



Characterization of Thermal Behaviour and Fatty Acid Profile of Coconut Based Chocolate Novelties

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ABSTRACT

A study was carried out to produce chocolates from coconut variants *viz.*, coconut oil, coconut cream and coconut milk as a substitute for cocoa butter. The chocolate prepared with 40% cocoa butter was taken as control. Cocoa butter substituted at the levels of 10%, 20% and 30% by coconut oil, coconut cream and coconut milk respectively were optimized based on the consumer acceptance. The fatty acid profile of the developed chocolate novelties were analysed using GC-MS and the lauric acid content was elevated to 1.92%, 1.04% and 1.17% in coconut oil, coconut cream and coconut milk chocolates respectively from 0.02% in control. The thermal behavior of the developed chocolate novelties were analyzed by using Differential Scanning Calorimetry which exhibited harmonious distinct endothermic transitions between 28°C and 53°C. The developed chocolate novelties exhibited stable melting ranges in comparison with control.

Key words: Chocolates, DSC, Fatty acid profile, Thermal behavior.

INTRODUCTION

Cacao” is the botanical name that refers to the tree that includes pods and the unfermented beans, while “Cocoa” refers to the final raw material applied for making of various cocoa based food products. Chocolates are preferred by consumers all over the world by all age groups. Chocolate and cocoa are the products derived from cacao beans, the seeds of the *Theobroma cacao* tree. Chocolate can be described as a suspension consisting of non-fat particles (sugar, cocoa solids and milk powder particles) dispersed in cocoa butter as a continuous phase (Beckett, 2009; Schantz and Rohm, 2005; Sokmens and Gunes, 2006).

Chocolates may have different percentages of cocoa liquor, cocoa powder, cocoa butter, sugar and milk powder based on different types of chocolates, namely dark, milk and white chocolates. Total solid content of chocolates varies from 65 to 75% depending upon the types of milk chocolate containing 20% of milk powder (Afoakwa *et al.* 2008; Lucisano *et al.* 2006). Cocoa butter is a pure vegetable oil derived from the beans of the cacao plant, which is the continuous phase of chocolate. It is responsible for dispersion of the other constituents of chocolate formulation during storage, handling and sensory evaluation (Nickless, 1996). Cocoa butter comprises a mixture of saturated and unsaturated fats which account for more than 95% of the fatty acids in cocoa butter. It contains high levels of triacylglycerols (TAGs) *viz.*, Palmitic acid, Oleic acid and Stearic acid.

In this research chocolates were developed with the substitution of cocoa butter with coconut fats namely, coconut oil (10%), coconut milk (20%) and coconut cream (30%). Coconut has numerous health benefits and is promoted as a dietary supplement. The main fatty acids in coconut belong to the group of fatty acids called medium

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chain fatty acids over 50% of the total fatty acids. The major fatty acids being lauric acid 46% (12:0), myristic acid 17% (14:0) and palmitic acid 9% (16:0) (Abrahamsson *et al.* 2008). These are absorbed intact from the small intestine and do not undergo degradation and re-esterification processes. They are directly used in the body to produce energy. Lauric acid, the integral component of coconut is comparable to fat in human milk and have similar nutraceutical effects as that of human milk (Kabara, 1978, 1990). It is transformed into a substance called “monolaurin” in the human body which has antibacterial and bactericidal effects (Hegde, 2006). Monolaurin is currently used as a GRAS (generally recognized as safe) food emulsifier, approved by the US Food and Drug Administration and is considered essentially a non-toxic compound even at relatively high dose levels (Skrivanova *et al.* 2006).

The health benefits of coconut fats can be obtained by substituting them in chocolates thereby reducing the cost of chocolate production. The chocolates developed during the current study were analyzed for their melting behavior and fatty acid profile which gives chocolate its unique properties.

MATERIALS AND METHODS

Raw materials and chocolate preparation

The chocolates were prepared with the commercially available ingredients such as cocoa butter, cocoa powder, icing sugar, lecithin, coconut oil, coconut milk and coconut cream. The control and chocolates substituted with coconut oil 10%, coconut cream 20% and coconut milk 30% were developed following the procedure given in Fig 1.

Differential scanning calorimetry

The thermal behaviour of chocolate was studied by using Differential Scanning Calorimetry (DSC). It is the technique in which the difference in energy input into a sample and a reference material is measured as function of time or temperature while the sample and the reference material are subjected to a controlled time - temperature program. Approximately 6-10 mg of sample was placed in an aluminum cup with a lid in hermetic pan and sealed with the lid. Temperature calibration was performed prior to measurements and an empty pan was used as reference which was about 56 grams. The DSC was calibrated and the samples were heated in the temperature range 25°C to 100°C at a heating rate of 5°C/min. Nitrogen was used to purge the thermal analysis system. Initial temperature, final

temperature, peak width, peak maximum and heat required (J/g) was computed from the thermograms obtained.

Gas chromatography

The Fatty acid profile of chocolates were analysed by GC-MS by using AOCS Official Method. Three drops of sample were taken in a vial and mixed with 9ml of hexane and 1ml of KOH with methanol solution. 1ml of the clear layer was transferred to the GC vial for analysis. The percentage of fatty acids present in the samples were estimated from the chromatograms obtained.

RESULTS AND DISCUSSION

Analysis of thermal behaviour of coconut based chocolate novelties by Differential Scanning Calorimetry (DSC)

The onset (T_{onset}) and end temperature of melting (T_{end}), peak width (J/g), peak maximum (T_{peak}) and heat flow (mW/mg) of control, $CO_{10\%}$, $CC_{20\%}$ and $CM_{30\%}$ analysed from DSC thermogram is given in Table 1. The onset temperature (T_{onset}) of melting was observed at 28.72°C, 30.04°C, 28.18°C and 28.37°C and the peak maximum (T_{peak}) was attained at a temperature of 39.9°C, 39.5°C, 39.7°C and 38.7°C for control, $CO_{10\%}$, $CC_{20\%}$ and $CM_{30\%}$ respectively. The specific heat (C_p) of the chocolates at which phase transition occurred were

Procedure for chocolate production

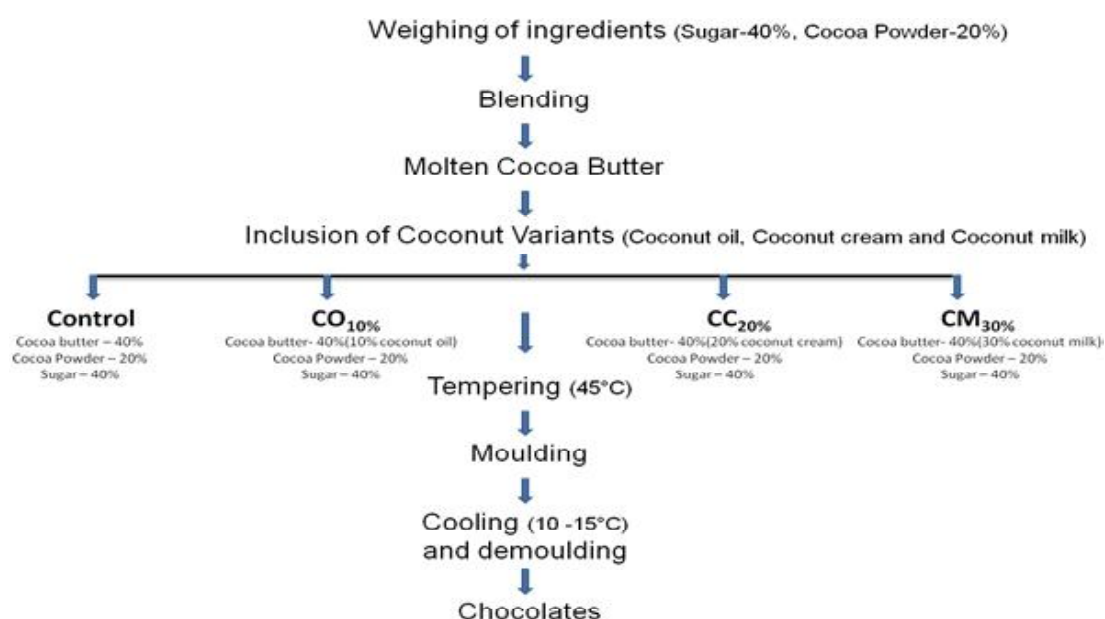


Fig 1: Procedure for preparation of chocolate.

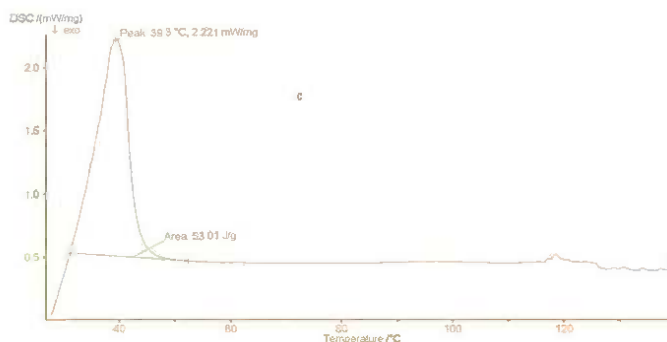
Table 1: Analysis of thermal behaviour of coconut based chocolate novelties by Differential Scanning Calorimetry (DSC).

Types of chocolate variants	Heat	Onset temperature	End temperature	Peak maximum	Area
	C_p mW/mg	T_{onset} °C	T_{end} °C	T_{peak} °C	
Control	2.221	28.72	52	39.3	53.01
$CO_{10\%}$	1.64	30.04	52	39.5	38.12
$CC_{20\%}$	2.1	28.18	52	39.7	56.49
$CM_{30\%}$	1.435	28.37	50	38.7	36.14

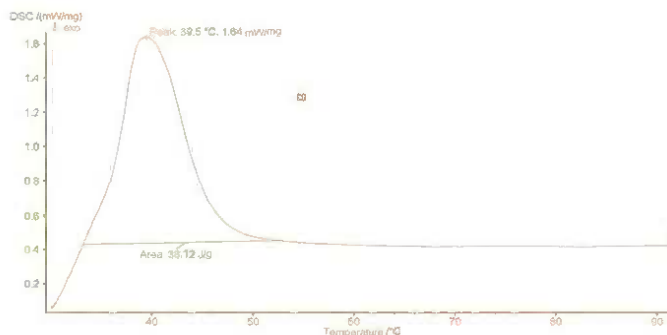
estimated to be 2.221, 1.64, 2.1 and 1.435 mW/mg for control, CO_{10%}, CC_{20%} and CM_{30%} respectively. The time taken for complete melting of the chocolates were found to be in relation with the peak width which were 53.01 J/g, 38.12 J/g, 56.49 J/g and 36.14 J/g for Control, CO_{10%}, CC_{20%} and CM_{30%} respectively. Fig 2 shows the thermograms obtained for the control and developed coconut based chocolate novelties (CO_{10%}, CC_{20%} and CM_{30%}).

The control of the molecular structure and polymorphic forms of cocoa butter is particularly important in the manufacture of chocolate. Cocoa butter is responsible for the smooth texture, contraction, flavour release and gloss of chocolate. It shows brittleness below 20°C, begins softening at 30°C to 32°C and exhibits a sharp complete melting below body temperature. This quick meltdown in a narrow range of temperature results in a cool sensation,

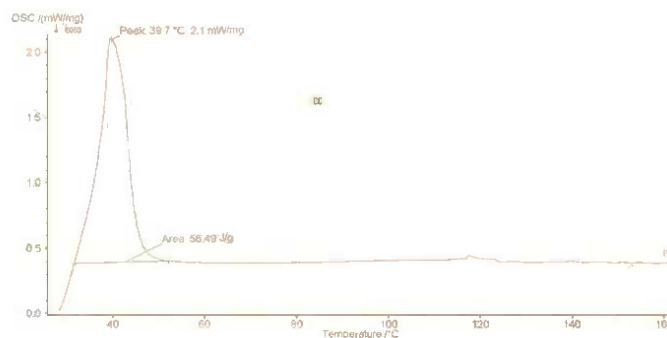
Thermogram illustrating the thermal behaviour of control chocolate



Thermogram illustrating the thermal behaviour of chocolate substituted with coconut oil (10%)



Thermogram illustrating the thermal behaviour of chocolate substituted with coconut cream (20%)



Thermogram illustrating the thermal behaviour of chocolate substituted with coconut milk (30%)

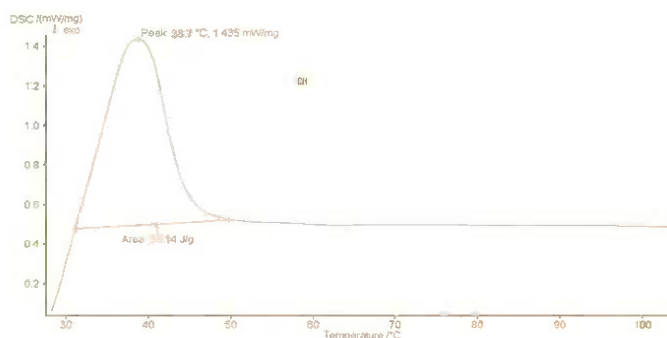


Fig 2: Thermograms illustrating the thermal behaviour of chocolates.

Table 2: Determinative analysis of Fatty Acid Profile of coconut based chocolate novelties using GC-MS.

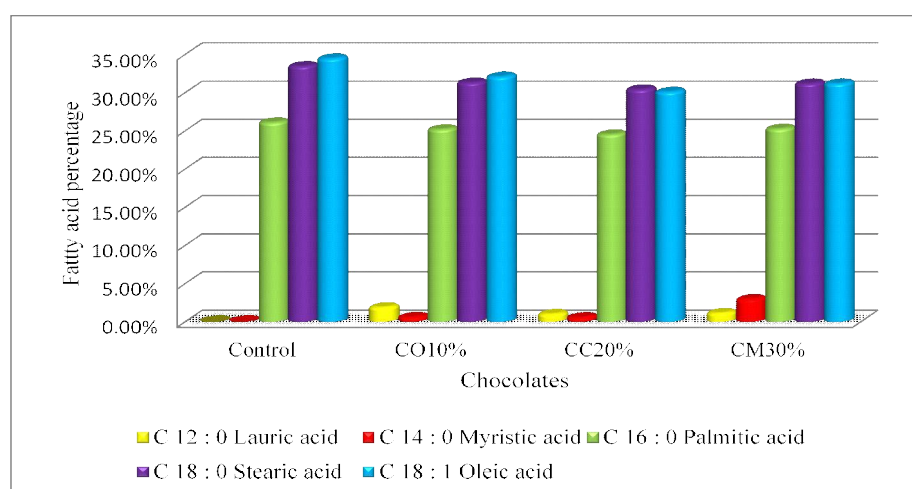
Fatty acid	Name of fatty acid	Control	CO _{10%}	CC _{20%}	CM _{30%}
C 12 : 0	Lauric acid	0.02%	1.92%	1.04%	1.17%
C 14 : 0	Myristic acid	0.04%	0.63%	0.59%	3%
C 16 : 0	Palmitic acid	26.13%	25.23%	24.56%	25.3%
C 18 : 0	Stearic acid	33.5%	31.34%	30.45%	31.22%
C 18 : 1	Oleic acid	34.5%	32.12%	30.13%	31.22%

Control - Chocolate was prepared with cocoa butter (40%).

CO_{10%} - Chocolate was prepared by substituting cocoa butter (40%) with 10% coconut oil.

CC_{20%} - Chocolate was prepared by substituting cocoa butter (40%) with 20% coconut cream.

CM_{30%} - Chocolate was prepared by substituting cocoa butter (40%) with 30% coconut milk.


Fig 3: Comparison of Fatty Acid Profile of developed chocolate novelties.

which is the appreciated organoleptic feature of cocoa butter. The melting behaviour of cocoa butter is not only responsible for mouth feel but also for flavour release from cocoa powder, which is dispersed within the fat (Schlichter-Aronhime and Garti, 1988).

Differential Scanning Calorimetry was utilized to exhibit the thermal behaviour of control and chocolates substituted with coconut variants. The peak onset corresponds to the temperature at which a specific crystal form starts to melt. The peak onset temperatures of all the chocolates were in the range of 28°C to 30°C. This implies that the crystal formed should be between IV (β') and V (β) form on correlating with the polymorphic forms of chocolate of which form V (β) was the most preferred crystal form for chocolates. The peak maximum denoted the temperature at which melting rate was the greatest and it was found that chocolate with coconut cream had the highest peak maximum followed by chocolate with coconut oil and control. The chocolate with coconut milk substitution had the lowest peak maximum indicating that the melting rate was high at a lower temperature when compared with other samples. There was a time delay in complete melting of the chocolate with coconut cream followed by control, coconut oil and coconut milk with respect to area. The heat capacity (C_p) gradually and consistently increased to onset temperature (T_{onset}) and then progressively increased more rapidly until peak

temperature (T_{peak}), after which it decreased to the end temperature (T_{end}). All the samples exhibited similar distinct single endothermic transitions between 28°C and 53°C, which was in agreement with the results furnished by Afoakwa *et al.* (2008) that the range expected for chocolate melting profiles were between 15°C and 55°C. The difference in melting range was due to the changes in sample composition and crystalline state distribution and the results were found to be in concurrence with studies by McFarlane (1999). The structure characteristics of chocolate by measuring the strength of cocoa butter crystal network with DSC melting curves is studied by Svanberg *et al.* (2013). Coconut oil substituted chocolate showed melting at a temperature slightly higher than the control but the melting time was highest for chocolate with coconut cream. All the chocolates exhibited desired polymorphs but chocolate substituted with coconut oil is more suitable than other substitutions.

Analysis of fatty acid profile of coconut based chocolate novelties using GC-MS

The chocolate prepared with cocoa butter which was taken as control contained large amount of Stearic, Oleic and Palmitic acid as it was highly present in the cocoa butter.

Table 2 shows the fatty acid profile of control and chocolates made by substituting cocoa butter with 10%

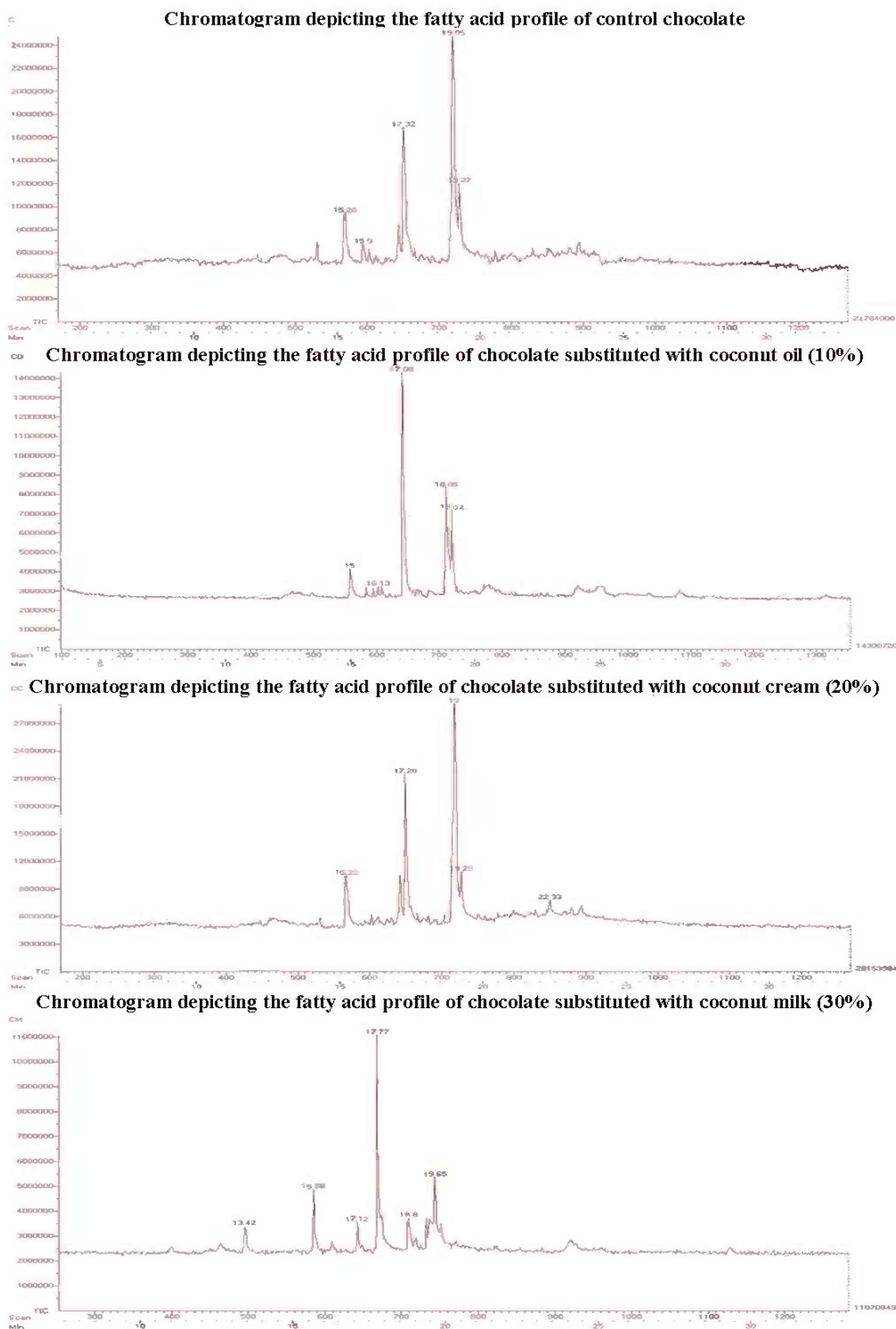


Fig 4: Chromatogram illustrating the fatty acid profile of chocolates.

coconut oil, 20% coconut cream and 30% coconut milk. Control sample was found to contain 26.13%, 33.5% and 34.5% of palmitic, stearic acid and oleic acids respectively. Lauric acid content of control was 0.02%, it was found that lauric acid content has increased to 1.92%, 1.04% and 1.17% in CO_{10%}, CC_{20%} and CM_{30%} respectively. Fig 3 depicts the comparison of fatty acid profile of control and coconut based chocolate novelties. Fig 4 shows the chromatograms of control, CO_{10%}, CC_{20%} and CM_{30%} obtained.

The fatty acid profile of the chocolates shows a higher amount of Palmitic, Stearic and Oleic acid in the range of 24-35% owing to the fact that cocoa butter had higher amount of these fatty acids which were in conformity with the findings by Naik and Kumar (2014). The lauric acid content of control chocolate was estimated to be lesser than 0.02%, whereas in chocolates substituted with coconut oil, coconut milk and coconut cream were 1.92%, 1.04% and 1.17% respectively. There observed a significant increase in lauric acid content of coconut based chocolate novelties due to the presence of high lauric acid content in coconut products which were correlated with the findings recorded by Hegde (2006) who stated that about 50% of the fats present in coconut was composed of the medium chain lauric fatty acid. Thus, chocolate substituted with coconut oil had the highest content of lauric acid making it a premium chocolate with a healthier fat that is responsible for many functional properties.

CONCLUSION

Coconuts are a rich source of Lauric acid and the chocolates developed with coconut variants were found to have significant amount of lauric acid in them in comparison to control. The lauric acid level is found to increase from 0.02% in control to 1.92% in the developed chocolate novelties especially in chocolates substituted with coconut oil. Also the thermal behaviour of chocolate with cocoa butter and coconut variants (coconut oil, coconut cream and coconut milk) showed minor changes in melting ranges due to changes in composition of chocolates and the temperatures were in ranges were in range with the control chocolates. The melting temperatures and fatty acid compositions play a major role in determining the flavour release and desirable mouth feel of the chocolates and among all variants, chocolates substituted with coconut oil exhibits consistent

results making it the most acceptable in terms of melting profile and presence of functional lauric acid.

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