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- Science/Technology
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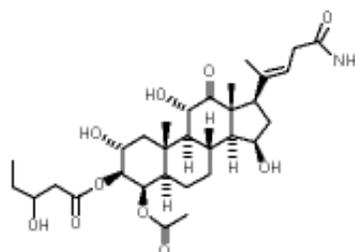
Volume 83, Number 33

p. 38

- [Unearthing rare treasures](#)
- [SF₆ is reactive fluorinator](#)
- [Cornflower pigment pictured](#)
- [Cholera toxin's harmful handshake](#)
- [Frogs eat ants for poisonous protection](#)

Unearthing rare treasures

The characterization of a crude mixture of natural products can be difficult, particularly when the sample is small and composed of a complex brew of low-concentration compounds such as steroids. But researchers continue to find ways to extract more information from ever-smaller samples. Frank C. Schroeder of Cornell University and colleagues now offer a powerful demonstration of the sensitivity that can be achieved by capillary NMR spectroscopy of biological samples (*J. Am. Chem. Soc.* **2005**, *127*, 10810). The researchers collected and combined whole-body extracts from just 50 members of a rare firefly species. They partially fractionated the mixture and analyzed each fraction by capillary NMR. The resulting spectra led to the identification of 13 new steroids, including the one shown here. Most of the steroids "could not have been characterized in a reasonable amount of time" without capillary NMR, according to Schroeder. "Crude or semipurified natural products extracts" can be characterized "without exhaustive purification," he adds. The approach should "greatly extend the range of accessible natural products research."

COURTESY OF FRANK SCHROEDER/
CORNELLSF₆ is reactive fluorinator

Sulfur hexafluoride (SF₆), a gas known for its extreme inertness and extraordinary stability, has now been shown to have promise as a selective fluorinating agent. [Richard D. Ernst](#) and coworkers at the University of Utah have discovered that SF₆ is quite reactive toward low-valent organometallic compounds of titanium and zirconium at room temperature and even below (*J. Am. Chem. Soc.* **2005**, *127*, 11924). And surprisingly, they report, the gas's reactivities "can rival or exceed those of some commonly employed fluorinating agents." For example, when they treated a titanium complex having three different ligands



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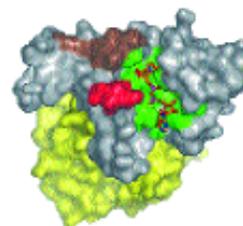
(one of them being a disubstituted cyclopentadienyl, R) with SF₆, they produced a cyclic tetrameric complex, [Ti(R)F₂]₄. The chemists believe that the SF₆ reactions leading to oxidation of the metal center occur when one or more of the fluorine atoms coordinate and then transfer to the metal center. They suggest that SF₆ may prove useful for preparing compounds "not normally obtained through other reactions."

Cornflower pigment pictured

My love is like a ... blue cornflower? Maybe not, but the same anthocyanin pigment that makes roses red also makes cornflowers blue. It's just packaged differently in the cornflower. A team of Japanese researchers led by Kosaku Takeda of Tokyo Gakugei University has obtained the crystal structure of the blue pigment in cornflowers. They find that the pigment is a complex of six anthocyanin molecules, six flavone molecules, one ferric ion, one magnesium ion, and two calcium ions (*Nature* **2005**, 436, 791). The ions line up along the pseudo-three-fold axis, with each Fe³⁺ and Mg²⁺ coordinated to three anthocyanin molecules and each Ca²⁺ coordinated to three flavone molecules. In the structure, stacking of the anthocyanin and flavone is evident. The C-C and C-O bond lengths indicate that the anthocyanin is in the 4'-keto-quinoidal form. The chelation of the Fe³⁺ and the Mg²⁺ with the 4'-keto-quinoidal base is important for the blue color, and the Ca²⁺ ions help stabilize the complex. The authors think that the tetranuclear metal complex may represent a new type of supramolecular pigment.

Cholera toxin's harmful handshake

A new study gives a peek at how cholera-causing bacteria trigger devastating bouts of diarrhea that can lead to severe dehydration and, if untreated, death (*Science* **2005**, 309, 1093). Cholera is caused by infection of the human intestine by *Vibrio cholerae*. When activated by its human host, the toxin produced by this bacterium catalyzes the transfer of an adenosine diphosphate ribosyl group from the cofactor nicotinamide adenine dinucleotide (NAD⁺) to the human signaling protein G_{sα}. This



COURTESY OF RANDALL HOLMES AND WIM HOL

chemical modification triggers a chain of events that result in the intestine being flooded with water and salts, generating the watery diarrhea characteristic of cholera. [Wim G. J. Hol](#) and Claire J. O'Neal of the University of Washington, Seattle, and Michael G. Jobling of the University of Colorado Health Sciences Center used X-ray crystallography to probe how a ubiquitous human G protein activates the cholera toxin to catalyze this crucial protein modification. They find that binding of the human G protein (yellow) induces a dramatic conformational change in the toxin (gray) that allows NAD⁺ (ball-and-stick model) to bind to the toxin's active site (green). The regions thought to bind G_{sα} are shown in red and brown.

Frogs eat ants for poisonous protection

The brightly colored Mantella frogs of Madagascar seem like they'd be an easy-to-spot snack. But for most predators, those vivid hues translate to "keep away" rather than "eat me." That's because the frogs' skin contains poisonous alkaloids. Despite the advantageous presence of the alkaloids, the frogs don't make the chemicals themselves. Instead, the frogs sequester the alkaloids from a steady

diet of alkaloid-rich ants, according to a new report from [Valerie C. Clark](#) of Columbia University and colleagues (*Proc. Natl. Acad. Sci. USA*, published online Aug. 8, dx.doi.org/10.1073/pnas.0503502102). Scientists had previously identified ants as the source of alkaloids in the neotropical poison dart frogs of South and Central America, but Clark's is the first study to identify the source of the Madagascar frogs' alkaloids. Clark notes that the finding is a striking example of convergent evolution--the phenomenon in which different species end up appearing superficially similar because they have taken the same approach to overcoming a challenge in their environment.

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