Natural Polymers: Polymers in Animals

Protein

The previous sections have summarized the important roles that polysaccharides play in plants. **Proteins** are also an integral part of the plant cell wall serving both structural and functional molecules. They determine the functionality and specificity of an organism (Perez 2005).

Proteins are made up of amino acid groups and sometimes other groups joined together by amide bonds, also known as peptide bonds. Proteins can be classified with regard to their shape, size, solubility, composition, and function.

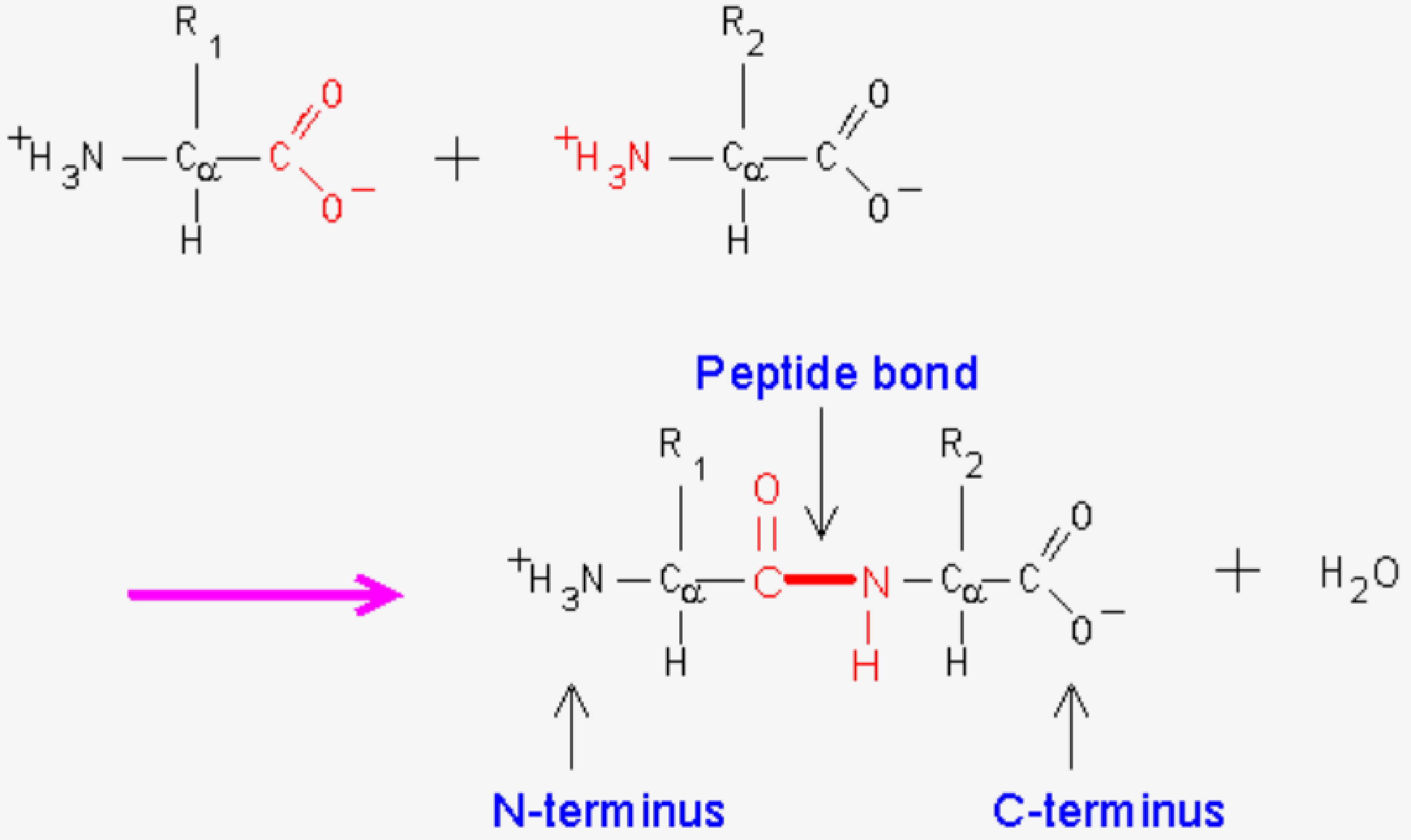


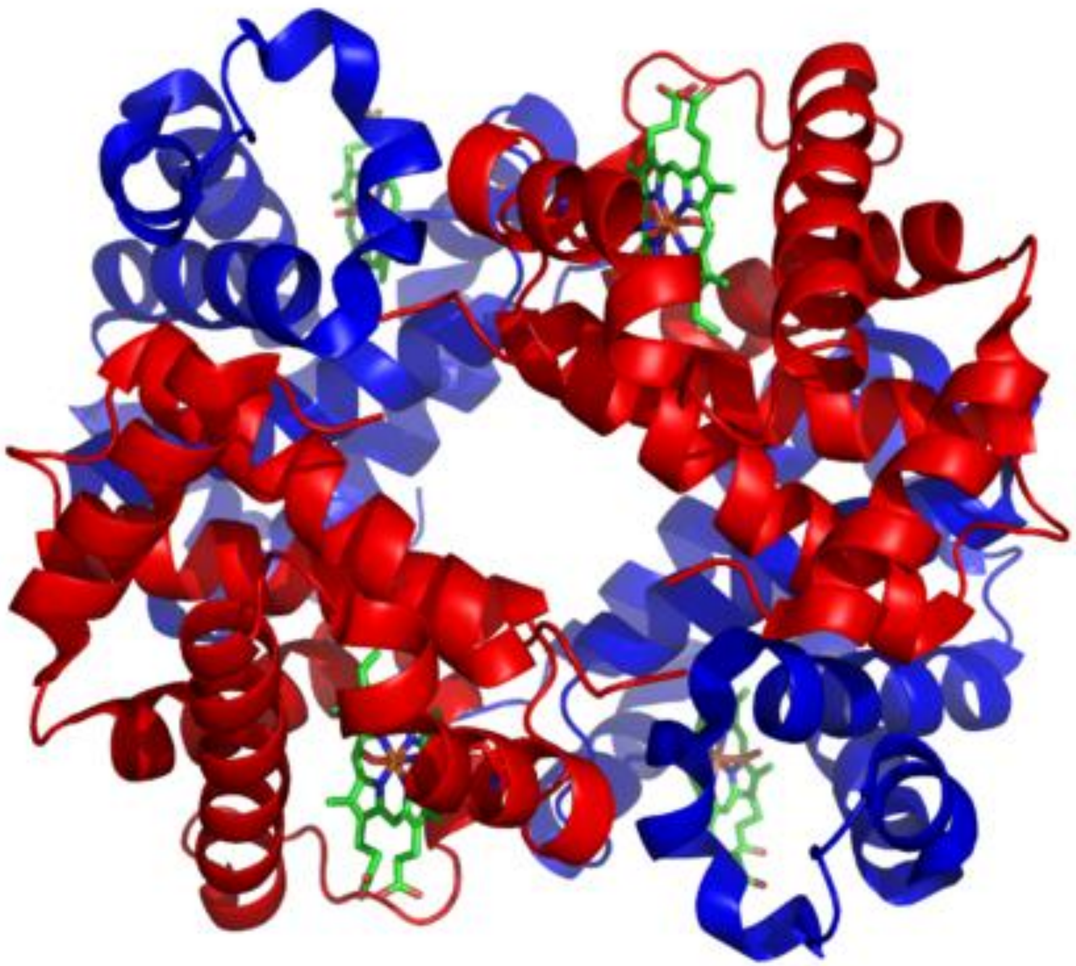
Figure 2-B-2. Formation of the peptide bond by condensation reaction.

Globular and fibrous proteins are the two types of proteins based on shape and size. Globular proteins are water soluble types which are rather fragile in nature.

Antibodies, enzymes, and hormones are typical examples of globular proteins.

Fibrous proteins are tougher water insoluble proteins. These are usually proteins found in structural tissues such as hair, nails, and skin.

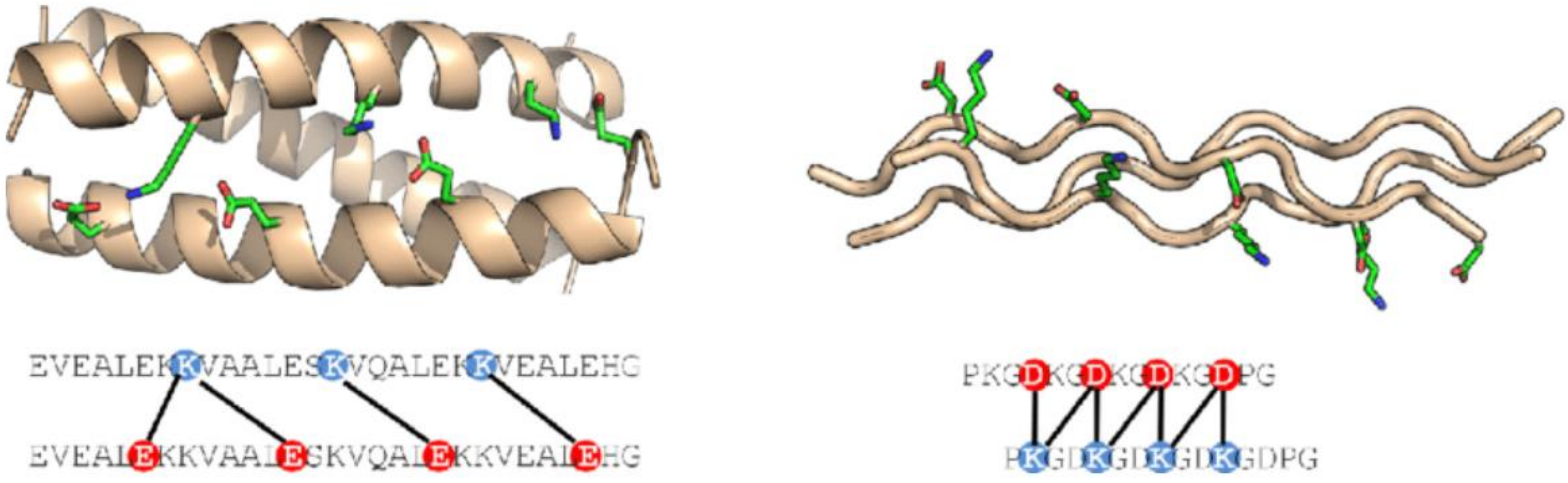
Globular proteins or spheroproteins are spherical ("globe-like") proteins and are one of the common protein types (the others being fibrous, disordered and membrane proteins). Globular proteins are somewhat water-soluble (forming colloids in water), unlike the fibrous or membrane proteins. There are multiple fold classes of globular proteins, since there are many different architectures that can fold into a roughly spherical shape



3-dimensional structure of hemoglobin, a globular protein.

Fibrous proteins are tougher water insoluble proteins. These are usually proteins found in structural tissues such as hair, nails, and skin.

Collagen
Elastin
Fibroins
Keratins



Charge-pair interactions can be inferred from the sequence for fibrous proteins with periodic structure. (LEFT) The seven-residue heptad of the repeat of the □-helix coiled-coil places acidic (red) and basic (blue) amino acids adjacent in structure. In this case, the interaction between two chains of a three-chain homotrimeric protein are shown (Ogihara et al. 1997). (RIGHT) The collagen triple-helix is another type of periodic structure where charge-pairs adjacent in structure can be inferred directly from the sequence. A theoretical model structure of two chains in the triple helix are shown highlighting an extensive chargepair network. E = glutamic acid, D = aspartic acid, K = lysine.

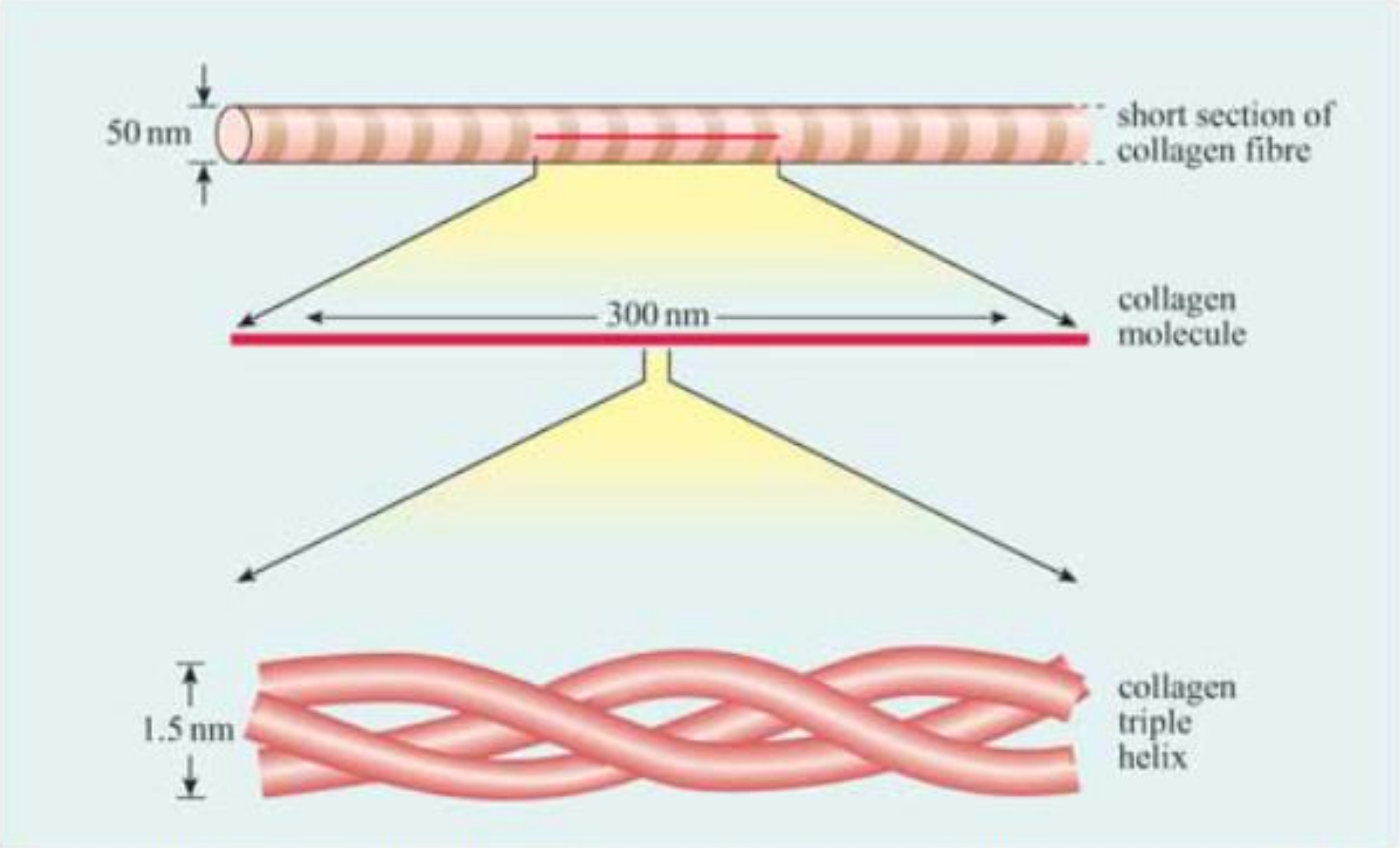
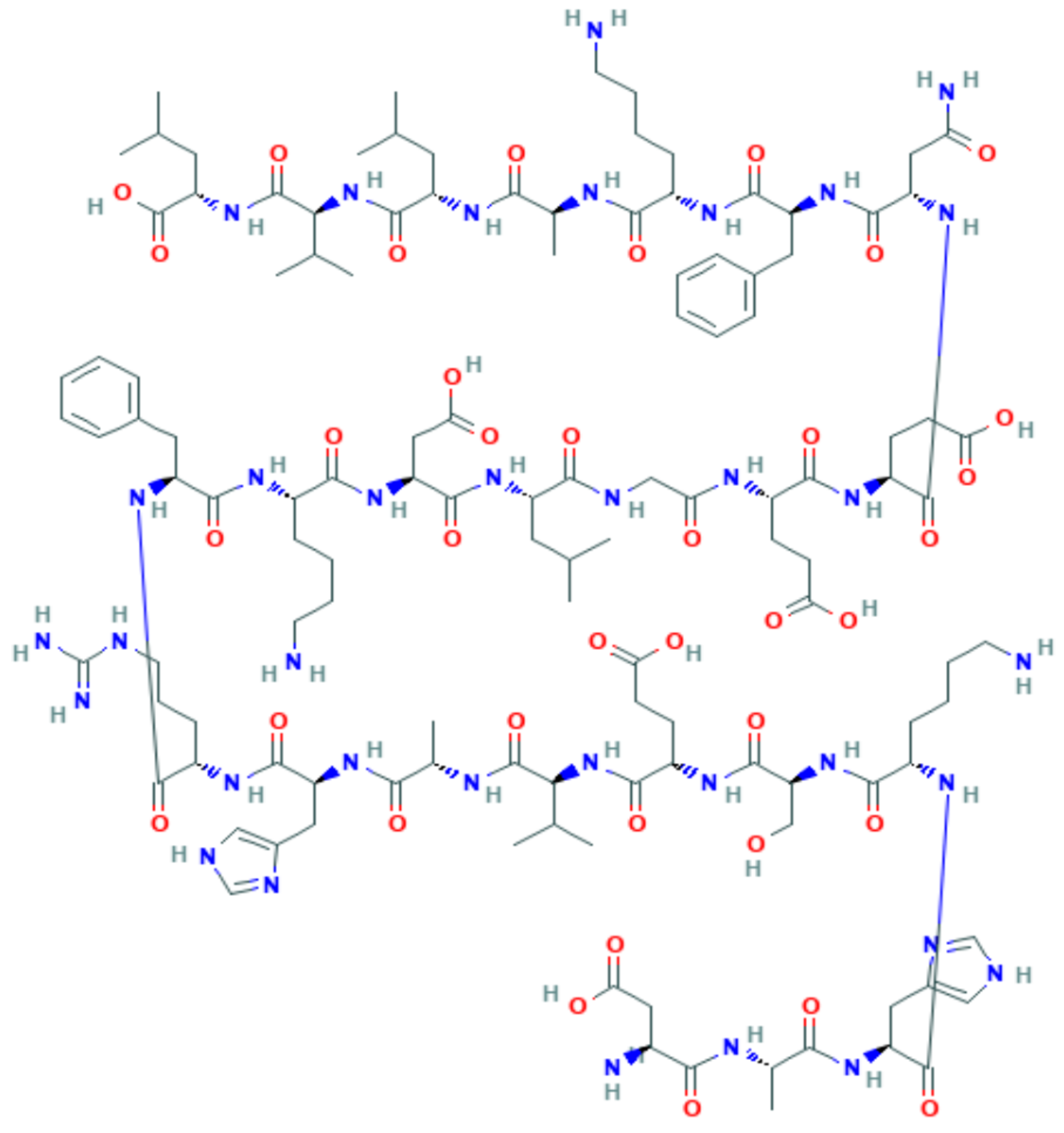


Figure 22 The triple helix structure of collagen. Collagen is a long (300 nm) rod-like protein consisting of three polypeptide chains wound together in a triple helix. Many such molecules are cross-linked in long fibres in the extracellular matrix. These collagen fibres are very strong and can not be extended, giving strength and resistance to the extracellular matrix.

Proteins can also be classified based on their solubility as **simple, compound, and derived proteins**.

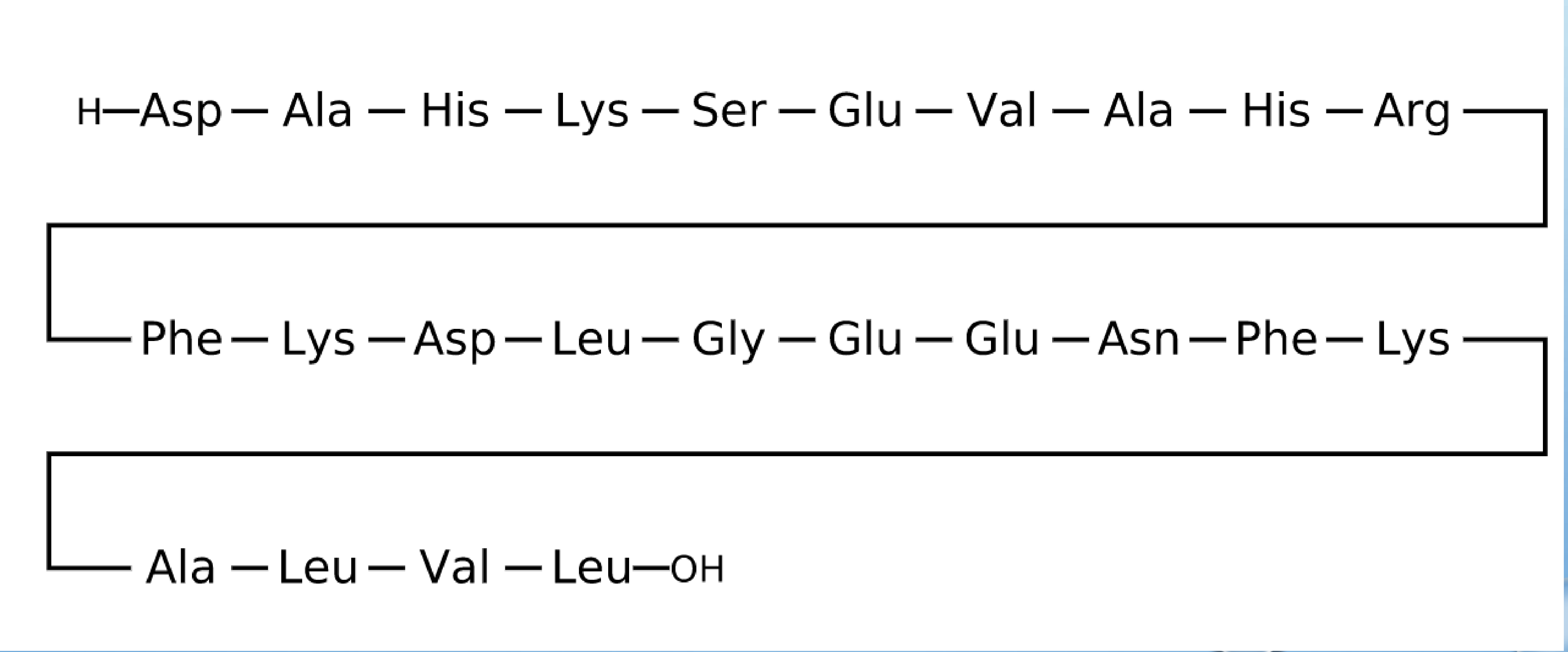
Simple proteins are those which when hydrolyzed produce amino acids only. These protein also have subcategories, which are albumins, globins prolamins, glutelins, histones, prolamins, and abuminoids.

Albumin is a family of globular proteins, the most common of which are the serum albumins. All the proteins of the albumin family are water-soluble, moderately soluble in concentrated salt solutions, and experience heat denaturation. Albumins are commonly found in blood plasma and differ from other blood proteins in that they are not glycosylated. Substances containing albumins, such as egg white, are called albuminoids.



Albumin

L-alpha-aspartyl-L-alanyl-L-histidyl-L-lysyl-L-seryl-L-alpha-glutamyl-L-valyl-L-alanyl-L-histidyl-L-arginyl-L-phenylalanyl-L-lysyl-L-alpha-aspartyl-L-leucyl-glycyl-L-alpha-glutamyl-L-alpha-glutamyl-L-asparagyl-L-phenylalanyl-L-lysyl-L-alanyl-L-leucyl-L-valyl-L-leucine



Compound proteins, also known as conjugate proteins, are a combination of simple proteins and prosthetic groups. Conjugate proteins are of various types depending on the prosthetic group attached. These could be nucleoproteins lipoproteins, glycoproteins, mucoproteins, phosphoproteins, metalloproteins, or chromoproteins

Derived proteins are those derived from complete or partial acidic alkali or enzymatic hydrolysis of simple or conjugate proteins. These derived proteins could be either primary or secondary derived proteins. Primary derived proteins are proteins, metaproteins, and coagulated proteins derived from partial hydrolysis of the protein molecule where very little or no peptide bonds are broken.

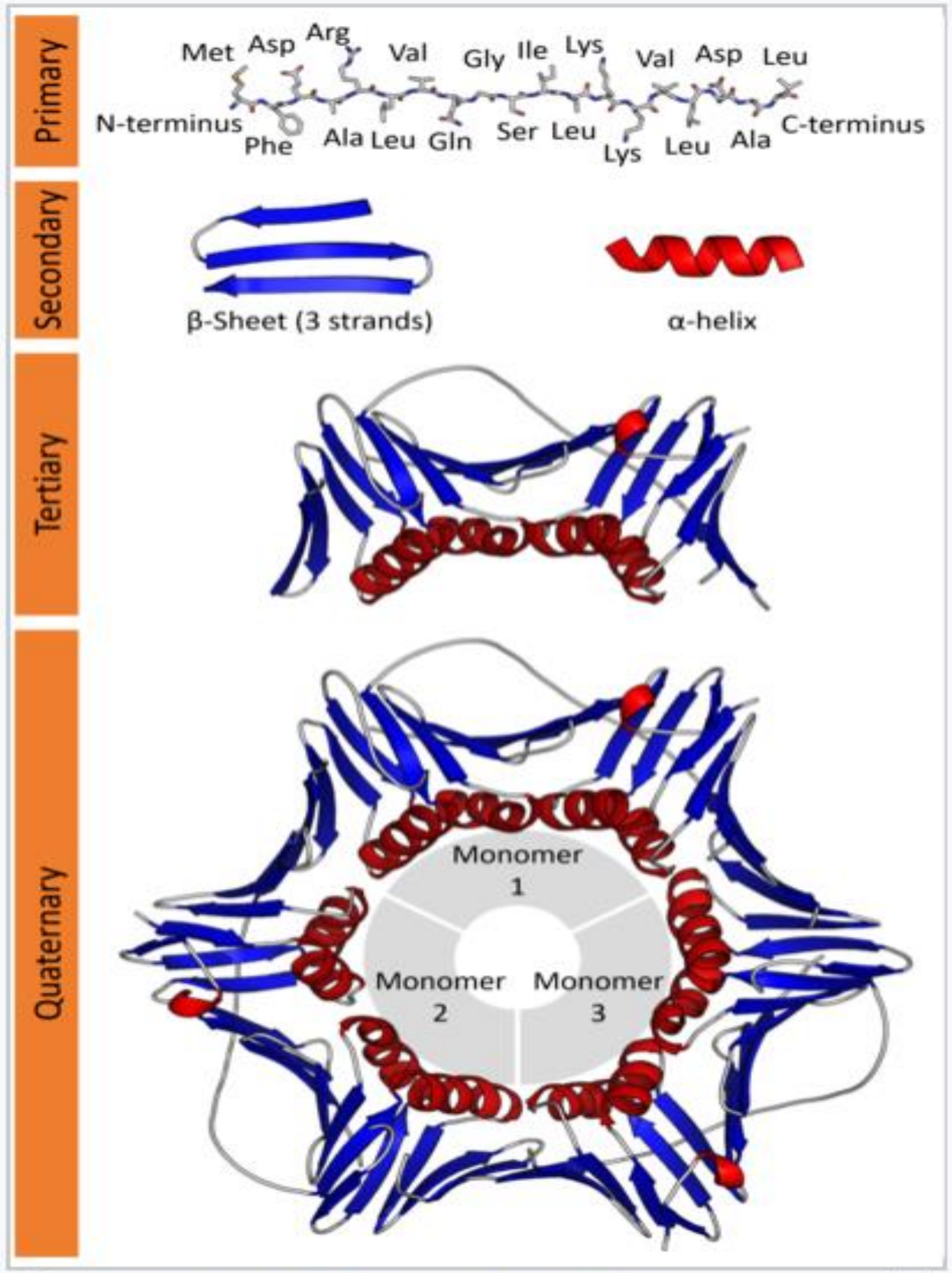
Secondary proteins are a result of more pronounced cleavage of the peptide bonds through hydrolysis. The main types are proteoses, peptones, and peptides.

Proteins are also classified based on their functions as catalytic, protective regulatory, storage, transport, toxic, exotic, contractile, secretary, and structural proteins.

Catalytic, regulatory, and protective proteins are enzymes, hormones, and antibodies respectively.

The following sections describe a few common proteins that are commonly applied in industries. These include silk fibroin, silk sericin, zein, collagen, gelatine, casein, wheat gluten, and soy protein.

Protein structure is the three-dimensional arrangement of atoms in an amino acid-chain molecule. Proteins are polymers – specifically polypeptides – formed from sequences of amino acids, the monomers of the polymer. A single amino acid monomer may also be called a residue indicating a repeating unit of a polymer. Proteins form by amino acids undergoing condensation reactions, in which the amino acids lose one water molecule per reaction in order to attach to one another with a peptide bond. By convention, a chain under 30 amino acids is often identified as a **peptide**, rather than a **protein**. To be able to perform their biological function, proteins fold into one or more specific spatial conformations driven by a number of non-covalent interactions such as hydrogen bonding, ionic interactions, Van der Waals forces, and hydrophobic packing. To understand the functions of proteins at a molecular level, it is often necessary to determine their three-dimensional structure.



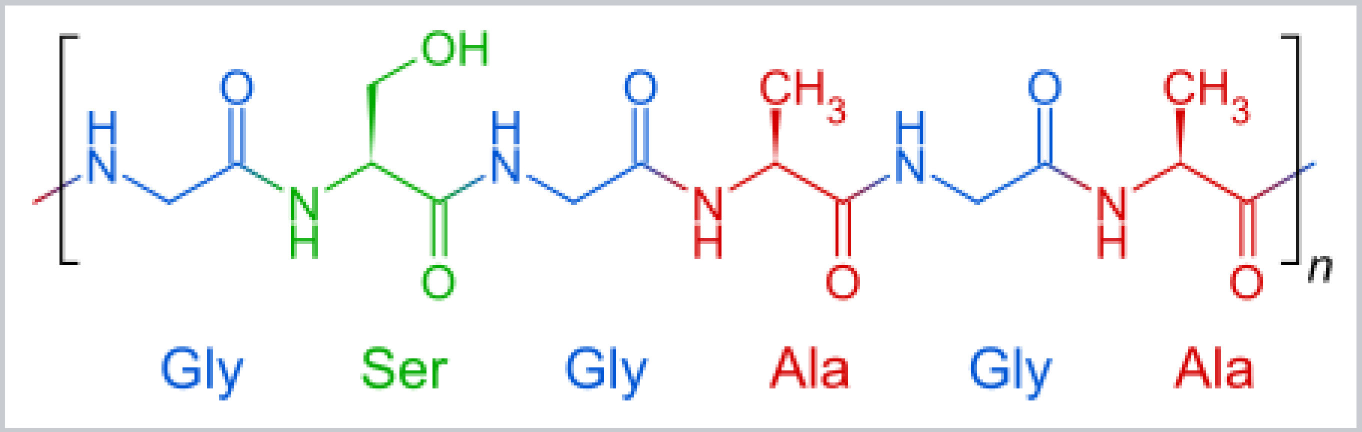
Interactive diagram of **protein structure**, using PCNA as an example.

Silk Fibroin

Silk fibroin is a fibrous protein found in silkworms, particularly the bombyx mori, a domestic insect of the Bombycide family. It is semicrystalline in nature with its main amino acid contents being tyrosine, glycine serine, and alanine. Silk fibroin makes up about 75–83 % of silk fibers with the rest of the silk fiber being made up of sericin, wax, and other components such as hydrocarbons.

Like other silks, the **silk fibroin** is attractive for biomedical application due to its nontoxic, biodegradable, and biocompatible nature. In addition, the silk fibroin shows desirable mechanical and chemical properties making it an excellent fiber for a variety of applications such as food additives, cosmetics, matrix for transdermal drug delivery, scaffolds, and fibers

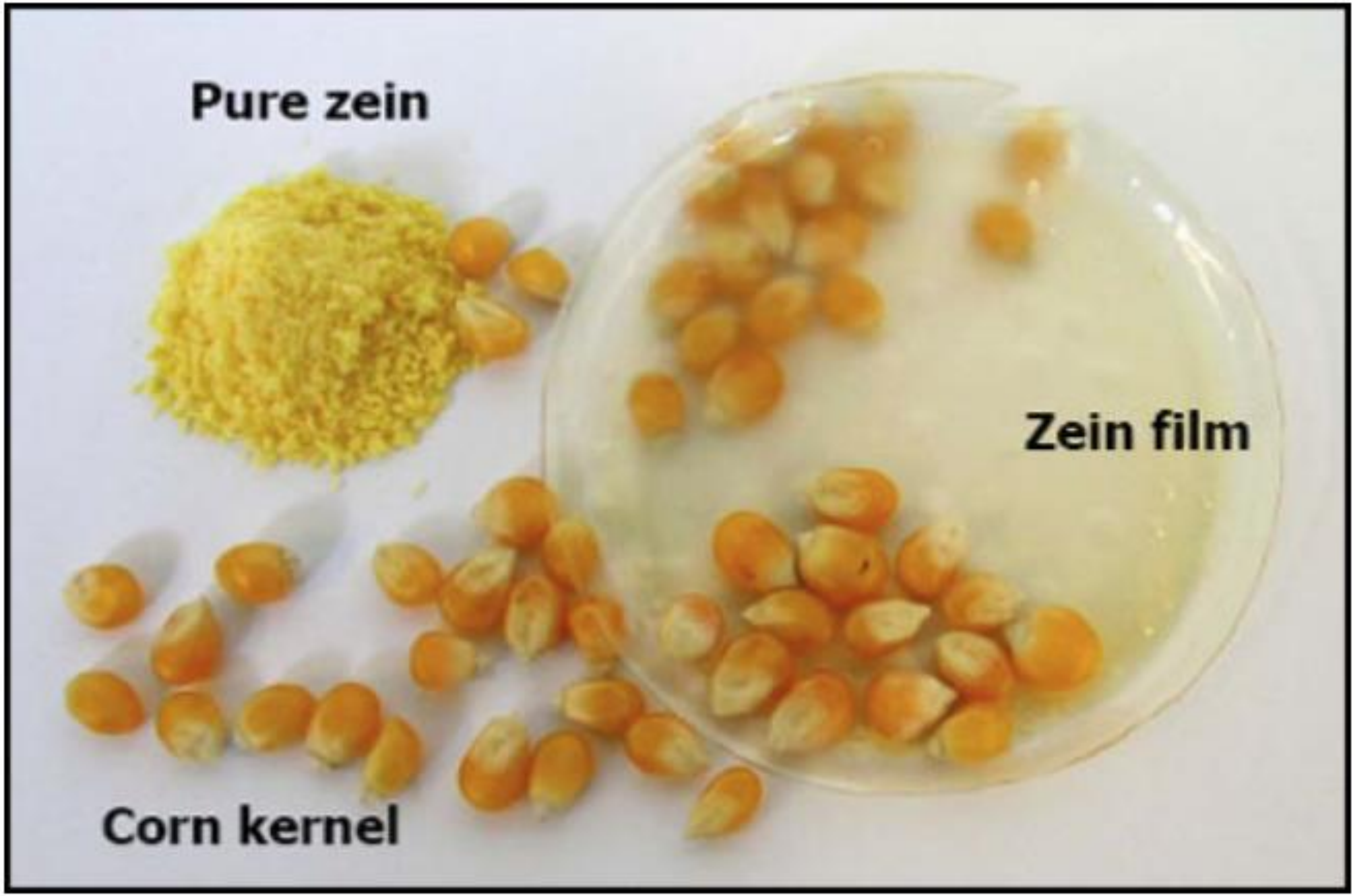
The silk fibroin is very versatile and can be prepared into various forms such as **gels, films, fiber, and powder** (Park 2004). The amount of silk fibroin obtained from a particular insect is affected by the nutritional intake and environmental conditions such that these insects can be cultivated for the purpose of producing the desired quantity and quality of silk fibroin.



Primary structure of fibroin, (Gly-Ser-Gly-Ala-Gly-Ala)$_n$

Zein

A by-product of corn processing, zein is a hydrophobic prolamin protein with thermoplastic property. It is soluble in alcohol and has good film forming properties albeit forming rather brittle films; the film property can be improved through use of other additives and by maintaining the right operating conditions (Guo 2012). It has potential for application as films and coatings in food and pharmaceuticals (Sharma et al. 2011; Elisangela 2007).


Pure zein
Zein film
Corn kernel

Zein: A natural Biopolymer from a Renewable Resource

Zein is the storage protein in corn kernels. It has a number of unique characteristics and functionalities which makes zein very valuable in diverse commercial applications.

It is: A natural film-forming polymer.

Inherently resistant to water and grease penetration .

Thermoplastic, which means biodegradable plastics can be made from zein.

Non-allergenic, which permits its use in food products.

Wheat Gluten

Gluten is a by-product from processing of starch present in wheat flour. It contains two prolamin proteins, gliadin a monomeric polypeptide soluble in dilute salt and glutenin a polymer complex soluble in acidic solutions.

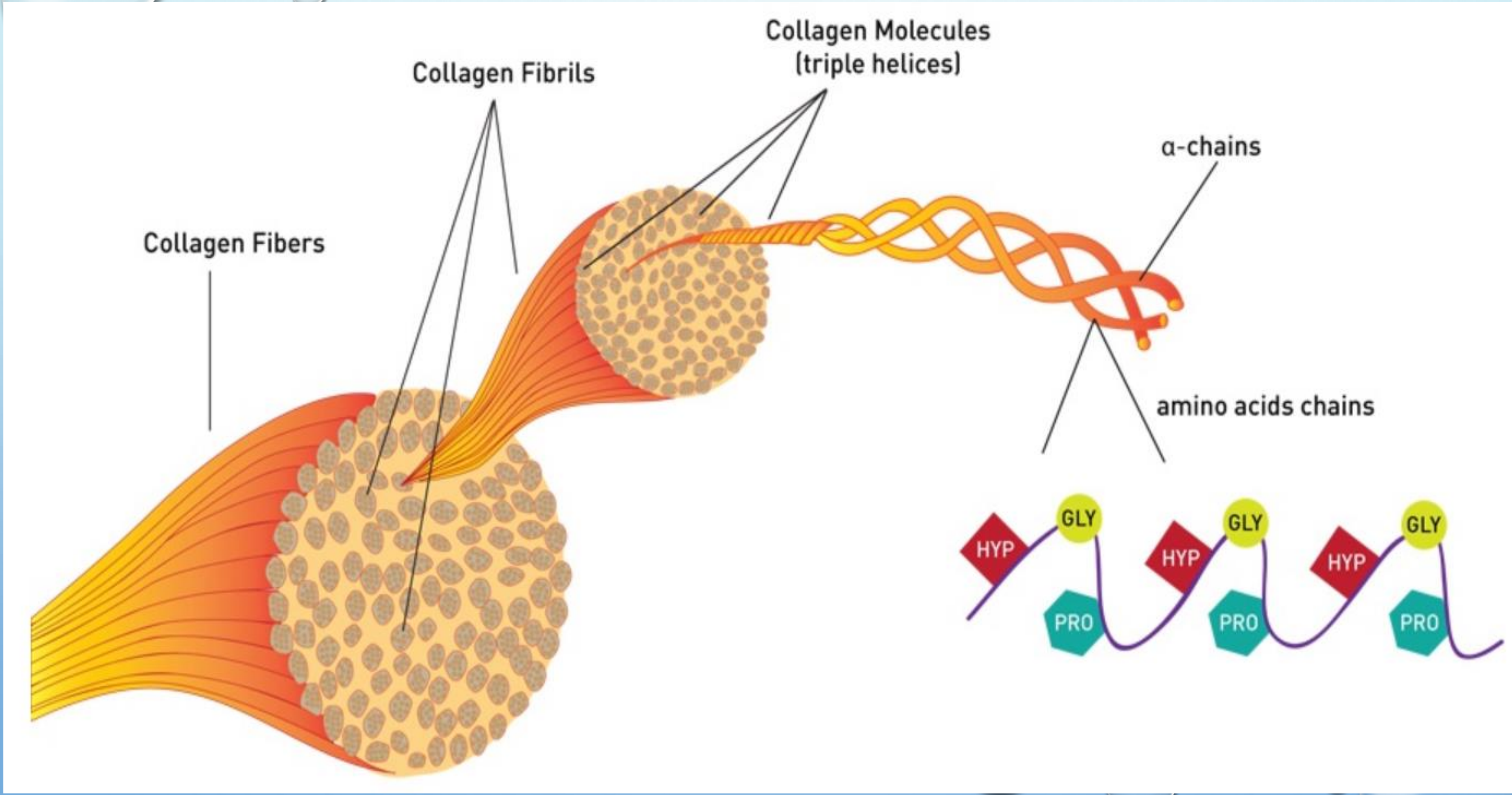
Although in the wheat plant these proteins serve mainly as storage protein, gluten has unique viscoelastic properties which make it commercially attractive in structural applications such as film forming and bread making

Wheat gluten

also contains other proteins, such as **albumins** and **globulins**, which serve mainly biological purposes as catalysts and regulators (Waga 2004). The film forming ability of wheat gluten can be modified through addition of plasticizer such as glycerol (Tanada-palmu 2000) or varying the pH (Herald 1995).

Collagen

Collagen is the most abundant protein in mammals making up about 25 % of the dry mass. It is a structural protein made of three polypeptide chains folded into a triple helix structure usually produced by fibroblast cells. Due to its biodegradability, biocompatibility, availability, and versatility, collagen is widely applied in: biomedicine, pharmaceutics, and cosmetics. It is found in tissues such as muscles, skin, and bone where it provides strength and flexibility.


Collagen Molecules
(triple helices)
Collagen Fibrils
α-chains
Collagen Fibers
amino acids chains
HYP
GLY
PRO
HYP
GLY
PRO
HYP
GLY
PRO

Collagen type varies
from source to source and also within sources, with the most common type used in industries being **type 1** collagen. Other types are listed in Table 1.2.

Table 1.2 Collagen type, forms, and distribution

	Type	Molecular formula	Polymerized form	Tissue distribution
Fibril—forming (fibrillar)	I	$[\alpha l(I)]_2\alpha 2(I)$	Fibril	Bone, skin, tendons, ligaments, cornea (represent 90 % of total collagen of the hitman body)
	II	$[\alpha l(n)]_3$	Fibril	Cartilage, intervertebrate disk, notochord, vitreous humor in the eye
	III	$[\alpha l(III)]_3$	Fibril	Skin, blood vessels
	V	$[\alpha l(V)]_2\alpha 2(V)$ and $\alpha l(V)\alpha 2(V)\alpha 3(V)$	Fibril (assemble with type I)	*Idem* as type I
	XI	$\alpha l(XI)\alpha 2(XI)\alpha 3(XI)$	Fibril (assemble with type II)	*Idem* as type II

			type II)	
Fibril—associated	IX	α1(IX)α2(IX) α3(IX)	Lateral association with type II fibril	Cartilage
	XII	$[\alpha 1(XII)]_3$	Lateral association with type I fibril	Tendons, ligaments
Network—forming	IV	$[\alpha 1(IV)]_2\alpha 2(IV)$	Sheet-like network	Basal lamina
	VII	$[\alpha 1(VII)]_3$	Anchoring fibrils	Beneath stratified squamous epithelia

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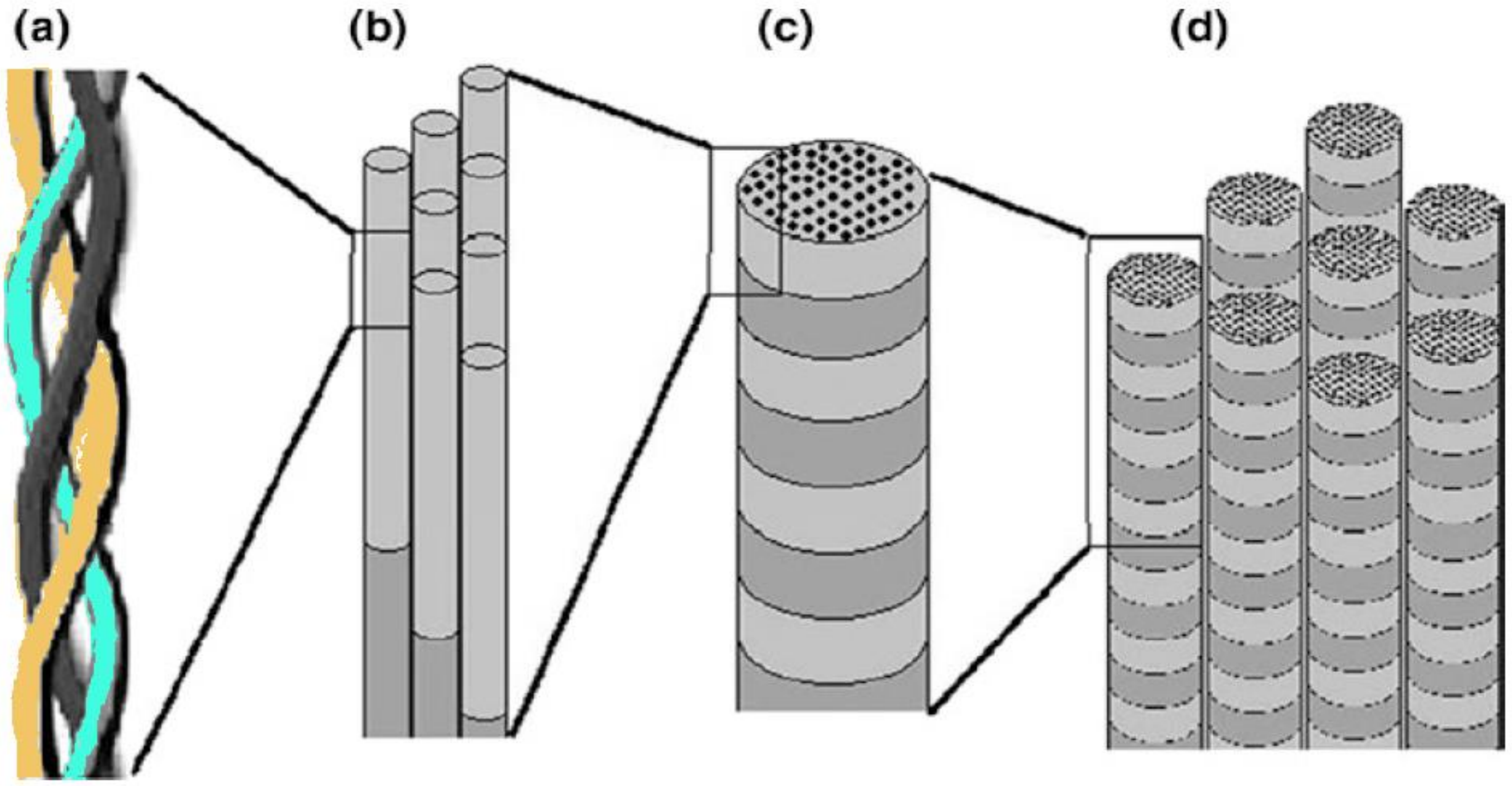
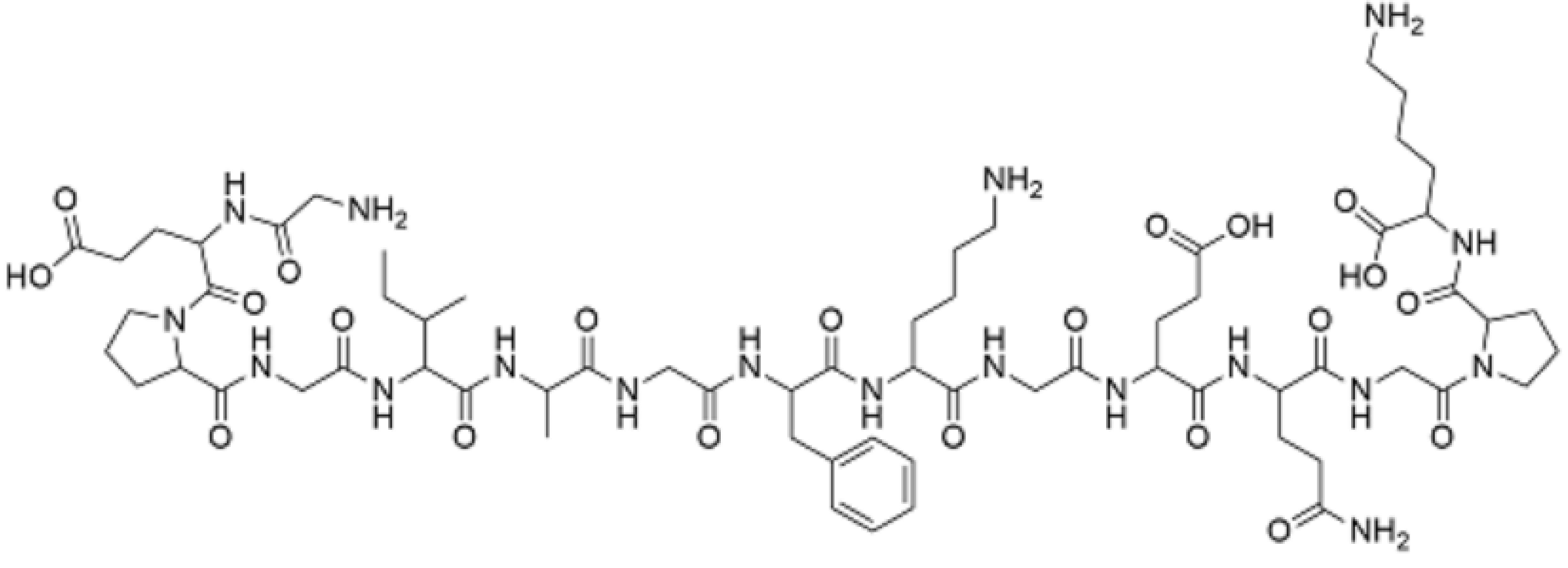


Schematics representing (a) a segment of a triple helix collagen chain, (b) collagen molecules, (c) collagen fibril made up of collagen molecules, (d) Collagen fibril aggregates forming collagen fiber. (Reproduced from Parenteau-Bareil (2010) under creative commons attribution license.)



Type II-Collagen

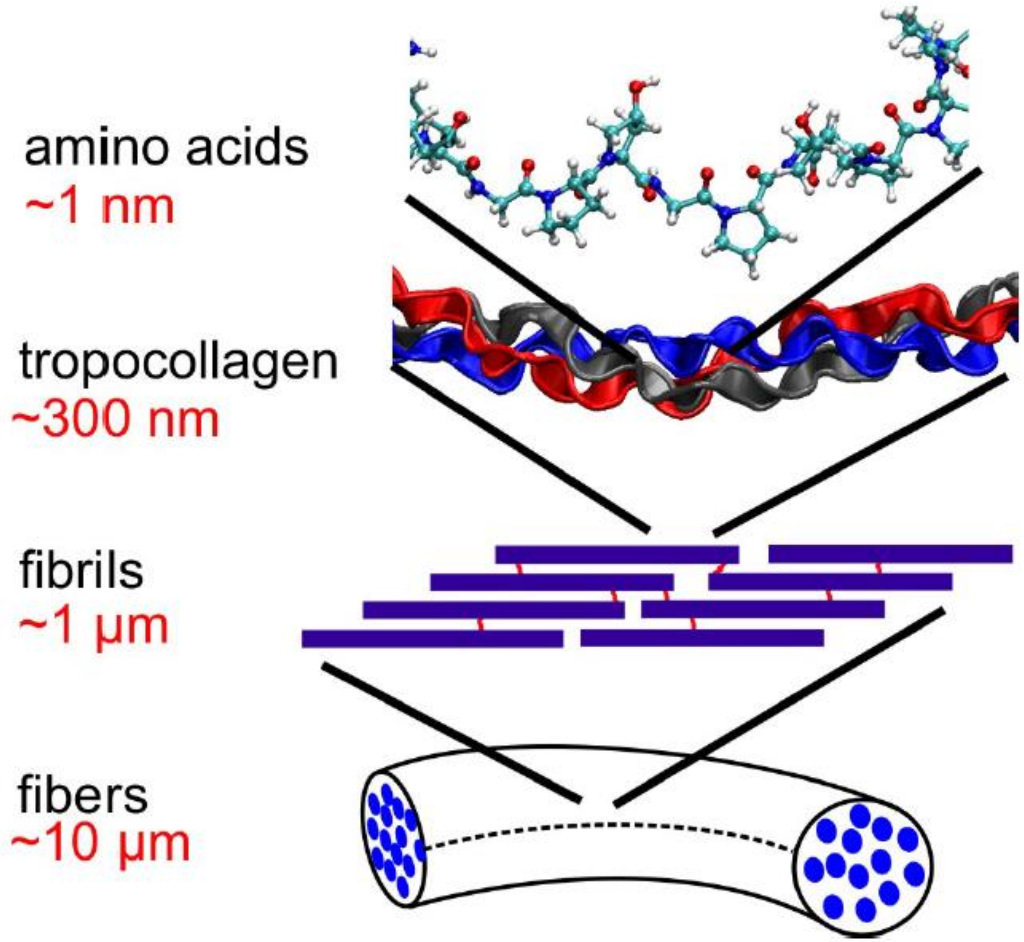
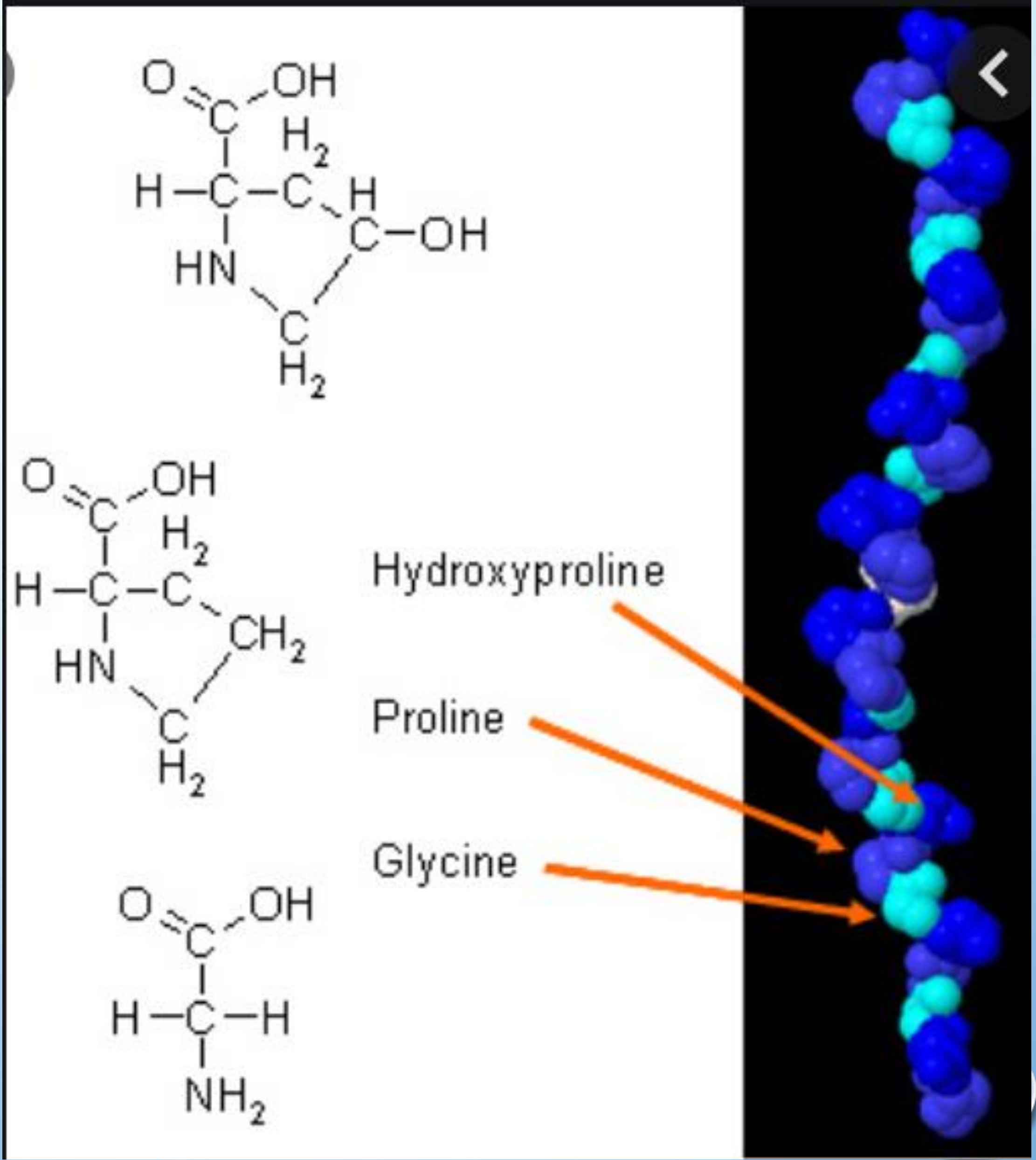


Figure 1: The hierarchical design of collagen. The structural features of collagen ranges from the amino acid sequence, tropocollagen molecules, collagen fibrils to collagen fibers. The new multi-scale model describes the mechanical properties of collagen fibrils using a hierarchical multi-scale scheme that starts from the atomistic level of amino acids (Figure created by M.J. Buehler / MIT).



Gelatine

Gelatine is a derived protein; it is the partially hydrolyzed form of collagen extracted from tissues such as bones and skins of animals through thermal hydrolysis using either an acid or alkali. There is also growing interest in extraction of gelatine from the scales of fish and insects as potential preferred alternatives to mammalian sourced gelatin.

It is a mixture of polypeptides and proteins formed as a result of irreversible hydrolysis of collagen, which results in the unfolding of the α triple helix structure by partially breaking some of the hydrogen bonds between the inter wound polypeptide chains.

Gelatin obtained from pig skin constitutes about 50% of world production and is mainly composed of collagen extracted from skin by acidic baths and thermal treatments. The gelatin is used to make various products, notably hard gelatin capsules (HGC) which of varying solubility in water. This issue has been known for many years and has been, and remains, a subject of study and debate.

The main reason for low gelatin dissolution rates is its tendency to form cross-links in the denatured collagen chains under specific conditions which stabilize the gel network and prevent dissolution. As it is extracted from animal tissues, gelatin may contain molecules other than collagen (sugars, lipids and other proteins) which may react with collagen chains to form covalent bonds. Although this biopolymer has been the subject ofnumerous publications, its structure and composition is not well defined. Indeed, there are many differences from an article to another.

Figure 4: Examples of hydrogen bond (dotted line) in gelatin chains (a) and between gelatin chains and water molecules (b)

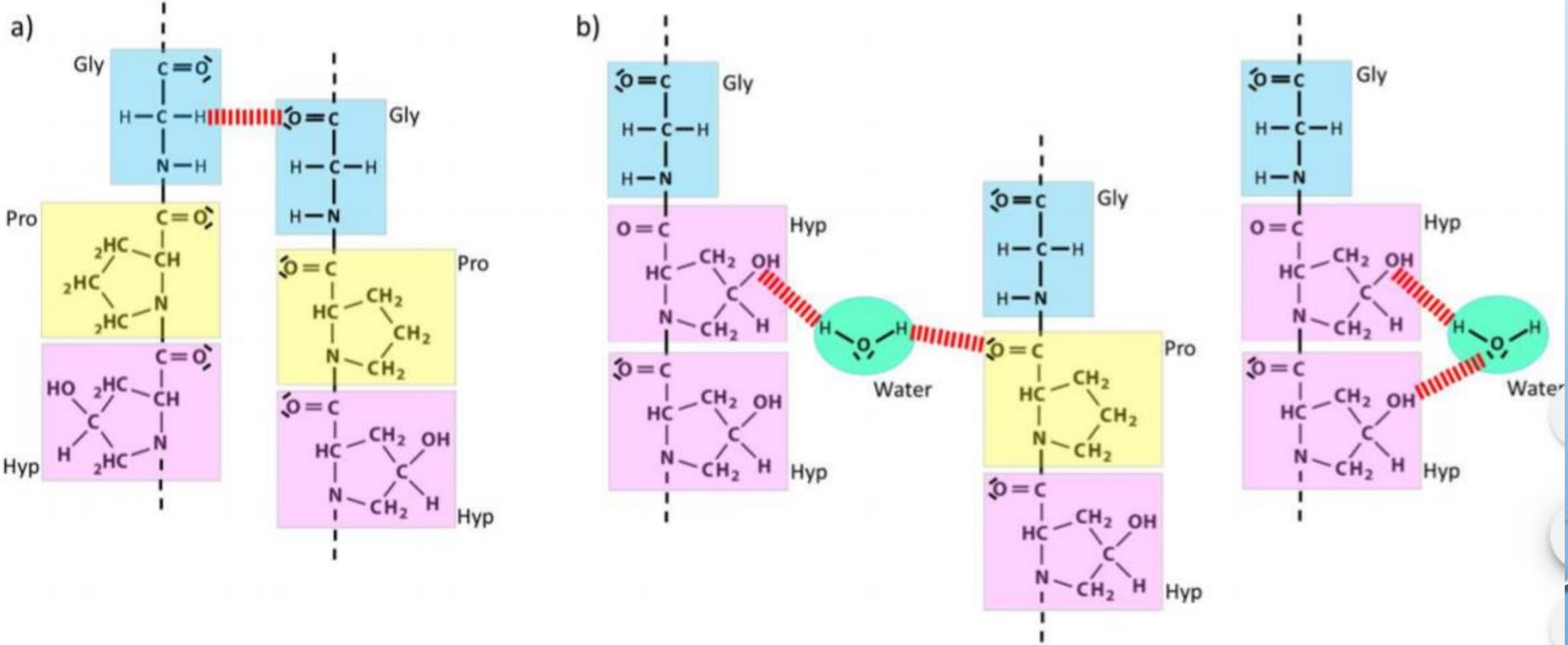


Figure 11: Aminal cross-links found in gelatin adapted from Digenis et al., (1994). Copyright (1994) Wiley. This material is reproduced with permission of John Wiley & Sons, Inc

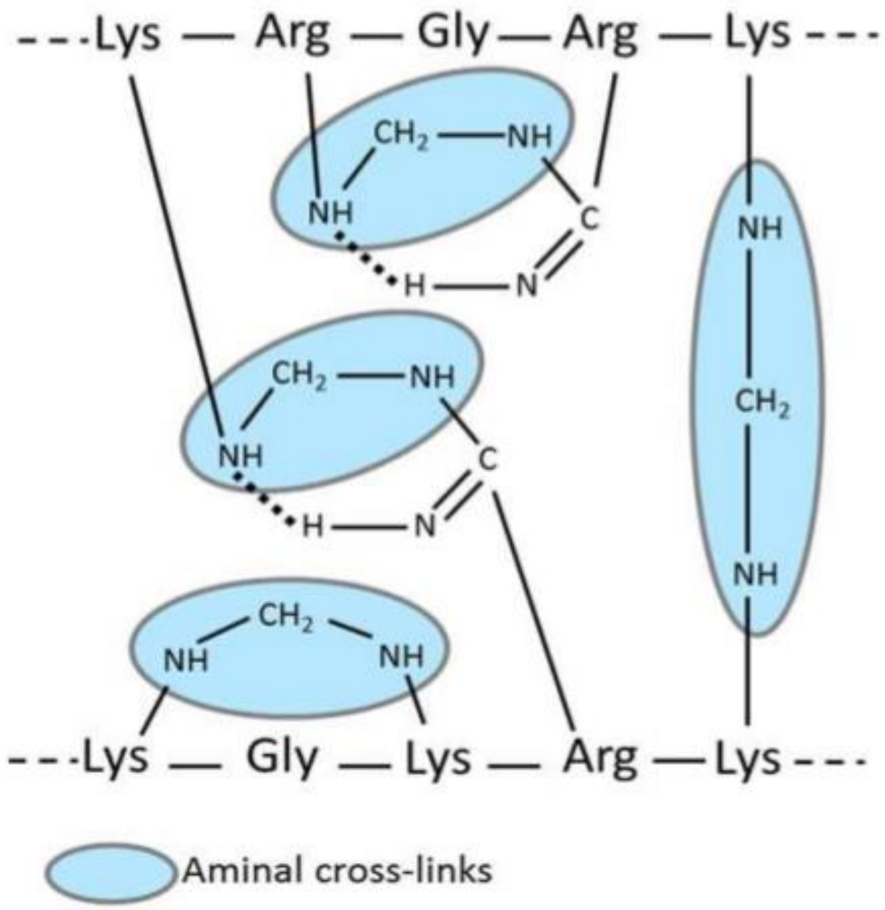


Figure 9: Methylene bond formation in gelatin adapted from Digenis et al., (1994). Copyright (1994) Wiley. This material is reproduced with permission of John Wiley & Sons, Inc

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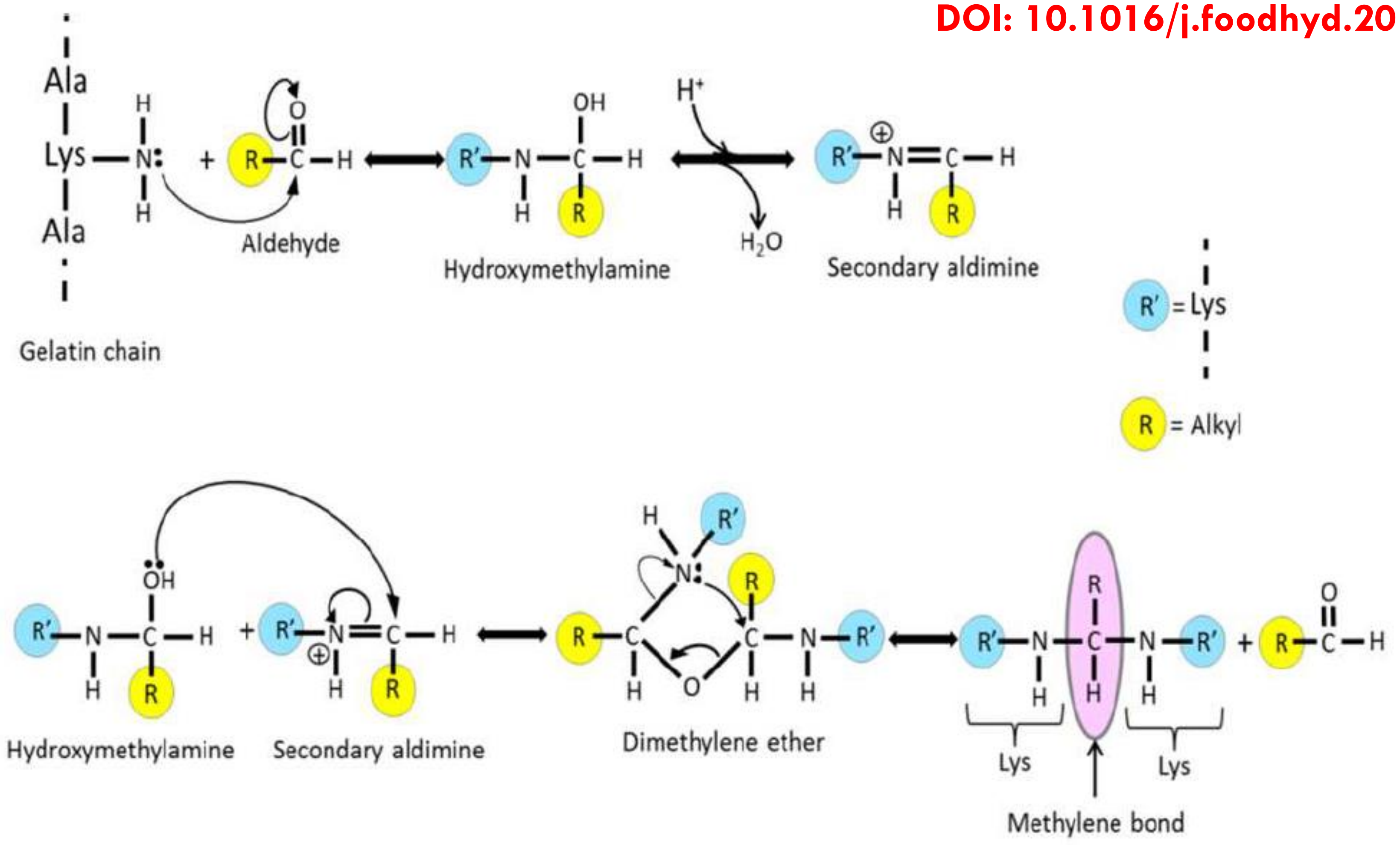

Gelatin is of two types, **type A** which is gelatine obtained through acid hydrolysis and **type B** obtained through basic (alkali) hydrolysis. The properties of gelatine depend on the source and extraction method; for instance, studies have shown that gelatine from insects have properties that are different from commercial gelatin. Studies also show that gelatine from different fishes and their parts also differ.

Gelatin is widely applied in foods, pharmaceutics, and cosmetics for its viscoelastic properties to act as gelling agent, thickener, or stabilizer.