Exploring Plant-Based Cooking Oils as a Promising Topical Alternative to Sunscreen

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ABSTRACT

Sunscreens protect the skin from the harmful effects of Ultraviolet radiation in the sunlight. However, most commercial sunscreens pose health and environmental hazards, lose effectivity over time, or are simply unpleasant to use, making it imperative to search for greener, safer, and efficacious alternatives. Plant-based oil extractions are promising given their hydrophobicity, nontoxicity, and availability. This paper aims to determine the absorptive capabilities of five common cooking (vegetable) oils using UVA spectrophotometry and analyze the properties of the oils that relate to their efficacy. Oils high in tocols, such as Rice Bran Oil, had the highest extinction coefficient. The analysis suggests that plant-based oil extractions high in phytonutrients with aromatic rings and π-systems, such as tocols and carotenoids, present the greatest potential to serve as UV chemical filters.

Background

Excessive exposure to the harmful ultraviolet (UV) radiation in sunlight can cause skin damage, from erythema to skin cancers. UV radiation wavelengths range from 200 nm to 400 nm and can be divided into UVA (320–400 nm), UVB (280–320 nm), and UVC (200–280 nm).[1,2] Although UVC is blocked by the ozone layer of the atmosphere, UVA and UVB can still pass through, of which UVA comprises over 90% of sun rays.[2] Since UVA has a longer wavelength, UVA can penetrate deeper into the skin as compared to UVB but has less energy.[1,3] UVA can especially reach keratinocytes of the stratum basale, where most of the damage manifests, such as immunosuppression and photocarcinogenesis.[4,5] Particularly, UVB is mostly absorbed by the epidermis (outermost layer) at most, while UVA can penetrate deeper into the dermis.[4]

Skin exposure to UV rays can induce a photoreactivation reaction in DNA and form UV-induced pyrimidine dimers or lead to oxidative damage by generating oxygen radicals.[1,3] Unless these photoreactions can be reversed by antioxidants such as Vitamin C and E, or DNA nuclear excision repair (NER), these damages can subsequently manifest into skin damage and malignancies.[6–8] Epidemiologic data suggest that UV radiation is directly responsible for most melanoma and non-melanoma skin cancers.[9] General protective measures have been developed and advocated to reduce the risk of UV-related pathologies from sunlight. These include preventative strategies such as minimizing outdoor times during peak UV hours, to incorporating protective attire.[10] Topical products known as sunscreens are also available commercially to protect against harmful UV radiation.

Sunscreens

Sunscreen chemicals can be categorized into two types: mineral filters and chemical filters.[11,12] Mineral filters serve to scatter UV radiation and are also known as sunblocks.[12] Common mineral filters include titanium dioxide (TiO_2) and zinc oxide (ZnO) due to their inert nature and broad-spectrum properties.[12,13] However, there are safety concerns with these nanoparticles.[13] TiO_2 has been classified by the International Agency for Research on Cancer (IARC) as an IARC Group 2B carcinogen, and topical application may impose risks through the respiratory or digestive tracts.[14–16]

Further, mineral filters are generally unpleasant due to their adhesive properties and are difficult to design.[17,18] Conversely, chemical filters absorb UV rays before they can penetrate the skin, and dissipate the radiation as heat.[19] Avobenzone, oxybenzone, and octinoxate are common active ingredients.[20] However, these ingredients contaminate marine ecosystems and are suspected to adversely impact the endocrine system given their transdermal penetration capabilities.[12,21–23]

In general, several compounds present in commercially available sunscreens, whether mineral or chemical filters, are not suitable for all populations and can serve as skin irritants themselves. They also may not be practical and can easily wash away with water. Several products also have questionable photostability or compound stability upon UV radiation exposure.[24,25] Therefore, regardless of how well a sunscreen can absorb or scatter UV rays, its efficacy deteriorates over time upon sunlight exposure.[25] Thus, it has been imperative in recent years to develop sunscreens that are effective and safe for wide use.

Whereas mineral filters are developed based on scattering capability, chemical filters are considered based on absorptive capabilities. However, across all sunscreens, inertness, photostability, hydrophobicity, nontoxicity, appeal, emollience, and acceptable smell are all qualities key to designing a good sunscreen.[26,27] Inertness and nontoxicity allow the filter for safe topical use without irritating the skin.[12] Hydrophobicity ensures that the filter does not wash away with water.[28,29] Emollience confers consistency and smoothness upon topical application.[30] Having good appeal and having an acceptable fragrance would not deter individuals from applying it.[18]

Chemical filters are typically molecules with extensive conjugated π systems leading up to a carbonyl group.[31,32] Conjugation refers to alternating double bonds, such that every adjacent carbon is sp^2-hybridized and connected by p orbitals. This extensive conjugation will allow the molecule to absorb at a longer wavelength, making it especially effective against UVA radiation. The body's natural pigment, melanin, protects against UV radiation and has extensive conjugation.[33,34] The absorptive power at a particular wavelength is also crucial in determining effectivity. A high molar absorptivity constant, or extinction coefficient, suggests that the compound can absorb more UV radiation and implies high photostability.[5,35]

Oils as Alternatives

Oils are triacylglycerols with melting points below room temperature and are therefore liquids.[36,37] As the degree of unsaturation increases, the melting point reduces. Further, *trans* π bonds (substituents about the π bond point in opposite directions) have higher melting points due to strong packing. Oils also contain emollient properties and their hydrophobicity, consistency, scent, and nontoxicity provide for widespread topical application.[38] Vegetable (cooking) oils, in particular, are unique in that they are triacylglycerols with different proportions along with free phytonutrients and tocols, such as vitamin E.[39,40] Tocopherols and tocotrienols demonstrate antioxidant ability and are amphipathic molecules, with a chromanol ring system and an alkyl chain.[41–43] Whereas tocopherols have a saturated alkyl chain, tocotrienols have units of unsaturation on their chain. Figure 1 depicts the general structure of tocols.

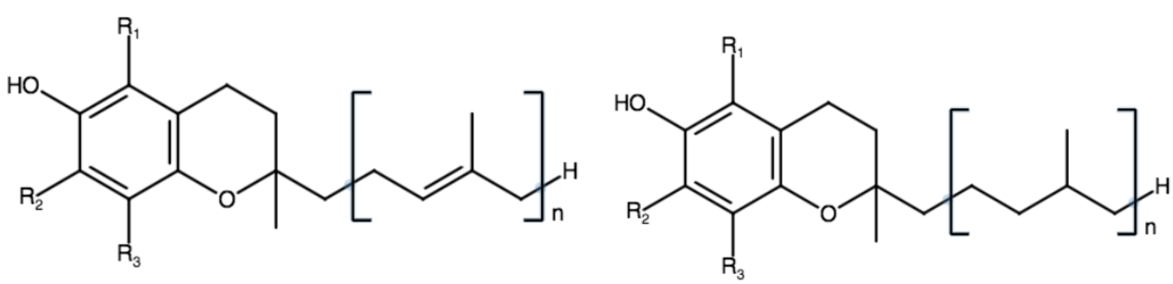

Figure 1. Tocotrienols (left) and Tocopherols (right)

Little research has been done in evaluating the potential of vegetable oils to serve as a chemical filter for sunscreens. The oils are obtained by extraction of dried plant leaves or fruit rind. Table 1 depicts the percent saturation and approximate concentration of tocols in various cooking oils used in the study.[44–46] Although exact figures may differ by brand and oil extraction method, Almond oil has the greatest concentrations of unsaturated fatty acids overall. Furthermore, Grapeseed oil has the highest concentration of polyunsaturated fats, particularly linoleic acid. Meanwhile, Rice Bran oil had the highest total tocopherols.

Table 1. Common Cooking oils, their percent saturated fat breakdown, and total tocols (mg/kg). Exact values vary by brand. *It is hypothesized that the oil with the greatest tocol content will be most effective in absorbing UVA radiation.*

Cooking Oil	% Saturated Fat	Total Tocols (mg/kg)
Almond	6%	528.28
Avocado	8%	222.65
Grape Seed	7%	454
Rice Bran	14%	867.2
Sunflower	8%	768

Methods

The objective of this investigation is to assess the UVA absorptive capabilities of common vegetable (cooking) oils.[47] UV-Vis spectrophotometry was used to obtain absorption spectra for the pure oils and determine the wavelength of maximum absorption (λ_{max}) in the UVA range. The photostability of the oils was determined by performing serial dilutions of the oils to obtain a standard curve and compute the extinction coefficient ε at the wavelength of maximum absorption using the Beer-Lambert Law, $A = \varepsilon Lc$, where A is the absorbance, L is the path length (1 cm), and c is the concentration (M).

5E-5 M solutions were made using molar equivalents of each cooking oil in a coconut oil solvent, followed by reflux. The standard curve was obtained following serial dilutions, to determine the concentration at 5E-5 M, 5.6E-5 M, 6.4E-5 M, 7.5E-5 M, and 9E-5 M. Observable properties such as hue were noted.

The following cooking oils were tested: Rice Bran Oil, Sunflower Oil, Grape Seed Oil, Avocado Oil, and Almond Oil. Coconut oil was used as a solvent. Distilled water was used as a blanking solution.

Results

The oils were tested in the UVA range, from 320–400 nm. Figure 2 depicts the absorption spectra of the oils, with the average peak absorption among the 100% cooking oils at λ_{max}=330 nm. For all oils, the absorbance spectra were right-skewed, and the peak for the average absorption was 330 nm.

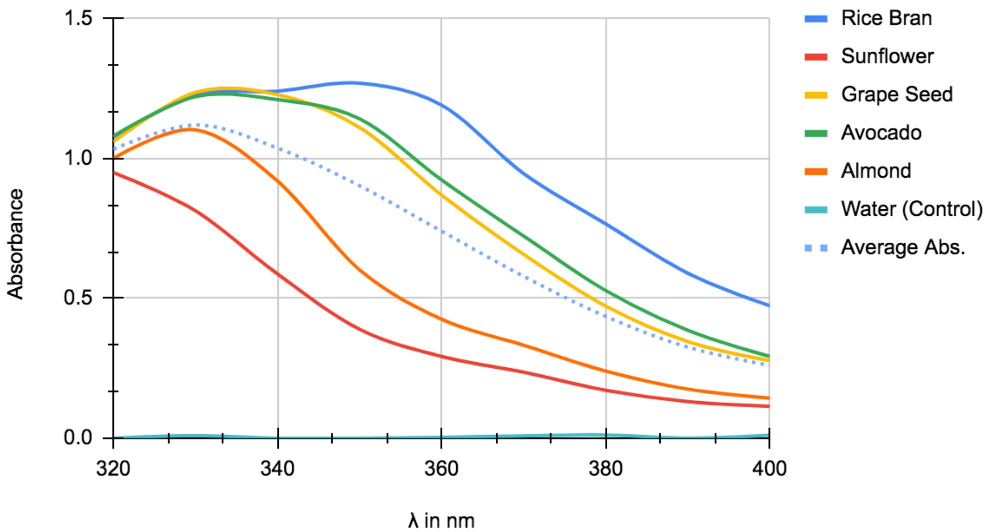

Figure 2. Absorption Spectra for Pure Oils. UVA absorption spectra of tested oils, blanking solution (water), and the average among oils.

The standard curve for each of the oils was made at λ_{max}=330 nm to calculate their extinction coefficient at 330 nm (ε_{330}). The solvent's absorbance at 330 nm was 0.620. Absorbances for each oil were obtained at the five different concentrations using serial dilutions. Points following the linear portion of the standard curve were used to determine ε_{330} for each oil (Table 1). The absorption maximum for sunflower oil could not be concluded from figure 1 as the UV-Vis spectrophotometer used only covered UVA-equivalent wavelengths.

Table 2. Extinction coefficient (ε_{330}) of tested oils.

Cooking Oil	Rice Bran	Sunflower	Grape Seed	Avocado	Almond
ε_{340} ($M^{-1}cm^{-1}$)	3825	661	2215	1676	550

After stirring and refluxing the cooking oil solutions in their coconut oil solvent, all of the oil solutions were transparent. The Rice Bran oil had an observable yellow hue, which was also faintly present in the Grape Seed and Avocado oils. These observations complement the results of the study.

Discussion

The absorbance spectra and extinction coefficient suggest that Rice Bran was able to absorb to the greatest extent at UVA-equivalent wavelengths without disintegrating. Particularly, Rice Bran oil had the highest absorbances among all the oils throughout the UVA range tested, followed by Avocado and Grape Seed oils. The extinction coefficients also agree with this analysis: Rice Bran Oil had more than double the ε_{330} as compared to Grape Seed Oil, and triple as compared to Avocado. The visual observations also complement the results of the study. The Rice Bran vial had a yellow hue, suggesting the ability to absorb deep-violet wavelengths. The yellow color could be due to the presence of tocopherols, which serve as yellow chromophores. Hence, Rice Bran can also be protective against some forms of visible-light-induced skin damage, such as erythema.[48,49]

It was originally expected that the oil with the most tocol content, in this case, Rice Bran oil, would have the greatest absorptive power. The results agreed with the hypothesis. The presence of the conjugated π-systems on the tocol allows for n-π^* and π-π^* electronic transitions. However, the results could not be explained by the proportion of unsaturated fatty acids. As the concentration of unsaturated fats increases, it would be expected that the λ_{max} and extinction coefficient would also increase. Nevertheless, this was not demonstrated. The conjugated π-systems of the tocols may have been more influential as compared to the presence of unsaturated fatty acids.

A similar study by Kaur et al. tested the absorbances of various herbal oils from 290–320 nm using the same UV spectrophotometric method applied in this study.[50] The study used absorbances to determine the sun-protection factor (SPF) of the herbal oils. Among the 12 herbal oils they studied, there was not a clear correlation between the concentration of unsaturated fats and absorptive power or SPF, which was also the case in this study. Coconut oil, consisting of almost 80% of saturated fat had one of the highest SPF. This points to other compounds present in the oils such as phytonutrients, or compounds present in plants, with aromatic ring structures and large conjugated π-systems, or traces of transition metals such as manganese.

Considering the natural antioxidant activity of tocols, sunscreens can incorporate oils high in antioxidants.[6,51,52] Antioxidants can protect against damage from oxygen radicals and stabilize UV chemical filters. The results present oils as a cost-effective chemical filter, as vegetable oils are much more widely available and economical as compared to other emulsifiers or chemicals in sunscreens with the same efficacy. Sunscreens can also incorporate plants high various phytonutrients with conjugated π systems, such as carotenoids, and perform extractions to produce and test their oils.

This paper adds to a growing collection of research searching for safe and efficacious sunscreen alternatives. The results and literature review point to the promising aspect of oils as a potential chemical filter. Future research can examine the potential of extracted tocols, conjugated fatty acid systems, or carotenoids and design chemical filters using these compounds. Studies can also test the absorptive capabilities of extracted oils from plants high in the abovementioned phytonutrients. Future studies can also test the efficacy of vegetable oils in other factors that are key to designing good sunscreens. The conclusions from this paper encourage studying or manipulating oils to design more efficient, safer, and economical sunscreens.

A future phase of this study can build upon the results and study the photostability of various cooking oils by identifying changes in the physical and chemical properties after sunlight exposure. A common problem with conventional sunscreens is the photo-destabilization of chemical filters upon sunlight exposure. The instability of chemical filters can jeopardize their efficacy in protecting the skin and thus warrant reapplication after a certain duration of time. This information can help determine other factors that are key to designing good sunscreens.

Conclusion

In conclusion, the objective of this study was to determine the efficacy of common household cooking oils in absorbing UVA-equivalent wavelengths. It was originally hypothesized that high tocol content would confer a greater influence over the degree of unsaturated fatty acids, and this was reflected in the UV spectrophotometric results. Rice Bran oil emerged as the most promising oil with the highest extinction coefficient (ε) at 330 nm, although all of the compounds tested have the potential to be incorporated as UV chemical filters. Oils high in various phytonutrients with aromatic structures, such as tocols and carotenoids, carry the highest potential to serve as UV chemical filters. Future studies can identify oil extractions high in these phytonutrients, test their efficacy and safety, and move forward to implement them in sunscreens.

Limitations

The study results are restricted to UVA-equivalent wavelengths and thus offer a limited view of how efficient the oils are in protecting against UVB wavelengths. Thus, the absorbance maximum for Sunflower Seed oil could not be determined. Although UVA wavelength comprises most of the sunlight and penetrates deeper into the skin, UVB has higher energy and can be much more detrimental. Another limitation is that the contribution of other compounds present in the oils in absorbing the UV radiation could not be determined. In future, this could be addressed by employing chromatographic techniques to separate compounds and individually test their function.

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