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Total Phenolic Content, Antioxidant Capacity and UV Radiation Protection Properties of Marigold (*Calendula officinalis*), Carrot (*Daucus carota*), Tomato (*Solanum lycopersicum*) and Hop (*Humulus lupulus*) Extracts

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Abstract: Total phenolic content using Folin–Ciocalteu method, antioxidant capacity by CUPRAC method and sun protection properties were measured for four different extracts of selected plants: marigold petals, carrot roots, tomato fruits and hop cones. Three types of extracts: water, oil and water-glycolic (1:4) were studied. Assessment of sun protection properties for extracts obtained from selected plants was first done by mathematical indication method and subsequently done spectrophotometrically. In a method of mathematical indication of UV protection based on absorption spectra, four parameters were determined regarding sun protection properties at different concentrations of selected plant extracts. Absorbance generally increased with an increase of concentration of extracts, but an expected increase of particular parameters was not obtained in all samples. The water-glycolic extract from hop cones was characterized by the highest content of phenolic compounds (among all studied samples) and high antioxidant activity. It also showed high radiation protection. Data for four parameters like UVA/UVB parameter, UVA1/UV parameter, SUI parameter and critical wavelength was generated, and the three first parameters were the highest for water and water-glycolic extracts of marigold. Among all plants, hop cones were characterized by the highest SPF for all types of extracts. SPF values increased with the concentration of extracts, but an increase of the weight of dried plants used to prepared extracts did not influence sun protection factor.

Keywords: antioxidant capacity; UV radiation protection; marigold; carrot; tomato; hop

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1. Introduction

Solar radiation or sunlight, emitted by the sun electromagnetic radiation, has a positive and a negative effect on the human organism. The undesirable effects include skin aging, generation of free radicals and the process of carcinogenesis. To avoid these negative effects, the protection is used in the form of a wide range of cosmetic products with UV radiation protection properties. New formulas, recipes, or forms of products and new sunscreen ingredients have been widely examined [1,2] In accordance with the growing needs of consumers and environmental aspects, natural plant sources of ingredients with UV radiation protection properties are essential to be studied and applied commercially. Solar radiation includes three types of light: infrared, visible and ultraviolet. The last one occurs in the smallest quantity, accounts for only 5% of all sunlight and can be divided into three ranges: UVA, UVB and UVC [1]. For UVA range the wavelength is from 320 to 400 nm and can be divided into UVA2 (wavelength 320–340 nm) and UVA1 (wavelength 340–400 nm). Among ultraviolet radiation, UVA makes up 95% of all UV range and can penetrate deeper layers of the skin, but its intensity depends only in small extent on different conditions like weather

or season [3]. UVA radiation influences the skin properties and structure of nucleic acids and proteins like elastin or collagen [4]. UVB radiation is characterized by a wavelength ranging from 290 to 320 nm and makes up only 5% of all UV radiation range [3]. UVB radiation affects the epidermis layer of the skin and may cause erythema, which can turn to sunburn, but it also takes part in a reaction related to the formation of vitamin D in the skin [5]. UVC radiation concerns the range of wavelength from 200 to 290 nm and is almost completely absorbed by the ozone layer. The human organism can be protected naturally against UV radiation. The skin has ability to protect itself after exposition to sunlight; unfortunately, the protection does not last for a long period of time [6]. One form of natural skin protection against UV radiation is the production of melanin. This pigment can also be applied to the cosmetic formulation as naturally obtained from octopus or cuttlefish or by chemical synthesis [7]. Other skin protection mechanisms are the production of urocanic acid, which protects against UVB radiation [5], or an increase in the thickness of the stratum corneum by a process of keratinization, which becomes a barrier for harmful radiation. Natural organism protection against radiation is a mechanism related to either disrupting the reactions that cause the formation of free radicals or directly destroying free radicals by compounds like carotenoids, vitamin C, coenzyme Q, tocopherols and lipoic acid [5]. In addition, anti-radical enzyme systems, which are based on such enzymes as catalase or superoxide dismutase, are also included in the above action [5,8]. To enhance the natural protection level, the topical application of cosmetic products onto the skin is advisable. Two types of sunscreen filters can be used: physical and chemical ones. Physical, mineral filters are very common in cosmetic applications by virtue of their stability and resistance to UV radiation, but their disadvantage is that they affect the decomposition of active substances. Among physical filters, we can distinguish titanium dioxide, zinc oxide, iron oxides, calcium carbonate, talc and kaolin. The above-mentioned substances can also act as pigments in cosmetic products [3,6,7]. Titanium dioxide and zinc oxide are also used as nanoparticles, with particle size smaller than 100 nm, which can penetrate deeper skin layers in contrast to pigments. Physical filters can be coated with hydrophobic compounds that reduce their negative impact on other substances in the formulation and allow to use them in an oil phase of cosmetics [7]. Another group of filters contains synthetic chemical compounds, which include chromophore groups [3]. These groups include unsaturated bonds as well as thiocarbonyl, indole, carbonyl, nitrate groups and nitrite [4,9,10] These filters penetrate into the surface layers of the epidermis. Their mechanism of action is based on the absorption of sunlight, in which the compound goes into an excited state. Then the molecule returning to its initial state gives off excess energy in the form of heat. Chemical filters absorb radiation in different wavelength ranges. For this reason, they have been divided into three main groups. UVB filters have the ability to absorb radiation in the wavelength range of 290–320 nm. They include, among others, terpene compounds, cinnamic, p-aminobenzoic and salicylic acid derivatives, as well as imidazole, quinoline and benzimidazole derivatives. UVA filters absorb light in the wavelength range of 320–400 nm. This group includes dibenzoylmethane derivatives, benzylidenecamphors and phenylbenzimidazole. The third group is UVB + UVA filters with a wide absorption range from 290 to 380 nm. These include single substances that are distinguished by their photoprotective ability in a wide spectrum, e.g., benzophenones, phenylbenzotriazoles and triazine [11–13]. Usually, sunscreen products are a mixture of physical and chemical filters in order to reduce the concentration of particular filters and provide maximum protection in a wide range of UV radiation [3,14,15] However, they are not the only substances that can protect human organisms against harmful radiation. Natural, isolated-from-plants chemical compounds also have such properties [3,9]. Moreover, due to their origin, they are safer for the human body, can protect from oxidative stress, absorb radiation in a wider spectrum of wavelength and may support the removal of negative effects of sun exposition, for example skin aging [8]. Natural filters can be the extracts obtained from plants due to the presence of numerous active compounds, as many of them have the ability to absorb radiation of wavelengths belonging to the UV range [11]. Based on the presence of compounds capable

of absorbing UV radiation, almost one hundred water-alcohol and water-glycolic plant macerates and tinctures had been divided into six groups: salicylates (present in willow and meadowsweet), p-aminobenzoic acid derivatives (found in extracts of chamomile, witch hazel, sage or arnica), anthracene derivatives (present in aloe, walnut, arnica or chamomile), coumarin derivatives (present in marigold, horse chestnut, fig-tree), benzophenone derivatives (present in arnica, chamomile, liquorice and rosemary) and cinnamic acid derivatives (found in rosemary, arnica, mint, dandelion and lemon balm) [11,16,17]. Different types of natural compounds with UV protective properties are vegetable fats like argan oil or macadamia oil, shea or cocoa butter and others containing unsaturated fatty acids which, just like plant extracts, do not indicate a very high level of protection, but a range of absorption of UV radiation is also broad. Furthermore, vegetable fats contain polyphenols which can exhibit the antioxidant properties. Another important group of chemical compounds with protective properties are carotenoids, such as β-carotene and lycopene which, applied in fatty medium, can support chemical filters, and when applied internally, cause an increase of skin resistance to the influence of sunlight. The research is conducted to search for and examine natural, plant-derived compounds with UV radiation protection properties and develop phyto sunscreens with satisfying effectiveness, whaich is confirmed by several examples. The photo-protective requirements may be met by numerous plant extracts containing either antioxidant, antiradical compounds or photoprotective substances. For example, extracts obtained from Brazilian plants were studied in terms of comparing their UVB radiation adsorption with total phenolic and flavonoid content and antioxidant activity. Flavonoids, phenolic compounds and esters of hydroxycinnamic acid present in plants protect their tissues from UV radiation [16,17]. The values for sun protection factor for plant extracts obtained from *Lippia microphylla* and *Dimorphandra gardneriana* were about 20, where results above 15 mean skin protection against UV radiation. In the case of these extracts, the protection was due to the presence of quercetin glycosides and sakuranetin flavonoids [10,11]. Secondary metabolites which are characterized by antioxidant properties could have the ability to indicate high absorption of UV radiation. For example, extracts of *Hibiscus furcatus*, *Leucas zeylanica* or *Ophiorrhiza mungos* displayed values for sun protection factor bigger than 25, which was higher in comparison to commercially available photoprotective cosmetic used as a reference. Furthermore, *Leucas zeylanica* or *Ophiorrhiza mungos* extracts have the potential for use in sunscreen of broad spectrum due to their high UV absorbance of wavelengths in a range from 260 to 350 nm. Extract of *Ophiorrhiza mungos* was also characterized by photostability after exposure to direct UV radiation for three weeks without significant reduction in its sun protection factor [17]. In other studies, four extracts of different species of *Lippia* plant were examined to develop sunscreen formulation with a single, natural UV filter. The results obtained in the experiment suggested that, among them, sunscreen with *Lippia sericea* indicated potential in a commercial application. Moreover, the total polyphenolic content of the plant was related to its photoprotective properties unlike its antioxidant capacity or flavonoid content [18]. Subsequent studies were also performed to develop an antioxidant phytocosmetic sunscreen product containing a mixture of plant extracts rich in flavonoids. Extracts of selected plants were used: *Vitis vinifera*, *Ginkgo biloba*, *Ruta graveolens* and *Dimorphandra mollis*. The results obtained for topical application showed sun protection properties and antioxidant activity of the created phytocosmetic formula [19]. Extracts obtained from *Moringa oleifera* leaves were examined as natural, herbal UV phytosunscreen ingredients [20]. All these examples of conducted research on UV radiation protection properties showed that numerous plant extracts had the potential to protect human skin from harmful radiation. In this study, four plants were selected to examine their total phenolic content, antioxidant capacity, UV radiation protection properties and spectrophotometric sun protection factor (SPF). One of them was marigold, which contains coumarin derivatives: esculetin and scopoletin; flavonoids and their glycosides for example rutin and quercetin; carotenoids like lycopene and carotenes; and polyphenols [4,21–23]. The second selected plant was hop characterized by a content of flavonoids: kaemferol, xanthohumulone or phytoestrogenic compounds and

tannins like caffeic or gallic acid and resins like humulon and lupulone [24]. Other plants rich in carotenoids responsible for their antiradiation and antioxidant properties, were carrot and tomato. Carotenoids can absorb radiation of wavelength from 400 to 700 nm, among them lycopene, which shows the best antioxidant properties [25]. Due to the presence of all listed chemical compounds, those four selected plants show potential for use as a natural and ecological sunscreen filter; consequently, their properties were examined.

The main purpose of the study was to determine the content of phenolic compounds, antioxidant activity of water, water-glycol and oil extracts from pot marigold, hops, carrot and tomato and to determine their radiation protection properties using methods based on spectrophotometric measurements.

2. Materials and Methods

2.1. Chemicals and Materials

Caffeic acid and neocuproine were purchased from Sigma-Aldrich, whereas other reagents (analytical grade) from Chempur, Poland. All analyzed raw materials were purchased from local markets.

Apparatus UV–Vis spectra were recorded on a UV–Vis HELIOS α spectrophotometer (Unicam, Cambridge, UK) in 1 cm quartz cell.

The extraction process was carried out using a water bath with a shaking function (Laboplay SWB, Białystok, Poland).

2.2. Sample Preparation

The extracts for this research were obtained from marigold flowers (*Calendula officinalis*), carrot root (*Daucus carota*), tomato fruit (*Solanum lycopersicum*) and hops cones (*Humulus lupulus*). The freeze-drying process was conducted for fresh carrot and tomato before extraction. Lyophilised and dried marigold flowers and hops cones were ground to powder. Unground marigold flowers were also used to prepare extract to compare if the degree of defragmentation of materials affects results. Two types of extractants were used to obtain extracts: water and a mixture of water and propylene glycol in a ratio of 1 to 4 to determine total phenolic compounds content and antioxidant capacity. Additionally, to examine the sun protection factor of extracts obtained from selected plants as a third extractant, sunflower oil was also used. The extraction process with application of the mixture of water and propylene glycol and sunflower oil was preceded by a maceration process at room temperature in the dark for 24 h using a water bath with a shaking function. To obtain extracts, the appropriate amounts of plant materials were weighted (from 0.5 to 5 g), and about 50 mL of extractants were added to each sample. All samples were placed in a water bath and shaken at a speed of 800 rotations per minute for 4 h in temperature 25 °C (water extracts) or 30 °C (water-glycolic and oil extracts). The next step was centrifugation to 9000 rotations for 10 min. Then, the solutions were filtered into volumetric flasks and refilled to appropriate extractant to a volume of 50 mL and stored in the fridge. The method of obtaining an extract from unground marigold flowers was similar, but the final process of filtration was different due to the fact that the research material absorbed a large part of the extractant, so filtration was conducted under reduced pressure.

2.3. Determination of Total Phenolic Content

Total phenolic content (TPC) in plant extracts was measured with Folin–Ciocalteu reagent using UV-VIS spectrophotometer. This yellow reagent consists of a mixture of phosphomolybdic and phosphotungstic acids, which reduce to blue-dyed oxides after oxidation of phenolic compounds [26]. Two types of solution were prepared: 0.29 mM solution of caffeic acid in ethyl alcohol and 1.132 M water solution of calcium carbonate for determination of the calibration curve of caffeic acid. Eight different concentrations of caffeic acid were prepared with the addition of Folin–Ciocalteu reagent, calcium carbonate and distilled water. The calibration curve of caffeic acid was prepared in the range from 1.3 to 9.1 mg/L. The absorbance for prepared samples was measured at a wavelength of 725 nm. The obtained

calibration curve equation was as follows: $y = (0.0985 \pm 0.0031) \times + (-0.0113 \pm 0.0170)$ with $r^2 = 0.999$. The calculated limit of detection (LOD) and limit of quantification (LOQ) were 0.36 mg/L and 0.88 mg/L, respectively.

Water and water-glycolic extracts of selected plants were analysed (5 samples of each extract). The amount of the extract used in the analysis was different for various plants due to the unequal quantity of phenolic compounds. The studied samples were analysed in similar way to that of determination of the calibration curve. Total phenolic content for plant extracts was calculated with the application of linear regression equation obtained from the calibration curve and was expressed as caffeic acid equivalent and calculated as a mean of five samples for each extract. The obtained results of F-C method for analysed samples are presented in Table 1.

Table 1. Total phenolic compounds content in analysed extracts.

Type of Extracts	TPC in 100 g Dried Plant [mg/100 g] CAE *
Water extract of marigold (unground petals)	368.51 ± 58.94
Water extract of marigold (powdered petald)	1140.53 ^{A} ± 55.47
Water-glycolic extract of marigold	1214.24 ^{B} ± 28.88
Water extract of hop cones	1009.58 ^{A} ± 31.60
Water-glycolic extract of hop cones	4017.41 ^{B} ± 131.56
Water extract of carrot	188.97 ^{B} ± 7.68
Water-glycolic extract of carrot	164.81 ^{A} ± 2.01
Water extract of tomato	314.41 ^{A} ± 8.65
Water-glycolic extract of tomato	386.28 ^{B} ± 3.46

* CAE—caffeic acid equivalent. Different letters (A–B) within the same column indicate significant differences (one-way ANOVA and Duncan test, $p < 0.05$) for tested samples; sorted from the lowest to highest values, where "A" was the lowest.

2.4. Determination of Antioxidant Capacity by CUPRAC Method

The CUPRAC method (Cupric Reducing Antioxidant Capacity) is based on SET (single electron transfer) mechanism [26]. This method relies on the reduction reaction of copper ions which create a yellow-orange complex with neocuproine as shown in [27,28]. To determine antioxidant capacity for studied extracts by CUPRAC method, 0.029 mM solution of caffeic acid in ethyl alcohol, 0.0075 M solution of neocuproin in ethyl alcohol, 0.01008 M copper(II) chloride and 1.004 M ammonium acetate buffer solution with pH = 7 were prepared. For construction of the calibration curve used in CUPRAC method, the samples containing copper(II) chloride, neocuproin and ammonium acetate were prepared with different concentrations of caffeic acid (from 0.52 to 4.16 mg/L). For calibration curve and prepared samples, the absorbance was measured at the wavelength 450 nm.

The obtained calibration curve equation was as follows: $y = (0.2859 \pm 0.0105) \times + (0.0031 \pm 0.0271)$ with r2 = 0.9993. The calculated LOD and LOQ were 0.17 mg/L and 0.41 mg/L, respectively.

Antioxidant capacity of plant extracts was calculated with the application of a linear regression equation obtained from the calibration curve and was expressed as caffeic acid equivalent and calculated as a mean of five samples for each extract.

In the experiment, five samples of water and water-glycolic extract of each plant were analysed. To the samples containing different amounts of extracts (from 0.1 mL to 2.0 mL) the following reagents were added: copper(II) chloride, neocuproin and ammonium acetate. The next steps of analysis were similar to the methodology of preparing the calibration curve, and the absorbance for each sample was measured. Antioxidant concentration was determined from the calibration curve expressed as caffeic acid equivalent [mg/L]. Subsequently, antioxidant content in 100 g of dried plant expressed as caffeic acid amount was calculated as a mean of 5 samples for each extract. Results are presented in Table 2.

Table 2. Results of antioxidant capacity for analysed extracts.

Type of Extracts	Antioxidant Activity [mg/100 g] CAE *
Water extract of marigold (unground petals)	75.76 ± 9.80
Water extract of marigold (powdered petals)	218.76 ^{A} ± 11.96
Water-glycolic extract of marigold	232.62 ^{A} ± 17.90
Water extract of hop cones	232.45 ^{A} ± 6.33
Water-glycolic extract of hop cones	1395.97 ^{B} ± 22.33
Water extract of carrot	32.30 ^{A} ± 2.38
Water-glycolic extract of carrot	38.59 ^{B} ± 0.02
Water extract of tomato	79.81 ^{A} ± 2.37
Water-glycolic extract of tomato	127.49 ^{B} ± 4.43

* CAE—caffeic acid equivalent. Different letters (A–B) within the same column indicate significant differences (one-way ANOVA and Duncan test, $p < 0.05$) for tested samples; sorted from the lowest to highest values, where "A" was the lowest.

2.5. Assessment of Sun Protection Properties of Plant Extracts by Mathematical Indication Method

All three types of extracts from selected plants were analyzed by mathematical indication method, which is based on UV-VIS spectra of examined extracts, to define whether the plant show radiation absorption. Extracts were diluted by the same extractants, in the case of oil extracts, isopropyl alcohol was used for dilution and for all samples absorbance was measured at a wavelength from 200 to 900 nm collecting data every 1 nm. For obtained values, area under the curve (AUC) were calculated for UVB (wavelength range from 290–319 nm), UVA1 (wavelength range from 320–339 nm), UVA2 (wavelength from 340–400 nm) and all range of UV. Those results were used to calculate four parameters: ratio of UVA/UVB, UVA1/UV, Spectral Uniformity Index (SUI) and critical wavelength informing about sun protection properties of analyzed samples. The above parameters were calculated using the Equations (1)–(4) [29,30]. All extracts were characterized by the assignment a degree of radiation protection based on the values of obtained parameters.

2.5.1. Critical Wavelength

Critical wavelength determines the width in which protection against UV radiation occurs, and for each extract it was calculated from the Equation (1):

$$\int_{290}^{\lambda c_i} A_\lambda d_\lambda = 0.9 \int_{290}^{400} A_\lambda d_\lambda \quad (1)$$

A_λ—monochromatic absorbance, λ—wavelength

While for the critical wavelength smaller than 325 nm, there is no protection against UV radiation, but in the case of critical wavelength bigger than 370 nm, the protection against UV radiation is maximum. The levels of radiation protection determined by this parameter can be characterized on a 5-point scale with grades from 0 to 4 meaning no protection, medium, good, excellent and maximum protection against UV radiation.

2.5.2. Ratio UVA/UVB

In method BSRS (Boat Star Rating System) the ratio is calculated using the Equation (2),

$$\frac{UVA}{UVB} = \frac{\int_{320}^{400} A_\lambda d_\lambda / \int_{320}^{400} d_\lambda}{\int_{290}^{320} A_\lambda d_\lambda / \int_{290}^{320} d_\lambda} \quad (2)$$

A_λ—monochromatic absorbance, λ—wavelength

On the base of the obtained results the ratio UVA/UVB to cosmetic products are assigned with the specific number of stars (0, 3, 4 or 5) that indicate the degree of protection against UV radiation. The higher number of assigned stars, the better the radiation protection of products.

2.5.3. Ratio UVA1/UV

This parameter is the ratio of area under curve (AUC) from *UVA*1 range to AUC, all *UV* range being the sum of half range of *UVB*, *UVA*2 and *UVA*1. Based on this indicator, four categories (low, medium, high and the highest) of radiation protection were created. Ratio *UVA*1/*UV* was calculated from the Equation (3):

$$\frac{UVA1}{UV} = \frac{\int_{340}^{400} A_\lambda d_\lambda / \int_{340}^{400} d_\lambda}{\int_{290}^{400} A_\lambda d_\lambda / \int_{290}^{400} d_\lambda} \quad (3)$$

A_λ—monochromatic absorbance, λ—wavelength

2.5.4. SUI (Spectral Uniformity Index) Parameter

This parameter concerns assessment of radiation protection from *UVA* range and depends on the obtained value; it can be expressed as low, medium, high and very high protection against radiation. The parameter was calculated using the Equation (4):

$$SUI = \frac{\sum_{290}^{380} A_\lambda}{\sum_{290}^{380} |A_\lambda - \hat{A}|} \quad (4)$$

A_λ—monochromatic absorbance, $\hat{A}$—mean value of absorbance in the wavelength range 290–380 nm [28].

2.5.5. Spectrophotometric Method of Sun Protection Factor (SPF) Determination

This method allows to assess the sun protection factor of extracts but also it can be used for sunscreen cosmetic products. Diluted solutions of samples (for example extracts or cosmetics) are characterized by spectrophotometric analysis. Using the Equation (5) below, the sun protection factor (*SPF*) can be calculated with the use of spectrophotometry.

$$SPF_{spectrophotometric} = CF \times \sum_{290}^{320} EE\ (\lambda) \times I\ (\lambda) \times Abs\ (\lambda) \quad (5)$$

EE (λ)—the spectrum of the erythema effect, *I* (λ)—the spectrum of the intensity of the sun, *Abs* (λ)—absorbance of examined extract/ cosmetic, *CF*—correction factor (=10).

The values of product $EE * I$ are constant values, normalized for a given wavelength [29,30].

3. Results

3.1. Total Phenolic Content

Total phenolic content (TPC) in plant extracts was measured using Folin–Ciocalteu method. The results of total phenolic content in analyzed extracts are shown in Table 1. The dependence of total phenolic content on the type of extractant has been shown in Figure 1.

The results show that the extracts contain different amounts of phenolic compounds. Extracts obtained from carrot contain the smallest amount of phenolic compounds among studied specimens. The amount of phenolic compounds in extracts of tomato is slightly greater than in carrot. Taking into account all analyzed extracts, marigold and hops contain a significant amount of phenolic compounds with water-glycolic extracts of hop cones showing the greatest amount.

3.2. Antioxidant Activity Determined by CUPRAC Method

Results of antioxidant capacity of analyzed extracts of marigold, hop, carrot and tomato have been shown in Table 2. The dependence of the antioxidant capacity on the type of extractant has been shown in Figure 2.

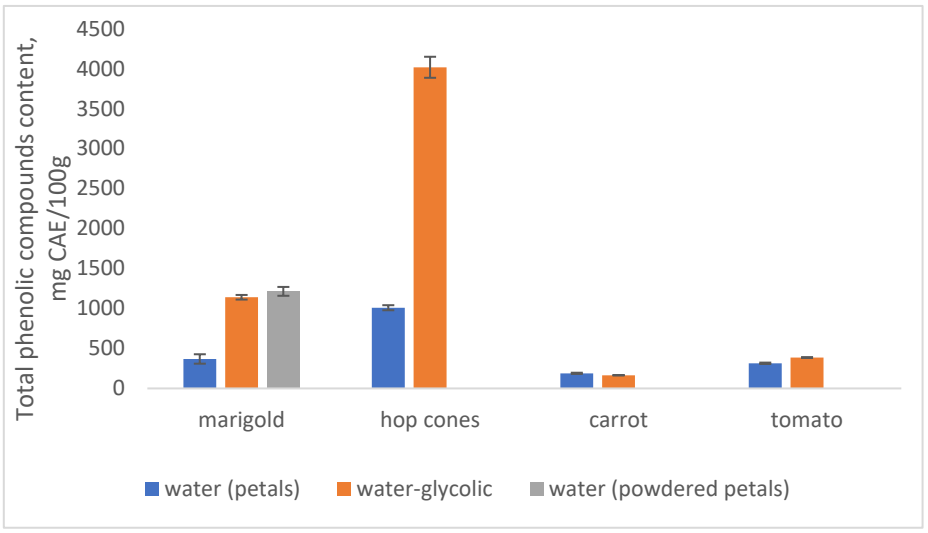

Figure 1. The dependence of total phenolic content on the type of extractant.

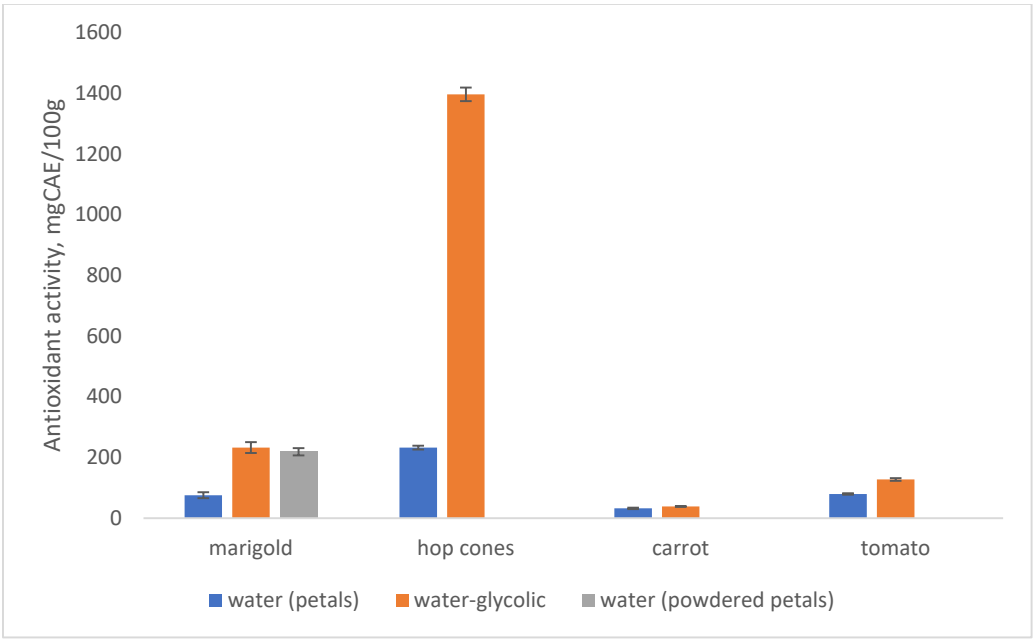

Figure 2. The dependence of antioxidant capacity on type of extractant.

Similar to the results obtained for total phenolic content analysis, the antioxidant capacity differs among analyzed plant extracts, and it is the highest for a water-glycolic extract of hop cones, while carrot extracts had the lowest antioxidant capacity. For statistical evaluation of the obtained result, Statistica Ultimate 13 (StatSoft Polska) was applied. Comparing results obtained by one-way ANOVA ($p < 0.05$), followed by the Duncan test, it is evident, that the mean value of Folin and Cuprac in the majority of tested samples reveal significant differences, except water and water-glycolic extract of marigold.

3.3. Assessment of Radiation Protection Properties of Selected Extracts by Mathematical Indication Method

For all types of extracts and for their three different concentrations, the absorbance for different wavelengths was measured in a range from 290 to 400 nm. The dependence of absorbance on the wavelength was plotted and compared. The area under the absorbance curve and four previously mentioned parameters was calculated by given equations and compared for all types of extracts and for their different concentrations [28–30]. All obtained

results of measured parameters for water, water-glycolic and oil extracts of marigold, tomato, hop cones and carrot and their different concentrations are collected in Table 3.

Table 3. Results of parameters: UVA/UVB, UVA1/UV, critical wavelength, SUI for different concentrations of plant extracts.

	Parameters			
	UVA/UVB	**UVA1/UV**	**Critical Wavelength [nm]**	**SUI**
Type of extract and its concentration	Number of stars assigned to cosmetic product	Protection level	Protection level	Protection level
Marigold water extract (0.4; 0.8; 1.6 mg/mL)	5	medium	maximum	high
Marigold water-glycolic extract (0.4; 0.8; 1.6 mg/mL)	5	medium	maximum	very high
Marigold oil extract (0.2; 0.4; 0.8; 1.6 mg/mL)	0	low	maximum	low
Hop cones water extract (0.2; 0.4; 0.8 mg/mL)	3/4- for concentration 0.8 mg/mL	low	excellent	low/medium- for concentration 0.8 mg/ml
Hop cones water-glycolic extract (0.1; 0.2; 0.4 mg/mL)	5	medium	maximum	high
Hop cones oil extract (0.2; 0.4; 0.8; 1.6 mg/mL)	5/4- for concentration 0.8 mg/mL	low	maximum	medium
Carrot water extract (0.2; 0.4; 0.8; 2,0; 4.0 mg/mL)	5	medium	maximum	medium
Carrot water-glycoli extract (0.4; 0.8; 2.0; 4.0 mg/mL)	5	Low- for concentration 0.8; 2.0 mg/mL, medium- for concentration 0.4; 4.0 mg/ml	maximum	medium
Carrot oil extract (0.2; 0.4; 0.8; 1.6 mg/mL)	0	Low- for concentration 0.2 mg/mL, no protection for the rest	Maximum- for concentration 0.2 mg/mL, excellent for concentration 0.4; 0.8 mg/mL, good for concentration 1.6 mg/mL	low
Tomato water extract (0.2; 0.4; 0.8; 2.0; 4.0 mg/mL)	5	low	maximum	medium
Tomato water-glycolic extract (0.4; 0.8; 1.6; 2.4; 3.2 mg/mL)	5	Medium- for concentration 0.4; 0.8; 1.6 mg/mL, low- for rest	maximum	High- for concentration 0.4 mg/mL, medium- for the rest
Tomato oil extract (0.2; 0.4; 0.8; 1.6 mg/mL)	3- for concetration 0.2 mg/mL 0- for the rest	Low- for concentration 0.2 mg/mL, no protection for the rest	Maximum- for concentration 0.2; 0.4 mg/mL, excellent- for 0.8; 1.6 mg/mL	low

The graphical comparison of the parameters mentioned in Table 3 has been shown in Figures 3–6. The comparison has been made for four measured and calculated parameters for all three types of extracts of marigold, tomato, hop and carrot for concentration 0.4 mg/mL.

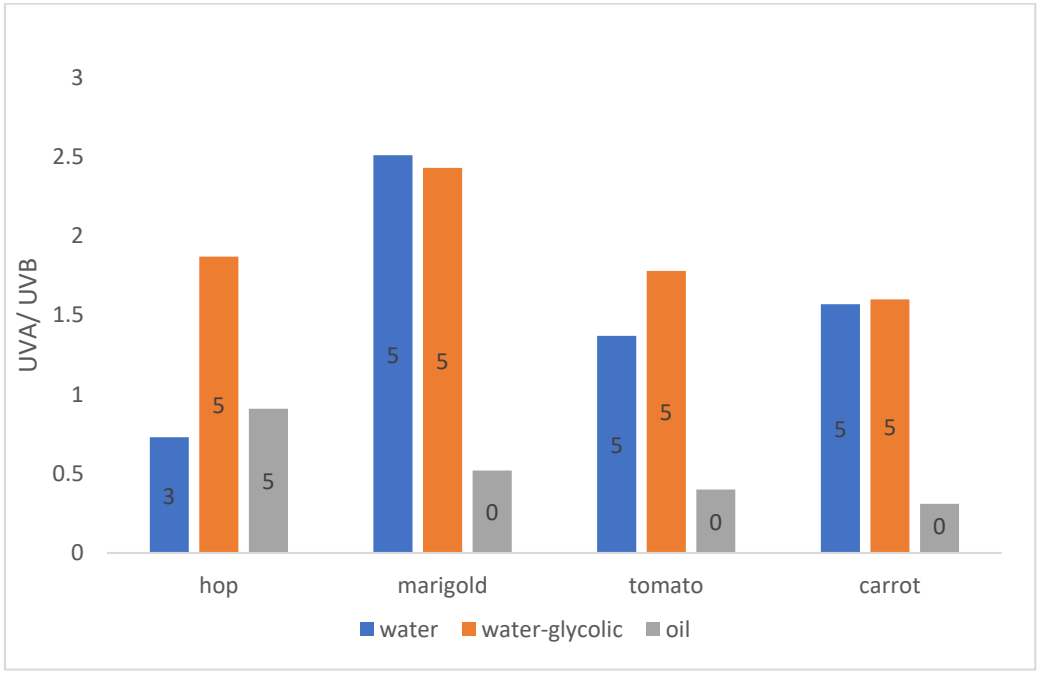

Figure 3. The results of parameter UVA/UVB for different plant extracts with a concentration 0.4 mg/mL. 0, 3, 5—number of stars assigned to cosmetic product.

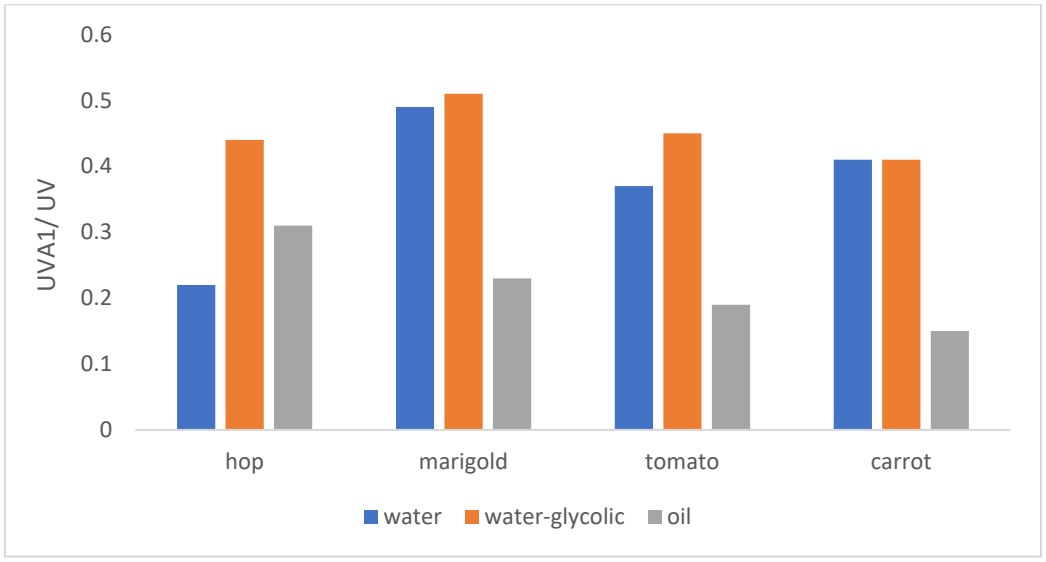

Figure 4. The results of parameter UVA1/UV for different plant extracts with a concentration 0.4 mg/mL.

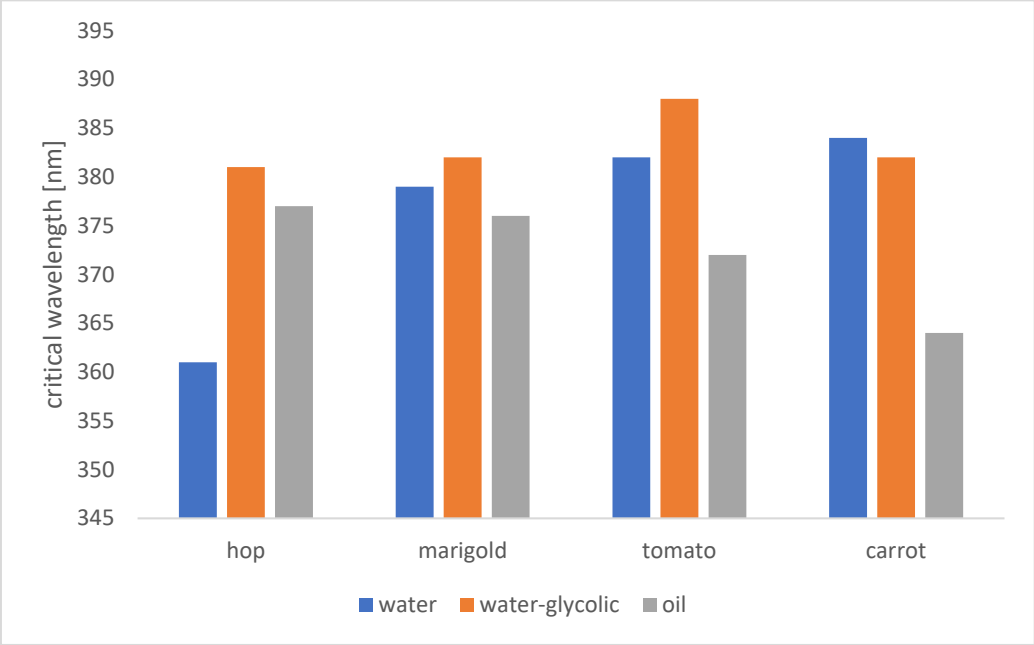

Figure 5. The parameter critical wavelength for different plant extracts with a concentration 0.4 mg/mL.

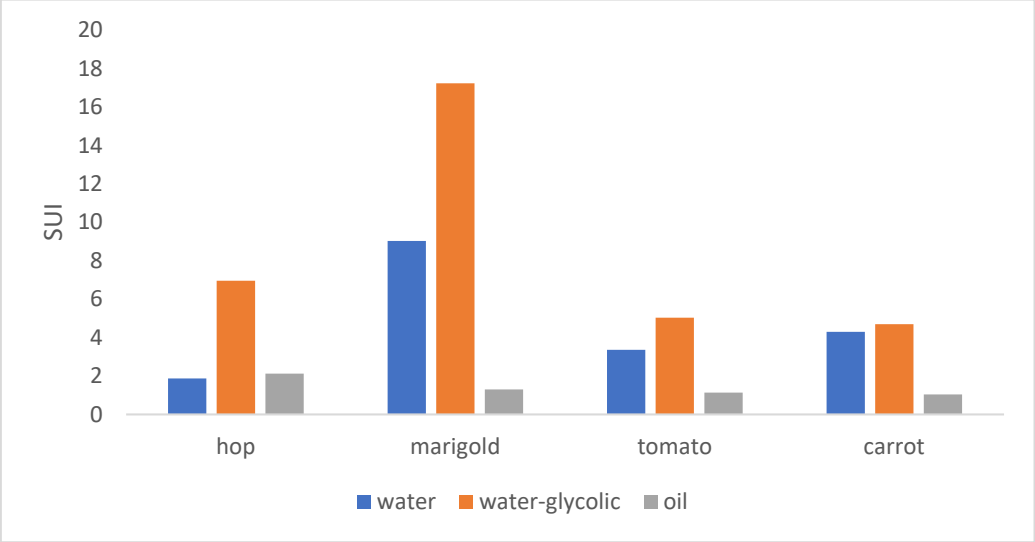

Figure 6. The parameter SUI for different plant extracts with a concentration 0.4 mg/mL.

3.4. Determination of Spectrophotometric SPF in Examined Extracts

In these studies, the following amount of extracts were used: one gram of water, 1 g of water-glycolic and 1 g of oil plant extracts, whereas for water extracts of hop cones and marigold, the amount of two-gram samples were prepared. In the analysis, the diluted samples were examined, and again to dilute the oil extract, we used isopropyl alcohol. The concentrations of extracts were chosen depending on their indicated detection intensity. For the diluted extracts, the spectrophotometric analysis has been done, and absorption spectra were collected in a range of wavelength from 290 to 320 nm. The results obtained were used for a determination of spectrophotometric SPF using the equation provided in the experimental part. All obtained values for spectrophotometric sun protection factor SPF of three types of extracts (water, water-glycolic and oil) and their different concentrations for marigold, hop, tomato and carrot were compiled in Table 4.

Table 4. The SPF for plant extracts at different concentrations.

Type of Extract		Water (1 g)	Water-Glycolic	Oil
Type of Plant	**Concentration [mg Dried Plants/mL Extractant]**	**SPF**	**SPF**	**SPF**
Marigold	0.2	-	-	1.59
	0.4	1.72	2.78	3.35
	0.8	3.70	4.93	6.79
	1.6	7.79	9.84	12.62
Hop	0.1	-	3.18	-
	0.2	1.27	5.80	4.30
	0.4	2.45	10.18	7.40
	0.8	5.58	-	14.19
	1.6	-	-	21.05
Carrot	0.20	0.95	-	1.54
	0.40	1.23	1.14	2.65
	0.80	1.87	1.31	5.54
	1.60	-	-	10.52
	2.00	4.10	2.33	-
	4.00	6.83	3.95	-
Tomato	0.2	0.90	-	1.95
	0.4	1.16	0.82	3.03
	0.8	1.58	1.28	6.24
	1.6	-	2.21	11.61
	2.0	2.99	-	-
	2.4	-	3.18	-
	3.2	-	3.56	-
	4.0	5.46	-	-

Additionally, for 2 g water extract of marigold at concentration 0.8 mg dried plant/mL extractant value for sun protection factor (SPF) was 3.74 and for 2 g water extract of hop of the same concentration was 5.47.

The dependence of spectrophotometric SPF from type of extractant for different plant extracts with a concentration 0.4 mg/mL has been shown in Figure 7.

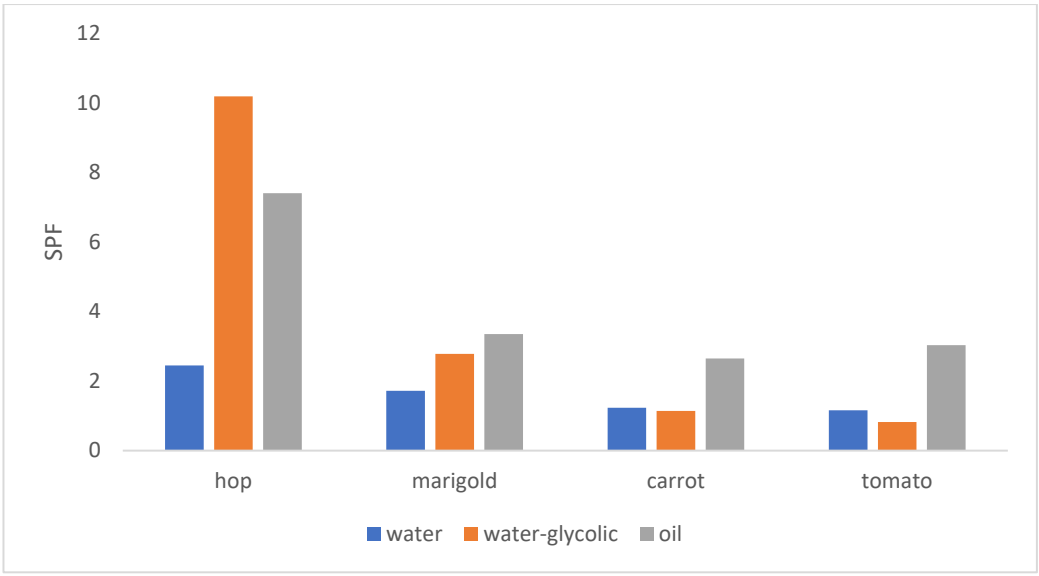

Figure 7. The dependence of spectrophotometric SPF from type of extractant for different plant extracts with a concentration 0.4 mg/mL.

4. Discussion

4.1. Total Phenolic Content

Total phenolic content (TPC) was measured by Folin–Ciocalteu method (TPC) in water and water-glycolic extracts of four different plants. For extracts of tomato, carrot and marigold the obtained results of TPC are similar in both extractants, water and mixture of water and propylene glycol. However, in extracts of hop, the difference in obtained results is significant; in water-glycolic extract, the content of total phenolic content is four times higher than in water extract, and it is the highest among all extracts; in the first extract, the result is 4017.41 ± 131.56 [mgCAE/100 g], while in the second extract it equals 1009.58 ± 31.60 [mg/100 g] of polyphenols expressed as caffeic acid equivalent. In tomato and carrot extracts the amount of investigated compounds is insignificant, with amounts less than 4 and 2, respectively. In water extracts of marigold, the method of fragmentation of material affected the amount of extracted substances. Grinding of dried flowers caused an increase in the extraction area which led to the increase of the quantity of extracted substances; for unground marigold petals, 368.51 ± 58.94 [mgCAE/100 g], and for powdered marigold petals, 1140.53 ± 55.47 [mgCAE/100 g].

The literature describes the methods of isolation and analysis of biologically active compounds, including phenolic compounds found in plant materials. Depending on the solvents used, larger amounts of hydrophilic or hydrophobic polyphenol compounds can be isolated. Our research indicates, except for the carrot extract, that the use of less polar extractant (water-glycol) increases the polyphenolic compounds in the extracts. This indicates that in these matrices, in addition to typically hydrophilic compounds, compounds of lower polarity are present. In the case of carrot extract, the change of the extractant from water to a water-glycol mixture causes a slight decrease in the content of polyphenols [23,24,31,32]. Sun et al. [33] describe research on the determination of the content of polyphenols in carrots. They indicate that the main polyphenols are chlorogenic and caffeic acids, hence the addition of glycol causes a lower extraction efficiency. The total content of polyphenols determined by the authors is at the level of 1.89–38.69 mg/g, depending on the type of raw material, which is a value comparable to the results of our research. Similar results were obtained by Bozolan and Karadeniz [34].

In a paper written by Cetkovic et al. [35], the content of polyphenols and flavonoids in two types of methanol and water marigold extracts was investigated. The authors proved that the content of the studied groups of compounds is slightly higher in water extracts than in methanol ones. The content of polyphenols determined by the Cetkovic et al. is comparable to the value obtained in our research. In the next study, the effect of various solvents on the content of polyphenols, including flavonoids, as well as on the antioxidant activity of marigold extracts was examined. The highest content of the tested compounds and the highest antioxidant activity were found in the aqueous ethanol extract (3:7 v/v). A high correlation was also observed between the content of polyphenols and the antioxidant activity determined by the DPPH, ABTS and FRAP methods [36].

The study of the composition of antioxidants in tomatoes and their antioxidant activity has been the subject of many studies [37–39]. As in the case of marigold, a close correlation was observed between the content of antioxidants (including polyphenols, vitamin C) and the antioxidant activity determined by various methods. Garcia-Alonso et al. studied the effect of the type of extractant on the composition of tomato extracts. Hydrophobic extractants have been found to isolate more carotenoids, including lycopene. In the hydrophilic extracts, polyphenolic compounds, including phenolic acids and flavonoids, constituted the predominant fraction [37]. Toor et al. studied the major antioxidants and antioxidant activity in different fractions (skin, seeds and pulp) of tomato. The obtained results pointed that the skin fraction had higher levels of total phenolics, total flavonoids, lycopene, ascorbic acid and antioxidant activity (ABTS method) [38]. Erge and Karadeniz studied the content of antioxidants (mainly polyphenols, vitamin C and carotenoids) and antioxidant activity of 16 tomato varieties. Like other researchers, they found that the content of antioxidant compounds is different in different varieties of raw material. In addition, they

also observed a close correlation between antioxidant content and antioxidant activity [39]. Bocquet et al. [40] studied the composition of hop secondary metabolites. They found that the tested extracts contain, among others: mono- and sesquiterpenes, polyphenols (phenolic acids, flavonoids, tannins, stilbenes, lignans), alkaloids and humulones and lupulones. Other researchers studied the antioxidant content and antioxidant activity of hop extracts. The results of these studies indicate their high antioxidant potential [41–43]. As in other publications, the authors of the cited works draw attention to the close relationship between the extractant used and the composition of phytochemicals in the extracts. In addition, the dependence of the composition of antioxidants on the type of hop and the part of the plant was observedand analyzed. Each time, attention was drawn to the high antioxidant activity of the extracts tested [41–43].

4.2. Antioxidant Capacity

CUPRAC method was used to determine the antioxidant capacity of extracts obtained from four different plants. In extracts of marigold, carrot and tomato, obtained results were similar in both extractants and the change of solvent did not affect significantly the solubility of substances present in the mentioned plants. However, in extracts obtained from hop cones, type of extractant was important and influenced the antioxidant capacity. In water extracts, results were 232.45 ± 6.33 [CAE mg/100 g], and in water-glycolic extracts, we found 1395.97 ± 22.33 [CAEmg/100 g]; and in the second case, antioxidant capacity was the highest among all extracts. Both carrot extracts containing water and a mixture of water and propylene glycol were characterized by low antioxidant activity (32.33/38.59 [mgCAE/100 g], slightly lower value was for tomato extracts (79.81/127 [mg/100 g] antioxidants expressed as caffeic acid). Similar to the previous investigation from powdered marigold petals, more substances were extracted with antioxidant properties than from unground flower petals. The results were 218.76 ± 11.96 [mgCAE/100 g] and 75.76 ± 9.60 [CAE mg/100 g], respectively. Our results confirm the well-known fact that the use of different extractants affects the amount of isolated compounds and the chemical composition of the extract [31,32]. The analysis of the literature reports on the antioxidant activity of the tested plants, leads to the conclusion that the authors of the works most often use the DPPH, ABTS and FRAP methods for this purpose, using various standard [33–43]. Our research results are similar to those of other researchers. Naturally, the following should be taken into account: the use of different extractants to obtain extracts, different standards, the testing of different parts of plants and different batches of raw materials.

4.3. Method of Mathematical Indication of Radiation Protection

Based on measured absorption spectra in the range of wavelengths from 290 to 400 nm, four parameters of UV protection properties of selected plant extracts of different concentrations were determined. With an increase of concentration of extracts, the absorbance increases relatively proportionally, but the calculated area under curve (AUC) showed that this dependence was not noticeable in every case. Due to this observation, not in all samples of extracts were the increasing values of determined parameters obtained with increasing concentration. The bar charts of four parameters for extracts with concentration equal 0.4 mg/mL showed some dependencies. Parameter UVA/ UVB indicates to what extent the radiation in range of UVA is absorbed in relation to UVB, and it showed that the majority of extracts obtained a maximum number of stars (which mean five stars). The highest values were in the water and water-glycolic extracts of marigold. However, for oil extracts obtained from carrot, tomato and marigold, the result was zero, so these extracts did not meet the conditions of this classification. Considering parameter UVA1/UV, the measured extracts were characterized by low and medium protection level against radiation. Again, the highest value was in the water and water-glycolic extracts of marigold. Generally, the lowest results and the weakest protection level against UV radiation were observed among oil extracts and the highest among water-glycolic extracts. Parameter SUI

indicating the level of protection in a range of UVA radiation for majority extracts were low or medium. As for the previous parameters, water and water-glycolic extracts of marigold obtained the highest results among all extracts; water extracts of this plant showed a high level of UV radiation protection while water-glycolic showed very high results. Again, the best examined properties were found for water-glycolic extracts and the lowest results and the worst properties for oil extracts. Critical wavelength concerning the width of sun protection in almost all extracts according to the classification was maximum, so results were above 370 nm. The longest critical wavelength was observed for water-glycolic tomato extract and was equal 388 nm. Only water extract of hop cones and oil extract of carrot showed an excellent level of radiation protection which means that all examined extracts can protect the skin against UVA and UVB radiation.

4.4. Determination of Spectrophotometric Sun Protection Factor (SPF)

Spectrophotometric SPF for extracts was determined by a method based on absorbance measurements with a range of wavelengths from 290 to 320 nm. Extracts were characterized by their protection against UVB radiation. Oil extracts of selected plants were characterized by the highest values of SPF, except the extract of hop for which the highest values were obtained when mixture of water and glycol was used as an extractant. Due to unsaturated fatty acids, which also have antiradiation protection properties, oil extracts indicated higher values of sun protection factor and increased protection against UVB radiation. In addition, sunflower oil contains vitamin E, which also has a protective effect against UV radiation [44,45] The lowest values were for water extracts of marigold and hop and for water-glycolic extracts of carrot and tomato. Among all extracts, carrot and tomato extracts had the lowest values of SPF and the lowest radiation protection, but significantly higher values of sun protection factor indicated water-glycolic and oil extracts of hop cones. In all measured extracts, with an increase of concentration, the sun protection factor increased linearly (Supplementary Materials). Prepared and examined 1 g and 2 g extracts of hop and marigold of the same concentration had the approximate values of sun protection factor which indicate that increasing amount of dried plant with the same amount of solvent did not cause an appearance of other compounds with radiation protection properties, an only proportional increase of phytochemicals occurred.

There are several analytical methods applied to antioxidant and antioxidant capacity assessment in plant-derived products. Some of them have been reviewed by Pisoschi et al. [46]. All the aspects related to oxidative stress, reactive oxidative species' influence on essential biomolecules, and antioxidant benefits and modalities of action are very crucial in the preparation of cosmetics with high antioxidative and protective potential. Several research results showed that the antioxidative effectiveness of plant extracts depends on the kind of species and the method of analysis [47–51]. Although our results showed that the extracts of marigold, tomato, hop and carrot in low concentrations did not show high protection against UV radiation, it can be assumed they have the potential to be applied in cosmetic formulations, particularly in sunscreen cosmetics. In our future work, several cosmetic formulations using the above-mentioned extracts are planned for study.

It has been shown that hop extract had not only antioxidant properties but also anti-inflammatory effects in human primary keratinocytes [52]. Moreover, the antimicrobial activities against both *P. acnes* and *S. aureus* have been found [53]. The usefulness of antioxidants in cosmetics has been reviewed by Lupo [54]. It is commonly known that the topical use of antioxidants in cosmetics can better protect and possibly correct the damage of the skin by neutralizing free radicals and, in the final effect, act as an antiaging agent. Human skin as the main organ of the human body, is constantly exposed to external factors, which can generate free radicals, so there is a continual need for testing the antioxidative properties of several plant extracts. Recently, natural antioxidants from plant extracts in skincare cosmetics have been reviewed by [55]. It has been stated that the interest in the health effects of natural antioxidants has increased due to their safety and applicability in cosmetic formulation. Without any doubt, natural plant extracts derived from both

naturally occurring plants and also from industrially processed plants have a great potential to create natural topical antioxidants.

5. Conclusions

To sum up, all obtained results showed that the extracts of marigold, tomato, hop and carrot in low concentrations did not show high protection against UV radiation, but they have the potential for application in cosmetic formulation, particularly in sunscreen cosmetics together with chemical and physical sunscreen filters enhancing the UV radiation protection effect. The results of sun protection factor (SPF) for oil extracts, especially for those in higher concentrations, are very promising and can have the potential to be used in cosmetic formulation. However, additional research should be conducted to check whether the analyzed concentrations of extracts can be applied in cosmetic formula and are safe for consumers. On the basis of the obtained results, we can conclude that the ability to absorb radiation showed extracts of marigold can be used as a valuable cosmetic ingredient in different products. The highest content of polyphenol compounds and the highest antioxidant capacity that can protect against the negative impact of free radicals was found for extracts of hop cones, which have the potential to be applied in anti-aging cosmetics.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cosmetics9060134/s1; Figure S1. The dependence of the protection factor on the concentration of the tomato water extracts. Figure S2. The dependence of the protection factor on the concentration of the tomato water-glycol extracts. Figure S3. The dependence of the protection factor on the concentration of the tomato oil extracts.

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References

1. Kiriiri, G.; Mwangi, A.N.; Maru, S.M. Sunscreen products: Rationale for use, formulation development and regulatory considerations. *Saudi Pharm. J.* **2019**, *27*, 1009–1018.
2. Schmalwieser, A.W.; Casale, G.R.; Colosimo, A.; Schmalwieser, S.S.; Siani, A.M. Review on Occupational Personal Solar UV Exposure Measurements. *Atmosphere* **2021**, *12*, 142. [CrossRef]
3. Egambaram, O.P.; Pillai, S.K.; Ray, S.S. Materials Science Challenges in Skin UV Protection: A Review. *Photochem. Photobiol.* **2019**, *96*, 779–797. [CrossRef] [PubMed]
4. Gromkowska-Kępka, K.J.; Puścion-Jakubik, A.; Markiewicz-Żukowska, R.; Socha, K. The impact of ultraviolet radiation on skin photoaging—Review of in vitro studies. *J. Cosmet. Dermatol.* **2021**, *20*, 3427–3431. [CrossRef] [PubMed]
5. Lopes, F.C.P.S.; Sleiman, M.G.; Sebastian, K.; Bogucka, R.; Jacobs, E.A.; Adamson, A.S. UV Exposure and the Risk of Cuta-neous Melanoma in Skin of Color a Systematic Review. *JAMA Dermatol.* **2021**, *157*, 213–219. [CrossRef]
6. Scheuer, C.; Pommergaard, H.C.; Rosenberg, J.; Gogenur, J. Melatonin's Protective Effect Against UV Radiation: A Systematic Review of Clinical and Experimental Studies. *Photodermatol. Photoimmunol. Photomed.* **2014**, *30*, 180–188. [CrossRef]
7. Priyanka, K.G.; Mayuri, S.; Rashmi, S. Natural Sunscreen Agents: A Review. *Sch. Acad. J. Pharm.* **2013**, *2*, 458–463.
8. Sarbak, Z.; Jachymska-Sarbak, B.; Sarbak, A. *Chemia w Kosmetyce i Kosmetologii*; MedPharm Polska: Wrocław, Poland, 2013.
9. Schueller, R.; Romanowski, P. *Beginning Cosmetic Chemistry*, 3rd ed.; Allured Business Media: Carol Stream, IL, USA, 2009.
10. Lamer-Zarawska, E.; Chwała, C.; Gwardys, A. *Rośliny w Kosmetyce i Kosmetologii Przeciwstarzeniowej*; Wydawnictwo Lekarskie PZWL: Warszawa, Poland, 2012.
11. Schueller, R.; Romanowski, P. *Multifunctional Cosmetics*; Marcel Dekker Inc.: New York, NY, USA, 2001.

12. Martini, M.-C. *Kosmetologia i Farmakologia Skóry*; Wydawnictwo Lekarskie PZWL: Warszawa, Poland, 2009.
13. Sikora, E.; Olszańska, M.; Ogonowski, J. *Chemia i Technologia Kosmetyków*; Wydawnictwo Politechniki Krakowskiej im. Tadeusza Kościuszki: Kraków, Poland, 2012.
14. Moyal, D. The development of efficient sunscreens. *Indian J. Dermatol. Venereol. Leprol.* **2012**, *78*, 31–34. [CrossRef]
15. Wang, S.Q.; Tanner, P.R.; Lim, H.W.; Nash, J.F. The evolution of sunscreen products in the United States—A 12-year cross sectional study. *Photochem. Photobiol. Sci.* **2013**, *12*, 197–202. [CrossRef]
16. Nunes, A.R.; Rodrigues, A.L.M.; de Queiróz, D.B.; Vieira, I.G.P.; Neto, J.F.C.; Junior, J.T.C.; Tintino, S.R.; de Morais, S.M.; Coutinho, H.D.M. Photoprotective potential of medicinal plants from Cerrado biome (Brazil) in relation to phenolic content and antioxidant activity. *J. Photochem. Photobiol. B Biol.* **2018**, *189*, 119–123. [CrossRef]
17. Napagoda, M.T.; Malkanthi, B.M.A.S.; Abayawardana, S.A.K.; Qader, M.M.; Jayasinghe, L. Photoprotective potential in some medicinal plants used to treat skin diseases in Sri Lanka. *BMC Complement. Altern. Med.* **2016**, *16*, 147. [CrossRef]
18. Polonini, H.C.; Brandão, M.A.F.; Raposo, N.R.B. A natural broad-spectrum sunscreen formulated from the dried extract of Brazilian *Lippia sericea* as a single UV filter. *RSC Adv.* **2014**, *4*, 62566–62575. [CrossRef]
19. Cefali, L.C.; Ataide, J.A.; Fernandes, A.R.; Sousa, I.M.D.O.; Gonçalves, F.C.D.S.; Eberlin, S.; Dávila, J.L.; Jozala, A.F.; Chaud, M.V.; Sanchez-Lopez, E.; et al. Flavonoid-Enriched Plant-Extract-Loaded Emulsion: A Novel Phytocosmetic Sunscreen Formulation with Antioxidant Properties. *Antioxidants* **2019**, *8*, 443. [CrossRef]
20. Baldisserotto, A.; Buso, P.; Radice, M.; Dissette, V.; Lampronti, I.; Gambari, R.; Manfredini, S.; Vertuani, S. *Moringa oleifera* Leaf Extracts as Multifunctional Ingredients for "Natural and Organic" Sunscreens and Photoprotective Preparations. *Molecules* **2018**, *23*, 664. [CrossRef]
21. Schueller, R.; Romanowski, P. *Conditioning Agents for Hair and Skin*; Marcel Dekker Inc.: New York, NY, USA, 1999.
22. Cieszyńska, A.; Wieczorek, D. Estimation and Comparison of Ultraviolet Protection Properties of Essential Oil, Infusion and Extracts of Hop (*Humulus lupulus* L.). *Towarozn. Probl. Jakości* **2016**, *1*, 115–125.
23. Unny, R.; Chauhan, A.K.; Joshi, Y.C. A Review on Potentiality of Medicinal Plants as the Source of New Contraceptive Principles. *Phytomedicine* **2016**, *10*, 233–260. [CrossRef]
24. Tiwari, B.K.; Brunton, N.P.; Brennan, C.S. *Handbook of Plant Food Phytochemicals Sources, Stability and Extraction*; John Wiley & Sons Ltd.: Oxford, UK, 2013.
25. Amparo, S.; Chisvert, A. *Analysis of Cosmetic Products*; Elsevier: Amsterdam, The Netherlands, 2007.
26. Rawson, A.; Patras, A.; Oomah, B.D.; Campos-Vega, R.; Hossain, M.B. Antioxidant Activity of Phytochemicals and Their Method of Analysis. *Adv. Food Sci. Nutr.* **2013**, *2*, 153–256. [CrossRef]
27. Apak, R.; Güçlü, K.; Özyürek, M.; Celik, S.E. Mechanism of antioxidant capacity assays and the CUPRAC (cupric ion reducing antioxidant capacity) assay. *Microchim. Acta* **2007**, *160*, 413–419. [CrossRef]
28. Timoumi, R.; Salem, I.B.; Amara, I.; Anabi, E.; Abid-Esefi, E. Protective Effects of Fennel Essential Oil Against Oxidative Stress and Genotoxicity Induced by the Insecticide Triflumuron in Human Colon Carcinoma Cells. *Environ. Sci. Pollut. Res. Int.* **2020**, *27*, 7957–7966. [CrossRef]
29. Suva, M.A. Evaluation of Sun Protection Factor of Zingiber Officinale Roscoe Extract by Ultraviolet Spectroscopy Method. *J. Pharma Sci. Technol.* **2014**, *3*, 95–97.
30. Dutra, E.A.; Oliveira, D.A.G.D.C.; Kedor-Hackmann, E.R.M.; Santoro, M.I.R.M. Determination of sun protection factor (SPF) of sunscreens by ultraviolet spectrophotometry. *Rev. Bras. Ciências Farm.* **2004**, *40*, 381–385. [CrossRef]
31. Conde, E.; Moure, A.; Domínguez, H.; Parajó, J. Extraction of natural antioxidants from plant foods. In *Separation, Extraction and Concentration Processes in the Food, Beverage and Nutraceutical Industries*; Elsevier: Amsterdam, The Netherlands, 2013; pp. 506–594. [CrossRef]
32. Cannell, R.J.P. *Natural Products Isolation*; Humana Press Inc.: Totowa, NJ, USA, 1998.
33. Sun, T.; Simon, P.; Tanumihardjo, S.A. Antioxidant Phytochemicals and Antioxidant Capacity of Biofortified Carrots (*Daucus carota* L.) of Various Colors. *J. Agric. Food Chem.* **2009**, *57*, 4142–4147. [CrossRef] [PubMed]
34. Bozalan, N.C.; Karadeniz, F. Carotenoid Profile, Total Phenolic Content, and Antioxidant Activity of Carrots. *Int. J Food Prop.* **2011**, *14*, 1060–1068. [CrossRef]
35. Ćetković, G.S.; Djilas, S.M.; Čanadanović-Brunet, J.M.; Tumbas, V.T. Antioxidant properties of marigold extracts. *Food Res. Int.* **2004**, *37*, 643–650. [CrossRef]
36. Gong, Y.; Liu, X.; He, W.-H.; Xu, H.-G.; Yuan, F.; Gao, Y.-X. Investigation into the antioxidant activity and chemical composition of alcoholic extracts from defatted marigold (*Tagetes erecta* L.) residue. *Fitoterapia* **2012**, *83*, 481–489. [CrossRef]
37. García-Alonso, F.; Navarro-González, I.; Ros, G.; Periago, M. Assessment of the antioxidant properties of tomato extracts: A synergistic approach using in vitro chemical tests and cell-based assays. *Acta Aliment.* **2015**, *44*, 297–303. [CrossRef]
38. Toor, R.K.; Savage, G.P. Antioxidant activity in different fractions of tomatoes. *Food Res. Int.* **2005**, *38*, 487–494. [CrossRef]
39. Erge, H.S.; Karadenism, F. Bioactive compounds and antioxidant activity of tomato cultivars. *Int. J Food Prop.* **2011**, *14*, 968–977. [CrossRef]
40. Bocquet, L.; Sahpaz, S.; Hilbert, J.L.; Rambaud, C.; Rivière, C. *Humulus lupulus* L., a very popular beer ingredient and medicinal plant: Overview of its phytochemistry, its bioactivity, and its biotechnology. *Phytochem. Rev.* **2018**, *17*, 1047–1090. [CrossRef]

41. Önder, F.C.; Ay, M.; Sarker, S.D. Comparative study of antioxidant properties and total phenolic content of the extracts of *Humulus lupulus* L. and quantification of bioactive components by LC-MS/MS and GC-MS. *J. Agric Food Chem.* **2013**, *61*, 10498–10506.
42. Maietti, A.; Brighenti, V.; Bonetti, G.; Tedeschi, P.; Prencipe, F.P.; Benvenuti, S. Metabolite profil-Metabolite profiling of flavonols and in vitro antioxidant activity of young shoots of wild *Humulus lupulus* L. (hop). *J. Pharm. Biomed. Anal.* **2017**, *142*, 28–34. [CrossRef]
43. Abram, V.; Čeh, B.; Vidmar, M.; Hercezi, M.; Lazić, N.; Bucik, V.; Možina, S.S.; Košir, I.J.; Kač, M.; Demšar, L.; et al. A comparison of antioxidant and antimicrobial activity between hop leaves and hop cones. *Ind. Crop. Prod.* **2015**, *64*, 124–134. [CrossRef]
44. Rowe, R.C.; Sheskey, P.J.; Owen, S.C. *Handbook of Pharmaceutic Excipients*, 6th ed.; Pharmaceutical Press and American Pharmacist Association: London, UK, 2009; pp. 721–722.
45. Idson, B. Vitamins in Cosmetics, An Update Part II: Vitamin E. *Drug Cosmet. Ind.* **1990**, *147*, 20–25.
46. Pisoschi, A.M.; Pop, A.; Cimpeanu, C.; Predoi, G. Antioxidant Capacity Determination in Plants and Plant-Derived Products: A Review. *Oxidative Med. Cell. Longev.* **2016**, *2016*, 9130976. [CrossRef]
47. Amendola, D.; De Faveri, D.; Spigno, G. Grape marc phenolics: Extraction kinetics, quality and stability of extracts. *J. Food Eng.* **2010**, *97*, 384–392. [CrossRef]
48. Ouchemoukh, S.; Hachoud, S.; Boudraham, H.; Mokrani, A.; Louaileche, H. Antioxidant activities of some dried fruits consumed in Algeria. *LWT* **2012**, *49*, 329–332. [CrossRef]
49. Adnan, L.; Osman, A.; Hamid, A.A. Antioxidant Activity of Different Extracts of Red Pitaya (*Hylocereus polyrhizus*) Seed. *Int. J. Food Prop.* **2011**, *14*, 1171–1181. [CrossRef]
50. Šamec, D.; Durgo, K.; Grúz, J.; Kremer, D.; Kosalec, I.; Piljac-Žegarac, J.; Salopek-Sondi, B. Genetic and phytochemical variability of six *Teucrium arduini* L. populations and their antioxidant/prooxidant behaviour examined by biochemical, macromolecule- and cell-based approaches. *Food Chem.* **2015**, *186*, 298–305. [CrossRef]
51. Arora, N.; Pandey-Rai, S. GC-MS analysis of the essential oil of *Celastrus paniculatus* Willd: Seeds and antioxidant, anti-inflammatory study of its various solvent extracts. *Ind. Crops Prod.* **2014**, *61*, 345–351. [CrossRef]
52. Weber, N.; Biehler, K.; Schwabe, K.; Haarhaus, B.; Quirin, K.-W.; Frank, U.; Schempp, C.M.; Wölfle, U. Hop Extract Acts as an Antioxidant with Antimicrobial Effects against *Propionibacterium acnes* and *Staphylococcus aureus*. *Molecules* **2019**, *24*, 223. [CrossRef]
53. Sinha, P.; Srivastava, S.; Mishra, N.; Yadav, N.P. New Perspectives on Antiacne Plant Drugs: Contribution to Modern Therapeutics. *BioMed Res. Int.* **2014**, *2014*, 301304. [CrossRef] [PubMed]
54. Lupo, M.P. Antioxidants and vitamins in cosmetics. *Clin. Dermatol.* **2001**, *19*, 467–473. [CrossRef] [PubMed]
55. Hoang, H.T.; Moon, J.-Y.; Lee, Y.-C. Natural Antioxidants from Plant Extracts in Skincare Cosmetics: Recent Applications, Challenges and Perspectives. *Cosmetics* **2021**, *8*, 106. [CrossRef]