Vanilla! It's Everywhere!

From steamy Mayan jungles to cold Norwegian pulp mills ... from the Aztec halls of Montezuma through Europe to Thomas Jefferson's plantation, one spice has been there. Chocoholics step aside, it is vanilla that reigns supreme as the world's most widely used flavoring!

By Gail Kay Haines

It's almost unbelievable the number of things vanilla is in. Vanilla can be produced from peanuts, grapefruit, cloves, rice bran, and even barrels of crude oil. Originally discovered in Mexican orchids, it has spread from a taste hoarded by royalty into the flavor in everybody's ice cream sundae. Vanilla is the world's most widely used flavoring, a long-believed aphrodisiac, and a contributor to the manufacture of specialty drugs.

A trip through the average home turns up vanilla in vanilla extract, room spray, soap, body lotion and massage oil, pudding mix, vanilla-scented candles, potpourri, and, of course, vanilla ice cream—the number-one seller. A flood of recent television ads—like the one featuring the bouncing Pepsi truck—signal that Coca-Cola and Pepsi are going head-to-head in the battle for *vanilla* cola supremacy.

Almost every chocolate recipe calls for it. Tobacco and cattle food are flavored with vanilla, and it is even used in baby food. Where does all this vanilla come from? The United States alone consumes more than 1000 tons of vanilla beans per year, just for "high-end" products. The world demand for vanilla far exceeds the natural supply.

Growth and harvesting

In order to meet demand, planters once carried cuttings of the tree-climbing vines from Mexico to Madagascar and other tropical areas, but the vines did not set pods. *Vanilla planifolia* (old name V. fragrans), which produces 99% of the pure vanilla sold, had been pollinated occasionally by hummingbirds, but mainly by a strain of Mexican Melipona bees. No bees meant no seedbeds and no vanilla. To make matters even more complicated, each flower opens for one day only. In 1841, growers began to hand-pollinate the orchids with a sharp bamboo stick—as they still do—and *V. planifolia* flourished. In Tahiti, vines mutated into a new species, *V. tahitensis*, the other commercial 1%.

Today, each ripening vanilla pod is so valuable that it is guarded and sometimes tattooed with its own I.D. number. Picked while green, the large pods have no characteristic smell. First, they must be "killed" in hot water, "sweated" in the sun, dried in the shade, and "conditioned" in a closed box until they turn brown, supple, and fragrant. This process, which promotes enzymatic action to develop the flavor, requires 3–8 months,

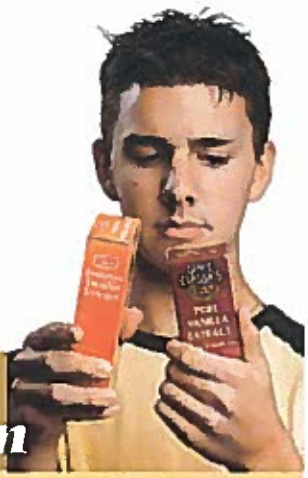
finally yielding long, skinny blackish-brown pods—each weighing about 5 grams—filled with tiny black seeds. From planting to market can take five years, making natural-grown vanilla the second most expensive flavor, after saffron.

Vanillin

Vanillin, $C_8H_8O_3$, is the major component (about 2%) of "pure vanilla", a complex mixture of four primary and nearly 300 minor chemicals. All four major compounds belong to the group called "aromatics", which means they contain a benzene ring—C_6H_6—with various side chains substituted for hydrogen.

To protect consumers, different types of vanilla have specific legal meanings. *Vanillin* is only slightly soluble in water, but it dissolves easily in ethanol (ethyl alcohol). Pure *vanilla extract* is made from chopped vanilla beans, soaked for days or weeks in dilute alcohol. It is the only flavoring to have a U.S. Food and Drug Administration standard of identity. Pure vanilla extract must contain "the extractive material from 13.35 oz. of vanilla beans per gallon and at least 35% alcohol by volume". The extract picks up hundreds of chemicals from the vanilla pod, giving "pure" vanilla its complex taste.

But vanillin is vanillin, whatever the source. In the 1880s, German chemists synthesized it as a cheap substitute for vanilla. "Imitation vanilla" is mainly synthetic vanillin. "Natural" vanilla is vanillin from other food sources mixed with a little pure extract. Since the price differences are huge, chemical tests exist to make sure each product is what the label says. But words do not always mean what they suggest. For instance, "vanilla bean" ice cream may contain, not tiny seeds, but flecks of ground pods left over from the extraction process. Vanillin



Legal Vanillin and Counterfeit Extract

Because synthetic vanillin is so much cheaper than natural vanillin and not subject to the fluctuations of supply and price that affect natural foods, it offers an inexpensive way for a food producer to impart a vanilla flavor to a food or beverage. Substituting synthetic vanillin for natural vanilla is safe, sensible, and legal—as long as the product is properly labeled as containing artificial vanilla flavoring.

But passing off synthetic vanillin for vanilla extract can be lucrative. A quick trip to the supermarket reveals that vanilla extract can sell for close to $3.50 per oz., whereas imitation vanilla sells for about $0.20 per oz. This presents a tempting situation for counterfeiters.

The possibility of cheating means that food chemists must devise a method to determine when a product contains natural or synthetic vanillin. But vanillin is the same chemical compound, whether it originates in the bean or is synthesized from lignin. Standard chemical analysis indicates the identity and quantity of a compound, but usually gives no clues about its sources. In the past few years, researchers have been able to distinguish between vanillin from fossil precursors, such as coal and petroleum, and vanillin of bean origin by using isotopic ratio mass spectroscopy and nuclear magnetic resonance.

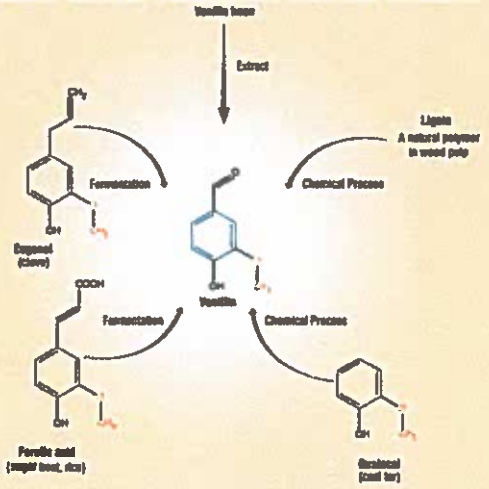
The source can be determined by inspecting the carbon atoms in the vanillin with a technique called stable isotope ratio analysis (SIRA). SIRA is based on the fact that not all carbon atoms have the same mass. Of the carbon atoms found in nature, 98.9% have a mass number of 12, and 1.1% have a mass number of 13. Most organic compounds contain these percentages of carbon-12 (^{12}C) and carbon-13 (^{13}C) atoms. However, the ratio of these isotopes is slightly different for natural vanillin than for synthetic vanillin. The synthetic vanillin is enriched in ^{13}C. This happens because of differences in biochemistry of the vanilla orchid and that of most other plants.

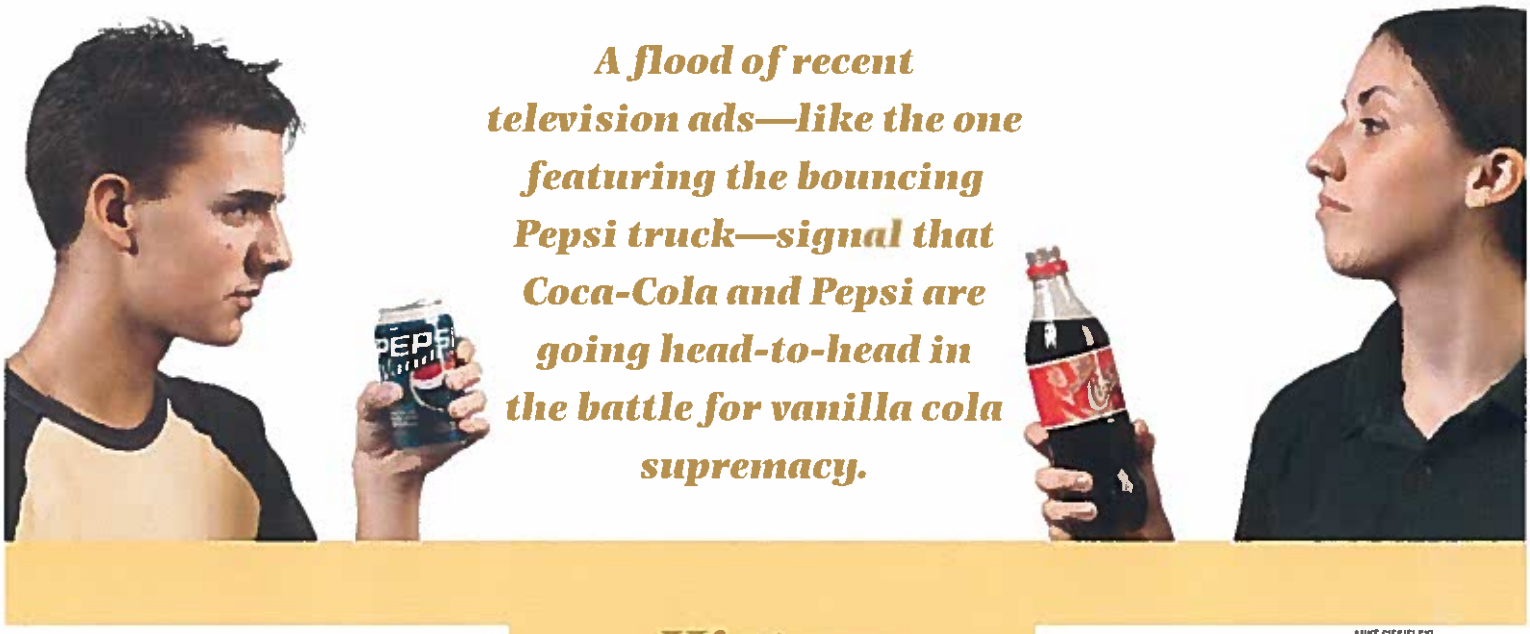
The vanilla orchid carries on photosynthesis by a series of reactions known as the Crassulacean pathway. Most plants, however, including trees, use the Calvin pathway, which involves a greater number of chemical reactions. Because ^{13}C is heavier than ^{12}C, ^{13}C reacts more slowly—and less ^{13}C is incorporated during each photosynthesis reaction step. Most plants that will eventually become oil, coal, and lignin use the longer pathway. So synthetic vanillin from these sources has a lower percentage of ^{13}C. By measuring the ^{13}C:^{12}C ratio with a mass spectrometer, scientists at the Bureau of Alcohol, Tobacco, and Firearms have been able to identify counterfeit vanilla extract, and federal attorneys have prosecuted unscrupulous suppliers.

But the detective story does not end here. When counterfeiters discovered that chemists could tell the difference between natural and synthetic vanillin by means of isotope ratios, they searched for ways to adjust the ^{13}C:^{12}C ratio in the synthetic product to more closely match that of natural vanillin. The easiest way is to remove the $-OCH_3$ group containing ^{12}C and replace it with another $-OCH_3$ group containing ^{13}C. But the government chemists were able to spot this ploy by removing the $-OCH_3$ group and testing for the presence of ^{13}C using mass spectrometry.

Adapted from a classic *ChemMatters* article by R. C. Breedlove, August 1988

Where does vanillin come from?





A flood of recent television ads—like the one featuring the bouncing Pepsi truck—signal that Coca-Cola and Pepsi are going head-to-head in the battle for vanilla cola supremacy.

MIKE CIESIELSKI

probably makes up the difference. And although high-fat ice creams require a higher concentration of vanillin—because there is less air to deliver the fragrance—no-fat ice creams require the most. A mixture of extract and concentrated vanillin seems to work best.

The scent in your hand lotion is likely synthetic, as is 95% of the world's vanilla supply. Once, most synthetic vanillin came from lignin—the natural polymer removed from wood pulp in papermaking. It was a good use for waste lignin, but the process gave off so much waste sulfuric acid that all such plants in North America have closed due to pollution.

Now, vanillin is more likely to be made from petroleum or coal tar. Ethyl vanillin from crude oil—which replaces the methyl (CH_3–) side chain in vanillin with ethyl, ($C_2 H_5$–)—has a vanilla taste that is 3 times stronger than vanillin, but it is insoluble in butter, caramel, and chocolate. It is used in perfumes and low-fat ice cream. Eugenol from clove oil and guaiacol from coal tar can both be turned into vanillin. As wines and liquors age in oak barrels, alcohol pulls vanillin right out of the wood. Both peanuts and their hulls contain vanillin, which, even at parts per million (ppm) levels, adds a major flavor note. Grapefruit contains vanillin in the ppm range too, but here it causes an "off" taste. In this case, less vanillin tastes better.

Medicinal use

Vanilla even has some medicinal uses. Vanillin is used in the manufacture of medications for Parkinson's disease and high blood pressure. Memorial Sloan-Kettering Cancer Center discovered that the vanilla-like scent of heliotropin—a compound in Tahitian vanilla—produced a 63% reduction in patient anxiety during MRI scans. Vanilla is one of the three most widely used flavoring/scents to mask the bad taste of medicine, and herbalists are reviving its popularity as a folk remedy to heal and soothe.

For hundreds of years, many people have ascribed aphrodisiac properties to vanilla. European physicians once believed that vanilla could cure sexual ailments and improve performance. Chocolate, also thought to have similar properties was considered "cold", while vanilla was "hot".

Before visiting his harem, the Aztec ruler Montezuma would consume large quantities of "chocolatl" containing vanilla extract. We'll never know if Montezuma's success with the ladies was a result of the smell of chocolate on his breath or vanilla's aphrodisiac qualities.

Maybe it's not quite that "hot", but modern research has shown men respond to vanilla more than to any other scent. Today, it is appreciated for its mood-lifting, romantic appeal to both sexes. Unless you happen to be a bug. Vanilla scent, alone or with DEET makes a good insect repellent, yet vanilla is used in flypaper, to attract flying pests. Go figure.

Either way, fans of vanilla owe a huge debt of gratitude to chemistry, for making so many sources of vanilla available. Otherwise, this "nectar of the gods", as the Totonacs called it, might still be property of the royal rich.

History

The Totonacs, in Mexico, first gathered seed pods of the wild orchid for their unique flavor. They traded pods as vine-grown "money" with the Maya, who paid the beans in taxes to the Aztecs. When Cortez invaded the New World, around 1520, his men named the pods "vainilla" (little sheath) and shipped them home as part of the Aztec treasure. From Spain, vanilla spread across Europe, sometimes as a flavoring for chocolate. Some 250 years later, when Thomas Jefferson was ambassador to France, he brought vanilla back to America. The popularity of ice cream took vanilla flavoring to the top, but chemistry brought it into everyone's life.

MIKE CIESIELSKI

Gail Kay Haines is a science writer and book author from Olympia, WA.