CHAPTER I

INTRODUCTION

1.1 Background

One of plant foods that has a great potential as source of antioxidant is curcumin, the major yellow pigment in turmeric, the ground rhizome of *Curcuma longa* Linn (Ohigashi *et al.*, 2014). While most of antioxidants present have either a phenolic functional group or a β-diketone group, curcumin is a unique antioxidant which contains a variety of functional groups such as β-diketone group, carbon-carbon double bonds, and phenyl rings containing hydroxyl and methoxy substituents (Aggarwal *et al.*, 2007).

Curcumin is a potent scavenger of a variety of reactive oxygen species such as peroxide anion free radical, hydroxyl radical, singlet oxygen, and nitrogen-centered free radical. Curcumin also has the capability to protect lipids, haemoglobin, and DNA against oxidative degradation. Pure curcumin has more potent superoxide anion scavenging activity compared to demethoxycurcumin (DMC) and bisdemethoxycurcumin (BDMC) in which three of them are parts of curcuminoids, a group of polyphenol in turmeric plant (Ohigashi *et al.*, 2014). Curcumin is found as the highest component of curcuminoids which is 77% while DMC and BDMC only 17% and 6% respectively (Jantarat, 2013). Therefore, curcumin is a high potential antioxidant and possible to be explored further.

However, there are limits to the use of curcumin given its susceptibility to hydrolysis at basic and neutral pH. Its half-life at neutral pH or phosphate buffer is less than 10 mins. Hence, in an attempt to enhance its stability to hydrolysis, synthetic derivatives of curcumin can be made. Furthermore, preceding modification of curcumin's α,β-unsaturated 1,3-diketone moiety as semicarbazone and pyrazole derivatives has been done and found to improve the antioxidant and anti-inflammatory properties over curcumin which is an interesting point in enhancing health benefit of curcumin (LaManna *et al.*, 2011).

As past modifications of curcumin as semicarbazone and pyrazole derivatives improve antioxidant activities of curcumin, pyrimidine derivative can also be a potential modification of curcumin with enhanced antioxidant property. Pyrimidines are heterocyclic aromatic compounds containing two nitrogen atoms at positions 1 and 3 of the six membered rings. Heterocycles containing pyrimidine subdivision are of great interest because many of which exhibit useful biological activities and clinical applications, such as vitamin B_1 (thiamine) and 2,4-diaminopyrimidine (Brodiprim) as an antibacterial compound, leading to an interest in researching further regarding modification of curcumin as pyrimidine derivative (Sharma *et al.*, 2014).

1.2 Research Problem

Modification of curcumin can enhance the antioxidant properties of curcumin. However, modification of curcumin with solvent and catalyst can lead to environmental damage. Therefore, solvent-free modification was performed in this research as an option in order to minimize environmental waste as well as make the modification easier and faster. While for catalyst, as catalyst is required to accelerate the modification reaction, green catalyst (eco-friendly catalyst) which is citric acid found in citrus fruits, was used in this research. Furthermore, modification of curcumin requires aromatic aldehyde as a modifier. However, as the final modified product was expected to be applicable in food industry, the aromatic aldehyde that was involved had to be food-grade. Thus, cinnamaldehyde and benzaldehyde which are simple aromatic aldehydes found in cinnamon and almond respectively, were used in this experiment.

1.3 Objectives

1.3.1 General Objective

The general objectives of this research were to conduct modification of curcumin and study the antioxidant activity of the modified compound.

1.3.2 Specific Objective

The specific objectives of this research were:

1. To compare modification products of curcumin from different use of ethanol as solvent which were with solvent and without solvent as well as from different concentration of citric acid as catalyst which were 5 mmol%, 10 mmol%, 20 mmol%, and 25 mmol% ($mmol/mmol_{substrate}$) in terms of yield and TLC spot in order to determine the best use of solvent and the best concentration of catalyst.

2. To apply the best use of solvent and the best concentration of catalyst into modification of curcumin and dimedone with two different aldehydes which were cinnamaldehyde and benzaldehyde each.
3. To characterize and compare modification products of curcumin and dimedone from both aldehydes in terms of yield, TLC spot, UV-Vis spectrophotometry graph, and antioxidant activity.
4. To compare modified compound with the highest antioxidant activity with commercial curcumin in terms of antioxidant activity.
5. To analyse structure and presence of the modified compound with the highest antioxidant activity with LC-MS.