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Analysis of Cyanide in Bulbs of Gadung Crackers For sale in Pelem Village, Tulungagung Regency using Complex Formation Titration Method

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Abstract: Gadung tubers or *Dioscorea hispida* are tubers that originally grew in the forest and are used as alternative food ingredients to replace rice and corn. One of the preparations from gadung tubers that is popular with the community is gadung tuber crackers. Before being processed into food, gadung tubers must be processed properly so that the cyanide content is reduced. Cyanide is a goitrogenic substance that is naturally found in foodstuffs. The purpose of this study was to determine the cyanide content in gadung root crackers. In this study, 3 samples were sold in Pelem Village, Tulungagung Regency. Cyanide analysis was carried out by qualitative test using picrate paper and quantitative test using complex formation titration. The cyanide content in the sample was 2.124 mg/kg; 0.9 mg/kg; 1,386 mg/kg.

Keywords: Umbi Gadung, Sianida, Complex Formation Titration

PRELIMINARY

Indonesia is an agrarian country where most of the population are farmers. As an agricultural country, Indonesia is expected to be able to meet the food needs of its people. However, until now Indonesia is still importing food from other countries (Aprilia, 2018).

Along with the increasing population of Indonesia, the need for food also increases. Therefore, alternative food ingredients are needed to support food needs. One of the alternative food ingredients with abundant availability is gadung tuber. However, gadung tubers cannot be utilized optimally because gadung tubers contain very high cyanide if eaten directly without proper processing (Aprilia, 2018).

Cyanide is an anti-nutritional compound contained in several types of plants such as gadung tubers, cassava, bamboo shoots and others. Based on medical studies, cyanide can interfere with health, especially in the respiratory system because cyanide compounds bind oxygen in the blood. Symptoms that arise due to consuming foods containing cyanide are vomiting, dizziness, weakness, stomach cramps and fainting (Ardiansari, 2012).

Cyanide is a goitrogenic substance that is naturally found in foodstuffs. Goitrogenic substances are substances that can block the thyroid gland from taking up iodine so that the concentration of iodine in the thyroid gland is very low. Therefore, consuming foods containing cyanide for a long time is not recommended because it can cause Iodine Deficiency Disorders (IDD). In addition, cyanide can also cause neurological diseases and damage essential amino acids such as cysteine and methionine (Ardiansari, 2012).

When foods containing cyanide are sliced, crushed, chewed or damaged, the hydrogen cyanide in these foodstuffs rapidly decomposes into cyanide. The cyanide will form a thiocyanate which will compete in taking up iodine with the thyroid gland. In addition to inhibiting the absorption of iodine, cyanide can also cause poisoning. If you often consume gadung tubers, the possibility of being exposed to cyanide poison is also greater (Ardiansari, 2012).

Based on the 2006 Indonesian National Standard (SNI) regarding food additives, the maximum limit of cyanide allowed in ready-to-eat foods is 1 mg/kg. Symptoms that occur when consuming foods containing cyanide are anxiety, dizziness and headaches. It is possible that the patient cannot focus his eyes and occurs mydriasis caused by hypoxia. Continued hypoxia causes decreased level of consciousness, seizures and coma (Cahyawati, 2017). Consuming foods containing cyanide in low doses continuously can cause various diseases such as stunting, goiter and neurological diseases (Arisanti et al., 2018).

According to the Department of Industry and Trade, Tulungagung Regency has an industrial center for gadung tuber crackers, precisely in Pelem Village, Campurdarat District. Before being processed into crackers, the cyanide in gadung tubers is removed first. The people of Tulungagung have a recipe for generations to get rid of the cyanide by thinly slicing gadung tubers and burying them in ash or charcoal for two days. Then the gadung tubers are soaked in water for days by regularly changing the soaking water. Furthermore, steaming and drying is carried out before the gadung tuber crackers are ready to be fried and consumed.

Reported by detik.com news on June 10, 2021, there was news of three Tulungagung residents being poisoned by gadung tubers with one of them dead. The gadung tuber was accidentally eaten by the victim because the gadung tuber has the same shape as gembolo. The victim's child brought the gadung tuber home and boiled it to be eaten together. After some time, the victim and the victim's child felt nauseous and dizzy due to the cyanide reaction. From the results of the medical examination, the victim died purely due to poisoning and there were no signs of violence. Furthermore, based on research (Ardiansari, 2012) in 2012, there was news that residents in Jangkang Village, Probolinggo Regency were poisoned by consuming gadung tubers. One of the victims said that residents took gadung tubers from the forest and immediately boiled them for 2 hours and then ate them with other residents. After that, they felt nauseous and the residents who consumed the boiled yam tubers vomited. After being diagnosed by the medical team, residents were poisoned by gadung tubers due to improper processing.

The presence of cyanide in gadung root crackers can be detected by many methods, one of which is complex formation titration. Determination of cyanide levels using this complex formation titration follows Deniges, where the indicator used is iodide ion derived from the added KI solution. Iodide ion is used as an indicator because the amount of silver iodide (AgI) that is precipitated is very large, it is possible to see it easily and has a lower solubility than silver cyanide (AgCN), so that at the end point of the titration it precipitates instead of silver cyanide. However, when the end point of the titration occurs too quickly, it is necessary to add ammonia before the titration which will form a solute $Ag(NH_3)^{2+}$ which will slow down the precipitation of silver iodide which is too fast (Kurnia and Marwateon, 2013).

From the above explanation, a research was conducted "Analysis of Cyanide on Gadung Bulb Crackers Sold in Pelem Village, Tulungagung Regency with the Titration Method of Complex Formation".

RESEARCH METHODS

Types of research

The type of research carried out was observative, qualitative and quantitative, namely collecting data according to what happened at the time of qualitative and quantitative research on gadung root crackers which were suspected to contain cyanide using the complex formation titration method.

Materials and tools

The materials used in this study were gadung crackers, 5% tartaric acid, saturated picric acid, 8% Na_2CO_3 solution, 2.5% NaOH, NH_4OH solution, 5% KI, $AgNO_3$ 0.02 N and distilled water. . The tools used in this study were 250 ml Erlenmeyer, 10 ml volume pipette, analytical balance, mortar and pestle, filter paper, water bath, Kjeldahl flask, distillation apparatus, burette.

Sampling

Samples were taken from 3 different traders in Pelem Village, Campurdarat District with different producers.

Qualitative Determination of Cyanide

Samples of gadung chips A were crushed using a pestle and mortar. Samples that have been finely weighed as much as 50 grams. The sample was macerated in 50 ml of water in a 250 ml Erlenmeyer and added 10 ml of 5% tartaric acid solution. Filter paper measuring 1×7 cm was dipped in a saturated solution of picric acid and then dried in air. After drying, it was moistened with 8% $Na_2CO_{3\ solution}$ and hung on the neck of the upper Erlenmeyer and closed in such a way that the paper did not come into contact with the liquid in the Erlenmeyer. Then heated on a 50ºC water bath for 15 minutes. If the pictate paper changes color to red, it means that the sample contains HCN. Qualitative analysis was also carried out on sample B and sample C.

Quantitative Determination of Cyanide

Samples of gadung chips were ground using a pestle and mortar. Samples that have been mashed weighed as much as 10-20 grams. The sample was macerated in 100 ml of distilled water in a Kjeldahl flask for 2 hours. Then 100 ml of distilled water was added and distilled using steam distillation. The distillate was accommodated in an Erlenmeyer which had been filled with 20 ml of 2.5% NaOH. after the distillate reaches 150 ml, the distillation is stopped. The distillate was then added with 8 ml of NH_4OH and 5 ml of 5% KI. The distillate was titrated $_{with\ 0.02\ N}$ AgNO3 solution until turbidity occurred. Quantitative analysis was also carried out on sample B and sample C. 3 times were replicated for each sample.

RESULTS AND DISCUSSION

Qualitative analysis on gadung tuber crackers was carried out to determine the presence of cyanide in the sample. The qualitative test of cyanide on gadung tuber crackers was carried out using picrat paper which was used as an indicator to determine the presence of cyanide in the sample. Picrate paper is made by dipping filter paper that has been cut in size 1×7 cm into a saturated picric acid solution and then aerated to dry. Next, samples of gadung tuber crackers were mashed and weighed as much as 50 grams. The weighed sample was macerated in 50 ml of distilled water with the aim of attracting the active components in the sample without heating or in a cold state (Wulandari and Zulfadli, 2017). The reactions that occur in the maceration process are:

$$CN^-_{(g)} + H_2O_{(l)} \rightarrow HCN_{(g)} + OH^-_{(g)}$$

In the maceration process, 10 ml of 5% tartaric acid was added to produce HCN vapor. Hydrogen from tartaric acid ($H_2.C_4H_4O_6$) produces steam which reacts with CN^- ions and dissolves in water to produce HCN vapor (Wulandari and Zulfadli, 2017). The reaction that takes place is as follows:

$$2\ CN^-_{(g)} + 2\ H_{(g)} \rightarrow HCN_{(g)}$$

The dried picrat paper was then moistened with 8% Na_2CO_3. The addition of Na_2CO_3 was carried out to ensure the picrate ion was stable and able to capture H^+ from cyanide because the optimum condition for the reaction to occur was at pH 10.8. Then the picrat paper was hung around the neck of the Erlenmeyer to prevent it from coming into contact with the liquid in the Erlenmeyer. In addition, hanging picrat paper will cause HCN vapor to be trapped in the acid, causing a color change from yellow to orange-brown (Wulandari and Zulfadli, 2017). The reactions that occur are:

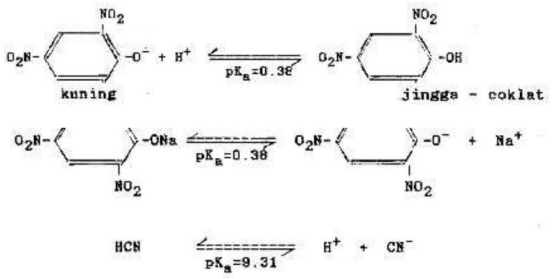

Figure 4.1. Reaction of picric acid with cyanide

Table 4.1 Results of qualitative examination of cyanide on samples

Sample Name	Initial Color	First Replication	Second Replication	Third Replication
Sample A	Yellow	Pink	Yellow	Orange
Sample B	Yellow	Yellow	Yellow	Yellow
Sample C	Yellow	Orange	Orange	Orange

Based on these results indicate that the sample A picrat paper changes color from yellow to pink in the first replication. While the results of the second replication of picrat paper remained yellow and the third replication of picrat paper showed a color change to orange. This indicates the presence of cyanide in the gadung tuber cracker sample with a small concentration. In sample B, after heating the picrat paper remained yellow. Because there is no color change, sample B is estimated to contain very little cyanide or still within the permissible limits. As for sample C, the picrate paper changed color to orange which indicates that the sample contains very low levels of cyanide.

Quantitative analysis was carried out to determine the levels of cyanide contained in samples of gadung root crackers. The steps involved include maceration, distillation and titration. A total of 20 grams of the mashed sample was macerated in 100 ml of distilled water for 2 hours. Then 100 ml of distilled water was added. Before the distillation begins, the Erlenmeyer where the distillate holds the distillate is given 20 ml of 2.5% NaOH so that the NaOH can bind cyanide gas into cyanide salt (NaCN). The sample is distilled until the distillate reaches 150 ml (Mardiyono, 2020).

The distillate was then added with 5 ml of 5% KI. The iodide ion from the KI solution is added as an indicator. Iodide ion is used as an indicator because the amount of silver iodide (AgI) that is deposited is very large so it is possible to be easily seen and its solubility is lower than silver cyanide (AgCN). So that when the end point of the titration will settle to replace the silver cyanide. However, because the end point of the titration occurs very quickly, before the titration, ammonia is added with the formation of solute $Ag(NH_3)^{2+}$ which will slow down the precipitation of silver iodide (KI). The basis of this titration is the formation of a stable complex ion $Ag(CN)^{2-}$ (Kurnia and Marwatoen, 2013).

$$2CN^- + Ag^+ Ag(CN)^{2-}$$

The end point of the titration is characterized by the occurrence of stable turbidity due to the precipitation of silver cyanide (Kurnia and Marwatoen, 2013). The reaction that occurs is as follows:

$$Ag^+ + Ag(CN)^{2-} 2AgCN.$$

The method used in determining cyanide levels is through titration of the formation of a modified deniges complex because the cyanide ion will react with silver nitrate solution to form a stable complex of AgCN which is characterized by the occurrence of turbidity. The disadvantage of this method is that it is difficult to obtain a clear end point for the titration because the precipitate dissolves very slowly as it approaches the end point. While the advantages of this method do not require large costs, the reagents are easy to obtain, easy to work with and do not require a standard solution of cyanide acid because cyanide acid is relatively stable. In addition, the cyanide content in gadung root crackers is small so it is enough to do it by titration (Mardiyono, 2020). The results of the titration and cyanide levels in the sample can be seen in table 4.2.

Table 4.2 Results of examination of cyanide levels in samples

No.	Sample Name	Average Titration Volume	HCN level
1.	Sample A	3,934 ml	2.124 mg/kg
2.	Sample B	1,667 ml	0.9 mg/kg
3.	Sample C	2,567 ml	1,386 mg/kg

Cyanide levels obtained in samples of gadung root crackers from sample A, sample B and sample C were 2.124 mg/kg, respectively; 0.9 mg/kg; 1,386 mg/kg. Meanwhile, according to the 2006 Indonesian National Standard (SNI) concerning food additives, the maximum allowed cyanide in food is 1 mg/kg. Based on this, from the 3 samples tested, there were 2 samples whose cyanide levels exceeded the specified limit, namely sample A and sample C. This was due to

improper processing of gadung tubers. This is in line with the research of Sari and Astili (2017) that the cyanide content of beef jerky made from cassava peel waste that has gone through several processes, namely washing, boiling, soaking, drying and frying is 4.8 mg/kg.

Eating foods that contain cyanide residues can be detrimental to health. Symptoms of poisoning caused by consuming foods containing cyanide are dizziness, weakness, vomiting, inflammation of the esophagus, fainting and stomach cramps. Cyanide compounds that enter through food into the body will react with sulfur to form thiocyanate compounds (SCN-). The sulfur used is derived from essential amino acids containing S, namely methionine and cystine. This can cause KKP (Less Calorie Protein) because the body lacks protein or amino acids. In addition, the thyroid gland that should absorb iodine will be bound by ionic compounds, including SCN^-. SCN^- in large quantities in the body can cause depletion of iodine compounds, resulting in goiter, hearing loss, slow growth with mental deficiency and confusion (Ardiansari, 2012).

CONCLUSION

Based on the results and discussion of cyanide analysis research on gadung root crackers sold in Pelem Village, it can be concluded that of the 3 samples of gadung root crackers tested, there were 2 samples that did not meet the specified requirements, namely sample A with a concentration of 2.124 mg/kg and sample C with levels of 1,386 mg/kg. The method used in determining cyanide levels is through titration of the formation of a modified deniges complex because the cyanide ion will react with silver nitrate solution to form a stable complex of AgCN which is characterized by the occurrence of turbidity.

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