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Weakening collagen evidences its strength over millions of years?

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Believers in deep time have been struggling with the question of soft tissue finds (intact biomolecules such as proteins and DNA)[1] in fossils purported to be many millions of years old. For instance, people who believe dinosaurs went extinct 65 Ma ago are desperate to come up with plausible explanations for these controversial discoveries in the fossils.

Suggestions that 'it is not what you think it is' have been mostly wiped off the table—together with the biofilm that was put forward as one of the possible alternatives. A likelier candidate is contamination, but even that is becoming more difficult to defend in some cases.[2–4] Yet a third justification is that such biomolecules can 'survive' for millions of years, after all! Can they?

Half-lives

A paper by Yang *et al.*, MIT scientists in the American Chemical Society publication *ACS Central Science*, refers to the fact that collagen—a common structural protein found in many tissues, including our skin and bones—has been detected in dinosaur fossils:

> "… collagen … has remained intact for (at least) hundreds of millions of years, exceeding the half-life of a peptide bond by a millionfold or more."[5]

The authors address the glaring problem in that statement, which is that in a neutral aqueous environment "peptide bonds have a half-life of only ~500 years".[5,6]

Peptide bonds (figure 3) are the connections between one amino acid building block with the next one in line. The amino group linked to the acid carboxyl group of the next amino acid forms the backbone of a peptide chain—the primary structure of a protein.

Using the half-life number of ~500 years, only about 0.2% of the initial peptide bonds persist after nine half-lives. Counting backwards from the present, that would be ~4,500 ka ago; i.e., when Noah was alive. After 10 half-lives, only a 1,000th of the original signal is left. With peptide bonds, going back 65 Myr equates to 130,000 half-lives! After millions of years, nothing larger than a dipeptide—containing a proline—should be found. There is no way we should be able to identify any protein in a sample if it truly was millions of years old.

Now, collagen is a robust protein, strengthened by its triple-stranded helix of polypeptides (called 'alpha chains'),[7] and also by the cross-links between these three strands.

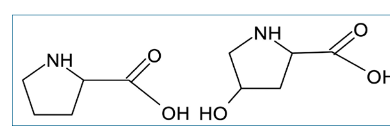

Figure 1. Proline and hydroxyproline

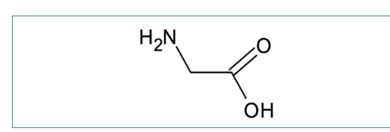

Figure 2. Glycine

Figs 1 and 2 drawn by LT using ChemSketch (by ACDLabs)

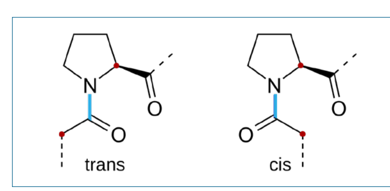

Figure 3. (trans and cis respectively). The peptide bond (N—C) is indicated in blue.

Hbf878, Wikimedia | PD

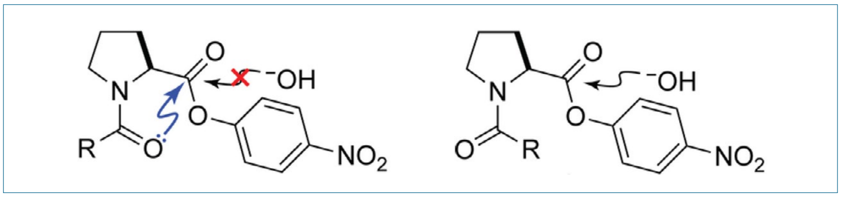

Figure 4. Synthetic molecules incorporating isomeric forms of proline (trans left, and cis right*)*

Yet, proteins more fragile have been discovered in fossil remains of similar alleged age—and older![8,9]

The chemistry

Studies that investigate the (half-life) decay of organic molecules have never shown evidence of such biomolecules lasting millions of years.[10–12] The authors of the paper described here[5] tried to explain how they possibly *could* have lasted that long, by using three different ester configurations around the amino acid proline. Proline and its hydroxylated version hydroxyproline (figure 1) together make up ~22% of the amino acids in collagen.[13] Glycine (figure 2) is the most ubiquitous amino acid in the collagen alpha chains, and usually occurs at every third position.

Molecules can exist in different forms—even with the same chemical formula. Stereoisomers possess handedness (left or right), formally called 'chirality', and molecules comprised of the same atoms are termed 'enantiomers' (mirror images). Another group of isomers with the same chemical formula is the diastereomers category; this includes *cis/trans* isomers. Proline in collagen is always present as a trans isomer (see figure 3).[13]

The experiments

Yang *et al.*[5] found that the synthetic molecule incorporating the trans isomer of collagenous proline did not allow water to hydrolyze the ester group (see figure 4). This is due to the Pauli exclusion principle, which explains how only a limited number of electrons can occupy any one of an atom's orbitals.[14] However, in the cis isomer, there was no such electron 'crowding', and water was able to 'get in' and hydrolyze the bond (see figure 4).[15]

It is important to note that the chemicals for these experiments, including different ratios of trans/cis isomers, were all synthesized in the lab—no bone remains were actually investigated. So all that the researchers have really shown is that when you decrease the amount of the trans isomer and increase the amount of the cis isomer, it becomes easier to break the peptide chain. That *does not prove* that collagen (containing only trans proline and mostly insoluble in water) can last for millions of years. If anything, it shows that if you alter the design to include the unnatural cis proline, it breaks down more quickly.

Conclusion

Synthetic chemistry may give clues about how organic chemistry works in nature, but, even so, it is important to compare like-for-like. Showing that cis isomers lead to more easily disrupted bonds does not mean that the less reactive trans isomer can therefore help collagen last for millions of years. Discoveries of original intact material can be better explained by exquisite preservation (of the naturally occurring trans isomer in collagen, rather than the synthetic cis isomer) due to the conditions during Noah's Flood, a little less than 4.5 ka ago. To stretch this preservation to millions of years is not credible and defies basic chemistry and physics.[16]

References

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7. Think of Ecclesiastes 4:12, a threefold cord is not quickly broken.
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14. The Pauli exclusion principle states that no two electrons can occupy the same atom with the same configuration defined by the four quantum numbers: the principal for the energy level orbital (n), angular moment describing the orbital shape (ℓ), magnetic orientation (m_ℓ), and electron spin (m_s).
15. The energy level of a non-bonding orbital is normally higher than that of valence shell bonding, but lower than what is called an anti-bonding orbital, designated by π*. In collagen, n→π* interactions are abundant, providing electron density around 99.9% of the carbonyl groups. This means that there is 'no room' for any negatively charged hydroxyl groups (deprotonated water) to disrupt the locality of the trans peptide bond and subsequently break it.
16. Quoting Matthew Collins; in: Morton, M.C., Cretaceous collagen: can molecular paleontology glean soft tissue from dinosaurs? *Earth*, 16 Oct 2017; earthmagazine.org.