SEBHA UNIVERSITY JOURNAL OF PURE & APPLIED SCIENCESVOL.24 NO.3 2025
DOI: 10.51984/JOPAS.V24I3.3761

مجلة جامعة سبها للعلوم البحتة والتطبيقية
Sebha University Journal of Pure & Applied Sciences

Journal homepage: http://www.sebhau.edu.ly/journal/jopas

Calculation of Sun Protection Factor (SPF) Values for Selected Organic Filters Using a UV Spectrophotometer

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Keywords:
Sunscreen.
Sodium Salicylate.
Ammonium Benzoate.
Cinnamic Acid.
SPF.

ABSTRACT

This study analytically investigated the ultraviolet (UV) absorption characteristics of various organic UV filters containing a benzoyl or benzylidene group, using a double-beam UV–Vis spectrophotometer to measure their absorbance. Additionally, the sun protection factor (SPF) of these compounds was calculated using Mansur's equation—a critical metric for assessing their effectiveness against harmful UV radiation. Absorbance measurements were conducted over the wavelength range of 290 to 320 nm in methanol, focusing on organic acid salts such as sodium benzoate, sodium salicylate, and ammonium benzoate, as well as organic acids and aldehydes. The results demonstrated that the organic filters provided varying levels of UV protection. The highest SPF value recorded was 54.5 for 4-methoxybenzaldehyde, followed by benzophenone at 44.6, trans-cinnamaldehyde at 41.4, and cinnamic acid at 39.3. These data suggest that benzoyl derivatives with conjugated double bonds exhibit significantly greater UV absorption than benzoic acid and salicylic acid, which displayed relatively modest SPF values. In light of these findings, it is recommended that benzophenone, trans-cinnamaldehyde, and cinnamic acid be considered for incorporation into sunscreen formulations due to their demonstrated efficacy in UV protection.

حساب قيم عامل الحماية من أشعة الشمس (SPF) لبعض المرشحات العضوية باستخدام مطياف الأشعة فوق البنفسجية

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قسم الكيمياء، كلية العلوم، جامعة سرت، سرت، ليبيا.

الكلمات المفتاحية:
واقي من الشمس.
ساليسيلات الصوديوم.
بنزوات الأمونيوم.
حمض السينامك.
SPF.

الملخص

تناولت هذه الدراسة تحليلياً خصائص امتصاص الأشعة فوق البنفسجية لمرشحات عضوية مختلفة للأشعة فوق البنفسجية تحتوي على مجموعة بنزويل أو مجموعة بنزيليدين، وذلك باستخدام مطياف الأشعة فوق البنفسجية المرئية ثنائي الحزمة لقياس امتصاصها للأشعة فوق البنفسجية. بالإضافة إلى ذلك، تم حساب عامل الحماية من الشمس لهذه المركبات باستخدام معادلة منصور، وهو مقياس مهم لتقييم فعاليتها ضد الأشعة فوق البنفسجية الضارة. أجريت قياسات الامتصاص على مدى نطاق طول موجي يتراوح من 290 إلى 320 نانومتر في الميثانول، مع التركيز على أملاح الأحماض العضوية مثل بنزوات الصوديوم وساليسيلات الصوديوم وبنزوات الأمونيوم، بالإضافة إلى الأحماض العضوية والألدهيدات. وتوضح النتائج أن المرشحات العضوية توفر مستويات متفاوتة من الحماية من الأشعة فوق البنفسجية. كانت أعلى قيمة لمعامل الحماية من الشمس (SPF) المسجلة 54.5 لـ4-ميثوكسي بنزالدهيد، يليه بنزوفينون عند 44.6، وترانس سيناماldهيد عند 41.4، وحمض سينامك عند 39.3. تشير هذه البيانات إلى أن مشتقات البنزويل ذات الروابط المزدوجة المترافقة تظهر امتصاصًا متفوقًا للأشعة فوق البنفسجية مقارنة بحمض البنزويك وحمض الساليسيليك، اللذين يمتلكان قيم معامل حماية من الشمس متواضعة نسبيًا. في ضوء هذه النتائج، يوصى بالنظر في دمج بنزوفينون وترانس سيناماldهيد وحمض سينامك في تركيبات واقي الشمس نظرًا لفعاليتها المثبتة في الحماية من الأشعة فوق البنفسجية.

1. Introduction

UV filters are essential components found in sunscreens that protect the skin from the damaging effects of the sun's ultraviolet (UV) rays [1]. These rays can cause immediate harm, such as painful sunburn, as well as long-term effects including premature ageing, skin discolouration, and an increased risk of skin cancer. To effectively combat these dangers, UV filters are classified into two main categories, each serving a distinct purpose [2]:

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Article History : Received 10 January 25 - Received in revised form 28 June 25 - Accepted 20 July 25

i. Inorganic UV Filters (also known as physical or mineral filters): This This category includes key ingredients such as titanium dioxide (TiO_2) and zinc oxide (ZnO), which are widely recognised for their effectiveness [2]. These filters work by forming a physical barrier on the outer layer of the skin. When sunscreen containing these ingredients is applied, the inorganic filters reflect and scatter both UVA and UVB rays away from the skin [3]. This protective mechanism prevents the rays from penetrating the skin and causing harm. One of the significant benefits of inorganic filters is that they begin working immediately upon application, making them ideal for active outdoor use. They are also gentle on sensitive skin, as they are less likely to cause irritation or allergic reactions [4–5].

ii. Organic UV Filters: Known as organic UV filters, these compounds operate differently than their inorganic counterparts. Instead of reflecting rays, organic filters absorb UV radiation and transform it into heat, which the body then releases [6]. Common ingredients in this category include avobenzone **4**, octocrylene **2**, octisalate **7**, and homosalate **8** (Fig. 1) [1, 2, 7]. These filters can penetrate the outer layer of the skin, providing a different type of coverage [8]. However, it's important to note that organic filters generally need about 15 to 30 minutes after application to become fully effective [6]. Many users appreciate that sunscreens with organic filters tend to have a lighter feel on the skin and often blend in more easily than those with only inorganic filters [9].

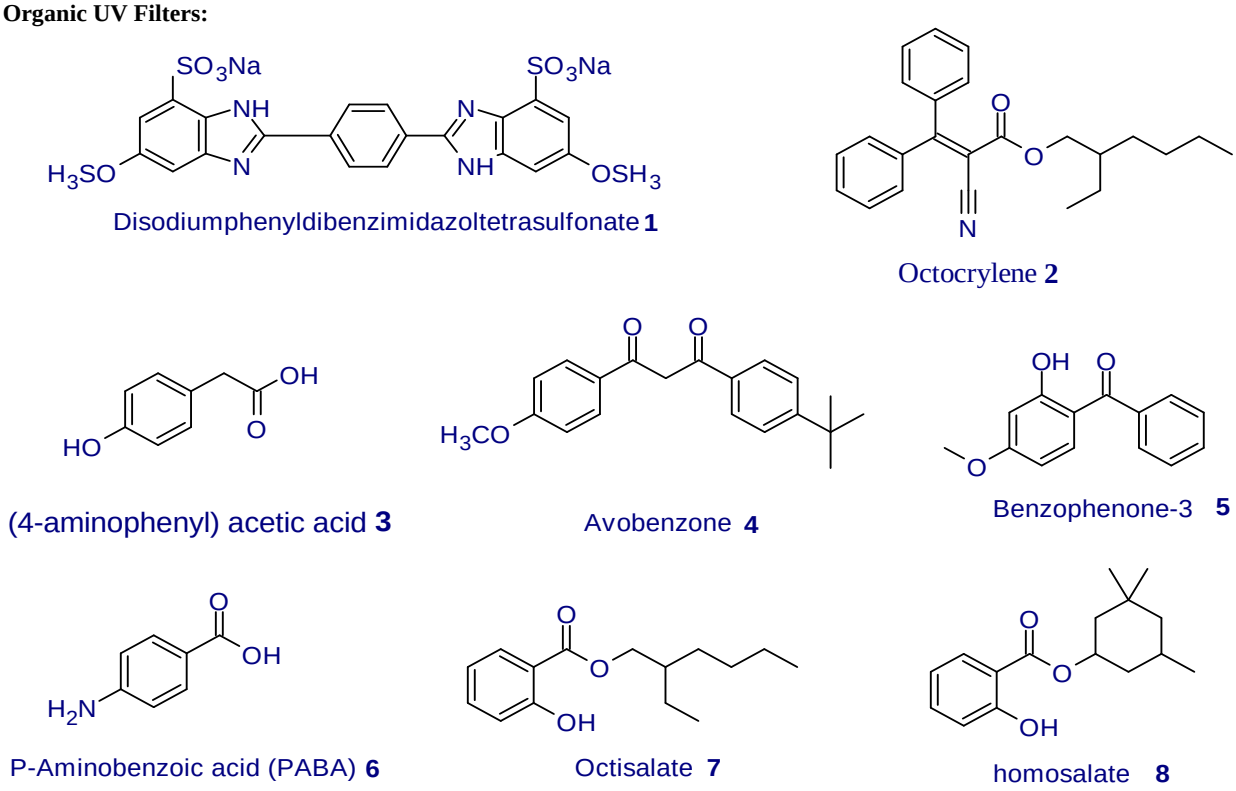


Figure 1: chemical structures of known organic UV filters were sketched by ACD/ChemSketch (Freeware) 2022.2.3

To maximize protection, many sunscreens today combine both inorganic and organic UV filters [10]. This combination ensures broad-spectrum coverage, protecting the skin from both UVA rays, which contribute to skin aging and can damage the skin's DNA, and UVB rays, which are primarily responsible for causing sunburn. [11]. Employing a broad-spectrum sunscreen that features both types of UV filters is vital for providing comprehensive defense against the dangers of sun exposure [12]. Regularly applying sunscreen—ideally every two hours, or more frequently when swimming or sweating—is crucial for maintaining skin protection throughout the day [13]. By understanding the roles of these filters, you can make informed choices about sunscreen products to safeguard your skin effectively.

Table 1 offers an overview of allowance levels for specific organic candidates across several countries, including Canada, Australia, the European Union, and the United States. This table serves as a representative sample that underscores the regulatory differences among these regions. Additionally, it is important to note that any organic filter employed in these countries must secure the appropriate licensing to comply with local regulations. This licensing may be issued by relevant authorities, such as the European Union for its member states or the Food and Drug Administration (FDA) in the United States. These regulatory measures are crucial for maintaining the integrity and safety of organic products in the marketplace [14].

Table 1: The levels of organic UV filters in four markets [14].

Organic UV filter	European Union	United States	Australia	Canada
Aminobenzoic Acid (PABA) **4**	5%	Up to 15%	----------	Up to 15%
Avobenzone (Butyl Methoxydibenzoylmethane) **6**	5%	Up to 3%	5%	Up to 3%
Oxybenzone (Benzophenone-3) **5**	10%	Up to 6%	10%	Up to 6%
Octocrylene **2**	10% (as acid)	Up to 10%	10%	Up to 10%
Disodium Phenyl dibenzimidazole tetraslfonate **1**	10%	----------	10%	----------
Octisalate **7**	5%	Up to 5%	5%	Up to 5%

2. MATERIALS AND METHODS

2.1. Chemicals and Equipment:

Cinnamic acid ($C_9H_8O_2$, 99%), salicylic acid ($C_7H_6O_3$, 99.8%), sodium benzoate ($C_7H_5NaO_2$, 99.5%), and trans-cinnamaldehyde (C_9H_8O, 98%) were purchased from RIEDEL-DE HAËN AG, Seelze-Hanover. Benzoic acid ($C_7H_6O_2$, 99.5%) was obtained from Clariant. Benzophenone ($C_6H_5COC_6H_5$, 98%) was acquired from MERCK-Schuchardt. Ammonium benzoate ($C_6H_5COONH_4$, 99%) was sourced from Panreac, and benzaldehyde (C_6H_5CHO) was purchased from AVONCHEM. 4-Methoxybenzaldehyde ($C_8H_8O_2$, >99%) was obtained from ACROS ORGANICS. Methanol (CH_3OH, 99%) was purchased from AnalaR NORMAPUR, and sodium salicylate ($C_7H_5NaO_3$, 93.5%) was obtained from BDH.

Spectrophotometric determination of UV absorbance was carried out using a 1 cm path-length quartz cuvette and a double-beam UV/Visible spectrophotometer (Specord 210 Plus, Analytik Jena). Sample mixing

was performed using a Vortex mixer (BioCote).

2.2. Sample Preparation and Measurement of UV Absorption: 500 500 mg of each sample was weighed and transferred to a 100 ml volumetric flask, then diluted to the mark with methanol. The mixture was stirred using a vortex mixer and filtered through filter paper. The absorbance of the prepared solutions for ten samples—cinnamic acid, salicylic acid, sodium salicylate, benzoic acid, sodium benzoate, ammonium benzoate, benzaldehyde, 4-methoxybenzaldehyde, benzophenone, and trans-cinnamaldehyde—was measured using a UV spectrophotometer in the range of 290–320 nm in 1 cm quartz cuvettes, with readings taken at 5 nm intervals. Each sample was measured three times at a single wavelength, and the average absorbance was calculated, as shown in Tables 3 and 4. The full optical absorbance data are summarised in Tables 2–5.

Table 2: shows the calculations for measuring the average absorbance of the cinnamic acid.

Wave length (nm)	absorbance (Abs)		Abs average (±) SD
	Abs (1)	Abs (2)	
290	1.532	1.691	**1.611±0.112**
295	1.981	2.107	**2.044±0.089**
300	2.439	3.018	**2.728±0.409**
305	2.963	4.255	**3.609±0.914**
310	4.178	9	**6.589±3.410**
315	3.028	9	**6.014±4.223**
320	2.028	2.056	**2.042±0.020**

Table 3: Absorbance average's values of benzoic acid and its salt samples.

Wave length (nm)	Benzoic Acid	Ammonium Benzoate	Sodium benzoate
290	0.565± 0.001	0.375±0.022	0.493±0.009
295	0.189±0.007	0.171±0.016	0.347±0.008
300	0.170±0.008	0.114±0.013	0.258±0.005
305	0.171±0.001	0.093±0.010	0.198±0.004
310	0.164±0.001	0.093±0.007	0.152±0.002
315	0.143±0.002	0.085±0.004	0.112±0.001
320	0.101±0.001	0.076±0.004	0.085±0.020

Table 4: shows the average optical absorbance of the tested aldehydes and ketones samples.

Wave length (nm)	benzaldehyde	4-Methoxybenzaldehyde	*trans*-cinnamaldehyde	Benzophenone
290	1.625±0.011	2.411±0.303	2.060±0.131	1.869±0.262
295	2.013±0.144	5.882±4.409	2.776±0.499	2.299±0.160
300	2.585±0.158	3.868±1.039	2.925±0.192	2.791±0.066
305	2.750±0.057	6.357±3.737	6.063±4.154	6.069±4.852
310	2.803±0.070	6.001±4.241	3.648±0.931	5.412±0.011
315	2.72±0.105	6.068±4.155	3.145±0.070	3.374±0.433
320	2.541±0.099	6.111±4.086	6.191±3.972	9±0.000

Table 5: shows the average optical absorbance of samples of salicylic acid and its sodium salt.

Wave length (nm)	Salicylic acid	Sodium salicylate
290	1.425±0.030	0.903±0.023
295	1.808±0.011	1.146±0.007
300	2.236±0.021	1.418±0.001
305	2.411±0.033	1.492±0.006
310	2.439±0.035	1.539±0.012
315	2.478±0.082	1.57±0.007
320	2.549±0.104	1.592±0.018

2.3. SPF Chemical Samples Account:

The Mansur mathematical equation (1) is used to evaluate the SPF values of the ten samples (cinnamic acid, salicylic acid, sodium salicylate, benzoic acid, sodium benzoate, Ammonium benzoate, benzaldehyde, 4-Methoxybenzaldehyde, benzophenone, *trans*-cinnamaldehyde) [15-17].

$$\mathbf{SPF= CF \times \sum_{290nm}^{320nm} EE\ (\lambda) \times I\ (\lambda) \times ABS(\lambda)} \quad (1)$$

Where: CF is the correction factor (=10); "EE", the erythemal effect of radiation at wavelength λ; "I", the intensity of the solar spectrum; and "ABS", the absorbance at wavelengths 290-320 nm. "EE", "I", and "ABS" are values obtained or applied for every wavelength (λ). The values for each of the [EE(λ) x I(λ)] are constants have been reported by the authors as normalized on the basis of the work by Sayre et. al., and are shown in Table 6 [18].

Table 6: The values of EE x I as they were determined by Sayre et al (1979).

Wavelength λ (nm)	Value of EE x I
290	0.0150
295	0.0817
300	0.02874
305	0.3278
310	0.1864
315	0.837
320	0.0180

EE – erythemal effect spectrum; I – solar intensity spectrum.

By applying Mansour's equation to calculate the SPF of the tested samples, we get the following (Table 7):

Table 7: shows the SPF values for the tested samples.

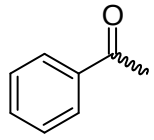
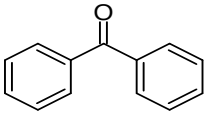
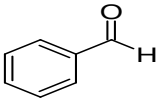
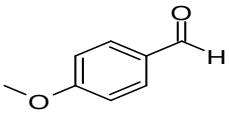
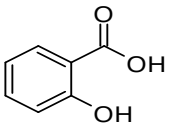
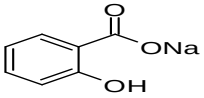
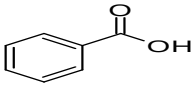
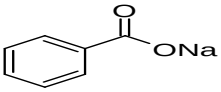
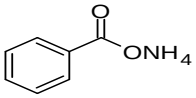
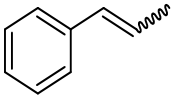
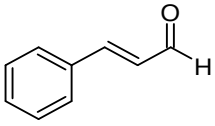
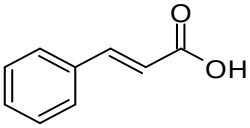
Sample Name	Calculated SPF
Cinnamic acid	39.3
Benzoic Acid	1.7
Sodium benzoate	2.1
Ammonium Benzoate	1.1
Salicylic acid	23.8
Sodium salicylate	39.2
Benzophenone	44.6
benzaldehyde	26.3
4-Methoxybenzaldehyde	54.5
***trans*-cinnamaldehyde**	41.4

3. Results and Discussion:

3.1. Research Approach

The proposed research focuses on assessing the light absorption properties of an organic filter by analyzing the chemical structures of derivatives from two specific groups recognized for their capacity to absorb light in the ultraviolet (UV) region. These groups include the benzoyl group (C_6H_5-C=O) and the benzylidene group (C_6H_5-CH=CH-), as depicted in Table 8. This investigation aims to enhance our understanding of the effectiveness of these compounds in UV light absorption.

Table 8: Chemical compositions of used organic filters in this study.

Chromophore type	Using compounds			
 Benzoyl derivatives	 Benzophenone **9**	 Benzaldehyde **10**	 4-Methoxybenzaldehyde **11**	 Salicylic acid **12**
	SPF= 44.6	**SPF= 26.3**	**SPF= 54.5**	**SPF= 23.8**
	 Sodium salicylate **13**	 Benzoic acid **14**	 Sodium benzoate **15**	 Ammonium Benzoate **16**
	SPF= 39.2	**SPF= 1.7**	**SPF= 2.1**	**SPF= 1.1**
 Benzylidene derivatives	 *trans*-cinnamaldehyde **17**		 Cinnamic acid **18**	
	SPF= 41.4		**SPF= 39.3**	

3.2. Solubility Test of Samples of Organic Filters in Polar Solvents:

Water (H_2O) was excluded from consideration as a solvent, despite its classification as the safest option, due to the limited solubility of most organic compounds in this medium. It is noteworthy to mention that certain organic salts, such as salicylates and benzoates, exhibit solubility in water. Consequently, methanol (MeOH) was employed as an alternative, as it enables optimal solubility for all filters utilized in the process.

3.3. SPF Values for Organic Filters

Sun Protection Factor (SPF) values are numerical indicators that measure how effectively a product protects the skin from the harmful effects of ultraviolet (UV) rays emitted by the sun. These values are especially important for understanding the protective capabilities of sunscreen formulations. In the case of organic filters, which are commonly used in many modern sunblock products, SPF values are specifically measured to provide clarity on their effectiveness. The results of these measurements are then compiled and presented in graphical form, as illustrated in Figure 2, allowing consumers and researchers to easily assess and compare the protective qualities of various used organic UV filters options.

3.4. UV Absorption Mechanism & Enhanced Electron Delocalization

Salicylic acid absorbs ultraviolet (UV) light through electronic transitions, where photons excite electrons from bonding (π) or non-bonding (n) orbitals to higher-energy antibonding (π*) orbitals. The **ortho-positioned hydroxyl (-OH) group** enhances electron delocalization across the benzene ring, increasing UV-B (290–320 nm) absorption—the range most linked to sunburn. This structural feature allows for more efficient photon capture compared to simpler aromatic acids like benzoic acid, which lacks this intramolecular electron-stabilizing effect.

3.5. Improved Stability Properties

When converted into salts (e.g., sodium salicylate), salicylic acid gains **higher water solubility and stability**, enabling it to form a uniform protective film on the skin. This contrasts with cinnamic acid salts, which are less effective at adhering evenly. The improved film formation ensures consistent UV blocking, while the molecule's extended conjugation absorbs a broader range of wavelengths. Additionally, its stability under sunlight reduces degradation, prolonging sunscreen efficacy.

3.6. Antioxidant Synergy & Multifunctional Protection

Beyond UV absorption, salicylic acid acts as an **antioxidant**, neutralizing free radicals generated by UV exposure. This dual role—blocking UV rays while mitigating oxidative stress—makes it more effective than benzoic acid derivatives, which lack significant radical-scavenging ability. Combined with its structural advantages, this synergy enhances photoprotection, reducing both immediate sun damage and long-term skin aging. These properties explain why salicylates are widely used in sunscreens alongside other organic and inorganic filters.

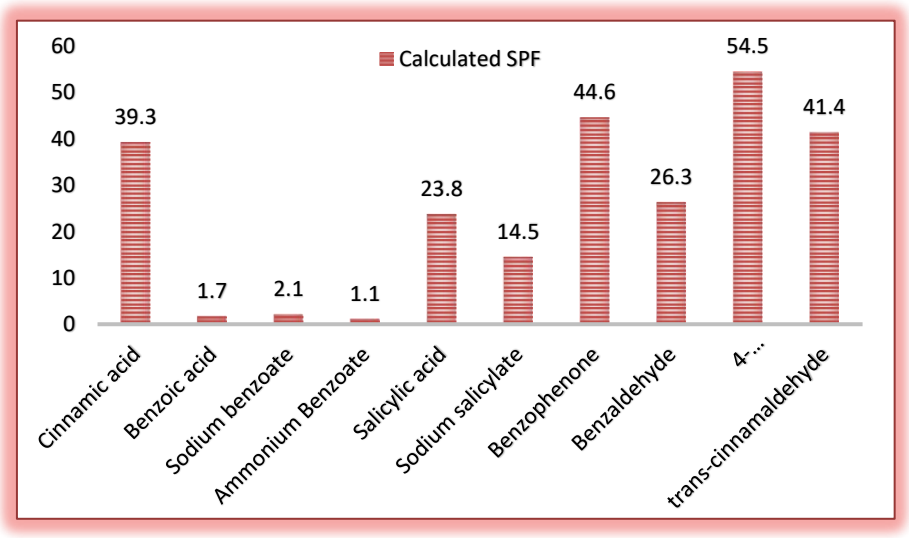


Figure 2: *Comparison of calculated SPF values for used organic filters in this study.*

3.7. SPF Values for Organic Filters Interpretation

Organic filters of benzoic acid and its salts showed very poor SPF values, while organic filters of salicylic acid and its salts showed much higher SPF values than benzoic acid salts with a value of 23.8. The reason may be attributed to the difference in the structure of salicylic acid from benzoic acid; the presence of the electron-donating hydroxyl group in the ortho position increased the exchange capacity of π bonds and gave the compound a more active character than benzoic acid, which lacks the presence of an electron-donating group on the aromatic ring (Figure 3). Also, we find 3,4-aminobenzoic acid widely used as a well-known organic filter in sunscreens as mentioned previously in Table 1, because it contains an electron-donating amine group, which is what benzoic acid lacks; the rest of the results for theses acids salts are shown in Tables 7.

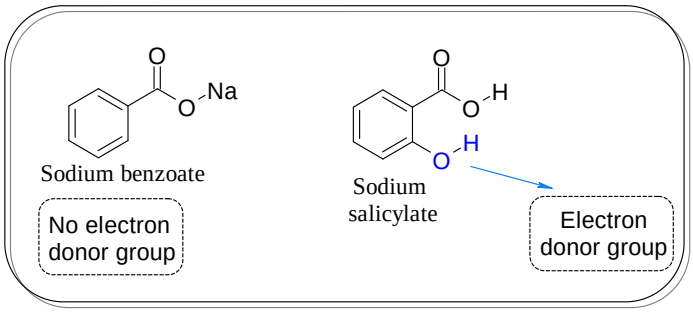


Figure 3: Comparison of the structures of salicylic salt and benzoic salt.

The large difference in SPF values between benzaldehyde and 4-methoxybenzaldehyde may be also due to the presence of an electron-donating group (-OMe) on the aromatic ring of the para moiety (Figure 4).

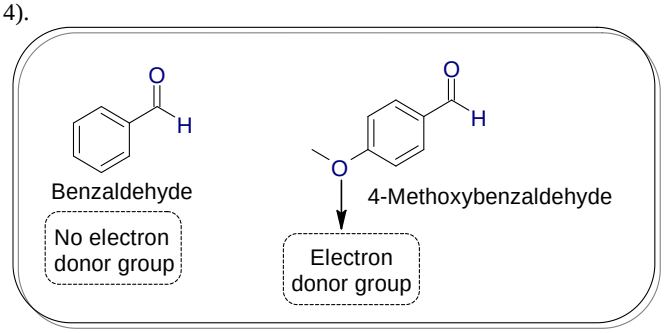


Figure 4: Comparison of the structures between benzaldehyde and 4-methoxybenzaldehyde.

The SPF values of compounds containing the benzylidene group (C_6H_5-CH=CH-) showed very high absorbance values, which is attributed to the presence of the alkene group exchanged with the aromatic ring (Figure 5).

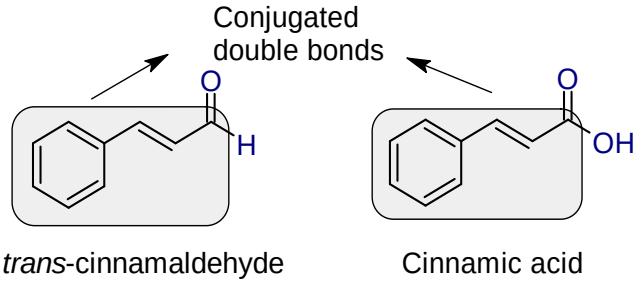


Figure 5: Structures of compounds containing the benzylidene group

The SPF values of benzophenone (Ph_2CO) are high, due to its high number of double bonds. It is no wonder that it is used as a photo-initiator in UV curing applications such as inks, photography, and transparent coatings in the printing industry. Benzophenone also prevents UV rays from damaging odors and colors in products such as perfumes and soaps [19-21].

The carbonyl group, commonly found in carboxylic acids, their salts, and aldehydes, serves as a prominent electron-withdrawing group. This characteristic significantly influences the reactivity and properties of these compounds. Notably, the electron-withdrawing capability of the carbonyl group is often stronger than that of many other functional groups, enhancing its importance in various chemical reactions and applications.

3.8. Comparison of the Obtained SPF Values with Previous Studies

In our previous research endeavors, we concentrated primarily on natural extracts, encompassing various plant sources and oils [22-25]. Importantly, these studies did not examine organic filters, which are the central focus of our current investigation. The sun protection factor (SPF) values reported in those earlier studies for natural sources were generally limited, with most not exceeding 10, indicating a restricted effectiveness in terms of sun protection. This observation underscores a notable distinction: many organic filters demonstrate the ability to provide higher SPF values in comparison to those extracted from plant samples. This is particularly relevant when considering the efficacy of different sun protection ingredients. For instance, salicylic acid, derived from the bark of the willow tree, plays a significant role in various skincare formulations, but its contributions to SPF appear to be less pronounced than those of organic filters. Similarly, while aspirin is synthesized from salicylic acid, it does not match the protective capabilities found in organic filters.

3.9. Absorbance vs. Wavelength

The absorbance vs. wavelength plots provide insight into how various aromatic compounds absorb ultraviolet (UV) light in the 290–320 nm range. These trends help reveal the influence of structural features, such as conjugation, substituents, and ionization state, on UV absorption behavior.

i. Cinnamic Acid

The cinnamic acid plot (Figure 6) shows a sharp rise in absorbance with increasing wavelength, peaking around 310–320 nm. This profile indicates strong π→π* electronic transitions due to the conjugated system involving a phenyl ring and an α,β-unsaturated carboxylic group. The elevated absorbance in the longer-wavelength region reflects extensive delocalization of electrons across the conjugated system.

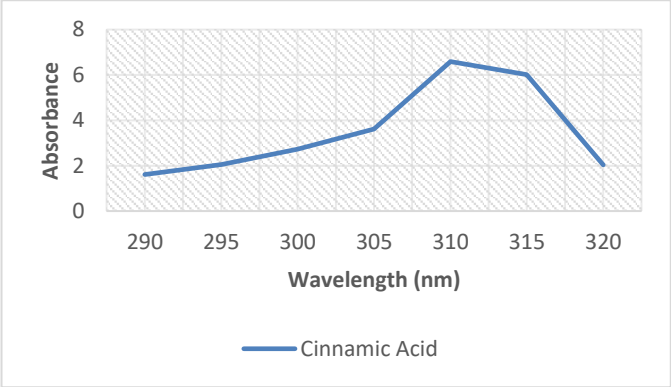


Figure 6: Absorbance of cinnamic acid.

ii. Benzoic Acid and its Salts

Benzoic acid, sodium benzoate, and ammonium benzoate all exhibit decreasing absorbance with increasing wavelength (Figure 7). Benzoic acid consistently shows the highest absorbance across the spectrum, while its salts display lower values, with ammonium benzoate having the weakest response. This suggests that ionization of the carboxylic acid group reduces the conjugation efficiency or alters the electronic environment, leading to diminished absorption. The trend emphasizes how molecular ionization affects UV activity.

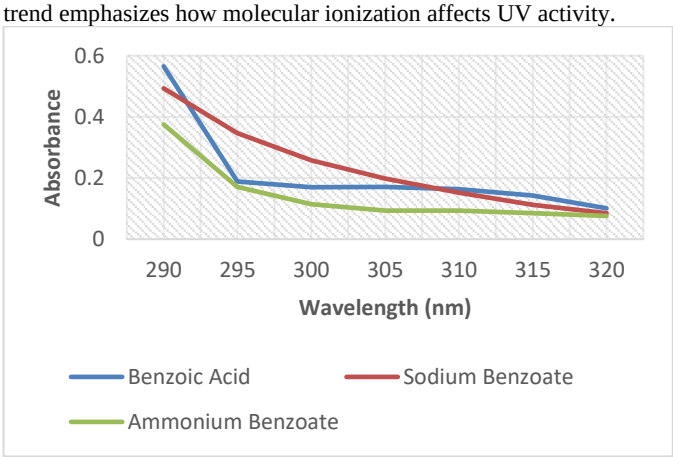


Figure 7: Absorbances of benzoic acid and its salts.

iii. Aldehydes and Ketones

This group exhibits the most variation and generally stronger absorbance: 4-Methoxybenzaldehyde shows the highest and broadest absorbance, especially around 295–320 nm. The methoxy group acts as an electron-donating substituent, enhancing conjugation and transition intensity. Cinnamaldehyde and benzophenone also exhibit significant absorbance at higher wavelengths, with benzophenone peaking around 305 and 320 nm. Both molecules benefit from extended conjugation and aromatic character. Benzaldehyde, which lacks strong substituents, displays a more moderate, narrow absorbance profile. This plot (Figure 8) underline the role of substituents and extended π-systems in increasing both absorbance intensity and wavelength range. underline the role of substituents and extended π-systems in increasing both absorbance intensity and wavelength range.

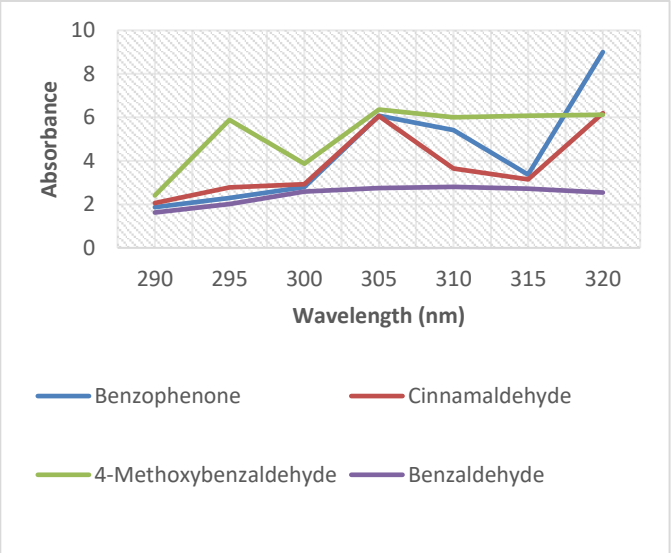


Figure 8: Absorbances of aldehydes and ketones.

iv. Salicylic Acid and Sodium Salicylate

Salicylic acid shows higher absorbance (Figure 9) than sodium salicylate across all wavelengths, with a peak near 320 nm. The difference can be attributed to the –OH group in salicylic acid forming intramolecular hydrogen bonds, stabilizing the molecule and favoring π→π* transitions. In the sodium salt, deprotonation likely disrupts this interaction, slightly reducing absorbance. Both compounds show increasing absorbance with wavelength, highlighting their capacity for UV absorption near the edge of the measured range.

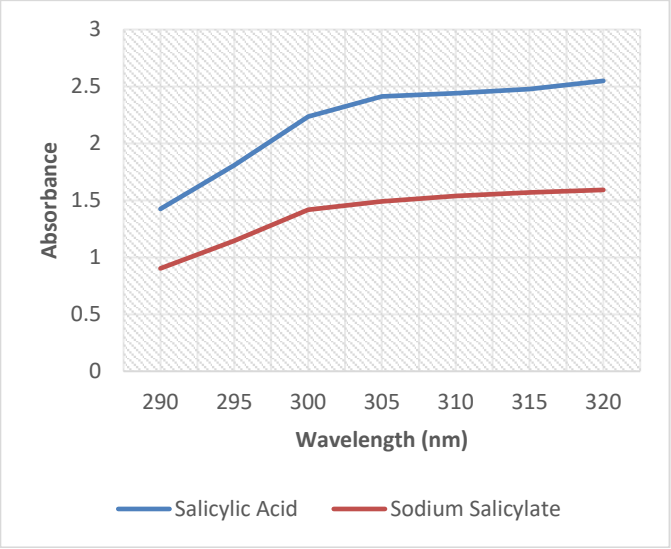


Figure 9: Absorbances of salicylic acid and sodium salicylate.

4. Conclusions

The evaluation of SPF values for organic filters is a critical method for determining the efficacy of sunscreens. It is widely recognised that an increase in SPF value corresponds to an enhanced level of protection against ultraviolet radiation. This study examined the SPF values of ten aromatic compounds, including ketones, aldehydes, carboxylic acids, and their respective salts. The results identified organic filters with high UV absorption capacity and elevated SPF values—such as cinnamic acid and trans-cinnamaldehyde—which may be suitable for incorporation into skincare products for sun protection.

5. Recommendations

Organic filters with strong light absorption characteristics are recommended for use in sunscreen formulations due to their significant UV-filtering capacity and effectiveness in preventing skin penetration by harmful rays. It is advisable to pursue further research into the development of safe organic filters that also exhibit high solubility in polar solvents—such as water—in order to enhance both their performance and formulation flexibility in sunscreen products.

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