

# FRAUDULENT MOLECULES

Roald Hoffmann

In the real world fraud is unlikely to be pleasant for the often ingenious people who engage in such nefarious activity. The whole enterprise is tarnished by association with criminality, pulled down by the darkness that comes with secrecy. A forger cannot publish.

To be at the receiving end of a forgery is certainly no fun, especially if your livelihood is undermined. In fact, the only person bound to enjoy himself or herself in the chain of deceit and its discovery is the scientific detective: If it be a challenge to make sense of the seeming tricks of nature (beautifully elaborated by evolution), so much more fun (and perhaps easier) to follow the clues of a chemical crime. Let me tell you of two examples—amber and vanilla.

## Amber

Amber is a complex, highly polymerized and cross-linked material resulting from the fossilization of coniferous (when the amber is from around the Baltic) and leaf-bearing (Dominican) tree resins, as well as other tree exudates. Its attractiveness and the relative scarcity of gem-quality pieces, as well as its unique color and feel, made amber a target for imitation thousands of years ago.

Amber forgeries of the ancient past used other natural resins—for instance, copal. Copal is a “very young” (from a few years to a few thousand years) resin—amber is always millions (from 5 to 130 or more) of years old. Things took another turn with the invention of the phenolic resins by Leo Baekeland. These first plastics were of great use and highly decorative, too. And it took only two to three years between the first “Bakelite” patents and the first documented Bakelite amber forgeries.

Alexander M. Shedrinsky, David A. Grimaldi, Jaap J. Boon and Norbert C. Baer, all active in the amber-analysis community, write the following:

In 1937 a new material, polystyrene, entered the polymer market. Over time its application grew from rubber for car tires to foam for in-

sulation and packing. Forgers learned to add colorants to obtain a very convincing amber-lookalike material of various colors (lemon-yellow to quite pronounced brown). However, this substitute did not give a transparency resembling that of real amber.

In recent times the interest has shifted to another quality of amber. This is the material's ability to preserve the remains of once-living objects, some dating back to the Jurassic period, 150 million years ago. Who can escape the tug of the spiritual connection with the past that one feels on seeing an ant, contorted in its death throes in amber? And *Jurassic Park* hardly hurt the price of fossilized amber specimens. Shedrinsky *et al.* continue:

It took another five to ten years before unsaturated polyesters and epoxy resins (1942–1947) were introduced by the chemical industry. These synthetic polymers created a small scale revolution in amber forgeries, particularly in the area of forged inclusions. With easy commercial availability and sophisticated “artwork” one can prepare convincing imitations of large transparent amber pieces with a wide variety of inclusions (*e.g.*, ants, bees, lizards and mosquitoes).

Shedrinsky knows whereof he speaks. He's an amber-forgery detective. His tools are pyrolysis—decomposition by heat—followed by gas chromatography and/or mass spectrometry. The pieces of the synthetic polymers (typical are the molecule of phthalic anhydride from polyesters, phenol from phenolic resins) are quite different from those of natural amber. The pyrolysis products and their yields are like a fingerprint, and that fingerprint serves to identify not only forgeries, but also natural amber from different sources.

Just to complicate things, and to provide a link with the mysteries of the natural, there are some authentic old resins that seem to consist of just polystyrene, a typical modern (we thought) synthetic polymer. How were these formed? We don't yet know.

## Plain Vanilla

The story shifts to vanillin, benzaldehyde and cinnamic aldehyde. The flavors of vanilla, al-

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National Gallery of Art

Figure 1. Relation between natural and synthetic worlds is the subject of René Magritte's painting, *La Condition Humaine*.

monds and cinnamon are largely, not entirely, the result of these simple molecules. They are available from natural sources, yet made ever more cheaply synthetically, often from petroleum-based feedstocks. Now popular taste comes in, and in particular the recent emphasis on the natural. What advantage accrues to the advertiser, if he can say "Natural Vanilla Flavor!" But ... vanilla beans are expensive. They are grown primarily in Madagascar, with lesser production elsewhere. Tara Patel, who has written on food authenticity, reports in *New Scientist* a French estimate that the

"French food industry would need ten times as many vanilla pods as it actually imports to account for all the 'natural' vanilla that companies claim is in milk products alone."

There is nothing wrong with synthetic vanillin. It is as healthful as the natural, and indubitably tastes the way it should—otherwise 12,000 tons of it wouldn't have been sold last year. Synthetic vanillin adds to life. No, the molecule is not at fault—the villain is the unscrupulous human being who labels the ingredient as natural when it is not. The incentive is nontrivial—the price of



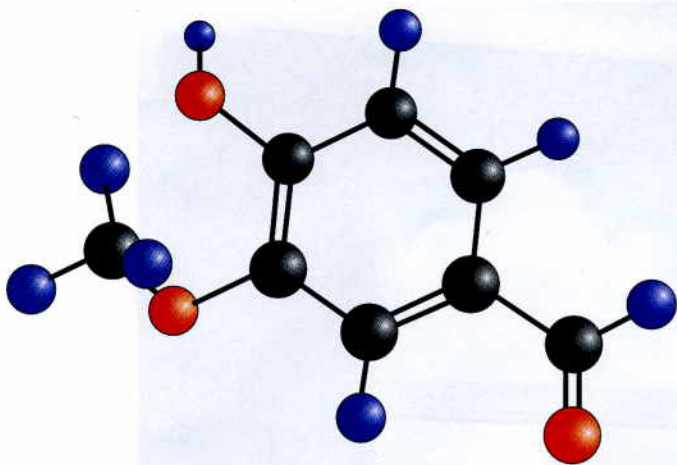


Figure 2. Vanillin molecule can be extracted from vanilla beans, or it can be produced in the lab. (Black balls are carbon atoms, blue balls are hydrogen and red balls are oxygen.)

vanilla from beans is more than 200 times that of synthetic vanilla. Elaborate forgeries have been done for much, much less.

The boundary between the natural and synthetic is continually confounded by normal human actions, and not just forgery. Of course it takes human transformations, many of them, to make vanilla ice cream. The cream and sugar are ultimately agricultural products, the freezing induced and not the product of an Ithaca winter. The vanilla beans cannot be just mixed in; what is used, natural or synthetic, is an alcoholic extract. Given all the forgery, it is good that there is a federal standard for that extract to be called “natural”—in fact vanilla is the only flavor extract for which there is a federal penalty for adulteration. But, as was brought to my attention by Scott R. Hagedorn, who works on the biocatalysis of flavor and fragrance chemicals, the federal standard, with all its good intentions, tends to impede new technologies for extracting natural vanillin. So, if one uses supercritical carbon dioxide (a wonderful solvent) instead of alcohol to get the vanillin out of the bean, the product cannot be labeled a natural vanilla extract! In the case of another flavor (governed by another federal guideline), a peach-flavoring ingredient can be labeled as natural even if the flavor molecules (lactones) never saw a peach but are made by fermentation of castor oil.

Faced with human nature, what is the seeker of the natural (often the seller of the natural) to do? He or she had better train as a chemist and buy some fancy equipment. It is possible to detect the natural product, but as one method to do so comes on line, the forgers get cleverer.

The first modern detection methods looked at the ratios of  $^{13}\text{C}$  and  $^{12}\text{C}$  and deuterium/hydrogen isotopes, and at the radioactive  $^{14}\text{C}$  content in the flavor molecules. The latter technique is easy to understand:  $^{14}\text{C}$  has a half-life of 5,730 years—in living material it is replenished by photosyn-

thesis. Petroleum’s carbon is essentially devoid of  $^{14}\text{C}$ ; it decayed a long time ago. So natural benzaldehyde (the almond-flavor chemical) is radioactive (just a little); synthetic benzaldehyde, made from a petroleum product, is not.

The forgers did not sit idle. They spiked the benzaldehyde with a little “hot” stuff, molecules containing a lot of  $^{14}\text{C}$ . So the flavor-chemist detectives turned to  $^{13}\text{C}/^{12}\text{C}$  ratios—the point there is that photosynthesis is accompanied by isotopic fractionation (the outcome of small differences in rates of biochemical reactions) in favor of  $^{12}\text{C}$ . And there are even different ratios of  $^{13}\text{C}/^{12}\text{C}$  for plants following different metabolic cycles.

Actually the  $^{13}\text{C}/^{12}\text{C}$  ratio analyses were needed from the beginning to detect vanilla forgeries. Cheaper, semisynthetic vanillin turns out to be made not only from petroleum products, but also by chemical and microbial transformation of lignin, a byproduct of wood pulping. Lignin from a recently living plant has just about as much  $^{14}\text{C}$  as the vanilla bean. Thus the need for an identification method that focused on biochemical differences between one natural product (vanillin) and another (lignin).

The forgers responded, adding vanillin labeled in a specific way with  $^{13}\text{C}$ . Economical, not lazy, they did not spread out the isotope over the whole molecule, as would be expected in a natural product. They just put it in where it was cheapest to put it, in the one  $\text{CH}_3$  group of the molecule.



Figure 3. Extinct termite, *Mastotermes electrodominicus*, included in Dominican amber is the kind of piece prized for its rarity and the possibility of extracting ancient DNA. (Photograph by Edward Bridges, from Grimaldi 1996; provided courtesy of David Grimaldi.)



The contest goes on. With newly devised nuclear-magnetic-resonance techniques (one of these is called "site-specific natural isotope fractionation by nuclear magnetic resonance," or SNIF-NMR) it is possible to measure the ratio of deuterium to hydrogen wherever a hydrogen atom appears in the molecule. Because of the biochemical reaction mechanisms involved, these ratios turn out to be different, and reasonably specific for most hydrogens in the molecule. As little as 10 percent of lignin-origin vanillin in a natural sample may be detected with SNIF-NMR. And the method, appropriately developed in France, has been adopted as the official European way to spot the addition of sugar in wines.

A forger could overcome this. But to do so he or she would have to synthesize the molecule in the laboratory much the same way nature does. It is possible, but it would be (a) in some cases a major scientific achievement, worth publishing, and (b) very expensive. The whole point of molecular forgery is the substitution of the cheap for the dear. But the spectroscopic tools of the chemical-forgery detective are also expensive. A stand-off in ingenuity, resolved by what usually resolves things: economics.

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