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SUN SCREENING METHOD USING ACETYLATED p-AMINO-CINNAMATES

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No Drawing. Continuation of application Ser. No. 679,123, Aug. 20, 1957. This application Dec. 10, 1959, Ser. No. 858,596

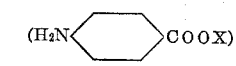
6 Claims. (Cl. 167—90)

The present invention is directed to sunscreen compositions and more particularly to such compounds which have improved protective properties. This application is a continuation of co-pending application Serial No. 679,123, filed August 20, 1957, now abandoned.

It is well established that the essential causative fact in producing sun burn on the human skin is the erythema producing radiation of the ultra-violet spectrum of sunlight and of artificial radiation, such as that produced by therapeutic lamps, mercury arc lamps and the like. The essential function of an effective sun-screening agent is the substantial absorption of radiant energy in the ultraviolet portion of the spectrum lying between approximately 2900 and 3200 Angstrom units. Sunscreen preparations have been formulated as alcoholic solutions or lotions and as emulsified products, such as non-toxic cosmetically acceptable creams.

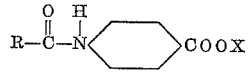
In the past, a wide variety of chemical compounds have been proposed for formulation into compositions which, when topically applied, afford protection to the human skin against such radiation-induced erythema. The purpose of these various compositions is to apply to the skin a film or coating in which the erythematogenic wave-absorbents are finely distributed. The compounds generally employed for this purpose comprise the alkyl and alkylol esters of p-aminobenzoic acid.

The amino group present in sunscreening compounds of this general type of aminobenzoic esters



is susceptible to oxidation and on exposure to air, it oxidizes with the consequent development of highly colored products which form difficultly removable stains on the apparel of the user. This staining has posed a problem to the art which is well recognized.

It is known that the staining propensities of this type of screening agent may be avoided by acylating the amino group in any convenient manner to form compounds of the general type:



However such acylation results in shifting of the ultraviolet absorption spectra of the compounds, thus drastically reducing the absorption efficiency of the essential absorptive agents and commensurably reducing the protective effect afforded by the original unacylated compounds. Up to the present time it was not possible to obtain effective stabilization of the basic sunscreening compounds without impairing their screening efficiency.

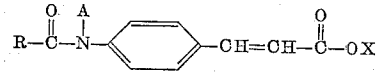
The present invention is intended and adapted to overcome the deficiencies in sunscreen compositions of the above type, it being among the objects thereof to provide a composition which is highly efficient in screening out erythema radiations and rendering the same safer to use.

It is also among the objects of the invention to provide a composition for the purpose described which avoids the staining characteristics of prior compositions.

It is further among the objects of the invention to provide stable compounds for said purpose having not only

a substantially higher ray-filtering or screening efficiency but having combined therewith the non-staining property.

In practicing the invention, it has been found that this desirable double function i.e. tinctorial stabilization and retention of filtering efficiency, may be achieved in a simple and efficacious manner. It has been determined that a series of non-staining sunscreening compounds of the desirable selective, specific absorption for the erythematogenic range of ultra-violet radiation, may be produced by acylating p-amino-cinnamic acid to produce compounds having the characteristic structure:



where R may be hydrogen, an alkyl group having 1 to 4 carbon atoms; and X may be hydrogen, and an alkyl group having 1 to 4 carbon atoms; and A may be hydrogen, alkyl having 1 to 4 carbon atoms.

These compounds are characterized by a high selective absorption for ultra-violet radiation of energy equivalent to wave lengths of from 2900 to 3200 Angstrom units. The compounds containing the acylated amino group of the amino-cinnamic acid all are characterized by a high resistance to oxidation and are therefore non-staining. The employment of the basic amino-cinnamic nucleus in the compounds does not inhibit or eliminate the shift in the spectral absorption pattern. But the basic amino-cinnamic nucleus absorbs at higher wave-lengths than does the aminobenzoic nucleus. Upon acetylation of the amino-cinnamic nucleus, the shift in absorption is such that the acetylated amino-cinnamate absorbs in the same spectral range as does the unacetylated aminobenzoic nucleus, thus preserving the absorption efficiency upon acetylation. The novel sunscreening agents may not only comprise acetylated p-amino cinnamic acid but also its derivatives.

Acetylated amino-cinnamates may be incorporated into cosmetic products by dissolution in suitable lower aliphatic alcohols to form lotions, or they may be incorporated in a sun-tan cream by emulsification with suitable vegetable or mineral oils together with the typical adjuvants of such creams, such as stearic acid, ethylene glycol monostearate, wetting agents etc. in the manner and procedures well-known to the art.

Typical examples of sunscreen compositions made in accordance with the invention are as follows:

Example 1

Typical lotion:	Parts by weight
Ethyl-p-acetamidocinnamate	1.5
SDA–40 (ethyl alcohol)	43.75
Water	43.75
Propylene glycol	11
Color and perfume to suit.	

Example 2

Typical cream lotion:	Parts by weight
Stearic acid	3
Glycerol monostearate	7
Mineral oil	4
Cetyl alcohol	1
Isopropyl linoleate	1
Methyl-p-hydroxybenzoate	0.1
Triethanolamine	1
Isopropyl-p-acetamidocinnamate	1.5
Propylene glycol	7
Water	73.4
Color and perfume to suit.	

Various lower alcohols may be used in such compositions, for instance, methyl, ethyl, butyl and propyl alco-

hols. The amounts of sunscreen compound given in the above examples have been found to be sufficient and effective, but lesser or greater amounts may be used. The preferred range of proportions in the vehicles is from about 1% to 5% by weight and from about .5% to 10% may be used. Larger amounts are usable but are most likely unnecessary for protection.

The following procedure may be used in the production of the esters of acylated p-amino-cinnamic acid:

One mole (151 gm.) of p-nitrobenzaldehyde is treated with 82 gm. of freshly fused sodium acetate and 204 gm. of acetic anhydride. The mixture is heated to refluxing with stirring and held at this temperature for eight hours. The mixture is then cooled slightly and poured into a mixture of ice and water. The pale yellow precipitate of p-nitrocinnamic acid is filtered from the resulting mixture and is washed with slightly acidulated water. The product is then dried.

One hundred and seventy-seven grams of the p-nitrocinnamic acid is dissolved in absolute ethyl alcohol (460 grams, 10 moles) and 6 grams of p-toluene sulfonic acid is added to the mixture. The mixture is heated to reflux for twenty hours, and then cooled. To this is added a solution of four grams of sodium carbonate in 20 grams of water, and the mixture is then heated to distill off about 200 grams of alcohol. The residue is then thrown onto 500 grams of crushed ice. When the ice was melted, the ethyl-p-nitrocinnamate is filtered from the residual liquor, water washed and dried.

One-tenth mole of ethyl-p-nitrocinnamate (20.5 gm.) is dissolved in absolute ethyl alcohol to which is added 2 gm. of a catalyst comprising 10% palladium on charcoal. To this mixture in a rocking autoclave is added pure hydrogen gas at a pressure of 45 pounds per square inch. The hydrogen is absorbed, and the reaction ceases when 0.3 mole of hydrogen gas is taken up. The resulting ethyl-p-aminocinnamate is isolated by filtering off the catalyst and evaporating the alcohol solvent, followed by chilling and filtration of the crystalline product.

The ethyl-p-aminocinnamate (17.8 gm., 0.1 mole) is dissolved in 500 cc. of water containing 3.7 gm. of hydrochloric acid. To this is added, at once, 10.2 gm. (0.1 mole) of acetic anhydride and 8.2 gm. (0.1 mole) of anhydrous sodium acetate which is dissolved in 80 grams of water. Within a few minutes the reaction is complete and ethyl-p-acetamidocinnamate is filtered from the liquid, washed with water until free of acid and dried at 50° C.

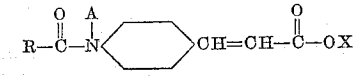
The unexpected effectiveness of the present compounds over the prior art analogous compounds is well illustrated by a comparison between the prior acylated amino-benzoic esters, and the present acylated amino-cinnamic esters wherein the essential difference is the presence of an ethylene radical, as set forth below:

Screen: 1% Concentration	Percent Erythemal Transmission	Percent Tanning Transmission
Ethyl-p-acetamidobenzoate	84.9	99.94
Ethyl-p-acetamidocinnamate	8.16	47.06

The above values indicate the percentage of physiologically active radiation which is transmitted through equal films of equal screen concentration. It is known that an effective screen must transmit no more than 15% of incident erythemal radiation. Thus it is evident that the p-acetamido-benzoates are completely ineffective, but the corresponding p-acetamidocinnamates are very effective cosmetic sunscreens.

I claim:

1. A method of protecting the skin against erythema producing radiation which comprises applying to the skin a film of a composition of a cosmetic carrier having disseminated therethrough at least .5% of a compound of the general formula:



wherein R is a radical taken from the class consisting of hydrogen, alkyl having 1 to 4 carbon atoms; A is a radical taken from the class consisting of hydrogen, alkyl having 1 to 4 carbon atoms; and X is a radical taken from the class consisting of hydrogen, alkyl having 1 to 4 carbon atoms.

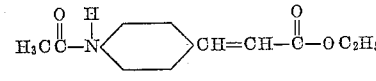
2. A method according to claim 1 in which the amount of said compound ranges from about .5% to 10%.

3. A method according to claim 1 in which the amount of said compound ranges from about 1% to 5%.

4. A method according to claim 1 in which the carrier is a monohydric alcohol having 1 to 4 carbon atoms.

5. A method according to claim 1 in which the carrier is a cosmetic cream lotion.

6. A method of protecting the skin against erythema producing radiation which comprises applying to the skin a film of a composition of a cosmetic carrier having disseminated therethrough at least .5% of a compound having the following formula:



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