



Clove Oil Extraction by Steam Distillation and Utilization of Clove Buds Waste as Potential Candidate for Eco-Friendly Packaging

Paramita Jaya Ratri[✉], Meri Ayurini, Khabib Khumaini, Azka Rohbiya

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Department Chemistry, Faculty of Science & Computer Science, Universitas Pertamina, Jalan Teuku Nyak Arief, Simprug, Kebayoran Lama, 12220 Jakarta, Indonesia

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Abstract

As a tropical country which has abundant of spices, Indonesia is challenged to increase the economic values of spices commodity in raw material form (wet or dry). One way to raise the economic values of these commodities is by modifying into its derivatives. Clove is one of spices commodity which can be processed furthermore into an essential oil. By transforming clove from raw material to essential oil, the economic value increases from 2 to 20 times per kilogram. In this present research, the extraction time of clove oil using steam hydro distillation is reported. The distillation procedure was conducted in various times, that was in 3, 4, 5, and 6 hours. Furthermore, the clove oil sample that obtained from optimum extraction time was characterized using FTIR and GCMS. Then the result was compared to the commercial clove oil (100 % of purity). In support of sustainability process, then the clove buds waste from steam distillation were challenging to be one of eco-friendly packaging candidates. Two compositions of waste and additional material have been investigated in this study. It found that the best composition was composed of clove buds waste powder: recycled paper (7:3). During the casting process, some additives material was added such as tapioca (20%) and chitosan (1 %) in acid solution in order to improve its mechanical properties. Furthermore, thermal degradability of the eco-friendly packaging was studied. It was started to degrade at 286.58°C. According to this research, the cloves buds' cardboard was quite potential to be developed as commercial eco-friendly packaging.

INTRODUCTION

Clove (*Syzygium aromaticum*), one of Indonesian native species, is an aromatic flower buds. Java and Manado are parts of the largest clove productions in Indonesia. Beside used as cooking ingredients directly, clove can be proceed furthermore as medicinal properties. As medicinal effect, clove buds need to undergo the extraction process to obtain the essential oil. Several researchers have been studied the medicinal application of clove such as on dental care (Mandava et al., 2019), effective against a large number of other bacteria *Eschericia coli* (Friedman et al., 2002; Cressy et al., 2003), antifungal (Chami

et al., 2005), anticarcinogenic (Ali et.al., 2019), antiallergic (Koshak, 2019), and antimutagenic activity (Miyazawa & Hisama, 2001).

In general, essential oils are composed of terpenes and aromatic polypropanoid compounds. Several techniques for essential oil isolation have been reported including hydrodistillation, steam distilation, solvent extraction, supercritical CO₂ extraction (Frohlich et al., 2019; Guan et al., 2007), and so on. Guan et al. (2007) reported that *Eugenia caryophyllata Thunb.*, one of clove species, are composed around twenty three identified compounds by gas chromatography using mass spectrometry detection (GC-MS). This result is similar to Jirovetz et al. studies (2006). Basicly, the

[✉]Corresponding author:

Department Chemistry, Faculty of Science & Computer Science, Universitas Pertamina,
Jalan Teuku Nyak Arief, Simprug, Kebayoran Lama, 12220 Jakarta, Indonesia
E-mail: paramita.jr@universitaspertamina.ac.id

primary compound in clove oil is Eugenol (Guan et al., 2007; Jirovetz et al., 2006). Eugenol is useful as antioxidant (Ogata et al., 2000) and insecticidal properties (Lambert et al., 2020). Ayoola et al. (2008) reported about the antimicrobial activity of clove oil (*Syzygium aromaticum*). They isolated the clove oil from the dry flower buds by steam distillation until no more difference in successive readings of the light yellow oil volume. The yield percentage of the clove oil isolation was around 7% (w/w) (Ayoola, et al., 2008).

In this present paper, to support the sustainability process, we studied the isolation process of clove oil by steam hydro distillation. Beside, we studied to utilize the residue of the clove oil extraction as an eco-friendly packaging.

MATERIALS AND METHODOLOGY

In this present study, the used materials and methods are described as follows.

Materials

Chemicals

The raw material of clove buds (*Syzygium aromaticum*) which was used in this research was a species from Magelang, Central Java, Indonesia. Chemicals including solvents were used in extraction of essential oil process, production of eco-friendly packaging candidate, or during characterization. N-hexane technical grade 96%, acetic acid glacial p.a. 100%, ethanol p.a. 99.9%, and acetone p.a. 99.0% were purchased from Merck Chemicals. Chitosan which was used for pulp production was industrial grade with 30 to 80 mesh of particle size from CV. ChiMultiguna. The used paper was added so that mechanical properties improvement. The type of used papers in the experiment is an HVS 80 gr.

Instrumentations

Instrumentations such as Gas Chromatography Mass Spectrometer (GC-MS), Fourier Transform Infrared (FTIR), Universal Testing Machine (UTM), and Thermogravimetric Analysis (TGA) were used for characterization and testing. The essential oil contents were detected by Thermo Trace 1310 GC with Mass Spectrometer Thermo ISQ Single Quad Detector and FTIR Spectrometer System Nicolet iS 5 in Attenuated Total Reflectance (ATR) mode.

Mechanical properties of eco-friendly paper candidate were conducted by Material Strength Testing, Zwick Roell Z100. Thermal degradation of eco-friendly paper candidate was measured by Discovery-650 SDT (Simultaneous DSC-TGA).

Methods

Extraction of Clove Oil

Steam hydro distillation is selected as a method to isolate clove oil. A twenty-five gram (25 g) of dried clove buds was put in steam flask as shown in Figure 1. The steam distillation was conducted in several times such as 3, 4, 5, and 6 h. The time started to be counted when first drop of distillate comes out. Then, the collected distillate was extracted furthermore with n-hexane as solvent using separatory funnel. Clove oil was obtained by evaporating the n-hexane.

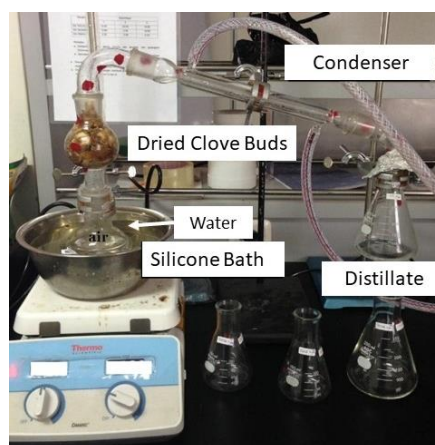


Figure 1. Steam Hydro Distillation Set

Characterization of Clove Oil

The composition and characteristic of clove oil were determined by using FTIR and GC-MS spectrum analysis the results were then compared to commercial product of clove oil (100% purity). Some drops of clove oil were measured by ATR-FTIR mode in order to check the similarity based on functional groups of compounds. Beside ATR results, GC-MS has been used to measure the clove oil contents based on mass-to-charge (m/z). The separation of clove oil was conducted by TraceGOLD™ TG-1MS column (length 30 m; ID 0.25 mm; film thickness 0.25 μm). A 1 μL of 1% diluted sample in methanol was injected into the column using split ratio of 1/50. Gradient elution has been applied to the instrument method so that gives good separation for its compounds. At first, the system

was equilibrated to 50°C. Then, the temperature was gradually raised to 100°C by rate 10°C/min and hold for 1 min, followed by gradually raised to 140°C by rate 5°C/min and hold for 1 min, to 160°C by rate 2°C/min and hold for 1 min, and finally to 245°C by rate 5°C/min and hold for 1 min. The mass-to-charge (m/z) of clove oil compounds were detected by electrospray ionization mode (EI). The temperature of ion source was maintained at 250°C, while injector and detector temperatures were programmed at 280°C. The sample was eluted and separated along the column by helium gas as mobile phase with flow rate 1 mL/min. The chemical compounds of clove oil are identified by comparing its m/z to their mass spectra library (NIST MS).

Eco-Friendly Packaging Candidate Preparation

Clove bud's residue from clove oil extraction were collected and utilized furthermore as eco-friendly packaging candidate for supporting the sustainability of industrial process. In general, the process was divided into three main steps such as making concentrated paper pulp, casting, and drying. First, the clove buds waste was dried and grinded to obtain a powder form. A 70 g of clove powder was mixed and blended together with 30 g of shredded used papers, 20 g tapioca flour commercial, and 1% of chitosan in 100 mL of acetic acid solution. In order to get the best pulp casting, the water content was needed to reduce by heating process. The eco-friendly packaging was made by pulp casting method. By casting and drying, a thick paper which cardboard look like was produced.

Mechanical and Degradation Testing

The mechanical properties of clove bud's cardboard were analyzed furthermore by comparing commercial cardboard and styrofoam. Its properties were studied using material strength testing (Zwick Roell Z100). Modified ASTM D638 was used as a standard method. The pre-load was set to 0.1 MPa, while test speed and tensile modulus were 5 mm/min. Grip to grip separation at the start position was 90.00 mm, and elongation preset was 1 %. Degradation ability of the clove bud's cardboard was analyzed by thermal process. The thermal degradation was studied by thermogravimetric analysis Discovery-650 SDT (Simultaneous DSC-TGA). The sample was

heated from ambient temperature to 600°C by 20°C/min heating rate.

RESULTS AND DISCUSSION

Clove Oil Extraction And Characterization

In this present study, clove oil was extracted by steam hydro distillation method in several hours followed by separatory funnel extraction of the distillate using n-hexane. The yield percentage are shown in Figure 2. According to Figure 2, the observed maximum yield of clove oil extraction was achieved in 6 hours, which the yield was 7.04 %. However, in this experiment, longer experiment time need to study furthermore.

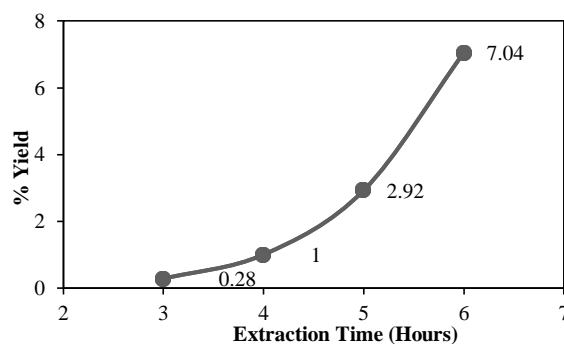


Figure 2. The obtained Yield Percentage Extraction of Clove Oil using Steam Hydro distillation Method in Several Hours.

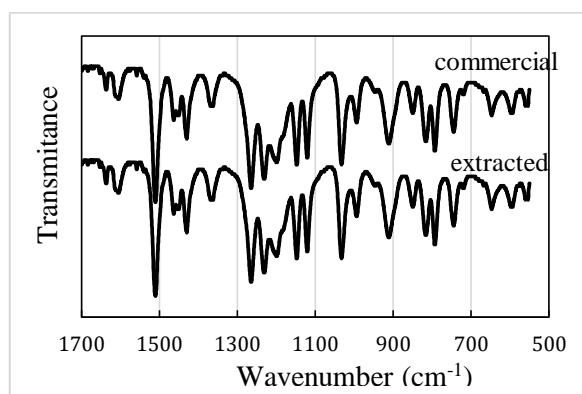


Figure 3. FTIR Spectra of Obtained Extraction and Commercially Available of Clove Oils

The clove oil which collected for 6 h by steam hydro distillation was characterized using FTIR and then compared to the commercially available clove (*Syzygium aromaticum*) oil (100 % pure) spectra. The comparison of FTIR spectra is shown in Figure 3. According to the

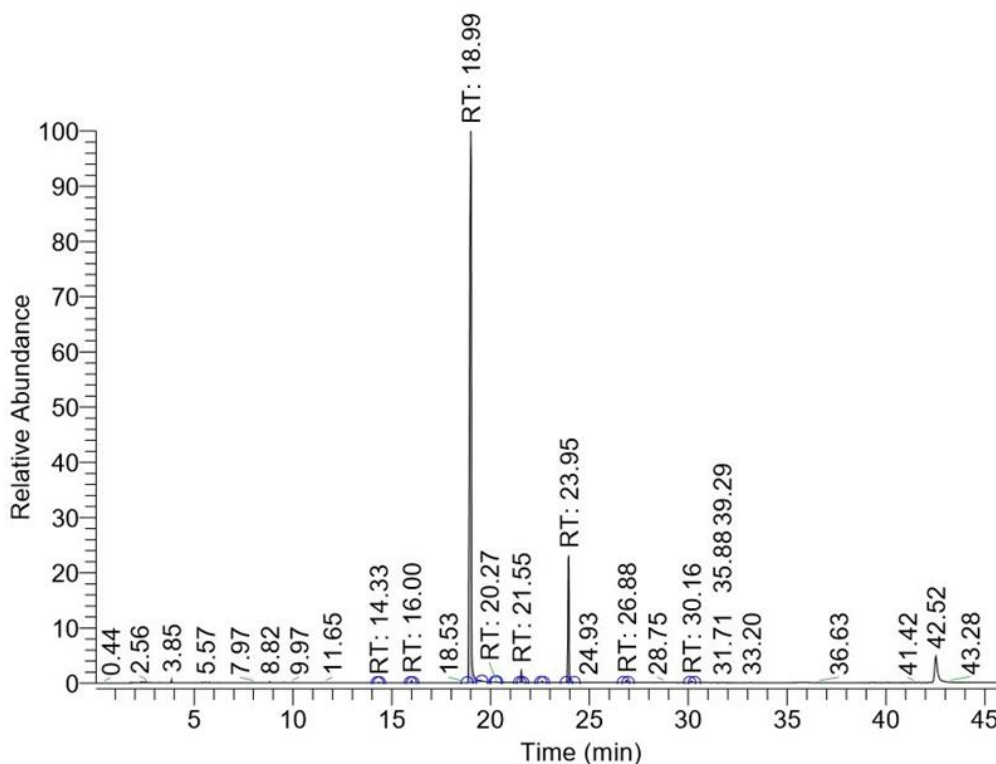


Figure 4. Chromatography Spectra of Obtained and Commercially Available Clove Oils

Table 1. Chemical composition of clove oil from local traditional market from Java Island and commercially available clove oil.

No.	Compounds	Obtained Clove Oil		Commercially Available 100% Pure Clove Oil	
		RT	% Area	RT	% Area
1	Methyl Salicylate	14.33	0.06	14.29	0.05
2	Chavicol	16.00	0.19	15.98	0.04
3	Eugenol	18.99	85.01	18.98	81.35
4	α -ylangene	20.27	0.04	20.23	0.11
4	Caryophyllene	21.55	1.14	21.52	5.05
5	Humulene	22.61	0.18	22.58	0.76
7	Eugenyl Acetate	23.93	13.06	23.90	12.50
8	Caryophyllene Oxide	26.88	0.32	26.83	0.14

FTIR spectra, by comparing the extracted clove buds' sample and commercial essential oil sample, both of samples have high similarity spectra which are around 98.88% of similarity. Therefore, it can be concluded that the extracted clove buds oil contains of similar constituent compounds to the commercially available clove oil.

Moreover, the clove buds oil contents were investigated by GC-MS spectroscopy. The chromatography spectra are shown in Figure 4. According to GC-MS spectra, there are two major constituents separated based on mass-to-charge ratio (m/z). The detailed compounds that found in clove buds' oil are pointed out in Table 1. Similar

results obtained either of extracted clove buds' oil or commercially available clove oil, which are composed of two major compounds. The two major components are eugenol and eugenyl acetate. The eugenol and eugenyl acetate contain in extracted clove buds' oil are around 85.01% and 13.06%, respectively. The percentage of these two compounds are slightly different for commercially available clove oil. In commercially available clove oil, the eugenol contents are 81.35% while eugenyl acetate 12.50%. These results are consistent to literatures that eugenol contains in clove oil is around 70-80%. According to these results, Eugenol is the highest abundance in clove oil

which is around 80 %. This constituent was reported as the most responsible components of clove buds that have a medicinal application (Milind & Deepa, 2011). Moreover, both clove oils also contain caryophyllene and humulene. Percent area of these components is in the middle compared to the rest constituents (Santin et al., 2011; Amelia et al., 2017). According to the data from GC-MS, clove oil also has some minor compounds such as methyl salicylate, chavicol, caryophyllene oxide, and α -ylangene which was also reported in literatures (Amelia et al., 2017).

Utilization of Clove Buds Waste as a Potential Candidates for Eco-Friendly Packaging

Since one of the components of clove buds is cellulose, then clove buds waste from clove oil isolation process can be utilized furthermore as a piece of paper for environmentally friendly packaging. This study will be supporting industrial process sustainability. In this research, some trial and error in composition of clove buds waste and some additives were conducted in order to find the best percentage to obtain good piece of hard paper. Beside the clove buds waste as a main component, the shredded used paper and some additive were added to improve its mechanical properties. The additive material which used in this present study are tapioca flour and chitosan. Tapioca flour is chosen as thickener while chitosan can be having a role as an antimicrobial agent and an adsorbent. In addition, both of tapioca flour and chitosan are quite cheap.

At first, a 100 g of clove buds waste, 20 g of tapioca, and 1 g of chitosan in 1% acetic acid solution were blended and casted. However, from this composition, the casting paper result was very brittle, perforated, and difficult to remove from the template without being broken. The characterization was difficult to perform. In order to increase its mechanical properties, the clove bud waste was decreased and combined with used paper. In this study, the casting process was successful by blending a 70 g of dried powder clove buds waste with a 30 g of shredded used paper then added some additives such as tapioca (20 g) and 1% chitosan in 1% acetic acid solution. This composition was obtained a cardboard look like. In each clove oil extraction time, around 25 g of dried clove buds were used. The extraction process produced waste almost the same as original

weight. From 70 g of clove buds waste, it produced three sheets of cardboard with size of 32.8 x 20.9 cm². The resulted piece of candidate green packaging of clove cardboard is shown in Figure 5 with 0.33 mm in thickness. The texture of the cardboard is smooth on the back side and rough on the front side. Apparently, the clove bud cardboard is as hard as the other cardboard but slightly brittle. The clove cardboard has a signature scents as clove essential oil. It is quite good of structure which looks like cardboard with unique odour. Up to nine months, there is no change in colours and no being mouldy when it is stored in dry place.

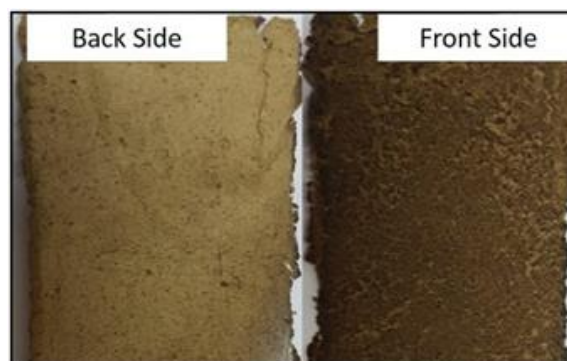


Figure 5. Piece of packaging cardboard from clove buds waste (left: back side, right: front side).

Furthermore, the mechanical properties of clove bud's cardboard were investigated using tensile strength testing. For comparison, a commercial cardboard and Styrofoam were used. The result is shown in Figure 6. According to the curves in Figure 6, clove buds cardboard has ultimate tensile strength of 1.48 MPa. This is three times higher when compared to Styrofoam (0,40 MPa) but under a half of commercial cardboard (3.34 MPa). However, percent elongation before break point for our sample was 2.11%. It was quite short compared to both Styrofoam and cardboard. Therefore, in the next study, improvement in the percentage of elongation by addition of plasticizer is needed.

The thermal degradation was also studied by Thermal Gravimetric Analysis (TGA). Degradation temperature was observed up to 600°C. Figure 7 shows at first the water content will be vaporized. Then start at 286.58°C, the clove bud's cardboard start to degrade up to 369.50°C. Finally, at 600°C the mass of clove buds paper decreased up to 27.63% of residue.

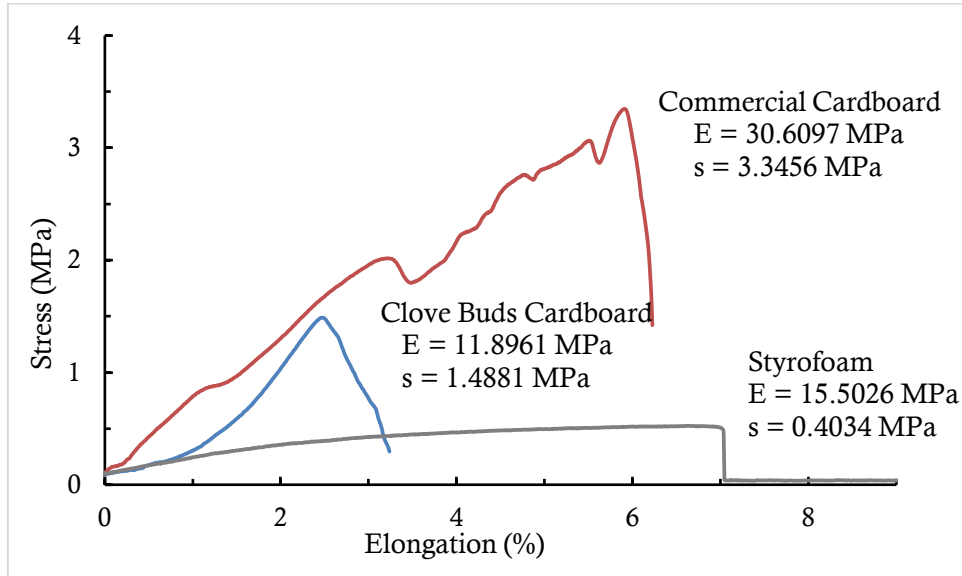


Figure 6. Tensile Strength Test of Clove Buds Cardboard, Commercial Cardboard, and Styrofoam Container.

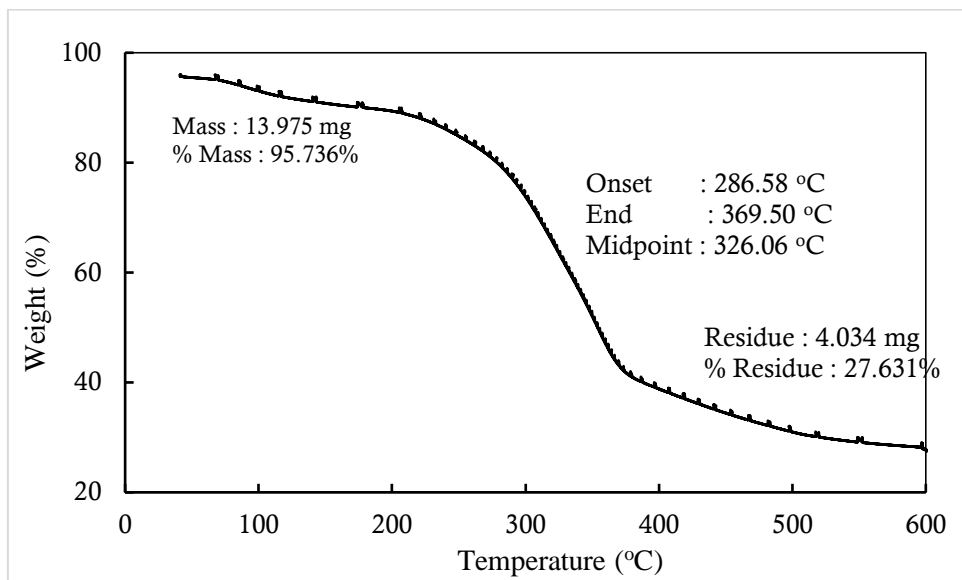


Figure 7. Thermal degradation ability testing of clove paper by Thermal Gravimetric Analysis

CONCLUSION

At the present research, steam hydro distillation was used as a method to isolate clove oil. According to the result, we need to lengthen the extraction time to observe the optimum result. By increasing the extraction time from 2 to 6 hours, the % yield also increased. The longest extraction time is 6 hours which has yield percentage around 7.04%. Both of clove oil which collected from experiment and commercially available have similar characteristic of their constituents. Two major components of clove oil are eugenol and eugenyl acetate, which have % area around 80 % and 12 %, respectively. By

supporting the sustainability process, the clove buds waste was successfully proceeds become an eco-friendly packaging as a cardboard. According to the mechanical properties, the clove bud's cardboard has quite good ultimate tensile strength, 1.48 MPa. However, this candidate of packaging needs to be improved by adding a plasticizer. The clove bud's cardboard started to degrade by heating at 286.58°C.

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AUTHOR'S CONTRIBUTIONS

Paramita Jaya Ratri and Meri Ayurini equally contributed of the presented idea, developed the theory, verified the analytical methods, wrote the manuscript. Khabib Khumaini supervised the project. Azka Rohbiya carried out the experiment. All authors discussed the results and contributed to the final manuscript.

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