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Differences in Physical-Chemical Character of Red and White Galangal (*Alpinia galanga*) Extract in Green Synthesis of Nanosilver

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This research is carried out on the physical-chemical characteristics of red and white galangal (Alpinia galanga) extracts in green synthesis of nanosilver. The study is carried out experimentally through an extraction process followed by instrumentation measurement and then through a redox reaction of nanosilver formation followed by instrumentation measurement. The results physically show that the red-galangal and white-galangal extracts are not too different as a raw material in green synthesis of nanosilver, whereas chemically there are 10 and more bioactive compounds detected in red galangal extracts compared to white galangal extracts. The percentage of bioactive compounds from red galangal extract, which became a reducing agent in the reaction of nanosilver formation, (81%) is smaller than the percentage of bioactive compounds from white galangal extract (92%). The oxidation efficiency of bioactive compounds from red galangal extract (an average of 4.04%, except galanganol of 0.05% and ellagic acid of 9.02%) is greater than the oxidation efficiency of bioactive compounds from white galangal extract (an average of 1.79%). The diameter of the nanosilver resulting from the reduction reaction of each galangal extract on silver ions calculated based on UV-Vis spectra is almost the same, which is around 16-17 nm. This fact is corroborated by TEM results, which show that the nanosilver produced from the reaction using red galangal extract reductant has a diameter of about 8-26 nm, while the nanosilver diameter of white galangal extract is around 10-26 nm. These results indicate that the particle size of the obtained nanosilver is in accordance with the standard nanoparticle size, which is of 1-100 nm.

Це дослідження проводиться стосовно фізико-хемічних характеристик екстрактів червоного та білого тайського імбиру (альпінії звичайної чи то калгану) заради зеленої синтези наносрібла. Дослідження проводиться експериментально за допомогою екстракційного процесу з подальшим апаратурним вимірюванням, а потім окиснювально-відновної реакції утворення наносрібла з подальшим апаратурним вимірюванням. Резуль-

тати фізично показують, що червоно-калгановий і біло-калгановий екстракти не надто відрізняються як сировина задля зеленої синтези наносрібла, тоді як хемічно виявлено 10 і більше біологічно активних сполук у екстрактах червоного калгану в порівнянні з екстрактами білого калгану. Відсоток біоактивних сполук з екстракту червоного калгану, який став відновником в реакції утворення наносрібла, (81%) менше відсотка біологічно активних сполук з екстракту білого калгану (92%). Ефективність окиснення біоактивних сполук з екстракту червоного калгану (в середньому 4,04%, крім 0,05% ґаланґанолу та 9,02% еллаґової кислоти) перевищує ефективність окиснення біоактивних сполук з екстракту білого калгану (в середньому 1,79%). Діяметер наносрібла в результаті реакції віднови кожного калганового екстракту на йонах Арґентуму, розрахований на основі спектрів у оптичному (видимому) діяпазоні довжин хвиль з прилеглим до нього ультрафіолетовим діяпазоном, майже однаковий, що становить близько 16-17 нм. Цей факт підтверджується результатами просвітлювальної електронної мікроскопії, які показують, що наносрібло, одержане з реакції з використанням червоного калганового екстрактувідновника, має діяметер близько 8–26 нм, тоді як діяметер наносрібла білого калганового екстракту становить близько 10–26 нм. Ці результати свідчать про те, що розмір частинок одержаного наносрібла відповідає стандартному розміру наночастинок, який становить 1-100 нм.

Key words: physical-chemical characterization, galangal extract, green synthesis, nanosilver.

Ключові слова: фізико-хемічна характеризація, калгановий екстракт, зелена синтеза, наносрібло.

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1. INTRODUCTION

Nanosilver has very good medical uses [1]. Nanoparticles can be synthesized physically or chemically by top-down or bottom-up methods [2]. The chemical synthesis of nanosilver is generally carried out through a redox reaction [3]. The silver ion is reduced to nanosilver, which is stable as a colloidal dispersion. Common reducing agents for silver ions are sodium citrate, ascorbate, sodium borohydride (NaBH₄), elemental hydrogen, the polyol process, Tollens reagent, N,N-dimethylformamide (DMF), and poly(ethylene glycol)-block copolymer, hydrazine, and ammonium [4]. The chemical synthesis of nanosilver often creates problems. This method often uses toxic solvents, produces hazardous waste, and requires high-energy consumption [5].

Alternative environmentally friendly methods need to be developed to produce nanosilver, for example using plant extracts as reducing agents [6]. This method uses secondary metabolite compounds as a reducing agent [7]. Plants, whose extracts are thought

to have potential, include galangal because they contain various secondary metabolites such as flavonoids and others that can function as reducing agents [8].

Galangal was chosen for the synthesis of nanosilver because it is an example of a biopharmaceutical plant [9]. Galangal has various medicinal properties, including being able to inhibit the xanthine oxidase enzyme in preventing cancer [10]. Galangal can be used as an ingredient to treat rheumatism and arthritis because it contains flavonoids that can inhibit fatty acid oxidation [11]. The essential oil from galangal is useful for increasing skin permeation from fluorouracil [12]. Galangal is also used as an alternative to heal burns and relieve pain [13]. Galangal is a natural antiseptic to keep skin clean, germ-free, bright, and smooth [14]. Galangal is a natural medicine to heal and prevent acne by cleaning bacteria from the skin [15].

The use of galangal extract in nanosilver synthesis is expected to produce a combination of properties and medical applications of the bioactive content of galangal secondary metabolites as well as properties and medical applications of silver. Because the galangal commonly circulating consists of white galangal and red galangal, what is being studied this time is the difference in the characteristics of white galangal extract and red galangal extract as a reducing agent in nanosilver synthesis.

2. METHODS

The main materials used in this study consisted of red galangal and white galangal which were harvested at the same time from plants with the same planting period, silver nitrate (AgNO₃) 1000 ppm, and aquademin.

Red galangal and white galangal that have been dried in the sun for 3–5 days and finely ground each weighed 10 g, added 50 mL of aquademin and then heated to boiling. Each mixture was allowed to simmer for 5 minutes. After that, the ultrasonication process was carried out for 30 minutes. After cooling to room temperature, each mixture was filtered. Each extract was tested with Shimadzu LCMS-8040 LC/MS to determine the content of secondary metabolites. Each extract that is produced is ready to be used for the synthesis of silver nanoparticles.

Silver nanoparticles were synthesized using $AgNO_3$ solution precursors with reducing agents, namely red galangal and white galangal extracts, respectively. The volume ratio of each galangal extract with $AgNO_3$ solution was 1:1, 1:2, and 1:3. The synthesis was carried out by adding $AgNO_3$ solution and each galangal extract to 200 mL of aquademin, which was heated to boiling. The nanosilver produced was then characterized using a UV-Vis spectrophotometer, transmission

electron microscopy (TEM), and Shimadzu LCMS-8040 LC/MS.

3. RESULTS AND DISCUSSION

White galangal and red galangal produce extracts of different colours, as shown in Fig. 1. White galangal extract has brownish yellow colour while red galangal extract has a bright yellow colour.

The physical properties of these two types of galangal extract can be seen in Table 1. Both types of extracts have almost the same physical properties such as density, viscosity, and pH.

The only difference is colour. The pH value that is not too acidic indicates that the potential of each extract is good enough to be used as a cosmetic raw material considering that the skin surface



Fig. 1. White galangal extract in the left bottle and red galangal extract in the right bottle.

TABLE 1. Physical properties of white galangal extract and red galangal extract.

Type of material	Colour	Density, g/mL	Viscosity, Pa·s	pН
White galangal extract	Brownish yellow	0.9899	0.0071693584	5
Red galangal extract	Yellow	0.9864	0.0072233143	5

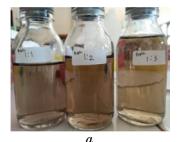




Fig. 2. Nanosilver using extracts of (a) red galangal or (b) white galangal.

has a pH of around 5.

The results of the nanosilver synthesis using the respective reducing agents for red galangal extract or white galangal extract and AgNO₃ solution with volume variations of 1:1, 1:2, and 1:3 are shown in Fig. 2. The use of white galangal extract produces blackish-brown nanosilver. The use of red galangal extract reducing agents resulted in a yellow-brown nanosilver. The greater the appeal numbers of the AgNO₃ solution, the darker the resulting colour.

Nanosilver produced through the reduction reaction of each galangal extract on $AgNO_3$ has a pH that is almost the same, which is around pH 6 as shown in Table 2. The value is slightly larger than the pH value of the pure extract in Table 1. This pH change is still safe, if the resulting nanosilver is applied to cosmetic raw materials [16].

The change of each galangal extract from the colour shown in Fig. 1 to the coloured material as shown in Fig. 2 above shows that there is a silver ion reduction reaction by each galangal extract to produce nanosilver which is not charged [17]. The determination of nanosilver formation is done by measuring the maximum wavelength with a UV–Vis spectrophotometer. The results are shown in Table 3.

Light absorption with a maximum wavelength in the range of values between 400–420 nm indicates the formation of nanosize particles [18]. Nanosilver has the appearance of surface local plasma in linear and nonlinear optical response. SPR plays an important role in the determination of the optical absorption of the nanosilver spectrum, which shifts to a longer wavelength as the particle size increases [19]. The maximum wavelength data in Table 3 is used to calculate the diameter of the nanosilver cluster using the Brus equation [20]:

TABLE 2. Nanosilver pH results.

Galangal extract + AgNO ₃ (Volume: Volume)	Red galangal	White galangal
1:1	6.7	6.5
1:2	6.6	6.4
1:3	6.4	6.8

TABLE 3. The maximum wavelength of the nanosilver.

Galangal extract + AgNO ₃ (Volume:Volume)		$\begin{array}{c} \text{Red} \\ \text{galangal} \\ \text{after 7 days} \\ \lambda_{\text{max}}, \text{ nm} \end{array}$	White galangal λ_{max} , nm	White galangal after 7 days λ_{max} , nm
1:1	410.50	414.20	415.40	415.40
1:2	416.60	416.60	419.60	419.00
1:3	413.60	419.60	421.60	421.60

$$E_{g} = E_{g}(\infty) + rac{14.84}{R^{2}} \left(rac{1}{m_{e}^{2}} + rac{1}{m_{h}^{2}}
ight) - rac{2.6}{kR}.$$

The results of calculating the nanosilver diameter obtained from the reaction between the reducing agents of each white galangal extract and $AgNO_3$ are shown in Table 4.

The results of calculating the diameter of the nanosilver obtained through the reaction between the reducing agents of each red galangal extract and $AgNO_3$ are shown in Table 5.

The nanosilver diameter resulting from the reduction reaction of each galangal extract on the silver ion is almost the same, which is about 16–17 nm. The difference in colour intensity that occurs is related to the cluster diameter and the density of the distance between the clusters. The greater the concentration, the narrower the distance between the clusters so that the colour intensity becomes stronger [1]. The nanosilver produced is also quite stable. This is shown by measuring the maximum wavelength using a UV–Vis Spectrophotometer after the silver nanoparticles were stored for 7 days. The result was almost the same as the maximum wavelength when the nanosilver was formed.

To ensure the size of the resulting nanoparticle cluster diameter through calculations using the maximum wavelength of the spectrophotometer, characterization was carried out using a TEM (transmission electron microscope) tool with a magnification of $\times 20,000$ as shown in Fig. 3. Nanosilver used for the TEM test was nanosilver formed from each of the galangal extracts, both red galangal extract and white galangal extract, and AgNO $_3$ solution with a ratio of 1:3.

The results of the TEM analysis showed that the nanosilver was well dispersed with mostly irregular shapes. The nanosilver produced from the reaction using red galangal extract reductant has a diameter of about 8–26 nm, while the diameter of the nanosilver produced from the reaction using a white galangal extract reducing agent is of about 10–26 nm. The measurement results using the UV–Vis spectrophotometer, which are strengthened by the TEM measurement results, show that the particle size of the nanosilver obtained is in accordance with the standard nanoparticle size, namely 1–100 nm [2].

The chemical content of each galangal extract was analysed using Shimadzu LCMS-8040 LC/MS, which has a library. The results are shown by the chromatogram in Fig. 4.

The nanosilver synthesis results were analysed using the Shimad-zu LCMS-8040 LC/MS, which has a library, shown in Fig. 5.

The chromatograms in Figs. 4, *a* and 5, *a* show that there are 64 bioactive compounds detected in white galangal extract and undergo changes in concentration in nanosilver synthesis as shown in Table 6.

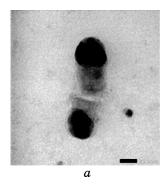
The chromatograms in Figs. 4, b and 5, b show that there are 74 bio-

TABLE 4. Size of the nanosilver particles formed using the white galangal reducing agent.

Galangal extract $+ AgNO_3$, (Volume: Volume)	λ, nm	Cluster diameter, nm
1:1	415.40	16.69
1:2	419.60	16.77
1:3	421.60	16.85

TABLE 5. Size of the nanosilver particles formed using the red galangal reducing agent.

Galangal extract + AgNO ₃ , (Volume: Volume)	λ, nm	Cluster diameter, nm
1:1	414.20	16.61
1:2	416.60	16.70
1:3	419.60	16.77



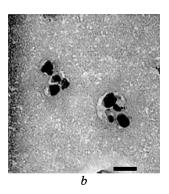


Fig. 3. TEM results of the nanosilver using reducing agents: (a) red galangal extract and (b) white galangal extract.

active compounds detected in red galangal extract and undergo changes in concentration in nanosilver synthesis as shown in Table 7.

The chromatogram results in Figs. 4 and 5, which are clarified by Tables 6 and 7, show that the number of bioactive compounds detected in the extract of red galangal is more than that detected in the white galangal extract. There were 10 compounds, which were only detected in red galangal extract and were not detected in white galangal extract. These compounds are shown in sequence in Fig. 6, namely: p Cymene, Ocimene, Camphor, Linalool, α Copaene, α Farnesene, Allo Aromadendrene, Spathulenol, Guaiol, and β Carotene.

The chromatogram in Figs. 4, a and 5, a which is clarified by Ta-

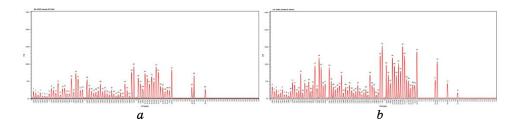


Fig. 4. Chromatograms of white galangal extract (a) and red galangal extract (b).

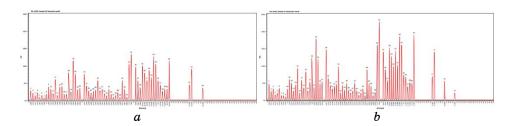


Fig. 5. Nanosilver chromatograms of white galangal extract (a) and red galangal extract (b).

ble 6 shows that about 92% or 59 bioactive compounds in white galangal extract reduce their concentration on the reduction of Ag^+ to Ag^0 in the formation of nanosilver. This reduction is predicted to occur because the bioactive compounds undergo oxidation reactions. The value of the oxidation efficiency of these compounds was the same, which was about 1.79%.

Only about 8% or 5 bioactive compounds in white galangal extract that do not participate in reducing silver ions in nanosilver formation, namely: camphene, gallic acid, 1 acetoxychavicol acetate, 1 acetoxyeugenol acetate, and capsaicin. This is indicated by the concentration of these compounds not decreasing, the concentration even increased with a growth of 0.10-0.49%. This increase in concentration may be caused by these compounds being terminal compounds in the oxidation reaction of bioactive compounds, which act as reducing agents in the formation of nanosilver.

Table 7, which clarifies the chromatograms in Figs. 4, b and 5, b, shows that about 82% or 61 bioactive compounds in red galangal extract have reduced their concentration in nanosilver synthesis.

The oxidation efficiency at reducing the concentration of these bioactive compounds is on average around 4.04%, with the exception of galanganol, which has the smallest efficiency, namely 0.05%, and ellagic acid, which has the largest efficiency, namely 9.02%.

TABLE 6. Changes in the concentration of bioactive compounds in white galangal extract on nanosilver synthesis.

	Concentration, %	ration,					Concent	Concentration,%	uo ui	
Bioactive compounds	initial	final	Difference concentrati	noitsbixO gansiaitts	.oV	Bioactive compounds	initial	final	Difference oncentrati	Oxidation goneioille
1. 4 Hydroxybenzaldehyde	96.0	96.0	0.02	1.79	33.	β Bisabolene	99.0	0.65	0.01	1.79
Chavicol	0.75	0.74	0.01	1.79	34.	α Humulene	0.48	0.47	0.01	1.79
α Pinene	0.46	0.45	0.01	1.79	35.	α Zingiberene	1.14	1.11	0.02	1.79
β Pinene	0.77	0.76	0.01	1.79	36.	α Cadinene	0.59	0.58	0.01	1.79
Sabinene	0.29	0.28	0.01	1.79	37.	Epizonarene	0.30	0.30	0.01	1.79
Camphene	0.29	0.46	-0.17	-60.54	38.	α Ylangene	0.47	0.47	0.01	1.79
α Thujene	0.20	0.20	0.00	1.79	39.	α Bergamotene	0.76	0.75	0.01	1.79
Myrcene	0.61	0.60	0.01	1.79	40.	α Santalene	0.29	0.28	0.01	1.79
4 Hydroxybenzoic acid	1.38	1.35	0.03	1.79	41.	p Methoxycinnamic acid ethyl ester	2.04	2.00	0.04	1.79
Carveol I	1.15	1.13	0.02	1.79	42.	Eugenol acetate	1.12	1.10	0.02	1.79
Carveol II	0.67	0.66	0.01	1.79	43.	Caryophyllene oxide	0.29	0.28	0.01	1.80
Cineol	2.14	2.11	0.04	1.79	44.	4 Hydroxy cinnamyl alcohol diacetate	3.73	3.66	0.07	1.79
Borneol	0.46	0.45	0.01	1.80	45.	1 Acetoxychavicol acetate	4.60	4.69	-0.10	-2.11
Fenchone	1.33	1.31	0.02	1.79	46.	1 Acetoxyeugenol acetate	2.91	3.39	-0.49	-16.71
p Coumaryl alcohol	1.42	1.40	0.03	1.79	47.	Galangin	2.05	2.01	0.04	1.79
4 Terpineol	0.61	0.60	0.01	1.79	48.	Galanganal	1.32	1.29	0.02	1.79

Continuation TABLE 6.

		Concentration,	ation, %					Concentration,	ation, %		
N o	Bioactive compounds	initial	final	Difference in concentration	noidation vonsioills	N o	Bioactive	initial	final	Difference in concentration	Oxidation vənəisiflə
17.	α Terpineol	0.59	0.58	0.01	1.79	49.	Kaempferol	3.56	3.49	90.0	1.79
18.	Methyl cinnamate	2.84	2.79	0.05	1.79	50.	Galanganol A	2.84	2.78	0.05	1.79
19.	$\mathbf{Eugenol}$	0.84	0.83	0.02	1.79	51.	Galanganol B	2.04	2.00	0.04	1.79
20.	Gallic acid	3.56	4.03	-0.47	-13.33	52.	Kaempferide	3.08	3.03	0.06	1.79
21.	Chavicol acetate		2.71	0.05	1.79	53.	8(17),12 Labdadiene 15,16 dial	2.38	2.33	0.04	1.79
22.	Eugenol methyl ether		1.10	0.02	1.79	54.	Ellagic acid	4.55	4.47	0.08	1.79
23.	Methyleugenol		1.20	0.02	1.79	55.	Quercetin	3.74	3.68	0.07	1.79
24.	. Coumaryl acetate	2.70	2.65	0.05	1.79	56.	Capsaicin	1.67	2.00	-0.33	-19.72
25.	Thymol acetate		1.44	0.03	1.79	57.	Galanal A	1.54	1.51	0.03	1.79
26.	Geranyl acetate	_	0.96	0.02	1.79	58.	Galanolactone	0.90	0.89	0.02	1.79
27.	Borneol acetate	_	0.73	0.01	1.79	59.	Galanal B	1.17	1.15	0.02	1.79
28.	Fenchyl acetate	_	0.00	0.02	1.79	90.	$\mathbf{Aframodial}$	1.14	1.11	0.02	1.79
29.	Citronellyl acetat		1.05	0.02	1.79	61.	Chlorogenic acid	4.08	4.01	0.07	1.79
30.	Curcumene	•	2.00	0.04	1.79	62.	Galanganol C	1.58	1.55	0.03	1.79
31.	β Caryophyllene	96.0	96.0	0.02	1.79	63.	Kaempferol 3 O rhamnoside	3.25	3.19	90.0	1.79
32.	Sesquiphellandrene	1.13	1.11	0.02	1.79	64.	$\mathbf{Raffinose}$	1.27	1.25	0.02	1.79

TABLE 7. Changes in the concentration of bioactive compounds in red galangal extract on nanosilver synthesis.

	noitsbixO vonsioills	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	4.04	-0.46 -10.74
	Difference ir	0.04	0.02	0.02	0.02	0.04	0.02	0.01	0.02	0.03	0.01	0.08	0.04	0.04	0.01	0.02	0.14	-0.46
ration, %	final	1.02	0.59	0.43	0.55	1.02	0.53	0.27	0.43	0.69	0.26	1.84	1.01	0.86	0.26	0.46	3.36	4.78
Concentration,	initial	1.06	0.62	0.45	0.57	1.07	0.56	0.28	0.45	0.72	0.27	1.92	1.05	0.89	0.27	0.48	3.50	4.32
	Bioactive compounds	Sesquiphellandrene	β Bisabolene	α Humulene	Allo Aromadendrene	α Zingiberene	α Cadinene	Epizonarene	α Ylangene	α Bergamotene	α Santalene	p Methoxycinnamic acid ethyl ester	Eugenol acetate	Spathulenol	Caryophyllene oxide	Guaiol	4 Hydroxy cinnamyl alcohol diacetate	1 Acetoxychavicol acetate
	No.	38.	39.	40.	41.	42.	43.	44.	45.	46.	47.	48.	49.	50.	51.	52.	53.	54.
	noitsbixO yonsioills	-7.50	4.04	4.04		4.04			4.04	4.04	-14.47	4.04	4.04	-18.34	-46.43	4.04	4.04	4.04
	Difference ir	-0.07	0.02	0.03	0.01	0.02	0.03	0.01	0.01	0.01	-0.08	0.05	0.04	-0.09	-0.29	0.08	0.03	0.05
ation, %	final	0.99	0.52	0.67	0.31	0.41	0.69	0.26	0.26	0.18	0.66	1.24	1.03	0.56	0.93	1.93	0.41	1.20
Concentration,	initial	0.92	0.54	0.70	0.33	0.43	0.72	0.27	0.27	0.19	0.57	1.29	1.08	0.48	0.63	2.01	0.43	1.25
	Bioactive compounds	4 Hydroxybenzaldehyde	p Cymene	Chavicol	Ocimene	α Pinene	β Pinene	Sabinene	Camphene	lpha Thujene	Myrcene	4 Hydroxybenzoic acid	Carveol I	Camphor	Carveol II	Cineol	Borneol	Fenchone
	No.	1:	2	е •	4.		9.	7.	∞	6	10.	11.	12.	13.	14.	15.	16.	17.

Continuation TABLE 7.

final final central No. Bioactive compounds 0.73 0.03 4.04 55. 1 Acetoxyeugenol of the compounds 1.71 -0.37 -27.75 56. Galanganal of the compounds 1.09 0.05 4.04 57. Galanganal of the compounds 2.56 0.11 4.04 57. Galanganal of the compounds 2.56 0.11 4.04 58. Kaempferol of the compounds 3.74 -0.40 -11.88 61. Kaempferol of the compounds 3.74 -0.40 -11.88 61. Kaempferol of the compounds 3.74 -0.40 -11.88 61. Galanganol of the compounds 3.74 -0.40 -11.8 62. Galanganol of the compounds 1.01 0.04 4.04 63. Ellagic acid the compounds 1.13 0.06 4.04 65. Capsaicin 1.33 0.06 4.04 66. Galanal B 0.88 0.04 4.04 66. Galanal B 0.89 0.09 4.04 68. Galanal B 0.80 0.09 4.09 69. Chlorogenic acid the compounds 2.05 -0.14 -7.06 71. Kaempferol 3 O 1.00 0.03 4.04 72. Kaempferol 3 O 1.00 0.03 4.04 72. Kaempferol 3 O 1.00 0.03 4.04 73 Raffinose 0.61 0.03 4.04 73 Raffinose			Concentration, %	ration,					Concentration, $\%$	ration,		
0.76 0.73 0.03 4.04 55. 1 Acetoxyeugenol 1.34 1.71 -0.37 -27.75 56. Galangin 0.57 0.55 0.02 4.04 58. Kaempferol 2.67 2.56 0.011 4.04 59. Galanganol A 2.67 2.56 0.11 4.04 60. Galanganol A 0.79 0.76 0.03 4.04 60. Galanganol B 3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.01 0.05 4.04 63. Ellagic acid 1.15 1.01 0.05 4.04 64. Galanal A 0.92 0.88 0.06 4.04 65. Galanal B 0.86 0.88 0.04 4.04 67. Galanganol 1.00 0.96 0.04 4.04 66. Galanganol	Bioactiv	e d	initial	final	Difference concentrat	oitsbixO onsioifts	No.	Bioactive compounds	initial	final	Difference concentrat	oitsbixO onsioiffs
1.34 1.71 -0.37 -27.75 56. Galangin 0.57 0.55 0.02 4.04 57. Galanganal 1.13 1.09 0.05 4.04 58. Kaempferol 2.67 2.56 0.11 4.04 59. Galanganol A 0.79 0.76 0.03 4.04 60. Galanganol A 3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.01 0.04 4.04 63. Ellagic acid 1.15 1.01 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal B 0.70 0.67 0.03 4.04 67. Galanganol 1.00 0.96 0.04 4.04 70. Chlorogenic acid	Linalo	ol	92.0	0.73	0.03	4.04	.66	1 Acetoxyeugenol acetate	2.73	2.94	-0.21	-7.64
0.57 0.55 0.02 4.04 57. Galanganal 1.13 1.09 0.05 4.04 58. Kaempferol 2.67 2.56 0.11 4.04 59. Galanganol A 0.79 0.76 0.03 4.04 60. Galanganol B 3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanal B 0.86 0.83 0.03 4.04 67. Galanganol C 1.00 0.96 0.04 4.04 70. Chlorogenic acid	p Coumaryl	alcohol	1.34	1.71	-0.37	-27.75	56.	Galangin	1.92	1.84	0.08	4.04
1.13 1.09 0.05 4.04 58. Kaempferol 2.67 2.56 0.11 4.04 59. Galanganol A 0.79 0.76 0.03 4.04 60. Galanganol B 3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanal B 0.70 0.67 0.03 4.04 67. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Galanganol C 0.43 0.41 -7.06 71. Galanganol C <	4 Terpi	neol	0.57	0.55	0.02	4.04	57.	Galanganal	1.24	1.19	0.05	4.04
2.67 2.56 0.11 4.04 59. Galanganol A 0.79 0.76 0.03 4.04 60. Galanganol B 3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanal B 0.70 0.67 0.03 4.04 67. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. rhamnoside	α Terpi	neol	1.13	1.09	0.05	4.04	58.	Kaempferol	3.34	3.20	0.13	4.04
0.79 0.76 0.03 4.04 60. Galanganol B 3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanal B 0.70 0.67 0.03 4.04 67. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. rhamnoside 0.52 0.08 0.04 4.04 73 rhamnoside	Methyl cin	ınamate	2.67	2.56	0.11	4.04	59.	Galanganol A	2.66	2.66	0.00	0.05
3.34 3.74 -0.40 -11.88 61. Kaempferide 2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanal B 0.70 0.67 0.03 4.04 68. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Raempferol 3 O 0.63 0.04 4.04 73 Raempferol 3 O 0.63 0.03 4.04 73 Raffinose 0.63	Euge	nol	0.79	0.76	0.03	4.04	.09	Galanganol B	1.91	2.05	-0.14	-7.07
2.59 2.48 0.10 4.04 62. 8(17),12 Labdadiene 1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanal A 0.70 0.67 0.03 4.04 68. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.63 0.08 0.04 4.04 73 Raffinose 0.63 0.03 4.04 73 Raffinose 0.63 0.61 0.03 4.04 73 Rapfinose	Gallic	acid	3.34	3.74	-0.40	-11.88	61.	Kaempferide	2.89	2.99	-0.10	-3.31
1.05 1.01 0.04 4.04 63. Ellagic acid 1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanolactone 0.70 0.67 0.03 4.04 68. Galanolactone 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 3 Carotene	Chavicol	acetate		2.48	0.10	4.04	62.	8(17),12 Labdadiene 15,16 dial	2.23	2.14	0.09	4.04
1.15 1.10 0.05 4.04 64. Quercetin 2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanolactone 0.70 0.67 0.03 4.04 69. Aframodial 0.86 0.83 0.03 4.04 70. Chlorogenic acid 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 3 Carotene	Eugenol me	thyl ether		1.01	0.04	4.04	63.	Ellagic acid	4.27	3.89	0.39	9.02
2.53 3.07 -0.54 -21.14 65. Capsaicin 1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanolactone 0.70 0.67 0.03 4.04 68. Galanolactone 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 3 Carotene	Methyle	ugenol		1.10	0.05	4.04	64.	Quercetin	3.51	3.37	0.14	4.04
1.38 1.33 0.06 4.04 66. Galanal A 0.92 0.88 0.04 4.04 67. Galanolactone 0.70 0.67 0.03 4.04 68. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 3 Carotene	Coumaryl	acetate		3.07	-0.54	-21.14	65.	Capsaicin	1.57	1.50	0.06	4.04
0.92 0.88 0.04 4.04 67. Galanolactone 0.70 0.67 0.03 4.04 68. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 B Carotene	Thymol ε	cetate		1.33	0.06	4.04	.99	Galanal A	1.44	1.39	0.06	4.04
0.70 0.67 0.03 4.04 68. Galanal B 0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 B Carotene	Geranyl a	acetate		0.88	0.04	4.04	67.	Galanolactone	0.85	0.81	0.03	4.04
0.86 0.83 0.03 4.04 69. Aframodial 1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 B Carotene	Borneol a	acetate		0.67	0.03	4.04	68.	Galanal B	1.09	1.05	0.04	4.04
1.00 0.96 0.04 4.04 70. Chlorogenic acid 1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 B Carotene	Fenchyl a	acetate		0.83	0.03	4.04	69.	$\mathbf{Aframodial}$	1.07	1.02	0.04	4.04
1.92 2.05 -0.14 -7.06 71. Galanganol C 0.43 0.41 0.02 4.04 72. Kaempferol 3 O 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 8 Carotene	Citronelly	acetate		0.96	0.04	4.04	70.	Chlorogenic acid	3.83	3.99	-0.16	-4.29
0.43 0.41 0.02 4.04 72. Kaempferol 3 O rhamnoside 0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 3 Carotene 0	Curcui	nene	1.92	2.05	-0.14	-7.06	71.	Galanganol C	1.48	1.42	0.06	4.04
0.92 0.88 0.04 4.04 73 Raffinose 0.63 0.61 0.03 4.04 74 B Carotene	α Copε	aene	0.43	0.41	0.03	4.04	72.	Kaempferol 3 O rhamnoside	3.05	2.93	0.12	4.04
0.63 0.61 0.03 4.04 74 B Carotene	β Caryop	hyllene	0.92	0.88	0.04	4.04	73	\mathbf{R} affinose	1.20	1.15	0.05	4.04
	α Farn	esene	0.63	0.61	0.03	4.04	74	β Carotene	0.43	0.41	0.02	4.04

Fig. 6. Bioactive compounds detected only in red galangal extract.

About 18% percent or 13 bioactive compounds in red galangal extract do not participate in reducing silver ions in the formation of nanosilver. The bioactive compounds are 4 hydroxybenzaldehyde, myrcene, camphor, kaempferide, curcumene, galanganol B, chlorogenic acid, 1 acetoxyeugenol acetate, carveol II, p coumaryl alcohol, gallic acid, 1 acetoxychavicol acetate, and coumaryl acetate. The concentration of each of these compounds increased with a growth of about 0.6–0.54%.

4. CONCLUSION

Physically, red galangal and white galangal extracts are not too different as raw materials in green synthesis of nanosilver, except for differences in colour intensity. Chemically, about 10 more bioactive compounds were detected in red galangal extract than in white galangal extract. The percentage of bioactive compounds from the red galangal extract, which became the reducing agent in the nanosilver formation reaction, (81%) was smaller than the percentage of bioactive compounds from the white galangal extract (92%). The oxidation efficiency of bioactive compounds from red galangal extract (on average 4.04%, except for galanganol 0.05% and ellagic acid 9.02%) was greater than the oxidation efficiency of bioactive compounds from white galangal extract (average 1.79%). The nanosilver diameter resulting from the reduction reaction of each galangal extract on silver ion calculated based on UV-Vis spectra is almost the same, which is about 16-17 nm. This fact is reinforced by the TEM results which show that the nanosilver produced from the reaction using red galangal extract reducing agents has a diameter of about 8-26 nm, while the nanosilver diameter of the reaction using

white galangal extract is about 10-26 nm. These results indicate that the particle size of the nanosilver obtained is in accordance with the standard nanoparticle size, namely 1-100 nm.

REFERENCES

- 1. L. Ge, Q. Li, M. Wang, J. Ouyang, X. Li, and M. M. Xing, *Int. J. Nanomedicine*, 9: 2399 (2014).
- 2. V. Pareek, A. Bhargava, R. Gupta, N. Jain, and J. Panwar, *Advanced Science*, *Engineering and Medicine*, 9: 527 (2017).
- 3. O. Długosz and M. Banach, Journal of Cluster Science, 30: 541 (2019).
- 4. J. V. Baudrit, S. M. Gamboa, E. R. Rojas, and V. V. Martinez, *International Journal of Biosensors & Bioelectronics*, 5, Iss. 5: 166 (2019).
- 5. X. F. Zhang, Z. G. Liu, W. Shen, and S. Gurunathan, *Int. J. Mol. Sci.*, **17**, Iss. 9: 1534, (2016).
- 6. S. Ahmed, M. Ahmad, B. L. Swam, and S. Ikram, *Journal of Advanced Research*, 7, Iss. 1: 17 (2016).
- 7. N. Sahu, D. Soni, B. Chandrashekhar, D. B. Satpute, S. Saravanadevi, B. K. Sarangi, and R. A. Pandey, *International Nano Letters*, 6: 173 (2016).
- 8. N. M. Al-Enazi, International Journal of Pharmacology, 14, Iss. 3: 301 (2018).
- 9. I. G. M. Sanjaya, I. Ismono, T. Taufikurohmah, and A. P. Wardana, *Proc. of Seminar 'Advances in Engineering Research'* (Sep. 22, 2018, Surabaya, Indonesia), vol. 171, p. 79.
- 10. M.-A.-R. Hajzadeh, H. Ghanbari, Z. Keshavarzi, and J. T. Afshari, *Iranian Journal of Cancer Prevention*, 7, Iss. 3: 142 (2014).
- 11. X. Xia, B. H. May, A. L. Zhang, X. Guo, C. Lu, C. C. Xue, and Q. Huang, Evidence-Based Complementary and Alternative Medicine, 2020: 1 (2020).
- 12. J. Dong, X.-M. Zhu, F.-Y. Wu, B.-Q. Yang, H. Feng, Y.-F. Dong, W. Gu, and J. Chen, *Drug Development and Industrial Pharmacy*, **46**, Iss. 1: 91 (2020).
- 13. A. M. Basri, H. Taha, and N. Ahmad, *Pharmacogn Rev.*, 11, Iss. 21: 43 (2017).
- 14. P. U. H. S. Karunarathne, M. G. Thammitiyagodage, and N. S. Weerakkody, *International Journal of Pharmaceutical Sciences and Research*, 8: 4582 (2018).
- 15. B. C. Joshi and A. Sundriyal, Inventi Rapid: Planta Activa, 2017, Iss. 2: 1 (2017).
- 16. H. Lambers, S. Piessens, A. Bloem, H. Pronk, and P. Finkel, *International Journal of Cosmetic Science*, 28: 59 (2006).
- R. A. H. Al-Khuzai, M. K. Aboud, and S. K. Alwan, Journal of Physics: Conf. Series, 1294, Iss. 6: 062090 (2019); https://doi.org/10.1088/1742-6596/1294/6/062090
- 18. K. Anandalakshmi, J. Venugobal, and V. Ramasamy, *Appl. Nanosci.*, **6**: 399 (2016).
- 19. L. Mahmudin, E. Suharyadi, A. B. S. Utomo, and K. Abraha, *Journal of Modern Physics*, 6, Iss. 8: 1071 (2015).
- 20. T. Taufikurohmah, D. Soepardjo, R. Rusmini, and H. Armadianto, *Proc. of Conf.* 'Advances in Social Science, Education and Humanities Research' (Sep. 7, 2019, Surabaya, Indonesia), vol. 390, p. 146.
- 21. S. H. Lee and B.-H. Jun, Int. J. Mol. Sci., 20, Iss. 865: 1 (2019).
- 22. P. Oberbek, P. Kozikowski, K. Czarnecka, P. Sobiech, S. Jakubiak, and T. Jankowski, J. Nanopart. Res., 21, Iss. 222: 1 (2019).