The use of glycosaminoglycans in cosmetic products

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Introduction

Dry skin is one of the most common ailments met most often in the persons over 30 years of age. The etiology of dry skin is not fully understood, it is assumed that it appears due to environmental and pathological factors, often in a synergistic manner. Symptoms of dry skin such as flaky surface roughness, loss of flexibility, often accompanied by itching, are very uncomfortable and aggravate in severe weather conditions such as winter frost, strong winds and reduced humidity.

The majority of cosmetic products currently available on the market contain moisturizing compounds. Among them, important are glycosaminoglycans as because of their structure they not only contribute to the improvement of skin hydration, but also strengthen the skin barrier and increase the resilience of the skin to harmful external factors [1, 2].

Overall information

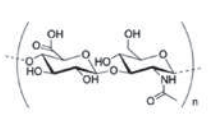
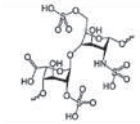
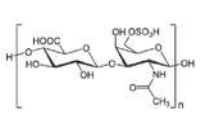
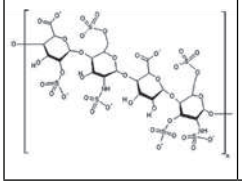
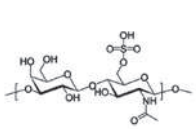
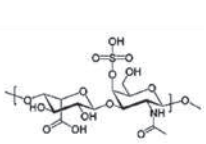
Glycosaminoglycans (GAG) are unbranched, linear polysaccharides composed of repeated disaccharide units. These units are composed of amino sugar (galactosamine or glucosamine) and uronic acid (glucuronic or iduronic), most often bonded through a 1,3-β or 1,4-β-glycosidic bond. Both uronic acids and aminosaccharides can be sulphated and/or acetylated [3, 4]. All glycosaminoglycans, except hyaluronic acid, contain in their composition sulphate groups and occur in complexes with proteins making proteoglycans. Unlike other types of GAG, hyaluronic acid does not form covalent bonds with proteins, but non-covalently interacts with several molecules present in the extracellular space [5].

Glycosaminoglycans are strongly hydrophilic and usually take the elongated configuration occupying a large volume relative to their weight. These compounds, even at very low concentrations form gels. Their strong negative charge, associated with the presence of acid sulphate residues and uronic acids, attracts cations such as Na^+, which are highly osmotically active, which results in binding of large amounts of water in the intercellular substance [4, 6].

We can distinguish seven types of glycosaminoglycans, their names and structural formulas are shown in Table 1 [3].

Table 1

Structural models of different types of GAG

Hyaluronic acid (HA)	*Heparin*	*Chondroitin sulphate (CS)*
		
Heparan sulphate	***Keratan sulphate (KSI or II)***	***Dermatan sulphate***
		

Both free glycosaminoglycans and their complexes with proteins (proteoglycans) are specific and richly represented components of extracellular matrix [4]. The primary function of these macromolecules is to sustain and join cells into tissues, tissues into organs and further on organise various parts of the body. Glycosaminoglycans are important in both physiology and pathology of individual cells and tissues. As all metabolites and nutrients are transported by the basic substance, changes in chemical composition and physicochemical properties of GAG in the basic substance of connective tissue affect the physiological and pathological processes in the surrounding cells and tissues.

The functions of GAG and proteoglycans are determined not only by their size and structure, but above all depend on the polyanionic nature of these compounds, which permits the following:

- participation in maintaining the structural integrity of the tissue matrix and in endowing it with desired elasticity and flexibility
- participation in intracellular transport processes
- affinity of these compounds to cations, which enables transport of cations and their deposition in tissues [7].

Biosynthesis of glycosaminoglycans

Glycosaminoglycans are synthesized in the cells of the connective tissue cells as proteoglycans, whose biosynthesis begins with the formation of core proteins on ribosome. Glycosaminoglycan chains are formed in the Golgi apparatus. The process of their synthesis begins with the recognition of the respective amino acid residues of the protein core and transferring to them, through glycosyltransferases, the residual sugar of the so-called connective region. Then N-acetylohexosamine and glucuronic acid (or galactose) are alternately attached to the non-reducing terminal of the last sugar residue of the linking region. Eventually this leads to the formation of a chain glycosaminoglycans [8]. The last stage of GAG biosynthesis takes place in the Golgi cisterns and involves a modification of the glycan chains synthesized. The character of this process depends on the class of GAG and is related to epimerization of some of glucuronic acid residues to iduronic acid and sulfonation of sugar residues. These modifications are responsible for differentiation of GAG types. Complete glycosaminoglycan polymers are released as a result of proteolytic degradation of the protein core of proteoglycans [9].

Characterisation of glycosaminoglycans

The types of glycosaminoglycans differ in composition of amino sugars, the presence of glucuronic or iduronic acid, chain length, type of bonding between the components of disaccharide units, the presence or absence of sulphate groups, amino acid composition of the core protein, a kind of bond between the core protein and GAG, distribution in subcellular and tissue structures and biological functions [3]. Because of considerable heterogeneity within this group of compounds in Table 2 shows a brief characterisation of each type of GAG.

Table 2

Characterization of different types of GAG: *GlcNAc*- D-glucosamine; *GlcUA*- D- glucuronic acid; *GalNAc*- D-galactosamine; *Gal*- D- galactose; *IdUA*- L- iduronic acid [3, 10]

GAG	Mono-saccharides	N-acetyl group	O-sulphate group	N-sulphate group	Occurrence
HA	GlcNAc GlcUA	+	-	-	Synovial fluid, the corpus vitreous, loose connective tissue
CS	GalNAc GlcUA	+	+	-	Bone, cartilage, cornea
KSI	GlcNAc Gal	+	+	-	Cornea
KSII	GlcNAc Gal	+	+	-	Loose connective tissue
Heparin	GlcNAc GlcUA IdUA	+	+	++	Mastocytes
Heparan sulfate	GlcNAc GlcUA IdUA	+	+	+	The wall of the aorta, skin fibroblasts
Dermatan sulfate	GalNAc IdUA GlcUa	+	+	-	Commonly present

The role of GAGs in the skin and their use in cosmetic formulations

Glycosaminoglycans occur in the skin tissue only in the form of proteoglycans, so in the form bonded with structural proteins such as collagen and elastin. These compounds maintain a proper level of hydration and proper structure of the skin, bond the epidermis to the proper skin, regulate transportation of raw materials and metabolites, regulate osmotic pressure and turgor. Thanks to their valuable properties glycosaminoglycans are widely used in cosmetic industry. Cosmetic products make use of their excellent moisturizing abilities, soothing and calming effects, ability to maintain adequate elasticity of the skin as they stabilise the firmness of skin cells. They are also able to significantly reduce the possibility of local irritation and allergies and strengthen the skin resistance to the harmful effects of external factors [1]. Besides the use of glycosaminoglycans in cosmetic products for skin care, such as creams or lotions [11], they are also applied for hair care. These compounds are naturally produced in the skin at the hair papilla supplied with blood. They play an important role in the proper nutrition of the matrix, in the metabolism and growth of hair. Larger concentrations of GAGs accumulate in the hair matrix in the growth phase, whereas they are not near the dying hair. These compounds have a stimulating effect on the hair matrix by which they control hair growth and may prevent hair loss. The main role of GAG is to control the proper transfer of nutrients between the cell and the blood. It has been confirmed that these compounds supply the matrix with nutrients, improve metabolism and have a positive effect on hair growth. They can improve the appearance of hair, which becomes stronger, thicker and more resistant [12].

Translation into English by the Author

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