UNIVERSITI PUTRA MALAYSIA

ENZYMATIC ESTERIFICATION OF DIHYDROCAFFEIC ACID AND EVALUATION OF ANTIOXIDANT ACTIVITIES OF THE SYNTHESIZED ALKYL-ESTERS

SOMAYEH GHOLIVAND

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By

SOMAYEH GHOLIVAND

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

December 2016

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DEDICATION

This thesis is dedicated to my family for nursing me with affections and love and their dedicated partnership for success in my life.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

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Chairman : Associate Professor Lasekan Olusegun Olaniyi, PhD
Faculty : Food Science and Technology

Solubility limitations of phenolic acids in many lipidic environments restrict their application as effective antioxidants. Enzymatic esterification of phenolic acids in a green media such as ionic liquid improves the lipophilicity of the resultant compounds. Herein, the investigation of a biocatalysts process for the esterification of dihydrocaffeic acid with different ionic liquids in order to improve the conversion of the phenolic acid in a shorter time and increase productivity of target product was carried out. To achieve the maximum conversion yield, the lipophilization of dihydrocaffeic acid (DHCA) by its enzymatic esterification with hexanol in the selected ionic liquid (as a model) was optimized by response surface methodology (RSM) using a five-level and four independent variables including: dosage of the enzyme (in relation to the total weight of substrates), hexanol/dihydrocaffeic acid mole ratio, reaction temperature and reaction time. The obtained optimal conditions were applied for the synthesis of the other n-alkyl esters with different chain lengths. Subsequently, the synthesized esters were separated from unreacted compounds and purified via a silica gel column. The purified alkyl-esters were identified by Fourier transform infrared (FTIR) and Nuclear magnetic resonance (NMR) analysis. Finally, the effects of alkyl chain length and concentration on the anti-oxidative properties of the resultant purified esters was investigated using *β*-carotene bleaching (*BCB*) and free radical scavenging method DPPH and also compared with butylated hydroxytoluene (BHT) as reference compound. According to the attained results, among ionic liquids tested, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide was the best solvent with the highest bioconversion. Furthermore, results of the optimization showed that hexyl dihydrocaffeate (HDHCA) conversion yield was significantly *($p<0.05$)* affected by the linear, quadratic and the interaction effects of all the variables examined. Thus, an empirical equation was developed to describe and predict the variation of the response variable. The optimization procedure showed that the optimum molar conversion yield for hexyl dihydrocaffeate (HDHCA) (Y_1 = 84.41%) was obtained using 41.6%

enzyme load at 39.4ºC for 77.5 h and 9.3 × 10^{-4} mM hexanol to DHCA ratio. According to the obtained results from synthesized alkyl esters, both esters' concentration and their chain-length had significant *($p<0.05$)* effects on their antioxidant assays. Moreover, the scavenging activity of the tested compounds was methyl ester > hexyl ester > dodecyl ester > octadecyl ester > BHT while the order of *BCB* anti-oxidative activity was BHT > octadecyl ester > dodecyl ester > hexyl ester > methyl ester. Therefore, in the emulsion system, the hydrophobicity and solubility of the tested esters affected the antioxidant activity of esters which revealed that the antioxidant with hydrophobic character had better anti-oxidative activity in an emulsion system.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENGESTERAN ENZIM ASID DIHIDROKAFEIK DENGAN HEXANOL DI DALAM CECAIR IONIK YANG BERBEZA DAN PENILAIAN AKTIVITI ANTIOKSIDAN DARIPADA ALKIL-ESTER YANG DISINTESIS

Oleh

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Keterlarutan asid fenolik yang terhad di dalam pelbagai persekitaran berlipid telah menyekat pengaplikasiannya sebagai antioksidan yang efektif. Pengesteran enzim asid fenolik di dalam media mesra alam seperti cecair ionik meningkatkan kecenderungan lipofilik bagi sebatian yang dihasilkan. Oleh itu, proses pemangkin biologi tentang pengesteran asid dengan pelbagai jenis cecair ionic dikaji untuk menyinkatkan masa penukaran asid fenolik dan meningkatkan produktiviti produk sasaran. Untuk mencapai hasil penukaran maksimum, kecenderungan lipofilik asid dihidrokafeik (DHCA) oleh pengesteran dengan heksanol di dalam cecair ionik terbaik (1-butil-3-methylimidazoliumbis (trifluorometilsulfonil) imida, dalam kehadiran *Candida antartika* lipase B (Novozyme 435) telah dioptimumkan dengan kaedah tindak balas permukaan (RSM) menggunakan lima peringkat dan empat pemboleh ubah bebas termasuk: dos enzim (berhubung dengan jumlah berat substrat); nisbah mol heksanol/asid dihidrokafeik; suhu tindak balas dan masa tindak balas. Syarat-syarat optimum yang diperolehi telah digunakan untuk sintesis ester n-alkil yang lain dengan panjang rantai yang berbeza. Selepas itu, ester yang tersintesis telah dipisahkan daripada sebatian yang tidak bertindak balas dan ditulenkan melalui kolum gel silika. Alkil-ester tulen telah dikenal pasti menggunakan analisis transformasi Fourier infra merah (FTIR) dan resonans magnetik nuklear (NMR). Akhirnya, kesan kepanjangan rantai alkil pada sifat-sifat antioksidan ester tulen disiasat menggunakan pelunturan β-karotena (*BCB*) dan kaedah memerangkap radikal bebas DPPH dan dibandingkan dengan butilated hidroksitoluen (BHT) sebagai sebatian rujukan. Selain itu, berdasarkan keputusan yang diperolehi, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ialah pelarut yang terbaik dengan kadar penukaran yang tertinggi antara cacair ionic yang diuji. Hasil pengoptimuman menunjukkan hasil penukaran heksil dihidrokafeik yang bersandar secara signifikan ($p<0.05$) terhadap linear, kuadratik dan kesan interaksi semua pemboleh ubah yang diperiksa. Oleh itu, persamaan empirikal telah dibangunkan untuk menerang dan meramalkan perubahan pemboleh ubah bergerak balas. Prosedur pengoptimuman menunjukkan bahawa hasil penukaran molar optimum

untuk heksil dihidrokafeik (Y1 = 84,41%) telah diperolehi dengan menggunakan 41.6% beban enzim pada 39.4ºC 77.5 jam dan 9.3×10^{-4} mM heksanol kepada nisbah DHCA. Berdasarkan keputusan yang diperolehi daripada sintesis ester alkil, kepekatan dan rantai panjang ester mempunyai kesan signifikan *($p<0.05$*) ke atas aktiviti antioksidan. Tambahan lagi, aktiviti memerangkap oleh sebatian ujian adalah metil ester > heksil ester ≥ dodesil ester > oktadesil ester > BHT manakala susunan aktiviti BCB antioksidan adalah BHT > oktadesil ester > dodesil ester > heksil ester > metil ester. Oleh itu, di dalam sistem emulsi, sifat hidrofobik dan keterlarutan ester yang diuji telah berhubung kait dengan aktiviti antioksidan ester, yang mendedahkan bahawa antioksidan dengan karakter hidrofobik mempunyai aktiviti pengantioksidaan yang lebih baik di dalam sistem emulsi.

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I certify that a Thesis Examination Committee has met on 9 December 2016 to conduct the final examination of Somayeh Gholivand on her thesis entitled "Enzymatic Esterification of Dihydrocaffeic Acid and Evaluation of Antioxidant Activities of the Synthesized Alkyl-Esters" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

AA	Antioxidant Activity
AILs	Aprotic ionic liquids
ANOVA	Analysis of variance
BCB	β-Carotene Bleaching
BF_4	Tetrafluoroborate
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
CA	Caffeic acid
CCD	Central composite design
CnMe3N	Alkyltrimethylammonium
Cm	Centimetre
D	Desirability
DHCA	Dihydrocaffeic acid
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DPPH	1, 1-diphenyl-1-picrylhydrazyl
DTGS	Deuterated Triglycine Sulphate
Emim (NTf2)	1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide
eNOS	Endothelial Nitric Oxide Synthase
FTIR	Fourier transform infrared
G	Gram
H	Hydrogen
HCAs	Hydroxycinnamic acids

HDHCA	Hexyl Dihydrocaffeate
HPLC	High Performance Liquid Chromatography
Hydro-PCs	Hydrophilic phenolic compounds
IL 1	1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide
IL 2	1-butyl-3-methylimidazoliumhexafluorophosphate
IL 3	1-hexyl-3-methylimidazolium hexafluorophosphate
IL 4	1-octyl-3-methyllidazolium hexafluolorophosphate
ILs	Ionic liquids
IM	Imidazolium
LDL	Low-Density Lipoprotein
Lipo-PCs	Lipophilic Phenolic Compounds
µL	Microliter
µm	Micrometer
Mg	Milligram
MHz	Megahertz
Min	Minute
mL	Millilitre
mM	Milimolar
Mm	Millimeter
MTOA	Methyl trioctylammonium
NMR	Nuclear Magnetic Resonance
NTf2	Bis (trifluoromethylsulfonyl)imide
°C	Celsius
OG	Octyl gallate

%	Percent
%T	Percent of Transmittance
P	Probability
PF_6	Hexafluorophosphate
Ph•	Phenoxyl radical
PhH	Phenolic antioxidant
PILs	Protic ionic liquids
PUFA	Polyunsaturated fatty acids
R^2	Regression
ROO•	Peroxyl radical
ROOH	Hydro peroxide
RSM	Response Surface Methodology
TBHQ	Tert-butylated hydroquinone
TLA	Trilinolein
TLNA	Trilinolenin
TLC	Thin-Layer Chromatography
TY	Trans-esterification Yield
3D	Three-dimensional
UV	Ultraviolet
v/v	Volume per volume
w/w	Weight per weigh

CHAPTER 1

INTRODUCTION

1.1 Background

The several thousand phenolic compounds naturally present in almost all plant materials, including food products of plant origin (Psomiadou & Tsimidou, 2002). Interest in food phenolic has grown greatly because of their antioxidant and free radical scavenging ability and potential health benefits as well. Attention has increased mostly in finding naturally occurring antioxidants for use in foods or medicinal materials to replace synthetic antioxidants that, in some cases, have been reported to be carcinogenic (Zheng & Wang, 2001).

Among natural antioxidants, phenolic acids as well as their derivatives are the major subgroup of phenolics broadly dispersed in the plant kingdom such as vegetables, fruits and cereals. There has been on-going research attention in phenolic derivatives acid as the common constituents of plant tissues not only due to antioxidant effects but also due to the variety of several pharmacological and biological applications such as neuroprotective, anti-carcinogenic and anti-inflammatory abilities (Castelluccio et al., 1996; Laranjinha et al., 1994; Rice-Evans et al., 1996). In addition, some of the phenolic acids have been reported to possess UV-absorbing efficiency for application in sunscreen formulation (Compton et al., 2000). Consequently, phenolic acids have the potential to be suitable components in cosmetics, health, food and pharmaceuticals.

Most of the food systems are emulsion. In general, due to the hydrophilic character of phenolic compounds, they will most probably be found in the aqueous phase (Frankel et al., 1994; Porter, 1993). One major barrier in the functional properties of phenolic acids, is their hydrophilicity character in non-polar media, emulsions and oil-based formulae which restricts their application in lipophilic formulation of food processing and cosmetic industries due to the reduction of their antioxidant capabilities in these systems (Figueroa-Espinoza & Villeneuve, 2005; Lue et al., 2005).

A practical approach to address the solubility limitation of phenolic acids is lipophilization through esterifying their carboxylic acid group with aliphatic side-chain groups (Buisman et al., 1998; Lue et al., 2005; Sabally et al., 2005b; Stamatis et al., 2001) or trans-esterification with triacylglycerols (Compton et al., 2000; Laszlo et al., 2003) so that it retains its original functional properties. Furthermore, conventional esterification such as chemical processes can be applied for synthesizing lipophilic compounds from phenolic acids; however, their disadvantages are loss of product yield due to oxidation under certain pH conditions besides the susceptibility of phenolics to heating. Thus, the various new synthesis

pathways are needed to utilize the esterification of natural antioxidants. As an alternative, enzyme-catalyzed biosynthesis of phenolic esters in ionic liquids or organic solvents is known as a suitable approach for esterification of phenolic compounds owing to its capability of product separation and recovering the used enzyme (Auerbach et al., 1998; Jain et al., 2005).

Enzymatic esterification of phenolic acid (using lipase) with short or medium chain length aliphatic alcohols has been studied (Buisman et al., 1998; Stamatis et al., 2001). A lipase-catalyzed reaction has been mostly applied in organic solvent medium in order to synthesize valuable esters under mild conditions with the purpose of their applications in food industries (Auerbach et al., 1998; Gandhi et al., 2000). The chief reason for the inefficiency of this kind of lipolization is low solubility of phenolic acids in most organic reaction solvents whereas the enzyme is active and *vice versa* (Eastoe et al., 2005).

Ionic liquids are able to give different reactivity and selectivity to various bio-catalytic reactions as a medium and also can dissolve numerous compounds due to existence of some properties compared with conventional organic solvents. In fact, their structures are composed of bulky cation and a small anion. The properties of ionic liquids can be easily altered by combination of different cations and anions as well. Besides, they possess no vapor pressures and entail a wide-ranging temperature for the liquid phase. Consequently, synthesis of plentiful ionic liquids with different compositions is possible (Jain et al., 2005). Many studies have been done on enzymatic transformation of various phenolic acids in several ionic liquids as a replacement reaction media with organic solvents (Jain et al., 2005; Kurata et al., 2010; Yang et al., 2012b).

Dihydrocaffeic acid (DHCA) is a hydrophilic compound and has low solubility in oil based foods. Thus, its modification via esterification with alcohols can be used as a tool to produce derivatives with increased lipophilicity and antioxidant potency. In comparison with caffeic acid, little information is presented about the anti-oxidative activity of dihydrocaffeic acid and its derivatives. Therefore, the specific objectives of this study were:

1. To investigate the enzymatic esterification of dihydrocaffeic acid (DHCA) and hexanol in different ionic liquids;
2. To optimize the enzymatic esterification conditions of dihydrocaffeic acid and hexanol in selected ionic liquid (NTf2) by response surface methodology (RSM); and
3. To evaluate the antioxidant activity of some synthesized alkyl dihydrocaffeic acid esters in the selected ionic liquid.

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