

## Nanogold as Supporting Activities of Conventional Sunscreen of Octyl-p-Methoxycinnamate to Inhibit Photoaging

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### Abstract

Research has been conducted in order to determine the potential of nanogold as a material and supporting material of sunscreen. It can contribute to the pharmaceutical design of cosmetics that much more effective, especially as a sunscreen as well as antiaging. Nanogold with various concentrations to be tested, was synthesized without using a matrix so that sunscreen activity really pure due to the activity of nanogold. Test of sunscreen activity and test of supporting capacity of sunscreen material is done by measuring the absorbance of nanogold, OPMC (Octyl-p-Methoxycinnamate) compound, and combinations of OPMC-nanogold using UV-Vis instrument of Simatzu-1700. The results showed that nanogold having sunscreen activity, especially in the high energy UV region at  $\lambda$  200 nm. Its activities will be higher if the concentration becomes higher. Nanogold also strongly supports the sunscreen activities of OPMC. This is evident from the increase in absorbance value of the combination of nanogold and OPMC.

**Keywords:** Sunscreen activity, Nanogold, OPMC compound, Combinations of OPMC-nanogold

### 1. Introduction

Skin aging is a complex process that evolved from two separate processes and affected the skin at the same time, i.e. the process of natural or intrinsic aging and extrinsic aging. Both the aging process is different for each person in which the person's aging process occurs according to age, but others occur earlier or later (Bauman, et al, 2009).

Skin aging is characterized by changes in the skin becomes wrinkled, dry, rough, and pigmentation changes. Skin aging like wrinkles and pigmentation especially from the view point of dermatologists may not be considered a serious disorder that requires special treatment. But from the view point of aesthetics, it is disturbing appearance that affected the quality of life of the majority of sufferers (Fisher, et al, 2002). The desire to look beautiful forever is very important in the social life of community. To that end, it is necessary to develop a strategy to accommodate the wishes and expectations of the treatment and prevention of human premature aging (Chung, 2003).

Intrinsic aging, also known as natural aging or chronological aging, is a fundamental biological process common to all living organisms. This process involves a low level of metabolic activity, characterized by damage to the function and structure of the skin that reflects a person's genetic base and is a result of the passage of time (Fisher, et al, 2002). It is unavoidable and occurs beyond our will. This process is a natural process that began in the mid age of 20 and is characterized by slowing the production of collagen, elastin (the substance important for skin elasticity) is not as flexible as before, the dead skin cells to flake off is not as fast as before, and turnover of new skin cell will decrease (Chung, et al, 2001). The changes in intrinsic aging process are due to the continuous damage by reactive oxygen species (ROS) that occurs in cellular oxidative metabolism (Puizina, 2008). ROS besides damaging cellular antioxidant systems is also causing damage to membranes, enzymes, DNA, protein, interactions of DNA-protein and interactions of proteins.

Extrinsic aging is the aging of the skin which aggravate intrinsic aging and is a superposition of the intrinsic aging causing premature aging of skin. Extrinsic aging is due to several external factors such as physical and psychological stress, smoking, excessive alcohol use, poor nutrition, environmental pollution, and exposure to sunlight. In many cases, extrinsic aging can be reduced and avoided by the willingness and effort (Chung, et al,

2001). Among all of these external factors, sun exposure contributes more than 80%. Premature skin aging due to sun exposure is known as photoaging (Yaar, et al, 2007). Commonly affected areas are the areas that are exposed to sunlight, such as: face, neck, back of the hand and wrist.

The efforts of antiaging material discovery cannot be separated from the fact that the cause of premature aging by external factors is largely from exposure to sunlight, which is more than 80%. Material antiaging would be better if it has support for the activities of the sunscreen to absorb sunlight, especially high energy of ultraviolet (UV). Nanogold as antiaging material has proven to reduce free radicals that can cause skin damage and aging (Taufikurohmah, et al, 2012).

Nanogold has been used by our ancestors to preserve the beauty and youthfulness of the skin in the form of gold implant. Furthermore, it has also conducted tests of safety material for nanogold as one constituent material of pharmaceutical cosmetics. Nanogold does not cause denaturation of proteins, so it does not cause damage of the skin that is composed of proteins. Nanogold has been successfully synthesized using glyceryl monostearate matrix which is a cosmetic material thus simplifying the preparation nanogold in cosmetics (Taufikurohmah, et al, 2011).

Conventional sunscreen compounds in cosmetics as ester derivative of cinnamate are ethylhexyl-p-methoxycinnamate (EHPMC), isoamyl-p-methoxycinnamate (IAPMC) and octyl-p-methoxycinnamate (OPMC). OPMC has absorption in the UV light at 305 nm and 315 nm due to the structure of the OPMC compounds containing a ketone group conjugated with benzene, which is one characteristic of sunscreen compounds (Taufikurohmah, et al, 2011).

It is necessary to test the activity of nanogold in support of sunscreen activity that has been used before, the OPMC. It is very important in order to know whether the presence of both compounds nanogold and OPMC, are mutually supportive or mutually exclusive. For this purpose, it is necessary to test the sunscreen activity gradually. To sunscreen compound of OPMC, has been obtained absorption data of UV-Vis.

The research activities begin with the synthesis of various concentrations of nanogold without matrix. When using a matrix, it is feared the matrix absorb UV, so the result is not valid. Synthesis performed at various concentrations of gold in  $\text{HAuCl}_4$  solution. Test of sunscreen activity of nanogold is done by measuring the UV-Vis absorption at each concentration of nanogold, OPMC compound, and a combination of various concentrations of nanogold and OPMC in a fixed concentration.

From the description of sunscreen compounds in cosmetics and its function, then the problems will be answered in this research include sunscreen activity of nanogold, effect concentration to the sunscreen activity of nanogold, and ability of nanogold to support the sunscreen activities of OPMC compound.

The research objective is to determine the ability of nanogold as sunscreen compounds and find support nanogold on the sunscreen of OPMC compound. The benefit of this research is to contribute to the design of pharmaceutical manufacture cosmetics, which is much more effective as a sunscreen as well as antiaging.

## 2. Method

### 2.1 Synthesis of Nanogold

Raw materials in this research are yellow solution of  $\text{HAuCl}_4$  1000 ppm and reducing agent of sodium citrate. A total of (1,000-x) ml of distilled water is heated in 1000 ml beaker glass to boiling. After that, add 2 g sodium citrate and stirred until homogeneous, and then add solution of  $\text{HAuCl}_4$  x ml (x = 5, 10, 15, 20, 25, 30, 35 and 40). Stirring is continued so that the solution becomes colorless and then changed to dark blue, red and burgundy. After that stirring and heating is stopped. This process produces nanogold 5, 10, 15, 20, 25, 30, 35 and 40 ppm. The colloidal nanogold is then used in the test of sunscreen activity of nanogold.

### 2.2 Test of Sunscreen Activity of Nanogold

Each 2 ml of colloidal nanogold mixed with 2 ml of distilled water. The absorbance is measured at a wavelength of maximum absorption by using UV-Vis instrument Simatzu-1700. The increase in absorbance is then calculated at each concentration of nanogold.

### 2.3 Test of Support of nanogold on the sunscreen activity of OPMC

Each 2 ml colloidal nanogold are mixed with 2 ml of solution of 4% OPMC. The absorbance is measured at a wavelength of maximum absorption by using UV-Vis instrument Simatzu-1700. The increase in absorbance is then calculated at each concentration of nanogold.

## 3. Results and Discussion

### 3.1 Synthesis of Nanogold

The result of the synthesis of nanogold with 5-40 ppm concentrations can be seen in figure 1. Observation of the color of nanogold, beside done manually by eyes senses, is also performed with the UV-Vis instruments.

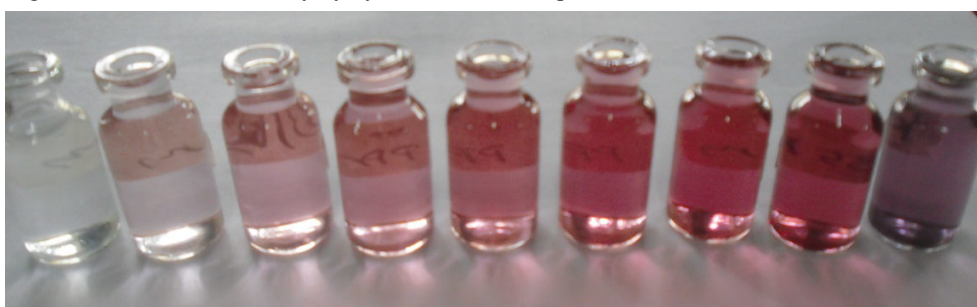


Figure 1. Synthesis results of nanogold with concentration 5-40 ppm and aquades (left).

According to analysis by UV-Vis instrument that can be seen in Figure 2 and Table 1, it is known that nanogold at various concentrations have maximum absorption wavelength and absorbance values different from one another. The highest absorbance appears on nanogold concentration of 25 ppm, with a wavelength of 520 nm and absorbance of 0.595. This result also is in accordance with visual observations that have the most intense color.

### 3.2 Sunscreen activity test of nanogold

The absorbance of UV-Vis of nanogold without sunscreen OPMC can be seen in Table 1 and Figure 2. Maximum absorbance occurs at nanogold concentration of 25 ppm, amounting to 0.595 at a maximum wavelength of 520 nm. The maximum absorbance is found to be in the region of maximum absorbance of DPPH at around 519-526 nm.

Table 1. Maximum absorbance of nanogold in UV-Vis instrument.

| No. | Nanogold concentration (ppm) | $\lambda$ max (nm) | Absorbance |
|-----|------------------------------|--------------------|------------|
| 1.  | 5                            | 520.00             | 0.121      |
| 2.  | 10                           | 520.50             | 0.209      |
| 3.  | 15                           | 523.50             | 0.323      |
| 4.  | 20                           | 526.50             | 0.392      |
| 5.  | 25                           | 520.00             | 0.595      |
| 6.  | 30                           | 523.50             | 0.286      |
| 7.  | 35                           | 525.00             | 0.273      |
| 8.  | 40                           | 523.50             | 0.102      |

Besides having absorption around maximum absorbance of DPPH, nanogold also has absorption at high energies of UV as shown on figure 2, i.e. in the region of 200 nm. The absorption peaks will become more apparent when using the standard addition method. This is an initial potential to be increased when reinforced with a compound that can synergize.

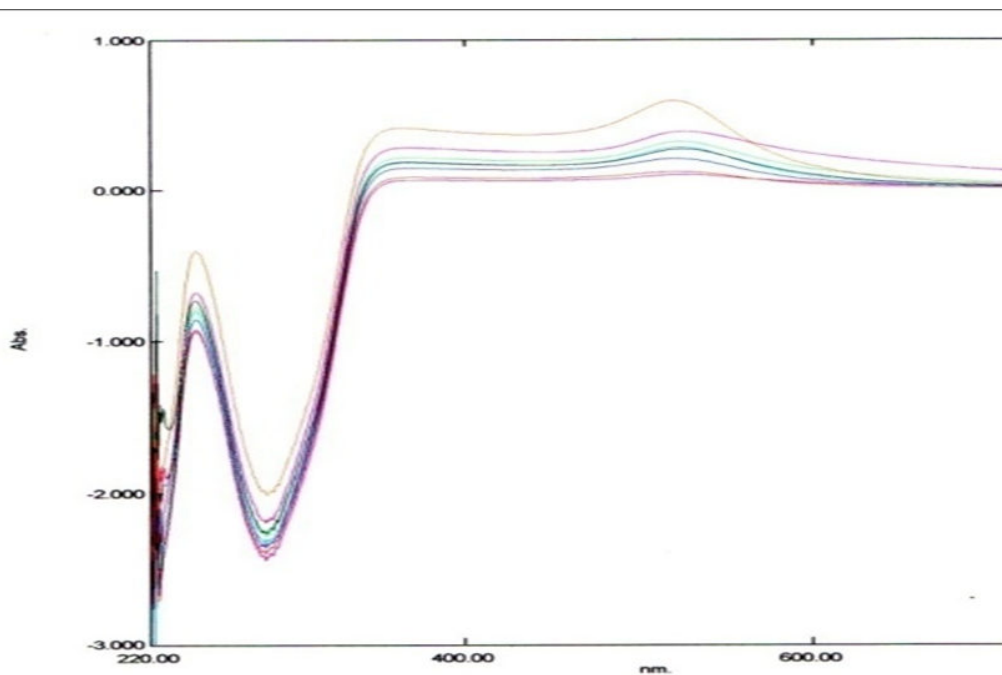


Figure 2. UV-Vis absorbance of nanogold (Taufikurohmah, et al, 2012)

### 3.3 Test of Support of nanogold on the sunscreen activity of OPMC

Both OPMC and nanogold have activity as a sunscreen because it had the same absorption of the UV-Vis. By looking at OPMC absorbance value of 0.667 at  $\lambda$  331 nm (figure 3) before interacting with nanogold and absorbance value after interacting with 5 ppm nanogold of 0.801 at the same  $\lambda$ , it is clear there appears to be an increase in activity of sunscreen.

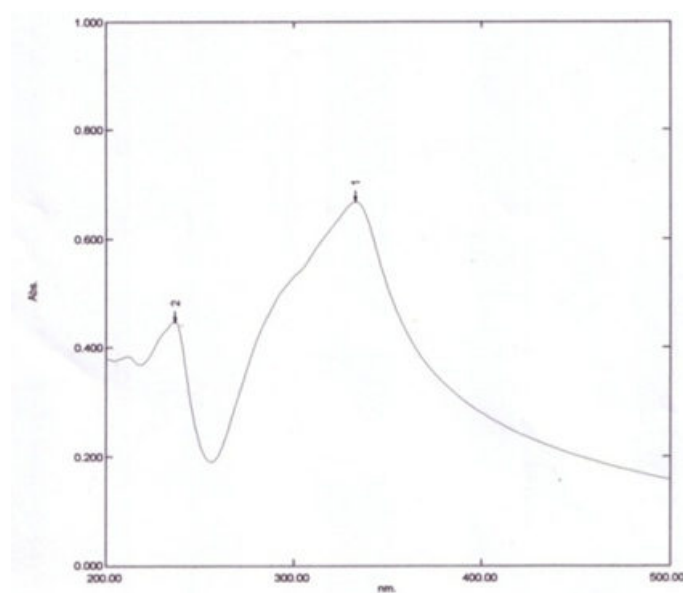


Figure 3. UV-Vis absorbance of OPMC sunscreen

Absorbance value of OPMC, nanogold, and OPMC-nanogold at various concentrations is presented in Table 2.

Table 2. UV-Vis Absorbance of OPMC, nanogold, and OPMC-nanogold.

| Concentration | OPMC             |                | Nanogold   |   | OPMC-nanogold                        |                                  |
|---------------|------------------|----------------|--|---|--------------------------------------|----------------------------------|
|               | $\lambda$ (nm)   | Absorbance     | $\lambda$ (nm)   | Absorbance  | $\lambda$ (nm)                       | Absorbance                       |
| 1% (b/v)      | 333,00<br>236,50 | 0,667<br>0,446 |  |   |                                      |                                  |
| 5 ppm         |                  |                | 735.00<br>520.00<br>370.00<br>246.00   | 0.014<br>0.121<br>0.087<br>-0.932   | 331.20<br>200.00                     | 0.801<br>2.982                   |
| 10 ppm        |                  |                | 520.50<br>369.50<br>246.00<br>217.50<br>208.00                               | 0.209<br>0.148<br>-0.859<br>-0.703<br>-0.730                              | 328.60<br>205.20<br>201.80           | 0.550<br>3.644<br>3.675          |
| 15 ppm        |                  |                | 523.50<br>369.00<br>246.00<br>222.50<br>214.00<br>208.50                     | 0.323<br>0.218<br>-0.774<br>-2.199<br>-1.382<br>-2.074                    | 331.80<br>206.60                     | 0.820<br>3.987                   |
| 20 ppm        |                  |                | 526.50<br>368.00<br>246.00<br>218.00<br>208.00                               | 0.392<br>0.286<br>-0.678<br>-0.967<br>-2.237                              | 310.20<br>291.80<br>207.20           | 0.573<br>0.578<br>4.000          |
| 25 ppm        |                  |                | 520.00<br>364.00<br>246.00<br>223.00<br>218.00<br>208.00                     | 0.595<br>0.417<br>-0.403<br>-1.823<br>-0.980<br>-1.641                    | 317.00<br>292.60<br>212.40           | 0.873<br>0.864<br>4.000          |
| 30 ppm        |                  |                | 523.50<br>369.00<br>246.00<br>215.00<br>207.50                               | 0.286<br>0.183<br>-0.805<br>-1.853<br>-1.999                              | 450.22<br>333.56<br>220.94<br>220.57 | 0.577<br>0.902<br>3.984<br>3.983 |
| 35 ppm        |                  |                | 525.00<br>368.00<br>245.50<br>224.50<br>218.00<br>207.50                     | 0.273<br>0.188<br>-0.733<br>-1.462<br>-1.276<br>-1.745                    | 447.09<br>331.22<br>222.12           | 0.687<br>1.028<br>4.001          |
| 40 ppm        |                  |                | 734.50<br>523.50<br>373.50<br>246.00<br>222.50<br>218.50<br>214.00<br>208.50 | 0.023<br>0.102<br>0.069<br>-0.925<br>-1.514<br>-1.327<br>-1.888<br>-2.766 | 283.00<br>214.00                     | 0.796<br>4.000                   |

In general, the value of OPMC-nanogold absorbance increased with increasing concentration of nanogold. However, there are exceptions where the increase in absorbance at  $\lambda$  maximum of OPMC not happen but at a certain  $\lambda$  increases. For example, 20 ppm nanogold has absorbance value at the maximum  $\lambda$  of OPMC only 0.573 but the absorbance at  $\lambda$  291.8 is 0.578. The same thing happened to nanogold 25 ppm, the value of absorbance at 331 nm is 0.873 and at 292.6 nm is 0.864.

According to table 2, it appears that the nanogold before combined whit OPMC giving absorbance at a wavelength of 200 nm with a negative value, but once combined with OPMC appears that absorbance values rose dramatically exceeds the maximum absorbance of OPMC even to the number 4. This shows the synergistic effect of the combination of the two types of material.

The combination of OPMC and nanogold has absorbance in the range of UV-Vis, toward shorter wavelength with higher energy. The combination of those materials is highly beneficial when used as a sunscreen in cosmetics. Skin damage from sun exposure causes aging can be prevented more leverage.

Aging due to sun exposure contributes about 80% of the overall aging. UV light causes crosslinking among collagen which is then followed by decreasing the quantity of soluble collagen. Crosslinking among collagen can also decrease skin turgor, increase the number of wrinkles, be skimming the surface of the skin, reduces moisture (hard to bind water molecules), increase skin dryness, cause rough skin and other aging parameters.

The whole explanation shows that activity of nanogold can be used as antiaging material through mechanism of UV absorption. In addition to direct damage, UV rays can also trigger the formation of free radicals that damage several tissues including skin tissue and causes aging. Lots of damage can be caused by UV rays, either directly or indirectly.

Interaction OPMC with nanogold 5 ppm give results as shown in Figure 4. Absorbance of both materials is synergy. Besides having absorbance at a wavelength of 305-315 nm (absorbance of OPMC), there is also a high absorbance in the region of 200 nm which is the absorbance of nanogold. Thus, the interaction of these two sunscreen compounds is complementary and synergistic to be the future of sunscreen compounds.

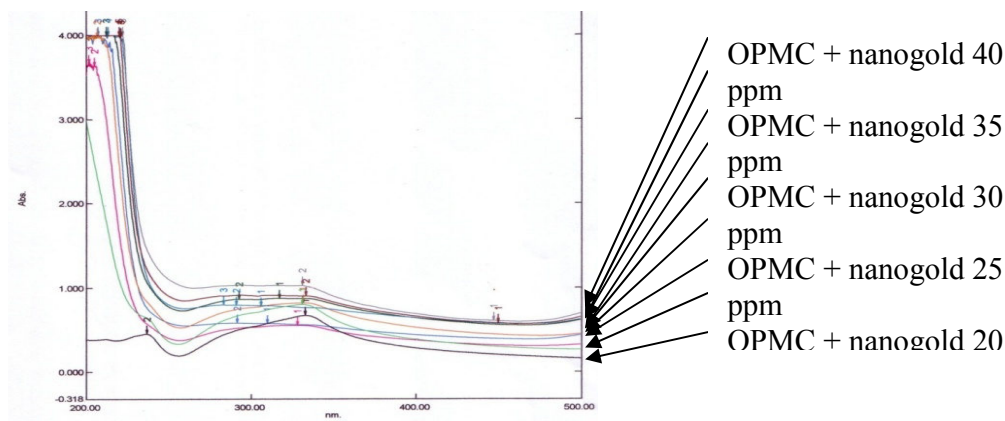


Figure 4. UV-Vis absorbance of OPMC and nanogold

From figure 2, it appears the synergetic of these two sunscreen compounds, nanogold and OPMC. Absorbance of pure OPMC has value under combination of OPMC and nanogold. In addition, new absorbance appears at a wavelength of 200 nm. It provides information that the combined both sunscreen materials can reduce the concentration of OPMC use in cosmetics. Of course this will reduce the production cost of the purchase of OPMC material.

The reaction mechanism between sunscreen of OPMC and nanogold, which can increase the ability to absorb UV rays even at the highest energy level, needs to be further discussed. OPMC structure consists of molecules containing conjugated electron system with double and single bond alternately which allowing the occurrence of resonance in the molecule that absorbs high-energy UV. Electron conjugated system consists of a ketone group with conjugated double bonds that connected to a benzene group which extends the possibility of the resonance process.

In OPMC, there is still one more group that has a function as a driver of electrons, namely -CH<sub>3</sub>.

Nanogold in this case took part in activating the resonance of the OPMC molecule. Resonance process runs faster and absorbed UV energy becomes greater. Therefore, there is a huge increase in absorption in the region of high energy UV at  $\lambda$  200 nm. This can be attributed to the ability of nanogold attract electrons (electron affinity) that quite large.

Nanogold can cause the resonance processes to be more stable, in the sense of resonance processes be connected one another so that more continuous. Resonance in the benzene ring circumference generally stopped in the ring while ketones with conjugated double bonds also perform its own resonance separately, so OPMC has two absorbance peaks. Nanogold make both the resonance are connected by strong attraction due to the high electron affinity owned by nanogold. This resonance produces greater energy absorption, since it appears the absorbance in the UV-Vis region at wavelength of 200 nm.

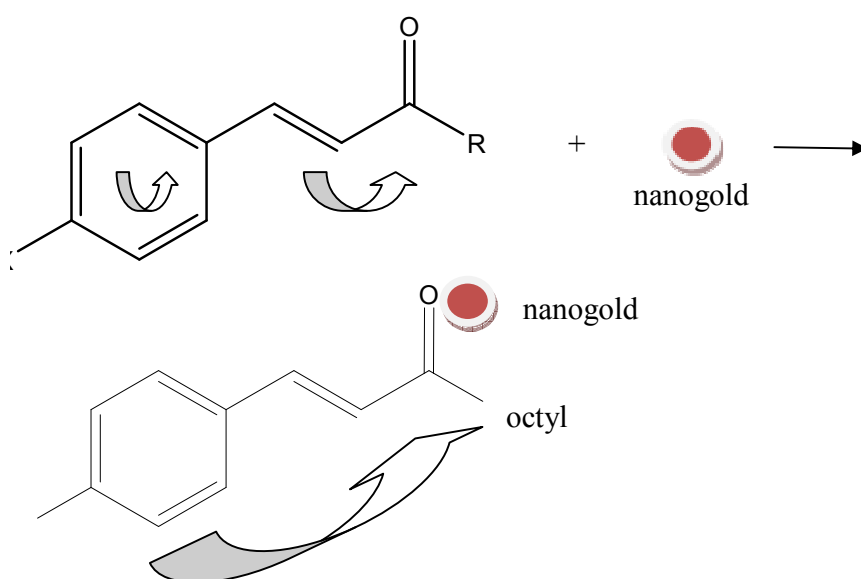


Figure 5. Nanogold increase molecule resonance of OPMC

#### 4. Conclusion

From absorption data of UV-Vis of nanogold various concentration, can be concluded that the nanogold has sunscreen activity especially in high energy UV region at  $\lambda$  200 nm. Sunscreen activity of nanogold becomes higher with higher concentrations. It can be seen from the absorbance values were greater when the concentrations increases.

Nanogold can support sunscreen activity of OPMC as seen from the rising of absorbance value on the combination of the two sunscreen nanogold and OPMC. Nanogold provides excellent absorbance at  $\lambda$  200 nm that is not owned by the OPMC compound.

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