

Analysis of Formaldehyde in Circulating Grapes in Makassar

Nurfathiyatul Izza, Aminah, Rais Razak*

Laboratory of Pharmaceutical Chemistry, Faculty of Pharmacy, Indonesian Muslim University, Makassar 90231, Indonesia

*Corresponding Author. E-mail: nurfathiyatulizza09@gmail.com

Received: 17 January 2023 / Revised: 22 February 2023 / Accepted: 11 March 2023

ABSTRACT: Formalin or formaldehyde is a chemical compound whose use is prohibited as a preservative in food additives. This study aims to analyze the content of formalin in red grapes (*Vitis vinifera*) circulating in the city of Makassar. The method used in this test is by using Schiff reagent and UV-Vis spectrophotometry. The results of the Schiff reagent test showed that two of the 10 grape samples were positive for formalin. Test results on UV-Vis Spectrophotometry at a wavelength of 556 nm, that all red grape samples obtained contained formalin with formalin levels as follows: Sample Tamalanrea 1 TD = 0.778%, Tamalanrea 2 TD = 0.483%, Manggala TD= 0.452%, Tamalate TD= 0.734%, Biringkanaya TD= 0.552%, Tamalanrea 1 SD= 0.452%.

KEYWORDS: Red grapes; Formalin; Schiff reagent; and UV-VIS Spectrophotometry.

1. INTRODUCTION

Grapes are one of the many types of fruits that contain lots of vitamins and nutrients; the body needs these vitamins and nutrients. There are so many benefits of grapes, therefore, it is necessary to preserve them to maintain their quality. Food preservation commonly used can include cooling, heating, drying, smoking, and preservatives (Mina NM, 2018). Formalin is one of the preservatives with a good preservative effect. However, formalin is a chemical that is prohibited from being used in food (Daelis, 2023). According to the Minister of Health of The Republic of Indonesia No. 033, 2012, concerning Amendments to Food Additives, 1168/Menkes/Per/X/1999 and Regulation of the Minister of Health Number 722/Menkes/Per/1988.

According to the BPOM Processed Food Standardization Directorate, in 2016 and 2017, several fresh food products were found that positively contained formaldehyde, namely grapes and tomatoes. It is known that exposure to formalin through digestion can have effects in the form of irritation and is corrosive to the digestive mucous membranes, as well as nausea, vomiting, and intense pain in the stomach (Namtini SS, 2019). Determination of formalin levels can be done using fluorimetry, HPLC, gas chromatography, and spectrophotometry. The method that is usually used is the spectrophotometric method because it is cheap and easy to use (U. Santoso, 2020). Therefore, it is necessary to make efforts to detect the presence or absence of formalin in food, especially grapes circulating in the community, especially those in the Makassar city area, by using qualitative and quantitative tests, namely by using a color reagent in the form of Schiff reagent and also using an instrument in the form of a spectrophotometer UV-Vis.

2. EXPERIMENTAL SECTION

2.1. Population and Sample

The population in this study were red grapes that circulated in the city of Makassar. The samples used in determining the level of formaldehyde were red grapes scattered in the Makassar city area, which consisted of 5 samples, then given 2 treatments where 5 samples were washed, and 5 other samples were not washed. The samples came from several sub-districts taken randomly in the Makassar city area. The samples were taken from 4 sub-districts, namely 1 sample in Biringkanaya sub-district, 1 sample in Manggala sub-district, 2 samples in Tamalanrea sub-district, and 1 sample in Tamalate sub-district. The washed samples have names, namely Tamalanrea 1 TD, Tamalanrea 2 TD, Manggala TD, Tamalate TD, and Biringkanaya TD. The unwashed samples have names, namely Tamalanrea 1 SD, Tamalanrea 2 SD, Manggala SD, Tamalate SD,

2.2. Materials and tools

The materials used are fuchsin, aquadest, formaldehyde 37% pa, HCl, universal pH paper, anhydrous sodium sulfite pa, and samples (red grapes). While the tools used were bulk, glassware in the form of a 50 mL beaker, 10 mL measuring cup, cuvettes, 5, 10 mL, and 25 mL volumetric flasks, mortar and pestle, micropipette, 1 mL volume pipette, knife, UV-Vis spectrophotometer, test tube and analytical balance.

2.3. Qualitative Analysis

A number of fruits crushed in a mortar, then add enough water about 2 mL, strain and take the filtrate. Then acidify with 2 drops of HCl until the pH obtained is less than 3. Add 3 mL of colorless Schiff reagent. After a while, a red-to-purple color will form if it is positive for formaldehyde (Mudaffar, 2018).

2.4. Quantitative Analysis

2.4.1. Preparation of stock solutions for standard formalin

From a 37% formaldehyde solution, 5 mL was used and diluted with distilled water up to 10 mL to obtain a concentration of 500 ppm, then 2.5 mL of this concentration was taken and diluted with distilled water up to 25 mL and a concentration of 50 ppm was obtained.

2.4.2. Maximum wavelength determination

Pipette 3.3 mL of the 50 ppm standard solution into a 5 mL volumetric flask, add distilled water to the mark and add 3 mL of Schiff's reagent to obtain a concentration of 33 ppm. The 33 ppm solution was then measured at a wavelength of 400-800 nm.

2.4.3. Standard curve creation

From a stock solution of 50 ppm, a formalin solution was prepared with 5 concentration series, namely 12 ppm, 14 ppm, 16 ppm, 18 ppm, and 20 ppm. For each of these concentrations, add 3 mL of Schiff's reagent. Dilute with distilled water up to 5 mL, then measure the absorbance value at the maximum absorption wavelength.

2.4.4. Sample preparation and measurement

Sample preparation was carried out by taking 10 samples from 5 of the same collection points and then dividing them into 2 treatments, where the first treatment consisted of 5 samples being washed and the second treatment was 5 samples not washed, then each sample was carefully weighed to as much as 15 g, then crushed in a mortar, added water to a volume of 25 mL in a volumetric flask, and filtered with filter paper. Take 0.01 mL of the filtrate, then add 0.01 mL of Schiff's reagent to a 10 mL volumetric flask and add distilled water up to the mark. In data analysis, the linear regression method is used by plotting the results of the sample absorbance on the standard curve that has been made before.

2.5. Data analysis

Data analysis was carried out by calculating the formaldehyde content in red grapes using the sample content equation formula (Lambert Beer):

$$\text{Concentration (\%)} = \frac{\text{C sample (ppm)} \times \text{Sample volume (L)} \times \text{Fp}}{\text{Sample weight (mg)}} \times 100\%$$

3. RESULTS AND DISCUSSION

The results of a qualitative analysis using Schiff reagent, as shown in **Table 1**, resulted in a yellow or yellow to pink color change where this color came from a sample of red grapes that had been crushed together with the skin and filtered and added about 1-2 mL of aquadest so that the filtrate was slightly pink in color, and the yellow color comes from a reagent that has removed the purple color so that it can detect the presence or absence of formaldehyde in the sample by seeing whether there is a change in color to purplish – red from the sample added with Schiff's reagent. Purplish-red color is present in the Tamalanrea 1 TD and Tamalate TD samples, yellow to pink in the Tamalanrea 2 TD sample, yellow to pink in the Manggala TD sample, yellow to pink in the Biringkanaya TD sample, yellow to pink in the Tamalanrea 1 SD sample, yellow to pink in the Tamalanrea 2 SD sample, yellow in the Manggala SD sample, yellow to pink in the Tamalate SD sample, and yellow to pink in the Biringkanaya SD sample. This is in accordance with the theory that Schiff's reagent and formaldehyde will react and produce a color change, which is the result of a condensation reaction between formaldehyde containing a carbonyl group (C=O) and Schiff's reagent (Pratiwi et al., 2019).

Formaldehyde reagent is used to test aldehydes, and formaldehyde, in this case, is formalin which is an aldehyde, so this reagent can be used to determine whether formaldehyde is present. Schiff's reagent consists of fuchsin, which has been decolorized and initially has a purple-black color and is then removed by sulfur dioxide, with the addition of formaldehyde containing aldehydes so that it returns a purple color. Formaldehyde can return to a purple color in a short time (NSKiroh, 2019) Schiff's reagent and formaldehyde will react and produce a purplish-red color (Junaini, 2016). From the qualitative analysis it can be seen that the samples tested in the form of red grapes were positive for formaldehyde. To make sure further.

Table 1. Qualitative identification of formaldehyde with Schiff reagent

Sample	Positive Results (Reference)	Test result	Information
Tamalanrea 1 TD	Purplish red	Purplish red	+
Tamalanrea 2 TD	Purplish red	Yellow to pink	-
Mangala TD	Purplish red	Yellow to pink	-
Tamalate TD	Purplish red	Purplish red	+
Bring it on TD	Purplish red	Yellow to pink	-

Tamalanrea 1 SD	Purplish red	Yellow to pink	-
Tamalanrea 2 SD	Purplish red	Yellow to pink	-
Mangala SD	Purplish red	Yellow	-
Tamalate SD	Purplish red	Yellow to pink	-
Biringkanaya SD	Purplish red	Yellow to pink	-

The maximum wavelength obtained is 556 nm, which is in the literature (Manoppo G, 2014) the maximum wavelength of formalin (Formaldehyde) is 550 nm. The wavelength obtained is 556 nm experiencing a bathochromic shift, namely a shift at the maximum wavelength towards longer wavelengths. Differences can cause this and influence temperature as well as pH. Standard curve solutions were made with several concentrations, as shown in **Table 2**. This solution was measured at the maximum wavelength so that the absorbance of each concentration was obtained, then a linear line equation was obtained, which would be used in determining the formaldehyde content in red grape samples.

Table 2. Standard curve measurement results

Concentration (ppm)	Absorbance (550 nm)
12	0.403
14	0.459
16	0.523
18	0.567
20	0.615

The calibration curve is a graph that forms a line (linear), which is the relationship between the levels of the test solution and the blank with a proportional response from the UV-Vis Spectrophotometer. The regression equation of the standard curve is $y = 0.0266x + 0.0878$, with the value of r being 0.9976. 0.0266x is the value of the slope (b), 0.0878 is the value of the intercept (a), and 0.9976 is the value of the correlation coefficient (r). The correlation coefficient obtained is close to 1 and in accordance with the requirements for acceptance of a good correlation coefficient, namely > 0.995 (Astuti et al., 2016).

On rate settings formaldehyde content of the red grape samples was determined by plotting the results of the linear regression obtained with the absorbance of the samples that were measured. The determination of the formaldehyde content is shown in **Table 3**. The results of the calculation of formaldehyde levels in 10 samples of red wine were taken from 5 traders and given 2 treatments. Of the 10 samples, 5 were washed and the other 5 were not washed, namely Tamalanrea 1 TD, Tamalanrea 2 TD, Manggala TD, Tamalate TD and Biringkanaya TD, which are the names of grape samples with unwashed treatment having absorbance values of respectively, 0.212, 0.165, 0.160, 0.205, and 0.176. Then the percentage of formaldehyde in each sample was obtained, namely 0.778%, 0.483%, 0.452%, 0.734% and 0.552%. In the other 5 samples that were given treatment in the form of washing with the name Tamalanrea 1 SD, Tamalanrea 2 SD, Manggala SD, Tamalate SD, and Biringkanaya SD. The absorbance values are sequentially 0.160, 0.160, 0.153, 0.161, and 0.156, and the percent concentrations obtained in each sample are 0.452%, 0.452%, 0.408%, 0.458 %, and 0.427%. From the results obtained, based on the Regulation of the Minister of Health of the Republic of Indonesia No. 033 of 2012 concerning Amendments to Food Additives, 1168/Menkes/Per/X/1999 and Regulation of the Minister of Health Number 722/Menkes/Per/1988, that one of the prohibited food additives for use is Formalin (Formaldehyde)

Table 3. Determination of formaldehyde levels in red grape samples

Sample	Absorbance (556 nm)	Rate (%)
Tamalanrea 1 TD	0.212	0.778%
Tamalanrea 2 TD	0.165	0.483%
Mangala TD	0.160	0.452%
Tamalate TD	0.205	0.734%
Bring it on TD	0.176	0.552%
Tamalanrea 1 SD	0.160	0.452%
Tamalanrea 2 SD	0.160	0.452%
Mangala SD	0.153	0.408%
Tamalate SD	0.161	0.458%
Biringkanaya SD	0.156	0.427%

4. CONCLUSION

There is a formalin (formaldehyde) content in grapes circulating in the city of Makassar. In the qualitative test, there were 2 samples that were positive for formaldehyde, namely the Tamalanrea 1 TD and Tamalate TD samples.

Followed by a formalin level test using a UV-Vis Spectrophotometer at a wavelength of 556 nm, and ten samples of red grapes containing formaldehyde in the form of Tamalanrea 1 TD = 0.778%, Tamalanrea 2 TD 0.483%, Manggala TD = 0.452%, Tamalate TD = 0.734%, Biringkanaya TD = 0.552%, Tamalanrea 1 SD = 0.452%, Tamalanrea 2 SD = 0.452%, Manggala SD = 0.408%, Tamalate SD = 0.458%, and Biringkanaya SD = 0.427%. Referring to the Regulation of the Minister of Health of the Republic of Indonesia No. 033 of 2012 concerning Amendments to Food Additives, 1168/Menkes/Per/X/1999 and Regulation of the Minister of Health Number 722/Menkes/Per/1988,

Acknowledgments: The authors are grateful to The Head of Pharmaceutical Chemistry Laboratory, Indonesian Muslim University. The authors are grateful to The Dean of Faculty of Pharmacy, Universitas Muslim Indonesia for the space to do this research.

Author contributions: Concept – MP, TN; Design – MP, ZA; Supervision –MB, MP, S., TN; Materials – RMJ, MB; Data Collection and/or Processing – RMJ, USA; Analysis and/or Interpretation – MP, MB, RMJ, AS; Literature Search – MP, MB, RMJ, US; Writing – MP, MB, A; Critical Reviews – MP, MB, A.

Conflict of interest statements: The authors declared no conflict of interest.

Ethical Approval: Not applicable

REFERENCES

- Astuti, Pudji, Nora I, Lia D. Validation of Methods for Measuring Humic Acid Levels Extracted from Potassium Hydroxide Using an Ultraviolet Spectrophotometer. *JKK*. 2016; 5(2): 69-77.
- Daelis A, Daramusseng, Hansen. Formaldehyde content in fruit (grapes and apples) and an overview of the seller's knowledge about the use of formaldehyde on Yos Sudarso street, Sangatta city. 2023; 11(1): 105–113.
- Junaini MA, Wibowo, Riyanto R. Qualitative Test of Natural Formaldehyde Content in Jambal Catfish (*Pangasius djambal*) During Cold Storage Using the Antiline Test Kit. *J. Kim. Equator*. 2016; 5(3): 8–12.
- Kiroh NS, Tiwow GA, VI Paat, Ginting AR. Analysis of Formalin in Tofu Circulating in Tomohon Market, Tondano Market and Karombasan Market. *Trop. J.Biopharm*. 2019; 2(2): 158–169.
- Manoppo G, Abidjulu J. Analysis of Formalin on imported fruit in the city of Manado. 2014; 3(3): 148–155.
- Mina NM, Sudarti, Yushardi. The Effect of Extremely Low Frequency (ELF) Magnetic Fields on the Capacitance of Red Grapes. *J. Educator. Fis*. 2018; 3(2): 216–220.
- Mudaffar RA. Qualitative and Quantitative Tests of Formalin on Apples, Grapes and Longans Sold in Makassar City. *J. Perbal*. 2018; 6: 59–65.
- Pratiwi D, Wardaniati I, Dewi AP. Reagent Selectivity and Sensitivity Tests for Formalin Detection in Foodstuffs. *Indonesian Pharmacy Journal*. 2019; 16 (1).
- Minister of Health of the Republic of Indonesia. Regulation of the Minister of Health of the Republic of Indonesia Number 033 of 2012 concerning Food Additives, Jakarta, 2012.
- Namtini SS, Presiana D, Restiani Y, Nurwanti D. Guidelines for Formaldehyde, Jakarta: BPOM, 2019.
- Santoso U, Setyaningsih W, Ningrum A, Ardhi A, Sudarmanto. Food Analysis, Yogyakarta: Gadjah Mada University Press, 2020.

This is an open access article which is publicly available on our journal's website under Institutional Repository at <https://www.umi.ac.id/id/>