ChemMatters February 1992 Page 8

Perfume

By Marilyn Linner-Luebe

What is your favorite aroma? Is it the tangy, salty smell of ocean air, lilacs in the spring, laundry dried out-of-doors, newly mown hay, or smoke from a campfire? When you smell one of these odors, it can change your mood and stir your emotions.

Smell, more than any other sense, has the capacity to vividly bring back the past. Scientists call this olfactory bonding and believe it is related to the unique way your brain is wired for smell. The sense of smell—probably our most primitive sense—operates differently than our four other senses. Other kinds of sensory information are interpreted by the thalamus, a region deep within the brain. Smell messages, however, are routed directly to the area of the brain that determines emotion, creativity, and memory. Thus, an odor can instantly trigger a feeling or recall a long-past event. Perfumes are attempts to capture those moods and emotions in a bottle.

Messages to gods

The first perfumers were priests who burned resins, leaves, and woods as incense. They believed the sweet-smelling smoke carried their prayers to the gods. The ancient Chinese burned musk, an animal substance, in their temples. These practices gave us the word perfume—from the Latin words *per*, meaning from, and *fume*, smoke.

The Egyptians were probably the first to use perfume lavishly in their private lives as well as in their ceremonies. To attract Marc Antony's attention, Cleopatra ordered the sails of her barge drenched with cyprinum, a fragrance extracted from the henna plant. Archaeologists who opened the tomb of King Tutankhamen in 1922 found vases of a fragrant oil known as kyphi. After 3300 years, traces of its aroma could still be detected.

The Greeks and Romans imported scents from Egypt and added them to rosemary and other Mediterranean plants. They often added fragrances to wine. At great feasts, the Romans sprinkled the wings of birds with fragrances and released them to carry the scent over the heads of their guests.

Meanwhile, the art of perfumery was developing in the Far East as well. When the Crusaders returned to Europe, they brought exciting new fragrances: jasmine, citrus, musk, and sandalwood. The passion for perfume reached its peak in 18th-century French courts. Louis XV decreed that a different scent be used every day in his "perfumed court." Fragrances for the household of his royal mistress, Madame Pompadour, cost as much as $100,000 a year.

Essential oils

Most natural fragrances come from essential oils found in plants, and they give flowers their scents and spices their flavors. They were named essential oils because they contain the essence—characteristic odor or flavor—of the plant. Although nearly 3000 essential oils have been identified in nature, only about 150 are important perfume ingredients. Some of their names are as lovely and mysterious as their scents: ylang ylang, patchouli, vetivert, jasmine, lavender, myrrh.

Although many oils are concentrated in the petals of flowers, others collect in leaves, buds, stems, bark, fruits, seeds, and roots. Peeling an orange, for example, frees tiny droplets of sweet-smelling oil located just beneath the skin.

Before they can be used in a perfume, the essential oils are separated from the rest of the plant—a challenging task. Over the centuries, perfumers devised clever techniques that relied on differences in solubility, volatility, and boiling point.

The Egyptians were among the first to capture the fragrance of flowers by steeping petals in warm liquid fat, a process called maceration. Every few hours, the petals were strained out and replaced with fresh ones. The process continued until the fat was saturated with oil, which was then cooled and mixed with ethyl alcohol.

Oil and alcohol don't mix

Oil and alcohol are not soluble; the oil forms a separate liquid layer, which floats on the alcohol. Though they dissolve in hot oil, the essential oils are more soluble in alcohol, which causes them to leave the oil and dissolve in the alcohol layer. Although this is an effective separation technique, some chemicals in the essential oil may be lost in the hot oil because their molecules are delicate and decompose when heated, or they are relatively nonpolar molecules with a low molecular

weight and so can evaporate more readily. Later, the French developed a gentle process called *enfleurage* that extracts oils without heat.

Enfleurage is used to extract essential oils (those that evaporate readily). Workers coat glass plates with a layer of purified fat, then freshly picked petals are spread on top of the fat. Each plate is in a frame about 8 cm deep. The workers stack the frames on top of each other, forming an enclosed chamber for each plate. Then they wait. As the oil evaporates from the petals, the molecules are absorbed by the fat. Every few days, the workers replace the petals with fresh ones and the process continues until the fat becomes saturated with oil. Then the fat is scraped from the plates and mixed with ethyl alcohol. As in the process described above, the essential oils dissolve in alcohol, but the fat does not. Finally, the alcohol is evaporated, leaving a concentrated mixture of plant substances and essential oils, which is called *floral absolute*.

Plants are not the only source of fragrance ingredients. Animal oils such as musk (from the Himalayan musk deer), civet (from an East African cat), and ambergris (from sperm whales) add a leathery or musky note and make the scent last longer. These materials are not used anymore because they come from species that are now protected. Fortunately, good synthetic replacements are available. (See "The Mystique of Musk," *Chem Matters*, April 1991.)

Solvent extraction

Today, solvent extraction has replaced enfleurage and maceration. An organic solvent, usually petroleum ether, runs through flowers placed on perforated trays in a sealed vat. After the solvent leaves the vat, a vacuum still separates the petroleum ether from the fragrance materials. The solvent is recycled, and the process is repeated until all of the oil has been removed. Because a flower may contain more than one essential oil, and the oils may not be equally soluble in petroleum ether, a variation called selective extraction may be used. A series of different solvents is passed through the vat to capture a larger number of fragrance components. The waxy residue obtained by solvent extraction is known as a *floral concrete*.

Steam distillation was used to make rose water, the first real perfume, in the 11th century. Today, distillation is the most popular way to extract rose, spice, and mint oils. The plants and water are heated in a distillation apparatus until the water boils. Steam and volatile oils pass into the cooling chamber where they condense. The immiscible liquids form two layers, and the water is drawn off. Vacuum

distillation, in which the water boils at a lower temperature, is used to recover less stable flower oils.

Citrus oils are extracted by a process called *expression*. Powerful presses squeeze the entire fruit, leaving an emulsion of oil and juice. This liquid is then spun in a centrifuge to separate the oil from the water-soluble material, which is made into beverage concentrate. A cheaper grade of citrus oil, used in household and industrial products, is made by distilling the rinds after the higher-grade oil has been expressed.

Synthetic aroma

Chemical analysis of essential oils shows that they are not pure substances, but mixtures of organic compounds. Before modern instruments were available, chemists could identify only the major components of an oil. Today, they are working to identify all molecules in an essential oil, even those present in smaller amounts.

When the chemical compounds in an essential oil have been identified, chemists can make them synthetically—sometimes from unlikely raw materials. Sulfate turpentine, a byproduct of paper making, is the starting material for making geraniol, a constituent of rose oil; linalool, an alcohol used in lavender, sweet pea, and lilac perfumes; and nerol, an ingredient that enhances the odors of rose and orange flower (see box, "Roses and oranges").

Most of the fragrance materials used in perfumes are now manmade. They are preferred because they are more uniform and stable than their natural counterparts, they are available from reliable sources that are not affected by the weather or other uncontrollable factors, and they are cheap. Many synthetics are copies of natural products, but others have completely new odors that allow fragrance compounders to develop imaginative new scents. Perfumes like Chanel No. 5, Charlie, and Fidji rely on synthetics.

Today, man-made fragrances are used not only in perfumes, but in a wide variety of products. They are used to enhance our "image" of soap, talcum powder, and fabric softener. They are used to mask other odors, as when fragrance is added to cat box litter. They are also used to create illusions, such as making vinyl automobile seats smell like leather, or fill the home of a busy two-career family with the aroma of freshly baked bread.

Man-made chemicals will never completely replace natural materials, however. According to perfumer Nigel Priest, "Synthetic reconstructions of most naturals still lack that certain something that the perfumer searches for in raw materials." For this reason, Priest says, the most expensive perfumers use synthetics to enhance a natural oil,

not to replace it. For some oils like sandalwood and patchouli, he adds, there are no satisfactory substitutes.

SIDE BARS

Making scents

Many synthetic aroma compounds contain a C6H6 ring, which is very stable. One example is synthetic eugenol, which has a spicy clove odor and has largely replaced the more expensive clove oil. Others are cinnamaldehyde, which adds cinnamon odor to perfume and food, and benzyl acetate, which was originally found in jasmine oil and is added to perfumes for its pearlike odor.

Perfume milestones

The Jean Maria Farina cologne 4711 is the fragrance product that probably has been in longest continuous use. The name came from the number of the house in Cologne, Germany, where it was originally made. Worn by men and women, Napoleon's troops bought this cologne when they occupied that city in 1792.

Aime Guerlain's Jicky, introduced in 1889, is often called the world's first modern perfume. A French perfume, it was the first fragrance compounded with synthetic oils and the first to use natural oils obtained by solvent extraction. It, too, was popular with both sexes.

Launched in 1923, Chanel No. 5 continues to be one of the most popular perfumes in the world. The fragrance, one of 10 samples submitted to designer Coco Chanel, was in bottle number 5. It was the first perfume to have a strong "alde-hydic" (synthetic) base, a truly modern scent.

In 1953, Estee Lauder introduced Youth Dew. Its powerful oriental scent, a radical change from the delicate floral scents then in style, marked the beginning of the American challenge to the French perfume industry.

Revlon's Charlie, introduced in 1972, was the first of the so-called life-style fragrances. The Charlie girl symbolized independence: she wore slacks and bought her own perfume.

Giorgio, launched in 1984 and named for an expensive Rodeo Drive boutique in Beverly Hills, was the first perfume advertised by scent strips attached to leading women's magazines. The practice became so popular that magazines now limit the number of strips they accept for each issue so the scents don't conflict.

Recently, "imposter" scents have hit the market. These products imitate such well-known fragrances as Halston, Chanel No. 5, and

Giorgio for a fraction of the price. These smell-alikes don't contain exactly the same ingredients as the originals, but they're close enough for many shoppers. Their manufacturers keep costs low by eliminating fancy bottles and expensive advertising campaigns.

Roses and oranges

Geraniol, top, has a sweet rose odor and is the chief component of the oil distilled from roses. Linalool, bottom, has a lavender smell and is found in sassafras, orange flower, and other natural oils. Originally these compounds were extracted from plants, but now they are both synthesized from a terpentine-like material that is a waste product of paper making.

CAPTIONS

Upgrading a fragrance. Your soap or perfume may smell like sweet blossoms when you buy it, but the fragrance material may not have started that way. This technician is pouring vetivert oil, which has a forest-like but somewhat harsh aroma, into the reaction flask. After reagents are added and a reflux condenser is fitted to the top, the flask will be heated and the vetivert oil will be converted into an acetate derivative with a richer, woody aroma. Vetivert oil is obtained from the root of vetivert grass in Indonesia and India.

Distillation on an industrial scale. The tank at the bottom contains hundreds of liters of yellow-brown raw cinnamon oil from China and Sri Lanka. It also contains some water and plant material because, in the far east, the oil was separated from the leavesand twigs of the cinnamon plant by a crude steam distillation. As the oil is heated, the key aroma compounds vaporize and rise through the condenser (the large vertical pipe) where they are cooled, condensed, and collected, leaving the impurities behind. The purified oil can be used in food and perfume.

A French perfume bottle from the 1920s. The bottle was trimmed with hand-applied gold gilt, and the label was removable so you could replace it with a photograph of your beau.

You can buy this modern, upscale perfume for $30 per ounce, though little of your money pays for the actual perfume. Much of the retail price pays for advertising, and the elegant bottle may cost as much as the contents. Manufacturers pay $3 to $4 per ounce wholesale for the fragrance ingredients.

BIOGRAPHY

Marilyn Linner-Luebe is a freelance science writer from Clinton, IA.

REFERENCES

Kaufman, W. *Perfume*; Dutton: New York, 1974.

Moore, D. R. *Journal of Chemical Education*, August 1960, *37*(8), pp. 434-5.