Today's Natural Aroma Chemicals and their Sources[a]

From essential oils and extracts to food byproducts and waste streams

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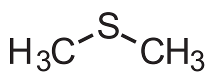
In the developed world, the desire for natural flavors, and hence natural aroma chemicals, continues unabated. Obtaining natural aroma chemicals by direct isolation from food sources is the oldest method of obtaining such materials, and indeed, as has been noted before, isolation of materials from natural sources is the de facto origin of organic chemistry. It is the method that produces the largest volumes of natural aroma chemicals, and it's also the method that is easiest for most lay persons to recognize as natural, without needing to consult the definitions of EU 1334/2008 or the US Title 21 Code of Federal Regulations.

Whilst the basic techniques of distillation and crystallization remain the cornerstones of isolation techniques, the increased demand for natural aroma chemicals means that greater effort is expended in isolating components at low concentrations, materials that might be said to be "down in the noise" on chromatographic traces. This is especially important as the industry obtains materials as byproducts of either food processing or byproducts of obtaining other materials. Dimethyl sulfide (**1**, **F-1**) is a good example; this as the "item of commerce" has moved from being a minor byproduct of mint oil production to a product isolated from the effluent gasses of ethanol fermentation.

Dimethyl sulfide **F-1**



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Natural Aroma Chemicals from Essential Oils and Extracts

This source is still the single most important approach for the production of natural aroma chemicals, especially in terms of sheer volume. While this article will try to avoid a "book of lists" approach featuring a table of citrus oils and their terpenes, it is important to note that citrus oils, produced in enormous quantities both in their own right and as the byproducts of the juice industry, are of great commercial importance as sources of natural aroma chemicals (including monoterpenes and their derivatives). Some of these chemicals are used to prepare other natural aroma chemicals, usually sesqui- and diterpenes and their derivatives.[1]

Citrus oils are often folded, i.e. the more volatile terpenes, frequently hydrocarbons which provide little organoleptic impact and have a negative effect on water solubility, are distilled off; the remaining pot fraction is the folded oil. For example, grapefruit oil can be folded to produce a terpene fraction, which along with the ubiquitous d-limonene (**2**) contains the grapefruit mercaptan, p-menthen-8-thiol (**3**) and the less volatile material; the folded oil can be further processed to produce the oxygenated sequiterpene nootkatone (**4**, **F-2**).

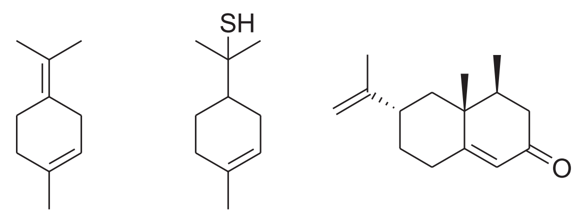
Orange oil, the cheapest and highest volume of all the oils, can be processed to give d-limonene, aliphatic aldehydes such as octanal (**5**) and decanal (**6**) from the terpene fraction, and the sesquiterpene valencene (**7**) from the folded oil (**F-3**).

Other examples of volatile derivatives are α-pinene (**8**) and β-pinene (**9**) from pine oils; these also yield α-terpineol (**10**). Mandarin oil is unusual in yielding a nitrogen derivative, methyl N-methylanthranilate (**11**; **F-4**).

This approach is not unique to the citrus oils; for example, mint oils (*Mentha arvensis* and variations thereof) yield menthol (**12**) very easily, simply by cooling the oil and filtering off the resulting crystalline menthol. Distillation of the resulting dementholized oil yields a terpene fraction, which can be fractionally distilled to give natural *cis*-3-hexenol (**13**; **F-5**).

Other important natural aroma chemicals from essential oils include linalool (**14**) from ho wood oil, cinnamaldehyde (**15**) from cinnamon bark oil and (primarily) cassia oil, eugenol (**16**) from clove oil, and citral (**17**) from

d-Limonene (2), p-menthen-8-thiol (3) and nootkatone (4) **F-2**



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[a]This article is based in part on Chapter 10, "Natural Aroma Chemicals for Use in Foods and Beverages," in *Natural Additives, Ingredients and Flavourings for Foods and Beverages*, Edited by D. Baines and R. Seal, forthcoming from Woodhead Publishing; ISBN# 978-1-84569-811-9.

Litsea cubeba oil (**F-6**); in the latter case, production is de facto solely for the production of natural citral.

Natural Aroma Chemicals from Food Byproducts and Waste Streams

This is potentially the most important approach for the future. There are ethical issues arising from the growth of non-food crops, most recently around palm oil and its contribution to deforestation in Indonesia. The growth of crops solely for "chemicals" is unlikely to win favor with the public. This is especially a concern in the production of natural aroma chemicals as marketing departments attempt to associate the word natural with a green, unspoiled picture—a veritable Garden of Eden. In this context, green credentials deriving from the use of material, which would otherwise be disposed of, can offer great advantage; sustainability is a good thing in chemistry, as well as marketing.

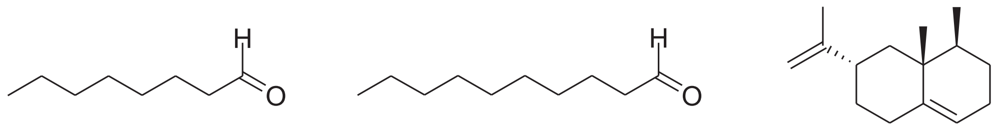
The stones, or pits, of peach and apricot can be processed to give natural benzaldehyde (**18**). The leaves and stems of tomato vine can be processed to yield 2-isobutylthiazole (**19**) and 2-isopropyl-4-methylthiazole (**20; F-7**).

Less obvious, but also of great importance, is the isolation from "off gasses." Since aroma chemicals are, by their nature, volatile components of food, it should be no surprise that when food and related natural materials are processed, useful materials emerge as byproducts. Unless trapped or in some way scrubbed from the effluent gasses, these byproducts would fill the surrounding manufacturing site's area with an unwanted miasma. Those who have lived or worked near to a brewery know the strength of aromas that are given off in fermentation; since this process is also used in the production of fuel alcohol, a lot of such effluent gas is produced. Trapping the volatiles, either cryogenically or by means of activated charcoal, both reduces the nuisance value of such odors and provides a feedstock for natural aroma chemicals, particularly the earlier mentioned dimethyl sulfide (**1**). Other examples include 2-methyltetrahydrofuranone (**21**), commonly known as coffee furanone, from, most appropriately, the effluent gasses from coffee roasting, and *trans*-2,*trans*-4-decadienal, (**22**), which is produced in the deodorization of vegetable oils (**F-8**). The latter can also yield saturated aldehdyes such as octanal (**5**) and decanal (**6; F-3**), highlighting an alternative route to the isolation from citrus oils mentioned earlier. There is, of course, an assumption in this—that the nature of the processing doesn't change and that the feedstock remains essentially unaltered. The vegetable oils with longer shelf lives tend to be so because they contain fewer unsaturated components; might that also mean that it contained less *trans*-2,*trans*-4-decadienal?

Future Trends

In terms of new aroma chemicals, continuing developments in isolations means that more materials become available; however, the industry is on a knife edge. Growing populations, especially in the developing countries, may lead to pressure to stop the use of valuable agricultural land to, in effect, grow chemicals; at the moment it's a rhetorical

Octanal (5), decanal (6) and valencene (7) **F-3**



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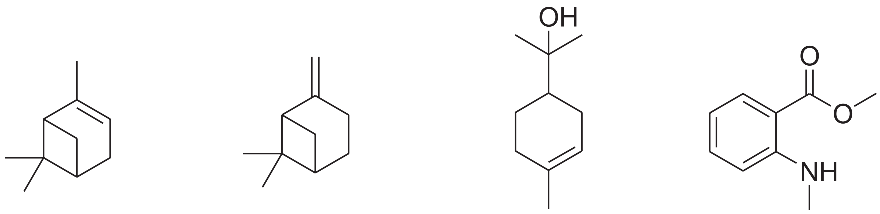
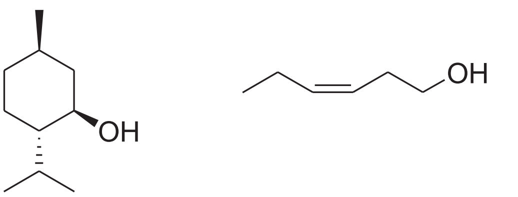
α-Pinene (8), β-pinene (9), α-terpineol (10) and methyl N-methylanthranilate (11) **F-4**



(8) (9) (10) (11)

Menthol (12) and natural *cis*-3-hexenol (13) **F-5**



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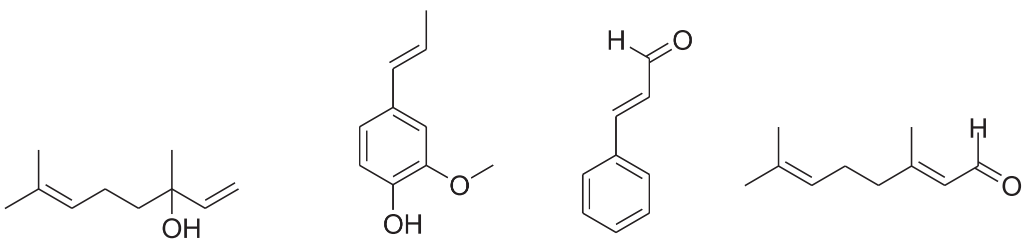
question (to which the author does not know the answer), but is the best use of land in India to grow mint in order to make menthol, when the same material is available from non-agricultural sources? Whither *Litsea cubeba*, grown solely to produce natural citral? Will a time come when petrochemical, currently a term of abuse, becomes fashionable, perhaps in the service of the product claim "this flavor contains no materials derived from food crops?"

Natural: Can We Have it Both Ways?

The industry is operating in an environment in which marketing departments are trying to have both "clean label" and an advantage over other suppliers. The difficulties associated with this, which are often associated with naturals, include religious matters (kosher, halal),

Linalool (14), cinnamaldehyde (15), eugenol (16) and citral (17) **F-6**



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social concerns such as sustainability, and fashions such as organic and GMO-free. This can best be illustrated, perhaps surprisingly, with solvents. Many natural materials are expensive per kilo; if they possess a strong odor, then using them in solution, typically at 1%, is a big advantage. But every solvent has potential disadvantages:

1. Ethanol; flammable and non-halal
2. Propylene glycol; petrochemical
3. Triacetin; made from glycerol, which can come from palm oil, one of the most vilified raw materials
4. MCTs (medium chain triglycerides); synthesized from glycerol and carboxylic acids, which can also be from palm oil
5. Vegetable oils; can be of GMO origin
6. Water; at present, no one has identified halal, kosher, organic, palm oil and GMO issues with water—though perhaps it's only a matter of time?—however, despite these massive advantages, there is the minor problem that most aroma chemicals don't dissolve in it

In choosing to use a natural aroma chemical, or even a solvent, issues above and beyond technical concerns such as solubility must be considered.

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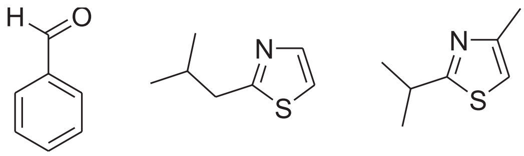
Benzaldehyde (18), 2-isobutylthiazole (19) and 2-isopropyl-4-methylthiazole (20) **F-7**



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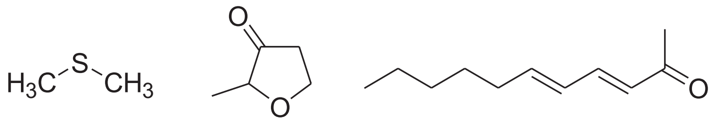
Dimenthyl sulfide (1), coffee furanone (21) and *trans*-2,*trans*-4-decadienal (22) **F-8**



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References

1. DJ Rowe, *Aroma Chemicals V: Natural Aroma Chemicals.* In: *Chemistry and Technology of Flavors and Fragrances.* J Margetts, ed., Wiley, Hoboken NJ (2009).