

## CHEMICAL REACTION BY STEVE HERMAN

# Non-Enzymatic Browning: Tan Minus Sun

The market for sunless tanners is destined to continue to grow, spurred by consumers' desire to look healthy while avoiding overexposure to the sun.

"The sun never gets tired of rising, but sometimes a person gets tired of being under the sun."

—Simone Schwarz-Bart

THE HUMAN RACE always has been fascinated with the sun, and primitive societies often worshiped the sun as a god. The ancient Greeks may have been the first to intentionally bask in its rays, calling sunbathing *heliotherapy*, yet, for most of history, light skin was preferred, indicating a leisurely life spent indoors, while the common workers darkened during their outdoor labors.

Three forces in the 1920s changed the attitude toward

tanned skin.<sup>1</sup> Coco Chanel, cruising aboard the Duke of Westminster's yacht, accidentally obtained a famous suntan. Lifestyles in general were changing, as women came out of the house to enjoy an outdoor life of hiking, picnics and tennis. Then, Parisians fell in love with the dark-skinned singer Josephine Baker.

Fashionable women everywhere suddenly needed to be tanned.

Bathing suits that once covered women's legs with bloomers now bared the legs, and brown powders and creams were created to color the places the sun had missed. A tan in the winter implied the resources to vacation in a warm climate, and the suntan became a symbol of wealth and leisure. By the 1960s, tanning became an art form and an entire generation baked in the sun, suffering sunburns that would develop into skin cancers 10–20 years later.

In 1979, the U.S. Food and Drug Administration (FDA) concluded that sunscreens could help prevent skin cancer and developed the first rating system for SPFs. Still, many medical experts concluded that there was no safe way to tan. The indoor tanning industry certainly did not provide a safe alternative.

The only way to attain a tanned look with complete safety was with a new product cate-

gory, sunless tanners. Man-Tan, in 1960, was the first self-tanning product to hit the market. Through the last decade ever-increasing acceptance of these products has developed and most major cosmetic marketers have become involved.

The poster child of self-tanning chemicals is dihydroxyacetone (DHA). DHA is a small and simple molecule—simple at first glance, that is. In powder form, DHA does not exist in its simple monomer configuration, but primarily as one of four possible dimers. The monomer and one of the dimer forms are shown in Figure 1. A few minutes in aqueous solution establishes the monomer as the dominant form. The monomeric structure in turn reacts to changes in pH, as shown in Figure 2. It is only as the monomer that DHA functions as a sunless tanning active. For its behavior on the skin, see Figure 3.

DHA is useful in self-tanning because its hydroxy groups make it behave as a simple sugar. The skin is composed of protein, which in turn is built of amino acids. The Maillard reaction takes place when components such as reducing sugars and amino acids or proteins react together. It occurs in most foods on heating, as can readily be observed by searing a piece of meat. The Maillard reaction products are responsible for

FIGURE 1. DHA STRUCTURES

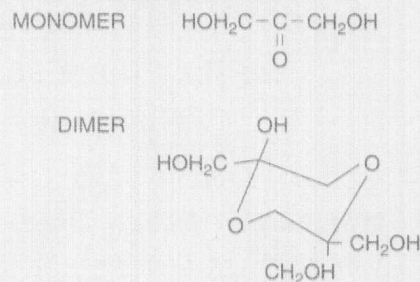


FIGURE 2. AQUEOUS DHA

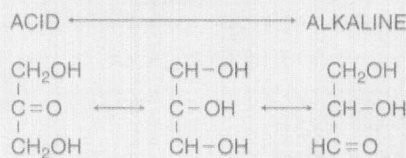


FIGURE 3. BEHAVIOR OF DHA ON THE SKIN

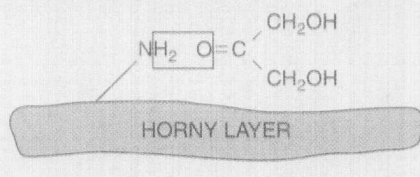
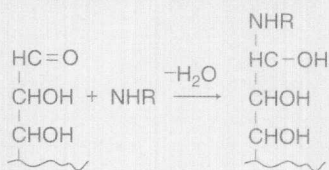


FIGURE 4. MAILLARD REACTION



much of the flavor of cooked food. The preponderance of the literature on the Maillard reaction, including some entire books, is concerned with the importance of the reaction in food processing.

The Maillard reaction produces a complex mixture of products through a daunting series of possible steps. Figure 4 shows only the most elementary reaction. The reaction of DHA with the skin can produce a variety of products so numerous as to elude any conclusive analysis. It is certain that the reaction of products will differ from individual to individual

and many of the resulting compounds are malodorous. Estée Lauder has used cyclodextrin to attempt to eliminate some of the undesirable notes.

The most innovative product of the past year was Coppertone's Endless Summer. Endless Summer has a double tube package, one side containing DHA and one side containing an amine.<sup>2</sup> The reaction is faster when the product is dispensed than if the skin supplies all the amine. A visible color change begins in less than 30 minutes, while one-phase products take several hours to show a darkening effect. Many users also notice a more natural tan color from the new technology.

DHA also can be encapsulated for enhanced skin penetration. A product from ROVI GmbH promises to increase the surface volume for the Maillard reaction to occur. With the trade name Rovisome DHS, its dihydroxyacetone, alcohol and lecithin complex is about 20 percent active DHA. It could possibly be most effective combined with DHA in the formula to provide dual action.

Other formulation variants have been placed on the market to enhance product performance. Thin emulsion sprays are available to improve uniform application on the skin, cosmetic dyes are added to the base to temporarily color the skin while the DHA reaction runs its course, and alpha hydroxyl acids and moisturizers are added for improved skin quality.

Not many alternatives are available for DHA, but Campo Research has a suggestion. Campo

identifies tanning as a consequence of the skin's response to UV damage. The repair enzymes, besides repairing gene damage, also stimulate the production of melanin. Makakanni STLC is a product derived from the herb *Eclipta alba*. Campo claims the development of a tan within three hours that is longer lasting than a DHA tan. Makakanni STLC also is recommended for use in conjunction with DHA. Campo offers Erythrulose as a self-tanning active.

DHA, as a reactive chemical, poses special challenges for the formulator. Most suppliers of DHA, such as Merck—available in the U.S. through Rona—can offer assistance. The market is destined to continue its growth, spurred by consumers' desire to look healthy while avoiding over-exposure to the sun. As knowledge of skin and its reaction to UV grows, so will the industry's ability to create improved generations of self-tanning products. **GCI**

#### References:

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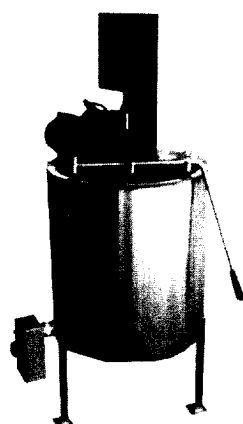
#### Additional Resources

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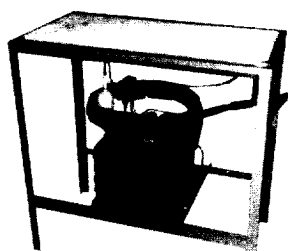
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