Natural Aroma Chemicals: More and Purer

How improvements in extraction, biotech processes and use of sidestream sources are changing the ingredient palette

"In chemistry you can do [almost] anything, as long as someone is willing to pay for it," says David Rowe, technical director of Riverside Aromatics Ltd., highlighting the potential and challenges in expanding the natural aroma chemical palette. Ingredient producers are able to isolate and extract ever smaller percentages of material from sources; the question is whether it is always economically viable to do so.

To take a simplistic example, Rowe notes that in theory one could isolate 2-methyl-3-furanthiol (FEMA# 3188, CAS# 28588-74-1, **F-1**), which is a powerful material with a roast beef odor, from meat. Yet, he says, the derivation of the material from a meat source would lead to a material more costly than its source, making it hugely and prohibitively expensive for flavor applications. When it comes to naturals, he says, "It's about identifying a more viable source."

In another example, *cis*-3-hexenol (FEMA# 2563, CAS# 928-96-1, **F-2**), which has been found in everything from apples to carnations to fresh cut grass, the chemical could theoretically be produced by harvesting enormous amounts of grass and distilling it. More realistically, the natural version has been derived as a component of mint oil, effectively making it a byproduct of a material that is already commercially viable as an essential oil or a derivative source for natural menthol.

"You could not grow mint simply to produce *cis*-3-hexenol, but when you're growing the mint for multiple products, it becomes economically viable," Rowe says. "There has to be an added value to using ingredients."

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—David Rowe

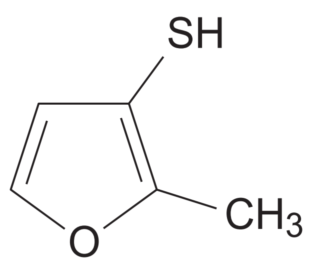
New Natural Materials, New Natural Sources

Flavor companies are particularly compelled to find new sources of natural aroma chemicals and are thus investing more R&D resources in this area. The technically driven work carried out by ingredient companies focuses on areas in which natural options may be lacking, such as in savory.

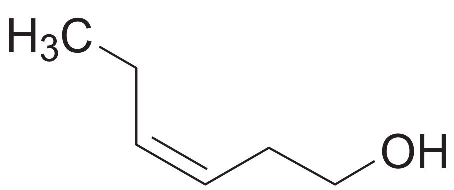
Fusel oil: Fusel oil, from which alcohol is derived, has provided a side stream of aroma chemicals for the flavor and fragrance industry which are present in the oil at low levels, including β-damascenone (FEMA# 3420) and pyrazines such as trimethyl pyrazine (FEMA# 3244, **F-3**). Unlike its synthetic counterpart, trimethyl pyrazine derived from fusel oil residues contains isomers—impurities—that impart a sweet, chocolate character. (See **The Pros and Cons of Impurities**.)

Sunflower oil: "Crude sunflower oil will sometimes have a quite rancid odor due to the oxidation of aldehydes," says Rowe. "Those are aroma chemicals in the wrong place. If you can get those aldehydes out, it will extend the life of the oil without damaging it." In turn,

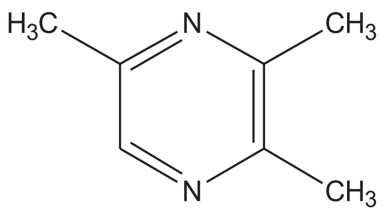
2-Methyl-3-furanthiol **F-1**



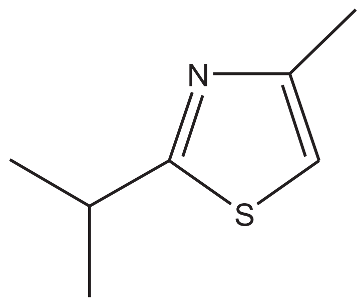
***cis*-3-Hexenol** **F-2**



Trimethyl pyrazine **F-3**



2-Isopropyl-4-methyl thiazole **F-4**



these valuable aroma chemicals, including decanal (FEMA# 2362) and (E,E)-2,4-decadien-1-al (FEMA# 3135), are valuable for formulators.

Tomato leaves and vine: 2-Isobutyl thiazole (tomato leaf thiazole, FEMA# 3134) and 2-isopropyl-4-methyl thiazole (peach thiazole, FEMA# 3555, **F-4**) can be derived from tomato leaves and vines. As with trimethyl pyrazine, natural 2-isopropyl-4-methyl thiazole differs from its synthetic counterpart in that it is softer, greener and less sulfurous due to impurities, including sub-trace levels of 2-isobutylthiazole.

"This is an example where the source has an influence on the quality of the end product," says Rowe. When there are differences between the natural and synthetic materials it is crucial for formulators and QC staff to understand the distinctions.

Biotech Future

Biotechnology/fermentation is not a new concept, says Rowe, but there may be innovations from other chemical sectors that the flavor and fragrance industry hasn't yet exploited. "There has been a realization that microorganisms can do a lot more than we normally ask them to do," he notes. Already, he says, fermentation has yielded a number of natural materials, including lactones.

"We can persuade microorganisms to do all sorts of things and make all sorts of transformations that we're not aware of [as an industry]," he adds. "In chemistry you can do [almost] anything, as long as someone is willing to pay for it. I think that will be true for biotechnology. As techniques [emerge], prices will be lowered and more materials will become available. An awful lot of materials that are not currently available naturally will be—sulfur compounds, pyrazines, thiazoles—a whole range of things. There is more to come."

The Pros and Cons of Impurities

"If everything was 100% pure, a natural aroma chemical and a synthetic aroma chemical would be exactly the same [olfactorily]," says Rowe, adding, "Of course things are never quite that pure." As with naturals such as trimethyl pyrazine and 2-isopropyl-4-methyl thiazole, it is crucial for formulators to determine when they can do a one-for-one swap of a synthetic for a natural and when there are sufficient differences that olfactory consistency will require extra technical and creative finesse.

The benefits and challenges of impurities in natural ingredients has long been a feature of isolates derived from essential oils. Rowe explains that linalool ex basil, for example, is likely to differ in some ways from linalool ex bois de rose or ex ho oil, while geraniol ex geranium oil will likely differ from geraniol ex citronella oil. Sometimes these differences can be due to differing isomer ratios (optical isomers in the case of linalool, geometric isomers in the case of geraniol), but often it's the influence of traces of other materials, the "impurity profile," as it were.

"Source has an impact," says Rowe.

Decanal ex orange oil may have been 40–50% pure 20 or 30 years ago, says Rowe. "At that level of purity you're really restricted in what you can use it for," he adds. "As the material became purer it extended its range [of potential applications]. If you have [impure] decanal from orange oil and it has a citrus note, that's not necessarily a positive thing. If you want to use that decanal in a savory flavor, it's not going to be so good. In the past 20 years there's been a move toward purer and purer natural materials."

However, he says, there is cause for caution. If isopropyl methyl thiazole natural and synthetic are identically pure, it becomes harder to verify which of the two is natural.

"You lose the impurity profile which actually tells you about its origins," says Rowe. "At super-pure levels you would have to carry out isotope testing to verify origin, which is very expensive. It is a real problem and means that increasingly it comes down to [whether] you are able to trust your supplier."

No matter the challenges ahead, however, the opportunities in new aroma chemical sources continues to expand.
