Sunless Tanning: An Alternative to Sun Exposure

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Many dermatologists are advocating the use of sunless tanning products as an alternative to sun exposure. Although sunless tanning products are able to simulate a beautiful tan, there are some important details for the dermatologist to know. This article is aimed at helping the dermatologist better advise patients on sunless tanning activities.

History of Dihydroxyacetone

Sunless tanning products are all based on the same chemical known as dihydroxyacetone (DHA).[1] Dihydroxyacetone was originally discovered in the 1920s as a sugar substitute for glucose. It was rediscovered in 1957 when Dr. Eva Wittgenstein, a physician at a children's hospital, discovered the tanning properties of DHA. Dr. Wittgenstein was studying the effect of orally administered DHA on a childhood glycogen storage disease when she noticed that the children were developing a brown color on the skin where they had spit up the sweet syrup. She subsequently applied the liquid to her own skin and noticed the tanned color.[2] The product was commercialized in 1959 as a shaving lotion known as "Man-Tan." It was a tremendous success, but the raw DHA was rather expensive at $2000/kg.

Chemistry of DHA

Dihydroxyacetone is the basis for all presently marketed sunless tanning products and is a 3-carbon sugar that is manufactured as a white, crystalline, hygroscopic powder. Dihydroxyacetone is formed when glycerol is fermented by *Gluconobacter oxydans*. It interacts with amino acids, peptides, and proteins to form chromophores known as melanoidins.[2] Melanoidins structurally have some similarities to skin melanin but are not photoprotective.[3] Dihydroxyacetone only interacts with the stratum corneum, as the entire brown color can be removed by tape stripping the skin. Thus, the thicker the stratum corneum, the more deeply the skin will pigment. For this reason, the brown is less intense on the face where the stratum corneum is thin and more intense on the elbows where the stratum corneum is thicker. The pH level of the skin and the formulation also can change the color of the DHA-induced skin stain. If the skin or the formulation is alkaline, the DHA color will be more orange. Conversely, if the skin or the formulation is acidic, the DHA color will be more natural in appearance. The optimal pH for the best color development is 5 to 6.

The amount of water in the formulation also can affect the DHA color. If too much water is present, the DHA color will be lighter. For this reason, DHA products are not formulated with glycerin, which inhibits the browning reaction. It has been noted that propylene glycol and sorbitol increase the tanning intensity.

Maillard Reaction

The browning reaction that occurs when DHA is exposed to keratin protein is known as the Maillard reaction.[4] Dihydroxyacetone is technically categorized as a colorant or colorless dye. It reacts with amines, peptides, and free amino acids in the stratum corneum. The first step is the conversion of DHA to pyruvaldehyde with the elimination of water. Then the keto or aldehyde interacts with skin keratin to form an imine.[5] The remaining specifics of the reaction are still unknown, but the resulting products are cyclic and/or linear polymers that have a yellow or brown color.

The chemical reaction usually is visible within 1 hour after DHA application, but maximal darkening may take 8 to 24 hours.[6] Many self-tanners contain a temporary dye to allow the user to note the sites of application and to promote even application, but this immediate color should not be confused with the Maillard reaction.

Self-tanners and Photoprotection

The brown color produced by self-tanners does not provide the same photoprotection as melanin. However, the DHA polymers absorb long-wavelength UVA from 300 to

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380 nm.[7] Dihydroxyacetone formally was listed on the sunscreen monograph, but it has since been removed, as DHA can only produce a sun protection factor of 3 to 4.[8] It is important to remind patients that they will still sunburn and tan while using a self-tanner; therefore, they must still use a sunscreen over sun-exposed skin.

Dihydroxyacetone can be combined with organic sunscreens that do not contain amino groups, such as octyl methoxycinnamate, homosalate, octocrylene, and benzophenone. It also can be combined with inorganic sunscreens, such as zinc oxide and titanium dioxide. The challenge with inorganic sunscreen combinations is that the zinc oxide and titanium dioxide can become discolored in the bottle if 5% DHA is combined with 5% inorganic sunscreen after only a few days.

Sunless Tanner Formulation

Dihydroxyacetone usually is added to a creamy base in concentrations of 3% to 5%.[9] Lower concentrations of DHA produce mild tanning, while higher concentrations produce darker tanning,[10] which allows self-tanning creams to be formulated in light, medium, and dark shades. The depth of color produced by self-tanning creams can be enhanced by increasing the protein content of the stratum corneum, which is accomplished by applying a sulfur-containing amino acid, such as methionine sulfoxide, to the skin just before applying the DHA.

Safety

Dihydroxyacetone is a nontoxic ingredient both for ingestion and topical application. It has a proven safety record with only a few reported cases of allergic contact dermatitis.[11] In the 1920s, it was determined that large quantities of oral DHA did not produce toxicity and the median lethal dose in rats is more than 16 g/kg. It is interesting to note that the phosphate of DHA is one of the intermediates in the Krebs cycle known as DHA monophosphate. Topically applied DHA reacts immediately on contact with the stratum corneum amines and is not absorbed for this reason. Dihydroxyacetone has not been detected in the urine or serum of volunteers following topical application.[9]

The staining reaction that occurs with DHA is limited strictly to the stratum corneum and can be readily removed with tape stripping and exfoliation. Thus, the product must be reapplied daily to maintain optimal skin darkening. There are no known side effects from frequent application, except for possible irritation. The DHA does have a distinct odor, which is difficult to mask with fragrances.

Summary

The American Academy of Dermatology has begun to promote the use of self-tanners in some of its safe sun messaging.[12] As consumers hear these public service announcements, more questions regarding the topical use of DHA may arise. This article has discussed some of the more important details regarding DHA and its formulation into self-tanning preparations. The formulations can be used safely but do not provide adequate photoprotection unless combined with a sunscreen. A natural-appearing tan can be created with even application of the self-tanner. Care should be taken to apply less product to easily stained areas, such as the ankles, knees, elbows, and toes. The hands should be washed immediately following application to prevent unnatural staining of the skin surface. The product should not be applied to the hair or nails. These few simple instructions can simulate a tanned appearance without photoexposure.

References

1. Maibach HI, Kligman AM. Dihydroxyacetone: a sun-tan-simulating agent. *Arch Dermatol.* 1960;82:505-507.
2. Wittgenstein E, Berry HK. Reaction of dihydroxyacetone (DHA) with human skin callus and amino compounds. *J Invest Dermatol.* 1961;36:283-286.
3. Meybeck A. A spectroscopic study of the reaction products of dihydroxyacetone with amino acids. *J Soc Cosmet Chem.* 1977;28:25-35.
4. Wittgenstein E, Berry HK. Staining of skin with dihydroxyacetone. *Science.* 1960;132:894-895.
5. Chaudhuri RK, Hwang C. Self-tanners: formulating with dihydroxyacetone. *Cosmet Toiletries.* 2001;116:87-96.
6. Goldman L, Barkoff J, Blaney D, et al. Investigative studies with skin coloring agents dihydroxyacetone and glyoxal. preliminary report. *J Invest Dermatol.* 1960;35:161-164.
7. Johnson JA, Fusaro RM. Protection against long ultraviolet radiation: topical browning agents and a new outlook. *Dermatologica.* 1987;175:53-57.
8. Muizzuddin N, Marenus KD, Maes DH. UVA and UVB protective effect of melanoids formed with dihydroxyacetone and skin. Poster presented at: 55th Annual Meeting of the American Academy of Dermatology; March 1997; San Francisco, CA.
9. Kurz T. Formulating effective self-tanners with DHA. *Cosmet Toiletriesx.* 1994;109:55-61.
10. Baran R, Maibach HI, eds. *Cosmetic Dermatology.* London, England: Murtin Dunitz; 1994.
11. Morren M, Dooms-Goossens A, Heidbuchel M, et al. Contact allergy to dihydroxyacetone. *Contact Dermatitis.* 1991;25:326-327.
12. How to apply self-tanner. American Academy of Dermatology Web site. http://www.aad.org/skin-conditions/skin-health-tips/how-to-apply-self-tanner. Accessed April 2, 2013.