

Chemical Reaction

What's That Smell?

Foul scents are always an industry concern. **BY STEVE HERMAN**

"...there was the rankest compound of villainous smell that ever offended nostril."

—Shakespeare,
The Merry Wives of Windsor

THE COSMETIC INDUSTRY provides consumers with pleasant aromas, from fine fragrances to perfumed bath gels. Nevertheless, foul smells are an industry concern, ranging from body odor to unpleasant base notes. If possible, malodors must be masked, prevented, or destroyed. Masking with a massive dose of aromatic compounds constituted malodor control in the fetid past. Modern approaches use carefully selected aroma chemicals, antibacterial and antiperspirant ingredients, malodor counteractants, and molecules capable of blocking the olfactory receptor sites.

The living symbol of malodor is the skunk. Figure 1 shows the principle components causing the foul odor of skunk spray. A common feature of many malodors is the presence of sulfur, nitrogen, or a halogen in the molecule.

Compare, for example, non-odorous water (H₂O) and carbon dioxide (CO₂) with their odorous counterparts, hydrogen sulfide (H₂S) and carbon disulfide (CS₂). The active atom must be available at the surface of the molecule to exhibit its characteristic malodor: A sulfur atom replacing a carbon in the middle of a hydrocarbon chain will not create a thiol odorant.

Human axillary odor is caused by the action of bacteria on the secretions of apocrine glands. Important odorous constituents include androstenone, androstenal, and isovaleric acid. The primary component of male underarm sweat is 3-methyl-2-hexenoic acid (Figure 2A, p. 18). The chemical components of human malodor are different from other malodors, since they aren't fundamentally foul—indeed, they can be important chemical signals. Remember Napoleon's message to Josephine: "Don't bathe. I'll be home soon."

Several of the "malodors" in sweat are human pheromones, and the modern American obsession with deodorizing may have profound negative consequences for non-visual sexual communication.

Napoleon notwithstanding, there is a demand for human

odor control. John D. Pierce¹ and his coworkers suggest an approach based on cross-adaptation, where there is a decrease in sensitivity to an odor following exposure to a structurally similar molecule. The pleasant-smelling methyl ester in Figure 2B (p. 18) reduces the perception of the odorous analog. A likely mechanism for this phenomenon involves the sharing of some of the same olfactory receptor sites by both molecules. A similar type of odor compensation is observed between coumarin and skatol. Odor compensation of this type requires correct levels of concentration between the two odorants, and the net result is a faint, pleasant smell resembling neither of the individual components.

The two most common ways of reducing malodor from sweat are blocking the apocrine pores with antiperspirants, or preventing the decomposition of the sweat with antimicrobials. Some deo-colognes are simply masks using perfume and alcohol. Other deodorants use triclosan as an antibacterial agent. Oral malodor, which afflicts 60 million Americans, also primarily is caused by bacterial action. Volatile sulfur compounds such as hydrogen sulfide, methyl

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FIGURE 1: EAU DE SKUNK

Principle components causing the foul odor of skunk spray.

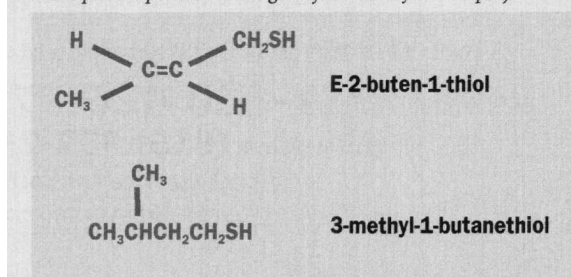


FIGURE 2A: MAIN COMPONENT, MALE UNDERARM SWEAT
E-Isomer of 3-methyl-2-hexenoic acid

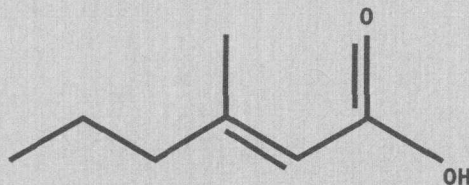
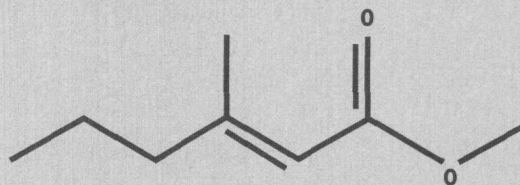


FIGURE 2B: PLEASANT-SMELLING METHYL ESTER
 Methyl ester of 3-methyl-2-hexenoic acid



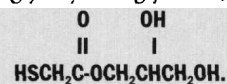
mercaptan, dimethyl sulfide, and dimethyl disulfide make up more than 90 percent of the putrid odors from the mouth. Good oral hygiene is the usual cure, although it is unfortunately not adequate for all individuals.

Most cosmetic bases have slightly undesirable odors. Emulsions typically have a fatty note that can be successfully overcome with a small percentage of an appropriate fragrance. Sometimes a "fragrance-free" claim is required, in which case, one or more aroma chemicals are listed separately on the ingredient label. Any aroma chemical listed in the CTFA Dictionary is a possibility: Examples are chamomile oil, geraniol, lavender oil, and phenylethyl alcohol. The dreaded word "fragrance" does not appear on the label, the base odor is tamed, and everyone is pleased with the deception.

Four cosmetic bases provide special perfuming challenges: permanent waves, depilatories, hair dyes, and hair relaxers. Depilatories, with a pH of 10 to 12, can destroy many fragrance chemicals. Ionones and rose alcohols such as geraniol and citronellol are among the few stable aroma ingredients. Relaxers provide even greater challenges, with a pH of 12.5 to 13.5. Phenylethyl alcohol, a simple rose note, has been the odorant most often employed.

Hair dyes present the combined challenge of a high pH, the presence of reactive chemicals, and the use of ammonia as a neutralizer. It is virtually impossible to deliver a uniform pleasant smell through the entire dyeing process.

The intrinsic base odor of perms is uniquely difficult to mask. The common active ingredients used for permanent waving are sulfur osmophores: ammonium thioglycolate ($C_2H_4O_2S \cdot H_3N$) and glyceryl thioglycolate,



Some methods are available to reduce the thioglycolate odor. Alkyl pyrrolidone surfactants can complex through hydrogen bonding at polar sites such as carboxylic acid and hydroxyl groups. The n-dodecyl version (ISP trade-name Surfadone® LP-300) is known for its ability to reduce the characteristic malodor of ammonium thioglycolate and glycerol monothioglycolate². The alkyl pyrrolidones also can complex with some fragrance materials in a useful manner, extending the fragrance life by increasing aroma substantivity to hair. Thioglycolic acid combines with benzaldehyde and cinnamic aldehyde in an exothermic reaction. A patent³ specifies selected materials for being more reactive with the cysteamine reducing agent

than with the aldehydes that naturally occur in hair. The reducing agent attacks the fragrance aldehydes rather than the hair aldehydes, resulting in reduced odor during the permanent waving process.

There is another location of foul smells in our industry—in perfumes. A fragrance composed only of pleasant-smelling components would be boring. The addition of small amounts of nasty odorants creates interest in the overall bouquet. Civet, for example, a far from attractive scent, provides a valuable nuance to many fine fragrances. Chanel No 5, with its overdose of an aldehyde bouquet, pioneered the use of unpleasant odors in perfumery. Malodors, thus, are not just something to be masked or destroyed, but occasionally a tool for bringing greater beauty to our world. **GCI**

References

1. Pierce, John D. et al., "Cross-Adaptation of Sweaty-Smelling 3-Methyl-2-Hexenoic Acid by Its Ethyl Esters Is Determined by Structural Similarity," *JSCC*, Vol. 47 No. 6, Nov./Dec. 1996.
2. Heliouff, Michael et al., "Alkyl Pyrrolidone Surfactants in Reactive Hair Care Products," *C&T*, Vol. 103, No. 5, May 1988.
3. US 5,554,363: Method of Reducing Malodors in Permanent Waving, Sept. 10, 1996.

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