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Composition of cocoa shell fat as related to cocoa butter

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Introduction

From a world production of over a million tons of cocoa beans, more than 100,000 tons are of cocoa shell produced annually (1). These amounts are removed from the beans in the chocolate factories. Usually cocoa beans are roasted at high temperature for a long period to remove the shell and germ, while the cotyledons are used for chocolate production. Cocoa shell is regarded by many investigators as the only important by-product of the cocoa. At present much of it is dumped. Particular interest has been given nowadays to the possible utilization of this by-product. Unfortunately, cocoa shell has the disadvantage of containing a considerable amount of theobromine, which limits its use for feeding purposes (1).

In the present work the composition of both the cocoa butter and shell fat obtained from the same sample of cocoa was of interest. The study involved the physical and chemical constants of shell fat and cocoa butter. To obtain more information on the relation between the shell fat and the cocoa butter, a study was carried out on their composition of the fatty acids and the unsaponifiable matter, using GLC. The stability of cocoa butter and shell fat was measured as they might be affected by heat treatment during roasting. The lipid classes and phospholipid content of cocoa shell fat and cocoa butter were extended in this investigation. Moreover, the chemical analysis of cocoa shell was studied.

Materials and methods

Materials

Samples of cocoa butter and cocoa shell from the same cocoa beans were obtained from the Egyptan Company for Foods (Bisco-Masr) Chocolate Factory, at Alexandria, Egypt. The shell fat was extracted by soaking cocoa shell in purified hexane (B.P. 65 °) for 48 hours, and this treatment was repeated three times for the same sample. The shell fat was obtained after evaporating the solvent by rotary evaporator under reduced pressure at 60 °) in the presence of nitrogen atmosphere.

Methods

Cocoa shell was subjected for the determination of moisture, fat, ash, and fiber (2). The determination of the protein was carried out by the micro-Kjeldahl method (3).

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The shell fat and cocoa butter were subjected for the determination of physical and chemical constants (2) with exception for specific gravity and acid value (4). The total phospholipids were determined and calculated as cephalin (5). The stability of shell fat and cocoa butter was measured by oxygen consumption during oxidation using Gallenkamp Warburg manometric apparatus (6). Lipid classes of the two samples were separated and identified by TLC method (7), while the fatty acids were determined quantitatively as methyl esters by GLC method (8). The unsaponifiable matter was identified, and the sterol content was determined quantitatively by GLC method (9).

Results and discussion

General analysis of cocoa shell

The preliminary analysis of cocoa shell showed that it contained moisture 4.79%, protein 14.13%, fat 5.54%, ash 5.49%, and fiber 19.42%. These results are in good agreement with many investigators (1, 10, 11, 12, 13). The higher value of fat in the present study than that of Knapp and Churchman (10) and Greenwood-Barton (1) is partly due to cocoa butter acquired from the cotyledons and adheres to the shell at the time of its separation during roasting the cocoa beans. A considerable amount of protein in the shell was found. Unfortunately it is known that 90 % of the alpha amino nitrogen in the extracted shell is strongly bound to oxidised polyphenols found in the shell, which are converted into polyphenoquinones. The latter compounds are combined with protein-NH_2 forming covalent bonds with the elimination of water. It follows, therefore, that only about 1 % of the protein in the cocoa shell exists in the free condition. The possibility of extracting a protein concentrate as a food suplement is, therefore, considered most unlikely (1). Cocoa shell is acceptable, however, to ruminants when small quantities of it are fed, but it is more dangerous to poultry for which deaths have been reported. The value of cocoa shell as a feed for cows varies considerably. One kilogram per cow per day increased percentage fat of the milk. Theobromine caused a definite increase in total protein and casein, a slight increase in ash, and decrease in lactose percentage (14) in cow milk.

Some physical and chemical constants of cocoa butter and shell fat

The physical and chemical constants of both cocoa butter and shell fat are given in table 1.

Table 1. Some physical and chemical constants of cocoa butter and shell fat.

Constant	Cocoa butter	Shell fat
Physical constants:		
Specific gravity at 40 °C	0.9012	0.9034
Melting point °C	34.10	31.00
Chemical constants:		
Acid value (as oleic %)	1.680	9.123
Saponification value	191.214	205.708
Iodine value	35.575	38.727

The specific gravity of cocoa butter and shell fat are 0.9012 and 0.9034 at 40 °C, respectively. The data of cocoa butter agreed with that found by Atawia (15) (0.9011 at 40 °C). The melting point of cocoa butter is 34.1 °C while it is 31.00 °C for shell fat. These results indicate that shell fat contains higher contents of short-chain and unsaturated fatty acids compared with cocoa butter. The melting point of cocoa butter agreed with that found by Pearson (13) and Atawia (15) (31–34 °C and 34.2 °C, respectively). The acid value of cocoa butter is 1.68. Similar observations were obtained by many investigators (13, 15, 16, 17) (1.1–2.8, 1.24, 1–4 and 1.3–1.88, respectively). The high acid value of shell fat (9.12), may be due to hydrolysis, occurred by heating the beans during roasting, and it must be neutralized before using for edible purposes.

The saponification value of shell fat is higher than that of cocoa butter (table 1). This indicates that shell contains higher contents of short-chain fatty acids compared with cocoa butter. The saponification value of cocoa butter is in good agreement with those reported by other investigators (13, 16, 17) (188–195, 192.5–196.7 and 190–200, respectively).

The iodine value of cocoa butter is lower than that of shell fat (table 1). This indicates that shell fat contains unsaturated fatty acids more than cocoa butter. The iodine value of cocoa butter agreed with the findings of Pietrzyk and Warzecha (16), Vasconcelos et al. (17) and Pearson (13) (32.15–37.61, 32–42 and 35–40, respectively).

Phospholipid content

Phospholipid contents were determined quantitatively, the results indicate that the amount of phospholipids (as cephalin) of cocoa butter was lower than that of shell fat (0.257 % and 1.35 %, respectively). Phospholipid content of cocoa butter is in good agreement with that of Parsons and Keeny (18), and Biino and Clabot (19) who reported that they are 0.05–0.57 %, and 0.29–0.55 %, respectively. Phospholipid amount and type affect lipid autoxidation. Farag (20) found that phosphatidyl ethanolamine enhanced the rate of linoleate oxidation, while phosphatidyl choline (lecithin) or phosphatidyl inositol had no effect.

Stability measurement

The rates of oxygen absorption at 100 °C by Warburg manometric method for cocoa butter and shell fat are given in table 2. The stability of

Table 2. Oxygen uptake for cocoa butter and shell fat.

Time in hours	ml oxygen absorbed per gram fat sample	
	Cocoa butter	Shell fat
4.00	0.5076	0.5231
6.00	1.3756	1.1209
8.00	2.0533	1.8193
10.00	2.9461	2.6139
10.30	3.1711	2.7800
10.45	5.5300	4.9078
12.00	5.8754	5.0437
stability in hours	10.5	10.5

Table 3. Lipid constituents of cocoa butter and shell fat and their R_f values.

Constituent	R_f value
Hydrocarbons	1.00
Squalene	0.95
Triglycerides	0.52
α-Tocopherol	0.29
Free fatty acids	0.235
Sterols	0.14
Diglycerides	0.11
Monoglycerides	0.07

the two samples expressed as the time elapsed before the propagation reaction occurred is the same (10.5 hrs). This low value may be due to the heat treatment of cocoa beans during roasting. El-Wakeil et al. (21) and Ahmed (22) reported that the heat treatment of kernels decreased the stability of the oils.

Identification of lipid classes

The lipid classes of cocoa butter and shell fat were identified by TLC analysis technique, the solvents applied for fractionation were petroleum ether : diethyl ether : acetic acid (90 : 10 : 1), and the results are given in table 3.

In both of the cocoa butter and shell fat eight spots are identified using known samples. An unidentified spot is presented only in shell fat with R_f value 0.172, which might be used to identify the adulteration of the cocoa butter or chocolate products with shell fat and evaluate the product quality. Fluorescent compounds peculiar to shell fat have been found, related to some 3–oxoergostane derivatives and can be used to recognize shell fat (23). The sequence and R_f values of all these known compounds were reported by several investigators (24, 25, 26, 27). The results show the presence of squalene and tocopherol, which are known as good antioxidant materials (27, 28, 29, 30).

Fatty acid composition

Fatty acids of cocoa butter and shell fat were identified and determined quantitatively as methyl ester derivatives in the presence of the methyl esters of authentic fatty acids by GLC analysis, and the results are given in table 4. The predominant fatty acids in cocoa butter are palmitic, stearic and oleic, whereas in shell fat they are palmitic and oleic. Shell fat contains higher palmitic values than cocoa butter, and they contain the same value of oleic acid. Less amounts of capric, myristoleic and linoleic are found in cocoa butter, whereas more amounts of these acids are found in shell fat. Cocoa butter contains higher values of stearic and myristic than those of shell fat. The nutritional value of shell fat is higher than that of cocoa butter, as its linoleic acid content is nearly twice compared with cocoa butter. Similar observation was obtained by Greenwood-Barton (1) who reported that shell fat differs in composition, than cocoa butter. The fatty

Table 4. Fatty acid composition of cocoa butter and shell fat %.

Fatty acids		Shell fat	Cocoa butter	Reported values for cocoa butter Reference 15	Reference 16	Reference 31
Caprylic	($C_{8:0}$)			0.341		
Capric	($C_{10:0}$)	16.89	12.95	0.299		
Lauric	($C_{12:0}$)	traces	traces	1.021		traces
Tridecanoic	($C_{13:0}$)	traces	traces			
Myristic	($C_{14:0}$)	3.19	4.32	0.653		trace – 0.2 %
Myristoleic	($C_{14:1}$)	2.43	1.29			
Palmitic	($C_{16:0}$)	27.27	23.31	22.155	22.5–28.2	24.9–29.2 (av. 25.7)
Palmitoleic	($C_{16:1}$)	2.55	0.95	1.618		0.2–0.5
Margaric	($C_{17:0}$)	traces	traces			0.2–0.4
Stearic	($C_{18:0}$)	12.05	24.51	32.163	33.2–33.6	32.5–37.0 (av. 35.1)
Oleic	($C_{18:1}$)	28.16	28.74	37.336	37.5–37.9	32.6–35.8 (av. 33.8)
Linoleic	($C_{18:2}$)	7.49	3.93	1.832	1.3– 3.9	2.6– 3.7
Linolenic	($C_{18:3}$)			1.232	0.0– 1.4	trace – 0.3
Arachidic	($C_{20:0}$)			1.091		0.9– 1.4
Behenic	($C_{22:0}$)			0.291		
Lignoceric	($C_{24:0}$)			0.112		

acid data of cocoa butter could be compared favorably with those reported by other investigators (15, 16, 31), and this may be due to the type of cocoa variety and environmental or seasonal conditions. The results of cocoa butter are in agreement with those reported by Van Wijngaarden et al. (31) only for lauric, palmitic, and linoleic acids. The data of Pietrzyk and Warzecha (16) and Atawia (15) are similar to those given in table 4 for palmitic acid only.

Unsaponifiable matter composition

Crude unsaponifiable matter was identified by GLC analysis in the presence of authentic compounds. Seventeen compounds were detected in the unsaponifiable matter of cocoa butter, and nine of them were identified as C_{22} hydrocarbon, C_{30} hydrocarbon, C_{32} hydrocarbon, squalene, α-tocopherol, cholesterol, campsterol, stigmasterol, and B-sitosterol, whereas the other eight compounds are unidentified. The data obtained are in good agreement with those given by Atawia (15) only for C_{22} hydrocarbon, campsterol, stigmasterol and B-sitosterol. The detected compounds in the unsaponifiable matter of shell fat were similar to those found in cocoa butter with exception to C_{22} hydrocarbon.

Table 5. Sterol composition of cocoa butter and shell fat.

Sterol	Cocoa butter	Shell fat
B-sitosterol	51.48 %	70.40 %
Stigmasterol	39.45 %	9.96 %
Campsterol	5.77 %	15.49 %
Cholesterol	3.29 %	4.15 %

The sterols were determined quantitatively following the same technique in the presence of authentic samples of sterols, and the results are given in table 5.

The predominant sterol in cocoa butter and shell fat is β-sitosterol, which was found in larger amounts in shell fat (table 5). Cocoa butter contained higher values of stigmasterol than that of shell fat, which contained higher values of campsterol.

Chaverson (32) reported that the sterol composition of eleven types of cocoa butter and plant oils were found to be β-sitosterol 29.8–64.7%, stigmasterol (27.0–30.3%), campsterol (7.7–10.4%) and cholesterol (0–2.8 %). The variation in data between the present study and Chaverson (32) may be due to the cocoa variety and seasonal or environmental conditions.

Summary

The physical and chemical constants of cocoa shell fat (a by-product resulted during the production of cocoa butter at chocolate factories) were almost identical with those of cocoa butter obtained from the same cocoa beans except for their high acid value. Shell fat contained more amount of phospholipid content (as cephalin) than cocoa butter. The lipid classes were almost the same in cocoa butter and shell fat, however, the latter contained an unidentified constituent which was not found in cocoa butter. The fatty acids were determined quantitatively by GLC, and the results showed that the predominant acids in cocoa butter were palmitic, and oleic. Less amounts of capric, myrisitic, palmitoleic and linoleic were found in cocoa butter, whereas more amounts of these acids were found in shell fat. Cocoa butter gave higher values of stearic and myristic acids than those of shell fat. Seventeen compounds were detected by GLC in the unsaponifiable matter of both cocoa butter and shell fat from which eight were identified as C_{30} hydrocarbon, C_{32} hydrocarbon, squalene, α-tocopherol, cholesterol, campsterol, stigmasterol and β-sitosterol in the two samples. The sterols were determined quantitatively, and it was found that the predominant sterol in cocoa butter and shell fat was B-sitosterol. Cocoa butter contained higher values of stigmasterol than that of shell fat, which contained increasing values of campsterol, low values of cholesterol were found in both samples. Stability of cocoa butter and shell fat towards oxidative rancidity at 100 °C was the same (10.5 hrs).

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