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Long Ago, Paris Was A Jungle

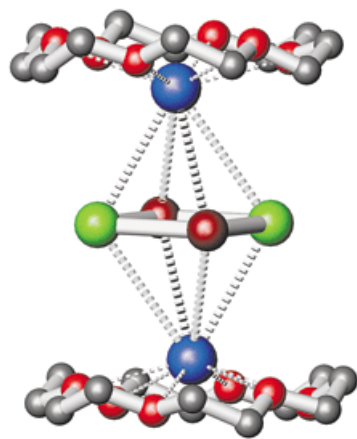


Modern-day Paris may have a reputation as being something of an urban jungle, but according to some new chemical evidence, tens of millions of years ago Paris was quite literally a jungle. Akino Jossang of Paris' National Museum of Natural History and colleagues did some detective work on a 55 million-year-old amber deposit found in the Oise River area of the Paris Basin. In extracts of the amber, they found a novel diterpene natural product (shown) that they named quesnoin (*J. Org. Chem.*, DOI: 10.1021/jo701544k). The researchers noted quesnoin's structural similarity to isoozic acid, a natural product isolated from tropical trees in the genus *Hymenaea*. Jossang's group suggests that quesnoin forms from isoozic acid via a Diels-Alder reaction initiated by a peroxy radical. If this theory is true, Jossang argues, then the Oise amber most likely came from an ancient ancestor of *Hymenaea oblongifolia*, a tree that is currently found only in the Amazon rain forest.

Immunoassay Based On Optical Diffraction

Purdue University scientists have developed a rapid and sensitive immunoassay method based on the spontaneous assembly of analyte molecules into an optical diffraction grating (*Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200703222). Ghanashyam Acharya, [David H. Thompson](#), and coworkers demonstrated the technique by trapping S-adenosyl homocysteine (SAH), a diagnostic marker for cardiovascular disease, in a molecular-sandwich-type configuration. Using standard microcontact printing methods, the team patterned gold chips with rows of nucleic acid aptamers designed to bind SAH's adenine group. The researchers also treated SAH samples with antibodies coupled to magnetic beads in order to bind the antibodies to SAH's homocysteine moiety. Exposure of the patterned chips to solutions of SAH bound to the tagged antibodies led to formation of micrometer-sized rows of sandwich-type complexes. By shining laser light on the assembly, the group produced characteristic diffraction patterns that enabled them to confirm the presence of SAH at concentrations in the low picomolar range.

Conflicting Inorganic Aromaticity



J. Am. Chem. Soc.

Aromaticity and antiaromaticity, once purely the domain of organic chemistry, has expanded in recent years to include organometallic complexes, all-metal clusters, and main-group compounds. In a new example, Angel Ugrinov and Ayusman Sen of Pennsylvania State University together with Shiv N. Khanna of Virginia Commonwealth University and coworkers report the synthesis and crystal structure of $\text{Te}_2\text{As}_2^{2-}$, the first four-membered ring anion made from a combination of group 15 and 16 elements (*J. Am. Chem. Soc.* **2008**, *130*, 782). The planar anion, sandwiched between two potassium 18-crown-6 units (shown), has alternating Te-As bond lengths and angles that give it a parallelogram geometry. The structure and molecular orbital analysis reveal a quite unusual electronic structure for the anion: δ -antiaromatic bonding coupled with π -aromatic bonding and a triplet electronic ground state, which leads to the distorted square shape and net aromatic character. While similar systems with this "conflicting aromaticity" have previously been observed in the gas phase, $\text{Te}_2\text{As}_2^{2-}$ is the first example isolated as a solid.

Organic Red Goo Found Outside Solar System

Collections of large organic molecules that form a reddish goo, seen in our solar system in places such as the surface of Titan, have now been spotted in a planet-forming disk of dust surrounding a star 220 light-years away (*Astrophys. J. Lett.*, DOI: 10.1086/527546). These molecules, dubbed "tholins" by the late astronomer Carl Sagan from the Greek word for muddy, couldn't exist on Earth—oxygen would destroy them. But in the environment of outer space, ultraviolet light interacting with compounds such as methane or ethane could produce tholins, which are thought to be biomolecule precursors. The newly sighted compounds were observed with the Near-Infrared Camera & Multi-Object Spectrometer aboard the Hubble Space Telescope. That these molecules exist in a system where planets are forming implies they might also exist on nascent planets. "If we see this kind of spectrum around other disks, we could be pretty confident that this is a common occurrence," says John H. Debes of the Carnegie Institution of Washington, one of the astronomers who made the discovery.

New Chorismate Metabolic Pathway

At least six bacterial biosynthetic routes to key biomolecules—including several amino acids, the vitamin folate, and the coenzyme ubiquinone—begin with the key metabolic intermediate chorismate. Researchers have now identified a seventh branching point in chorismate metabolism and determined that a product of this pathway is a major component of the enediyne antitumor antibiotic C-1027, one of the most cytotoxic natural products known (*Proc. Natl. Acad. Sci. USA*, DOI: 10.1073/pnas.0708750105). Ben Shen and coworkers at the University of Wisconsin, Madison, show that the benzoxazolinolate moiety of C-1027 is derived from chorismate by the sequential action of two enzymes: SgcD, a 2-amino-2-deoxyisochorismate (ADIC) synthase, and SgcG, an ADIC dehydrogenase. The reactions catalyzed by these enzymes yield 3-enolpyruvoylanthranilate, an intermediate that is further modified to form C-1027's benzoxazolinolate group. The findings could "provide the inspiration to search for other variations of chorismate-using enzymes" and could facilitate "genetic engineering and combinatorial biosynthetic approaches aimed at harnessing the inherent power of the C-1027 scaffold," the researchers write.

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