelco's sp - phase (3% Me-Silicon fluid) coated on 80/100 (mesh Supelcoport).
- Column temperature: programmed from 70 to 270 °C, elevation rate 10 °C/min.
- Injection port temperature: 25 °C.
- Detector temperature : 300 °C.
- Flow rate : nitrogen – 30 ml/min; hydrogen 33 ml/min; air 330 ml/min carrier gas.
- Chart speed : 0.4 cm/min.

Identification was attained with the aid of standard compounds. Each component on the chromatogram was calculated as a percentage out of the total areas under peaks according to A.O.C.S (1998) at Principal Central Laboratory, Faculty of Agriculture, Cairo University, Giza, Egypt.

RESULTS AND DISCUSSION

The Physical and chemical characteristics of cocoa butter substitutes and their blends are presented in Table 1. Slight differences could be noticed in the refractive index of CLSP 555/E, Kerme and blends from CLSP 555/E and Kerme at ratio 3:1 and 1:1 being 1.44205, 1.44324, 1.44238 and 1.44264, respectively. The aforementioned values are in agreement with those reported by Abd-El- Hady (1987). The melting point of CLSP 555/E, Kerme and blends from CLSP 555/E and Kerme at ratio 3:1 and 1:1 were 37.0-38.0, 34.0- 35.1, 35.0- 36.5 and 34.8- 35.0, respectively. Generally, the CLSP555/E has a higher melting point than Kerme. This could be attributed to the higher content of saturated fatty acids in CLSP555/E than Kerme as shown in Table 4. The obtained results are in agreement with those reported by Vissotto *et al.*, (1999). The color of Kerme appeared a high value by Lovibond units (red/yellow, 1.5/15) than the color value of CLSP555/E (1.0/10). Those both cocoa butter substitutes and their blends were very lower than the color value of palm kernel oil (Tan *et al.*, 2004). These results may be due to the refining process

Table 1. Some physical and chemical properties of cocoa butter substitutes and their blends

Property	CLSP555/E	Kerme	Blend from CLSP555/E and Kerme	
			(3:1)	(1:1)
Refractive index at 60 °C	1.44205	1.44324	1.44238	1.44264
Melting point (°C)	37 – 38	34 - 35.1	35.0 – 36.5	34.8 - 35.0
Colour (R/Y, 1.5/ 15)	1/10	1.5/15	1/10	1.5/15
Free fatty acid (%)	0.036	0.054	0.042	0.050
Iodine value	1.05	9.75	2.13	4.47
Peroxide value	0.106	0.183	0.120	0.143
Saponification value	248	250	249.8	250
Unsaponifiable matter (%)	0.57	1.24	0.72	0.83

during production of cocoa butter substitutes.

Results concerning the chemical characteristics of CLSP 555/E, kerme and blends from CLSP 555/E and Kerme at ratio of 3:1 and 1:1 are shown in Table 1. The results showed that the free fatty acids (FFA) was higher in Kerme (0.054) than CLSP555/E (0.036) and being 0.042 and 0.05 for blends from CLSP 555/E and Kerme at ratio of 3:1 and 1:1, respectively. However, the FFA among the cocoa butter substitutes and blends were lower than those in palm olein (0.069%) as reported by Sulieman *et al.*, (2006). Iodine value in oils reflects the degree of unsaturation. The iodine value of CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 were 1.05, 9.75, 2.13 and 4.47, respectively. The iodine value of CLSP 555/E was extremely low, this could be attributed to the very low concentration of unsaturated fatty acids (Table 4). The peroxide value is not constant of any oil but reflected its tendency towards oxidation. The peroxide value of CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 were 0.106, 0.183, 0.120 and 0.143, respectively. In generally the peroxide value of both cocoa butter substitutes and their blends was lower than 2 meq/kg. Che Man and Wan Hussin (1998) mentioned that good quality vegetable oils should have a peroxide value lower than 2

meq/kg. Saponification value which is reflected for the average molecular weight of fatty acids. A comparison of the data Table 1 showed that the saponification value of both cocoa butter substitutes and their blends was ranged from 248 to 250 which indicate a higher content of short chain fatty acids (Table 4). Results obtained are in accordance with those reported by Abd-El-Hady (1987) and Talbot and Smith (2005). The unsaponifiable matter of CLSP 555/E, and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 were relatively low, being 0.57%, 0.72% and 0.83%, respectively, while it was 1.24% for kerme. These results are in harmony with those reported by Abd-El- Hady (1987), who mentioned that such matters related to the oil stability.

Solid fat contents (SFC) of CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 are presented in Table 2. The results showed that solid fat contents at 20°C were lowered. However, CLSP 555/E and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 had solid fat contents of more than 70%. According to Traitler and Dieffenbacher (1985), this is an important criterion for cocoa butter equivalent. At 30°C the solid fat contents showed that CLSP 555/E (42.29%) was still markedly higher than kerme and their blends. At 35°C the solid fat contents were lowered to 2.53, 5.63, 3.02 and 4.51% for CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio of 3:1 and 1:1, respectively. This indicated that the kerme had the highest solid fat contents at 35°C. This result mainly attributed to the high content of stearic acid in kerme than CLSP 555/E (Table 4). However, all samples melted completely at 40°C and are therefore not expected impart any waxy taste to product. The solid fat content profile of cocoa butter at 20, 30, 35 and 40°C was 79.2, 52.7, 3.0 and 0.0, respectively (Samsudin and Rahim, 1996).

Unsaponifiable Matter Composition

Unsaponifiable matter composition of CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 is presented in Table 3. The results showed that twenty four compounds were detected in the unsaponifiable matters of CLSP555/E; nine of them which

Table 2. Solid fat content (%) of cocoa butter substitutes and their blends

Temperature (°C)	CLSP555/E	Kerme	Blend from CLSP555/E and Kerme	
			(3:1)	(1:1)
20 °C	94.93	66.09	92.51	85.46
30 °C	42.29	13.81	29.03	18.58
35 °C	2.53	5.63	3.02	4.51
40 °C	0.00	0.00	0.00	0.00

Table 3. Unsaponifiables matter (%) composition of cocoa butter substitutes and their belends

No. of peak	Component	Retention time	Clsp555/E	Kerme	Blends from clsp555/Eand kerme	
					3:1	1:1
1	Unknown	3.433	-	0.447	-	-
2	Unknown	4.683	-	0.014	-	-
3	Unknown	5.133	-	0.114	-	-
4	Unknown	5.550	-	0.048	-	-
5	Unknown	6.600	-	0.281	-	-
6	Unknown	7.550	-	0.021	-	-
7	Unknown	8.117	-	0.356	-	-
8	Tetradecane	9.833	-	0.311	-	0.047
9	Unknown	10.450	-	-	-	-
10	Unknown	11.200	-	0.432	1.042	0.222
11	Unknown	11.783	0.048	0.040	0.231	0.205
12	Unknown	12.467	-	0.160	0.073	0.226
13	Unknown	12.917	-	-	0.191	-
14	Unknown	13.30	0.528	0.057	15.797	6.875
15	Unknown	14.53	0.360	0.0578	-	-
16	Octadecane (18:0)	15.65	2.510	0.234	0.821	0.884
17	Unknown	16.740	1.392	0.323	-	-
18	Unknown	17.383	0.621	1.167	-	-
19	Eicosane (20.0)	17.933	3.883	1.097	4.237	5.535
20	Unknown	18.160	-	-	-	15.676
21	Unknown	18.95	0.733	1.890	14.892	9.456
22	Unknown	19.27	1.022	-	0.177	-
23	Docosane (22:0)	19.917	2.754	5.175	8.436	3.167
24	Unknown	20.417	4.395	11.814	-	-
25	Unknown	21.217	2.419	5.293	21.20	14.121
26	Tetracosane (24: 0)	22.167	3.338	2.479	2.152	2.998
27	pentacosane (25:0)	22.817	-	13.408	16.957	0.768
28	Hexacosane (C26:0)	23.850	-	12.017	3.598	3.854
29	Unknown	24.383	15.959	.822	8.431	11.321
30	Unknown	25.583	8.007	4.621	5.95	7.101
31	Octacosane (C28:0)	26.650	2.719	17.418	24.462	13.493
32	Unknown	27.233	15.127	4.826	0.956	0.339
33	Nonacosane (C29:0)	29.300	-	3.847	0.895	1.199
34	Triacontane (C30:0)	31.100	2.252	0.757	0.504	0.404
35	Unknown	32.650	3.024	-	0.138	0.179
36	Dotriacontane (C32:0)	33.717	-	-	-	-
37	Unknown	34.683	0.366	1.333	0.952	0.038
38	Unknown	36.633	0.305	1.455	1.228	1.617
39	Cholesterol	39.250	2.981	0.516	0.984	1.548
40	stigma-sterol	41.950	14.33	0.816	10.081	13.101
41	B-sitosterol	47.083	2.014	-	2.800	2.014

constituted 36.781% were identified. While 34 compounds were detected in unsaponifiable matter of kerme, twelve of them which constituted 58.075% were identified. The unsaponifiable matters of blend from CLSP 555/E and kerme at ratio 3:1 contained twenty six compounds; twelve of them which constituted 75.927% were identified. Therefore, the blend from CLSP 555/E and kerme at ratio 1:1 contained twenty six compounds, thirteen of them which constituted 49.012% were identified. Also, the results showed that CLSP555/E contained higher value of stigma-sterol than that of kerme; whereas kerme contained higher value of octacosane (C28:0) than that of CLSP 555/E. These results are in agreement with those reported by Abd- El-Hady (1987).

Fatty Acids Composition

The fatty acids composition of CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 is presented in Table 4. The results showed that the major fatty acids in CLSP555/E and kerme were C12:0, C14:0, C16:0 and C18:0, recorded 53.70, 21.10, 9.13 and 10.41%, respectively for CLSP555/E and 43.75, 12.94, 8.29 and 16.18%, respectively for kerme. Besides these fatty acids, both cocoa butter substitutes contained also caprilic, capric, oleic and linoleic with minor amounts. From tabulated data it could be noticed that the portion of saturated fatty acids in CLSP555/E (99.12%) was markedly higher than kerme (89.14%) especially in C12:0 and C14:0, whereas the stearic acid (C18:0) was higher in kerme (16.18%) than CLSP555/E (10.41%). The obtained results of fatty acids composition for CLSP555/E are in harmony with those stated by Talbot and Smith (2005), they reported that almost 60% of the lauric fats (fully hydrogenated palm kernel stearines) was lauric acid (C12:0) and no more than 16 - 17% was made up of longer chain palmitic, stearic and oleic acids. In contrast, about 95% of cocoa butter is composed of these three longer chain acids. Therefore, the ratio between saturated and unsaturated fatty acids were 354.00, 8.98, 19.10 and 42.40 for CLSP 555/E, kerme and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1, respectively. These results are in agreement with those reported by Abd Al-Hady (1987).

A comparison of the data showed the FFA, peroxide value and unsaponifiable matter were lower in CLSP555/E than kerme.

Therefore, the CLSP555/E contained more than 99.0% saturated fatty acids. These results indicated that the CLSP555/E cocoa butter substitute is more stable than kerme. In conclusion this study demonstrated that CLSP 555/E and blends from CLSP 555/E and kerme at ratio 3:1 and 1:1 (w/w) could be used as cocoa butter substitute in formulation of chocolate coating and kerme for filling.

Table 4. Fatty acids composition of cocoa butter substitutes and their blends

Fatty acid	CLSP555/E	Kerme	Blends from CLSP555/E and Kerme	
			3:1	1:1
Caprilic ($C_{8:0}$)	2.04	4.42	3.18	3.86
Capric ($C_{10:0}$)	2.74	3.56	3.11	3.36
Lauric ($C_{12:0}$)	53.70	43.75	48.73	46.74
Myristic ($C_{14:0}$)	21.10	12.94	17.06	15.14
Palmitic ($C_{16:0}$)	9.13	8.29	8.76	8.58
Stearic ($C_{18:0}$)	10.41	16.18	13.33	14.85
Oleic ($C_{18:1}$) cis	0.13	3.15	1.64	0.00
Linoleic ($C_{18:1}$)trans	0.09	6.71	3.20	0.00
Linolenic ($C_{18:2}$)cis	0.06	0.06	0.09	0.00
Others	0.53	0.87	0.84	0.27
Total saturated*	99.12	89.14	94.17	97.53
Total unsaturated**	0.28	9.92	4.93	2.30
S / U */**	354.00	8.98	19.10	42.40

- ratio of SFA* to USFA**

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الخواص الطبيعية والكيميائيـــة لبعض بـــدائـــل زبـــدة الكـــاكـــاو

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تتميز بدائل زبدة الكاكاو التى تكون من النوع لوريك والتى تشتق طبيعيا من زيت نوى النخيل بثباتها الجيد وكذلك قوامها. و تقارن هذه الدراسة بين نوعين من البدائل هما Croklaan Special 555/E (CLSP 555/E), والبديل kerme ومخلوطين منهما بنسبة(٣: ١)،(١:١) وزن/ وزن على التوالى. تم تقدير بعض الخواص الطبيعية والكيميائية لهذين البديلين ومخلوطيهما. حيث اظهرت النتائج المتحصل عليها اختلافا طفيفا فى معامل الانكسار للبديلين ومخلوطيهما. وان نقطة الانصهار للبديل Croklaan Special 555/E (CLSP 555/E), تتراوح ما بين ٣٧,٠ – ٣٨,٠م° والبديل Kerme ٣٤ – ٣٥,١م° والمخلوط (١:٣) ٣٥,٠ – ٣٦,٥م° فى حين كانت للمخلوط (١:١) ٣٤,٨ – ٣٥,٠م° وقد سجلت الاحماض الدهنية الحرة لكل من البديل Croklaan Special 555/E (CLSP 555/E), والبديل Kerme والمخلوط (١:٣) والمخلوط (١:١) القيم التالية ٠,٠٣٦%، ٠,٠٥٤%، ٠,٠٤٢% و٠,٠٥% على التوالى. كانت قيم الرقم اليودى للبديل Croklaan Special 555/E (CLSP 555/E), والبديل Kerme والمخلوط (١:٣) والمخلوط (١:١) هي ١,٠٥ ، ٩,٧٥، ٢,١٣ و ٤,٤٧ على التوالى. وأن قيم البيروكسيد كانت على النحو التالى ٠,١٠٦ ، ٠,١٨٣ ، ٠,١٢٠ و ٠,١٤٣ لكل من Croklaan Special 555/E (CLSP 555/E), و Kerme والمخلوط (٣: ١) والمخلوط (١:١) على الترتيب. وكان رقم التصبن لكل من البديلين والمخلوطين يتراوح ما بين ٢٤٨ – ٢٥٠. وقد لوحظ أن المواد غير المتصبنة لكل من Croklaan Special 555/E (CLSP 555/E),و Kerme والمخلوط (٣: ١) والمخلوط (١:١) كانت ٠,٥٧%، ١,٢٤%، ٠,٧٢% و ٠,٨٣%، على التوالى. كذلك كان البديل Croklaan Special 555/E (CLSP 555/E), والمخلوط (١:٣) هما الأعلى فى محتوى الدهون الصلبة مقارنة بالبديل Kerme والمخلوط (١: ١) على درجات حرارة ٢٠ و ٣٠°م.