Effect of Heating on the Stability of Curcumin on *Temulawak* Oleoresin Encapsulated in Arrowroot Starch Nanoparticles

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Abstract. Storage and heat exposure will cause water absorption and oxidation which lead to degradation and changes in physicochemical properties of the active ingredient and will affect its performance in-vivo. The purpose of the study was to determine the effect of storage and heat treatment on the stability of *temulawak*-curcumin oleoresin encapsulated with arrowroot starch nanoparticles. The treatments tested included the type of encapsulant which was two kinds of matrixes: two kinds of storing temperature, oven drying, and sunlight exposure. The results showed that the nanoparticle starch matrix had good stability during storage as well as against heat and sun exposure compared to the maltodextrin matrix. The matrix of ethanol precipitation results in better stability during storage than that of butanol precipitation. After storage for 60 days, the reduction of curcumin content was half at room temperature compared to 40°C (20 and 40% respectively). Storage at 40°C temperature at butanol matrix showed drastic curcumin degradation compared to other matrixes. Meanwhile, the butanol starch matrix showed better protection against curcumin degradation against oven drying heat treatments. Curcumin was too susceptible to sunlight exposure with a level below 10% for both matrixes used.

1 Introduction

Curcuma xanthorrhiza Roxb. (Family: Zingiberaceae) is one of the native Indonesian medicinal crops with high value locally familiar as "*Temulawak*" or Java turmeric. More than 40 active compounds, such as terpenoids, curcuminoids, and other phenolic compounds, have been isolated and identified from *C. xanthorrhiza* [1]. Curcumin is a kind of active ingredient in turmeric and *temulawak*/curcuma rhizome which have many health benefits for many kinds of curatives and preventive treatments, due to such activity as the antioxidant, anti-inflammatory, anti-cancer, anti-cholesterol, etc. Moreover, turmeric-based dietary supplements, including standardized extracts with high concentrations of curcumin, becoming more popular in the United States and elsewhere [2]. Globally, the market size of

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curcumin was valued at USD 58.4 million in 2019 and is expected to experience a CAGR (compound annual growth rate) of 16.1% from 2020 to 2028 [3]. Curcuma rhizome/*temulawak* as a source of curcuminoid is more beneficial than turmeric rhizome even though the content of *temulawak* is lower than that of turmeric. The curcuminoid content of *temulawak* powder rhizome is 4866 ppm, while the turmeric powder curcuminoid is 229,99 ppm [4].

Although it has good properties, curcumin has low solubility in water. Curcumin is also not resistant to changes in pH and temperature. In addition, curcumin is absorbed slowly and rapidly metabolized so that its bioavailability is low in the blood [5]. Moreover, curcumin application in an aqueous solution has a limitation for its basic pH range [6]. Curcumin solubility can be enhanced by chemical modification or by encapsulation into surface micelles, liposomes, emulsions, solid lipid particles, and biopolymer particles [7]. The spray drying technique represents a good alternative to obtain a soluble system for the industrial application of curcumin. Moreover, microparticulate solid dispersions using a spray drying technique is another method for improving the stability and solubility of compounds [8]. The solubility of microparticles of *C. longa* improved 100-fold compared to its extract [9]. Other methods to improve its solubility include preparing into oil in water emulsion (o/w emulsion), and encapsulation [10]. Encapsulation or incorporation of active components in the matrix also improves the stability of curcumin. Starch is a kind of polymer that has been widely used as an encapsulation matrix. Starch also can act as a sustained release agent due to its gel-forming ability, biodegradability, and biocompatibility [11].

The previous research showed that starch nanoparticles resulting from ethanol and butanol precipitation complex have been applied as encapsulation matrix for andrographolide extract [12] and *temulawak* oleoresin [13]. The complex of starch nanoparticles resulting from butanol and ethanol precipitation has a type of crystalline with a helical cavity that can be a host for organic and inorganic molecules, including curcumin. The starch nanoparticle has an advantage due to its greater surface area and higher entrapment of active ingredients. In addition, the guest encapsulation component or the active ingredient entrapped in the inclusion complexes, these complexes will stabilize the active ingredient being shielded from the influence of oxygen or light [12].

Storage and heat exposure will cause water absorption and oxidation of active ingredients, which lead to degradation and changes in physicochemical properties of an active ingredient and will affect its performance. Curcumin can easily lose about 27-53% due to heat processing [14]. Other research mentions that due to high light sensitivity it is further lost in the commonly practiced open sun drying methods [15]. Moreover, certain processing conditions or exposure to UV radiation in storage could affect the stability and bioactivity of curcumin [16]. Curcumin contents in various commercial turmeric powders from all over the world range from 0.58 to 1.2% on average, but it drops dramatically become less than 1% in curry powders [17]. Research by Kumavat [18] showed that less than 1% of curcumin decomposed within 6 hours of the total curcumin in the absence of light while it was more than 40% in the presence of light. Furthermore, research) on the effect of UV radiation on turmeric powder using different packaging materials (glass, aluminum foil bag, and low-density polyethylene bag), using several drying methods [19]. The results show that convection and fluidized bed drying had no significant impact on turmeric quality. However, solar drying degraded curcuminoids by 36.5%, and the antioxidant value decreased by 14%. The objective of the study was to determine the effect of storage temperature and heat treatment on the stability of curcumin of *temulawak* oleoresin encapsulated with arrowroot starch nanoparticles.

2 Material and methods

2.1 Material

The research was conducted at the Chemical Laboratory of the Indonesian Center for Agricultural Postharvest Research and Development (ICAPRD), and the Laboratory of Agro-industrial Technology Process, Bogor Agriculture University. The raw material used was *temulawak* oleoresin prepared from *temulawak* rhizome, extracted by ethanol. The coating material used was arrowroot starch nanoparticles derived from arrowroot starch which experienced a double modification process namely acid hydrolysis (*lintnerization*) followed by butanol or ethanol precipitation process.

2.2 Preparation and Characterization of Nanoparticle Starch

The nanocrystalline starches were prepared by two successive processes, i.e., *lintnerization* and ethanol or butanol precipitation, according to Winarti et al. [20] methods. About 50% of the starch slurry was dispersed in 2.2 N of HCl at 35oC and then incubated on a shaking incubator at 120 rpm for 6 h. The slurry was neutralized by 1 N of NaOH, then washed with distilled water and ethanol, and oven-dried at 40°C overnight. The *lintnerized* starch was then completely gelatinized. Ethanol was added to the solution drop by drop with slow stirring. The precipitate was then oven-dried at 40°C overnight.

2.3 Process of Encapsulation of Curcumin Extract

The procedure for the encapsulation process of curcumin extract used previous methods from [20]. Each nanoparticle starch was mixed with maltodextrin. About 10 g of the nano-starch matrixes were diluted in 150 ml of warm water (70°C) to produce a 10% of starch solution. The mixture was then dispersed and stirred thoroughly for 30 minutes using a magnetic stirrer bar, and then stood to rehydrate overnight. 10% (v/v) of *temulawak* oleoresin, which had been diluted with ethanol with total dissolved solids ~20°Brix, was mixed with a starch solution, and then homogenized with Ultra Turrax for 10 minutes at 11000 rpm. The next process was atomization and dried with a spray dryer with inlet temperature conditions around 80°C and outlet temperature of 170°C. The obtained microcapsules were weighed and stored in a tight plastic bag until it was used. The microcapsule also measured their yield and curcumin content.

The treatments tested included the type of coating materials which were two kinds of starch nanoparticles matrix (ethanol and butanol starch nanoparticles) treated at the heat treatments such as storing at ambient (room temperature 27-30°C) and 40°C, heat treatment using oven drying at 100 and 150°C for 1 and 2 hours, and sun exposure for 5 hours per day for 2 weeks. Some treatments were compared with maltodextrin matrix as an encapsulant. The parameter observed was curcumin content before and after treatment. Curcumin content analysis using UV-Vis Spectrophotometer at 462 nm wavelength.

2.4 Heat stability

This test was done using an oven apparatus. The known weight microcapsules samples are stored in the oven at temperatures of 100° and 150°C for 1 and 2 hours. All the samples that have been treated were then tested for their active ingredient levels.

2.5 Stability during storage

The weighed sample was placed in a closed glass bottle. Then samples were stored in an incubator using 40°C temperature and at room temperature. Storage was conducted for 2 months. The observation took place every week. Each sample taken was analyzed at the rate of its active content.

2.6 Sunlight stability

The microcapsule sample weighing is placed in a closed glass bottle and then stored in a place exposed to direct sunlight for about 5 hours a day. Storage is for 2 weeks. Observations were conducted every 2 days. Each sample taken analyzed the rate of the active ingredient.

3 Result and discussion

3.1 Characteristics of microcapsule

The yield of *temulawak* microcapsules produced using the different matrixes with the ratio of matrix: extract ranged between 26.45 and 29.86 % for the matrix: oleoresin ratio = 3:1 and between 32.09 – 30.08% for the 3:2 ratio; with curcumin levels ranging from 3536.6 – 8849.6 ppm (Table 1). Furthermore, the main treatment of the effect of storage and stability on heat was carried out at a ratio of 3:1 by considering the viscosity of the slurry to be processed further for spray drying. Emulsion viscosity is an important factor that affects the microencapsulation rate [23]. The ratio of core material (*temulawak* oleoresin) and wall material (starch NP) affects the encapsulation rate. The levels of curcumin in microcapsules were relatively low compared to the levels of curcumin powder and turmeric extract. As mentioned before the curcuminoid content of *temulawak* powder rhizome is 4866 ppm, while the turmeric powder curcuminoid is 229,99 ppm [4].

Table 1. Yield and curcumin content of microcapsule prepared from different matrix.

Matrix treatment	Ratio Matrix: oleoresin	Yield (%)	Curcumin (ppm)
Butanol precipitation	3:2	32.09	4457.20
	3:1	29.86	3536.60
Ethanol precipitation	3:2	30.08	4107.62
	3:1	26.45	3064.05

3.2 Effect heat exposure (oven drying)

The results showed that the higher the temperature and the longer the heating, the lower the curcumin content (Table 2). Curcumin content of *temulawak* oleoresin encapsulated with maltodextrin matrix tends to decrease higher than that of NP starch matrix. While the butanol NP matrix decreased the lowest or was more effective in preventing the degradation of curcumin levels. The active ingredients of curcumin are sensitive to changes in environmental conditions, both in the form of temperature, pH, and sun exposure. Storage conditions are very critical for storing microcapsule products. During storage, the microcapsules will absorb water and cause degradation and changes in physicochemical properties that can affect performance in-vivo. In addition to water absorption, another problem that is often faced in storing products containing active ingredients is damage due to oxidation. The research by Paramera et al. [21,22] showed that encapsulation increases heat resistance. According to Raza et al. [24], as temperature increases during heat treatment using a convection oven or hot air drying, the drying duration and curcumin concentration decrease, which clearly indicates that temperature has a direct effect on curcumin content in turmeric. During the heating process of curcumin, there were several modifications, including shifting of double bonds, polymerization, or degradation into lower molecular weight components which showed the susceptibility of bridges to diketones of curcumin caused by heat exposure. The heating treatment, namely boiling turmeric powder for 20 minutes, caused the curcumin content to decrease by 32% [25].

Table 2. Effect of oven drying on the declining of curcumin content using the matrix of ethanol and butanol starch nanoparticle.

Matrix	Temperature (°C)	Length of heating (hour)	Curcumin content (ppm)	Curcumin reduction (%) *
Butanol SNP	100	1	3,104.15	4.32
		2	2,820.57	7.16
	150	1	2,178.65	13.58
		2	1,499.39	20.37
Ethanol SNP	100	1	1,883.86	11.46
		2	1,770.65	12.59
	150	1	1,161.55	18.68
		2	937.74	20.92
Maltodextrin	100	1	1,185.70	23.51
		2	1,426.40	21.10
	150	1	1,198.25	23.38
		2	1,139.75	23.97

Note: * Curcumin reduction was determined based on the curcumin initial curcumin content (3536.6 ppm)

3.3 Sun Exposure

Several studies have been done to evaluate the degradation of curcuminoids at different temperatures with light exposure, showing that light radiation can accelerate the drying process but detriments the curcuminoid content [26]. Figure 1 showed a decrease in the level of curcumin after sun exposure for about 5 hours per day for 2 weeks. The longer exposure to curcumin levels decreases. After exposure for 10 days, the curcumin content was still around 265.1 ppm for microcapsules with butanol precipitation matrix and 213.7 ppm for the ethanol precipitation matrix. Whereas at the end of the 16th day of storage, curcumin levels remained below 10% (Figure 1). Microencapsulation has long been used to protect photosensitive compounds against photodegradation [27]. Curcumin is highly light-sensitive nutrient [15]. The mechanism is that direct exposure to UV radiation causes a photodegradation reaction that favors oxidation processes. These processes generate compounds that increase the green hue [19]. In addition, photoreactions affect the nutritional composition, such as fats and vitamins, the color, and the concentration of the food bioactive compounds, such as curcuminoids in turmeric. Therefore, these products might have a shorter shelf life. The curcumin decomposition, when exposed to UV light radiation is through the breakdown of β-diketone bonds, causing the formation of smaller phenolic components of curcumin, such as vanillin, ferulic acid, feruloyl methane, vanillic acid, and aldehyde spherulites [28]. Meanwhile, the main photodegradation product is a cyclization product formed by the loss of two hydrogen atoms. Direct and indirect sunlight has the highest effect on curcumin concentration as shown from the results of sun drying and solar tunnel if compared to shade drying [24]. Compared to other treatments, direct sunlight affects the curcumin concentration significantly followed by drying temperature and drying duration [23].

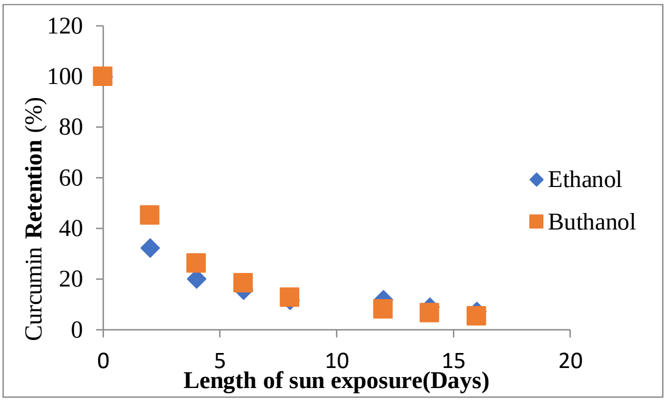

Fig. 1. Effect of sun exposure on the declining of curcumin content using matrix of Ethanol (◆) and Butanol (■) starch nanoparticle

3.4 Effect of Storage

The use of a matrix is expected to protect the active ingredients from damage that occurs during storage. The effect of storing at room temperature on decreasing curcumin retention is presented in Figure 2. It can be seen that the decrease in curcumin levels is relatively low after storage for 60 days the levels are still around 80% or only around 20% decrease. Storage carried out using dark glass bottles proved to be quite effective in reducing the degradation of curcumin. Research by Esmaeili et al. [29] the content of curcuminoids, decreased about 61% after 12 months of storage.

Effect of storage temperature of 40°C showed a rapid decline compared to the storage of room temperature (Figure 3). As previously stated, curcumin is sensitive to heat and temperature changes. Graph 3 also shows that the nanoparticle starch matrix resulting from butanol precipitation can hold the active material better than that ethanol precipitation matrix and maltodextrin at 40°C temperature storage. The difference in response between the two types of matrices to the two different types of active materials is due to different matrix characteristics after going through different nanoparticle formation processes. The butanol precipitation method is dominated by amylose and crystalline structure, while ethanol precipitation methods mainly contain amylopectin and amorphous.

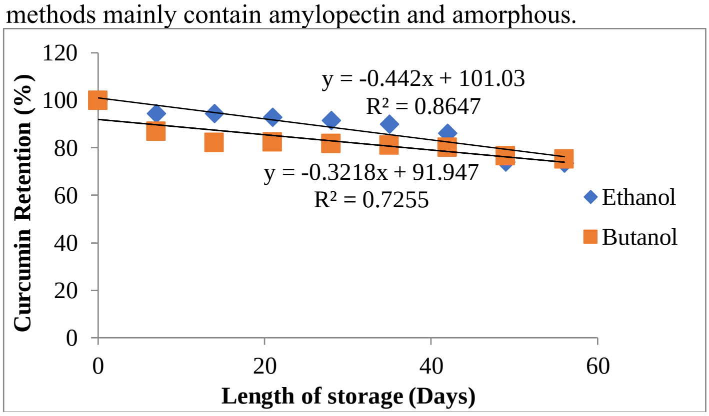

Fig. 2. Effect of storage at ambient temperature on the curcumin retention during storage using matrix of ethanol (◆) and butanol (■) starch NP

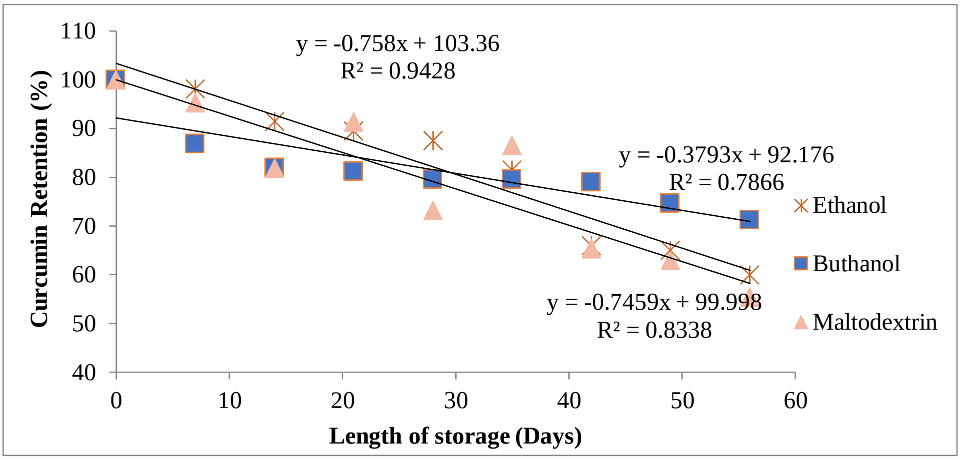

Fig. 3. Effect of storage at 40°C on the curcumin retention during storage using matrix of ethanol (✕) and butanol (■) starch NP and maltodextrin (▲)

4 Conclusion

The stability of microcapsules of curcuma extract on heat and sunlight exposure showed that the matrix of nanoparticle starch from ethanol precipitation was better than butanol precipitation and maltodextrin; except for oven drying treatment. During oven drying treatment, the highest degradation of curcumin occurred at sample using maltodextrin, followed by ethanol and butanol matrix. The longer the exposure the lower the curcumin level. The stability of curcumin during storage at room temperature almost similar for all matrix used. However, storage at 40°C temperature for butanol matrix showed the drastic curcumin degradation compared to other matrixes.

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