Characterization of catechin microcapsules from gambier using modified flour coatings from bengkuang

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Abstract. Active compounds of catechin from gambier have several disadvantages, which include being difficult to dissolve in water and not easily oxidized. Therefore, to overcome these disadvantages, they are coated with starch matrix. The modified starch from jicama (bengkuang) was produced from acid hydrolysis process, precipitated with alcohol therefore, it has a helical hole, porous structure and functions as a matrix. The aim of this study was to determine the effect of modified starch from bengkuang as a matrix on the characteristics of catechins microcapsules from gambier. The treatments tested include the ratio of catechins in modified starch (25%, 50%, 75%), a speed of 6000 rpm, and stirring time of 15 minutes on the emulsification process. The parameters observed consisted of the loading capacity of catechins in coatings, morphology (SEM), antioxidant activity, and Fourier Transform Infrared (FTIR) analysis. The results of this study showed that catechins which were encapsulated at a ratio of 1:3, had the highest antioxidant activity, i.e. 15.30 ppm with morphology of the sphere being smooth. The material ratio which affects the surface of the catechin microcapsules with elemental mapping, showed that the brighter the colour, the higher the amount of catechin concentration in encapsulation. Furthermore, the FTIR analysis showed the binding of catechins ingredient in the matrix with new absorption peaks at wavelengths of 1240 cm\(^{-1}\), 1286 cm\(^{-1}\) and 1366 cm\(^{-1}\). Therefore, catechin microcapsules encapsulated with modified starch, have shown good resistance to air/oxygen diffusion during storage.

1. Introduction
The catechins obtained from gambier are phenolic compounds that can serve as antioxidants, and the potency have also been tested in vitro. Furthermore, research has been carried out on their utilization, antiradicals function, and properties [1,2,3,4,5,6,7]. Catechins are characteristically unstable and are very susceptible to oxidation during processing and storage. This is because they possess many unsaturated bonds which cause their activity to decrease [8,9,10].

In order to keep this compound from the effect of oxidation, microencapsulation is employed, which is a method of protecting active ingredients to maintain bioavailability and stability, from environmental influences (light, humidity and oxygen). The technology employed in this process coats the core substance as a physical protection. In addition, the enclosed material can be released back to its normal form based on the targeted purpose. The microcapsules formed can be single, and also possess very small particles with a size range between 5-5000 µm [11,12,13,14].

One of the methods used in making microcapsules includes solvent evaporation and emulsification which are often performed by spray drying. The type of particles obtained through this technique is
able to protect the coated core substance for a long time and then release it back to the initial form. Therefore, this process is suitable for increasing the stability of active ingredient during long term storage. The microcapsule is made by a coating of the polymer derived from carbohydrate. The coat is chemically compatible with the core material and can be widely used in all the manufacturing methods [15,16,17,10,18,19].

In the production of the microcapsules, the modified flour extracted from bengkuang is a potential material for protecting the active ingredient from environmental influences [20]. This particular starch flour is a renewable, natural, non-toxic, and edible biopolymer. Besides being a coating for catechin, this also can be used simultaneously as a raw material for cosmetics and pharmaceuticals. Meanwhile, there has been no research on the use of modified bengkuang flour as a catechin coating. The starch is used as a sunscreen and catechins function as antioxidants, which indirectly increase the added value of these two raw materials. This is also supported by the high public awareness of natural ingredients utilization, especially for cosmetics and pharmaceuticals. Therefore, it is necessary to obtain natural ingredients that can be used for these needs.

Microcapsules produced from the modified flour coatings are needed as suitable encapsulates that can increase the stability of catechins in storage. Furthermore, the success of this process is determined by the existence of equilibrium between the active ingredient and the coating material used when manufacturing an emulsion. The substance covering ability of bengkuang flour was tested by drying the emulsion into microcapsules. Therefore, this study aimed to determine the effect of modified bengkuang powder on catechin microcapsules characterization and its coating ability. These microcapsules were studied in relation to their morphology, chemical configuration, and antioxidant activity. The characterization process was employed in the production of catechin microcapsules which are raw materials for cosmetic preparations.

2. Material and methods

2.1. Material and tools

The raw materials used in the manufacturing of the coating include bengkuang flour from Padang city, West Sumatra, HCl, NaOH, aquades, and ethanol. Catechins were made by using ethyl acetate and ethanol, while encapsulates were produced from 70% ethanol and analysis chemicals. The tools used in this study were a shaker, erlenmeyer flask, beaker glass, 100 mesh sieve, balance, water bath, oven, high pressure homogenizer (GEA Niro Soavi-Panda PLUS), spray dryer (LabPlant SD-05), Scanning Electron Microscope (SEM-Zeiss EVO MA 10), Fourier Transform Infrared Spectroscopy (FTIR), and spectrophotometer.

2.2. Research procedure

2.2.1. Preparation of modified bengkuang flour. The production of modified flour from bengkuang which is subsequently used as an encapsulant matrix, is carried out through the method described by [20]. This flour was hydrolyzed with 2% HCl for ±72 hours over a water batch at ±40°C. The hydrolysate was filtered and the result was soaked in 70% ethanol solution for ±5 hours and then separated. Furthermore, the precipitate obtained afterwards was dried in an oven at a temperature of 50±5°C, sifted with a 100 mesh sieve and packed.

2.2.2. Emulsion manufacturing. The emulsionification process was carried out by dissolving the modified bengkuang flour (coating) with deionized water in a ratio of 1:4 (w/v) at a temperature of ±50°C. The mixture was made to become uniform by using a high-pressure homogenizer at a speed of 6000 rpm for ±5 minutes. The catechins were dissolved with 70% (1:10) (w/v) ethanol, and stirred at 3000 rpm for ±5 minutes. The resulting solution was added to a homogeneous mixture of the coating produced from bengkuang flour, and then stirred at a speed of 6000 rpm for ±15 minutes. The emulsion was prepared by using 3 (three) variations of catechins concentration in the coating, namely 25%:75% (E1), 50%:50% (E2) and 75%:25% (E3). The mixture was then desiccated with a spray dryer at an
inlet temperature of 175±5°C, an outlet temperature of 60±5°C and a solution flow rate of 20 ml min\(^{-1}\). The resulting product was catechin microcapsules and analysis was carried out.

3. Result and discussion

3.1. Scanning electron microscopy

The appearances of the microcapsules produced range from white to yellowish powder. The higher the catechin ratio compared to the modified bengkuang flour as a coating, the lighter the product color. The observation of the microcapsule morphology was carried out by using Scanning Electron Microscopy (SEM). Furthermore, the results obtained from this process generally showed a round shape, smooth surface, microcapsules with basin on top and wrinkles with a size between 5-20 µm. The shape of the microcapsules and particle size were influenced by the amount of coating, stirring speed, and solvent evaporation in the spray drying process. Therefore, the faster the agitation during encapsulation, the smaller the particles produced. The temperature effect indicated higher degrees or rapid solvent evaporation, which resulted in a smoother particle surface. Meanwhile, low temperatures produced microparticles that are irregular in shape with wrinkled exteriors [11,16,21,17,15,18,19].

The morphological observation results of the microcapsules (figure 1) were treated with 25% catechins and 75% coatings (E1), generally having a smooth, regular round and irregular semi-spherical shapes, with various sizes. The treatment of 50% catechins and 50% coatings (E2) caused the microcapsules to contain the core material that is evenly dispersed in the coating material, having a smooth, regular, and irregular semi-spherical shapes, slightly hollow and wrinkled with various particle sizes. Meanwhile, the treatment of 75% catechin and 25% coating (E3) caused the microcapsules to be finely spherical, irregular semi-spherical, and with more wrinkled shapes.

![Figure 1. Morphology of catechin microcapsules treated by ratio of catechins and modified bengkuang flour E1 (25%:75%), E2 (50%:50%), and E3 (75%:25%).](image)

The roughness can be due to improper covering of the core by the coating material. The microcapsules, which have a deflated shape, are suspected to be the consequence of a ballooning event that occurred during the spray drying process. The morphology of the microcapsules formed will also affect the release of coated active ingredient [11,22,19]. SEM observations of catechin microcapsules showed that bengkuang modified flour could be used as a coating. In addition, the data obtained will support the conclusions on FTIR analysis and antioxidant activity.

3.2. FTIR spectrometry analysis

The process was carried out in order to elucidate the position of phthalate groups that were bound or substituted into the coating structure. The substitution or cross-linking of phthalates is measured at a wavelength of 1300-1700 cm\(^{-1}\). The FTIR spectrophotometer results (table 1 and figure 3) showed that the catechins from gambier extract contain weak C=C stretching aromatic compounds with an absorption of 1680-1640 cm\(^{-1}\), and strong OH carboxylic acid functional group stretching with 3350-
3310 absorption cm\(^{-1}\). The modified bengkuang flour contained a strong stretching of OH carboxylic acid functional group with an absorption of 3350-3310 cm\(^{-1}\), a stretching of the CH aldehyde functional group with an absorption of 2830-2695 cm\(^{-1}\), a bending of the CH functional group of an alkena compound with an absorption of 1450-1375 cm\(^{-1}\), and a bending of the functional group OH carboxylic acid functional group with an absorption of 1440-1395 cm\(^{-1}\). The infrared absorption spectrum of catechin microcapsules had a moderate peak at a wavelength of 1628.65 cm\(^{-1}\), 1628.55 cm\(^{-1}\) and 1628.03 cm\(^{-1}\).

![Figure 2](image-url) Catechin and bengkuang starch structure.

### Table 1. FTIR spectrum of catechin microcapsules treated by catechin ratio and coating of modified bengkuang flour.

| Functional groups | Standard of wavenumber (cm\(^{-1}\)) |
|-------------------|-------------------------------------|
| O-H Stretching    | Carboxylic acid 3350-3310           |
| C-H Stretching    | Aldehid 2830-2695                   |
| C=C Stretching    | Alkena 1680-1640                    |
| C-H Bending       | Alkena 1450-1375                    |
| O-H Bending       | Carboxylic acid 1440-1395           |

|                        | 25:75     | 50:50     | 75:25     |
|------------------------|-----------|-----------|-----------|
| Wavenumber (cm\(^{-1}\)) of sample catechin : coating |           |           |           |
|                        | 3305.95   | 3307.22   | 3304.76   |
|                        | 2929.12   | 2929.42   | 2929.56   |
|                        | 1628.65   | 1628.55   | 1628.03   |
|                        | 1460.75   | 1462.46   | 1463.73   |
|                        | 1369.75   | 1370.18   | 1370.39   |

![Figure 3](image-url) FTIR spectrometry indicating catechin and coating ratio of (E1) as 25\%:75\%; (E2) as 50\%:50\%; (E3) as 75\%:25\%; while (K) represented catechins; and (P) coatings.
3.3. Antioxidant activity (IC$_{50}$)

The evaluation of antioxidant activity of catechin microcapsules was carried out by using DPPH free radicals (1,1-diphenyl-2-picrylhydrazyl), while the absorbance was read at a wavelength of 517 nm and the concentration was expressed with the IC$_{50}$ value. Furthermore, this value can be used to provide an estimate of the ability to ward off the DPPH in a solution. In fact, antioxidant activity increases proportionally with decreasing value of IC$_{50}$. Catechin with activity level of 5.03 ppm as a raw material has higher ability to ward off free radicals than modified bengkuang flour, a coating (148 ppm). Therefore, this shows that the capacity of catechins to prevent oxidation is 50% greater than the flour's [20].

Table 2. Shows the IC$_{50}$ test results of catechin samples and encapsulates obtained from spectrophotometry.

| Sample        | Antioxidant activity (IC$_{50}$) (ppm) |
|---------------|---------------------------------------|
| Catechin (K)  | 5.03                                  |
| E1            | 18.46                                 |
| E2            | 15.76                                 |
| E3            | 15.30                                 |
| Coating (P)   | 148                                   |

The IC$_{50}$ analysis of the microcapsules (table 2) with E3 treatment (catechin 70% : coating 25%) had a higher antioxidant activity and was not significantly different from E2 treatment (catechin 50% : coating 50%). This shows that more catechins were added to E3 treatment, therefore there was a loss of phenolic compounds which caused a decrease in their activity. In addition, his reduction must have occurred because the catechins were not coated, thus the applied heat caused damage to the active compound. According to [11], the decrease in the total compound content can be caused by synthesis factors, phenol polymerization and flavonoids as well as uncontrolled sample drying process conditions.

4. Conclusion

The use of modified bengkuang flour as catechin coating at different ratios produced microcapsules with different characteristics. Although the catechin concentration ratio in E2 treatment (catechin 50% : coating 50%) was lower than in E3 (catechin 75% : coating 25%), yet the antioxidant activity of both was not significantly different, and the SEM image appearances were relatively the same. The utilization of the flour as a coating is an alternative to the use of natural ingredients for protecting catechins from environmental influences and also possesses good microcapsule characteristics.

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