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Red Pigmented Natural Extract as Potential Organic UV Filter and Its Use in Combination with ZnO as Sunscreen Cream

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Keywords: SPF, red pigment; natural extract; organic UV filter; secang, zno, sunscreen.

Abstract: Sunlight consists of ultraviolet (UV) light and organic Ultraviolet (UV) filters can be found in plants and fruits which have orange-red or pink colors, such as watermelon, tomato, Secang (*Caesalpinia sappan*), carrot, dragon fruit, faloak (*Sterculia quadrifida* R.Br), strawberry, papaya, and rosella. Most of these plants contain active compounds such as carotenoids and anthocyanin. Determination of the effectiveness of the extracts as potential sunscreen was carried out by determining the Sun Protecting Factor (SPF) value *in vitro* by UV spectrophotometry. Maceration technique was used for the extraction process by using ethanol with a ratio of 4:1. Each of dried extract (100 mg) was then mixed well in the ethanol (96%, 50 mL) until the extract was dissolved and then filtered. The SPF values were determined by the Equation of Mansur. It was observed that all of the red pigmented extracts showed UV protection capabilities, with Secang extract gave the highest SPF value of 18.490. The Secang extract would have good potential to be developed as one of the ingredients in the sunscreen cream. Sunscreen cream combination between Secang extract and ZnO showed good quality and significant SPF value than ZnO and extract Secang sunscreen cream.

1 INTRODUCTION

Indonesia is a country with a tropical climate so that it gets more sunlight intensity than other countries. Sunlight, called ultraviolet (UV) light based on its wavelength, is divided into UVA, UVB and UVC. UVA has the longest wave of 320-400 nm and causes skin cancer in the epidermal layer, UVB with a wavelength of 290-320 nm gives an effect on the epidermis and dermis layer causing the skin to burn and UVC with the shortest wavelength 180-280 nm (Manuaba, 2010). UVC and most of the UVB radiation is absorbed by the ozone layer in the earth's atmosphere, therefore UVA accounts for 95% of UV radiation to the earth's surface which affects the entire organism. UVA is a major cause of skin injury and disease in humans, also indirectly affects DNA / RNA damage (Zhong et al., 2011).

Sunscreens initially developed to prevent sunburn and have evolved to protect against other harmful effects of ultraviolet radiation (UVR). UVB (280-320

nm) typically induces erythema and direct DNA damage via pyrimidine dimer formation, whereas UVA (320-400 nm) is associated with tanning, photo aging, (R, BA and MD, 2011). Sunscreens can absorb at least 85% of the sun's rays at a wavelength of 290-320 nm for UVB but can continue to light at wavelengths of more than 320 nm for UVA (Amnuakit and Boonme, 2013).

Sunscreen products consist of several chemicals that can absorb UV radiation or commonly called UV filters or UV light retaining. UV filter is an individual compound or mixture that is useful to prevent UV light from passing through it. Based on its function, the active ingredient of sunscreen is divided into two, namely absorbing compound as an absorbent of UVB rays to filter incoming light, for example Octyl dimethyl PABA, Octylmethoxycinnamate, Octocrylene, tinosorb and reflecting compounds which mechanism inhibit the absorption of UVA rays, for example TiO₂ and ZnO (Agustin, Oktadefitri and Lucida, 2013). Semiconductor TiO₂

is used as an inorganic UV filter for sunscreens. TiO₂ is used as a filter on sunscreen because it is widely used as an agent to absorb or spread UV radiation and has many characteristics that can be described, including long-term topical use such as cream, broad spectrum absorption, high photo stability, and low irritation (Ko *et al.*, 2012). In addition, TiO₂ has a deficiency if applied to the skin leaving white and opaque marks and inducing free radical formation under light exposure. This is an initial research of sunscreen formulations made by combining organic and inorganic solar filters because inorganic filters can block UVA radiation and most organic filters protect from UVB radiation (Reinosa *et al.*, 2016).

Inorganic filters work by filtering or blocking UV light throughout the UVA and UVB ranges at 290-400 nm waves through absorption, scattering and reflection (Serpone, Dondi and Albini, 2007). While the organic filter in the results of Jacek and Katarzyna's research in 2014 (Arct and Pytkowska, 2014) has the property of penetrating the skin, affecting the body's hormones, having photochemical activities and reactions that occur in infected skin.

A study conducted by (Suwami and Supriyono, 2014) about making creams from natural ingredients using extracts of ant nests with carica fruit (mountain papaya) that these two ingredients can improve the stability of the preparation with the formation of physical characteristics a good SPF values. Another study showed that ethanolic bark extract of *Prosopis cineraria* which is an excellent source of natural flavonoids and polyphenols showed decrease in skin melanin, erythema and sebum contents by the application of the formulation by in vivo method (Mohammad *et al.*, 2018).

Organic UV filters are found in plants and fruits that are orange-red or pink, such as tomatoes, watermelons, dragon fruit, papaya, carrots, rosella, faloak, Secang and strawberries. Most of these plants contain active compounds such as carotenoids and anthocyanins. Carotenoids are known as compounds that have antioxidant activity because they have conjugated double bonds. Carotenoids such as β -carotene or lycopene are efficient antioxidants in binding of oxygen singlet molecules and peroxy radicals produced during the photo oxidation process (Prasiddha *et al.*, 2016). The anthocyanin group is a natural pigment with a red range that is abundant in flowers, this pigment is able to fight the oxidation process in the body (Zafra-Stone *et al.*, 2007). Natural pigments from several types of plants can disguise and even cover the white marks caused by the use of TiO₂ as an inorganic UV filter. In one study entitled Determined by In Vitro Method "Effect of The

Organic and Inorganic Filters on The Sun Protection Factor" shows a synergistic effect when TiO₂ is combined with anisotriazine or PABA octyl dimethyl. The combination of ZnO and organic filter also had the same synergistic effect (El-Boury *et al.*, 2007). Therefore, this research was conducted to determine if ZnO has synergistic effect when combine with red pigmented extract plant in enhancing the SPF value.

2 METHODS

Materials used were Ethanol p.a. (Sigma), Ethanol 96%, Watermelon, Tomato, Secang, Carrot, Dragon Fruit, Strawberry, Papapaya, Rosella, and Faloak, ZnO, IKA Rotary Evaporator, Spectrophotometer UV-Vis (Jasco)

Ethanol extraction were obtained from maceration with ratio 1:4 in ethanol 96%. Filtrat was then evaporate using rotary evaporator and dried. Determination of the effectiveness of the potential sunscreen extract was carried out by determining the SPF value in vitro by UV-Vis spectrophotometry. The extracts of each ingredient were weighed as much as 100 mg, 50 ml of 96% ethanol was added and shaken until homogeneous then filtered. Ethanol 96% was used as blank. The absorbance were measured, with wavelengths between 290-320 nm. Then the average absorption (Ar) is set at 5 nm intervals. The results of the absorbance of each concentration are recorded and then the SPF value is calculated by the Equation of Mansur.

$$SPF = CF \sum_{290}^{320} EE(\lambda) I(\lambda) Abs(\lambda) \quad (1)$$

CF = Correction Factor (10)
 EE(λ) = Erythema Effect Spectrum
 I(λ) = Intensity of UV
 Abs(λ) = Absorbance of Extract

Whereas EE(λ) x I(λ) value is a constant (Malsawmtluangi *et al.*, 2013) shown in table 1.

Table 1: EE(λ) x I(λ) values in mansur equation (Dutra *et al.*, 2004).

Wavelength (nm)	EE(λ) x I(λ)
290	0,0150
295	0,0817
300	0,2874
305	0,3278
310	0,1864
315	0,0839
320	0,0180

SPF values from different extract by three replications were analysed with ANOVA using R Studio

Table 2: Sunscreen formula with variation of secang extract and ZnO.

Formula	F1	F2	F3
Secang Extract	20%	10%	0%
ZnO	0%	10%	20%
Tween 80	1,95%	1,95%	1,95%
Cetyl Alkohol	5,55%	5,55%	5,55%
TEA	2,5%	2,5%	2,5%
Dimethicone	0,5%	0,5%	0,5%
Spermaceti	6%	6%	6%
Isopropyl Myristate	4%	4%	4%
Propilenglikol	23%	23%	23%
Asam Stearat	5%	5%	5%
Aerosil	0,3%	0,3%	0,3%
Asam benzoat	0,1%	0,1%	0,1%
Parfume	0,1%	0,1%	0,1%
Aquadest	31%	31%	31%

Table 4: Absorbance of watermelon, tomato, secang, carrot, dragon fruit, faloak, strawberry, papaya, and rosella extract.

Wavelength	EE×I	Absorbance				
		Watermelon	Tomato	Secang	Carrot	Dragon Fruit
290	0.015	0.789±0.014	0.568±0.077	1.014±0.06	0.518±0.052	0.557±0.065
295	0.0817	0.869±0.016	0.601±0.095	1.171±0.007	0.534±0.056	0.543±0.069
300	0.2874	0.893±0.017	0.598±0.104	1.290±0.007	0.519±0.056	0.527±0.070
305	0.3278	0.876±0.019	0.572±0.106	1.373±0.008	0.487±0.053	0.510±0.069
310	0.1864	0.945±0.025	0.580±0.118	3.327±0.435	0.485±0.056	0.531±0.077
315	0.0839	0.868±0.026	0.519±0.106	3.027±0.290	0.431±0.051	0.512±0.076
320	0.018	0.736±0.026	0.430±0.082	2.412±0.161	0.358±0.044	0.477±0.072

Table 5: Absorbance of watermelon, tomato, secang, carrot, dragon fruit, faloak, strawberry, papaya, and rosella extract (continued).

Wavelength	EE×I	Absorbance			
		Faloak	Strawberry	Papaya	Rosella
290	0.015	1.138±0.013	0.871±0.009	0.867±0.027	0.912±0.012
295	0.0817	1.287±0.012	0.994±0.013	0.976±0.032	1.046±0.025
300	0.2874	1.390±0.012	1.011±0.019	1.017±0.042	1.128±0.040
305	0.3278	1.451±0.015	0.944±0.022	0.997±0.051	1.173±0.054
310	0.1864	2.071±0.109	0.987±0.028	1.137±0.086	1.665±0.185
315	0.0839	2.029±0.117	0.889±0.026	0.994±0.088	1.760±0.211
320	0.018	1.719±0.092	0.780±0.028	0.829±0.086	1.745±0.205

17 3 RESULTS AND DISCUSSION

The results of the statistical analysis showed that extracts from the nine plants differs significantly (Sig. 0.000) between extract groups. As can be seen in Table 3, Secang showed the largest SPF results that were significantly different from all of the herbal groups, which amounted to 18,490. The effectiveness of sunscreen is usually stated with SPF (Sun Protecting Factor) which is a comparison of the UV energy needed to make a minimum of erythema effect on protected and unprotected skin.

Table 3: SPF values of different red pigmented herbal extracts.

Herbal Extracts	SPF Value
Watermelon	8.889±0.198
Tomato	5.764±1.062
Secang	18.490±1.116
Carrot	4.933±0.543
Dragon Fruit	5.220±0.713
Faloak	15.842±0.373
Strawberry	14.437±0.215
Papaya	10.221±0.569
Rosella	12.973±0.875

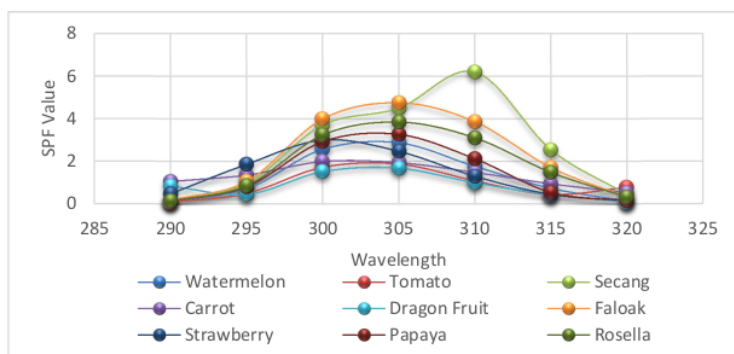


Figure 1: SPF value of various natural extract.

Table 6: Physical quality test of sunscreen cream.

Test	F1	F2	F3
Organoleptic	Semisolid, Magenta, Parfume Aroma, Soft Texture, Homogen	Semisolid, Pink, Parfume Aroma, Soft Texture, Homogen	Semisolid, White, Parfume Aroma, Soft Texture, Homogen
pH	8,01±0,02	8,31±0,01	8,66±0,03
Type of emulsion	Water in Oil	Water in Oil	Water in Oil
Stickiness Ability Test	3,88±0,37	1,58±0,49	7,5±2,2
SPF Value	19.68 ± 0.024	19.38 ± 0.95	15.83 ± 0.07

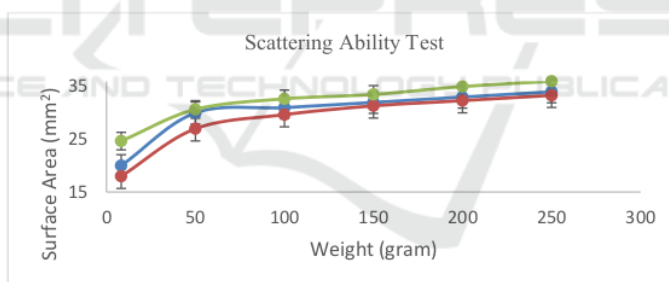


Figure 2: Scattering ability test diagram.

Some herbal extracts have SPF values that do not differ significantly from one another, which are watermelon, strawberry and papaya extract, show a range between 8,889 to 14,437 and another group that are not significant is tomato, carrot and dragon extract with a range of 4,933 to 5,764. It is known that Secang extract has the highest SPF value, this is supported by the red pigment from Secang extract which is more concentrated than the red pigment obtained from other extracts. Secang extract contains Brazilian compounds in which these compounds is the characteristic compound of Secang. Brazilian have several functions and one of them is antioxidants. As

the previous study, it is suggested that plant extracts acted by capturing ROS, thus minimizing erythema and collaborating indirectly to in vivo SPF enhancement (Cristina *et al.*, 2016).

Therefore, Secang extract could potentially formulated as sunscreen and could give synergistically effect of reducing the white effect of inorganic active substances and at the same time has antioxidant benefits for the skin in order to counteract free radicals due to induction of UV light exposure.

4 CONCLUSIONS

SPF is a standard that has been used throughout the world as a measure of the effectiveness of sunscreens. Some of these herbal extracts have SPF capabilities. The SPF value of several herbal extracts which have red pigment with Mansur equation shows the variation in the range between 4.933 to 18.490 and the herbal extract which has the high SPF value is Secang extract. The Secang extract has the potential to be developed into a natural pigment-based sunscreen preparation formulation or to be combined with an inorganic sunscreen active ingredient ZnO.

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