Beauty Secrets: Hydroxy Acids in Cosmetics

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Introduction

When Cleopatra set sail to greet Marc Antony's fleet, sailors reported that the entire sea smelled of incense to announce her arrival. The ancient Egyptians were famous for their lavish use of cosmetics and perfume and Cleopatra, the Queen of Egypt was doubly so. She was rarely seen in public without a face made up of blush, lipstick, multicolored eyeshadow, darkened eyebrows, and flattened eyelashes.

Cleopatra has used honey, sour milk, and cucumber to enhance the glow of her skin. Ancient French women have washed their faces with fruit wine to make their skin more attractive. Scientists have later found that hydroxy acids are the workhorses of these natural skin care agents.

What are hydroxy acids?

Hydroxy acids are a group of organic chemical compounds that consists of a carboxylic acid group and one or more hydroxyl groups. These acids naturally occur in sugarcane, sour milk, honey, cucumber, lemon, grape, apple etc. Hydroxy acids are also called fruit acids as they mainly present in fruits. α-hydroxy acids, β-hydroxy acids, polyhydroxy acids, polyhydroxy bionic acids and aromatic hydroxy acids are the groups of hydroxy acids that can be found in skin care formulations. α-hydroxy acids are carboxylic acids with hydroxyl groups attached to the alpha carbon (E.g., glycolic acid and lactic acids). If the hydroxyl group is attached to the beta carbon that hydroxy acids are considered as β-hydroxy acids. (E.g., β-hydroxybutyric acid). Polyhydroxy acids are hydroxy acids that contain

more than one hydroxyl group (E.g., Gluconolactone). Poly hydroxy acids with an additional sugar molecule are known as polyhydroxy bionic acids (E. g., maltobionic acid and lactobionic acid). Aromatic hydroxy acids are the carboxylic acids with phenolic rings (E.g., salicylic acid). [1, 2, 3]

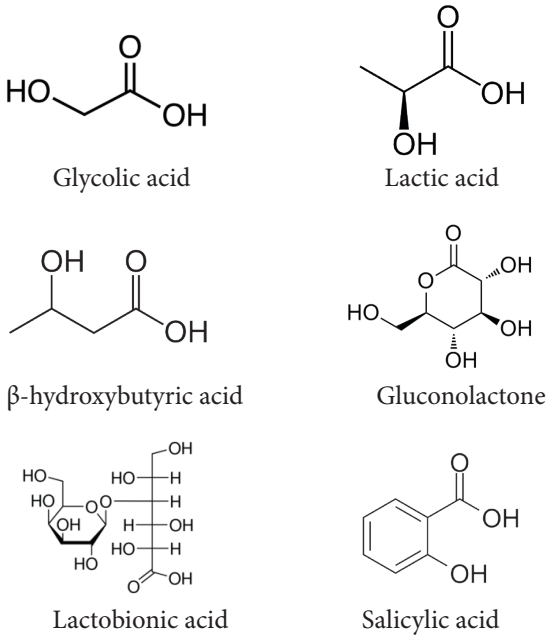


Figure 1: Structures of common hydroxy acids

Chemistry of hydroxy acids

Solubility and the ability to penetrate the skin are the major properties that are important in skin care product formation. Based on the solubility the applications of hydroxy acids vary. α-hydroxy acids, β-hydroxy acids, polyhydroxy acids, and polyhydroxy bionic acids are highly soluble in water because of their polar nature. However, salicylic acid is sparingly soluble in water. Due to the close proximity, hydroxyl group and carboxylic group, salicylic acid forms strong intramolecular hydrogen bonds instead of forming hydrogen bonds with water molecules. In addition to that, benzene rings of salicylic acid molecules tend to form strong π-π interaction with each other. Therefore, salicylic acid shows non-polar properties.

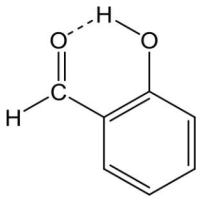


Figure 2: Salicylic acid with intramolecular H-bonds

The ability of hydroxy acids to penetrate the skin depends on the size of the molecule. If the molecule is smaller it can penetrate deeper in the skin and cause exfoliation of deep skin layers. This can cause severe side effects such as enhanced photosensitivity. Amongst the groups of hydroxy acids used in skin care products, polyhydroxy acids and polyhydroxy bionic acids show the lowest ability to penetrate into the deeper layer of the skin since they are relatively larger in size. Hence polyhydroxy acids and polyhydroxy bionic acids are considered as the most appropriate type of hydroxy acids which can be used to treat the sensitive skins with minimal risk of side effects. [2]

What are the skin conditions that can be treated with hydroxy acids?

Based on the properties of hydroxy acids, they have been incorporated into many skin care formulations such as exfoliants, anti-acne creams, anti-pigmentation creams and anti-aging creams to treat skin conditions including dry skin, acnes, hyperpigmentation, and aged skin respectively.

Some of the hydroxy acids can be used in sunscreens as photoprotective agents to protect the skin from UV radiation.

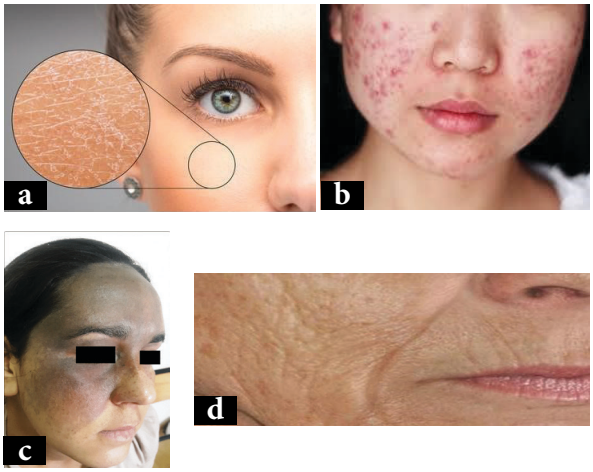


Figure 3: a) Dry skin, b) Acnes, c) Hyperpigmentation, d) Aged skin

Mechanisms of action of hydroxy acids

The mechanisms of action of hydroxy acids in skin care products that have been developed to treat different skin conditions differ from each other based

on the purpose.

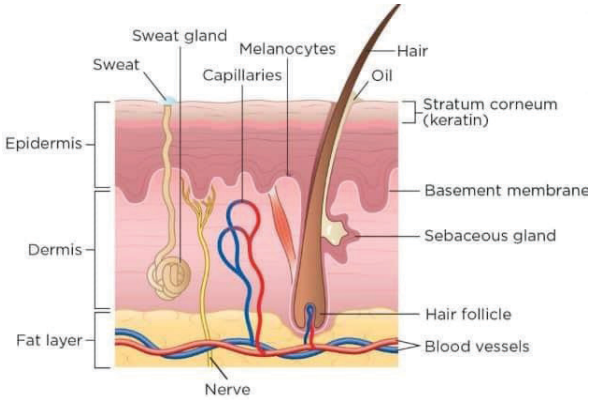


Figure 4: Cross section of the skin

α-hydroxy acids, β-hydroxy acids, polyhydroxy acids, and polyhydroxy bionic acids have been incorporated into exfoliants that are being used to treat skin conditions such as dry skin, roughness of the skin and aged spot. They can thin or remove the stratum corneum, the outermost layer of the skin. It consists of dead keratinocytes called corneocytes. Ionic interactions are responsible for keeping corneocytes in contact with each other. These ionic interactions arise as a result of the electrostatic interactions between Ca^{2+} ions and the negatively charged ions like SO_4^{2-} and PO_4^{3-}. Hydroxy acids can weaken these interactions by chelating Ca^{2+} ions. The ability of α-hydroxy acids, β-hydroxy acids, polyhydroxy acids, and polyhydroxy bionic acids to hydrate the skin by absorbing water also can cause the exfoliation of the outermost dead cell layer of the skin. When the water content in the stratum corneum is high the distance between charged ions becomes increased and the ionic interactions become weakened. As a consequence of the weakening of ionic interactions, exfoliation of corneocytes occurs. [2, 3, 6, 7]

Anti-acne products are considered as a type of exfoliants. Most anti-acne products contain salicylic acid as their working agent. Acne occurs when the hair follicles are blocked by dead cells, oils and/or bacteria. Due to the nonpolar nature of salicylic acid, it can penetrate through clogged hair follicles and dissolve oily intercellular cement. This causes the exfoliation of dead skin cells and bacterial cells that are present in the clogged hair follicle. As a result of that, the acne will disappear. [2, 8]

Moisturizers are skin care products that are applied on the skin to keep it hydrated. Since α-hydroxy acids, β-hydroxy acids, polyhydroxy acids, and polyhydroxy bionic acids can absorb water, they are present in most of the moisturizers as a major ingredient. [2, 3]

Hyperpigmentation is a common skin condition in which some area of the skin appears darker compared to the surrounding skin. This occurs due to the localized accumulation of melanin pigments. Anti-pigmentation creams are used worldwide to treat this condition. Some α-hydroxy acids such as glycolic acid and lactic acid are the major active compounds in most anti-pigmentation creams. α-hydroxy acids help to get rid of hyperpigmentation by exfoliating the stratum corneum that contains a higher amount of melanin. In anti-pigmentation creams, lactic acid shows a specific mechanism of action by on-competitively inhibiting tyrosinase enzyme. Tyrosinase is a major enzyme that is required for the melanogenesis process. Therefore, the inhibition of tyrosinase causes the suppression of melanin formation. [2, 9]

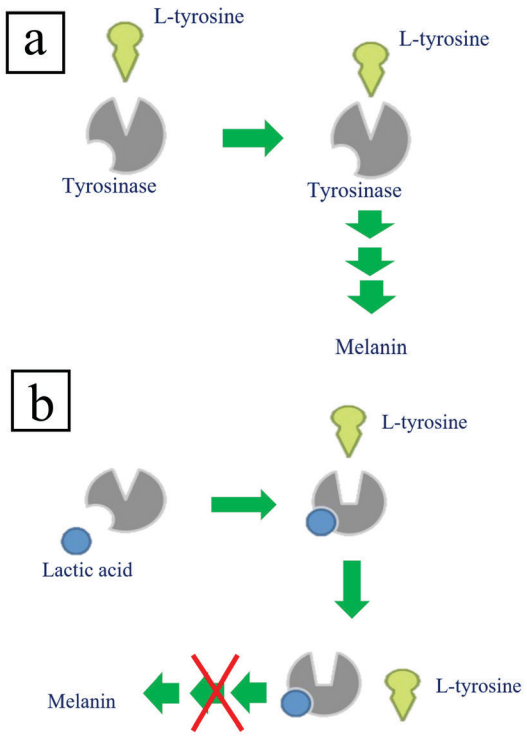


Figure 5: Effect of lactic acid on melanogenesis process; (a) schematic diagram of melanin formation in the absence of lactic acid, and (b) schematic diagram of the suppression of melanin formation in the presence of lactic acid.

Anti-aging formulations contain α-hydroxy acids, polyhydroxy acids, and polyhydroxy bionic acids as their active compounds. The loss of elasticity and the strength of the skin and increased thickness of the stratum corneum are major reasons for the aging of the skin. The elasticity and the strength of the skin are maintained by a protein called collagen. Polysaccharide which are known as glycosaminoglycans physically supports the collagen molecules to do their functions. α-hydroxy acids, polyhydroxy acids, and polyhydroxy bionic acids act in anti-aging creams via stimulating the synthesis of collagen and exfoliating the stratum corneum. [3, 10]

Hydroxy acids such as salicylic acid, polyhydroxy acids and polyhydroxy bionic acids show sunscreen properties. Salicylic acid and its salts like sodium salicylate show their sunscreen properties by directly absorbing UV radiations. Polyhydroxy acids and polyhydroxy bionic acids minimize the effect of UV exposure by scavenging the formed free radicals. [2, 11]

Beware of side effects

Despite all the benefits of hydroxy acids, sometimes they might cause severe side effects such as stinging or burning sensation, persistent erythema, blistering, purpura, skin irritation and increased photosensitivity.

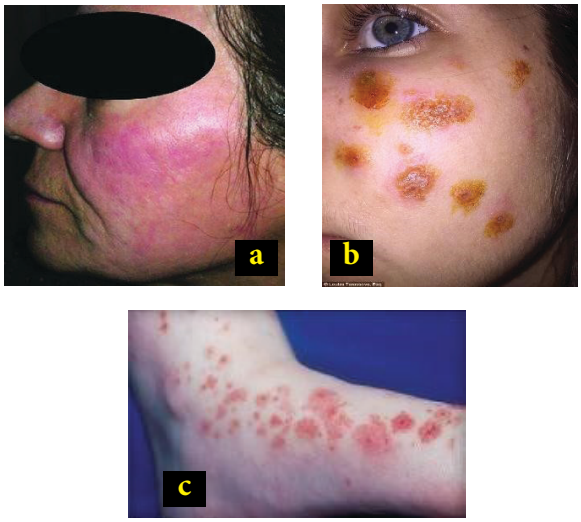
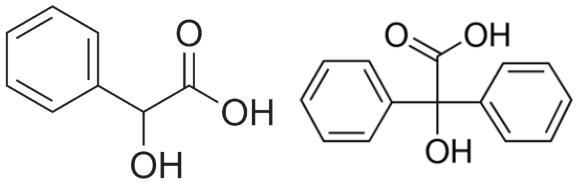


Figure 6: a) Erythema b) Blistering c) Purpura

The side effects depend on the concentration of hydroxy acids, pH and the time duration of the treatment. If the concentration of hydroxy acids and the time duration of the treatment is higher and the pH is very low the risk of causing side effects is higher. [3, 6]

Next generation hydroxy acids

Since polyhydroxy acids and polyhydroxy bionic acids show similar mechanisms of action as α-hydroxy acids in a milder manner, they will be used as the major ingredient in skin care products in the future. Due to the presence of multiple hydroxyl groups, polyhydroxy acids and polyhydroxy bionic acids can function as anti-oxidants and better humectants such as propylene glycol and glycerol. Therefore, by incorporating them into cosmetic formulation instead of α-hydroxy acids multiple benefits can be obtained. Hence, polyhydroxy acids and polyhydroxy bionic acids are known as the next generation of α-hydroxy acids. Lactobionic acid, a well-known polyhydroxy bionic acid, has shown inhibitive effects on matrix metallo-proteinase (MMP) enzymes. MMPs are responsible for the photoaging process since they catalyze the degradation of collagen after exposure to sunlight. By inhibiting this enzyme, the photoaging process can be suppressed. Since, traditionally used α-hydroxy acids in skin care products are highly polar, they do not effectively act on oily skin. Therefore, skin care products with lipophilic α-hydroxy acids such as mandelic acid and benzilic acid can be produced to specifically treat oily skins. [1, 12]



Mandelic acid Benzilic acid

Figure 7: Structures of Mandelic acid and Benzilic acid

Summary

Hydroxy acids, which are used in skin care products can be classified into different groups as α-hydroxy acids, β-hydroxy acids, polyhydroxy acids, polyhydroxy bionic acids and aromatic hydroxy acids. These hydroxy acids are widely used in chemical peelers, anti-acne creams, moisturizers, anti-pigmentation creams, and anti-aging creams due to their specific chemical properties.

Amongst the above mentioned groups of hydroxy acids, polyhydroxy acids and polyhydroxy bionic acids show milder mechanisms of action in the skin compared to the others. Therefore, they can be used to treat more sensitive skins. Since traditionally used α-hydroxy acids are highly polar, lipophilic hydroxy acids should be incorporated into the skin care products to treat oily skins.

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