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Substituting of Cacao by Carob Pod Powder In Milk Chocolate Manufacturing

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Abstract: The current study aimed to utilize the carob pod powder (due to its nutritional and healthy values) through addition in varied amounts (25, 50, 75 and 100%) to the milk chocolate as a cocoa replacer. Studying the impact of carob pod powder substitution instead of cocoa seeds on the nutritional and sensory properties were also carried out. The results showed that addition of the carob pod powder to the milk chocolate samples slightly enhanced the protein contents and highly increased reducing sugars, ash and fiber contents. It decreased the total and non reducing sugars, fats and carbohydrate contents in relative to the control sample. caffeine, the galactomannan, Consequently, it is advisably to utilize the carob pod powder in order to enhance the nutritional values, functional, sensory properties and a successful tool to substitute the cocoa seeds in chocolate products manufacturing.

Kew words: Carob pod powder, Cacao ,milk chocolate, protein contents reducing sugars.

INTRODUCTION

The carob, *Ceratonia siliquagenus*, Ceratonia, belongs to the Fabaceae (legume) family, and is believed to be an archaic remnant of a part of this family now generally considered extinct. It grows well in warm temperate and subtropical areas, and tolerates hot and humid coastal areas (Batlle and Tous 1997).

Santos *et al*., (2005) reported that carob (*Ceratonia siliqua*) is a perennial leguminous tree, native to the Mediterranean basin and Southwest Asia. It has been cultivated throughout the Mediterranean region for approximately 4000 years. Portugal and Spain have approximately 100,000 ha of carob trees and process approximately half of the world's commercial carob supply. World carob pod production is approximately 315,000 t per year and the main carob bean producers and exporters are Spain (42%), Italy (16%), Portugal (10%), Morocco (8%), Greece (6.5%), Cyprus (5.5%) and Turkey (4.8%). Carob is drought-resistant, requires little maintenance and produces a range of products from the seed and the pod. The endosperm is extracted from the seeds to produce a galactomannan, which forms locust bean gum, a valuable natural food additive used also in textile and cosmetic industries. The pod is useful for high-energy stock feed and the human food industry as a cocoa substitute and in syrups Carob pod is also an anti-diarrheic product because of its high tannin content (Loeb *et al*., 1989).

Both its economical and ecological value makes carob (*Ceratonia siliqua* L.) one of the most important Mediterranean trees The economic importance of this species comes from the industrial utilization of the locust bean gum (E410, also called carubin) obtained from its pods. This gum is employed in a wide range of products in the food industry; among the most important of which are ice cream, baby foods and pet foods. (Custódio *et al*., 2005).

Extracts from pods and leaves of carob showed a marked alteration inhibition of cell proliferation of mouse hepatocellular carcinoma cell line in a dose-related fashion reaching the maximal effect at 1 mg/ml. *Ceratonia siliqua* L. is a typical plant of the Mediterranean area, which is mainly used in the food industry as source of gum extracted from the seeds. Carob meal contains among total polyphenols a high level of proanthocyanidins in comparison to hydrolysable ones represented by ellagitannins and gallotannins. Interest has focused on flavonoids potential benefits to human health, as they are ubiquitously present in foods of plant origin and some epidemiological studies evidenced that the consumption of foods rich in these compounds could reduce the risk for certain types of cancer and heart diseases mortality. In this context, it has been shown that oral consumption of polyphenols offers protection against all stages of carcinogenesis (Corsia *et al*., 2002).

Avallone *et al*., (1997) reported that carob pod characterized by a high content of carbohydrates (45%, sucrose at more than 30%), appreciable amounts of protein (3%), low levels of fat (0.6%) and also a high tannin content is present in carob pod composition, which limits the consumption by cattle because of reduced digestibility (Priolo *et al*., 2000).

Another potential area of economic benefit is new uses of milk sugar, which presents a challenge to dairy research and the industry. Indeed, the market for lactose in the pharmaceutical industry is over-saturated and all the routes to chemically modify this sugar in products, such as lactulose, lactitol and detergents involve only small markets. The dairy industry worldwide is investigating markets for by-products containing high lactose content, such as whey. The worldwide lactose surplus is actually 550,000 t per year (Lifran *et al*., 2000).

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Environmental constraints fully justify discouraging direct discharge of such a large amount which has the equivalent polluting potential of 18 million people. The potential to create economical value from lactose containing liquids exists by fermentation (Santos *et al*., 2005).

It is common sense to avoid the excessive use of caffeinated beverages and the use of chocolate altogether. It is also found the benefits of using Carob as a substitute for Chocolate are very positive. Carob is high in calcium and has neither the addictive qualities of chocolate, nor the caffeine. The large red pods have been used for food for animal and man since prehistoric times. Non-fleshy and bean-like, the carob would not be generally regarded as a fruit, in the food-use sense, except for its sweetness. A powder made from the ground pods and seeds of this tree and used in cooking. It especially makes an excellent substitute for cocoa in recipes.

There was a flurry of activity in producing "health food" products from the imported carob pods. Some of these products are still sold today, especially as substitutes for chocolate. In Germany, the roasted seeds have served as a substitute for coffee. In Spain, they have been mixed with coffee. Historically it was claimed that the seeds of carob were used as a standard for measuring. Thus, the origin of the term "carat" is the measure of weight for precious jewels and metals. Cocoa is the common name for a powder derived from the fruit seeds of the cacao tree and for the beverage prepared by mixing the powder with milk. It is also mildly stimulating because of the presence of theobromine, an alkaloid that is closely related to caffeine. Research has found that pets, especially dogs, are sensitive to theobromine. Several cases of dog poisoning have been reported and the amount of chocolate eaten varied between 100g and 1kg. The dog's symptoms were mainly neurological (trembling and convulsions), but others such as diarrhea also occurred. Chocolate, is a preparation made from the fruit of the cacao tree and used as a flavoring and as an ingredient of beverages and various kinds of confectionery. The craving for chocolate is related to psychoactive ingredients. Like Cocoa, chocolate contains theobromine, a central nervous system stimulant which does not have strong subjective effects. Chocolate also contains caffeine but compared with tea and coffee it is a fairly insignificant amount. Chocolate is not viewed as a staple food, it is considered more of an indulgence. Resisting the desire to eat chocolate could cause the desire to eat it to become more prominent. On the other hand, the effects of caffeine on the body have been widely disputed. Mainstream medical research does not show a direct link to lasting negative effects of either blood pressure or heart conditions from using caffeine, although it may make those with weak hearts experience the racing of the heart beat which is a bit frightening. They have also not proved a direct link between caffeine and cancer, but this is only the isolated effects of the caffeine itself. Though long term studies on the effects of excessive use of strong coffee and cola type beverages on the kidneys, liver, and bladder has not been conducted, health journals all advise using them with extreme care. With the epidemic of prostate cancer in men it has been advised that those with prostate trouble avoid all coffee and cola and chocolate. There are some studies that show that large doses of caffeine, that would be three to seven cups of coffee a day, can delay fertility. That means you get pregnant a couple of months later than you otherwise would have gotten pregnant. There's also a warning for pregnant women who drink a lot of coffee or beverages containing caffeine that says drinking five cups of coffee per day more than doubles your risk of miscarriage (Rogers, 1998).

MATERIALS AND METHODS

Materials and Chocolate Manufacture:

The tested chocolate samples were manufactured at Food Manufacturer's Company known as "ULKER" a manufacturing company for Tea Biscuits, Chocolates, Cakes, Wafers, Sandwich biscuits, etc in Industrial City of Jeddah, the Kingdom of Saudi Arabia (KSA) and the carob pods were obtained from local markets at Mecca, KSA.

The whole carob pods were grinded to fine powder and dried at 60°c for 3 hr. The milk chocolate control (carob pod powder free) and the tested milk chocolate (substitute 25, 50, 75 and 100% of cocoa seed weights by the same amounts of carob pods powder) was manufactured at ULKER company.

Methods of Analysis

The physical properties of carob pod (length, width and weight) as well as seeds (weight and count) were estimated while, the seeds/pods weight ratio was calculated as described in AACC (2002).

The chemical composition (moisture, ash, protein, fat and fiber) of carob pod and the tested milk chocolate samples were determined while the carbohydrate content was calculated (100- (moisture + ash + protein+ fat + fiber)) according to the AOAC (2000) methods. The mineral (by The Perkin Elmer 100 Atomic Absorption Spectrometers) and sugars (total, reducing and non reducing) contents of carob pod powder and the tested milk chocolate samples were determined by the AOAC (2000) methods. The galactomannan content was estimated utilizing 1050 HP HPLC instrument equipped with a Quartenery Pumb, a Degaser and HP 1047 A Detector as described by Southgate (1976). Caffeine content was also determined by 1050 HP HPLC instrument equipped with a Quartenery Pumb, a Degaser and HP 1047 A Detector as described by Madison *et al*., (1976). The sensory evaluation of the tested samples attributes were determined by well trained panelists (15 judges) for general appearance (GA), color, taste, odor, texture, emulsification degree (ED) and aftertaste as suggested by Hoda *et al*., (2006).

Data analysis was performed using SAS (1987) software. Analysis of variance was used to test for differences between the groups. Least Significant Differences (LSD) test which was used to determine significant differences ranking among the mean values at P< 0.05 was recorded.

RESULTS AND DISCUSSION

Physical Properties of Carob Pod Parts:

Physical properties of carob pod parts of both pod (length, width and weight) and seeds (numbers, weight and seed weight / pod weight ratio) are found in Table (1). It showed that the pod length was ranged between 15.00 and 21.00 cm, its width reached from 2.50 to 3.00 cm and its weight averaged 17.37-22.53 g. On the other hand, the carob seeds characteristics, numbers, weight and seed weight / pod weight ratio were fall in the range of 6.00-14.00, 1.09-2.52pod and 6.20-11.18 %, respectively. Such results were concurrent with that found by Biner *et al*., (2007) and Yousif and Alghzawi (2000), who stated that the long length pod average recorded 15.06 cm, the seed numbers average in each pod ranged 6.4 - 12.0 and the seed weight average was about 1.0 to 2.4 g/pod.

Table 1: Physical properties* of carob pod parts.

Physical properties	Carob pods	Carob seeds
Pod length (in cm)	15.00-21.00 ± 5.80	----
Pod width (in cm)	2.50-3.00 ± 0.40	----
Pod weight (in g)	17.37-22.53 ± 2.32	----
Seed numbers	----	6.00-14.00 ± 3.20
Seed weight (in g/ pod)	----	1.09-2.52 ± 0.56
Seed weight / Pod weight ratio (%)	----	6.20-11.18 ± 1.88

* Range average ± Standard Deviation (SD).

Chemical Compositions of Carob Pod Powder:

The moisture content value of the carob pod (9.30%) as mentioned in Table (2) was agreed with that found by Lipumbu (2007) and Yousif and Alghzawi (2000) who reported that it was ranged between 9.00 and 9.87%. It was, also, found that the protein content was recorded a high amount (8.45%, on wet weight basis) agreed with that found by Owen, *et al*., (2003), who stated that the protein content in carob pod was 8.0%. The current study showed also that the carbohydrate content represented the highest ingredient value (51.76%) and the fats were the lowest one (4.80%) among all the other ingredients. Carob pods contained remarkable amounts of both of fiber and ash (16.86 and 8.83%, respectively). A similar trend was, also, found in case of the determination on dry weight basis (Table 2) concurrent with that found by Abd El-Lateef and Salem (1996) .

Chemical Compositions of Milk Chocolate Samples:

Chemical compositions of the tested milk chocolate sample and that contained 25, 50, 75 and 100% of their weights carob powder are found in Table (3). The data showed that there were significant increases in moister contents as a result of the increasing of the carob proportions in the chocolate formula. The same pattern could be also detected in case of the protein contents and the highest protein content was found in the sample manufactured by 100% carob powder. Such results were agreed with Avallone *et al*., (2002) who explained that the carob pod powder contained numerous nutrients included the high quality protein reached 15%. On contrary, the carbohydrate contents were lowered as a result of the increasing of the carob proportions in the chocolate formula. The lowest amount was detected in case of 100% carob proportions in the chocolate formula. Such results were in agreement with that found by Schenker (2000), who found that chocolates were contained 63.5 g carbohydrates/100g. The same trend was, also, obvious in case of fat contents, concurrently with that found by Glenn (2005) who reported that 50 g of milk chocolate contained 16 g of fats.

Table 2: Chemical compositions (%)* of carob pod.

Components	As wet weight basis	As dry weight basis
Moisture	9.30 ± 1.00	----
Protein	8.45 ± 0.01	9.32 ± 0.01
Carbohydrates	51.76 ± 0.76	57.06 ± 0.76
Crude fats	4.80 ± 0.87	5.29 ± 0.87
Crude fibers	16.86 ± 0.15	18.59 ± 0.15
Ash	8.83 ± 0.20	9.74 ± 0.20

* Average ± Standard Deviation (SD).

Table 3: Chemical compositions (%)* of milk chocolate manufactured by different amounts of carob pod powder.

Chocolate samples	Moisture	Protein	Carbohydrates	Fats	Fibers	Ash
Control (carob free)	3.53 ± 0.50	7.91 ± 0.30	58.55 ± 0.12	29.66 ± 0.33	2.55 ± 0.78	1.33 ± 0.57
25% carob powder	3.20 ± 0.34	8.10 ± 0.66	56.89 ± 0.12	28.10 ± 0.69	4.22 ± 0.31	2.69 ± 0.33
50% carob powder	3. 68 ± 0.23	8.21 ± 0.16	54.34 ± 0.24	26.99 ± 0.33	6.61 ± 0.46	3.85 ± 0.57
75% carob powder	3.73 ± 0.23	8.39 ± 0.50	52.51 ± 0.12	26.61 ± 1.00	8.19 ± 0.43	4.30 ± 0.037
100% carob powder	4.53 ± 0.68	8.47 ± 0.62	51.12 ± 0.12	24.09 ± 0.50	10.22 ± 0.20	6.10 ± 0.47
LSD at 0.05	0.01	0.32	1.25	1.19	1.98	1.11

* Average as dry weight basis ± Standard Deviation (SD)

Data presented in Table (3) showed, also, highly significant differences in fiber contents among milk chocolate samples contained 25, 50, 75 and 100% carob powder of their weights than the control (free carob powder) sample. Wherein, there was a progressive increment as a result of increase the carob powder amount. The same model was also achieved in case of ash contents of the milk chocolate samples provided by carob powder. The highest ash content was detected in the 100% carob powder replacement sample, while the lowest one was in case the 25% carob powder replacement sample. However, milk chocolate samples manufactured by all the carob powder tested amounts were contained a higher ash contents than the control sample.

Chemical Compositions of Milk Chocolate Samples:

Total, reducing and non reducing sugars (%) in the carob pod powder and the tested milk chocolate samples are found in Table (4).

Table 4: Total, reducing and non reducing sugars (%)*in carob pod powder and chocolate manufactured by different amounts of carob pod powder.

Chocolate samples	Total sugars	Reducing sugars	Non reducing sugars
Carob pod powder	29.94 ± 0.37	7.46 ± 0.25	22.48 ± 0.12
Control (carob free)	50.24 ± 0.01	7.67 ± 0.25	42.57 ± 0.25
25% carob powder	44.46 ± 0.01	9.49 ± 0.02	34.97 ± 0.01
50% carob powder	40.55 ± 0.12	12.02 ± 0.12	28.53 ± 0.01
75% carob powder	40.01 ± 0.10	11.15 ± 0.24	28.86 ± 0.34
100% carob powder	39.35 ± 0.25	9.84 ± 0.12	29.51 ± 0.12
LSD at 0.05	0.34	0.33	0.33

* Average as dry weight basis ± Standard Deviation (SD)

The non reducing sugars amounts (22.48%) were higher than the reducing sugars (7.46%) in the carob pod powder, consequently, the total sugars reached 99.94%, concurrent with that reported by Lipumbu (2007). The same pattern was also found in the control (free carob powder) sample (42.57 and 7.67%, respectively). But the non reducing sugars amounts in the control sample seemed to be two folds of the amount of the carob pod powder. Such findings led to make the total sugars in the control sample seemed to be two folds of that in the carob pod powder. On the other hand, due to the higher contents of total and non reducing in the control sample than the carob pod powder, the increasing amounts of carob powder (from 0 to 25, 50, 75 or 100%) in the tested sample lowered such constituents in the final milk chocolate products. Such results could be confirmed by Abd El- Lateef and Salem (1996) and Rizzo *et al*., (2004) who mentioned that 100 g of carob pod powder contained 15.21 and 22.5% reducing and non reducing sugars, respectively.

Mineral Contents of Milk Chocolate Samples:

Data presented in Table (5) show the mineral contents of the carob pod powder and the milk chocolate samples contained 25, 50, 75 and 100% carob powder of their weights. It could find that potassium, calcium and sodium were the highest minerals in the carob pod powder (1486.25, 220.41 and 110.93 mg/100g, respectively). On contrary, iron, zinc and magnesium were the lowest minerals in the carob pod powder (2.23, 0.62 and 0.44 mg/100g, respectively). The minerals pattern was also the same in case of the control sample of milk chocolate with variation in each mineral. Wherein, the potassium, calcium, sodium, and magnesium contents in the carob pod powder were higher than that found in milk chocolate control sample, therefore, their amounts were increased as a result of increase carob pod powder proportions (25, 50, 75 and 100%) in the tested milk chocolate samples. On contrary, the iron and zinc contents in the carob pod powder were lower than that found in the milk chocolate control sample, therefore, their amounts were decreased as a result of increase carob pod powder proportions in the tested milk chocolate samples. Such results were concurrent with that found by Glenn (2005), Rizzo *et al*., (2004), Owen *et al*., (2003) and Avallone *et al*., (2002).

Galactomannan Contents of Milk Chocolate Samples:

Galactomannan contents in the carob pod powder and the milk chocolate samples are found in Table (6). It showed that the carob pod powder contained 17.03% galactomannan but the control milk chocolate sample was free. Such results were agreed with Bouzouita *et al*., (2004) who reported that carob pod powder contained a higher amount of galactomannan. Consequently, addition of 25, 50, 75 and 100% carob pod powder to the milk chocolate resulted in samples contained detectable gradient amounts of galactomannan (7.41, 9.32, 12.66 and 14.70%, respectively).

Caffeine Contents of Milk Chocolate Samples:

Data presented in Table (7) show the milk chocolate samples contents of caffeine. It showed that the control sample of the milk chocolate (carob free) possessed the highest amount of caffeine (2720.26 mg/100kg). Addition of the carob powder (25, 50 and 75%) gradually significantly lowered the milk chocolate contents of caffeine (to be 22382.44, 1059.16 and 740.678 mg/100kg, respectively) agreed with Apgar and Tarka (1999). The milk chocolate sample manufactured by 100% carob pod powder was caffeine free which was previously confirmed by Rogers (1998)،

Table 5: Mineral contents* in carob pod powder and milk chocolate manufactured by different amounts of carob pod powder.

Chocolate samples	Calcium	Iron	Magnesium	Zinc	Potassium	Sodium
Carob pod powder	220.41 ± 4.22	2.23 ± 0.42	0.44 ± 0.04	0.62 ± 0.02	1486.25 ± 2.00	110.93 ± 3.80
Control (carob free)	207.48 ± 5.11	2.40 ± 0.32	0.26 ± 0.01	0.72 ± 0.01	357.09 ± 16.20	105.85 ± 5.20
25% carob powder	212.18 ± 3.22	2.31 ± 0.22	0.32 ± 0.01	0.70 ± 0.03	354.80 ± 18.40	109.5 ± 4.40
50% carob powder	226.77 ± 4.26	2.27 ± 0.11	0.36 ± 0.03	0.68 ± 0.02	376.25 ± 16.60	112.31 ± 3.80
75% carob powder	230.50 ± 3.36	2.18 ± 0.09	0.39 ± 0.02	0.65 ± 0.04	379.37 ± 12.20	124.79 ± 4.00
100% carob powder	234.38 ± 4.00	2.12 ± 0.12	0.42 ± 0.01	0.60 ± 0.04	389.09 ± 14.30	130.37 ± 3.46
LSD at 0.05	2.38	0.63	0.14	0.20	4.53	6.04

* Average (in mg/100g dry weight basis) ± Standard Deviation (SD)

Table 6: Galactomannan and Caffeine contents in carob pod powder and milk chocolate manufactured by different amounts of carob pod powder.

Chocolate samples	Galactomannan contents (%)*
Carob pod powder	17.03 ± 0.62
Control (carob free)	0.00
25% carob powder	7.41 ± 0.22
50% carob powder	9.32 ± 0.42
75% carob powder	12.66 ± 0.24
100% carob powder	14.70 ± 0.52

* Average as dry weight basis ± Standard Deviation (SD)

Table 7: Caffeine contents in milk chocolate samples manufactured by different amounts of carob pod powder.

Chocolate samples	Caffeine contents (mg/kg)*
Control (carob free)	2720.26 ± 11.20
25% carob powder	2382.44 ± 9.23
50% carob powder	1059.16 ± 12.40
75% carob powder	740.678 ± 6.42
100% carob powder	0.00

* Average as dry weight basis ± Standard Deviation (SD)

Sensory Evaluation of Milk Chocolate Samples:

The sensory properties of the tested milk chocolate samples (Table 8) showed that there was a significant difference in general appearance attribute between the control sample and the other samples. It was also found that there were significant differences among the carob powder samples as a result of increasing the carob amounts. Such trend was also observed by Anonymous, (1997). On the other hand, there was a slightly significant difference in color attribute of the tested samples agreed with that found by Rogers (1998). On contrary, with respect to the taste and odor attributes, there was no significant difference either between the control sample and the other samples or among the carob powder samples as a result of increasing the carob amounts. Such pattern was concurrent with that found by .Bonvehi and Coll (2002) and Hoda *et al*., (2006), respectively. The emulsification degree and aftertaste attributes showed a slightly enhancement as a result of increasing the carob powder amounts. Since the highest value was detected in the 100% sample and the lowest value was found in the control value agreed with Urdiain *et al.,* (2004).

Table 8: Sensory evaluation of the tested milk chocolate, manufactured by different amounts of carob pod powder.

Chocolate samples	GA	Color	Taste	Odor	Texture	ED	Aftertaste
Control (carob free)	9.25 ±0.35	9.12 ± 0.82	8.71 ± 0.82	8.71 ± 0.92	8.96 ± 0.69	8.61 ±1.07	8.85 ± 0.61
25% carob powder	8.31 0.37	8.95 ± 0.21	8.63 ± 0.06	8.56 ± 0.42	8.18 ± 0.23	8.60 ±0.20	8.20 ± 0.01
50% carob powder	8.24 ±0.26	8.85 ± 0.15	8.31 ± 0.37	8.25 ± 0.50	8.31 ± 0.37	8.42 ±0.25	8.03 ± 0.06
75% carob powder	8.53 ±0.66	8.65 ± 0.34	8.37 ± 0.57	8.53 ± 0.61	8.53 ± 0.48	8.77 ±0.32	7.87 ± 0.14
100% carob powder	8.78 ±0.52	8.81 ± 0.42	8.18 ± 0.23	8.31 ± 0.55	8.50 ± 0.35	8.85 ±0.50	7.96 ± 0.15
LSD at 0.05	0.069	0.79	0.70	0.94	0.68	0.85	0.43

GA= General Appearance ED= Emulsification degree

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