Hair 101
Steve Herman
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Understanding the architecture of a hair shaft can help in formulating treatment products. BY STEVE HERMAN

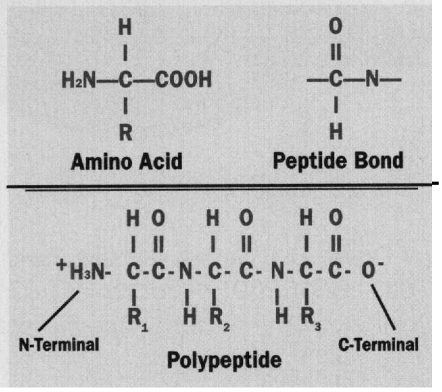
"Forget not that the earth delights to feel your bare feet, and the winds long to play with your hair."

—Kahlil Gibran

COSMETICS CAN be defined as "products for the treatment of dead body parts," since neither the stratum corneum nor hair shafts are vibrant with life. Of the two, hair is the least vital, since a haircut prompts neither pain nor blood flow. The skin keeps the rest of the body from oozing out, but hair is little more than decoration. Despite its superficial importance, hair treatment products generated $26 billion in worldwide sales in 2000, so making lifeless protein attractive has very real rewards.

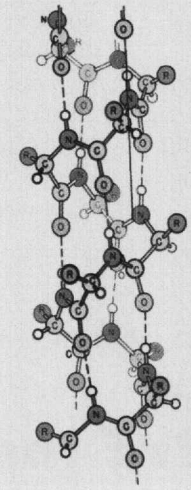
The basic building block of hair, responsible for 91 percent of its dry weight, is keratin. This protein is a biopolymer built of amino acid units. Wool, horns, claws, fur, nails, and quills are also mainly keratin. An amino acid has two functional groups, an amine and a carboxylic acid, which allow polymerization through the peptide bond to form polypeptides (Figure 1).

FIGURE 1: FORMING POLYPEPTIDES



Not all amino acids are created equal—some have a third functional group that creates the opportunity for cross-linking. Of particular importance for hair structure is the diamino acid, cysteine, with an –SH group capable of creating disulfide bonds. The bonds can form between cysteine groups in the same chain (intramolecular cross-linking) or in adjacent chains (intermolecular cross-linking). The composition of amino acids in hair, or any other biopeptide such as wool or wheat protein, has a well-defined distribution of amino acids: In humans, 16.73 percent of keratin is cysteine. The disulfide group provides significant structure to hair, and the breaking and reforming of these bonds is the key to the mechanism of permanent waving. Other contributors to the three-dimensional structure of keratin are Van der Waals interactions, hydrogen bonding, and coulombic interaction (salt links).

FIGURE 2: α-HELIX



The tertiary structure of polypeptides was determined in 1951 by Linus Pauling and his co-workers, using the results of X-ray diffraction on protein crystals. Pauling found that although a polypeptide chain can assume an infinite number of configurations, the most stable are those in which all the –NH groups of the peptide bonds are hydrogen bonded to C=O groups. Two types of stable organization are thus possible: sheets (where the hydrogen bonding exists between polypeptide chains) and helices (where the hydrogen bonding exists between peptide bonds of the same peptide chain). The right-handed α-helix is shown in Figure 2.

Why was Linus Pauling investigating hair structure? Well, he really was not. The goal was much bigger: the elucidation of the structure of

DNA. Pauling lost the DNA race to Watson and Crick, having to settle for a mere two Nobel Prizes in his lifetime.

The α-helix is a building block for the complete structure of the hair shaft, a simplified form of which is shown in Figure 3. A cross-section of the hair can be divided into three sections: the medulla, the cortex, and the cuticle. The medulla is the innermost structure: It has no important function in humans and has no significance for formulators. While the nomenclature for the cuticle and cortex is universally used, the inner part of the hair is subject to some variation: One alternate term is "pith."

The cortex is the central core of the hair shaft and accounts for 75 percent of the cross-sectional area of the shaft. It gives hair strength and color. Keratin itself is essentially colorless but contains melanin in a variety of forms that provide the full range of human hair color. Hair has considerable polarity and can absorb up to 30 percent of its weight in water, primarily through hydrogen bonding. Water swells the hair and allows penetration by large molecules such as hair dye, accounting for the other major source of modern hair color.

The cortex provides a wonderland of chemical construction. The α-helices are coiled together in little bunches called microfibrils, which form hexagonal assemblies immersed in an amorphous matrix rich in cysteine. This larger structure becomes the cylindrically shaped macrofibrils, which, in turn, are packed together to comprise the cortex cells.

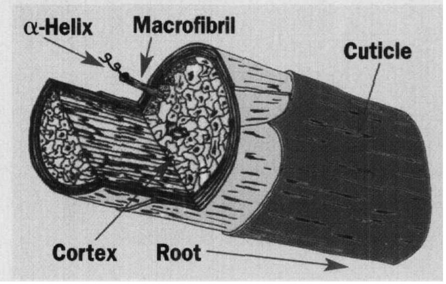
The cuticle is about 5 μm thick, composed of overlapping sheets of 0.5 μm thickness, arranged in a scale-like structure. The cuticle protects the cortex and gives hair its glossy appearance. It is the part of the hair treated by cosmetics, and it must be penetrated for perms or dyes to be effective. The isoelectric point of the cuticle is approximately 3.7, making it acidic and creating an electrical environment where quaternary hair conditioners can be effective.

Cuticle cells have a complex structure, each scale having several layers separated by a cell membrane complex (CMC). The top layer is the epicuticle or ß-layer. The second layer, the A layer, provides mechanical support through its cross-linked structure. Moving further through the layers, the endocuticle is followed by the inner layer, similar in structure to the exocuticle.

The cuticle cells can be subjected to extensive damage during many hair treatments. The "teasing" or "back combing" of hair—combing against the grain of the cuticular layers—is an obvious example, but wet combing is also destructive. When the cuticle finally unravels, the result is "split ends," which can only be eliminated by a haircut. Hair always suffers a progressive decrease in scale structure from root to tip, a condition somewhat alleviated by hair conditioners, which reduce the frictional force on the surface of the hair shaft.

As is so often found, the science behind personal-care categories leads to the technical frontiers of human knowledge. A few pages cannot do full justice to the fascinating architecture of a hair shaft, but they do allow a basic understanding of some modern approaches to hair treatment, the subject of next month's Chemical Reaction. GCI

FIGURE 3: HAIR SHAFT



Hair has considerable polarity and can absorb up to 30 percent of its weight in water.

References

Most of the primary information for this column came from:

Hillary Beaton, "Hair Structure and New Methods of Treatment, Independent Study," Fairleigh Dickinson University Masters in Cosmetic Science Program, Spring 2001 (unpublished manuscript).

There are many volumes dedicated to the science of hair. A recent compilation, containing a chapter on "Fragrance for Hair-Care Products" by *GCI* contributor Peter Dichter is: Johnson, Dale H., ed., "Hair and Hair Care," Marcel Dekker, NY, 1997.

Steve Herman is director of R&D of AFF International. He has more than 30 years of experience in the industry, primarily in fragrance application. He serves as an adjunct professor in the FDU Masters in Cosmetic Science program, and has been active in numerous capacities with the SCC. He may be reached at (973) 244-5880, or by e-mail: GCISteve@aol.com.