Molecular backstories

Michelle Franci reminds #ChemistsWhoCook to look at the chemistry behind the cooking.

It was the pandemic that drove me to it. Not the baking of sourdough, though like many #ChemistsWhoCook I produced a surfeit of loaves. No, I bought ikasumi: powdered squid ink. Like many of my coronavirus cooking adventures, this one was rooted in nostalgia: my strategy to avoid facing the daily uncertainties of living through a global pandemic. I wanted to recreate a dish from a memorable summer meal enjoyed in a small town outside Rome, a tangle of black pasta and fresh seafood. Besides, kneading the pasta dough would be an anodyne for my anxiety. It was, I confess, efficacious in both regards.

For me, the nostalgic appeal of colouring food ran deeper than that Roman *pranzo*. The synthetic target of my long-ago and short-lived career as a natural products chemist was carminic acid, a red-hued anthraquinone extracted from cochineal — insects that infest prickly pears. Used as a pigment for centuries, in the modern era cochineal has been used to colour food from strawberry yogurt to grapefruit juice. Bugs in your food, who knew?

Though I made no progress on a synthetic route to carminic acid in my undergraduate days, the project gave me a taste for the weirder backstories of the molecules I cook with. Bonus points if the narrative invokes one or more of the seven classic motifs of disgust, such as creatures in your food or weird smells¹. Herewith are three of my favourite tales, literal backstories all: of squid ink, of skunks, and of faux vanilla flavouring exuded from a beaver's posterior.

A few years ago I reviewed² food blogger Vani Hari's book, *The Food Babe Way*³. In it, Hari lists 'The Sickening 15'. Number ten on her list of gross food additives is castoreum, a creamy brown substance that is extracted from sacs on the hind end of a beaver, typically harvested from the pelts, not from live animals. The beavers mix the castoreum with urine and apply it to their fur to increase its water repellence, as well as to mark out their territory. I agree this sounds unappealing, but I imagine pretty much anything mixed with beaver urine is unappetizing. Like cochineal, castoreum has a long history of use, extending back to at least 2,000 years ago when it could be found on sale in Roman marketplaces⁴, through the early twentieth century when Dr Jones' Beaver Oil was hawked as a remedy for

Seeded yeast rolls made with powdered squid ink.

aching joints⁵. Nowadays it is used in perfumes, where it adds a leathery note.

Castoreum is reputed to taste of vanilla and raspberry, which has given rise to the urban legend that it is used to flavour vanilla ice cream as a cheap alternative to vanillin. It's more likely to be the other way round, because castoreum is far more expensive than even the priciest of vanilla extracts. So enjoy that vanilla ice cream cone, secure in the knowledge that it contains no extract of beaver. Castoreum is packed with a wide range of phenolic compounds derived from the beaver's diet, including salicylates, so it is unsurprising (at least to chemists) that it could taste of vanilla and ease a headache or joint pain⁶.

The French biochemist Edgar Lederer used his 1946 letter to *Nature* on castoreum to mark his research territory⁶. He'd read Philip Stevens' paper, *American Musk II. A Preliminary Note on the Scent Glands of the Beaver* and feared losing credit for his own earlier work on beaver secretions⁷. I had in fact read Stevens' third instalment⁸ in that series, *The Scent of the Common Skunk*, while engaging in what might have

been my peak moment of domestic organic chemistry. In case you are wondering, instalments I and IV take up the scent of the muskrat. The skunk in question was not the main course that evening in 2007, though my mother's 1958 Betty Crocker cookbook contains a recipe for squirrel that I suspect could be readily adapted to use skunk. The dog had cornered the skunk. The skunk had expressed (literally) its displeasure with the situation. As a result, both the dog and I were redolent with the volatile oils Stevens described as "repulsive in odor" and a seventeenth century Jesuit likened to the stench of sin. I concurred with both assessments.

Miles from town, with no tomato juice — the traditional folk remedy for skunk odours — on hand, and wishing to be allowed back in the house to sleep, I sought salvation in organic chemistry. The malodorous components of *Mephitis mephitis* (skunk) musk comprise a mixture of low-molecular-weight thiols — principally 2-butene-1-thiol and 3-methyl-1-butanethiol. Weird fact: as awful as 3-methyl-1-butanethiol smells at high

Box 1 | A recipe for *tenebris* rolls with squid ink

Original recipe developed by Eugene J. Miller, modified by Christopher Donnay.

For 12 rolls:

60 ml (1/4 cup) water
1 tbsp ikasumi (dried squid ink powder)
10 g (1 1/8 tsp) dry yeast
475 ml (2 cups) warm water
2 1/4 teaspoons salt
650 g (5 cups) flour

Add ikasumi to 60 ml of water and stir to combine; the ink doesn't dissolve, you will get a suspension. Sprinkle yeast into 475 ml warm water in a large mixing bowl. Let stand until dissolved. Sprinkle in the salt, stir in ikasumi mixture and add flour, beating until smooth. Turn dough out onto a lightly floured board and knead until smooth and satiny. Place in a greased bowl

and turn dough to coat. Cover bowl with a moist towel and let rise in a warm place until doubled in size, about 1.5 hours.

Punch down, cover with a towel and let rise again until doubled in size. Turn out onto floured board and knead lightly.

Cut dough into 12 pieces. Shape each piece into a long rope, about 8 inches long, and tie into a trefoil knot (3₁). Place on a greased baking sheet and brush with a beaten egg. Sprinkle with white poppy seeds or sesame seeds and place in a warm place to rise. When rolls have doubled in size, bake in a 190 °C oven for 25 to 30 minutes. Rolls are done when they sound hollow when tapped on the bottom or when their internal temperature is 90 °C.

Notes: The squid ink may come off on your hands when kneading, but it readily washes off.

concentrations, it is an approved flavouring agent in food and it has the scent of alliums at low levels. Humans can detect thiols at very low concentrations, often less than 1 ppm, so flushing with water isn't an efficient way to completely deodorize either human or Labrador Retriever. The trick is to convert the thiols to less mephitic molecules. They readily oxidize to odourless sulfonic acids when treated with hydrogen peroxide or bleach⁹. A wash with an alkaline solution of 3% hydrogen peroxide with a touch of dish soap followed by a thorough hosing off and the dog and I were none-the-worse for the adventure. Note that tomato juice doesn't do a thing. Should you have some on hand, save it to make a Bloody Mary when you're done solo wrestling 25 kg of damp, disgruntled dog.

Marcella Hazan, who wrote the iconic *Essentials of Classic Italian Cooking* with my go-to recipe for homemade pasta, considered pasta tinted black with squid ink deplorable¹⁰. Personally, I enjoy its subtle briny notes and visual contrast to the fish I toss with it, but until I decided to make the inky black pasta from scratch I hadn't given much thought to the chemistry behind the colouring. One line of marine biologist Charles Derby's beautifully written review¹¹ of 2,500 years of cephalopod ink science nearly put me off the entire project: "ink has a significant volume of mucus". Was I

really going to stir a couple of tablespoons of reconstituted squid snot into my dinner? While snotty ink expelled through the anus of a squid surely could compete with castoreum for a spot on anyone's list of disgusting degustations, I was (mostly) undeterred. The pasta was fabulous — and my foraging in the literature about squid ink equally delightful.

Culinary squid ink doesn't actually come from squid, but is extracted from cuttlefish, *Sepia officinalis*, a related cephalopod. Melanin is what gives rise to the deep brown-black of cuttlefish ink; it is roughly 15% by weight eumelanin. Cephalopods have been using the ink to hide from predators and as a chemical deterrent since at least the Jurassic period — usable ink has been reconstituted from fossilized relatives of the modern cuttlefish¹².

Cuttlefish ink also contains significant concentrations of free amino acids — principally taurine and glutamate. Interestingly, the concentrations of glutamate are high enough to trigger the umami receptors in humans. This suggested to me that if Parmesan cheese could add a whiff of umami to bread, ikasumi might too. I recruited a research assistant and we modified a family recipe for seeded yeast rolls to test the theory. The results are shown in the picture; the recipe can be found

in Box 1. Despite looking like charcoal briquettes, we report the texture to be unaffected. There is a faint hint of umami. They are great with butter.

Not all cephalopod ink is black, which gives me yet wilder ideas. Could you make bright magenta pasta using the ink of the California sea hare? Or phosphorescent bread using the ink of deep-water cephalopods, such as *Vampyroteuthis infernalis* (literally the vampire squid from hell)? And why hasn't a murder mystery turned on the poisoning of a dinner guest with fettuccine coloured by the tetrodotoxin-laced ink of a blue-ringed octopus?

Chemists who cook know that just as the glutamates in that squid ink subtly enriched the flavour of my bread, so too does our understanding of the stories behind the molecules enrich our experiences in the kitchen and at the table. All that pandemic cooking has reminded me to slow down, back up, and smell the molecules at play on the stove. □

Michelle Franci^{1,2} ✉

¹Department of Chemistry, Bryn Mawr College, Bryn Mawr, PA, USA. ²Vatican Observatory, Vatican City, Vatican City State.

Twitter: @MichelleFranci

✉e-mail: mfranci@brynmawr.edu

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Competing interests

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