### Formulation of Watermelon Rind (Citrullus vulgaris schard) and Secang (Caesalpinia sappan L.) Jam as Functional Food Rich in Antioxidants

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#### Abstract

The body's immune system is one of the natural defenses in the human body, functioning to ward off various diseases, including those that emerged after the Covid-19 pandemic. One plant with potential as an antioxidant and easily found in the environment is watermelon. Jam made from watermelon rind and secang wood, with various formulations, namely 100% watermelon rind: 0% secang (F1), 90% watermelon rind: 10% secang (F2), 80% watermelon rind: 2% secang (F3), and 70% watermelon rind: 3% secang (F4), is expected to possess good antioxidant properties. A promising antioxidant formulation for watermelon rind jam and secang is the one with 70% watermelon rind and 30% secang (F4), having an IC<sub>50</sub> value of 144.27 g/mL, which is classified as a moderate antioxidant. Among the four jam formulations, panelists preferred the jam formulation (F4) without the addition of sweetened condensed milk in terms of color and texture. However, for the jam formulation (F4) with the addition of sweetened condensed milk, panelists favored it in terms of aroma and taste. The jam formulation (F4) meets the quality standards for fruit jam based on INS 3746:2008, including total plate count, arsenic, and tin categories.

Keywords: Jam, watermelon rind, secang, antioxidant

#### INTRODUCTION

After the Covid-19 pandemic, it is important to consume minerals and vitamins that contain high antioxidants. Apart from their ability to ward off free radicals, antioxidants can also enhance the strength of the body's immune system. The body's immunity is one of the natural defenses in the human body and various serves to protect against diseases. Antioxidants are chemical compounds capable of donating one or more electrons to reactive free radicals, thereby forming free radicals that are unreactive and relatively more stable (Brewer, 2013).

One of the plants that holds potential as an antioxidant and is readily available in the surrounding environment is watermelon (Mariani, 2018). Watermelon (Citrullus vulgaris schard) is a popular fruit among Indonesians due to its sweet, crunchy, and refreshing taste, along with its high water content. The watermelon fruit consists of several parts, namely the red or yellow flesh, albedo (white flesh), and the green, hard outer rind. Watermelon fruit is typically consumed either directly as fruit or in the form of juice, with the rind usually discarded. Currently, watermelon rind waste is underutilized (Siregar, 2015).

The albedo of the watermelon rind contains high levels of antioxidants that can neutralize free radicals and reduce cell damage in the body (Tahir, 2016). Phytochemical screening of the white rind juice reveals the presence of phenolics. Phenolic compounds are phytonutrients known for their antioxidant properties (Ismayanti, 2013). Additionally, the watermelon albedo serves as a potential source of pectin, comprising approximately 21.03% of the pectin compound (Sutrisna). Therefore, the albedo presents a promising opportunity for utilization and development in Indonesia as a new food source, especially during the ongoing Covid-19 pandemic.

The role of pectin as a thickening agent in the albedo is crucial in the processing of food products that require thickening or gelling agents, such as jam. Jam comprises food products derived from fruits (Yenrina, 2019). Fruit jam is widely enjoyed by people of all ages and backgrounds, making it a promising candidate for development. However, the white color of watermelon albedo can result in unattractive-looking jam. To address this issue, it becomes necessary to incorporate other ingredients to achieve a more appealing color (Novidahlia, 2019).

One of the additives that can be used is sappan wood. Secang (Caesalpinia sappan L.) is an herbal plant known for its high antioxidant activity. Secang wood has been traditionally used as an herbal beverage, particularly in Bulukumba Regency, due to its numerous beneficial properties. The red dye present in secang, referred to as the brazilin group, belongs to a class of antioxidant compounds containing catechols in their chemical structure. These compounds have the ability to safeguard the body from damage caused by free radicals (Utari, 2017). Moreover, sappan wood has been reported to possess various medicinal properties, including treating the blood, impurities in antidiabetic effects, anticoagulant properties, anti-tumor activity, antimicrobial and antiviral effects, anti-inflammatory properties, and detoxification (Badami, 2015).

The body has antioxidants as a defense mechanism to neutralize formed free radicals. Antioxidants are compounds that can inhibit free radical activity by giving up one or more electrons to free radicals resulting in excessive oxidation reactions in the body (Fadiyah dkk, 2020). Free radicals contain one or more unpaired electrons in their outer orbitals (Andriana dan Tantawi, 2017). The nature of free radicals is very reactive and unstable, causing radicals to seek and grab electrons from other nearby molecules to release energy and return to a stable state. If free radicals do not bind to antioxidants, they will cause ongoing oxidation reactions that can cause damage to cells in the body.

Sources of antioxidants are naturally present in fruits, vegetables, and whole grains. These include vitamin C, vitamin E, carotenes, phenols, and phytoestrogens (Murray, 2017). The mechanism of antioxidant reactions in natural products is based on reducing oxidative stress by scavenging free radicals through three primary methods: the donation of hydrogen ions by tocopherols and polyphenols, quenching singlet oxygen facilitated of by carotenoids, and electron donation through the role of ascorbate. If not addressed, free radical reactions can persist in the body and lead to various ailments like cancer, heart disease, cataracts, premature aging, and diseases other degenerative (Rustiah. 2018). Watermelon rind jam is a food product that utilizes waste and contains antioxidants, thereby enhancing its market value.

Based on this context, the current study aimed to develop a formulation for watermelon rind and secang jam, creating a functional food product abundant in antioxidants. The goal was to produce jam items that meet the standardized requirements set by the Indonesian National Standard (INS) and offer health benefits to individuals during the Covid-19 pandemic. Additionally, these jam products were designed to cater to consumer preferences and garner popularity among them.

#### METHODOLOGY

#### **Tools and materials**

The materials used in this study were sulfuric acid ( $(H_2SO_4)$  99%, distilled water, iron (III) chloride (FeCl<sub>3</sub>), watermelon rind, 10% sodium hydroxide (NaOH) 10%, secang plant. The tools used in this study were a hotplate, mortar, pestle, stir bar, beaker, measuring flask, funnel.

#### Preparation of Watermelon Rind Jam and Secang

This study used watermelon and sappan wood Bukit Harapan, Gantarang, Bulukumba from Regency, South Sulawesi. In general, jam processing consists of three stages: preparation of ingredients, cooking, and packaging. The preparatory stage separates the albedo of the watermelon and then pulverizes it with a blender until a fruit pulp is formed. The next step is cooking, which aims to make a homogeneous mixture of granulated sugar, lime juice, cinnamon sticks, and boiling water of sapphire and fruit pulp, produce a good taste, and obtain a gel structure. The resulting jam products are then packed into containers that have been sterilized and tightly closed.

# Phytochemical test of Watermelon Rind Jam extract and secang extract

Phytochemical screening for phenolic compounds was carried out with FeCl<sub>3</sub>, flavonoids using 10% NaOH and 5% FeCl<sub>3</sub>, saponins with shaking, terpenoids, and steroids with libermann burchard reagent. As for the alkaloids, it was carried out using Mayer's and Wagner's reagents.

### **Antioxidant Activity Test**

Antioxidant activity test using the DPPH method used samples of jam formulas F1, F2, F3, and F4 taken 50  $\mu$ L and put into the plate. The DPPH blank was 50  $\mu$ L methanol, and the sample blank was 50  $\mu$ L aquadest. After that, 80 $\mu$ L of DPPH 80 $\mu$ L/mL was added. Cover the plate with aluminum foil. The mixture was incubated for 30 minutes in a dark place at room temperature. The absorbance of the sample was measured with *a microplate reader* at a wavelength of 515 nm.

#### Organoleptic Test with the Hedonic Method

The hedonic test on jam used 30 panellists with an average age of 20-50 years. panelists tasted samples, and between each sample, tasting were required to consume drinking water as a neutralizer, then panelists were asked to fill out a questionnaire. The organoleptic test used the hedonic scale for the jam with the highest antioxidant activity.

#### Jam Quality Standard Test

Testing for jam quality standards follows procedures set by the 2008 National Standardization Agency.

### **RESULTS AND DISCUSSION**

#### **Phytochemical Test**

The phytochemical test was carried out qualitatively by using several specific reagents. The results of the phytochemical analysis can be seen in Table 1

Table 1. Result of Phytochemical Test of Watermelon
rind and Secang

Compound	Reagent	Watermel on rind extract	Secang extract
Fenolik	FeCl <sub>3</sub>	+	+
	$H_2SO_4$	+	+
Flavonoid	NaOH 10%	+	-
	FeCl <sub>3</sub> 5%	-	+
	Dragendorff	+	+
Alkaloid	Mayer	-	-
	Wagner	-	+
Terpenoid/	Lieberman	-	+
Steroid	n-Burchard		
Tanin	FeCl <sub>3</sub>	-	+
Saponin	Bubble	+	-

Note : (+) = positive and (-) = Negative

Phytochemical tests were conducted to determine the class of compounds present in the water extract of watermelon peels and secang when exposed to specific reagents. The aim of the phytochemical tests on jam products was to identify the chemical compounds that contribute to the assessment of jam quality, including phenolic, flavonoid, alkaloid, terpenoid/steroid groups, tannins, and saponins (Widowati, 2013). The results of the phytochemical tests using water extracts on watermelon peels and secang are presented in Table 1.

Specifically, the watermelon peels were found to contain phenolics and flavonoids, as indicated by

reactions with concentrated  $H_2SO_4$  and 10% NaOH reagents, alkaloids detected by the Dragendorff reagent, and saponins, which were characterized by the formation of foam. As for secang, the phytochemical tests revealed the presence of phenolics and flavonoids with concentrated  $H_2SO_4$ and 5% FeCl<sub>3</sub> reagents, alkaloids detected by Dragendorff and Wagner reagents, as well as terpenoids/steroids and tannins.

## Jam Formulation of Watermelon Rind (*Citrullus* vulgaris schard) and Secang (*Caesalpinia sappanL.*)

The results of the formulation of watermelon rind jam and secang can be seen in Figure 1. Jam formulation of watermelon rind and secang was made with four formations, namely F1 ((100% watermelon rind : 0% secang), F2 (90% watermelon rind: 10% secang), F3 (80% watermelon rind: 20% secang) and F4 ( 70% watermelon rind: 30% cup). Watermelon rind is the main ingredient for making jam because it contains pectin, or a thickening agent at albedo, which is very important in manufacturing processed food products that require a thickening agent or gelling agent, such as jam.





The results of making jam formulations can be seen in Figure 1 shows that the color of jam F1 (without the addition of secang) looks brownish green. Formulations F2, F3, and F4 have a bright color, namely brownish red. This is due to the presence of a red dye contained in secang known as the brazilin group, a group of antioxidant compounds with catechol in their chemical structure that can protect the body from poisoning due to free radicals.

#### Antioxidant Test

The recapitulation results of antioxidant activity can be seen in Table 2. This study employed the DPPH method to determine the antioxidant content in jam, utilizing the  $IC_{50}$  (inhibition concentration) as a parameter. The IC<sub>50</sub> represents the concentration of the sample solution required to reduce DPPH activity by 50%. According to Molyneux (2004), the categorization of antioxidant strength based on IC50 values is as follows: very strong if IC<sub>50</sub><50 ppm, strong for 50<IC<sub>50</sub><100 ppm, moderate for 100-IC<sub>50</sub><150 ppm, weak for 150 ppm-IC<sub>50</sub><200 ppm, and very weak if IC<sub>50</sub>>200 ppm. The process of obtaining IC<sub>50</sub> values involves various steps, such as calculating concentration and inhibition values for each percentage of DPPH free radical inhibition in jam formulations (Taba et al., 2019).

Table 2. Results of Antioxidant Analysis on Jan	n
Formulations of Watermelon Peel and Secang	

No	Sample code	IC <sub>50</sub> (µg/mL)
1	F1	180.79
2	F2	149.50
3	F3	146.01
4	F4	144.27

$IC_{50} \le 50 \ \mu g/mL = very strong$
$IC_{50}: 50 - 100 \ \mu g/mL = strong$
$IC_{50}$ : 101 - 150 µg/mL = moderate
$IC_{50}$ : 150 - 200 µg/mL = weak
$IC_{50} \ge 200 \ \mu g/mL = very \ weak$

Table 2 reveals that the  $IC_{50}$  value for F1 was 180.79 µg/mL (ppm). Interpreting this IC<sub>50</sub> value, it can be deduced that the antioxidant activity is relatively weak, falling within the IC<sub>50</sub> range of 150-200. This implies that a concentration of 180.79 ppm of watermelon rind and secang jam is needed to radicals. capture 50% free Conversely, of formulations F2, F3, and F4 are categorized as having moderate antioxidant activity, as their IC<sub>50</sub> values fall within the range of 101-150 µg/mL (ppm). This suggests that adding secang to the jam enhances its antioxidant activity compared to the jam without secang. This improvement is attributed to the presence of phenolic and flavonoid compounds in secang, which contribute to its high antioxidant potency (Aisyah, 2021).

Notably, a study by Mariani (2018) found that the IC<sub>50</sub> value of red watermelon rind extract was 14,729 mg/L, classifying it as a very strong antioxidant. Additionally, research by Setiawan (2018) indicated that the ethanol extract of secang exhibited an IC<sub>50</sub> value of 11.37 mg/L, signifying its classification as a very strong antioxidant. However, when watermelon rind and secang are processed into jam, their respective IC<sub>50</sub> values decrease, indicating a reduction in antioxidant activity. This decline can be attributed to the heating process involved in jammaking. The heat causes cell walls in the plant material to break down, enabling the release of compounds, including antioxidants, into the water solvent. Moreover, the heating process can lead to the breakdown of chemical bonds in macromolecules, resulting in smaller molecules with higher solubility in water, including antioxidant compounds (Momuat, 2010).

#### **Organoleptic Test**

The watermelon rind and secang jam formulation with the highest antioxidant content is labeled as F4. Subsequently, F4 underwent organoleptic testing, where various parameters were evaluated, including color, aroma, taste, and texture. Figure 2 illustrates the data, revealing distinctive observations.



Figure 2. Organoleptic Test on Jam of Watermelon rindand Secang (F4 Formulation)

Concerning color, the dominant panelists favored the F4 jam formulation without the inclusion of SKM (sweetened condensed milk). This preference is attributed to the natural brownish-red hue derived from secang, a natural dye, which produced a superior color compared to the SKM-added version, characterized by a less vibrant color.

In terms of aroma, the F4 jam formulation without SKM received positive feedback due to the notable aroma from the watermelon rind. Conversely, the F4 jam formulation with SKM garnered high approval due to the additional aroma contributed by the SKM, eliciting a heightened sensory experience among panelists. Addressing taste, the F4 jam formulation without SKM was favored by panelists due to the robust and pronounced sweetness, showcasing a rich flavor akin to concentrated sugar. Despite the inclusion of sugar in the jam, the distinct sugary taste remained prominent. On the other hand, the F4 jam formulation with SKM gained favor for its heightened sweetness, effectively masking the intense secang flavor inherent in the jam.

Regarding texture, the F4 jam formulation without SKM was preferred by panelists due to its fibrous and substantial texture. Conversely, the F4 jam formulation with SKM was slightly favored in terms of texture, although its consistency was perceived as less fibrous and more adhesive, which led to a stickiness on the hands. Therefore, the researcher's inclination leans towards the jam formulation (F4) without SKM for its superior color and texture characteristics. Meanwhile, the jam formulation (F4) with SKM found favor among panelists for its appealing aroma and taste.

# Jam Quality Standard Test (ALT, Arsenic, and Tin)

The parameters of the fruit jam quality standard used in this study were ALT, arsenic, and tin. Table 3 explains that the total plate count in the F4 jam formulation is  $8.6 \times 10^{11}$  colonies/g. This indicates that the result is within the safe limits set by INS 3746: 2008, which specifies a maximum count of  $1 \times 10^{3}$ . The arsenic content in the F4 jam formulation was <0.001 mg/kg, indicating compliance with the requirements of INS 3746: 2008, which has a maximum limit of 1.0 mg/kg.

Table 3. Results of jam quality standards test (ALT,<br/>Arsenic and Tin)

Parameter	Unit	result	Requirements		
Total Plate	colony/g	8.6×10 <sup>1</sup>	Max $1 \times 10^3$		
Number					
(ALT)					
Arsenic	mg/kg	< 0.01	Max. 1.0		
Tin	mg/kg	1.47	Max 250.0		

In contrast, the F4 jam formulation contains 1.47 mg/kg of tin. These results demonstrate that they are still safe and meet the criteria outlined in INS 3746: 2008, which sets a maximum limit of 250.0 mg/kg for tin. Therefore, the F4 jam formulation with the best antioxidant content continues to meet the quality standards for fruit jam as specified by INS 3746: 2008, in terms of total plate count, arsenic, and tin content.

#### CONCLUSIONS

The formulation of watermelon rind and secang jam using the 70%:30% secang ratio (F4) proved to be the most effective, exhibiting superior antioxidant activity compared to formulas F1, F2, and F3. The IC-50 value ( $\mu$ g/mL) for F4 was 144.27. Regarding organoleptic evaluation, the F4 jam formulation without the addition of SKM was favored for its color and texture, whereas the F4 jam formulation with the inclusion of SKM was preferred in terms of aroma and taste. Additionally, it has successfully met the quality standards set by INS 3746: 2008 for fruit jam, particularly in the aspects of total plate count, arsenic content, and tin content.

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#### REFERENCES

- Aisyah, D.N, Nety Kurniaty & Gita Cahya Eka Darm.(2021). Antioxidant Activity Test of Red Dragon Fruit (*Hylocereus polyrhizus* L.) and Jam Formulation. *Pharmaceutical Proceedings*, 7(1): 37-41.
- Andiana R, & Tantawi D. Antioxidants in Detmatologyi. JKK, 4(1): 39-48.
- Badami S, Moorkoth S, Rai SR, Elango L,Bhojraj S. (2015). Antioxidant activity of Caesalpinia sappan heartwood. *Biol. Pharm*, *26*(11), 1534-1537.
- Brewer MS. (2013). Natural Antioxidant: Sources, Compounds, Mechanisms of Action and Potential Applications.Compr Rev Food Sci Food Saf. *Journal Food Sains*, 10(4): 221-247

- Fadiyah I, Iin L, dan Robby G.M. (2020). Antioxidant Capacity of Rukam Fruit Extract (Flacourtia Rukam) Using Microwave Assisted Extraction (MAE) Method.. *Indonesian Journal of Chemical Research* 7(2): 107-113.
- Ismayanti, Bahri S, Nurhaeni. (2013). Study of Phenolate and Antioxidant Levels of Watermelon (*Citrullus lanatus*). Journal Natural Science, 2(2): 36-45.
- Mariani S, Nurdin R, Supriadi. (2018). Antioxidant Activity Test of Watermelon Fruit Extract (*Citrullus lanatus*). Jurnal Akademika Kimia, 7(3): 107-114.
- Molyneux P. (2004). The Use of The Stable Free Radical Diphenylpicrylhydrazil (DPPH) for Estimating Antioxidant Activity, *Journal Science Technology*, 26(2): 211-219.
- Momuat L, Feti F, Frenly W, & Oktavianus Mamondol. (2010). The Effect of Heating on the Total Antioxidants of Several Types of Tinutun Vegetables. *Chemistry Progress*, 3(2): 85-90.
- Murray B. (2017). Hydration and physicalperformance. J. Tthe American CollNutr, 26(sup5), 542S–548S.
- Novidahlia, N, Titi R, & Yuni N. (2019). Physochemical Characteristics of Jelly Drink Meat of Watermelon, Albedo of Watermelon, and Tomato with Addition of Carrageenan and Porang (Amorphophallus muelleri Blume) Starch. Jurnal Agroindustri Halal, 2(2): 57-66.
- Rustiah W, dan Nur U. (2018). Antioxidant Activity Test of Kawista Fruit Extract (*Limonia Acidissima*). Indo. J. Chem. Res. 6(1), 22-25.
- Setiawan F, Oeke Y, & Ade K. (2018). Antioxidant Activity Test of Secang Wood (*Caesalpinia* Sappan) Ethanol Extract Using DPPH, ABTS and FRAP Methods. *Media Pharmaceutica* Indonesian, 2(2): 82-89.

- Siregar S. (2015) The Effect of Comparison of Watermelon Peel Extract with Passion Fruit Extract and the Amount of Sucrose on the Quality of Hard Candy, *Tesis*, Universitas Sumatra Utara.
- Souhoka F.A, Nikmans H, dan Marsye H. (2019). Antioxidant Activity Test of Kesumba Keling (*Bixa Orellana* L) Seed Methanol Extract. *Indonesian Journal of Chemical Research*, 7(1): 25-31.
- Taba P, Nadya Y.P, dan Syahruddin K. (2019). Synthesis of Silver Nanoparticles Using Bay Leaf Extract (*Syzygium polyanthum*) As a Bioreductor And Test Its Activity As An Antioxidant. *Indonesian Journal of Chemical Research*, 7(1), 51-60.
- Tahir M, Heluyh AC, Widiastuti H. (2016). Test the antioxidant activity of watermelon (*Citrullus lanatus*) using the FRAP method. *As-Syifaa*. 8(1): 31-38.
- Utari FD, Sumirat, Djaeni M. (2017). Production of Antioxidants from Secang Wood Extract (*Caesalpinia sappan* L.) using Low Humidity Dryer. Journal Food Technology Application, 6(3): 1-4.
- Widowati W. (2013). Phytochemical test and antioxidant potential of the ethanol extract of secang wood (*Caesalpinia sappan* L.). *Journal Maranatha Medicine*, 11(1): 23-31.
- Yenrina R, Hamzah N, Zilvia R. (2019). Quality of jam sheet mix of pineapple (Anans comusus L.) with pumpkin seeds (Curcubitamoschata), *Education Journal 1*(2): 33-42.