UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF ANTIOXIDANT-RICH COCOA LIQUOR MASK FOR SKIN REJUVENATION

ALYAA NURATHIRAH BINTI ABD HALIM

IPPH 2021 3

DEVELOPMENT OF ANTIOXIDANT-RICH COCOA LIQUOR MASK FOR SKIN REJUVENATION

By

ALYAA NURATHIRAH BINTI ABD HALIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

May 2021

DEDICATION

This thesis is dedicated to
My loving Ayah, Ibu, Along, Angah & Future…

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

DEVELOPMENT OF ANTIOXIDANT-RICH COCOA LIQUOR MASK FOR SKIN REJUVENATION

By

ALYAA NURATHIRAH BINTI ABD HALIM

May 2021

Chairman : Associate Professor Siti Salwa binti Abd Gani, PhD
Institute : Halal Product Research

Halal cosmetics generally derive from plant-based materials. Cocoa liquor (CL), a paste produced from ground cocoa (*Theobrama cacao* L.) beans, is a natural source of antioxidants with high potential health benefits. The present study was conducted to determine the prospect of incorporating CL in skin care cosmetics, complementing its ability in protecting the skin by warding off free radicals from the environment. Polyphenols and methylxanthines in CL extract were assayed using Liquid Chromatography-Mass Spectroscopy (LC-MS/MS). In formulating cocoa facial mask (CFM), the chemical components in each ingredient were analyzed and characterized in terms of either thickness or watery texture. The final formulation was optimized and characterized by pH, rheology, texture and color measurements. In accelerated stability, freeze-thaw cycles and centrifuge studies were conducted to determine the stability of CFM in the parameters under study. The CFM was determined of its antioxidant activities including total phenolic content (TPC), total flavonoid content (TFC), 1,1-diphenyl-2-picryhdrazyl (DPPH), Ferric Ion Reducing Power (FRAP) and β-carotene linoleate bleaching (β-CB). Results showed that TPC and TFC were recorded at 131.97±0.06 mg GAE/g and 4.10± 0.0 mg RE/g dried weight of sample, respectively. DPPH free radical scavenging activity was observed at the highest concentration of 87.99± 0.03 % with EC_{50} of 30.33± 0.0 mg/mL. The FRAP reading was recorded at 252.31 ± 0.001 mmol Fe^{2+}/g dry weight at 1000 mg/mL. The β-carotene linoleate bleaching (β-CB) assay was detected at the highest concentration of 83.42 ± 0.03 % with EC_{50} of 2.92 ± 0.03 mg/mL. In microbiological studies, oven, room temperature and chiller treatments recorded microorganism growth of 1.0 x 10^1 cfu/g, < 1 cfu/g and < 1cfu/g on Day 28, meanwhile yeast and mould growth yield were recorded at < 10 cfu/g for all treatments. Heavy metals such as arsenic, lead, cadmium and mercury were detected below the range as suggested by ASEAN. Eye and skin irritation tests depicted the CFM irritant in eye and non-irritant in skin applications. The efficacy of the CFM was measured by *in-vitro*. The CFM acted as good natural inhibitors in collagenase, tyrosinase and elastase activities on the skin. The study presented scientific validation on phytochemical contents of CL showing presence of bioactive compounds with

nutritional and therapeutic values which had positive impact on skin health due to the cocoa butter contained in CL, suggesting its prospective use in value-added products such as skin care cosmetics.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PEMBANGUNAN TOPENG MUKA YANG KAYA DENGAN ANTIOKSIDAN LIKUOR KOKO UNTUK KEREMAJAAN KULIT

Oleh

ALYAA NURATHIRAH BINTI ABD HALIM

Mei 2021

Pengerusi : Profesor Madya Siti Salwa binti Abd Gani, PhD
Institut : Penyelidikan Produk Halal

Kosmetik *halal* umumnya diperolehi daripada bahan berasaskan tumbuhan. Likur koko (LK), sejenis pes yang dihasilkan daripada biji koko (*Theobrama cacao* L.) yang telah dikisar, adalah satu sumber antioksidan semulajadi yang mengandungi faedah kesihatan yang berpotensi tinggi. Kajian ini telah dijalankan bagi menentukan prospek menggabungkan LK dalam kosmetik penjagaan kulit bagi melengkapkan kemampuannya dari segi melindungi kulit dengan menangkis kesan radikal yang bebas di persekitaran. Polifenol dan metilxanthine yang terkandung dalam ekstrak LK telah diuji dengan menggunakan Liquid Chromatography-Mass Spectroscopy (LC-MS/MS). Dalam merumuskan topeng muka koko (TMK), komponen kimia bagi setiap bahan telah dianalisis dan dilakukan pencirian dari segi tekstur ketebalan atau berair. Pada formulasi terakhir, pengoptimuman dan pencirian telah dilakukan mengikut pH, reologi, tekstur dan warna. Bagi ujian kestabilan, kitaran beku-cair dan kajian empar telah disempurnakan bagi menentukan kestabilan TMK pada parameter kajian. Aktiviti antioksidan TMK telah ditentukan melalui jumlah kandungan fenolik (TPC), jumlah kandungan flavonoid (TFC), ujian-ujian 1,1-diphenyl-2-picryhdrazyl (DPPH), Ferric Ion Reducing Power (FRAP) dan β-carotene linoleate bleaching (β-CB). Keputusan menunjukkan TPC dan TFC masing-masing merekodkan 131.97±0.06 mg GAE/g dan 4.10± 0.0 mg RE/g sampel kering. Aktiviti mengikis radikal yang bebas DPPH didapati pada kepekatan tertinggi iaitu 87.99± 0.03 % dengan EC_{50} pada 30.33± 0.0 mg/mL. Bacaan FRAP adalah pada 252.31 ± 0.001 mmol Fe^{2+}/g berat kering pada 1000 mg/mL. Ujian β-CB direkodkan pada kepekatan 83.42 ± 0.03 % dengan EC_{50} of 2.92 ± 0.03 mg/mL. Dalam kajian mikrobiologi, rawatan ketuhar, suhu bilik dan rawatan penyejuk masing-masing mendapati pertumbuhan pada 1.0 x 10^1 cfu/g, < 1 cfu/g and < 1cfu/g pada hari 28, sementara itu, pertumbuhan yis dan jamur merekodkan pada < 10 cfu/g bagi semua rawatan. Logam berat seperti arsenik, plumbum, kadmium dan merkuri dikesan pada julat rendah daripada syor ASEAN. Ujian kerengsaan mata dan kulit menyamai kerengsaan TMK dalam merengsa mata semasa aplikasi pada kulit. Keberkesanan TMK telah diukur secara *in vitro*. TMK bertindak sebagai perencat semula jadi yang baik sebagai kolagenase, tyrosinase, elastase pada kulit. Kajian ini

memberi pengesahan saintifik ke atas kandungan fitokimia LK yang mengandungi kompaun bioaktif dengan nilai pemakanan dan terapi yang memberi impak positif ke atas kesihatan kulit oleh kerana mentega koko yang terkandung dalam LK, sekaligus mencadangkan prospeknya dalam produk bernilai tambah seperi kosmetik penjagaan kulit.

ACKNOWLEDGEMENTS

In the name of Allah, the most Gracious and the Most Merciful

All praises to Allah and His blessings for the completion of this thesis. I thank The Almighty Allah for all opportunities, trials and strength that have been showered upon me to finish writing the thesis. I have experienced so much during this process, not only in academic aspects but also from the aspect of personality. My humble gratitude to the holy Prophet Muhammad (Peace be upon him) whose way of life has been a continuous guidance for me.

First and foremost, I would like to sincerely thank my honoured supervisor Assoc. Prof Dr. Siti Salwa Abd Gani for her guidance, understanding, patience and most importantly, positive encouragement and a warm spirit to finish this thesis. It has been a great pleasure and honour to have her as my supervisor. I sincerely wish to thank both of my co-supervisors Assoc. Prof Dr. Uswatun Hasanah Zaidan and Dr. Mohd Izuan Effendi Halmi for lending and spending time towards this effort.

My gratitude to Malaysian Cocoa Board especially Dr. Norliza Abdul Wahab for giving me great opportunities to join her Cocoa Facial Mask research project and encouraging me to further my studies towards Master of Science, helping me in solving problems in my studies as well as in other personal issues. Thank you to all the staff of Malaysian Cocoa Board who willingly spent time helping and guiding me in completing my laboratory work and thesis.

My deepest gratitude to my parents, dearest father En. Abd Halim bin PA Mohd Noordin and most adorable mother Pn. Zulina binti Mat Tasim, and my respected brothers Muhammad Haziq and Muhammad Yazid for their support and sharing of experiences with me towards successful completion of this thesis, cheering me up when I was feeling down. Lastly, my special thanks to all my beloved friends who were with me and supported me through thick and thin. Most importantly I would like to thank to all who were involved directly or indirectly in the completion of this study and thesis.

This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Siti Salwa Abd Gani, PhD
Associate Professor
Faculty of Agriculture
Universiti Putra Malaysia
(Chairman)

Uswatun Hasanah Zaidan, PhD
Associate Professor
Faculty of Biotechnology and Biomolecular Science
Universiti Putra Malaysia
(Member)

Mohd Izuan Effendi Halmi, PhD
Senior Lecturer
Faculty of Agriculture
Universiti Putra Malaysia
(Member)

_____
ZALILAH MOHD SHARIFF, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 09 September 2021

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software

Signature: _____ Date: _____

Name and Matric No: Alyaa Nurathirah binti Abd Halim, GS52118

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature: _____
Name of Chairman of Supervisory Committee: Associate Professor Dr. Siti Salwa Abd Gani

Signature: _____
Name of Member of Supervisory Committee: Associate Professor Dr. Uswatun Hasanah Zaidan

Signature: _____
Name of Member of Supervisory Committee: Dr. Mohd Izuan Effendi Halmi

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

AA	Ascorbic acid
$AlCl_3$	Aluminium chloride
ASEAN	Association of Southeast Asian Nations
BHT	Butylated hydroxytoluene
Cd	Cadmium
CFM	Cocoa facial mask
CL	Cocoa Liquor
Cr	Chromium
Cu	Copper
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DPPH	DPPH Scavenging Activity
ECVAM	European Centre of the Validation of Alternative Methods
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
$FeSO_4.7H_2O$	Ferrous sulphate
FRAP	Ferric Ion Reducing Power
GMO	Genetically Modified Organisms
HCl	Hydrochloric acid
Hg	Mercury
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
LC-MS/MS	Liquid Chromatography-Mass Spectroscopy
L-DOPA	L-3.4-dihyroxyphenylalanine

LK	Likur Koko
MCB	Malaysian Cocoa Board
MTT	(3-[4,5-dimethyltriazole-2-yl]-2,5-diphenyltetrazolium bromide)
$NaCO_3$	Sodium carbonate
NC	Negative control
Ni	Nickle
NIST	National Institute of Standard and Technology
NPRA	National Pharmaceutical Regulatory Agency
OD	Optical Density
OECD	Organisation of Economic Co-operation and Development Guidelines for Testing of Chemicals No 439
Pb	Lead
PC	Positive control
RhCE	Reconstructed Human Cornea-like Epithelium
RhE	Reconstructed Human Epidermis
ROS	Reactive Oxidative Stress
TFC	Total Flavonoid Content
TMK	Topeng Muka Koko
TPC	Total Phenolic Content
UV	Ultraviolet radiation
β-CB	β-carotene Linoleate Bleaching

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Cocoa (*Theobroma cocoa* L.) is an important industrial crop that has contributed significantly to the economies of many countries worldwide. The crop is widely cultivated in Ivory Coast, Ghana, Indonesia, Brazil, Nigeria, Cameroon, Ecuador, Dominican, Republic and Papua New Guinea. Ivory Coast has been the largest cocoa producing country, with output of about 33% of global supply, followed by Ghana. The World Cocoa Foundation estimated that about 6 million farmers produced about 500 kg cocoa beans per hectare in Asia (Beg et al., 2017). Malaysia, Madagascar, Mexico and the Carribbean Islands also cultivate cocoa on smaller scales (Verna, 2013; Hagiwara & Wright, 2015; de Souza et al., 2018).

The demand for cocoa as raw material in chocolate making and cosmetics has never ceased. The present study was undertaken to investigate the potential of cocoa liquor (CL), the pure cocoa mass which possesses antioxidant, antiradical, anticarcinogenic properties, as the main ingredients in formulating cocoa facial mask (CFM). The study was conducted with the view that CL affords to protect the skin from rapid aging resulting from collagen and elastin fibre damage which compromises skin barriers thus causing the skin to sag with deep wrinkles and less skin smoothness.

Various studies documented that CL had high concentrations of polyphenols due to the presence of varieties of bioactive compounds including catechin, epicatechin, procyanidin, and tannin known to give beneficial effects on skin health. In addition, polyphenolic compounds, which are secondary metabolites, have been reported to aid in reducing oxidative stresses produced in the body (Epstein, 2009). Reactive oxidative stress (ROS) had also been documented to affect collagen production due to excessive free radicals, more than antioxidants in the body, resulting in unhealthy skin and affecting daily life and self-confidence. It is known that polyphenolic compounds have good effects as cosmetics due to several properties that could be delivered to the skin, for instance, UV-protecting, antiviral, antiallergic, antifungal, anti-inflammatory and many more (Adamska-szewczyk & Zgórka, 2019).

Cosmetics have been used by both men and women to improve personal appearances and hygiene while protecting and maintaining skin conditions from ultraviolet (UV) radiations (Hashim & Mat Hashim, 2013). In the Asian Pacific region, demand for cosmetics and skincare products rises every year with the market value of more than US70 billion. In 2015, Malaysian consumers spent more than US229 million in skincare and cosmetic products (Abd Rahman et al. 2015), an amount considerably larger compared to other essentials. Presently, Muslim consumers are more aware of the *halal*

status of skincare and cosmetics products doubting ingredients, raw materials and hygiene involved in the production of same. Abd Rahman et al. (2015) cited that global consumers spent more US26 billion on *halal* cosmetics products over concern of their *halal* status opined to be safer than non-*halal* competitors.

In the cosmetics industry, adulterating of ingredients in terms of exceeding the range of allowable heavy metal contents without clinical test procedures on the products, has been the general scenario. Unsuspecting consumers, without any knowledge of the side effects of excessive percentage of heavy metals contents, generally fall prey. Irresponsible manufacturers used toxic ingredients, often acquired more cheaply than premium grades, to enjoy hefty profits. Cosmetics products with mercury, arsenic, lead and more toxic metals contents have been reported to result in skin being more sensitive to sunlight, causing peeling, rashes and at worst, fatal due to high levels of toxicity in the body (Bocca et al., 2014; Chen et al., 2018). In Malaysia, there have been several cosmetics products that have been banned from entering the market due to toxic contents often exceeding the permitted range (ASEAN, 2017). Plant-based ingredients have been the alternatives for use in cosmetics products due to their conditions being safer with good functionality to the skin.

Enzymes in the skin such as tyrosinase, collagenase and elastase are naturally produced and are being degraded with increase in age. It has been documented that enzymes collagenase and elastase are responsible for elasticity, strengthening the skin structures under the dermis layer, while tyrosinase is responsible for melanin synthesis absorbing ultraviolet (UV) radiations from causing deleterious effects on the skin (Lawton, 2019). This suggests that age spots, melasma, pigmentation of the skin are due to long term exposure of UV radiations. There have been various cosmetics and skincare products claiming to reduce skin issues for example sagging, wrinkles, sun spots with the use of plant-based ingredients in numerous forms such as cleansers, toners, moisturizers, serums, lotions and gels in attempts to maintain the enzymes of interest from degradation and thus, slowing the aging process.

The present study was aimed primarily at using CL as the main component in a CFM formulation. CL encompasses cocoa butter and cocoa powder that gives powerful positive effects on skin. Premium cosmetic grade ingredients were selected to maintain quality of CFM and for safer use by consumers. The bioactive compounds in CL are said to be responsible for the functionality of CFM when delivered by topical application to the skin. These compounds also contribute in combating free radicals as antioxidant activities. CL is generally not used in cosmetic products but mostly in food and beverages products.

1.2 Problem Statement

The present study explored the use of cocoa liquor (CL) as a natural coloring with beneficial antioxidant contents. The potentiality of CL comprising of cocoa powder and cocoa butter in facial mask has not been established as there has been limited references

on use of CL in cosmetics. Issues on *halal* status of products have recently taken center stage impacting much of the lifestyle of people. The issues have gained much attention worldwide particularly in most Islamic countries. Cosmetic and personal care products have become doubtful to Muslim consumers of their sources of raw materials, cleanliness of the products, contents and other aspects. In terms of raw materials, for examples, some products are doubtful of their gelatin and collagen contents due to sources that could originate from animals forbidden in the teaching of Islam such as swine, dogs or animals not slaughtered according to Islamic Laws (Hashim & Mat Hashim, 2013; Abd-Gani et al., 2018).

Numerous cosmetic and personal skin care products have ingredients that give immediate effects on the skin such as mercury, arsenic, lead, hydroquinone, tretinoin, cadmium, nickel and other toxic metals. These toxic metals are known not only to beautify the skin surface, but they have adverse long terms toxic effects associated with cardiovascular and reproductive systems, cancer, miscarriages and decrease in immune system due to long term exposure of adulteration of the products (Orisakwe & Otaraku, (2013); Eldin.Elhag et al., (2015); Borowska & Brzóska, (2015); Pereira & Pereira, (2018)). Toxic metals have also been known to reduce skin thickness following shedding of healthy skin resulting in the skin being more sensitive and itchy, and eventual peeling, rashes, sensitive to ultraviolet (UV) radiation and becoming dry due to damaged skin barrier system.

1.3 Objectives

The objectives of the present study included the following:

i) To characterize and analyze bioactive compounds of pure cocoa liquor (CL) by using liquid chromatography-mass spectrometry (LC-MS/MS);
ii) To analyze and evaluate antioxidants properties in cocoa liquor and antioxidant-rich CFM;
iii) To optimized the formulation of antioxidant-rich CFM;
iv) To evaluate safety in antioxidant-rich CFM of heavy metals, skin and eye irritation and microbiological stability;
v) To evaluate the efficacy of antioxidant-rich CFM through *in vitro* methods.

1.4 Scope of Study

In the present study, the levels of polyphenols (catechin and epicatechin) and methylxanthine (theobromine and caffeine), extracted from pure cocoa liquor, were examined. CFM was formulated with appropriate range of ingredients. The amount of CL was fixed in the experiment to explore the reaction of individual ingredient's behaviour. The selected percentage of each ingredient was based on the best physicochemical reactions with CL. The stability of CFM at different temperatures and

freeze-thaw studies were based on pH, color, viscosity. Shear measurements and centrifugal tests were also conducted.

Bioactive compounds in pure CL of CFM contributed to antioxidant activity such as total phenolic content (TPC), total flavonoid content (TFC), DPPH radcial scavenging activity, ferric ion reducing power (FRAP) and β-carotene linoleate bleaching (β-CB).

Safety evaluation of CFM in terms of heavy metals, eye and skin irritations and microbiological tests were also conducted. The efficacy of CFM were conducted *in vitro* and *in vivo* with *in vitro* determining the cosmeceutical properties of CFM for elastase, collagenase and tyrosinase inhibitions. *In vivo* studies involved human subjects by surface evaluation of living skin (SELS) and high resolution ultrasound skin-imaging.

1.5 Significance of Study

The present study presents antioxidant and cosmeceutical potentials in CFM particularly delivered by CL as bioactive compounds' carrier. The involvement of CL in CFM from plant sources is to maintain environmental sustainability. CFM offers good hygiene and sources of ingredients complying with Islamic Law, presenting a *halal* and safe cosmetic products.

REFERENCES

Ababneh, F. A., & Al-Momani, I. F. (2018). Assessments of toxic heavy metals contamination in cosmetic products. *Environmental Forensics*, *19*(2), 134 – 142

Abbe Maleyki, M. J., & Ismail, A. (2010). Antioxidant properties of cocoa powder. *Journal of Food Biochemistry*, *34*(1), 111–128.

Abd Gani, S. S., Basri, M., Abdul Rahman, M. B., Kassim, A., Abd Rahman, R. N. Z. R., Salleh, A. B., & Ismail, Z. (2010). Characterization and effect on skin hydration of engkabang-based emulsions. *Bioscience, Biotechnology and Biochemistry*, *74*(6), 1188–1193.

Abd Rahman, A., Asrarhaghighi, E., & Ab Rahman, S. (2015). Consumers and halal cosmetic products: Knowledge, religiosity, attitude and intention. *Journal of Islamic Marketing*, *6*(1), 148–163.

Abd-Gani, S. S., Abd-Gani, S. S., Mustafa, S., Desa, M. N. M., Mokhtar, N. F. K., Hanapi, U. K., Zakaria, Z., Yahaya, N., & Sulaiman, W. M. A. W. (2018). Detection of porcine adulteration in cosmetic cream formulation via TaqMan Probe Real-Time Polymerase Chain Reaction. *International Journal of Engineering & Technology*, *7*(4.14), 112–115.

Abdul Karim, A., Azlan, A., Ismail, A., Hashim, P., Abd Gani, S. S., Zainudin, B. H., & Abdullah, N. A. (2014). Phenolic composition, antioxidant, anti-wrinkles and tyrosinase inhibitory activities of cocoa pod extract. *BMC Complementary and Alternative Medicine*, *14*(1), 1–13.

Abdul Wahab, N. (2014). Assessment of antioxidant capacity, anti-collagenase and anti-elastase assays of malaysian unfermented cocoa bean for cosmetic application. *Natural Products Chemistry & Research*, *2*(3).

Adamska-szewczyk, A., & Zgórka, G. (2019). Plant polyphenols in cosmetics – A review. *European Journal of Medical Technologies*, *3*(24), 1–10.

Alam, M. F., Akhter, M., Mazumder, B., Ferdous, A., Hossain, M. D., Dafader, N. C., Ahmed, F. T., Kundu, S. K., Taheri, T., & Atique Ullah, A. K. M. (2019). Assessment of some heavy metals in selected cosmetics commonly used in Bangladesh and human health risk. *Journal of Analytical Science and Technology*, *10*(1), 1-8.

Alara, O. R., Abdurahman, N. H., Abdul Mudalip, S. K., & Olalere, O. A. (2019). Effect of drying methods on the free radicals scavenging activity of *Vernonia amygdalina* growing in Malaysia. *Journal of King Saud University - Science*, *31*(4), 495–499.

Ali, F., Ranneh, Y., Ismail, A., & Esa, N. M. (2015). Identification of phenolic compounds in polyphenols-rich extract of Malaysian cocoa powder using the HPLC-UV-ESI—MS/MS and probing their antioxidant properties. *Journal of*

Food Science and Technology, *52*(4), 2103–2111.

Ali, S. M., & Yosipovitch, G. (2013). Skin pH: From basic science to basic skin care. *Acta Dermato-Venereologica*, *93*(3), 261–267.

Al-Saleh, I., Al-Enazi, S., & Shinwari, N. (2009). Assessment of lead in cosmetic products. *Regulatory Toxicology and Pharmacology*, *54*(2), 105–113.

Amarowicz, R., Wanasundara, U., Wanasundara, J., & Shahidi, F. (1993). Antioxidant activity of ethanolic extracts of flaxseed in a B-Carotene-Linoleate Model System. *Journal of Food Lipids*, *1*(2), 111–117.

A, Beringhs., J, M, Rosa., H, K, Stulzer., R, M, Budal. & D, Sonaglio. (2013). Green clay and *Aloe vera* peel-off facial masks: Response Surface Methodology applied to the formulation design. *Pharmacy Science Technology*, *14*(1), 445-455.

Andújar, I., Recio, M. C., Giner, R. M., & Ríos, J. L. (2012). Cocoa polyphenols and their potential benefits for human health. *Oxidative Medicine and Cellular Longevity*, *2012*,1-23.

Angelis, A., Mavros, P., Nikolaou, P. E., Mitakou, S., Halabalaki, M., & Skaltsounis, L. (2020). Phytochemical analysis of olive flowers' hydroalcoholic extract and *in vitro* evaluation of tyrosinase, elastase and collagenase inhibition activity. *Fitoterapia*, *143*(2020), 1-12.

Angkatavanich, J., Dahlan, W., Nimmannit, U., Sriprasert, V., & Sulongkood, N. (2009). Development of clay liquid detergent for Islamic cleansing and the stability study. *International Journal of Cosmetic Science*, *31*(2), 131–141.

ASEAN. (2017). ASEAN Guidelines on Limits of Contaminants for Cosmetics. *Association of South East Asian Nations (ASEAN)*, 1–5. http://www.hsa.gov.sg/content/dam/HSA/HPRG/Cosmetic_Products/ASEAN Guidelines on Limits of Contaminants for Cosmetics.pdf

Azila, A.K. and Nur Azilah, A. (2012). A comparison of cocoa heel cream and selective commercial heel creams on several skin surface parameters. *Malaysian Cocoa Journal*, *7*, 34–41.

Azmi, N., Hashim, P., Hashim, D. M., Halimoon, N., & Nik Majid, N. M. (2014). Anti-elastase, anti-tyrosinase and matrix metalloproteinase-1 inhibitory activity of earthworm extracts as potential new anti-aging agent. *Asian Pacific Journal of Tropical Biomedicine*, *4*(Suppl 1), S348–S352.

Bandeira, R. D. da C. C., Uekane, T. M., Cunha, C. P. da, Cunha, V. S. da, Rodrigues, J. M., Godoy, R. L. de O., & la Cruz, M. H. C. de. (2012). Development and validation of a method for detection and quantification of ochratoxin A in green coffee using liquid chromatography coupled to mass spectrometry. *Food Science and Technology*, *32*(4), 775–782.

Beg, M. S., Ahmad, S., Jan, K., & Bashir, K. (2017). Status, supply chain and processing of cocoa - A review. *Trends in Food Science and Technology*, *66*, 108–116.

Belščak, A., Komes, D., Horžić, D., Ganić, K. K., & Karlović, D. (2009). Comparative study of commercially available cocoa products in terms of their bioactive composition. *Food Research International*, *42*(5–6), 707–716.

Bhaigyaba, T., Bag, G. C., & Grihanjali Devi, P. (2015). Assessment of total flavonoid content and antioxidant activity of methanolic rhizome extract of three *Hedychium* species of Manipur valley. *International Journal of Pharmaceutical Sciences Review and Research*, *30*(1), 154–159.

Björklund, S., Engblom, J., Thuresson, K., & Sparr, E. (2013). Glycerol and urea can be used to increase skin permeability in reduced hydration conditions. *European Journal of Pharmaceutical Sciences*, *50*(5), 638–645.

Blois, M. S. (1958). Antioxidant determinations by the use of a stable free radical [10]. *Nature*, *181*(4617), 1199–1200.

Bocca, B., Pino, A., Alimonti, A., & Forte, G. (2014). Toxic metals contained in cosmetics: A status report. *Regulatory Toxicology and Pharmacology*, *68*(3), 447–467.

Bogacz-Radomska, L., & Harasym, J. (2018). β-Carotene-properties and production methods. *Food Quality and Safety*, *2*(2), 69–74.

Boligon, A. A. (2014). Technical evaluation of antioxidant activity. *Medicinal Chemistry*, *4*(7), 517–522.

Bonina, F., Lanza, M., Montenegro, L., Puglisi, C., Tomaino, A., Trombetta, D., Castelli, F., & Saija, A. (1996). Flavonoids as potential protective agents against photo-oxidative skin damage. *International Journal of Pharmaceutics*, *145*(1–2), 87–94.

Bonne, K., & Verbeke, W. (2008). Religious values informing halal meat production and the control and delivery of *halal* credence quality. *Agriculture and Human Values*,*25*(1), 35–47.

Borowska, S., & Brzóska, M. M. (2015). Metals in cosmetics: Implications for human health. *Journal of Applied Toxicology*, *35*(6), 551–572.

Brabo de Sousa, S. H., de Andrade Mattietto, R., Campos Chisté, R., & Carvalho, A. V. (2018). Phenolic compounds are highly correlated to the antioxidant capacity of genotypes of *Oenocarpus distichus* Mart. fruits. *Food Research International*, *108*, 405–412.

Brunetto, M. del R., Cayama, Y. D., Gutiérrez, L., Roa, S. C., Méndez, Y. C., Gallignani, M., Zambrano, A., Gómez, Á., & Ramos, G. (2009). Headspace gas chromatography-mass spectrometry determination of alkylpyrazines in

cocoa liquor samples. *Food Chemistry*, *112*(1), 253–257.

Caligiani, A., Marseglia, A., & Palla, G. (2015). Cocoa: Production, Chemistry, and Use. In *Encyclopedia of Food and Health* (1st ed.). Elsevier Ltd.

Cartea, M. E., Francisco, M., Soengas, P., & Velasco, P. (2011). Phenolic compounds in *Brassica* vegetables. *Molecules*, *16*(1), 251–280.

Charanjit Kaur & Harish C. Kapoor. (2009). Antioxidant activity and total phenolic content of some Turkish pomegranate varieties. *Acta Horticulturae*, *818*, 241–248.

Chang, C., Yang, M., Wen, H., & Chern, J. (2002). Estimation of Total Flavonoid Content in propolis by two complementary colorimetric methods. *Journal of Food and Drug Analysis*, *10*(3), 7802.

Chen G., S, Chen., Y, Xie., F, Chen.,Y, Zhao., C, Luo., Y, Gao. (2015). Total phenolic, flavonoid and antioxidant activity of 23 edible flowers subjected to *in vitro* digestion. *Journal of Functional Foods*, *17*, 243–259.

Chen, X., Sullivan, D. A., Sullivan, A. G., Kam, W. R., & Liu, Y. (2018). Toxicity of cosmetic preservatives on human ocular surface and adnexal cells. *Experimental Eye Research*, *170*, 188–197.

Chengcheng Zhang, Daqun Liu, Liehong Wu, Jianming Zhang, X. L. and W. (2019). Chemical characterization and antioxidant properties of ethanolic extract and its fractions from sweet potato (*Ipomoea batatas* L.) leaves. *Foods (MDPI)*, *18*.

Chiocchio, I., Mandrone, M., Sanna, C., Maxia, A., Tacchini, M., & Poli, F. (2018). Screening of a hundred plant extracts as tyrosinase and elastase inhibitors, two enzymatic targets of cosmetic interest. *Industrial Crops and Products*, *122*(June), 498–505.

Cortex Technology. (2012). Instruction Manual SkinLab Z5010108 UK.docx. DermaLab® Series SkinLab Combo Instruction Manual. 38.

Dai, J., & Mumper, R. J. (2010). Plant phenolics: Extraction, analysis and their antioxidant and anticancer properties. *Molecules*, *15*(10), 7313–7352.

Department of Standards Malaysia. (2008). Islamic Consumer Goods - Part 1: Cosmetic and personal care - General guidelines. *MS 2200: P*, 1–17. https://law.resource.org/pub/my/ibr/ms.2200.1.e.2008.pdf

de Souza, P. A., Moreira, L. F., Sarmento, D. H. A., & da Costa, F. B. (2018). Cacao - *Theobroma cacao*. *Exotic Fruits*, *3*(2001), 69–76.

Eldin.Elhag, D., Osman, H. O., & Dahab, A. A. (2015). Investigation of mercury content in cosmetic products by using direct mercury analyzer. *American Journal of Pharmacy Technology Research*, *5*(June), 205–212.

Elmorsy, T. H. and Hafez, E. A. (2016). Microbial contamination of some cosmetic preparations in Egypt. *International Journal of Agricultural Technology*, *12*(3), 471–481.

Emad, A. S. and Sanaa, M. M. S. (2013). Antioxidant compounds, assays of determination and mode of action. *African Journal of Pharmacy and Pharmacology*, *7(10)*, 528-539.

Enzolifescience. *Neutrophil Elastase Colorimetric Drug Discovery Kit*. www.enzolifesciences.com. https://www.enzolifesciences.com/BML-AK497/neutrophil-elastase-colorimetric-drug-discovery-kit/.

Epstein, H. (2009). Cosmeceuticals and polyphenols. *Clinics in Dermatology*, *27*(5), 475–478.

Ersoy, E., Eroglu Ozkan, E., Boga, M., Yilmaz, M. A., & Mat, A. (2019). Anti-aging potential and anti-tyrosinase activity of three *Hypericum* species with focus on phytochemical composition by LC–MS/MS. *Industrial Crops and Products 141(2019)*, 1-9.

Gasser, P., Lati, E., Peno-Mazzarino, L., Bouzoud, D., Allegaert, L., & Bernaert, H. (2008). Cocoa polyphenols and their influence on parameters involved in *ex vivo* skin restructuring. *International Journal of Cosmetic Science*, *30*(5), 339–345.

Gattefossé. Personal Care Product guide. https://www.gattefosse.com/

Gowder, S. K. M. and S. J. T. (2015). *Members of Antioxidant Machinery and Their Functions. 60-85*.

Hagiwara, K. A., & Wright, A. D. (2015). Tea Leaf Age, shade and characteristic levels of l-theanine, caffeine, (-)-epigallocatechin gallate (EGCG), (-)-epigallocatechin (EGC), (-)-epicatechin (EC), and (-)-epicatechin Gallate (ECG). In *Processing and Impact on Active Components in Food*. Elsevier Inc.

Hashim, P., & Mat Hashim, D. (2013). A review of cosmetic and personal care products: Halal perspective and detection of ingredient. *Pertanika Journal of Science and Technology*, *21*(2), 281–292.

Hermund, D. B. (2018). Antioxidant properties of seaweed-derived substances. In *Bioactive Seaweeds for Food Applications: Natural Ingredients for Healthy Diets*. Elsevier Inc.

Hernández-Hernández, C., Viera-Alcaide, I., Morales-Sillero, A. M., Fernández-Bolaños, J., & Rodríguez-Gutiérrez, G. (2018). Bioactive compounds in Mexican genotypes of cocoa cotyledon and husk. *Food Chemistry*, *240*(2017), 831–839.

Hiroshi, U., Shizuka, Y., Riya, S. A., Takumi, O., and Ken, K. (2014). Systematic evaluation and mechanistic investigation of antioxidant activity of fullerenols

using β-Carotene bleaching assay. *Journal of Nanomaterials, 2014*, 1-7.

Hsu, C. K., Chang, C. T., Lu, H. Y., & Chung, Y. C. (2007). Inhibitory effects of the water extracts of *Lavendula sp*. on mushroom tyrosinase activity. *Food Chemistry*, *105*(3), 1099–1105.

Huang, D., Boxin, O. U., & Prior, R. L. (2005). The chemistry behind antioxidant capacity assays. *Journal of Agricultural and Food Chemistry*, *53*(6), 1841–1856.

Information and Operating Instruction (2005). Visioscan® VC 98 and the Software SELS (Surface Evaluation of the Living Skin). 1-53

Iris F. F. Benzie, and J. J. S. (1996). The Ferric Reducing Ability of Plasma (FRAP) as a measure of "'Antioxidant Power"': The FRAP Assay Iris. *Analytical Biochemistry*, *239*, 70–76.

Jalil, A. M. M., & Ismail, A. (2008). Polyphenols in cocoa and cocoa products: Is there a link between antioxidant properties and health? *Molecules*, *13*(9), 2190–2219.

Jerkovic, V., Broihan, M., Monnart, E., Nguyen, F., Nizet, S., & Collin, S. (2010). Stilbenic profile of cocoa liquors from different origins determined by RP-HPLC-APCI(+)-MS/MS. Detection of a new resveratrol hexoside. *Journal of Agricultural and Food Chemistry*, *58*(11), 7067–7074.

José, T., Alexandra, G., E. Manuela, G., Jorge, G. & Fernanda, B. (2013). Hydroxycinnamic acid antioxidants: An Electrochemical Overview. *BioMed Research International, 2013*, 1-11.

Kapoor, C. K. & H. C. (2002). Anti-oxidant activity and total phenolic content of some Asian vegetables. *International Journal of Food Science and Technology*, *37*, 153–161.

Katz, D. L., Doughty, K., & Ali, A. (2011). Cocoa and chocolate in human health and disease. *Antioxidants and Redox Signaling*, *15*(10), 2779–2811.

Kavitha, J. V. H. (2018). Microbial analysis of cosmetics and design of an effective preservative. *International Journal of Pharmaceutical Sciences Review and Research*. *51*(14), 76–79

Kedare, S. B., & Singh, R. P. (2011). Genesis and development of DPPH method of antioxidant assay. *Journal of Food Science and Technology*, *48*(4), 412–422.

Kim, E., Kim, S., Nam, G. W., Lee, H., Moon, S., & Chang, I. (2009). The alkaline pH-adapted skin barrier is disrupted severely by SLS-induced irritation. *International Journal of Cosmetic Science*, *31*(4), 263–269.

Kim, J., Lee, K. W., & Lee, H. J. (2011). Cocoa (*Theobroma cacao*) seeds and phytochemicals in human health. *Nuts and Seeds in Health and Disease*

Prevention, 351–360.

Kozłowska, A., & Szostak-Wegierek, D. (2014). Flavonoids-food sources and health benefits. *Roczniki Państwowego Zakładu Higieny*, *65*(2), 79–85.

Lamuela-Raventós, R. M. (2017). Folin-Ciocalteu method for the measurement of total phenolic content and antioxidant capacity. *Measurement of Antioxidant Activity and Capacity: Recent Trends and Applications*,107–115.

Lawton, S. (2019). Skin 1: the structure and functions of the skin. *Nursing Times*, *115*(12), 30–33.

Magi, E., Bono, L., & Di Carro, M. (2012). Characterization of cocoa liquors by GC-MS and LC-MS/MS: Focus on alkylpyrazines and flavanols. *Journal of Mass Spectrometry*, *47*(9), 1191–1197.

MakingCosmetics. Stability testing of cosmetics. https://www.makingcosmetics.com/Stability-Testing-of-Cosmetics

Makrantonaki, E., & Zouboulis, C. C. (2007). Molecular mechanisms of skin aging: State of the art. *Annals of the New York Academy of Sciences*, *1119*(1), 40–50.

Malaysian Cocoa Board. (2010). Manual of Semi-Finished Cocoa Products Analysis. 1-104. ISBN 978-983-2433-07-1.

Manach, C., Scalbert, A., Morand, C., Rémésy, C., & Jiménez, L. (2004). Polyphenols: Food sources and bioavailability. *American Journal of Clinical Nutrition*, *79*(5), 727–747.

Mandrone, M., Lorenzi, B., Venditti, A., Guarcini, L., Bianco, A., Sanna, C., Ballero, M., Poli, F., & Antognoni, F. (2015). Antioxidant and anti-collagenase activity of *Hypericum hircinum* L. *Industrial Crops and Products*, *76*, 402–408.

Mat Jusoh, N. H., & Panatik, S. A. (2016). The effects of safety climate on safety performance: An evidence in a Malaysian-based electric electronic and manufacturing plant. *Sains Humanika*, *8*(4–2), 52–63.

Mendes, V. M., Coelho, M., Tomé, A. R., Cunha, R. A., & Manadas, B. (2019). Validation of an LC-MS/MS Method for the quantification of caffeine and theobromine using non-matched matrix calibration curve. *Molecules*, *24*(16) 1-14.

Micheli, F., Guiltinan, M., Gramacho, K. P., Wilkinson, M. J., Figueira, A. V. de O., Cascardo, J. C. de M., Maximova, S., & Lanaud, C. (2010). Functional genomics of cacao. *Advances in Botanical Research*, *55*(C), 119–177.

Microchem Laboratory. Freeze-Thaw Stability Testing. http://microchemlab.com/test/freeze-thaw-stability-testing.

Miller, N. J., Rice-Evans, C., Davies, M. J., Gopinathan, V., & Milner, A. (1993). A novel method for measuring antioxidant capacity and its application to monitoring the antioxidant status in premature neonates. *Clinical Science*, *84*(4), 407–412.

Mueller, L., & Boehm, V. (2011). Antioxidant activity of β-carotene compounds in different *in vitro* assays. *Molecules*, *16*(2), 1055–1069.

National Pharmaceutical Regulatory Agency. (2017). *Guidelines for Control of Cosmetic Products in Malaysia National Pharmaceutical Regulatory Agency Ministry of Health, Malaysia*. 1–13. https://www.npra.gov.my/images/Guidelines Central/Guidelines on Cosmetic/2017/feb2017/guidelines for control of cosmetic products in Malaysia.pdf

Natsume, M., Osakabe, N., Yamagishi, M., Takizawa, T., Naka-Mura, T., Miyatake, H., Hatano, T. And Yoshida, T. (2000). Analyses of polyphenols in cacao liquor, cocoa, and chocolate by normal-phase and reverse-phase HPLC. *Bioscience Biotechnology Biochemistry 64*(12),2581–2587.

Neukam, K., Stahl, W., Tronnier, H., Sies, H., & Heinrich, U. (2007). Consumption of flavanol-rich cocoa acutely increases microcirculation in human skin. *European Journal of Nutrition*, *46*(1), 53–56.

Nishikawa, D., Zague, V., Vieira, R., Kaneko, T., & Baby, A. (2007). Avaliação da estabilidade de máscaras faciais peel-off contendo rutina. *Rev. Ciênc. Farm. Básica Apl*, *11*, 227–233.

Norliza, A.W., Russly, A.R., Puziah, H., Amin, and Shuhaimi, M. (2016). Human cheek skin texture improvement by cocoa bean extract incorporated in a cosmetic formulation. *Malaysian Cocoa Journal*, *9*(1), 160–169.

Orisakwe, O. E., & Otaraku, J. O. (2013). Metal concentrations in cosmetics commonly used in Nigeria. *The Scientific World Journal*, *2013*, 1-7.

Osakabe, N., Yamagishi, M., Sanbongi, C., Natsume, M., Takizawa, T., & Osawa, T. (1998). The antioxidative substances in cacao liquor. *Journal of Nutritional Science and Vitaminology*, *44*(2), 313–321.

Othman, A., Ismail, A., Abdul Ghani, N., & Adenan, I. (2007). Antioxidant capacity and phenolic content of cocoa beans. *Food Chemistry*, *100*(4), 1523–1530.

Panche, A. N., Diwan, A. D., & Chandra, S. R. (2016). Flavonoids: An overview. *Journal of Nutritional Science*, *5(47)* 1-15.

Pandey, K. B., & Rizvi, S. I. (2009). Plant polyphenols as dietary antioxidants in human health and disease. *Oxidative Medicine and Cellular Longevity*, *2*(5), 270–278.

Pellevoisin, C., Videau, C., Briotet, D., Grégoire, C., Tornier, C., Alonso, A., Rigaudeau, A. S., Bouez, C., & Seyler, N. (2018). SkinEthic™ RHE for *in*

vitro evaluation of skin irritation of medical device extracts. *Toxicology in Vitro, 50,* 418–425.

Pereira, J. X., & Pereira, T. C. (2018). Cosmetics and its health risks. *Global Journal of Medical Research*, *18*(2), 63–70.

Pientaweeratch, S., Panapisal, V., & Tansirikongkol, A. (2016). Antioxidant, anti-collagenase and anti-elastase activities of *Phyllanthus emblica*, *Manilkara zapota* and silymarin: an *in vitro* comparative study for anti-aging applications. *Pharmaceutical Biology*, *54*(9), 1865–1872.

Puziah, H., Shahab, N., Masilamani, T., Rozita, B., & Rohaidah, I. (2009). A cosmetic analysis in compliance with the legislative requirements, *halal* and quality control. *Malaysian Journal of Chemistry*, *11*(1), 81–87.

Quelal-Vásconez, M. A., Lerma-García, M. J., Pérez-Esteve, É., Arnau-Bonachera, A., Barat, J. M., & Talens, P. (2020). Changes in methylxanthines and flavanols during cocoa powder processing and their quantification by near-infrared spectroscopy. *LWT-Food Science and Technology 117*, 108598.

Rabeta, M. S. & An, Nabil. (2012). Total phenolic compounds and scavenging activity in *Clitoria ternatea* and *Vitex negundo* linn. *International Food Research Journal, 20*(1), 495-500.

Ramli, N., Yatim, A. M., Said, M., & Hok, H. C. (2001). HPLC Determination of Methylxanthines and Polyphenols Levels In Cocoa and Chocolate Products. *Malaysian Journal of Analytical Sciences, 7*(2), 377–386.

Redovniković, I. R., Delonga, K., Mazor, S., Dragović-Uzelac, V., Carić, M., & Vorkapić-Furač, J. (2009). Polyphenolic content and composition and antioxidative activity of different cocoa liquors. *Czech Journal of Food Sciences*, *27*(5), 330–337.

Rusconi, M., & Conti, A. (2010). *Theobroma cacao* L., the Food of the Gods: A scientific approach beyond myths and claims. *Pharmacological Research*, *61*(1), 5–13.

Sabahannur, S., Alimuddin, S., & Rahmawati, -. (2018). Changes in phenol level and antioxidant activity of cocoa beans during fermentation and roasting. *Journal of Food Research*, *7*(4), 23.

Sánchez-Rabaneda, F., Jáuregui, O., Casals, I., Andrés-Lacueva, C., Izquierdo-Pulido, M., & Lamuela-Raventós, R. M. (2003). Liquid chromatographic/electrospray ionization tandem mass spectrometric study of the phenolic composition of cocoa (*Theobroma cacao*). *Journal of Mass Spectrometry*, *38*(1), 35–42.

Scapagnini, G., Davinelli, S., Di Renzo, L., De Lorenzo, A., Olarte, H. H., Micali, G., Cicero, A. F., & Gonzalez, S. (2014). Cocoa bioactive compounds: Significance and potential for the maintenance of skin health. *Nutrients*, *6*(8),

3202–3213.

Schinella, G., Mosca, S., Cienfuegos-Jovellanos, E., Pasamar, M. Á., Muguerza, B., Ramón, D., & Ríos, J. L. (2010). Antioxidant properties of polyphenol-rich cocoa products industrially processed. *Food Research International*, *43*(6), 1614–1623.

Shahidi, F. (2015). Antioxidants: Principles and applications. In *Handbook of Antioxidants for Food Preservation*. Elsevier Ltd.

Sjerobabski-Masnec, I., & Šitum, M. (2010). Skin aging. *Acta Clinica Croatica*, *49*(4), 515–518

Sorrenti, V., Ali, S., Mancin, L., Davinelli, S., Paoli, A., & Scapagnini, G. (2020). Cocoa polyphenols and gut microbiota interplay: Bioavailability, prebiotic effect, and impact on human health. *Nutrients*, *12*(7), 1–16.

Stanner, S., & Weichselbaum, E. (2012). Antioxidants. *Encyclopedia of Human Nutrition*, *1–4*, 88–99.

Sugibayashi, K., Yusuf, E., Todo, H., Dahlizar, S., Sakdiset, P., Arce, F. J., & See, G. L. (2019). Halal cosmetics: A review on ingredients, production, and testing methods. *Cosmetics*, *6*(3), 1–17.

Sveikata, K., Balciuniene, I., & Tutkuviene, J. (2011). Factors influencing face aging. Literature review. *Stomatologija, Baltic Dental and Maxillofacial Journal*, *13*(4), 113–116.

Syafiq, A., Amir, I. Z. & Sharon, W. X. R. (2014). Mixture experiment on rheological properties of dark chocolate as influenced by cocoa butter substitution with xanthan gum/corn starch/ glycerin blends. *International Food Research Journal*, *21*(5), 1887-1892

Tapas, A., Sakarkar, D., & Kakde, R. (2008). Flavonoids as Nutraceuticals: A Review. *Tropical Journal of Pharmaceutical Research*, *7*(3).

Thring, T. S. A., Hili, P., & Naughton, D. P. (2009). Anti-collagenase, anti-elastase and anti-oxidant activities of extracts from 21 plants. *BMC Complementary and Alternative Medicine*, *9*, 1–11.

Tobin, D. J. (2017). Introduction to skin aging. *Journal of Tissue Viability*, *26*(1), 37–46.

Verna, R. (2013). The history and science of chocolate. *Malaysian Journal of Pathology*, *35*(2), 111–121.

Vieira, R. P., Fernandes, A. R., Kaneko, T. M., Consiglieri, V. O., Pinto, C. A. S. D. O., Pereira, C. S. C., Baby, A. R., & Velasco, M. V. R. (2009). Physical and physicochemical stability evaluation of cosmetic formulations containing soybean extract fermented by Bifidobacterium animalis. *Brazilian Journal of*

Pharmaceutical Sciences, *45*(3), 515–525.

Vijayakumar, R., Gani, S. S. A., & Mokhtar, N. F. (2017). Anti-elastase, anti-collagenase and antimicrobial activities of the underutilized red pitaya peel: An *in vitro* study for anti-aging applications. *Asian Journal of Pharmaceutical and Clinical Research*, *10*(8), 251–255.

Vivek, P. V. and Lata, I. S. (2017). Gamma irradiation of medicinally important plants and the enhancement of secondary metabolite production. *International Journal of Radiation Biology*, *93(9)*, 967–979.

Wilson, D. W., Nash, P., Singh, H., Griffiths, K., Singh, R., De Meester, F., Horiuchi, R., & Takahashi, T. (2017). The role of food antioxidants, benefits of functional foods, and influence of feeding habits on the health of the older person: An overview. *Antioxidants*, *6*(4), 1–20.

Yagi, M., & Yonei, Y. (2018). Glycative stress and skin aging. *Glycative Stress Research*, *5*(1), 50–54.

Yusof, N. Z., Abd Gani, S. S., Azizul Hasan, Z. A., & Idris, Z. (2018). Skin and eye irritation assessment of oil palm (*Elaeis guineensis*) leaf extract for topical application. *International Journal of Toxicology*, *37*(4), 335–343.

Zhou, S., Shao, L., Wang, L., Yi, Y., Deng, B., & Wen, N. (2012). Masking ability of IPS e.max all-ceramics system of HO series. *Key Engineering Materials*, *512–515*(2012), 1784–1787.

Zolghadri, S., Bahrami, A., Hassan Khan, M. T., Munoz-Munoz, J., Garcia-Molina, F., Garcia-Canovas, F., & Saboury, A. A. (2019). A comprehensive review on tyrosinase inhibitors. *Journal of Enzyme Inhibition and Medicinal Chemistry*, *34*(1), 279–309.