Ideas and comments about mechanisms and pathways and verifying the molecules or elements with them.

Cells in the human body require many compounds to survive. The main substances found in every cell are a combination of lipids, carbohydrates, nucleic acids and proteins. Each of these substances plays a different role in the body, and all of them must either come from the diet or be manufactured using other chemicals in the body.

The genetic information of cells

Cells can thus be seen as a self-replicating network of catalytic macromolecules engaged in a carefully balanced series of energy conversions that drive biosynthesis and cell movement. But energy alone is not enough to make self-reproduction possible; the cell must contain detailed instructions that dictate exactly how that energy is to be used. These instructions are analogous to the blueprints that a builder uses to construct a house; in the case of cells, however, the blueprints themselves must be duplicated along with the cell before it divides, so that each daughter cell can retain the instructions that it needs for its own replication. These instructions constitute the cell's heredity.

Coupled chemical reactions

Cells must obey the laws of chemistry and thermodynamics. When two molecules react with each other inside a cell, their atoms are rearranged, forming different molecules as reaction products and releasing or consuming energy in the process. Overall, chemical reactions occur only in one direction; that is, the final reaction product molecules cannot spontaneously react, in a reversal of the original process, to reform the original molecules. This directionality of chemical reactions is explained by the fact that molecules only change from states of higher free energy to states of lower free energy. Free energy is the ability to perform work (in this case, the "work" is the rearrangement of atoms in the chemical reaction). When work is performed, some free energy is used and lost, with the result that the process ends at lower free energy. To use a familiar mechanical analogy, water at the top of a hill has the ability to perform the "work" of flowing downhill (i.e., it has high free energy), but, once it has flowed downhill, it cannot flow back up (i.e., it is in a state of low free energy). However, through another work process—that of a pump, for example—the water can be returned to the top of the hill, thereby recovering its ability to flow downhill. In thermodynamic terms, the free energy of the water has been increased by energy from an outside source (i.e., the pump). In the same way, the product molecules of a chemical reaction in a cell cannot reverse the reaction and return to their original state unless energy is supplied by coupling the process to another chemical reaction.

All catalysts, including enzymes, accelerate chemical reactions without affecting their direction. To return to the mechanical analogy, enzymes cannot make water flow uphill, although they can provide specific pathways for a downhill flow. Yet most of the chemical reactions that the cell

needs to synthesize new molecules necessary for its growth require an uphill flow. In other words, the reactions require more energy than their starting molecules can provide.

Cells use a single strategy over and over again in order to get around the limitations of chemistry: they use the energy from an energy-releasing chemical reaction to drive an energy-absorbing reaction that would otherwise not occur. A useful mechanical analogy might be a mill wheel driven by the water in a stream. The water, in order to flow downhill, is forced to flow past the blades of the wheel, causing the wheel to turn. In this way, part of the energy from the moving stream is harnessed to move a mill wheel, which may be linked to a winch. As the winch turns, it can be used to pull a heavy load uphill. Thus, the energy-absorbing (but useful) uphill movement of a load can be driven by coupling it directly to the energy-releasing flow of water.

In cells, enzymes play the role of mill wheels by coupling energy-releasing reactions with energy-absorbing reactions. The mushroom chemistry provides many enzymes for mammalian chemistry support. As discussed below, in cells the most important energy-releasing reaction serving a role similar to that of the flowing stream is the hydrolysis of adenosine triphosphate (ATP). In turn, the production of ATP molecules in the cells is an energy-absorbing reaction that is driven by being coupled to the energy-releasing breakdown of sugar molecules. In retracing this chain of reactions, it is necessary first to understand the source of the sugar molecules.

Elements

Of all the elements found on Earth, about 25 are essential for life. Just 6 elements account for about 99 percent of the mass of the human body. But very little of this matter exists as pure elements. Instead, most is in the form of compounds, which are substances made up of two or more different elements. For example, water is a compound made of hydrogen and oxygen. The smallest unit of any element is called an atom. In a compound, atoms of two or more elements are joined together by chemical bonds. Most compounds in cells are made up of atoms bonded together in molecules. For example, a molecule of water is made of one atom of oxygen bonded to two atoms of hydrogen. Most activities that take place within cells involve atoms and molecules interacting. In this process, called a bond between atoms are broken and new bonds form to make different molecules. Energy is needed to break bonds between atoms, and energy is released when new bonds form. Cells use chemical energy for life activities.

Elements in the Human Body

Oxygen 65.0% Carbon 18.5% Hydrogen 9.5% Nitrogen 3.3% Calcium 1.5% Phosphorus 1.0% other 19 elements 1.2%

Mechanisms and pathways

These Mushroom Strains of various species contain bioactive metabolites capable of healing, revitalize and modulate our immune system. These biological response modifiers help activate macrophages and T-cells and produce cytokines, including interleukins as well as tumor necrosis factors (TNF).

The beta-D-glucan, a polysaccharide in these strains of medicinal mushrooms are oxygen-bearing molecules. In the process of breakdown, this oxygen is released and made available at a cellular level. Polysaccharides are poorly digested and are acted upon by intestinal bacteria to release oligosaccharides. The main immunological activity is believed to be due to the interaction of the oligosaccharides with gut-associated lymphoid tissue. Immune cells associated with (GALT) gut-associated lymphoid tissue, activated by beta-glucans in the gut, may migrate to other tissue and thereby exert immune -modulating activity. Beta-glucans stimulate interferon, interleukin, TNF, NK, B and T-lymphocytes, tumor-infiltrating lymphocytes, lymphokine-activated killer cells, macrophages, granulocytes in bone marrow, and production of platelets in bond marrow. Beta-glucans also attach themselves to the receptor sites on the immune cells and activate them and other fungi enzymes attach themselves to the cancer cells, allowing them to be recognize as "foreign body" and create a higher level of response.

Dectin-1, on macrophages, is a receptor that mediates beta-glucan activation of phagocytosis and production of cytokines, an action coordinated by the toll-like receptor-2.

Activated complement receptors on natural killer cells, neutrophils, and lymphocytes are associated with tumor cytotoxicity, Scavenger and lactosyl-ceramide bind beta-glucans and mediate a sequence of pathways leading to immune activation.

TNF is a pro-inflammatory cytokine that activates nuclear factor-kB (NFkappaB) and c-Jun N-terminal kinase (JNK0. NFkappaB is anti-apoptotic, and JNK contributes to cell death. In cancer, TNF is a double-edged sword. It can be an endogenous tumor-promoter, because TNF stimulates the growth, proliferation, invasion and metastasis, and tumor angiogenesis of cancer cells. On the other hand, TNF is also a cancer-killer, and the mushroom chemistry appear to sensitize cancer cells to TNF-induced apoptosis by inhibiting NFkappaB, etc. The mushroom mycelium produce natural antibiotic enzymes that are antiviral, antibacterial, antiprotozoal, and antifungal.

One study has shown that post-menopausal women eating various strains of the medicinal mushrooms received more breast cancer protection than women who were still ovulating (S. A. Hong et al. 2008)

Large molecules support cell function.

In living things, there are four main types of large molecules: (1) carbohydrates, (2) lipids, (3) proteins, and (4) nucleic acids. Thousands of these molecules work together in a cell. The four types of molecules in all living things share one important characteristic. They all contain carbon atoms. These large molecules are made up of smaller parts called subunits.

Carbohydrates

Carbohydrates provide the cell with energy. Simple carbohydrates are sugars made from atoms of carbon, oxygen, and hydrogen. Inside cells, sugar molecules are broken down. This process provides usable energy for the cell. Simple sugar molecules can also be linked into long chains to form more complex carbohydrates, such as starch, cellulose, and glycogen. Starch and cellulose are complex carbohydrates made by plant cells. When a plant cell makes more sugar than it can use, extra sugar molecules are stored in long chains called starch. Plants also make cellulose, which is the material that makes up the cell wall. Animals get their energy by eating plants or other animals that eat plants. Cells use carbohydrates as energy as well as store energy. They also help with the breakdown of fatty acids and help with cell functions like cell growth. Carbohydrates are also used in cells because they provide a structural material for cell walls.

Lipids

Lipids are the fats, oils, and waxes found in living things. Like carbohydrates, simple lipids are made of atoms of carbon, oxygen, and hydrogen and can be used by cells for energy and for making structures. However, the atoms in all lipids are arranged differently from the atoms in carbohydrates. Many common lipids consist of a molecule called glycerol bonded to long chains of carbon and hydrogen atoms called fatty acids. This structure gives lipids unique properties. One extremely important property of lipids is that they cannot mix with water.

Proteins

Proteins are made of smaller molecules called amino acids. Amino acids contain the elements carbon, oxygen, hydrogen, nitrogen, and sometimes sulfur. In proteins, amino acids are linked together into long chains that fold into three-dimensional shapes. The structure and function of a protein is determined by the type, number, and order of the amino acids in it. Your body gets amino acids from protein in food, such as meat, eggs, cheese, and some beans. After taking in amino acids, your cells use them to build proteins needed for proper cell functioning. Some amino acids can be made by the body, but others (essential amino acids) must be taken in from an outside food source. There are many types of proteins. Enzymes are proteins that control chemical reactions in the cells. Other proteins support the growth and repair of living matter. The action of proteins in your muscles allows you to move. Some of the proteins in your blood fight infections. Another protein in your blood delivers oxygen to all the cells in your body. Proteins are also important parts of cell membranes. Some proteins in the cell membrane transport materials into and out of the cell.

Technically mechanisms are disproven. You can find evidence supporting your mechanism- computational, kinetic, what have you- but the process of studying a mechanism involves making a set of assumptions about the possible pathways, ruling out all but one, and trying to find evidence to support the one left. What you end up with is a "proposed mechanism consistent with all the data obtained", not a proven mechanism.

That said, it's generally accepted that some mechanisms are essentially proven because they've been tested from so many different fronts, and since computations have gotten so accurate you can in essence prove a mechanism, if not technically.

Nucleic acids

Nucleic acids are the molecules that hold the instructions for the maintenance, growth, and reproduction of a cell. There are two types of nucleic acids: DNA and RNA. Both DNA and RNA are made from carbon, oxygen, hydrogen, nitrogen, and phosphorus. The subunits of nucleic acids are called nucleotides. DNA provides the information used by the cell for making proteins a cell needs. This information takes the form of a code contained in the specific order of different nucleotides in the DNA.

The pattern of nucleotides in DNA is then coded into RNA, which delivers the information into the cytoplasm. Other RNA molecules in the cytoplasm produce the proteins.

Water

All of the chemical reactions inside the cell take place in water. Water is also in the environment outside the cell. For example, water inside cells makes up about 46 percent of your body's mass, and water outside the cells in body fluids accounts for another 23 percent. A water molecule consists of two atoms of hydrogen bonded to one atom of oxygen. Because of its structure, a water molecule has a slight positive charge near the hydrogen atoms and a slight negative charge near the oxygen atom. Molecules that have slightly charged ends are said to be polar. Like a magnet, the ends of a polar molecule attract opposite charges and repel charges that are the same. Because water is a polar molecule, many substances dissolve in water. However, not all materials dissolve in water. If you have ever shaken a bottle of salad dressing, you've probably observed that oil and water don't mix.

History

Photosynthesis, the beginning of the food chain.

Sugar molecules are produced by the process of photosynthesis in plants and certain bacteria. These organisms lie at the base of the food chain, in that animals and other no photosynthesizing organisms depend on them for a constant supply of life-supporting organic molecules. Humans, for example, obtain these molecules by eating plants or other organisms that have previously eaten food derived from photosynthesizing organisms.

plants: photosynthesis The location, importance, and mechanisms of photosynthesis.
Encyclopedia Britannica, Inc.

Plants and photosynthetic bacteria are unique in their ability to convert the freely available electromagnetic energy in sunlight into chemical bond energy, the energy that holds atoms together in molecules and is transferred or released in chemical reactions. The process of photosynthesis can be summarized by the following equation: (solar) energy + CO_2 + H_2O → sugar molecules + O_2.

The energy-absorbing photosynthetic reaction is the reverse of the energy-releasing oxidative decomposition of sugar molecules. During photosynthesis, chlorophyll molecules absorb energy from sunlight and use it to fuel the production of simple sugars and other carbohydrates. The resulting abundance of sugar molecules and related biological products makes possible the existence of no photosynthesizing life on Earth.

ATP: Fueling chemical reactions

Certain enzymes catalyze the breakdown of organic foodstuffs. Once sugars are transported into cells, they either serve as building blocks in the form of amino acids for proteins and fatty acids for lipids or are subjected to metabolic pathways to provide the cell with ATP. ATP, the common carrier of energy inside the cell, is made from adenosine diphosphate (ADP) and inorganic phosphate (P*i*). Stored in the chemical bond holding the terminal phosphate compound onto the ATP molecule is the energy derived from the breakdown of sugars. The removal of the terminal phosphate, through the water-mediated reaction called hydrolysis, releases this energy, which in turn fuels a large number of crucial energy-absorbing reactions in the cell. Hydrolysis can be summarized as follows: ATP +H_2O → ADP + P*i*+ energy.

adenosine triphosphate (ATP) Adenosine triphosphate, or ATP, is the primary carrier of energy in cells. The water-mediated reaction known as hydrolysis releases energy from the chemical bonds in ATP to fuel cellular processes.

Comments

Experimentally, you can determine if a reaction mechanism is correct by isolating the transition state intermediates of the reaction. That is, if the reaction mechanism is true, then there physically exists the middle step or transition molecule for the mechanism. However, most reactions occur too fast for one to isolate an intermediate and analyze using x-ray diffraction, NMR, or the like. This is where theoretical computational chemistry and quantum chemistry come into play. I work for a computational chemistry group mapping enzyme mechanisms, energy profiles, and catalysis surfaces. Basically, we prove or disprove mechanisms in a theoretical and computational way. We build the starting molecule, and input restrictions such as solvents and give the ending molecule. Then we optimize the structure, meaning we run calculations using quantum mechanics to determine the lowest energy conformation of the structure. From here we can see exactly how specific atoms will move based on mathematical calculation and determine if a proposed mechanism is correct.

Ether isolate the intermediates experimentally or run quantum computational calculations to asses viability of the mechanism.

From a theoretical perspective

I study organic mechanisms (frequently) using ab initio molecular dynamics and electronic structure methods. To understand the answer to your question, you must realize that real reactions do not proceed by one mechanism (in most cases). They don't even proceed by one pathway along a given mechanism. Think about an arbitrary dimer single-coordinate reaction (like a proton transfer between two DNA base pairs or even proton shoveling in water). The reaction proceeds in one basic "direction", but it can still occur along a spectrum of kinetic

energies. Not only can the exact reaction path differ, but all kinds of really unexpected side reactions can occur. The recent organic craze in roaming radicals is one example of this.

With this in mind: you can absolutely prove mechanisms within the framework of accepted assumptions. If you find a transition state, refine it, link to reactants to products and connect the intermediates; one can calculate effectively exact barrier heights and the pathway is established. Do this with a variety of exact methods and you've got a mechanism. You can use the details of this pathway to run MD simulations and get an approximation of things like branching ratios.

Understanding the barrier heights gives you an idea of kinetic control while understanding intermediate stability tells you about thermodynamic control in a reaction.
In short, yes. You can prove mechanisms mathematically. The SN2 case is fairly easy to prove and certain parts of the job are used frequently as test files in many QC engines. I think Q-Chem and GAMESS both have one. I should also mention that finding transition states is a process with ludicrously unpredictable difficulty.

To prove a reaction mechanism, what you want is to either directly or indirectly discover the intermediates and possibly the transition states.
The classical way has been to try the reaction many times, with different reactants, then analyze the products and figure out what happened. While it has worked for many reactions, it can be time-consuming.
In some cases, it is possible to isolate the intermediates by choosing the reactants such that severe steric impediment will keep the reaction from going through entirely, or by using an appropriate solvent to stabilize the intermediate.
Direct detection is hard because chemical reactions are very quick, happening on the order of picoseconds or even less. Femtosecond spectroscopy is quite new but has already been used to decipher reaction mechanisms, even being the subject of the 1999 Nobel prize in Chemistry.

In recent years, computational chemistry is becoming better and better, with more advanced functionals and forcefields to properly simulate atoms and the astounding increase in computational capacity that has been going on for decades. With calculations it is possible to investigate the potential energy landscape of an interaction between reactants, allowing the discovery of energy barriers and low energy pathways, so that after a sufficient number of geometries and techniques have been considered, a reasonable mechanism can be proposed.

Another way that I don't think has been mentioned is labeling. If you have starting materials that are isotopically labeled, the location of the labeled atoms in the product can confirm or disprove a mechanism.

As trad_is_rad wrote, "proving" a mechanism is looking at science the wrong way. This really is a microcosm of how all science operates. Karl Popper (for example) had a lot to say about how theories must be falsifiable, but it is impossible to prove a theory absolutely true. For example,

Newtonian mechanics was "proved" to be absolutely true, up until the time that people started looking at the motion of very small (quantum mechanics) or very fast (relativity) things.

Anyhow, back to the original question. Others have mentioned theoretical models, and in modern science, these can help corroborate a mechanism. Even in the era before computers though, chemists still discussed, defended and disproved mechanisms, generally based on various indirect evidence. For example, you may have studied in your general chemistry course how to derive a rate law from a mechanism. If your mechanism predicts that a certain reaction should have a rate proportional to the concentration of reactant X, it is straightforward to imagine (if not to conduct) the relevant experiment. If you double the amount of X and the reaction goes only 140% faster or goes 400% faster (instead of 200% faster), you have evidence to eliminate that possible mechanism. In short, you made a quantitative prediction about rates and saw whether it held up.

There are other even less direct methods. For example, the reaction of H2 and I2 was once thought to be a very straightforward bimolecular collision. An alternative mechanism was proposed, which involved cleavage of the I2 molecules and propagation by free iodine atoms. This resulted in the same empirical rate law, so kinetics measurements alone could not distinguish these two mechanisms. It was shown that irradiation of the reaction mixture with ultraviolet light accelerated the reaction. It was known the UV light would cause the cleavage of the I-I bond in I2. So, this evidence, which the simple bimolecular mechanism could not explain, supported the more complex mechanism.

To add what others have said about computational modelling being useful because it gives you information about the molecular geometries and energies along the reaction path, there is also a lot of other data that can be gleaned from a good model. Any electronic structure calculation will give you the wavefunction for the system you are studying. From that wavefunction you can look at the shapes and energies of the molecular orbitals, especially of course the HOMO and LUMO. You can look at the molecular electrostatic potential, for example to understand why a nucleophile will preferentially attack one end of a molecule over another, and the atomic charges, which allow you to see how the electron density of a system changes over the course of the reaction (it's never as simple as the curly arrows would lead you to believe). There are methods like QTAIM, ELF, and NBO that can give you information on the bonding within a system.