



# Properties of *Aspalathus linearis* extracts as sunscreen agents in combination with standard UV filters

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## Abstract

The new horizons in sunscreen development are based on the discovery of novel active ingredients, and those from natural sources are the most promising. The objective of the work was to analyze the potential of different *Aspalathus linearis* (AL) extracts as natural photoprotective ingredients to be used in combination with standard UV filters in topical formulas. The impact of AL extracts on different biological protection factors, as well as on the photostability of standard organic UV filters, was measured. Under this aim, and employing in vitro techniques, UV transmittance properties, solar protection factor, UVA protection factor, and immune protection factor were analyzed for the extracts formulated alone or in combination with the UVB and UVA standard filters Octyl-methoxy-cinnamate (OMC) and Butyl-Methoxy-dibenzoylmethane (BMDDBM). Water containing AL extracts showed a significant UV absorbance in the entire UV spectrum with an absorption peak around 285 nm. The addition of AL extracts to sunscreen galenic formulas, including OMC and BMDDBM, increased the protection factors up to 50%. AL extracts were also able to protect BMDDBM and OMC against photodegradation under increasing radiation doses up to 14.4 standard erythemal doses. In conclusion, the addition of AL extracts in topical photoprotective formulas provides the double benefit of increasing the protection values against different biological effects, as well as improving photostability. Thus, these natural extracts appear as valuable candidates for the development of safer and more efficient sunscreens.

**Keywords** Sunscreens · Natural extracts · Booster · Solar protection factor · Biological protection factors · Photostability

## 1 Introduction

Exposure to high levels of UV increases the risk of developing the three main forms of skin cancer [1], namely basal cell carcinoma, squamous cell carcinoma, and melanoma. In fact, squamous cell carcinomas and basal cell carcinomas

develop almost exclusively on sun-exposed areas of the skin, and the estimates suggest that approximately 65–90% of melanomas are also caused by exposure to UV radiation. Limiting and protecting against solar and artificial UV overexposure is the main preventive strategy for controlling the appearance of these kinds of tumors [2, 3]. In this context, the use of topical sunscreens is considered the most valuable preventive measure, especially for parts of the body that are directly sun-exposed. Clinical trials have found that sunscreens effectively reduce the incidence of actinic keratosis, squamous cell carcinoma precursors, and the number of moles (the most important precursors and risk factor for melanoma) [4–6]. Consequently, sunscreen application is one of the most common practices to prevent skin cancer [4].

To protect humans from sun damage, scientists have developed sunscreen formulations containing different filters [7, 8]. Filters are compounds able to absorb and/or

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reflect specific wavelengths, such as UVA (320–400 nm), UVB (280–320 nm), and visible radiation, thereby preventing the radiation from reaching and penetrating the skin surface and causing damage. As the UV part of the spectrum is considered to produce the most deleterious effect in the skin, currently all sun protection offered by commercial products is based in either protecting against the generation of skin erythema (mainly due to the UVB band) or the biological effects dependent on the UVA part of the electromagnetic solar spectrum, such as the generation of permanent pigmentation [9, 10]. Each photoprotector released on the market must meet the efficacy and safety requirements established by regulatory agencies [10], and the efficacy and safety of most artificial sunscreen components are hindered by their photostability, toxicity, and damage to marine ecosystems [7, 11, 12]. Thus, maintaining high efficacy with increasing photostability, along with insignificant toxicity, is an uncovered need of the field and one of the goals of these formulations.

In this scenario, the use of natural compounds is attracting considerable attention. Natural selection and evolution have ensured that plants and animals developed effective protective mechanisms against the harmful effects of UV radiation and the related oxidative stress [13, 14]. Thus, some substances found in living organisms, as plant polyphenols, can exert photoprotective activities through antioxidant properties, controlling skin inflammation, alleviating skin barrier deterioration, and preventing UV-induced aging [13–15]. Hence, the incorporation of natural substances and ethnobotanical antioxidants into sunscreen formulas is on the rise.

*Aspalathus linearis* (Brum.f) Dahlg. (Fabaceae) (AL), is a fynbos shrub native to the Cape Floristic Region of South Africa [16]. While it is widely consumed globally as an herbal tea, it is increasingly being incorporated into skincare products. Two typical types of AL can be found, known as green and red. The green (unfermented form of AL, ALU hereinafter) has a chemical profile rich in chalcones, including the unique chalcone, aspalathin. The red type (fermented form of AL, ALF hereinafter) results from the oxidative/enzymatic fermentation of green AL form under certain conditions, which alters the plant's chemical profile and reduces the content of dihydrochalcone derivatives, especially aspalathin [17]. Therefore, ALU is preferred for isolating aspalathin and other polyphenolic compounds of interest, which are active ingredients in cosmeceutical products. Extracts from ALU exhibit potent antioxidant, anti-inflammatory, and antitumor properties, with evidence supporting their photoprotective effects on the skin [18–20]. Indeed, different studies demonstrated the protective effects of compounds such as linearthin, aspalathin, and nothofagin from *Aspalathus linearis* against UVB-induced oxidative

stress and toxicity in human skin cells [21, 22]. In a recent study by our group, we explored the photoprotective properties of both ALF and ALU, assessed individually and combined. ALF showed higher photoprotective capabilities than ALU in terms of increasing human dermal fibroblast survival, with synergistic properties observed when both extracts were combined [23]. Therefore, AL extracts appear as attractive candidates for exploring their inclusion in topical and systemic photoprotective strategies. However, even when their role in photoprotection has been studied using cellular models, no references have been reported on their photoprotection capabilities in terms of radiation absorption properties. At this respect, plant-based compounds that possess antioxidant, anticarcinogenic, and anti-inflammatory features, such as flavonoids or other polyphenols (as the ones present in AL extracts), can usually absorb UVA and UVB rays, which contribute to their photoprotective effect [24, 25]. Apart from flavonoids, other natural products such as certain vegetable oils, carotenoids, stilbenes, and ferulic acid are also able to absorb UV radiation [7]. These UV-absorbing properties support their use as UV blockers. Accounting for AL composition and reported properties, it is then interesting to address the unexplored AL filtering activities. Considering that they could additionally provide other cellular and antioxidant photoprotective benefits, the cosmeceutical potential of the photoprotective ingredient derived would be enviable.

Another photoprotective role of active compounds derived from plant extracts is related to the stabilization of the filtering components of the sunscreen. It is well known that UV filters can gradually degrade under high doses of UV radiation. Two of the most used filters in the design of commercial sunscreen are the octyl-methoxycinnamate (OMC, UVB absorbing filter) and butyl methoxy dibenzoyl methane (BMDBM, UVA absorbing filter). They are easily solubilized, inexpensive, and have high molar extinction coefficients; conversely, they also show significant photoinstability [26–28]. To overcome this weakness, other UV filters such as octocrylene have been included in the formulas as photostabilizers; unfortunately, they have been found to cause photosensitivity pathologies in many patients [29]. So, the search for safer and more effective filters is still ongoing, and testing natural substances can be of central interest due to their plausible potential as photostabilizers, radiation absorption properties, and antioxidant capabilities.

Therefore, the present study aims to explore the UV absorption properties of *Aspalathus linearis* extracts (fermented and unfermented), their synergistic effects when combined with organic sunscreens such as OMC and BMDBM, and their potential to enhance the photostability of these standard filters under high doses of solar simulated UV radiation.

## 2 Materials and methods

### 2.1 Natural extracts

Unfermented and Fermented dried leaves in the form of lyophilized powder from *Aspalathus linearis* were supplied by Rooibos Ltd (Western Cape, South Africa). The material was stored at room temperature and shielded from light following the supplier's instructions. From this unfermented and fermented material, stock solutions were prepared at a concentration of 100 mg/ml in distilled water, under agitation at room temperature ( $23 \pm 2$  °C).

### 2.2 AL absorbance properties in water solution

First, in order to analyze the light absorbing potential of AL extracts (fermented and unfermented) that we received in the laboratory in form of lyophilized powder, they were dissolved in distilled water at a final concentration of 6.25 mg/ml and their absorbance in the UV - visible part of the spectrum (250–750 nm) was measured in quartz UV-transparent cuvettes using the UV-visible spectrophotometer Shimadzu UV-1607 (Shimadzu Co. Kyoto, Japan).

### 2.3 Preparation of galenic formulations

A second step was the analysis of AL extracts included in galenic formulations, similar to the ones used in commercial

**Table 1** The different combinations of extracts and UV filters used for each sunscreen sample. AL fermented (ALF) and unfermented (ALU), as well as their combination (ALU/ALF), were used at 2 different concentrations (1 and 2.5%). The oil phase was maintained at the same concentration of the compounds NeoPCL 20% +PPG 5%. AL extracts were dissolved in aqueous solution, and standard UV filters were included in the oil phase. In all cases, 10 g of total formula cream was prepared

Sample	AL extracts at 1% concentration	AL extracts at 2.5% concentration
ALF	ALF at (1%)	ALF at (2.5%)
ALU	ALU at (1%)	ALU at (2.5%)
ALU/ALF	ALU/ALF combination (1%)	ALU/ALF combination (2.5%)
ALF + Filters	ALF (1%) + OMC (4%) and BMDBM (2.5%)	ALF (2.5%) + OMC (4%) and BMDBM (2.5%)
ALU + Filters	ALU (1%) + OMC (4%) and BMDBM (2.5%)	ALU (2.5%) + OMC (4%) and BMDBM (2.5%)
ALU/ALF + Filters	ALU/ALF combination (1%) + OMC (4%) and BMDBM (2.5%)	ALU/ALF combination (2.5%) + OMC (4%) and BMDBM (2.5%)
Filters	OMC (4%) and BMDBM (2.5%)	OMC (4%) and BMDBM (2.5%)
Blank	Excipient (Neo PCL 20% + PPG 5% + H <sub>2</sub> O)	Excipient (Neo PCL 20% + PPG 5% + H <sub>2</sub> O)

sunscreens. All formulations were performed using a simple preparation base in which both the AL extracts as well as UV standard filters were dissolved. This preparation base was a self-emulsifiable O/W “NeoPCL” base (20% w/w), propylene glycol (5% w/w), and distilled water was used to reach a total weight of 10 g of cream formula. Each mixture was assayed in different variations: extracts independently, extracts in combination, filters, or combinations of both extracts and filters. The different combinations are shown in Table 1. AL extracts were assayed at 1% (0.1 g/10 g of cream) and 2.5% (0.25 g/10 g of cream). The combination of filters used to analyze the booster effect of the extracts was octyl methoxycinnamate for the UVB region (4%; 0.4 g/10 g of cream) and butyl methoxydibenzoylmethane for the UVA region (2.5%; 0.25 g/10 g of cream). The standard UVB and UVA filters were dissolved in the oil phase, and the AL extracts were dissolved in the aqueous phase of each cream preparation.

### 2.4 Determination of protection factors of sunscreen formulations

The in vitro protection factor of each formulation was determined by measuring the spectral transmittance and calculating the absorbance of the formulations across the UV and High Energy Visible Light (HEVL) range (290–420 nm) on PMMA plates (Schönberg, Hamburg, Germany). This protocol was based on ISO 24443:2022 specifications for evaluating the solar protection factor of sunscreens [30], with some variations. Since we observed a significant absorbance of AL extracts in water solutions in the HEVL range, we introduced a variation of the method, extending the evaluation from 400 nm to 420 nm for absorbance/transmittance calculation. The second variation of the ISO was that no in vivo SPF was performed before analysis. Third, the final SPF and UVAPF were calculated not based on exposure to solar simulated radiation at a dose of  $1.2XUVAPF_0$ , but with controlled exposures corresponding to 3.6 up to 14.4 standard erythemal doses.

This protocol specifies spreading  $1.3 \text{ mg/cm}^2$  of the formulation over a  $5 \times 5 \text{ cm}^2$  PMMA plate. These plates simulate the relief of the real skin surface and are specific to this ISO protocol. After 15 min in the darkness where the emulsion was stabilized, the sample was measured in a Shimadzu UV 3101 PC spectrophotometer (Shimadzu, Japan), equipped with three photodetectors covering transmittance and spectral absorbance measurements from 190 to 3200 nm. The spectrophotometer also includes an integrating sphere for diffuse transmittance and reflectance measurements (240–2600 nm), in accordance with ISO 24443:2022. The transmittance spectrum was analyzed at 1 nm intervals within

the 290–450 nm range, using the spectral transmittance of a blank PMMA plate coated with glycerol.

#### 2.4.1 Solar protection factor calculation

Solar protection factor (SPF) or protection potential against skin erythema was calculated using the following formula:

$$SPF = \frac{\int_{290}^{400} (E_{\lambda} \times \epsilon_{\lambda})}{\int_{290}^{400} (E_{\lambda} \times \epsilon_{\lambda} \times T_{\lambda})}$$

Where: SPF=sun protection factor, E=spectral irradiance of solar simulator,  $\epsilon$  = biological action spectrum of erythema (290–400 nm), T=transmittance spectrum of the sample.

#### 2.4.2 UVA protection factor calculation

Following the same procedure as for the calculation of the SPF, the UVA protection factor was also calculated by using the action spectrum of Persistent Pigment Darkening as shown in the ISO 24443:2022, and as specified in the ISO, considering the range between 320 and 400 nm.

#### 2.4.3 Human immune protection factor calculation

Finally, in the case of protection factors related to photo immunosuppression (HIF), the sample transmittance in the UV region was weighted by the action spectra published for the human skin photo immunosuppression [31]. The photo immunosuppression action spectra data between 290 and 400 nm, were calculated from cubic spline interpolation between the data points of the respective action spectrum employed to provide values of 1 nm increments. Spline interpolation was made by the software Table Curve 2D 5.0. The error in the interpolation and summation in 1 nm steps is estimated to be lower than 5%.

For all cases, the final protection factor was calculated from 3 samples per treatment (4 PMMA plates/sample), obtaining a total of 12 replicas. Complying with ISO guidelines, protection factors were calculated by the mean value of the 12 replicas, followed by the standard deviation. Also complying with ISO guidelines, the confidence interval of 95% was less than 17% of the mean value.

### 2.5 Analysis of the photostability of sunscreens

The photostability tests were assayed by irradiation of the plate's samples and subsequent measurements at the spectrophotometer, to observe the reduction of absorbance. After an initial absorbance spectrum analysis (SED 0), PMMA

plates were situated under a solar simulator light beam and exposed to increasing doses of UV corresponding to 3.6, 7.2, 10.8, and 14.4 standard erythemal doses (SEDs). One SED corresponds to 10 mJ/cm<sup>2</sup> of UV erythemal effective dose [32]. Irradiation was carried out employing a solar-simulating setup using an Oriel 1000 W Solar Simulator (Cleveland, USA) with Xenon Arc Lamp with continuous spectrum emission from 290 to 400 nm. The solar simulation spectrum is achieved through the combination of dichroic filters (which eliminate the UVC, part of visible light, and infrared range above 1350 nm), interference filter UG11 (which eliminates total visible radiation), and Schott UG320 for selecting the final solar simulating spectra. Spectral characteristics as well as irradiance emitted were in accordance with ISO 24443:2022. Final dose of 14.4 SEDs corresponds to approximately the number of SEDs that one person would receive after approximately 2 h of exposure at midday on a typical summer day in mean Mediterranean latitudes.

### 2.6 Statistics

Calculated data on the protection factor for various UV-induced skin biological effects (erythema, PPD, and HIF), as well as the critical wavelength, were determined from transmittance measurements taken from three different locations on the PMMA plates. Statistics were based on 4 plates per sample (glycerol, base formulation with extract, base formulation with filters, and complete formula with both extract and filters), with each plate recording 3 measurements from different areas, covering a total surface of 2.8 cm<sup>2</sup> per plate (complying with the ISO requirement of at least 2 cm<sup>2</sup> per plate). The final values represent the mean absorbance across different spectral bands, calculated from the 3 sub-replicates of the 4 plates per sample ( $n=12$ ), accompanied by the standard deviation. Mean values are considered valid if the upper limit of the 95% confidence interval falls within 17% of the mean. The percentages of change for the different combinations of AL with standard filters compared to filters alone were evaluated by One-way ANOVA. The significance level was  $p<0.05$ . In case of the photostability experiment for different combinations of AL with UVB and UVA standard filters, the changes in parameters from absorbance curves (mean UVB absorbance, UVA absorbance, as well as changes in biological protection factors) were expressed in terms of % of decay from the initial value (at SED 0). The best-fitting model for the curves was a second-degree polynomial. To analyze the statistical significance of the fitted curves, a Student's t-test for the comparison of the slopes was used, accounting for the homogeneity of the variances. This homogeneity was calculated using the F test.

### 3 Results

#### 3.1 AL UV absorbance properties

The different AL extracts (ALU, ALF, or their combination ALU/ALF) dissolved in distilled water to a concentration of 6.25 mg/ml, produced a gradual increase of absorbance in the UV spectral region, from 250 to 400 nm, with a peak value around 285 nm (Fig. 1). AL extracts also show a low (compared to UV) but significant absorbance in the range of the High Energy Visible Light (short blue light wavelengths from 400 to 450 nm).

The fermented AL extract (ALF) showed significantly higher absorption properties in the whole spectrum than the unfermented one (ALU). Finally, a previously reported specific combination of both extracts (ALU/ALF) [23] led to a slightly but significantly lower absorbance than the fermented fraction (ALU), yet higher than the unfermented one (ALU). We found that all extracts tested showed very high absorbance in the part of the UV spectrum wavelengths, the part of the solar spectrum that generates both erythema (mainly UVB from 290 to 320 nm) and skin pigmentation (mainly UVA 320–400 nm).

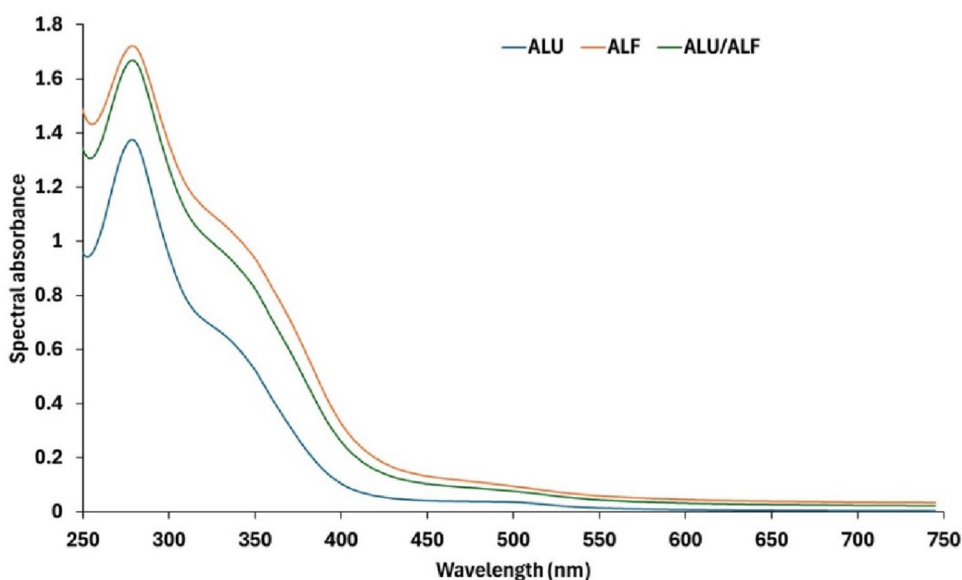
#### 3.2 AL booster effect when combined with standard UVB and UVA filters

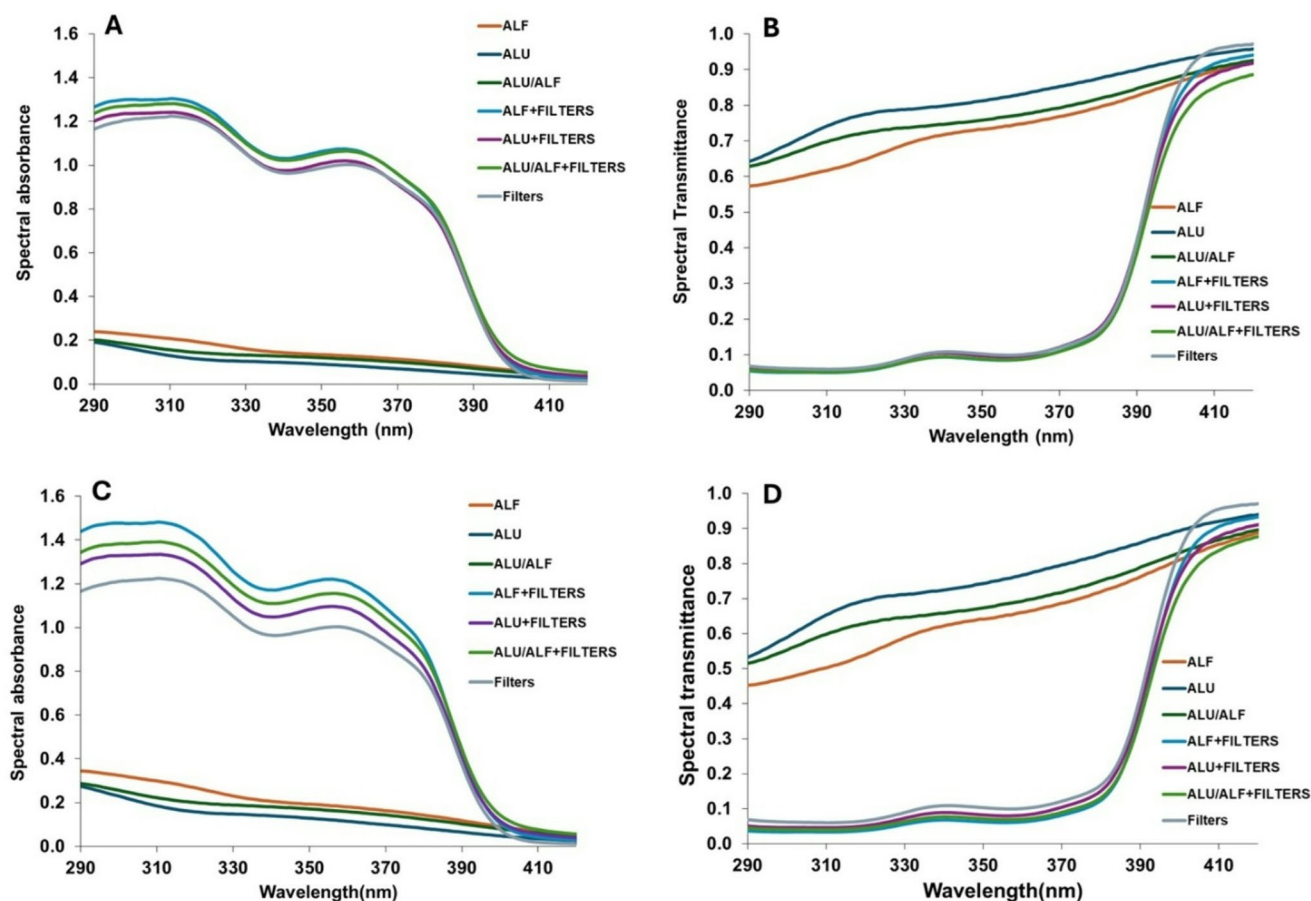
For the case of AL formulated as cosmetic sunscreens, their photoprotection potential was analyzed by calculating the spectral absorbance obtained from the transmittance in the region of 290–420 nm. With the obtained data, SPF, UVAPF, and HIF values were calculated. The spectral characteristics were analyzed at 2 different concentrations of the AL extracts (1% and 2.5% in galenic formula for topical

application). The absorption and transmittance spectra of ALF and ALU at 1% are shown in Fig. 2A–B; and at final concentration of 2.5% in Fig. 2C and D. The sunscreen formulas with ALF and ALU, as well as the combination of both, showed a gradual increase in the absorbance along the UV spectrum with maximum absorbance values of 0.23 for ALF at a concentration of 1% (Fig. 2A), and 0.35 of ALF at 2.5% (Fig. 2C).

The combination of filters OMC at 4% and BMDDBM at 2.5% increased absorbance up to maximum values of absorbance of around 1.2 in the UVB region (due to OMC absorbance) and with a second peak of 1 around 365 nm (due to the absorbance of BMDDBM). This combination of standard UVB and UVA filters leads to SPF of  $15.43 \pm 1.4$ ,  $8.35 \pm 1.05$  UVAPF, and  $10.5 \pm 1.15$  for the human immunological protection factor (HIPF), as shown in Table 2. The addition of 1% of ALU slightly but significantly increased the protection factor of erythema (SPF) to 104%, relative to the value of standard filters alone (100%, Table 2). In contrast, adding 1% of ALF to the filters significantly increased SPF (up to 119%), as well as the other biological factors. When the specific combination of ALU/ALF was added to the filters, the values of protection factors importantly increased compared to standard filters, although not as high as with ALF. Interestingly, a role of AL extracts as a booster in photoprotection was clearly observed when combined with standard filters at concentrations, similar to them (2.5% in formula). In this case, the protection factors markedly increased, reaching 128% for SPF, 118% UVAPF, and 120% HIPF, when the ALU extract was incorporated into the formula. When the addition of ALF extract was tested, the protection factors increased even more significantly, reaching 176% in the case of SPF, 150% corresponding to UVAPF values, and 156% for HIPF. The combination of ALU/ALF increased

**Fig. 1** Absorbance spectrum of the *A. linearis* fermented (ALF), unfermented (ALU), and a specific combination of fermented and unfermented (ALU/ALF) water dissolved extracts in the UV and the visible spectrum range (250–750 nm). All 3 types of extracts were dissolved at a concentration of 100 mg/ml in distilled water and diluted to a final concentration of 6.25 mg/ml in distilled water. Tests were made at room temperature ( $23 \pm 2$  °C)





**Fig. 2** Spectral absorbance and transmittance of ALF, ALU, and ALU/ALF in galenic formulations, at 1% (A-B) or 2.5% (C-D), alone and when combined with the solar filters Octyl Methoxy Cinnamate (4%) and Butyl methoxy dibenzoyl methane (2.5%)

protection factors at intermediate levels, higher than ALU but lower than ALF (Table 2).

Remarkably, AL combinations in galenic formulas alone showed a UVAPF/SPF value over 0.77 and up to 0.9. In case of the addition of standard UV filters to the formula, the UVAPF/SPF ratios decreased, but still yielded values around 0.5. These values are, in any case, much higher than the minimum established in ISO 24443:2022 (0.33). This indicates that the absorbance features of AL extracts, alone or in combination with standard UV filters, confer broad-spectrum benefits to the photoprotective properties of the formulas.

### 3.3 Photostability assay

Since the composition of AL extracts is rich in substances with antioxidant potential, we considered that AL extracts could play a dual role in photoprotection. On one hand, as a booster of standard filters, and on the other hand, photo-stabilizing filters that are known to be unstable. To address that hypothesis, PMMA plates with the different AL extracts at 2.5% combined with or without the same standard of OMC

and BMDDBM filters in galenic formulations, were exposed to increasing solar simulated UV doses corresponding to 0, 3.6, 7.2, 10.8, and 14.4 SEDs. In Fig. 3, the changes in the absorbance curves for the different samples after exposure to increasing doses of UV radiation are shown. Based on Fig. 3 absorbance curves, the different biological photoprotection factors were calculated, and their changes represented in Fig. 4. In the case of the AL extracts in the absence of the standard filters, both ALU, ALF, and their combination showed a very high photostability performance, with no changes in the absorption properties along the exposure to up to 14.4 SEDs (Figs. 3A, B and C and 4;  $p < 0.01$ ). In Table 3, the number of SEDs necessary for a decrease of the biological protection factors to 50%, with respect to the initial values, were calculated using the regression fitting of the curves (second grade polynomic model) obtained in Fig. 4. No doses for biological factors 50% decay could be estimated when AL extracts were exposed in the absence of the filters, reflecting the high photostability of both AL extracts and their combination. In contrast, the exposure of the standard filters OMC and BMDDBM to the same increasing UV doses led to a gradual decrease in the absorbance

**Table 2** Biological protection factors (SPF, HIPF, and UVAPF) as well as the ratio of UVAPF/SPF of the different combinations in Galenic formulations. AL extracts (ALF, ALU, and ALU/ALF) were analyzed alone and in combination with standard UV filters, including octyl methoxy cinnamate (4%) and Butyl methoxy dibenzoyl methane (2.5%). AL extracts were assayed at 2 different concentrations: 1% (0.1 mg/10 g cream) and 2.5% (0.25 mg/10 g cream). Filters alone were used as sunscreen control for the different biological protection factors. In the specific case of UVAPF/SPF, the asterisks mean significant increments compared to the minimum value established for broad-spectrum at ISO 24443:2022. For the rest of the cases: \* = significant difference between AL combinations with filters with respect to filters alone (100%) at  $p < 0.05$ ; and \*\* = significant differences at  $p < 0.01$ ; one-way ANOVA

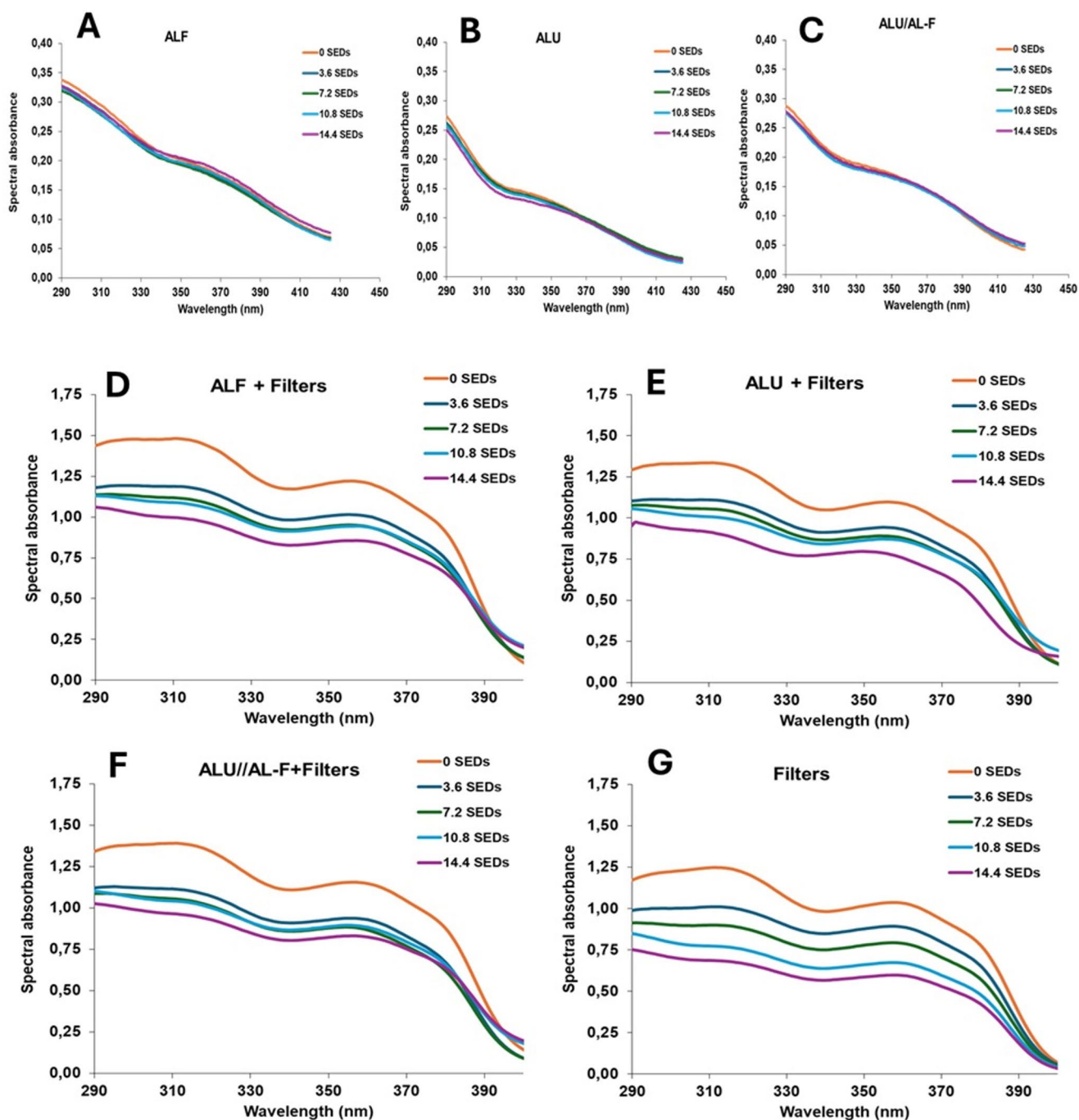
<i>A. linearis</i> 1% in galenic formula				
COMBINATIONS	SPF	HIPF	UVAPF	UVAPF/SPF
ALU	1.35±0.22	1.26±0.15	1.2±0.10	0.89±0.09**
ALF	1.59±0.29	1.45±0.17	1.33±0.09	0.90±0.03**
ALU/ALF	1.43±0.06	1.35±0.04	1.29±0.03	0.83±0.10**
ALU+FILTERS	16.06±2.7	10.63±2.15	8.44±1.83	0.52±0.02*
ALF+FILTERS	18.38±5.4	11.88±2.53	9.36±1.66	0.5±0.07*
ALU/ALF+FILTERS	17.54±6.2	11.73±3.72	9.34±2.85	0.53±0.02*
FILTERS	15.43±1.4	10.5±1.15	8.35±1.05	0.54±0.02*
AVERAGE BOOST	SPF	HIPF	UVAPF	
% increment ALU+FILTERS	104.11*	101.28	101.19	
% increment ALF+FILTERS	119.13*	113.2*	112.16*	
% increment ALU/ALF+FILTERS	113.69*	111.72*	111.92*	
Filters	100	100	100	
<i>A. linearis</i> 2.5% in galenic formula				
COMBINATIONS	SPF	HIPF	UVAPF	UVAPF/SPF
ALU	1.53±0.27	1.40±0.18	1.30±0.12	0.85±0.10**
ALF	1.95±0.34	1.69±0.20	1.51±0.11	0.77±0.12**
ALU/ALF	1.67±0.08	1.53±0.05	1.44±0.04	0.86±0.04**
ALU+FILTERS	19.76±3.3	12.60±2.57	9.86±2.2	0.50±0.02*
ALF+FILTERS	27.24±6.5	16.35±3.02	12.53±1.9	0.46±0.08*
ALU/ALF+FILTERS	22.46±7.4	14.39±4.4	11.27±3.4	0.50±0.02*
FILTERS	15.43±1.6	10.50±1.37	8.34±1.25	0.54±0.02*
AVERAGE BOOST	SPF	HIPF	UVAPF	
% increment ALU+FILTERS	128.08**	120**	118.16**	
% increment ALF+FILTERS	176.52**	155.75**	150.14**	
% increment ALU/ALF+FILTERS	145.57**	137.05**	135**	
Filters	100	100	100	

properties (Fig. 3G). The regression models (Fig. 4) showed that exposure to 6.15 SEDs led to a 50% decrease in the initial SPF; a decrease that was achieved with 9.4 SEDs for HIPF and 7.9 SEDs for UVAPF (Table 3;  $p < 0.05$ ). When ALU was added to the standard filters, the stability of the combination increased slightly but significantly (Figs. 3E and 4), and 7.9 SEDs were necessary for a 50% of SPF decay, as well as 12.1 and 9.8 SEDs for HIPF and UVAPF, respectively (Table 3;  $p < 0.05$ ). The higher photostability was offered by the addition of ALF, as can be observed in Figs. 3D and 4, increasing the SEDs necessary for 50% of SPF decay to 14.1 (Table 3;  $p < 0.01$ ). More than the maximal SEDs used in the experiment appear to be necessary for the 50% decay of HIPF and UVAPF (Table 3). The combination of both extracts also provided significant photostability, close to that offered by the fermented extract (Figs. 3F and 4, and Table 3).

## 4 Discussion

The present study demonstrates that all *Aspalatus linearis* (AL) extracts tested, including fermented (ALF), unfermented (ALU), and their combination (ALU/ALF), exhibit enviable optical properties supporting their consideration for the development of future photoprotective formulas.

Initially, a broad UV absorption spectrum increasing gradually from UVA up to UVB, with the highest absorption peak around 285 nm, was observed for AL water extracts. The high absorbance characteristics of natural extracts have also been reported in a previous work of our research group [7], and could be due to the presence of UV-absorbing phytochemicals within the plant tissue [33, 34]. One of the most probable groups of compounds contributing to the observed effect is flavonoids. Flavonoids possess a typical UV-VIS spectra including two bands, corresponding with the absorption of the B ring (band I: 310–385 nm), and the A ring (band II 250–285 nm) [35]. They have been reported

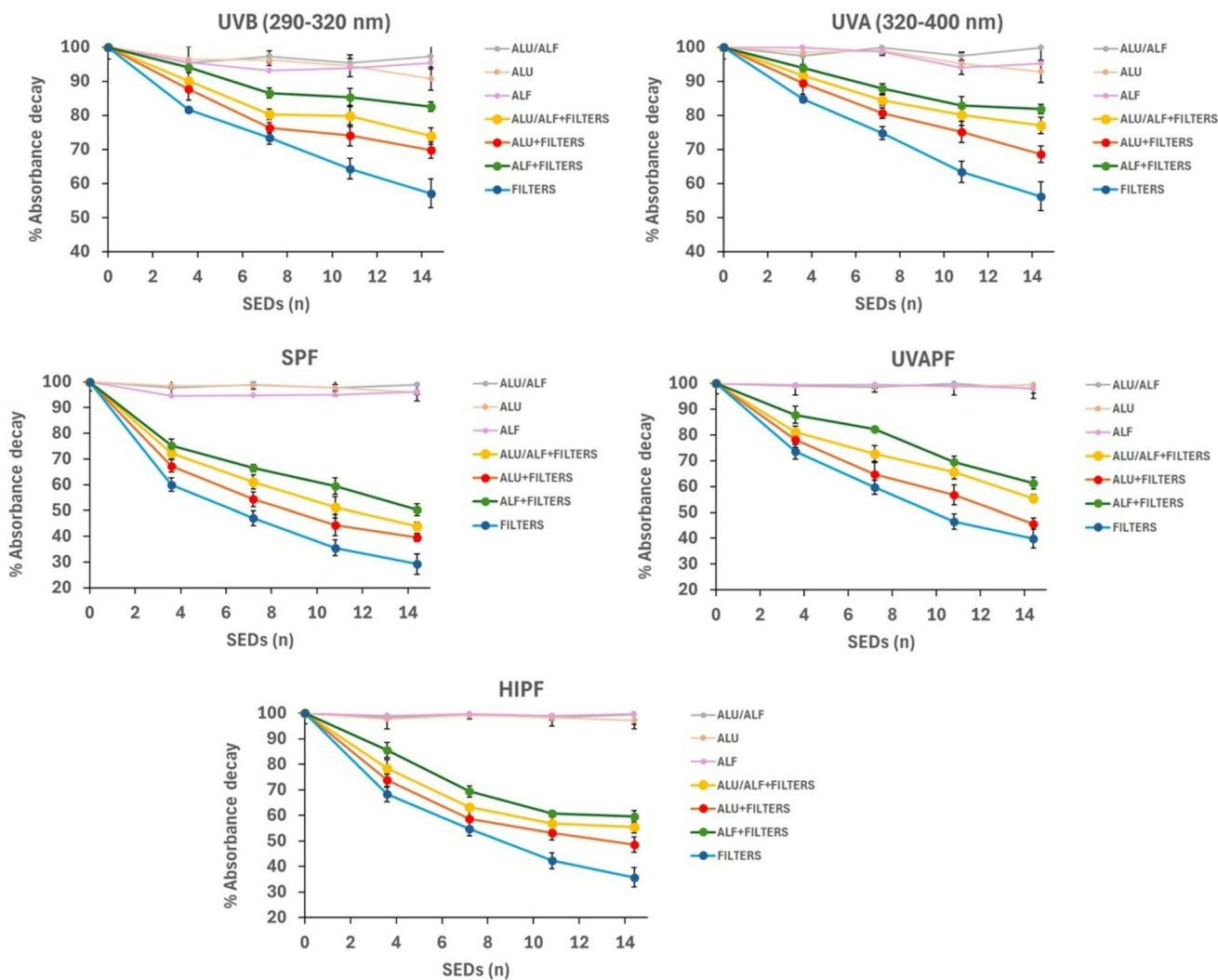


**Fig. 3** Photostability assays. PMMA plates with the different extracts and standard filters were exposed to increasing doses of solar simulated UVB+UVA from 0 to a dose corresponding to 14.2 Standard Erythemal Doses (1 SED=10 mJ/cm<sup>2</sup>). Then UVB and UVA absor-

bance means are represented. (A-C) Spectral absorbance changes ALF, ALU, and ALU/ALF at 2.5% alone, and (D-G) when combined with OMC (4%) and BMDBM (2.5%)

previously as natural UV filters [14], and some of them have been tested against keratinocyte damage in experimental settings [21, 22]. The water extracts of AL contain high concentrations of different phenolic compounds known to absorb UV radiation, including 3 dihydrochalcones (aspathin, nothofagin, and linearthin), and other flavonoids such

as orientin, isorientin, quercetin, and luteolin [33]. Given their structure, the presence of the C-glycoside dihydrochalcones could confer a high absorption peak at 286 nm, while the presence of rutin, quercetin, or other flavonoids could explain the UVA peak at 353 nm. Interestingly, our data showed that the UV absorbance of ALF was higher than



**Fig. 4** The photostability impact in UVB and UVA spectral regions, and the protection factors. Different biological photoprotection factors were calculated from the absorbance curves of Fig. 3. Results are expressed as mean percentage of decay ( $\pm$  standard deviation) of absorption in the UVB (290–320 nm), UVA (320–400 nm), and bio-

logical protection factor (SPF, UVAPF, and HIPF) under increasing UV doses, from 0 to 14.4 SEDs. The changes in UVB, UVA, and the biological factors are expressed in % relative to the initial value (values measured at SED 0 – non-irradiated- are taken as 100%)

**Table 3** Number of standard erythemal doses applied to the different samples containing ALU, ALF, and ALU/ALF independently and when combined with the solar filters octyl methoxy cinnamate (4%) and Butyl methoxy dibenzoyl methane (2.5%) necessary for the 50% decay of the different biological protection factors (SPF, HIPF, and UVAPF). Data are extracted from second-degree polynomial fitting regression lines of the biological protection factors (BPF) decay curves of Fig. 4

Number of SEDs for 50% decay of BPFs			
COMBINATIONS	SPF	HIPF	UVAPF
ALU	> 14.4	> 14.4	> 14.4
ALF	> 14.4	> 14.4	> 14.4
ALU/ALF	> 14.4	> 14.4	> 14.4
ALU+FILTERS	7.9*	12.6*	9.8*
ALF+FILTERS	> 14.1**	> 14.4**	> 14.4**
ALU/ALF+FILTERS	10.5**	> 14.4**	> 14.4**
FILTERS	6.15	9.4	7.9

that of ALU. It is well known that during the plant processing (known as fermentation), the dihydrochalcones are rapidly oxidized by nonenzymatic mechanisms to flavanones and polymeric brown products [36–39], then noticeable browning takes place [17]. Therefore, the appearance of the oxidized forms from the pool of flavonoids and hydrochalcones may change the absorption properties of the extracts, increasing ALF UV absorbance. It is worth noticing that the autooxidation process decreases the antioxidant potential of the extracts, underlying the lower antioxidant capability ascribed to ALF vs. ALU [23, 40]. Thus, considering the important benefits attributed to AL extracts as antioxidant ingredients in sunscreens, plus the recent synergistic biological photoprotective effect shown by a specific combination ALU/ALF [23], we decided to include the spectral

properties analysis of that combination. As expected, we found intermediate absorbance properties, lower than ALF but significantly higher than ALU, which would support the use ALU/ALF combination to take advantage of maintaining high antioxidant capacities, optimal absorption properties, and the synergistic biological photoprotective effect.

We are in a new era, where we aim natural compound combination providing the sunscreen formula absorption properties as “real biological” filters for UVB and UVA bands of the solar spectrum. Walking towards the practical inclusion of AL extracts in commercial sunscreens, our next step was to assess the performance of the extracts when incorporated into real sunscreen formulas, testing their absorption properties following the international standards outlined in ISO 24443:2022, and calculating SPF, UVAPF, and HIF values. SPF and UVAPF are reference parameters commonly tested in sunscreens, and account for the specific spectrum of action for erythema and permanent pigmentation darkening, respectively. However, Damian et al. 2011, determined 2 peaks of UV radiation (310 and 370 nm), key for immunosuppression, which is one of the most relevant factors in the steps previous to skin carcinogenesis [31]. Then, a biological protection factor against human photoimmunosuppression can be calculated (named as HIPF). We considered including HIPF as other biological protecting factors beyond erythema and permanent pigmentation darkening since AL extracts show broadband absorbance properties in the whole UV region. This HIPF has been previously used with *Polypodium leucotomos* extracts in assays for their photoprotection properties [41]. AL extracts, individually and combined, showed a significant absorbance increment from UVA to UVB, leading to SPF values close to 2 at concentrations of 2.5%, reinforcing their properties as radiation filters. Few works in the literature have reported the absorption properties of phenolic compounds for photoprotection purposes. For instance, quercetin and especially rutin offer high UV absorption potential, reaching SPFs above 30 [42], and total polyphenols extracted from some plant leaves can achieve SPF values above 20 [43]. The traditional herbal formulation, Ubtan, based on different plant seeds (rich in flavonoids), can reach SPF values above 30 [44]. Although those works showed higher SPF values, it is worth mentioning that they used methanol and other organic extractions, which yield much higher concentrations. Conversely, the water extractions used in this work are considerably less toxic, affordable, and environmentally sustainable, which represents a strong advantage for their industrial implementation. Additionally, those works did not include the extracts in galenic formulations or test the regulated standards for real sunscreens. Therefore, the results presented here demonstrate not just the enviable broadband absorbing properties of aqueous extracts of AL, but also its performance in

complex formulations analyzed under regulated standards, which strongly support and facilitate its practical inclusion as natural filters in current sunscreens.

Surprisingly, the most interesting results were obtained when AL extracts were combined with other filters (OMC and BMDBM). The addition of 2.5% ALF was able to increase the SPF of the reference filters from 15.43 to 27.24, an increase of 76.52%. Similarly, the UVAPF increased 50% and the HIPF increased 56%. ALU extract showed lower values than ALF, yet conferred a very important increase in all biological protection factors, and the combination ALU/ALF showed intermediate photoprotection factors closer to ALF (increment of 45,57% SPF, 35% UVAPF, and 37.5% HIPF). Given the potential adverse effects of certain organic filters on human health and the environment, the incorporation of natural products into cosmetic formulations is a growing trend, aiming to reduce reliance on high concentrations of synthetic UV filters [45, 46]. In this scenario, this work demonstrates a booster effect on commonly used synthetic UV-filters when AL is included in the formula. This would allow reducing the amount of filters used, maintaining the efficacy of the sunscreen while improving safety and sustainability.

Interestingly, the AL combinations in galenic formulations alone showed very high UVAPF/SPF ratios. Even when those ratios decrease when the extracts are included together with standard UV filters, they were still maintained close to 0.5. UVAPF/SPF ratios reflect the broad-spectrum character of the formula. Actually, one of the goals in the new sunscreen photoprotection consensus is to raise UVAPF/SPF ratios, therefore increasing the confidence of the users in being protected from the UVA part of the solar spectrum. Thus, the incorporation of AL extracts in future topical photoprotectants would also fit this new goal.

Finally, the additional role of the AL extracts as photostabilizers was demonstrated. It is well known that the combination of BMDBM and OMC, with very extended use as UVB and UVA filters in commercial sunscreens, is photounstable. This process is initiated by BMDBM, which, after absorbing UVA radiation, reacts with OMC to form cycloaddition products [47]. To palliate this effect, other molecules are included in sunscreen formulations not just as UV filters, but as stabilizers. This is the case of bis-ethylhexyloxyphenol methoxyphenyl triazine (tinosorb S), methylbenzylidene camphor, diethylhexyl 2,6-naphthalate, or octocrylene [28, 48–50]. However, in the current scenario where synthetic filters are under scrutiny, octocrylene, due to its toxic potential in humans and animals, is currently being phased out by industry, justifying the need for alternatives [29]. As the light-induced degradation mechanism of BMDBM and OMC proceeds through the initial formation of free radicals and singlet oxygen [51, 52], scavenging these reactive

species by antioxidants has been proposed as an approach for photo-stabilization [53, 54]. In this context, triplet–triplet energy transfer is an important photo-stabilization mechanism for organic UV filters [48], and the stabilizing potential of flavones and flavonoids, including quercetin, has been described [55, 56]. In this study, both AL extracts, especially ALF and the combination ALU/ALF, were able to significantly prevent the absorbance decrease of the reference filters under UV radiation. This importantly reinforces their double role, not just as filtering ingredients but as alternative photo-stabilizers.

In conclusion, the evidence presented herein highlights the promising potential of natural extracts as components for advanced solar photoprotection. Up to now, none of the commercially available sunscreen molecules present ideal behavior as a photoprotection ingredient, which implies very high absorption properties in the UV region, high photostability, and negligible toxicity or phototoxicity. AL extracts combination demonstrated in the present work that they can play this role, acting as biological filters and photo-stabilizers, allowing the development of future topical photoprotective agents based on natural sources, effective, and safer for human health and the environment, which in current times could potentially enhance user adherence to the recommended photoprotection protocol.

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**Author contributions** Authorship contribution: José Aguilera: Writing – original draft, Conceptualization, Methodology, Investigation. Pablo Sepulveda: Writing- original draft, Investigation. Ana López Sánchez: Methodology, Investigation, Review & editing. Luisa Haya: Conceptualization, Review & editing, Salvador González: Review & editing, María Victoria de Gálvez: Review & editing.

**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Declarations

**Competing interests** JA, PS and MVG received a grant for the present research project. S.G. has a consultant role for Cantabria Labs, ALS and LH. belong to the Research, Development and Innovation Department at Cantabria Labs SA.

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