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PRODUCING COCOA BUTTER SUBSTITUTES BY BLENDING PROCESS OF SOME VEGETABLE OILS

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ABSTRACT

The objective of this study was to produce cocoa butter substitutes (CBSs) from some vegetable oils by blending process avoiding hydrogenation and esterification processes. The vegetable oils used in this study were palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut oil as well and were mixed in different proportions according to the presence of lauric acid ($C_{12:0}$) and the melting point to produce cocoa butter substitutes (CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7). The physico-chemical properties (specific gravity, refractive index, color index, acid value, peroxide value, iodine number, saponification number, and induction period by Rancimat method) have been determined for vegetable oils and the produced CBSs. Also, fatty acid composition was identified by Gas liquid chromatography and solid fat content of the produced CBSs were measured by Nuclear Magnetic Resonance (NMR). The results indicate that all the values of melting and slip point were about the human body temperature (37°C), specially the CBS7 and CBS5 whose melting point were (33°C and 35°C); respectively. Also CBS1 and CBS6 which had the highest values of oxidative stability. Finally, the results of all the samples indicated their conformity with the Egyptian standard specifications.

Key words: Blending, Cocoa butter, Cocoa butter substitutes, Melting point, Palm oil, Solid fat content

INTRODUCTION

Fats and oils play a vital role in the formulation and preparation of a variety of foods. In some food industries the properties of these products are attributed to the presence of particular fats or oils, like icing, toppings, coatings, coffee whiteners, cheeses and imitation dairy products. All these food products as well as certain confectionary like chocolate require special types of oils and fats, which perform functions that normal fats are not capable of and do one or some functions in food industry that cannot any other fats do it like margarines and shortening, and that can be wide used in infant's food (milk) known as specialty fats (**Henry, 2008**).

The cocoa bean only contains small amounts of cocoa butter (CB), and thus the price of CB is one of the highest among all commercial fats and oils. As only a few countries cultivate cocoa, supply can be unstable therefore industries are looking for Cocoa butter alternatives to CB (**Zaidul *et al.*, 2007** and **Biswas *et al.*, 2016**).

Cocoa butter is a natural and highly valued fat that contributes to the desirable textural and sensory properties of chocolate and confectionery products. Thanks to its unique triglyceride composition cocoa butter is responsible for the most important qualities of produced chocolate, namely gloss, brittleness, hardness, and rapid and complete melting in the mouth (**Joanna *et al.*, 2015**).

Cocoa butter contains three main fatty acids: palmitic, stearic and oleic acid the saturated fatty acids, palmitic and stearic, are predominantly found in the sn-1 and sn-3 positions of the glycerol backbone, with the unsaturated oleic acid occupying the sn-2 central position. This distribution results in a triacylglycerol (TAG) composition rich in di-saturated species, with 1,3-dipalmitoyl-2-oleoyl glycerol (POP), (1-palmitoyl-3-stearoyl-2-oleoylglycerol (POSt) and 1,3-distearoyl-2-oleoyl glycerol (StOSt) being the most abundant TAG species. This TAG composition is responsible for the characteristic melting profile of cocoa butter, highly solid at 20° C; sharp melting between 20 and 30° C, and complete melting by 30–35° C this melting profile is desirable for confectionery applications. In CB, the lauric acid (C₁₂) and myristic acid (C₁₄) fatty acid constituents are present as a trace or very low amounts whereas the palmitic acid (C₁₆), stearic acid (C_{18:0}) and oleic acid (C_{18:1}) constituents are high (**Biswas *et al.*, 2018**; **Yongjun *et al.*, 2018** and **Miguel *et al.*, 2012**).

Cocoa butter substitutes (CBSs): lauric plant fats containing (lauric acid), chemically totally different to cocoa butter, with some physical similarities suitable only to substitute cocoa butter to 100 %. **(Lipp and Anklaam, 1998).**

Currently, Egypt is importing (CBSs) of great amounts yearly. However, they are produced by hydrogenations in the most time, so the objective of the present study is to produce some types of cocoa butter substitutes by using blending of some vegetable oils.

MATERIALS AND METHODS

Materials:

Cocoa butter substitute: a cocoa butter substitute delivered from local market used in this study as a reference guide was obtained from El Shamadan Company for Food Industries Alexandria Egypt.

Source of palm oil, palm olein, palm stearin, palm kernel oil and coconut oil: Refined, bleached and deodorized (RBD) palm oil, palm olein, palm kernel oil coconut oil and palm stearin which used in the present study were obtained from the Extracted Oils and Derivatives Company (Arma Company), 10th of Ramadan City, Egypt. The samples were analyzed then kept at $-18 \pm 2^{\circ}\text{C}$ in deep freezer until used.

Olive oil: Oil was extracted from the olive samples as follows:(A): Crushing of olive fruits were performed using experimental crusher mill.(B): (Carver) press, the pressure used was 12.000 lb/in^2 , which was reached gradually. The resulting liquid phase was put in a separator funnel and allowed to settle for 50 mins. The upper oil layer was decanted then dried over anhydrous sodium sulphate then filtered through Whatman No. 1 filter paper and kept in brown glass bottle (120ml) at $-18 \pm 2^{\circ}\text{C}$ until analysis.

Reagents:

All chemical and reagents of the analytical methods used in present study were analytical grade purchased from El- Gamhouria Trading Chemicals and Drugs Company, Egypt. Pure standards of fatty acids methyl esters used in this study were obtained from Koch light Laboratories, Ltd, England.

Methods:

Preparation of blends:

Seven cocoa butter substitutes (CBSs) have been produced by blending process of palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut oil and were prepared according to the presence of lauric fatty acid C_{12:0} (Lipp and Anklam, 1998). The melting point and slip point behavior theoretically calculated then modifying the blend ratios. The blends components mixture designs as described in **Table (1)**. All tested samples were individually melted at $70 \pm 2^\circ\text{C}$ in water bath prior to blending process. A cooling unit (Refrigerated Temperature Bath Model TC-500 serial 194042101, USA) fixed on $5 \pm 1^\circ\text{C}$ was used as well as homogenizing stirrer (Fisher Scientific Mix Model 143, USA) was, fixed on 300 RPM. This process take within 1 min to 3 min to get the desire texture of cocoa butter substitutes the times was measured by calibrated stopwatch to produce 100g of blends samples (Smith, 2001). The liquefied tested samples were mixed in proportions ranging as follows:

Table (1): Blends percentage (%) of the investigated vegetable oils used in producing cocoa butter substitutes (CBSs)

CBSs	Blends percentage (%) of the investigated vegetable oils					
	Palm oil	Palm olein	Palm stearin	Palm kernel oil	Olive oil	Coconut oil
CBS1	33.33	0.00	33.33	33.33	0.00	0.00
CBS2	25.00	25.00	25.00	25.00	0.00	0.00
CBS3	22.00	22.00	34.00	0.00	0.00	22.00
CBS4	0.00	31.00	38.00	31.00	0.00	0.00
CBS5	0.00	33.33	33.33	0.00	0.00	33.33
CBS6	0.00	0.00	65.00	15.00	20.00	0.00
CBS7	0.00	0.00	22.00	0.00	10.00	68.00

Analytical methods:

The analytical methods used in the present investigation were carried out according to the methods described in (AOAC, 2012) as follows:

1-Physical properties:

The refractive index at (25, 40 and 60°C), specific gravity at (25, 40 and 60°C), the slip and melting point and color index were determined According to (AOAC, 2012).

2. Chemical properties:

The Acid value (mg KOH/g oil), Peroxide value (meq.O₂/kg), unsaponifiable matter (%), The Saponification value (mg KOH/ g oil), The Iodine (I₂/ 100g oil) value was determined using Hanus solution (AOAC, 2012).

The induction period measurements are carried out on the tested samples in order to provide a quick indication of the trends in resistance to the oxidative rancidity as well as of the shelf-life of samples. The induction periods, as the oxidative stability index, of the tested samples were measured by an automated Rancimat (MetrohmUd. CH-9100 Herisau, Switzerland, model 679), comprises of the control unit and the wet section containing 6 reaction vessels, according to the method described by (Berrin and Feral, 2008).

The Ultra-violet absorption of the tested oils was determined using the method described by IUPAC (1987). The conjugated diene and triene fatty acids were determined in absorbance at 232 and 268 nm; respectively.

3. Determination of fatty acids composition:

a- Preparation of fatty acids methyl esters: Fatty acid methyl esters were prepared from total lipid by using rapid method according to the method of ISO 12966-2 (2011).

b-Gas Liquid Chromatographic(GLC) of fatty acids methyl esters.

Fatty acid methyl esters were injected into (HP 6890 series GC) apparatus provided with a DB-23 column (60m × 0.32mm × 25 µm). Carrier gas was N₂ with flow rate 2.2 ml/min, splitting ratio of 1:50. The injector temperature was 250°C and that of Flame Ionization Detector (FID) was 300°C. The temperature setting was as follows: 150°C TO 210°C at 5°C /min, and then held at 210°C for 25 min. Peaks were identified by comparing the retention times obtained with stander methyl esters.

4. Solid fat content: The solid fat content (SFC) of the tested samples was determined by Nuclear Magnetic Resonance (NMR) using a Bruker Minispec Analyzer (Model NO.120, Rheinstetten, Germany) according to the (AOCS, 2012). The tested samples were measured at 10, 20, 25, 30, 35, 40, 45 and 50°C.

5. Statistical analysis: Statistical analysis of data was performed using one-way and two-way analysis of variance (ANOVA).

Significant differences between means were determined using Duncan's multiple rang testes (**SAS, 1985**).

RESULTS AND DISCUSSION

Cocoa butter is the high valued ingredient in chocolate and some confectionery and it plays a special role according to its physical and chemical properties which made it a unique ingredient. But because of the shortage of supply, the high demand and the raising prices every year it was necessary to get some specialty fats used as cocoa butter substitutes to face these challenges. The produced cocoa butter substitutes studied to stop on its values.

1. Physico-chemical properties of the investigated vegetable oils used in producing cocoa butter substitutes (CBSs).

a-Physical properties:

Physical characteristics of the edible fats and oils such as refractive index, melting point, slip point and colour play an important role in assessing their quality and palatability, as well as the consumer acceptability of these products. The physical characteristics of fats or oils are dependent on the degree of unsaturation, carbon chain length, isomeric fatty acid forms, and molecular configuration (**Zaidul et al., 2007**).

The above properties were determined to ensure the compliance of the investigated vegetable oils used with their **Egyptian Standard Specifications (2005)**. The specific gravity of vegetable oils used palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut were 0.888, 0.8996, 0.8849, 0.8990, 0.9091 and 0.9081 respectively; all these results are compatible with those found by (**Kiritsakis et al., 1983; Lalas, 1998 and Onwuliri et al., 2011**). From the results obtained in **Table (2)**, it could be observed that refractive index was determined at 60°C ±1 for palm stearin, 40°C ±1 for palm oil, palm olein, palm kernel and coconut oil and 25°C±1 for olive oil. The refractive index values were ranged from 1.4473 to 1.4701 for all the investigated samples that showed clearly the difference degree of unsaturation. All these results agreed with (**Hui. 1996; Onwuliri et al., 2011 and Yap et al., 1989**). The melting and slip point of the investigated vegetable oils used in producing (CBSs) are shown in **Table (2)**, where palm stearin represented to have the highest values

of melting and slip point being (53.50 - 52.00° C) respectively; followed by palm oil (35.00 - 33.80 °C). On the other hand, coconut oil and palm kernel oil showed melting and slip point (27.00-25.20°C) and (23.00-21.30°C) respectively. Meanwhile the olive oil recorded the lowest melting and slip point which were (- 4.00°C and -2.20°C). The obtained data illustrate obviously that the vegetable oils used are significantly variable in their melting and slip point which make more choices in using in the current investigation (**Jin et al., 2008; Eskin et al., 1996 and Berger., 1996**). It could be clearly noticed that palm oil and olive oil nearly had the same values of yellow scale which recorded 35.00. On the other hand, palm olein and palm stearin had the same yellow scaled 30.00. Meanwhile, the coconut oil showed only 5.00 as yellow scale value. Also the red color was scaled for palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut oil and they were 2.00, 2.20, 2.40, 1.00, 2.1 and 0.8 respectively. May be the colour of olive oil was based upon pigments such as carotenoids and both carotenoids and chlorophyll (**Grati et al., 1999; Ayton et al., 2007 and Endo 2018**).

Table (2): Physical properties of the investigated vegetable oils used in producing cocoa butter substitutes (CBSs).

Physical properties	Investigated vegetable oils						
	Palm oil	Palm olein	Palm stearin	Palm kernel oil	Olive oil	Coconut oil	LSD $p \leq 0.05$
Specific gravity at 25-40-60 °C	0.8888	0.8996	0.8849	0.8990	0.9091	0.9081	0.01
Refractive index at 25-40-60 °C	1.4559	1.4580	1.4473	1.4517	1.4701	1.4490	0.002
Melting point °C	35.00	21.40	53.50	23.00	-4.0	27.00	0.40
Slip point °C	33.80	18.92	52.00	21.30	-2.2	25.20	0.30
Colour Index	yellow	35.00	30.00	30.00	35.00	35.00	0.50
	Red	2.00	2.20	2.40	1.00	2.10	0.1

LSD determination to least significant differences test at $p \leq 0.05$.

1.1. Chemical properties:

The chemical characteristics of edible lipids play an important role in the assessing of their quality assurance, palatability and consumer acceptability, in addition to their relation with the healthy safe quality criteria of these fats and oils by using them. Therefore, the chemical quality assurance criteria, including the acid value (mg KOH/ g oil), peroxide value (meq.O₂/kg), iodine value (I₂/100g.oil), unsaponifiable matter (%), oxidative stability (Induction period by

Rancimat), conjugated diene and triene, fatty acids and saponification value for the vegetable oils used in this investigation for producing cocoa butter substitutes.

According to data showed in **Table (3)**, the acid value of palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut oil amounted in 0.17, 0.27, 0.16, 0.20, 0.56 and 0.33(mg KOH/g oil); respectively. Lower acid value content of palm stearin and palm oil may be due mainly to high content of saturated fatty acids specially the content of palmitic acid ($C_{16:0}$) (**Onwuliri et al., 2011**). Whereas, peroxide values ranged from 1.01 to 3.78 (meq O_2 /kg oil) are found to be much greatly lower than that recommended values (within the permissible values) which should not exceed 15 meq O_2 / kg oil as reported by the **Egyptian Standard Specifications (2005)**.

The iodine value is considered to be one of the most important chemical properties for quality assurance of lipids and as a good successful measure for changes occurs in the unsaturation degree of their content of fatty acid profiles. The data showed in **Table (3)**, illustrate that the iodine value of the vegetable oils used which ranged from (6.97 to 85.09 I_2 /100g oil) are variable in their characteristics which make more choices in using in the current investigation. The present results are approximately similar with those obtained by (**Codex Stan 210. 1999; Hui, 1996 and Onwuliri et al., 2011**).

The induction period (IP), measuring the increase in the volatile components by- products released from the oxidizing fats and oils. According to data showed in **Table (3)**, the markedly highest oxidative stability was to palm stearin then much later comes palm oil in contrast with coconut oil which was the corresponding the lowest oxidative stability. The significant differences in the induction period were mainly due to the different level of total saturated fatty acid not only but also the long or short carbon chain fatty acid and rather than tocopherol content and other antioxidant compounds for olive oil (**Hui, 1996**). The specific extinction values; ultra- violet absorptions at 232 and 268 nm are taken as a good successful index for measuring the formation degree of conjugated fatty acids dienes and trienes, respectively (**Yap et al., 1989; Allen and Hamilton 1983; Hui 1996 and Endo 2018**). It could be observed that the formation extent of conjugated fatty acid dienes were 1.142, 1.022, 1.124, 1.154, 1.323 and 1.198; respectively for palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut oil. Meanwhile, the formation of

conjugated fatty acid trienes were 0.165, 0.132, 0.165, 0.170, 0.465 and 0.364; respectively (**Dimitra *et al.*, 2002**).

From the tabulated data in **Table (3)**, it could be observed that olive oil contains the highest amount of unsaponifiable matter (%). Meanwhile, the palm oil, palm olein and palm stearin contain the lower. The above mentioned data are in accordance with those reported by (**Codex Stan 33, 1981; Codex Stan 210, 1999 and Onwuliri *et al.*, 2011**).

Saponification values for all the tested vegetable oils are all in the accepted range with (**Codex Stan 33, 1981; Codex Stan 210, 1999 and Egyptian Standard Specifications 2005**).

Table (3): Chemical properties of the investigated vegetable oils used in producing cocoa butter substitutes (CBSs).

chemical properties	Investigated vegetable oils used						LSD value at $p \leq 0.05$
	Palm oil	Palm olein	Palm stearin	Palm kernel oil	Olive oil	Coconut oil	
Acid Value (mg KOH/g oil)	0.17±0.03	0.27±0.07	0.16±0.04	0.20±0.04	0.56±0.04	0.33±0.04	0.02
Peroxide value (meq O ₂ /kg oil)	1.80±0.04	1.01±0.04	1.78±0.04	1.90±0.04	3.78±0.04	2.08±0.04	0.14
Iodine value (I ₂ /100g oil)	53.75±0.45	59.21±0.40	35.40±0.45	16.90±0.30	85.09±0.70	6.97±0.20	1.99
Induction period (hr) / 110 °C	26.50±0.30 ^b	17.10±0.25 ^a	42.00±0.50 ^a	22.50±0.30 ^c	19.29±0.50 ^d	14.12±0.40 ^f	0.99
Conjugated fatty acids diene at 232 nm	1.142±0.04	1.022±0.03	1.124±0.04	1.154±0.04	1.323±0.04	1.198±0.03	0.07
Conjugated fatty acid triene at 268 nm	0.165±0.04	0.132±0.04	0.165±0.04	0.170±0.04	0.465±0.04	0.364±0.04	0.02
Unsaponifiable matter (%)	0.33±0.03	0.29±0.04	0.45±0.04	0.70±0.04	1.46±0.04	0.91±0.04	0.01
Saponification value (mg KOH/g oil)	198.11±0.44	194.34±0.45	194.56±0.74	234.23±0.74	188.24±0.98	254.21±1.75	1.80

Values are ± mean SD of three estimations and LSD determination to least significant differences test at $p \leq 0.05$.

2. Fatty acids composition (%) of the investigated vegetable oils used in producing cocoa butter substitutes (CBSs).

From the results presented in **Table (4)**, it could be concluded that major saturated fatty acid of palm kernel oil and coconut oil is lauric acid (C_{12:0}), which amounted in 41.24 and 45.27% respectively. Meanwhile, it was found in neglected amount in all the other used tested samples. Therefore palm kernel and coconut oil, (one or both) is important to be found in all the produced CBSs which are the (lauric plant fats containing) the main source of this fatty acid. It could be observed that palmitic acid (C_{16:0}) is found to be the major saturated fatty acid in palm oil, palm olein and palm stearin as well, where it was 42.08, 39.06 and 59.67%; respectively. Meanwhile, higher content of oleic fatty acid the major monounsaturated fatty acid was

represented about 69.64% in olive oil. In contrast the lowest content of oleic fatty acid was represented about 6.85% in coconut oil. On the other side it was represented 41.25, 43.44 and 27.26%; respectively for palm oil, palm olein and palm stearin (**Codex Stan 33-1981 and Codex Stan 210-1999**). The data showed in **Table (4)**, that all tested samples had no Trans fatty acids which are very harmful to human health (**FAO, 2010**).

Concerning the total saturated fatty acids (TSFAs) where shown in **Table (4)**, it could be remarked that the values of palm oil, palm olein, palm stearin, palm kernel oil, olive oil and coconut oil were 48.23, 45.23, 66.80, 73.79, 17.65 and 92.15%; respectively hence the unsaturated fatty acids were 51.68, 54.66, 33.19, 26.06, 82.10 and 7.85%; respectively.

In general, it could be concluded that coconut oil followed by palm kernel oil and palm stearin recorded the high content of TSFAs and low amount of TUSFAs when compared with olive oil. In contrast, olive oil had the highest content of TUSFAs and low content of TSFAs that also explain the melting and slip point for all tested samples, which indicate low melting and slip point of olive oil. Meanwhile, the highest value of melting and slip point of palm stearin may due to the highest amount of palmitic acid (59.67%). On the other hand, the coconut oil and palm kernel oil were lower in melting and slip point however they contain high amount of TSFAs that maybe due to the high amount of lauric acid the major fatty acid which is lower in its melting and slip point characteristics. The differences in melting point of tested samples were mainly due to the different type and concentrations of triacylglycerols (TAG) in these lipids, Which is constituted by a mixture of triacylglycerol molecules with large differences of acyl chain length and degree of unsaturation, leads to the formation of several types of crystals (**Jirasubkunakorn et al., 2007**).

Table (4): Fatty acid profile (%) of the investigated vegetable oils used in producing cocoa butter substitutes.

Fatty acid (%)	Investigated vegetable oils					
	Palm oil	Palm olein	Palm stearin	Palm kernel oil	Olive oil	Coconut oil
C _{4:0}	N.D	N.D	N.D	N.D	N.D	N.D
C _{6:0}	0.00	0.00	0.00	0.31	N.D	0.66
C _{8:0}	0.029	0.15	0.023	4.30	N.D	9.01
C _{10:0}	0.023	0.17	0.001	3.51	N.D	7.30
C _{12:0}	0.241	0.19	0.110	41.24	N.D	45.27
C _{14:0}	1.09	0.98	1.243	12.73	N.D	16.98
C _{16:0}	42.08	39.06	59.67	8.83	15.30	9.34
C _{16:1}	0.166	0.22	0.023	0.03	0.57	0.00
C _{17:0}	0.099	0.091	0.126	0.02	0.57	0.014
C _{18:0}	4.33	4.16	5.17	2.67	1.78	3.44
C _{18:1}	41.25	43.44	27.26	22.21	69.64	6.85
C _{18:1trans}	N.D	N.D	N.D	N.D	N.D	N.D
C _{18:2}	9.95	10.60	5.68	3.66	11.32	0.95
C _{18:2trans}	0.137	N.D	N.D	N.D	N.D	N.D
C _{18:3}	0.189	0.24	0.13	0.007	0.82	0.05
C _{20:0}	0.34	0.37	0.40	0.14	N.D	0.133
C _{20:1}	0.126	0.16	0.097	0.15	N.D	N.D
C _{22:0}	N.D	0.06	0.061	0.037	N.D	N.D
C _{24:0}	N.D	N.D	N.D	N.D	N.D	N.D
*T.S.F.A	48.23	45.23	66.80	73.79	17.65	92.15
**T.U.S.F.A	51.68	54.66	33.19	26.06	82.35	7.85

* T.S.F.A Total saturated fatty acids.

**T.U.S.F.A Total unsaturated fatty acids.

3. Producing cocoa butter substitutes (CBSs) by using blending process.

For blending, certain process conditions need to be taken into account that all components should be liquid, the agitation should be effective without introducing too much air into the oil and to blend the fats homogeneously, sufficient time is required. Palm mid-fraction (PMF), which contains high concentration of POP can sometimes be used to give a softer texture to the chocolate. (Norberg, 2006 and Timms 2003).

a. Physico-chemical properties of the produced cocoa butter substitutes (CBSs).

1. Physical properties of the produced cocoa butter substitutes (CBSs).

According to **Table (5)**, the specific gravity of seven produced (CBSs) where it was 0.889, 0.889, 0.889, 0.888, 0.890, 0.888 and 0.898; respectively for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7 c. In addition there was no significant differences were observed between all the produced cocoa butter substitutes and the CBS0

The refractive index at 60° C for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7 was 1.4515, 1.4529, 1.4503, 1.4510, 1.4512, 1.4514 and 1.4499; respectively compared with CBS0 1.4500 that showed clearly the narrow range degree of unsaturation. All these results agreed with **(El-Mallah and Megahed, 1998)**.

The melting and slip point of the produced cocoa butter substitutes are very important to be determined, as it will specify the aim they could be produced for using in the confectionary industry with no harms to human body. As are shown in **Table (5)**, all the produced cocoa butter substitutes recorded the melting and slip point around the human body temperature 37°C except CBS6 which were (37.10 and 36.60°C) respectively; compared with CBS0 (43.12 and 40.40°C). That may due to the high saturated fatty acids it contained next to its fatty acid composition. On the other side, it could be illustrated that CBS7 had the lowest values of melting and slip point where they were (33.00and 30.89°C) respectively; however it contained the highest amount of TSFAs. That may return to the major saturated fatty acid (lauric acid C_{12:0}), where was represented to be 31.11%. **(Biswas et al, 2017)**.

From the obtained data in **Table (5)**, it could be clearly noticed that CBS1, CBS4, CBS6 and CBS7 had the same value of yellow scale as they were 35.00. On the other hand CBS5 has the lowest value of yellow scaled in 28.00. Also the red color was scaled for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7 and it was 1.10, 1.80, 2.40, 0.80, 1.50, 0.90 and 1.10; respectively all these results were compared with CBS0 which scaled only 3.00 for yellow scale and 0.3 for red scale .

Table(5):Physical properties of the produced cocoa butter substitutes (CBSs).

Physical properties		Cocoa Butter Substitutes (CBSs)								
		CBS0*	CBS1	CBS2	CBS3	CBS4	CBS5	CBS6	CBS7	LSD value at $p \leq 0.05$
Specific gravity at 60 °C		0.8878±0.01	0.889±0.01	0.889±0.01	0.889±0.01	0.888±0.01	0.890±0.01	0.888±0.01	0.898±0.01	0.01
Refractive index at 60°C		1.4559±0.001	1.4515±0.001	1.4529±0.001	1.4503±0.001	1.4510±0.001	1.4512±0.001	1.4514±0.001	1.4499±0.001	0.003
Melting point °C		43.12±0.50 ^a	36.30 ±0.50 ^c	36.90 ±0.55 ^c	36.60 ±0.45 ^c	36.90 ±0.55 ^c	35.00±0.40 ^c	37.10±0.60 ^b	33.00 ±0.35 ^e	0.50
Slip point °C		40.40±0.32 ^a	34.50±0.45 ^d	36.00 ±0.40 ^b	34.50 ±0.35 ^d	35.50 ±0.35 ^c	33.80±0.35 ^a	36.60±0.45 ^b	30.89 ±0.35 ^f	0.35
Colour	3.00	3.00	35.00	34.00	32.00	35.00	28.00	35.00	35.00	0.45
	0.30	0.30	1.10	1.80	2.40	0.80	1.50	0.90	1.10	0.20

Values are $\pm$ mean SD of three estimations and LSD determination to least significant differences test at $p \leq 0.05$.

CBS0* is a cocoa butter substitute delivered from the local market.

2. Chemical properties of the produced cocoa butter substitutes (CBSs).

Results in **Table (6)**, indicated that the acid value (mg KOH/g. oil) for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7 was 0.20, 0.21, 0.22, 0.20, 0.26, 0.25 and 0.30; respectively compared with CBS0 which was 0.32 mg KOH/g oil.

The present results are found to be much greatly lower within than that recommended (within the permissible values) for human consumption as reported by **the Egyptian Standard specifications (2005)** for edible fats and oils.

All the present results for peroxide value of tested samples are in accordance with those found by **(Hui, 1996)**. Also, the peroxide value of tested fats are found to be much greatly lower than that recommended value which should not exceed 15 meq O₂/kg as reported by **the Egyptian Standard Specifications (2005)**.

The data showed in **Table (6)**, also exhibited that the iodine value for all produced samples CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7 were 41.87, 42.21, 41.99, 47.90, 30.99, 39.87 and 23.87(I₂ /100g) oil; respectively compared with CBS0 4.22 (I₂ /100g oil) which showed the highest values of saturated fatty acids.

Actually, higher induction period (hrs) for CBS1 and CBS6 where represented to be 34.09 and 32.99; respectively suggests their

stronger oxidative stability when compared with CBS0 which recorded 17.23. The differences in the oxidative stability were mainly due to the different level of total saturated fatty acids not only but also due to the long or short carbon chain fatty acid and rather than tocopherol content and other antioxidant compounds (**Imegon, 2003**).

It could be observed that the formation extent of conjugated fatty acid dienes were 1.140, 1.110, 1.113, 1.108, 1.114, 1.210 and 1.196; respectively for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7. Meanwhile, the formation of conjugated fatty acid trienes were 0.166, 0.158, 0.201, 0.155, 0.220, 0.220 and 0.315; respectively.

Table (6): Chemical properties of the produced cocoa butter substitutes (CBSs).

Chemical properties	Cocoa Butter Substitutes								LSD value at $p \leq 0.05$
	CBS0*	CBS1	CBS2	CBS3	CBS4	CBS5	CBS6	CBS7	
Acid Value (mg KOH/g oil)	0.32 $\pm$ 0.02	0.03 $\pm$ 0.20	0.03 $\pm$ 0.210	0.03 $\pm$ 0.22	0.03 $\pm$ 0.20	0.04 $\pm$ 0.26	0.03 $\pm$ 0.25	0.05 $\pm$ 0.30	0.06
Peroxide value (meq.O ₂ / kg oil)	1.09 $\pm$ 0.05	1.82 $\pm$ 0.05	1.60 $\pm$ 0.04	1.68 $\pm$ 0.03	1.59 $\pm$ 0.03	1.69 $\pm$ 0.04	2.12 $\pm$ 0.05	2.10 $\pm$ 0.04	0.11
Iodine value. (I ₂ /100g oil)	4.22 $\pm$ 0.09	41.87 $\pm$ 0.38	42.21 $\pm$ 0.40	41.99 $\pm$ 0.38	47.90 $\pm$ 0.45	30.99 $\pm$ 0.42	39.87 $\pm$ 0.40	23.87 $\pm$ 0.35	2.2
Induction period (hr)/110°C	17.23 $\pm$ 0.01 ^f	29.09 $\pm$ 0.30 ^a	26.78 $\pm$ 0.40 ^b	25.90 $\pm$ 0.35 ^c	27.09 $\pm$ 0.45 ^b	23.90 $\pm$ 0.35 ^d	30.09 $\pm$ 0.40 ^a	20.09 $\pm$ 0.35 ^e	0.90
Conjugated fatty acids diene at 232 nm	1.001 $\pm$ 0.03	1.140 $\pm$ 0.03	1.110 $\pm$ 0.03	1.113 $\pm$ 0.03	1.108 $\pm$ 0.03	1.114 $\pm$ 0.03	1.210 $\pm$ 0.03	1.196 $\pm$ 0.04	0.03
Conjugated fatty acid triene at 268 nm	0.138 $\pm$ 0.04	0.166 $\pm$ 0.03	0.158 $\pm$ 0.03	0.201 $\pm$ 0.03	0.155 $\pm$ 0.03	0.220 $\pm$ 0.04	0.220 $\pm$ 0.03	0.315 $\pm$ 0.04	0.001
Unsatifiable matter (%)	0.13 $\pm$ 0.03	0.46 $\pm$ 0.03	0.44 $\pm$ 0.04	0.48 $\pm$ 0.03	0.47 $\pm$ 0.03	0.54 $\pm$ 0.04	0.68 $\pm$ 0.03	0.86 $\pm$ 0.03	0.02
Saponification value (mg KOH/g.oil)	203.23 $\pm$ 0.99	207.44 $\pm$ 0.60	203.11 $\pm$ 0.35	209.23 $\pm$ 0.45	204.77 $\pm$ 0.52	211.23 $\pm$ 0.55	200.94 $\pm$ 0.64	236.44 $\pm$ 0.88	3.2

Values are $\pm$ mean SD of three estimations and LSD determination to least significant differences test at $p \leq 0.05$.

CBS0* is a local cocoa butter substitute delivered from local market.

b. Fatty acids composition (%) of the produced cocoa butter substitutes (CBSs).

From the data showed in **Table (7)**, it could be concluded that all the produced (CBSs) had a respective amount of lauric acid (C_{12:0}) and the major was belonged to CBS7 which was 31.11% compared with CBS0 which recorded 43.58%. In contrast the minor was belonged to

CBS6 and it was 7.68 %. Also, it could be observed that CBS6 recorded the highest major saturated fatty acid palmitic acid (C16:0), which is represented 45.67 %. In contrast CBS7 recorded the lowest amount 15.73%. All the other tested produced (CBSs) contained it in respective amount. Besides, Stearic acid (C_{18:0}) was found in small amount for all the tested samples compared with CBS0 which recorded the highest respective amount in 25.06%. All the tested CBSs contained the monounsaturated fatty acid (oleic acid C_{18:1}) in respective amount about 31.00, 30.67, 33.20, 32.00, 24.76, 30.10 and 18.97 for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7; respectively. Also data showed that all the tested samples had no Trans fatty acids which achieved the current investigation aim, when compared with CBS0 that recorded 1.39% to (C_{18:1} trans)

Concerning the total saturated fatty acids as shown in **Table (7)**, it could be remarked 62.15, 62.27, 60.74, 61.96, 70.67, 63.14 and 81.17%; respectively for CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7, However the total unsaturated fatty was 37.85, 37.73, 39.26, 44.65, 29.33, 36.86 and 22.83%; respectively compared with CBS0 which recorded the highest saturated fatty acid 98.33%.

According to the fatty acid profile it could be noticed that CBS7 remarked the highest total saturated fatty acids but the lowest melting point 33.30°C which may be due to that the major saturated fatty acid in its TAG structure of fat was lauric acid.

Table (7): Fatty acid (%) profile of the produced cocoa butter Substitutes (CBSs).

Fatty Acid (%)	Cocoa butter Substitutes (CBSs)							
	CBS0*	CBS1	CBS2	CBS3	CBS4	CBS5	CBS6	CBS7
C _{4:0}	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
C _{6:0}	0.34	0.12	N.D	0.19	0.14	0.28	N.D	0.27
C _{8:0}	4.65	1.52	1.72	2.18	1.50	3.24	1.04	5.1
C _{10:0}	3.73	1.18	1.35	1.57	1.18	2.46	0.74	4.17
C _{12:0}	43.58	13.40	13.86	13.94	14.40	18.70	7.68	31.11
C _{14:0}	11.44	4.81	4.40	5.48	4.99	7.45	3.12	11.57
C _{16:0}	8.36	35.93	36.58	35.55	34.93	33.82	45.67	15.73
C _{16:1}	0.00	0.166	0.12	0.12	0.166	0.29	0.11	0.37
C _{17:0}	0.02	0.07	0.08	0.081	0.07	0.07	0.10	0.4
C _{18:0}	25.06	4.01	3.77	2.00	4.03	4.20	4.39	8.87
C _{18:1}	0.67	31.00	30.67	33.20	32.00	24.76	30.10	18.97
C _{18:1trans}	1.39	N.D	N.D	N.D	N.D	N.D	N.D	N.D
C _{18:2}	0.017	6.63	6.71	5.84	5.63	3.96	6.39	3.24
C _{18:2trans}	0.10	0.09	N.D	N.D	N.D	N.D	N.D	N.D
C _{18:3}	0.00	0.096	0.11	0.11	0.096	0.20	0.15	0.18
C _{20:0}	0.25	0.67	0.29	0.30	0.67	0.30	0.33	0.22
C _{20:1}	N.D	0.13	0.12	0.11	0.13	0.12	0.11	0.07
C _{22:0}	N.D	0.05	0.05	N.D	0.05	0.06	0.05	0.04
C _{24:0}	N.D	N.D	N.D	N.D	N.D	0.05	0.01	N.D
**T.S.F.A	98.33	62.15	62.27	60.74	61.96	70.67	63.14	81.17
***T.U.S.F.A	1.67	37.85	37.73	39.26	38.02	29.33	36.86	22.83

CBS0* is a cocoa butter substitute delivered from the local market.

** T.S.F.A Total saturated fatty acids.

***T.U.S.F.A Total unsaturated fatty acids

c. Solid fat content (SFC) of the produced cocoa butter substitutes (CBSs).

Solid fat content, the quantity of fat crystals in a fat or fat blend has a great influence on the suitability of the fat or fat blend for a particular application. The solid fat content is responsible for many product characteristics in margarines, shortenings and fat spreads, including their general appearance; ease of packing, spread ability, and for sure for cocoa butter alternatives in confectionary industry, oil oxidation and organoleptic properties (**Jahurul *et al.*, 2014**). SFC (%) versus temperature (10–50 °C) for the produces CBSs are given in **Table (8)**, SFC versus temperature plot generally gives not only the

information on how hard or soft a fat is at different temperatures but also the melting behavior of the fat.

Regarding to the solid fat content at 10°C of the produced cocoa butter substitutes CBS1, CBS2, CBS3, CBS4, CBS5, CBS6 and CBS7. **Table (8)**, showed that solid fat content of CBS3, CBS4 and CBS7 was found to be higher than found in other produced samples that illustrated the high ability of the substitutes to be solid on low temperature. However CBS5 and CBS7 had no solid fat content at 40°C compared with CBS0 which indicated high value of solid fats at 40°C represented in 10.01%. The CBS4 and CBS6 remarked to still have a little solid fat content at 40°C which may cause a little waxy mouth feel in confectionery and chocolate according to (Sonwai *et al* 2014 and Fiebig and Lüttke 2003).

Table (8): Solid fat content (%) of the produced cocoa butter substitutes (CBSs).

CBSs	Solid fat content (%) at °C							
	10°C	20°C	25°C	30°C	35°C	40°C	45°C	50°C
CBS0*	65.23	47.19	35.99	25.11	19.33	10.01	3.20	0.12
CBS1	45.58	24.80	17.14	12.69	6.58	0.22	0.00	0.00
CBS2	49.38	23.88	16.13	11.02	6.88	0.29	0.00	0.00
CBS3	60.58	32.10	22.89	16.86	8.51	0.29	0.00	0.00
CBS4	68.21	41.11	29.19	19.20	11.11	0.50	0.00	0.00
CBS5	43.70	32.70	20.70	10.10	3.00	0.00	0.00	0.00
CBS6	54.09	47.80	36.60	27.20	10.80	0.72	0.00	0.00
CBS7	63.07	27.54	11.07	6.95	4.11	0.00	0.00	0.00

CBS0* is a cocoa butter substitute delivered from the local market

CONCLUSION

In general, it could be recommended from the results obtained, using blending process of vegetable oils with ones rich in lauric acid in producing CBSs. Specially, CBS7 (coconut oil 68%, palm stearin 22% and olive oil 10%) and CBS5 (palm olein 33.33%, palm stearin 33.33% and coconut oil 33.33%) which were judged to be the most suitable oil blends for using in the manufacturing.

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انتاج بدائل زبدة الكاكاو باستخدام عملية الخلط لبعض الزيوت النباتية

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كان الهدف من هذه الدراسة هو إنتاج بدائل زبدة الكاكاو (CBSs) المحتوية على حمض اللوريك باستخدام عملية الخلط لبعض الزيوت النباتية دون استخدام أى من عمليات الهدرجة أو الإسترة. وكانت الزيوت النباتية المستخدمة في هذه الدراسة هي زيت النخيل، زيت أولين النخيل، زيت استيارين النخيل، زيت نواة النخيل، زيت الزيتون وأخيرا زيت جوز الهند. وقد تمت عملية الخلط للزيوت النباتية بنسب مختلفة وفقا لوجود حمض اللوريك (0:12C) مع الاخذ في الاعتبار قيم نقطة الانصهار وذلك لإنتاج سبع بدائل لزبدة الكاكاو هي (CBS1 و CBS2 و CBS3 و CBS4 و CBS5 و CBS6 و CBS7). وقد تم دراسة الخواص الفيزيائية والكيميائية لكلا من الزيوت النباتية وبدائل زبدة الكاكاو المنتجة (الكثافة النوعية، معامل الانكسار، اللون، رقم الحامض، قيمة البيروكسيد، الرقم اليودي، رقم التصبين، وقياس ثبات الزيت بطريقة الرانسيمات).

كما تم التعرف على تركيب الأحماض الدهنية بواسطة جهاز التحليل الكروماتوجرافى. بالإضافة الى محتوى الدهون الصلبة لبدائل زبدة الكاكاو المنتجة والتي تم تقديرها بواسطة جهاز الرنين المغناطيسي النووي (NMR). وقد أشارت النتائج إلى أن جميع قيم نقطة الانصهار والانزلاق لبدائل زبدة الكاكاو المنتجة كانت جميعها حول درجة حرارة جسم

الإنسان 37°م ، ولا سيما 5CBS و 7CBS التي كانت نقطة الانصهار لهما (35 و 33°م)؛ على التوالي. كما أظهرت النتائج طول فترة الثبات الاكسیدی للبدائل 1CBS و 6CBS عن باقي البدائل المنتجة. وفي النهاية يمكن الاستنتاج أنه بعملية خلط الزيوت النباتية التي شملتها الدراسة لإنتاج بدائل زبدة الكاكاو المحتوية على الحامض الدهنى اللوريك اتضح ان هناك تباين عام فى قيم الصفات الطبيعية والكيميائية وأيضاً فى تركيب الاحماض الدهنية بالاضافة الى التباين فى قيم الثبات الاوكسیدی للبدائل المنتجة. الا ان مجمل نتائج العينات المنتجة تشير الى مطابقتها للمواصفات القياسية المصرية.
