Role of protein in cosmetics
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Abstract Many authors recognize the beneficial effects of using protein-rich substances in formulations of various topical applications. Proteins quickly were considered useful ingredients for creating a suitable environment for healthy skin and hair because of their ability to bind water with the horny layer of skin and its annexes. Most protein derivatives that are used for cosmetic purposes are obtained from simple proteins, whereas conjugated proteins are used far less frequently. In this article, the role and efficacy of proteins used in cosmetics are reported and discussed.

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Preliminary Proteins (from the Greek word proteins, which means “of primary importance”) play dominant roles in almost all biological processes in living beings. Principal functions are: enzyme catalysis, transfer and accumulation of small molecules and ions, coordinated movement, mechanical support, immunity protection, production and transmission of nervous impulses, and control of growth and differentiation. Therefore, the importance of protein use in each kind of cosmetic product is easy to understand.

The target of the finished product could be whether the skin, hair, or both lose their main component (proteins) in everyday situations. In addition, it is well known that some of the raw materials used in cosmetic formulations interact with the skin barrier and are responsible for the modification (mostly weakening) of the horny layer, which compromises the skin’s hydration, elasticity, firmness and softness.

Today all of this skin damage is easy to analyze and control with different, well known, and internationally approved skin measurement devices, like Corneometer (hydration), Cutometer (elasticity), Tewameter (TEWL), and Visioscan VC98 (SELS).

Surfactant skin irritation

The mechanisms of the adverse effects produced by surfactants upon contact with skin and hair are not elucidated fully, but there is general agreement that the adsorption and interaction of their molecules to the keratin of the stratum corneum and hair cuticle is the initial step when determining tissue damage. Only monomeric surfactant can penetrate when the hydrated micelles are too large to enter the tight network of keratin fibres; thus, the concentration of tenside monomers (and hence the critical micelle concentration [CMC]) should be related to the skin and hair damage. Once surfactant monomers or small aggregates initially attach to the keratin surface, additional events and transformations may take place. This partial denaturizing effect is based on a combination of the following mechanisms: the hydrocarbon tail of the surfactants penetrate the polar regions of the keratin, replacing the conformation-stabilizing hydrophobic interactions by ligand-segment interactions; the ionic head of the surfactant produces attraction-repulsion forces on the charged groups of the keratin, disordering its architecture;...
and the formation of excess positive or negative charge causes additional osmotic pressure, leading to swelling of the matrix and increased permeability. Adding protein derivatives to cleansing formulations can reduce their adverse effects by forming complexes (Fig. 1) with surfactants within the detergent formulation, which produces larger micelles and consequently lowers the CMC of the system.²

Proteins in cosmetics

Direct information on the ancient use of protein materials (cereal flours, animal blood, milk, and egg whites) for cosmetic purposes is available from all great ancient civilizations. The spontaneous and practical use of protein substances (which, with no fundamental modifications, presently are used and appreciated in modern cosmetology) includes migrant Eritrean shepherds’ use of camel milk to clean skin and hair, Cleopatra’s legendary use of donkey milk, and Hokkaido island fishers’ use of soy flour to prepare facial masks, and so forth. The first rational use of proteins in cosmetics dates back the 1950’s.

The beneficial effects of using protein-rich substances in formulations of various topical applications are recognized by many authors.³,⁴ Proteins quickly were considered useful ingredients for creating a suitable environment for healthy skin and hair because of their ability to bind water with the horny layer skin and its annexes. Supplementary scientific investigations were conducted on the binding properties of proteins and peptides to skin and hair, and their potential role as hair conditioning agents was suggested in following years and at the beginning of the 1960’s. Proteins were considered useful for imparting gloss, softness, and manageability because of their substantivity, and hydrolyzed protein was proposed for permanent waving treatments to prevent damage to hair fibres because of their amphoteric and buffering properties.⁵

Most protein derivatives used for cosmetic purposes are obtained from simple proteins (fibrous and globular), whereas conjugated proteins (proteoglycans and nucleoprotein derivatives) are used far less frequently. Proteins from both animals (mammals, fish) and plants (angiosperms) could be used for the formulation of cosmetic ingredients; proteins obtained from lower organisms (algae, fungi) have been considered only recently.⁶ Availability and the economy have been the principal criteria for the selection of the protein sources. However, since the early 1980’s, bovine spongiform encephalopathy epidemiology, consequent health authority regulations, and speculation of advertising have moved the consumer association against the use of animal-derived ingredients, which allowed vegetable protein derivatives to become more important.
Soluble native protein or soluble protein hydrolyzed?

To make proteins suitable for use in water-based cosmetics, it is necessary to convert them into a soluble form, which is easier to manipulate and is more practical for formulating purposes. This form is obtained by the hydrolysis procedure, i.e., by cleavage of the protein macromolecule by disruption of some of the peptide bonds. Cutting native proteins into smaller pieces with water and a catalyst will produce water soluble peptides (more pieces of proteins) that could have useful cosmetic effects. It is important to distinguish hydrolyzed protein from simple protein pieces. The surprising differences make it possible to observe and test their cosmetic performances. A very clear example is the comparison between the cosmetic activity of soluble native collagen and hydrolyzed collagen, which is presented often as soluble collagen or other more fantastic adjectives (fish collagen, native collagen precursor, etc).

There are also different cosmetic properties that are strongly dependent of the molecular structure between hydrolyzed proteins. The number, type, and sequence of the 20 basic amino acids that compose all natural proteins are the factors that determine all of their biological properties.

Hydrolyzed proteins are made of the same 20 amino acids, and the sometimes striking differences (quantitative and qualitative differences and effects on the skin and hair) are related to the number, type, and sequence of the constituent amino acids. Proteolytic enzymes (special proteins obtained from animal, vegetable, and microbial sources) are able to catalyze the protein cleavage by lowering the energy barrier of the peptide bond with a 3-step mechanism. The specific interaction of the enzyme with the side chains of adjacent amino acids with formation of an activated protease-protein complex is the base of enzymatic hydrolysis and should make it possible control and determine most of the molecular features of the resulting peptides.

Protein efficacy

Peptide hydrophobicity \( ^7 \) (Fig. 2) is the critical parameter for cosmetic efficacy, and this peculiarity depends on its amino acid composition (i.e., the relative amount and lipophilicity of nonpolar residues in the molecule). For hydrolyzed protein, a theoretical relationship between molecular size, location of hydrophobic residues along the protein chain, and actual hydrophobicity has been observed.

Considering that proteolysis with enzymes that have different specificity leads to peptides with different locations of hydrophobic/hydrophilic amino acids, the hydrophobicity level of protein hydrolysates may, to a certain extent, be planned by selection of a particular enzyme or enzyme pool and reaching a certain degree of hydrolysis. The relationship of enzyme specificity to molecular size and hydrophobicity of hydrolyzed peptides is illustrated in Fig. 2.

Since the hydrophobicity of peptides influences many of their properties that have cosmetic relevance (substantivity to hair and skin, tenside binding capacity, foaming and emulsifying performance, interaction with radical species, and solubility), there is a chance to determine their functionalities

<table>
<thead>
<tr>
<th>Product of Hydrolysis</th>
<th>ENZYME SPECIFICITY</th>
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<tbody>
<tr>
<td></td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>Long peptides</td>
<td>More hydrophobic</td>
</tr>
<tr>
<td>Medium length peptides</td>
<td>Average hydrophobic</td>
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<tr>
<td>Short peptides</td>
<td>More hydrophobic</td>
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\( ^7 \) Hydrophobic amino acid
\( \bullet \) Nonhydrophobic amino acid

Fig. 2  Relationship between the peptide character and the cosmetic efficacy.
by properly managing their manufacturing process. Enzymatic hydrolysis allows protein cleavage to occur at pH values close to neutrality and temperatures approaching those of living beings, with the important advantage of preventing possible degradation of amino acids and formation of unsafe by-products. Such mild process conditions preserve the thiol groups of cysteine.

Apart from the unknown effects of the no-physiological molecule that the chemical hydrolysis of proteins could produce, loss of cysteine, serine, and other amino acids also occurs, which impairs the keratin binding capacity of the resulting peptides. Many of the interactions of protein substances with skin and hair and other molecules present in cosmetic products are of ionic nature; consequently, the isoelectric point and pH of the medium play a fundamental role on their cosmetic effects.

The isoelectric point of a peptide occurs at the pH where the number of protons combined with basic groups equals the number of protons liberated from acid groups. Mild enzymatic process prevents deamidation of glutamine and asparagine, respectively, to glutamic and aspartic acid. Glutamine and asparagine are more able to link skin/hair keratin, because their isoionic values are far higher than related acids.

**International Nomenclature Cosmetic Ingredient name**

At this point, it is necessary to emphasize that protein hydrolysates with the same International Nomenclature Cosmetic Ingredient name, may have different efficacy. The substantivity of protein hydrolysates of the same origin increases with increased hydrophobicity, decreased molecular size, and increased isoelectric point. Unfortunately it is not always easy to distinguish an enzymatic protein derivative from a chemical one. Chemical proteins are usually rich in inorganic salts, darker in color, and have a stronger (bitter) smell. The presence of unnatural amino acids (lysinoalanine, lanthionine, ornitoalanine, and β-aminoalanine) or a high percentage of cysteic acid are much more significant indicators that result from the strong conditions involved in chemical hydrolysis.

**Practical use of proteins in cosmetic products**

Protein derivatives are used in a variety of skin care and makeup formulations. Soluble protein ingredients are appropriate for almost all type of cosmetic forms (emulsions, lotions, gels, and powders). Insoluble proteins also are used in particular applications. Examples of these applications include: fibrous insoluble collagen (obtained by liophilization of aqueous dispersions of the native protein) in facial masks, where transitory moisturization, increased, skin smoothness, and shine are obtained; or silk powder that is produced with finely ground purified silk fibroin, which can be used in anhydrous decorative preparations.

Native proteins and hydrolysates with high molecular weight generally are preferred in skin care applications for their film-forming properties. Soluble collagen and its partially deamidated derivative (Desamidocollagen) are traditional examples. These particular big molecules are able to form a continuous colloidal film on the skin surface, giving a smooth feeling and softness. It is important to avoid exposing these proteins to heat and denaturing agents, because (1) the film-forming properties of these substances are determined mainly by the length of the molecules, (2) the hydrating effect of these substances is related to the high number of exposed hydrogen binding sites available for linking water, and (3) the properties of these substances is determined by their conformation in the triple helix structure. For this reason, proteins usually are added after emulsification and after the batch has cooled to a temperature at least 3-5 below the melting temperature of the molecule (about 35°C for native soluble collagen, 42°C for desamidocollagen and 24°C for fish collagen).

**Formulation highlights**

1. Avoid combining of protein derivatives of different sources or manufacturers; the functionalities of proteins do not always accumulate with each other and sometimes mutual inactivation occurs.
2. Refuse chemically hydrolyzed proteins if a lot of useless dehydrating salts are not needed; unnatural amino acids are not wanted, but functional and reactive disulphide bonds are needed.
3. Formaldehyde released from donor preservatives can be consumed by condensation with free amino groups of peptides, so avoid using HCHO donors in formulations, or keep the pH as low as possible to make a careful challenge test on the finished product.
4. Avoid combinations with some vegetable extracts containing tannins and other polyphenol derivatives (rathany, tormentil, and witch hazel), because they can form insoluble aggregates with large peptides.
5. Insoluble aggregate can be formed by the combination of large polyanions like hyaluronic acid and cellulose gum; quaternized guar may precipitate proteins with a net negative charge.

**References**

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