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Original Research Article

Photostability of avobenzone in a commercial sunscreen SPF 50 with the addition of quencher upon sun exposure

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ABSTRACT

Background: Sunscreen can prevent acute and chronic skin damage, acute skin damage includes the burning effect that is felt on the skin, chronic skin damage due to exposure to UV A and UV B rays, namely skin cancer. Avobenzone is a UV filter that is often used but is unstable when exposed to sunlight, for this reason a quencher is added as an avobenzone photostabilizer in commercial sunscreen SPF 50.
Methods: Photostability of avobenzone sunscreen formula SPF 50 before and after adding the quencher was tested in the sun using a quartz plate, then analyzed using UV vis spectrophotometer and high-performance liquid chromatography (HPLC).
Results: Testing using a UV vis spectrophotometer, SPF 50 sunscreen with the addition of solastay S1® is the best quencher because it can reduce the photodegradation of avobenzone compared to octocrylene, polycrylene (Polyester-8) and Sinoxyl HSS® (trimethoxybenzylidene pentanedione). FSOL2 is the best formula than FSOL1 and FSOL3 because it is more photostable in reducing avobenzone photodegradation. Follow-up testing with HPLC, FSOL2 can retain 50.56% avobenzone after 120 min of sun exposure.
Conclusions: The addition of solastay as a quencher is proven to reduce the photodegradation of avobenzone under sunlight.

Keywords: Sunscreen, UV filter, Photostability of avobenzone, Quencher

INTRODUCTION

The recommended exposure to sunlight is below 10.00 am, an inappropriate hour and too long can cause many health problems, such as sunburn, allergic reactions to light or photoallergy and even skin cancer.[1] Sunlight which is good for health starts at 07.00 am in the morning, but at 11.00 am - 14.00 pm the intensity of sunlight will increase so it is not recommended to bask in direct sunlight, then the next hour the intensity of sunlight will decrease again.[2]

UV radiation is grouped into 3 groups, namely UV A, UV B and UV C. Most of the sunlight in the environment is UV A and UV B, while UV C does not reach the earth's surface because in the earth's atmosphere UV C rays are absorbed by ozone. UVA rays which, if exposed directly to the skin, will enter the dermis layer, whereas if exposed to UVB rays, a small portion reaches the dermis because most of the UVB rays will be absorbed by the epidermis of the skin, resulting in mutations that cause skin cancer. Previous research on sunscreen proved that sunscreen is effective in preventing several types of skin cancer.[3]

Overcoming this problem, we need an ingredient that can protect the skin from the dangers of solar radiation. The ingredients used can be natural ingredients, but the preparation of these materials for use on the skin is quite time-consuming and the risk of contamination is greater and does not last long in storage.[4-6] People tend to use commercial sunscreen products that are easy to find and practical because they can be applied directly to the skin and have a long shelf life. Sunscreen can prevent acute and chronic skin damage. Acute skin damage includes sunburn or the burning effect that is felt on the skin, chronic skin damage due to exposure to UV A and UV B rays, namely skin cancer.[7]

Sunscreen must have good photostability when exposed to sunlight. The main ingredient of sunscreen is a UV filter which functions to absorb energy in radiation UV by converting it into electronic excitation energy. The most commonly used sunscreen filter today is Avobenzone (butyl methoxydibenzoylmethane or BMDM) since the 1980s in Europe and in the United States in the early 1990s.[8]

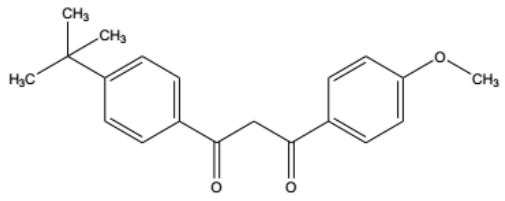
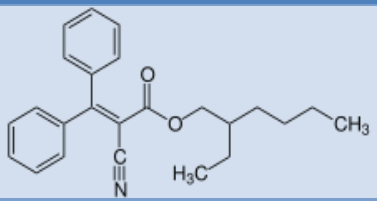
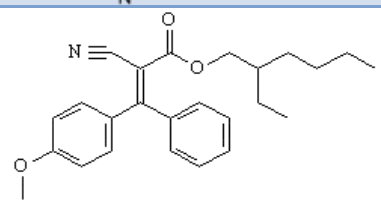
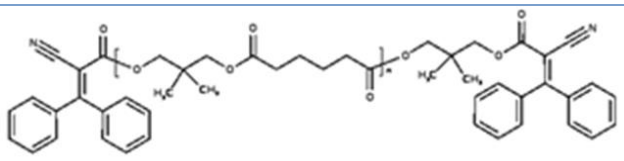


Figure 1: Structure of avobenzone.[9]

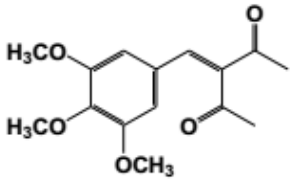
Avobenzone is the most widely used UVA protector in the cosmetic industry for sunscreen products worldwide which can absorb light in the UV range. In sunscreen products, avobenzone is generally added at concentrations between 3-10% and is often combined with other compounds that can absorb UVB light and also added several other compounds such as quenchers, antioxidants and moisturizers for the skin.[10-13] Avobenzone is known as an unstable UV filter, it has been proven in several studies that avonenzone has been degraded due to UV exposure even up to 90%.[14,15] The way to overcome the instability of avobenzone is by adding a fotostabilizer, which is a compound that helps prevent UV filters from losing their effectiveness when exposed to sunlight.[16] Materials used as stabilizers for avobenzone include adding antioxidants and quenchers as well as other ingredients that act as photostabilizers. The addition of antioxidants in sunscreen products can increase SPF such as vitamin E and vitamin C, addition of lignin and silymarin, fruit extracts containing flavonoids, but the use of these antioxidants has drawbacks because Antioxidants are easily damaged when exposed to light and heat generated by the sun.[17-21] Quencher is a photo stabilizer in sunscreens, which plays a role in transferring avobenzone excited energy so that it can return to its ground state.[8]

Quenchers can be photosensitizers, namely compounds that are sensitive to light, where photosensitizers will absorb light so that it will be excited to form photons which will then transfer this energy to other compounds, causing other compounds to be degraded.[22] Therefore, researchers want to know how the effect of photostability of avobenzone on commercial sunscreen SPF 50 with the addition of quencher by sunlight. Several quenchers used in this study were Octocrylene, Solastay S1®, Polycrylene (Polyester-8) and Sinoxyl HSS®. The concentration of quenchers used to stabilize UV filters in sunscreens are octocrylene with a maximum concentration of 10%, Solastay S1® with an additional concentration of 3-5%, Polycrylene with an additional concentration of 1-4 % and Sinoxyl HSS® with an addition of 1-2%.[23-26]

Table 1: Structure and formula of quencher.

Quencher	Structure		Molecular formula
Octocrylene		27	$C_{24}H_{27}NO_2$
Solastay S1®		28	$C_{25}H_{29}NO_3$
Polycrylene		29	$C_{37}H_{30}N_2O_4$ $(C_{11}H_{18}O_4)n$

Continued.

Quencher	Structure		Molecular formula
Sinoxyl HSS®		30	$C_{15}H_{18}O_5$

Objectives

The objective is to determine the best quencher in reducing the photodegradation of avobenzone in a commercial sunscreen SPF 50 upon sun exposure.

METHODS

This research method is an experiment with quantitative measurements.

Measurement

This research was conducted at Andalas University (Padang, Indonesia) from September to December 2022.

Reagents and samples

Commercially available SPF 50 sunscreen, Quencher (Octocrylene, Solastay S1®, Polycrylene and Sinoxyl HSS®, ethanol, methanol (merck) and distilled water.

Instrumentation

Sunscreen photostability as measured by Spectrophotometer (UV/Vis T70 UV / Spectophotometer and high-performance liquid chromatography (HPLC) (CBM-20A SHIMADZU).

Sample preparation

Commercial sunscreen SPF 50, sunscreen added with 3 variations of quencher concentration, namely Octocrylene, Solastay S1®, Polycrylene, Sinoxyl HSS® which can be seen in Table 2.

Sunscreen irradiation

The sunscreen formula sample was weighed and spotted on a quartz plate and then affixed to a second quartz plate, then irradiated with sunlight between 11.00 - 14.00 (UTC+7).

Table 2: Sample name and composition.

No	Formula	Sunscreen SPF 50	Quencher (%)			
			Octocrylene	Solastay S1®	Polycrylene	Sinoxyl HSS®
1.	F0	✓	-	-	-	-
2.	FOCT1	✓	3	-	-	-
3.	FOCT2	✓	5	-	-	-
4.	FOCT3	✓	7	-	-	-
5.	FSOL1	✓	-	3	-	-
6.	FSOL2	✓	-	4	-	-
7.	FSOL3	✓	-	5	-	-
8.	FPOL1	✓	-	-	1	-
9.	FPOL2	✓	-	-	3	-
10.	FPOL3	✓	-	-	5	-
11.	FSIN1	✓	-	-	-	1
12.	FSIN2	✓	-	-	-	1.5
13.	FSIN3	✓	-	-	-	2

Sunscreen photostability testing

Samples that had been irradiated by the sun for 0 min, 30 min, 60 min, 90 min and 120 min were dissolved in ethanol and distilled water (40:60) in a 50 ml volumetric flask. Then it was stirred using a magnetic stirrer for 30 min, during which the volumetric flask containing the sample was mixed was covered with aluminum voil so that it was not exposed to sunlight. After that, it was measured using a UV-Vis spectrophotometer and the percent photodegradation of avobenzone was found before and after irradiated sunlight.

Photostability testing using high-performance liquid chromatography

Samples before and after irradiated sunlight were dissolved in a solution of methanol and distilled water

(88:12). The treatment of dissolving the sample was the same as the procedure above, using methanol and distilled water (88:12) as mobile phases and a flow rate of 1 mL/min. Then the sample was injected, the chromatogram results were obtained in the form of peak retention time and area.

RESULTS

Measurement of sunlight intensity was carried out in an open field for 10 days in sunny weather at 10.00-15.00 UTC+7. The measurement results from 10:00-11:00 UTC+7 the intensity of sunlight is less than 90,000 lux and there is an increase in intensity from 11:00-14:00 UTC+7 with a peak at 12:00 UTC+7 of 114,880 lux, then after 14:00 00 UTC+7 the intensity of sunlight decreases again. The next sunscreen irradiation formula will be carried out at 11.00-14.00 UTC+7, because at that time the sunlight reaches its optimum state.

Solastay S1® is the best quencher as photostable avobenzone in commercial sunscreen spf 50 compared to Octocrylene, Polycrylene and Sinoxyl HSS®. The advantages of solastay are that it includes singlet and triplet quencher types which are able to extinguish excited energy in the singlet and triplet state, while Octocrylene, Polycrylene and Sinoxyl HSS® are triplet quencher types which can only extinguish excited energy in the triplet state.

In the variation of adding solastay S1®, FSOL2 was the formula that suppressed the photodegradation of avobenzone the most. Furthermore, further testing was carried out with HPLC to see the remaining avobenzone more accurately. The remaining avobenzone from 30 min, 60 min, 90 min and 120 min irradiation respectively were 87.38%, 54.42%, 51.90% and 50.56%.

DISCUSSION

Effect of irradiation time on avobenzone photodegradation using a UV-VIS spectrophotometer

UV-VIS spectrophotometer analysis to determine the percent degradation of avobenzone in sunscreen and determine the SPF value after adding quencher. This analysis was carried out before and after being irradiated with sunlight at 11.00 - 14.00 UTC+7 because at that time the sunlight is maximum with light intensity above 10,000 lux which is sunny weather.[31] The reactor used when irradiating the sample is a quartz plate, because the quartz plate can penetrate light so that sunlight will directly reach the sample.[32,33]

Avobenzone is a UV filter that is unstable when exposed to UV light, as shown in research to experience up to 90% degradation with sunlight as a source.[15] In Figure 2 it can be seen that the photodegradation of Avobenzone F0 is directly proportional to the irradiation time, the greatest degradation was at 120 min, namely 48.36%. This is because commercial sunscreens contain several ingredients added to stabilize avobenzone.

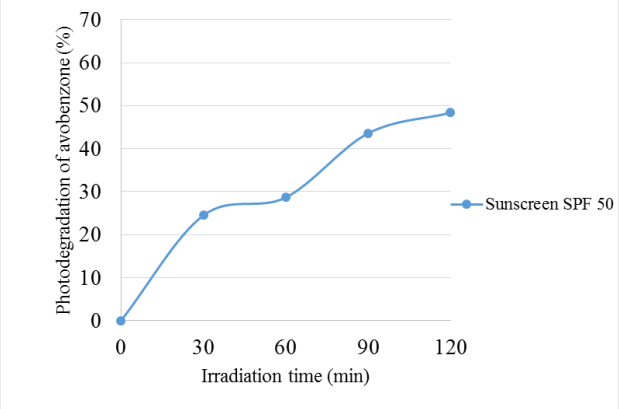


Figure 2: Effect of irradiation time on avobenzone photodegradation (F0).

The F0 sunscreen formulation initially provides high UVA protection, and this protection slowly decreases when irradiated time is added, therefore sunscreen is recommended to be applied every 2 hours.[10] The photodegradation of avobenzone in sunscreen F0 is quite large, so one way to reduce damage to avobenzone can be done by adding a quencher, namely a photostabilizer, which can maximize the effectiveness of sunscreen during its application.

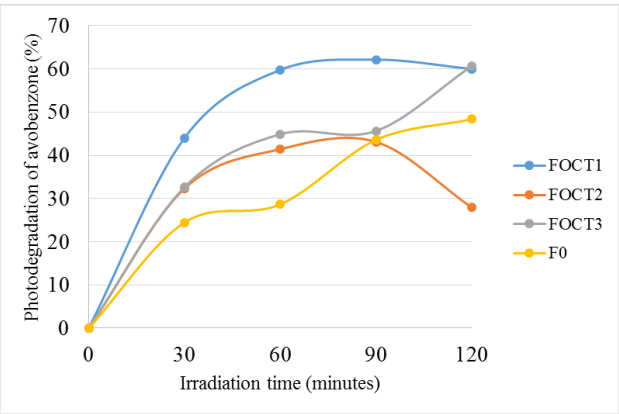


Figure 3: The effect of irradiation time on the photodegradation of avobenzone in sunscreens with the addition of octocrylene.

Octocrylene can absorb UV light in the range of 290-360 nm with an absorption peak of 307 nm and can increase the SPF in sunscreen formulas, but octocrylene can release free radicals that can cause photoallergy on the skin.[34] In Figure 3 it can be seen that the addition of octocrylene to sunscreen cannot reduce the photodegradation of avobenzone after being exposed to the sun. This is due to the nature of octocrylene as a photosensitizer, namely a light-sensitive compound, where the photosensitizer will absorb light so that it will be excited to form photons which will then transfer this

energy to other compounds causing the compound to be degraded, this is what causes the photodegradation of avobenzone which added octocrylene greater than F0.[22] The sequence of sunscreen formulas that have the best photostability based on irradiation time and octocrylene concentration variations are FOCT2, FOCT3 and FOCT1.

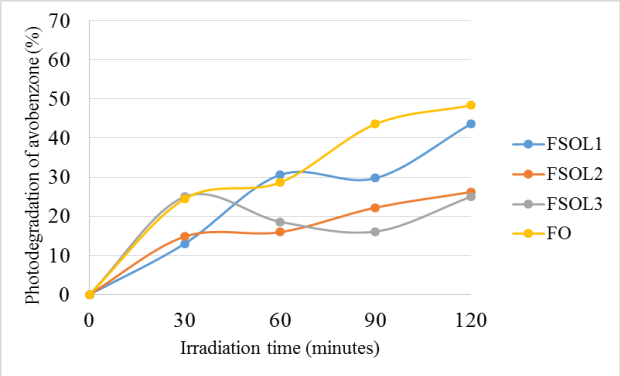


Figure 4: The effect of irradiation time on the photodegradation of avobenzone in sunscreens with the addition of Solastay S1®.

Photodegradation of avobenzone with the addition of Solastay S1® can be seen in Figure 4 directly proportional to the duration of irradiation, FSOL1 could only slightly reduce photodegradation of avobenzone, while FSOL2 and FSOL3 reduced more photodegradation of avobenzone, but in FSOL3 there was a skin effect at 60 and 90 min of irradiation. The highest photodegradation of avobenzone FSOL1, FSOL2 and FSOL3 occurred at irradiation time of 120 min with degradation of 43.63%, 26.21% and 25.00% respectively. The sequence of sunscreen formulas that have the best photostability based on the duration of irradiation and variations in octocrylene concentrations are FSOL2, FSOL3, FSOL1.

The addition of Solastay S1® can reduce the photodegradation of avobenzone in sunscreen after sun exposure and is more effective than using octocrylene according.[35] This is due to the nature of Solastay S1® as a photostabilizer, namely the ability to take excited state energy from avobenzone and dispose of energy safely so that it can reduce the degradation of avobenzone in sunscreens so that avobenzone will return to its basic state and can work again as a UVA filter in sunscreens. Solastay S1® works very fast, and it is good to be formulated with a combination of unstable active ingredients such as avobenzone to be more effective in its use.[36] Further research conducted by showed that the photostabilizer Solastay S1® from HallStar proved to act as a quencher which could quench the excited state of avobenzone in 1.86/10-12 seconds thereby preventing unwanted chemical reactions, and thereby contributing safely to photoprotection with Avobenzone stabilization.[37]

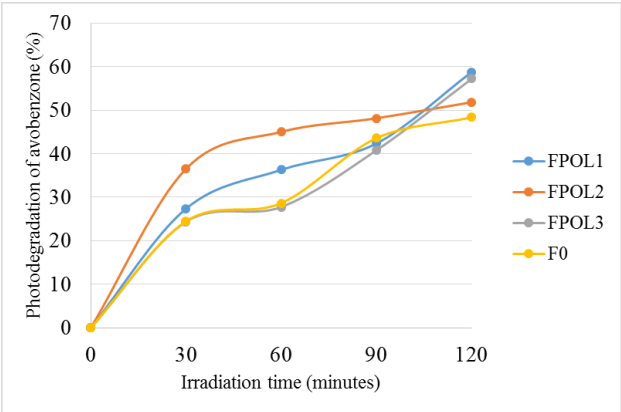


Figure 5: The effect of irradiation time on the photodegradation of avobenzone in sunscreens with the addition of polycrylene.

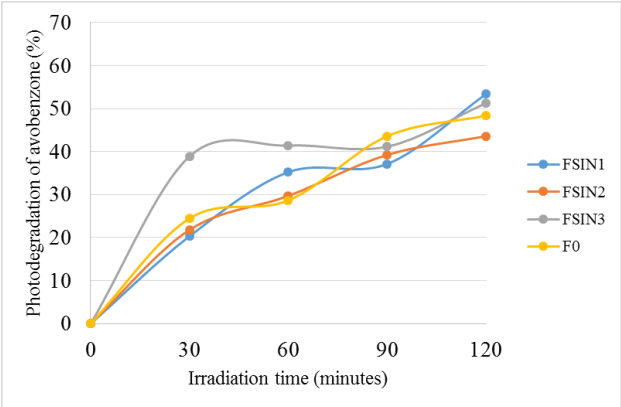


Figure 6: The effect of irradiation time on the photodegradation of avobenzone in sunscreens with the addition of Sinoxyl HSS®.

Polycrylene is often combined with sunscreen with the active ingredient avobenzone because it has the ability to absorb UVB in the range with a peak at 303 nm.[38] In sunscreen, polycrylene also acts as water resistant. A sunscreen formulation with 3% polycrylene will be more water resistant than a similar formulation without polycrylene. In Figure 5, the photodegradation of avobenzone in sunscreen with the addition of Polycrylene with variations of 1%, 3% and 5% is proportional to the length of irradiation time. The highest percentage of avobenzone degradation in FPOL1, FPOL2 and FPOL3 was after 120 min of irradiation, namely 58.79%, 51.84% and 57.22%. As can be seen in the figure, FPOL3 sunscreen has a similar photodegradation of avobenzone to F0, but FPOL1 and FPOL2 cannot reduce the damage to avobenzone in sunscreen.

Figure 6 shows the percent degradation of avobenzone in sunscreen with the addition of Sinoxyl HSS®. The photodegradation of avobenzone is proportional to the irradiation time, in FSIN1, FSIN2 and FSIN3 the highest photodegradation was 120 min of irradiation time with 53.39%, 43.60% and 51.26% respectively. The addition

of Sinoxyl HSS® to sunscreen could not optimally reduce the degradation of avobenzone. According to Sinoxyl HSS® and avobenzone in a 1:1 ratio makes avobenzone stable and works optimally and can also increase the SPF value.[36,39]

Results of analysis using HPLC

This HPLC analysis aims to find out how much avobezone remains after being irradiated by sunlight. The test used the mobile phase of methanol and aquabides (88:12) with a flow rate of 1 ml/min. The following is the HPLC chromatogram of the sunscreen formula FSOL2 before and after sunlight irradiation.

Avobenzone has an area that is inversely proportional to the length of irradiation time, the longer the irradiation time, the more avobenzone will be degraded. Testing of sunscreen formulation samples before and after irradiation using HPLC is more accurate than using a UV VIS spectrophotometer because the HPLC test is based on the principle of specific compound separation. The area of the sample is presented in Table 3.

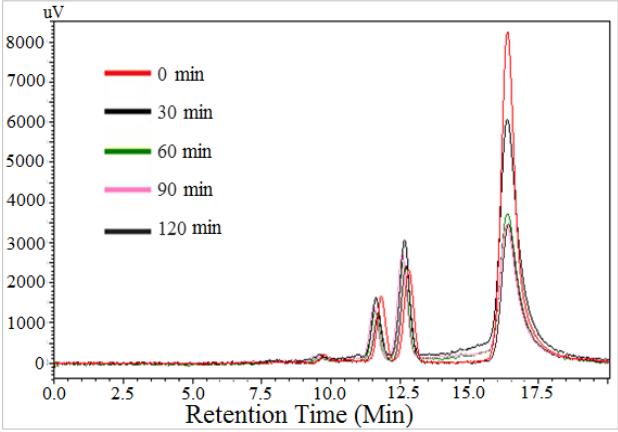


Figure 7: Chromatogram HPLC of FSOL2.

Table 3. Avobenzone remained (%).

Irradiation Time (Min)	Peak Area	Avobenzone (%)
0	307.688	100
30	268.868	87.38
60	167.442	54.42
90	159.685	51.90
120	155.581	50.56

Limitations

The limitations of this study discuss the photostability of avobenzone with the addition of a quencher.

CONCLUSION

The best sunscreen formul is FSOL2, showed a formula that was able to stabilize avobenzone because it was able to reduce the photodegradation of avobenzone after being irradiated by sunlight.

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Ethical approval: Not required

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