Effectiveness of Reducing Cyanide Levels in The *Dioscorea hispida Dennst* Bulbs Through Soaking in Seawater and Interaction with Ash scrub

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**Abstract.** The high concentration of cyanide in *Dioscorea hispida dennst* should be reduced through immersion in seawater and interaction with rubbing ash. Soaking seawater prepared in immersion time 12, 24, and 36 hours accompanied by the replacement of seawater every three hours, while interaction with rubbing ash was ready with 75% and 100% concentration of ash on 12, 24, and 36 hours of storage time respectively. Measurement of cyanide concentrations of *Dioscorea hispida dennst* samples was prepared by argentometry titration with Liebig method after through the steam distillation process. Based on the results of this study, it found that immersion time for 12, 24, and 36 hours could reduce cyanide concentrations about 48.30%, 64.44%, and 70.88%, respectively. The interaction by using 75% rubbing ash for 12, 24, and 36 hours, it can reduce 24.09%, 38.69%, and 51.42% cyanide concentration in *Dioscorea hispida dennst* tubers, respectively. The *Dioscorea hispida dennst* tubers smeared with100% rubbing ash for 12, 24, and 36 hours, it can reduce cyanide content in *Dioscorea hispida dennst* by 36.26%, 49.92%, and 59.63%, respectively. Further treatment with drying and fermentation produces *Dioscorea hispida dennst* with a lower concentration of cyanide about 88.68% with a soft and white texture.

1. Introduction

According to the National Socio-Economic Survey in 2012, the average consumption of rice per capita of Indonesia's population has reached 87.235 kg. Over time, the high consumption of rice due to population growth, will not be offset by the amount of production due to decreasing agricultural land, coupled with the potential for crop failure in each season. In addition, excessive consumption of rice can trigger an increase in blood sugar levels due to high glucose levels in rice, which has the potential to cause diabetes and obesity that recently affects many Indonesians. Therefore, we need an alternative food besides rice as a source of carbohydrates [1–4].

One foodstuff with a high nutritional content is *Dioscorea hispida dennst* tubers, including food sources from tubers, it can use as a source of carbohydrates. Cassava tubers are commodities that have good prospects because they contain fat, protein, and vitamins. In the *Dioscorea hispida dennst* tubers
also contained more resistant starch (amylopectin), it can use to prevent the onset of obesity and diabetes [5–8].

To date, the main problem the use of Dioscorea hispida dennst as a food source for the community is the high content of toxic substances. The types of poisons contained include alkaloids and cyanides bound with linamarin and lautostralin compounds with concentrations of 15-400 mg/kg [6,9]. Other problems are high water content and high susceptibility to gradual physiological damage after harvest. In addition, the content of toxic compounds such as dioscorine, dihydrodioscorine, and saponins in the form of dioscin in Dioscorea hispida dennst bulbs are also hazardous when consumed. The content of this compound can cause poisoning with symptoms of vomiting, nausea, abdominal pain, and diarrhea. The high content of cyanide in the bulb is a challenge to process it into a food source. Various methods can be used to reduce the cyanide content in a material such as using nanomaterials, fermentation, drying, oxidation with ozone, in-exchange, photocatalytic degradation, and adsorption [10–16] However, based on the literature study shows that until now studies to reduce the levels of Dioscorea hispida dennst bulbs cyanide effectively and simply have never been done. In this research, the study has been conducted methods to reduce the levels of Dioscorea hispida dennst bulbs cyanide effectively.

2. Experimental

2.1 Tools and materials

The tools used in this experiment knives, basins, blenders, burettes, Erlenmeyers, analytical scales, spatulas, porcelain cups, ovens, fillers, glassware, weighing bottles, adapters, three-flask, flask distillation, volumetric electromantel flask, condenser, thermometer. The materials used in this experiment are Dioscorea hispida Dennst tubes obtained from the Baadia Village, Bau-bau City, seawater, scrub ash, KI, K$_2$CrO$_4$, NaCl, NaOH, AgNO$_3$, NH$_4$OH, and distilled water.

3. 2.2. Reduction of cyanide levels using seawater

Dioscorea hispida Dennst bulbs are peeled and sliced to a thickness of approximately 0.5 cm. A total of 400 grams put into three containers that contained 650 mL of seawater. The sample soaked for 12, 24 and 36 hours, respectively with water replacements every 3 hours. Then, the sample washed clean and dry until they are free of water, and the sample fermented for 48 hours. The fermented sample is mashed, and its cyanide content analyzed.

2.2 Reduction of cyanide by using rub Ash

The contents of the Dioscorea hispida Dennst bulbs are sliced at a thickness of approximately 0.5 cm and sprinkled with ashes with a concentration of 75% and 100% (w/v). A total of 400 grams of samples rubbed with rubbing ash were put into 6 containers. The first three containers contained sliced of Dioscorea hispida Dennst bulbs interacted with pure rubbing ash. The other three containers contained rubbed ash with a concentration of 75% (w/v) with a storage time of 12 hours, 24 hours and 36 hours, respectively. The Dioscorea hispida Dennst bulbs slices are washed thoroughly and dried in the sun to dry. Sample fermented for 48 hours. The fermentation results are washed clean, mashed, and analyzed for cyanide content.

2.3 Determining of cyanide content in Dioscorea hispida dennst bulbs

The content of cyanide was performed by argentometric titration using a standard 0.02 N AgNO$_3$ solution. Steam Dioscorea hispida dennst bulbs that have been through the distillation process are passed through a 2.5% NaOH solution as a cyanide acid capturing solution (HCN) in a distillate holding flask. The series of steam distillation apparatus is shown in Fig. 1.

2.4 Data analysis technique

The actual concentration determined by AgNO$_3$ after standardization using NaCl solution using
equation 1.
\[ N\text{AgNO}_3 = \frac{N\\text{NaCl}xV\\text{NaCl}}{V\\text{AgNO}_3} \]

The levels of cyanide acid (ppm) in the sample determined by equation 2.
\[ HCN = \frac{V\\text{AgNO}_3 x M\\text{AgNO}_3}{ massa \ sampel} \times 1000 \text{ mg/kg} \]

Cyanide levels in cyanide acid determined by equation 3.
\[ CN^- = \frac{Mr\\text{-CN}^-}{Mr\\text{-HCN}} \times \text{HCN content (ppm)} \]

3. Results and Discussion

3.1 Cyanide content in Dioscorea hispida dennst bulbs
Cyanide in Dioscorea hispida dennst still bound to another molecule (cyanogenic glycosides) in the form of linamarin and lautostralin compounds, which mostly contained in the skin and surface of the flesh of the Dioscorea hispida dennst bulbs. The cyanide bound in the linamarin compound converted into an intermediate compound, namely cyanohydrin acetone by the linamarase enzyme, then becomes HCN by the hydroxy nitrile liaise enzyme [1,9,17]. Cyanide levels measurements of yam tuber only through stripping, slicing, and refining stages show that cyanide concentrations are still quite high at 76.10 ppm and are very dangerous to consume because the safe limit according to FAO is 10 mg/kg. The skin-stripping process can also reduce cyanide levels in the yeast by up to 50%, while the process of reducing size through slicing, grating and grinding can reduce the cyanide content by about 22% [4].

In this study, periodic seawater changes are conducted every 3 hours to anticipate the accumulation of cyanide and tannin poisons. After soaking for 12, 24, and 36 hours, the tuber slices show a soft, white texture. However, the process of immersion using seawater, Dioscorea hispida dennst tubers interaction results with rubbing both 75% concentration and 100% showed a harder texture in the presence of a red part on the surface of the tuber slices. The results of the fermentation of the tubers of Dioscorea hispida dennst that through soaking, the seawater produces white slices with a softer texture. Interaction results with rubbing ash produce a texture that becomes harder with brownish-red spots on some parts of the surface of the tuber slices.

![Figure 1. Steam distillation apparatus to isolate of cyanide content](image)

HCN resulted in the distillation stage will enter into a container containing 2.5% NaOH solution. The result of the distillate is a cyanide salt solution titrated with a standard AgNO\textsubscript{3} 0.02 N. These
deposits will again dissolve by shaking and then form stable white deposits $\text{Ag}[\text{Ag(CN)}_2]$ in accordance with the following reaction equation:

$$\text{NaCN}_{(aq)} + \text{AgNO}_3_{(aq)} \rightleftharpoons [\text{Ag(CN)}_2]^-_{(aq)} + \text{NaNO}_3_{(aq)} \quad \text{(4)}$$

Further addition of the $\text{AgNO}_3$ solution to the complex ion $[\text{Ag(CN)}_2]^-$, will form a stable precipitate of the salt of the argentum disianoargentate (I) complex according to the reaction equation:

$$\text{Na}[\text{Ag(CN)}_2]_{(aq)} + \text{AgNO}_3_{(aq)} \rightleftharpoons \text{Ag}[\text{Ag(CN)}_2]_{(s)} + \text{NaNO}_3_{(aq)} \quad \text{(5)}$$

From the reaction equation 5, it is known that in the potentiometric titration of CN ions, the equivalence point marked by the formation of a permanent precipitate of the $\text{Ag}[\text{Ag(CN)}_2]$ complex salt. However, determining the endpoint of the titration through this method becomes less effective because it is prone to irregularities in concluding the endpoint of the titration. For this reason, the Liebig method of argentometric titration can be applied with $\text{KI}$ as an indicator of the endpoint of the titration, because the reaction of the $\text{I}^-$ ion with the $\text{Ag}^+$ ion will form a constant AgI precipitate, then the precipitate from the $\text{Ag}[\text{Ag(CN)}_2]$ complex salt must first be dissolved. Therefore, the addition of a concentrated $\text{NH}_4\text{OH}$ solution before titration needs to be done because the $\text{NH}_4\text{OH}$ solution serves to dissolve the $\text{Ag}[\text{Ag(CN)}_2]$ complex salt that will be formed then converted into a compound $[\text{Ag(NH}_3)_2]^+$. It will slow down the precipitation of silver iodide (AgI) until the correct time (endpoint of the titration) [18]. When the iodide ion has been bound with silver ions from $\text{AgNO}_3$ as shown by the reaction below:

$$\text{Ag}[\text{Ag(CN)}_2]_{(s)} + 4\text{NH}_4\text{OH}_{(aq)} \rightleftharpoons 2[\text{Ag(NH}_3)_2]^+_{(aq)} + 2\text{CN}^-_{(aq)} + 4\text{H}_2\text{O}_{(l)}$$

$$[\text{Ag(NH}_3)_2]^+_{(aq)} + \text{I}^-_{(aq)} \rightleftharpoons 2\text{(AgI)}_{(s)} + 2\text{NH}_3_{(aq)}$$

### 3.2 Cyanide content in Dioscorea hispida dennst bulbs results of seawater immersion

Levels of cyanide in $\text{Dioscorea hispida dennst}$ tubers without given particular treatment and the results of seawater immersion without drying and fermentation are shown in Table 1.

| Samples | V $\text{AgNO}_3$ (ml) | P1 (ppm) | P2 (ppm) | Yield average content of CN (ppm) |
|---------|------------------|---------|---------|-------------------------------|
| TP      | 3.2              | 78.5142 | 73.6901 | 76.1022                       |
| 12JPAL  | 1.6              | 39.4514 | 39.2335 | 39.3424                       |
| 24JPAL  | 1.1              | 27.0564 | 27.0643 | 27.0604                       |
| 36JPAL  | 0.9              | 22.2084 | 22.1087 | 22.1586                       |

Remarks:
- TP : Without seawater immersion and interaction with rubbing ash
- JPAL : Time of seawater immersion (hour)
- P1 : Cyanide levels in the first measurement
- P2 : Cyanide levels in the second measurement.

Based on Table 1 shows the levels of yam tuber cyanide decreased by 48.30% for 12-hour immersion, 64.44% for 24-hour immersion, and 70.88% for 36 hours. These results indicate that soaking yam in seawater can reduce cyanide levels. During the immersion process, the linamarin compounds which are hydrolyzed and form volatile cyanide acid will then dissolve in water. The greater the ratio of circulating water-volume-the weight of the yam used causes the concentration difference between the two (driving force) also to increase. This condition increases the speed of
diffusion [19]. In addition to hydrolyzing and mobilizing the release of cyanide compounds, another purpose of immersion is to activate enzymes that produce cyanide poisons and poisons such as tannins. It makes the cyanide no longer produced after immersion is carried out.

3.3 Cyanide content of the Dioscorea hispida dennst bulbs as a result of interaction with ash rub

Content of cyanide in Dioscorea hispida dennst bulbs resulting from interaction with rubbing ash at a concentration of 75% without drying and fermentation are shown in Table 2.

| Samples | V AgNO₃ (ml) A | V AgNO₃ (ml) B | P1 (ppm) | P2 (ppm) | Yield average content of CN (ppm) |
|---------|----------------|----------------|----------|----------|-------------------------------|
| TP      | 3.2            | 3              | 78.5142  | 73.6901  | 76.1022                       |
| 12JPAG75% | 2.4          | 2.3            | 59.0036  | 56.5291  | 57.7664                       |
| 24JPAG75% | 1.9          | 1.9            | 46.6109  | 46.7061  | 46.6585                       |
| 36JPAG75% | 1.5          | 1.5            | 37.0290  | 36.9084  | 36.9687                       |

Note:
TP : Without seawater immersion and interaction with rubbing ash
JPAG : Time of interaction and storage of rubbing ash (hour)
P1 : The content of cyanide in the first measurement
P2 : The content of cyanide in the second measurement

Furthermore, the cyanide content in the Dioscorea hispida dennst bulbs results from interactions with rub ash at a concentration of 100% without drying and fermentation, as shown in Table 3.

| Samples | V AgNO₃A (ml) | V AgNO₃B (ml) | P1 (ppm) | P2 (ppm) | Yield average content of CN (ppm) |
|---------|--------------|--------------|----------|----------|-------------------------------|
| TP      | 3.2          | 3            | 78.5142  | 73.6901  | 76.1022                       |
| 12JPAG100% | 2            | 1.95         | 49.0429  | 47.9632  | 48.5030                       |
| 24JPAG100% | 1.6          | 1.5          | 39.3309  | 36.8870  | 38.1090                       |
| 36JPAG100% | 1.3          | 1.2          | 31.9366  | 29.5152  | 30.7259                       |

Note:
TP : Without seawater immersion and interaction with rubbing ash
JPAG : Time of interaction and storage of rubbing ash (hour)
P1 : The content of cyanide in the first measurement
P2 : Cyanide content in the second measurement

Based on Table 3, it appears that the interaction of rubbing ash with the Dioscorea hispida dennst bulbs with a concentration of 75% or 100% can reduce cyanide levels. The concentration of rubbing ash 75% in 12, 24, and 36 hours can reduce cyanide levels 24.09%, 38.69%, and 51.42% respectively the Dioscorea hispida dennst bulbs with 100% concentration of ashes without drying and fermentation can reduce tuber cyanide content by 36.26% in 12 hour storage, 49.92%, and 36 hour storage 59.62%.

These results indicate that the sliced the Dioscorea hispida dennst bulbs are 100% rub ash can reduce the concentration of cyanide more than the yam tuber slices that given interaction with rub ash concentration 75%. It due to the presence of water molecules in the rubbing ash to cause competition of metal ions in the rubbing ash with H₂O molecules in binding to cyanide ions. In addition, these metal ions can be polluted by water molecules, thereby reducing their binding capacity to cyanide ions. Whereas on the slices of the Dioscorea hispida dennst bulbs given 100% scouring ash, there will be maximum absorption of cyanide by alkali metal ions.
3.4 Analysis of cyanide levels by drying and fermentation of bulbs

Drying and fermentation, including methods that widely applied in the processing of the *Dioscorea hispida* dennst bulbs. The cyanide content in the *Dioscorea hispida* dennst bulbs soaked in 12, 24 and 36 hours, then samples dried and fermented for 48 hours is shown in Table 4.

Table 4. Content of cyanide bulbs of the *Dioscorea hispida* dennst

| Samples | V AgNO₃ A (ml) | V AgNO₃ B (ml) | P₁ (ppm) | P₂ (ppm) | Yield average content of CN (ppm) |
|---------|----------------|----------------|----------|----------|---------------------------------|
| TP      | 3.2            | 3              | 78.5142  | 73.6901  | 76.1022                         |
| 12JPAL  | 1.5            | 1.4            | 37.0289  | 34.4201  | 35.7245                         |
| 24JPAL  | 0.9            | 0.8            | 22.1122  | 19.6743  | 20.8932                         |
| 36JPAL  | 0.4            | 0.3            | 9.8325   | 7.3948   | 8.6136                          |

Note: JPAL : Time of seawater immersion (hour)

The results in Table 4 show the storage time for the *Dioscorea hispida* dennst bulbs that soaked with seawater will largely determine the amount of cyanide that can be reduced. The longer the storage time, the more cyanide concentrations can be reduced. These results also show that there is a more significant decrease in cyanide levels in the *Dioscorea hispida* dennst bulbs which have undergone drying and fermentation compared to without drying and fermentation. Furthermore, the results of the analysis of the content of the *Dioscorea hispida* dennst bulbs cyanide with rub ash concentration of 75% that have passed the additional treatment of drying and fermentation shown in Table 5.

Table 5. Content of cyanide bulbs of the *Dioscorea hispida* dennst (drying and fermentation)

| Samples   | V AgNO₃ A (ml) | V AgNO₃ B (ml) | P₁ (ppm) | P₂ (ppm) | Yield average content of CN (ppm) |
|-----------|----------------|----------------|----------|----------|---------------------------------|
| TP        | 3.2            | 3              | 78.5142  | 73.6901  | 76.1022                         |
| 12JPAG75% | 1.5            | 1.4            | 36.8179  | 34.5530  | 35.6854                         |
| 24JPAG75% | 1.1            | 1.05           | 27.0750  | 25.8037  | 26.4394                         |
| 36JPAG75% | 0.8            | 0.8            | 19.6756  | 19.6517  | 19.6636                         |

Note: JPAG: Time of interaction and storage of rubbing ash (hour)

Furthermore, cyanide levels in the *Dioscorea hispida* dennst bulbs result from interactions with scrub ash concentrations of 100% without drying and fermentation as shown in Table 6.

Table 6. Content of cyanide bulbs of the *Dioscorea hispida* dennst (without drying process)

| Sample   | V AgNO₃ A (ml) | V AgNO₃ B (ml) | P₁ (ppm) | P₂ (ppm) | Yield average content of CN (ppm) |
|----------|----------------|----------------|----------|----------|---------------------------------|
| TP       | 3.2            | 3              | 78.5142  | 73.6901  | 76.1022                         |
| 12JPAG100% | 1.5           | 1.3            | 36.7844  | 31.9964  | 34.3904                         |
| 24JPAG100% | 0.9            | 0.8            | 22.0900  | 19.6473  | 20.8686                         |
| 36JPAG100% | 0.6            | 0.65           | 15.9530  | 14.7419  | 15.3474                         |

Note: JPAG: Time of interaction and storage of rubbing ash (hour)

Based on Table 5 and Table 6 shows that at the same drying and fermentation time, the *Dioscorea hispida* dennst bulbs that interacted with 100% ash concentration gave a more significant decrease in the cyanide levels of the *Dioscorea hispida* dennst bulbs compared with 75% rub ash concentration. The result shows the storage time factor of the *Dioscorea hispida* dennst bulbs that given rubbing ash
will significantly determine the amount of cyanide that can be reduced. The longer the storage time, the more cyanide can be derived.

The drying process aims to reduce the water content in each slice of the Diascorea hispida denst bulbs because the water content itself is one of the determinants of the taste quality and durability of the Diascorea hispida denst bulbs. Through the drying process, dissolved water and cyanide will quickly evaporate. The longer the drying time, the breakdown of material components increases so that the amount of bound water that is released. After dehydration and cell structure breakdown due to drying, there will also be degradation of linamarin glycosides in the Diascorea hispida denst bulbs by linamerase enzyme that produces glucose and cyanohydrin acetone to release HCN gas further. In addition to the drying process of yam tuber slices, it fermented by utilizing the growth of Saccharomyces cerevisiae to remove the remnants of free or cyanide compounds that are still bound in the Diascorea hispida denst bulbs [9,19,20].

4. Conclusions
The method of seawater immersion and rub ash interaction is a method that can reduce the levels of cyanide in the Diascorea hispida denst bulbs. The remaining cyanide levels in the Diascorea hispida denst bulbs which were the result of seawater immersion through the drying and fermentation process for storage of 12, 24, and 36 hours respectively were 35.7245 ppm, 20.8932 ppm, and 8.6136 ppm. Interaction with 75% rubbing ash for the three storage times through the drying and fermentation process respectively of 35.66854 ppm, 26.4394 ppm, and 19.6636 ppm. The remaining levels of cyanide in the Diascorea hispida denst bulbs with interaction results with 100% scrub ash for 12, 24, and 36 hours storage through drying and fermentation processes were respectively 34.3904 ppm, 20.8686 ppm, and 15.33474 ppm. Immersion treatment with seawater for 36 hours, followed by 48 hours of drying and fermentation. This process can reduce cyanide levels up to 91.3954 ppm or still remaining 8.6136 ppm.

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