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UV Study of the Sun Protection Factor of Some Peels and Seeds in Ethanolic and Methanolic Solvents

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Abstract
Sunscreen formulation forms a protective layer on the skin to protect it from the harmful impact of UV radiation. The effectiveness of sunscreen is determined by the sun protection factor (SPF). The higher the SPF, the more active the product is in avoiding sunburn. Thus, it is compulsory to determine the SPF value of the products used to stop sunburn. The present study aimed to determine the ultraviolet (UV) absorption properties of alcoholic herbal extracts of peels and seeds of vegetable and fruit sources by determining the SPF number as an alternative to synthetic sunscreen using the spectrophotometric method. Alcoholic extract was prepared by dissolving the ground form of green produce (Watermelon, Orange, and Lemon seeds and peels of Banana, Lemon, and Orange), and the absorbance was recorded between 290-320 nm. A spectroscopic study revealed that all of the tested samples of vegetables and fruits in both ethanolic and methanolic extracts showed UV protection capabilities related to their high absorbance, which was satisfactory in finding their SPF values. The analysis of SPF values showed that variations were observed in both ethanolic and methanolic extracts, followed by exhibiting the highest absorbance value in normal, UV, and dark exposure. Moreover, the results after 7 days of exposure to solar radiation (UV) radiation in the ethanolic extract of green produce showed an increase in the SPF, indicating that extracts were not photosensitive in the range between 290 and 320 nm while a decrease in SPF to methanol, revealing that all samples were photosensitive in the range between 290 and 320 nm. The values of the SPF showed that peels and seeds may also be considered for the formulation of the green sunscreen cream.

Keywords: sunscreen, peels, seeds, ethanol, methanol, SPF

1.0. INTRODUCTION

Exposure to ultraviolet radiation results in acute and chronic sunburn, leading to various skin changes. Sunscreen products include chemical and physical filters that are used in multiple forms to save skin from the harmful UV radiation coming from the Sun. These synthetic formulations have adverse effects in chronic conditions. Thus, the involvement of herbal extracts could be of great choice owing to their specific radiation-absorbing capacity. It created the need for new ingredients that not only contain a high Sun Protection Factor (SPF) but also protect from the side effects of synthetic sunscreens. For these reasons, new ultraviolet ray blockers are determined from naturally available sources. Each year in the US, more than 1 million people are identified with skin cancer, making it the most common form of cancer in the country [1-5].

It is estimated that 90% of non-melanoma skin cancers and 65% of melanoma skin cancers are connected with exposure to ultraviolet (UV) radiation from the Sun [1]. Radiations from solar systems are comprised of three types: i) UV-C or ultraviolet C(200-280nm), UV-B or ultraviolet B(280-320nm), which is not entirely filtered by the ozone layer and is one of the reasons for sunburn, and UV-A or ultraviolet A(320-400nm) relatively longer wavelength, reaches to deeper layer of the epidermis, dermis and contributes to skin aging and wrinkling. In addition, it has various adverse effects, including immune suppression, eye injury and cancer of the skin. It is also responsible for generating free radicals, provoking early aging of the human skin, and irritating the pre-maturation of the skin [7]. Therefore, diverse sunscreens are employed to protect the dermis and epidermis from UV-A radiation. In contrast, UV-C radiation is the most damaging radiation of the ultraviolet region due to its shortest wavelength. It has the most extraordinary energy but filters out from the atmosphere by stratospheric (ozone) layer and doesn't reach the Earth's surface [5].

Wearing sunscreens can prevent these harms because sunscreen agents protect against the range of UV-B radiation [6]. People are conscious of the possible dangers of photo-aging, sunburn and skin cancer due to sun overexposure. Two factors are accountable for the defence of the skin: a) thickness of layer corneum and b) pigmentation of the skin. Sunscreen is an expanded foam, whipped or gel lotion, cream, or spray that absorbs (chemical sunscreen) or reflects (physical sunblock) some of the UV radiations and helps to protect against suntan or sunburn [8]. Sunscreen agents can be classified into organic, inorganic and hybrid, as shown in Fig.(1). The commercially available formulations combine these agents to cover a broad spectrum of UV radiation. These sunscreen agents' actions can vary from blocking, reflecting, and scattering sunlight.

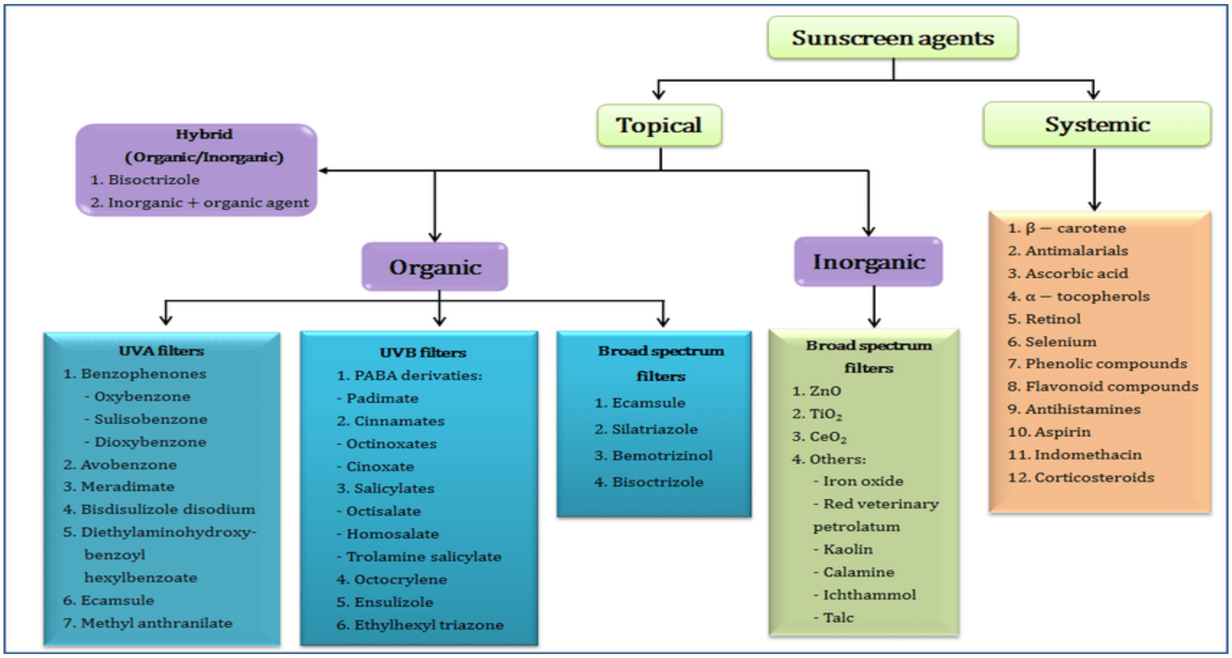

Figure 1: Classification of Sunscreen Agents

The sun protection factor (SPF) represents the efficacy of sunscreen or sunblock (2 to as high as 100). This number refers to the product's ability to screen or block out the sunburning rays. If SPF is 15, it indicates that the UV radiation influences the skin through the recommended thickness of sunscreen. If the product refers to SPF 15, it means that 1/15th of the burning radiation grips the skin through the recommended thickness of sunscreen. The higher the SPF, the more influential the product will prevent sunburn [9]. In general, there are two methods to determine the efficiency of UV blockers: a) In Vivo, it is expensive, time-consuming, and complex, and it requires ethical consideration, while b) in Vitro is rapid and cost-effective compared to in vivo [10-19].

This study aimed to determine and compare the SPF values of some natural ingredients like Watermelon Seeds, Banana, Orange Seeds, Lemon, Ginger, Lemon Seeds and Orange Peels in alcoholic (ethanolic and methanolic) extracts. In addition, the effects of solvent and sunlight on the available natural sources in ultraviolet and dark conditions through UV/Vis Spectroscopy were also reported to validate the SPF values for the formulation of green sunscreen.

2.0. MATERIALS AND METHODS

2.1. Collections of Seeds, Peels, Chemicals, and Instrumentation

The seeds of Watermelon, Orange, and Lemon were purchased from the local markets of Karachi, Pakistan, while peels of Banana, Lemon, and Orange were collected domestically after their prime use. The Westpoint Electronics France of the model WF-9292 grinder was used for grinding peels to increase the surface area of the material to observe rapid reaction.

Ethanol (C_2H_5OH) of E-Merck and Methanol (CH_3OH) of BDH AnalaR were used to perform the experiments. The digital balance Mettler Toledo PL202-S had the least count of ± 0.001g. The absorbance was recorded by UV/Visible Spectrophotometer (Beckman Coulter DU730) in the range(200 nm-1100nm) of extracts as natural sunscreen agents in ethanol and methanol.

2.2. Sample Preparation:

The selected ingredients were dried in the shade (protected from UV) and ground separately in a mixer grinder, then passed through a sieve to convert all of them into fine powdered form except the ginger one. The extracts of each material were prepared by transferring 1.0 g of each of the powdered forms into 10.0 mL of methanol and ethanol separately in 15 ml vials for each sample. The ginger was the same weight as the others, and it was cut into tiny pieces and used without drying and grinding. Like the other ingredients, 1.0 g of ginger was introduced to methanol and ethanol separately. After one month, when all the natural ingredients had been extracted, filtration of the extract was conducted through Whatman filter paper having a pore size of 110mm and no. of 41, residues were discarded, and filtrates were taken to measure the absorbance of all the selected natural ingredients.

2.3. Measurement of UV Absorptions

After diluting both filtrates, the absorbance was measured in the 290-320 nm range using a 1 cm quartz cell at an interval of every 5 nm using a UV-Vis Spectrophotometer. The determinations were made at each point using ethanol and methanol as blanks for their respective absorbance readings of the extracts. After taking all the absorbance, the Mansur Equation was applied to calculate the SPF values. All the samples were divided into halves; one was directly irradiated sunlight, and the other was kept in the dark. Their absorbance values were measured again after one week to study the effects of UV radiation,

2.4. Determination of SPF

The SPF is determined by the *In Vitro* method by measuring the absorption characteristics of different peels and seeds alcoholic extracts using the Mansur equation method [12]. For *In Vivo* method, SPF can be determined by the given formula,

$$\text{SPF} = \frac{\text{Minimal erythemal dose in sunscreen−protected skin(MEDp)}}{\text{Minimal erythemal dose in unprotected skin(MEDu)}} \quad \_\_\_\_\_\_\_\_ \ (1)$$

The minimal erythemal dose (MED) is defined as the lowest time interval or dosage of UV light irradiation sufficient to produce minimal, perceptible erythema on unprotected skin [12]

For In Vitro method, SPF can be determined by the Mansur mathematical equation [12] (Equation 2),

$$\text{SPF Spectrophotometric} = \text{CF} \times \sum_{290}^{320} \text{EE}(\lambda) \times \text{I}(\lambda) \times \text{Abs}(\lambda) \ \_\_\_\_\_\_\_\_\_\_\_\_ \ (2)$$

Where, EE = Erythema effect spectrum;

I = Solar intensity spectrum

Abs = absorbance of sunscreen product

CF = Correction factor (= 10).

The values of EE x I are constants. They were determined by Sayre et al. [13] as shown in the Table (1)

Wavelength (λ nm)	EE × I (Normalized)
290	0.015
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0837
320	0.018
Total	1

Table 1: Normalized product function used in the calculation of SPF; adapted [13]

3.0. RESULTS AND DISCUSSION

There is a lack of awareness regarding toxic chemical agents used in sunscreens, leading to increased demand for adequate protection against sunburn without any adverse effect on any sensitive skin of human beings. While several synthetic sunscreens are available, their use in cosmetics is limited due to their potential toxicity in humans and their ability to target only specific pathways of carcinogenesis. In contrast, herbal agents are considered safer and have gained popularity nowadays. They also work in various ways by stimulating the immune response, inducing gene suppression, detoxifying carcinogens, blocking oxidative DNA damage, and initiating selected pathways or other mechanisms [15-23]. Thus, these herbal agents play multiple roles in facilitating the process of clearing carcinogenesis. Therefore, these herbal formulations at optimum concentrations could produce several beneficial effects on the skin apart from functioning as UV filters,

Accordingly, in the present work, some naturally available ingredients, which are also cheap and considered waste most of the time and used for skin protection in ancient times, were analyzed and tested for SPF. It includes

Watermelon, Orange and Lemon Seeds, Banana, Lemon and orange Peels, and Ginger. Their alcoholic extracts were subjected to spectrophotometric analysis, and the absorbance of all samples was recorded in the range of 290-320 nm to determine the SPF values using the Mansur Equation [12]. The determination of SPF values for all seven samples under different conditions (normal, UV, and dark) was done through absorbance measurement via scanning extracts under the UV spectrophotometric method. Spectral analysis showed high absorbance, which resolute high SPFs in ethanolic and methanolic extracts. The Mansur equation[12] was applied to calculate SPF values which indicated that under UV irradiation, ethanolic extract displayed high SPF values (Table 2), whereas the SPF of ethanolic extracts for normal solar radiation was in the range of 22.261 (Ginger) to 25.846 (Lemon Peels), while under UV radiations, SPF values for Orange Seeds (26.443) to Banana Peels (28.175) and for non-radiative condition ginger (26.229) to orange peels are (27.943). The calculated SPF values of methanolic extracts for normal conditions are in the range of 27.534 (Lemon Seeds) to 28.428 (Orange Seeds), for UV radiations, 14.517 (Ginger) to 28.402 (Banana Peels) and for non-radiative-condition-25.232 (Watermelon Seeds) to 27.791 (Banana Peels). The SPF values for orange seeds are lower in normal conditions in the ethanolic and higher in methanolic extracts (Table 2). The ginger had the lowest calculated SPF (from UV condition) in both alcoholic extracts.

In general, it can be observed that the in vitro study of the SPF values in the methanol and ethanolic extracts showed variations under UV radiation and non-radiative conditions. These values indicate that the organic materials selected for the study are suitable and have the benefit of less degradation under normal, UV and dark conditions (Table 2).

Samples	**SPF values under Different Conditions in Ethanol**			**SPF values under Different Conditions in Methanol**		
	Normal	**UV**	**Dark**	**Normal**	**UV**	**Dark**
Watermelon Seeds	24.855	26.872	26.765	28.289	25.173	25.321
Orange Seeds	24.036	26.443	27.317	28.428	28.385	26.859
Lemon Seeds	24.729	26.661	27.592	27.534	27.672	26.076
Banana Peels	25.483	28.175	27.149	28.405	28.402	27.791
Lemon Peels	25.846	27.847	27.295	28.024	27.803	27.136
Orange Peels	25.178	28.011	27.943	27.556	27.742	27.076
Ginger	22.261	25.289	26.229	28.324	14.517	26.251

Table 2: Comparison between SPFs of the alcoholic extracts

Among the samples analyzed, a Lemon peel extract in ethanol exhibits the highest SPF (25.846) before any exposure to sunlight. In contrast, Ginger extract in the same solvent exhibits the lowest SPF value (25.289) compared to other samples, which is 22.261 before exposure. The SPF value of the ginger showed that it can effectively protect the skin from solar radiation. Interesting results are observed in the orange seed extract, where high SPF in UV radiation (26.443) in ethanol and methanol was higher (28.402), which showed the effectiveness of the orange seeds that may be used in the formulation of suncream. The sample of lemon seed extract in methanol exhibits the lowest SPF value among its other co-solvent samples, which is 27.534 before exposure.

The other remaining ingredients also gave significant values of sun protection factors before exposure to ultraviolet radiation or in dark conditions. Among all the samples extracted and tested, it was found that solvent also affected extraction. The difference in the SPF under different conditions, such as before exposure to sunlight and with one week of exposure to ultraviolet radiation and dark, showed that there was also the effect of both temperature and solvent. That's why, in the present work, both the difference between solvent and degradation was studied. The SPF value for watermelon obtained in the current search was higher (Table 2) when compared to the value in the aqueous extract as reported by (SPF= 0.97±0.41) [24] which showed that method adopted in the present search was adequate while it was slightly lower (Table 2) in comparison of the report of the Perkins & Davis [22] (32 SPF) for both UVA and UVB for the watermelon sunscreen.

The SPF of banana peels in both alcoholic extracts showed (Table 2) a notable value comparable to that reported by Lopes et al. [23]. The Mansur equation [12] determined a sun protection factor (SPF) of up to 36.4 in aqueous extract [23]. Putri et al. [24] determined SPF factor of banana peel in different percentages of alcohol (96,70 and 50%). They reported SPF values are 7.613870, 7.656650 and 8.9874, respectively, which were less than in the comparison of the current investigation. The current investigation is similar to those of Panchal et al. [25], who reported the highest value of SPF of orange juice at different concertations reported the SPF values to varying concentrations for Orange 13.32 (10ppm) 27.54(20ppm) and for Lemon 7.61(10ppm) 16.06 (20ppm).

Based on the SPF values obtained, a comparison between the SPFs of natural ingredients in alcoholic solvents showed that the lemon peels exhibited the highest SPF (25.846) among the ethanol extracts under normal conditions. However, after seven days of UV exposure, banana peels exceeded lemon peels with the highest SPF of 28.175. In dark conditions, orange peels recorded the highest SPF of 27.943 in the ethanol solvent. These findings suggest that such natural materials can effectively block UV rays and maintain their efficacy over time in ethanol, making them potentially long-lasting UV protectants.

In the methanol extracts, orange seeds initially showed the highest SPF of 28.428 under normal conditions, but after seven days of UV exposure, banana peels took the lead with an SPF of 28.402. In dark conditions, banana peels again showed the highest SPF of 27.791. However, unlike ethanol, methanol extracts demonstrated decreased SPF values under UV and dark conditions, suggesting that methanol-based products may not be as durable. Both ethanol and methanol solvents influence the SPF performance of natural ingredients differently. These organic solvents can easily blend with sunscreen agents and may have potential applications in commercial sun protection products. Additionally, using these extracts in spray form offers a sustainable alternative, contributing to advancements in green chemistry.

Such results prove the superiority of natural ingredients over chemical sunscreens. It is recommended that the use of natural ingredients or wastes has the advantage not only in the form of money as they are cheap as well as harmless but also in the form of long-lasting periods for running. In light of such results, naturally formulated sunscreens can last longer than chemically formulated ones.

4. CONCLUSION

It was concluded that the high SPF value of alcoholic extract indicates less degradation and is suitable for sunscreen formulation due to the maximum absorption. These products absorb UV radiation (290 to 320 nm) and may play a role in preventing sunburn, leading to skin cancer, wrinkle formation, photo aging, and other skin damage. However, more research is recommended on using peel and seed waste in green formulations to control the sunburn effect on the skin.

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