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Spotlights on Recent *JACS* Publications

CRACKING THE SEA'S SYNTHESIS SECRETS

Marine invertebrates play host to a library of structurally diverse molecules with potent pharmaceutical properties—for example, some didemnin natural products have been in clinical trials for various cancers—but these organisms' unique chemistry and limited natural supply make it difficult to fully explore the compounds' potential. Bradley Moore, Pei-Yuan Qian, and colleagues discover that a strain of the marine bacterium *Tistrella mobilis* from the Red Sea makes didemnin compounds, which were first isolated some 30 years ago from filter-feeding tunicates (DOI: 10.1021/ja301735a).

The researchers demonstrate that the didemnin compounds are biosynthesized by the oceanic bacterium, and they sequenced the microbe's entire genome to identify a gene cluster that encodes a synthesis pathway for didemnin B. But the process has another twist—the bacterium biosynthesizes didemnin B lipid derivatives that are targeted for active membrane transport and extracellular processing into the active didemnin B molecule with the help of a secreted enzyme that the researchers are now trying to pinpoint. The didemnin B lipid modification not only may help in actively targeting the compound for cellular secretion but also may serve a prodrug-like activity to reduce its biological activity while inside the cell.

Identifying the bacterial origin of these compounds and providing a blueprint of their unexpected biosynthesis pathway could help ease the supply bottleneck of these promising marine natural product drugs. **Kenneth J. Moore**

TOXIC COMPOUND REMOVAL BY SELECTIVELY CONSUMING IT

Hydrodesulfurization leads to reduced sulfur dioxide emissions during gasoline consumption, but it can be costly in terms of energy used and waste produced. Valentine Ananikov and co-workers report an efficient and selective reaction that could be used as an alternative to hydrodesulfurization to remove thiols from refined petroleum products and selenols from technological sources (DOI: 10.1021/ja210596w). The researchers' catalytic system turns a selenol (PhSeH) and two thiols (PhSH and CySH) into less toxic functionalized vinyl monomers, which can subsequently be reused for organic synthesis and polymer science.

When a mixture of the three compounds react with an alkyne in the presence of a heterogeneous catalyst, the reaction proceeds according to the order of decreasing toxicity: PhSeH > PhSH > CySH. This means that the reaction will completely consume PhSeH first before moving to PhSH and then CySH. The selective order of the reaction holds even in the presence of up to seven additional sulfur and selenium species.

Removing an unwanted or toxic component from a mixture of chemicals has typically been a complicated and expensive procedure. The group has successfully produced a model for consuming specific reagents in a mixture to produce functional and less toxic products, a process that could benefit the environment and save natural resources. **Yun Xie, Ph.D.**

SEEKING OUT THE HIDDEN HYDROGENS IN RNA

Investigation of the structure of biomolecules such as RNA, DNA, and proteins contributes to our understanding of their roles in biology and facilitates our ability to manipulate or target them, such as for the design of novel materials or the development of new drugs. Hydrogen bonds are among the most important contributors to biomolecular structure, and NIH researchers Grishaev, Ying, and Bax report on density functional theory computations to more accurately determine the locations of hydrogen-bonded hydrogen atoms in an RNA molecule called RiboA (DOI: 10.1021/ja301775j).

Of all the atoms that make up these biomolecules, determining the exact position of hydrogen atoms participating in H-bonding is particularly challenging. Now, the researchers find that their location relative to the plane of an RNA base is influenced significantly by the H-bonded base partner, and the researchers develop a model to account for these influences and get much improved agreement with experimental NMR data.

This report provides a general method for predicting hydrogen atom positions in RNA, which can be integrated into X-ray and nuclear magnetic resonance characterization—which are often too low resolution or not precise enough to provide information regarding the exact positions of the hydrogen atoms—of these important biomolecules. This approach can also be extended to the structural determination of other hydrogen-bond-containing biomolecules such as DNA and possibly proteins. **Eva J. Gordon, Ph.D.**

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