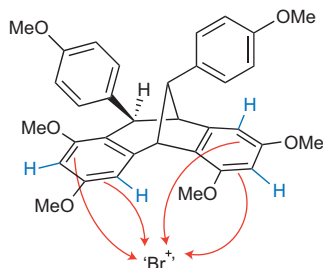


the energy barrier is not overcome, but the migrating hydrogen quantum-mechanically burrows through the narrower energy barrier. Although hydrogen tunnelling is not new to chemists, it has never been seen to have such an influence on the outcome of a reaction. *GA*

### NATURAL PRODUCT SYNTHESIS

## Optimizing oligomers

*Nature* **474**, 461–466 (2011)



Resveratrol has been the subject of much attention because it is widely credited as being responsible for the so-called French paradox — a diet high in saturated fat accompanied by a low rate of coronary heart disease. This simple polyphenol is also the building block for several hundred oligomeric natural products. The formation of these oligomers can involve several different reaction pathways that — coupled with the various stereochemical possibilities — lead to structures with diverse architectures and biological activities. These compounds are, however, difficult to isolate from natural sources and, when synthesized, uncontrolled oligomerization is not an option on account of the variety of reaction pathways.

Building on their work to develop selective routes to dimeric structures from an alternate precursor (that is, not resveratrol itself), Scott Snyder and co-workers from Columbia University have reported a strategy for the selective synthesis of several trimeric and tetrameric oligomers. The strategy relies on the development of selective bromination reactions of two dimeric cores. In both cases, theory suggested that there was a not a significant difference in reactivity between possible bromination sites, but extensive experimentation eventually showed otherwise.

Routes to ampelopsin H and carasiphenol C required selective mono- and dibromination of a core with four (two pairs of equivalent) electrophilic sites. Related routes to ampelopsin G, carasiphenol B and vaticanol C required the more challenging task of selective bromination of a core featuring four distinct sites and even resulted in the development of a new electrophilic bromination reagent. The strategy should allow the optimization of biologically relevant properties in unnatural analogues of resveratrol oligomers. *SD*

### PROTEIN NMR

## Spectroscopy of sediment

*Proc. Natl Acad. Sci. USA* **108**, 10396–10399 (2011)

Nuclear magnetic resonance spectroscopy is the structural tool of choice for chemists of many different disciplines, who make use of its ability to probe the chemical environment of different atoms. As the molecules being studied increase in size, however, the resolution becomes worse and worse. For studying proteins, with molecular weights in the hundreds of thousands of Daltons, the technique is increasingly difficult. Using solid-state NMR to study crystalline proteins is one answer, but proteins are notoriously difficult to encourage into the crystalline state.

Now, Ivano Bertini, Claudio Luchinat and colleagues from the Universities of Florence and Munich have side-stepped the crystallization problem. They realized that solid-state NMR probes, which are commonly rotated at high speeds to enable ‘magic-angle spinning’ experiments, act like ultracentrifuges. This, they reasoned, could be used to spin proteins into a solid sediment that could be studied using solid-state NMR techniques. As a proof of principle, Bertini, Luchinat and colleagues studied a solution of apoferritin, a 480 kDa protein that is almost impossible to analyse using solution NMR, but which can be obtained in microcrystals for comparison.

The team observed no signal when the solution was stationary, but peaks began to emerge when the rotor was spun at 3 kHz. Between 6 and 8 kHz the resolution of the spectrum was almost as good as the one obtained from crystalline solid samples. Encouraged by this, they tried a complicated 2D experiment and the spectrum obtained from the sediment had resolution as good as the solid-state experiment. Bertini, Luchinat and colleagues hope that their simple method will allow a range of future uses: following structural changes after addition of reagents, for example, or studying larger biomolecules such as the ribosome or proteasome. *NW*

Written by Gavin Armstrong, Stuart Cantrill, Stephen Davey, Anne Pichon and Neil Withers.

### Correction

In the Research Highlight ‘High-pressure materials: Diamonds are for aerogels’ (*Nature Chem.* **3**, 498; 2010), the reference DOI should have been ‘10.1073/pnas.1010600108’. This error was corrected online in the HTML and PDF versions on 23 June 2011.

## blogroll

### What’s in a name?

**Those famous reactions that you might never have used, a chemical-free quest and an unpleasant organocatalyst.**

Named reactions represent a fascinating subsection of chemistry, so we eagerly awaited the answers to Derek Lowe’s ‘Name Reactions You’ve Never Run’ blogpost (<http://go.nature.com/zTUwHt>). Lowe starts things off with the confession of a colleague who, despite years of experience, has never run a Diels–Alder reaction and continues with his own admission “I’ve never done a straight aldol condensation”, nor a Fischer indole synthesis. The comments thread was soon filled with people happily admitting which famous reactions have passed them by.

Who could fail to click on a blogpost with the title ‘Is earwax an organocatalyst?’ (<http://go.nature.com/UMNsvZ>). We certainly couldn’t and were rewarded with an informative post on the Chemistry Blog by Chemjobber, picking up on a Newsprints item by Steve Ritter in *Chemical and Engineering News* (**89**, 56; 2011). Way back in 1960 — in the days before blogs — budding chemist Charles Johnson discovered that his earwax accelerated the process of making colourful lake pigments. In his later life, as an undergraduate student, Johnson further found that earwax worked as a catalyst to make *trans*-stilbene, “although his professor didn’t seem impressed.” Chemjobber reminds us of Dylan Stiles’s blogpost on the now-defunct Tenderbutton in which he took a TLC of his earwax, which Chemjobber describes as “one of the initial triumphs of the chemblogosphere”. Who knew such an unpleasant substance was so interesting?

And finally... Mary Carmichael ([http://twitter.com/mary\\_carmichael](http://twitter.com/mary_carmichael)) got so fed up with seeing marketing spiel that uses the phrase ‘chemical-free’ to describe products that she started a blog, ‘F No, “Chemical Free!”’ (<http://fnochemicalfree.tumblr.com/>). Among the products named and shamed so far are “chemical free sunblock and bug spray” and even a chemistry set that offers “60 fun activities with no chemicals”. That doesn’t sound like much fun to us.