

# Natural Aroma Chemicals: Nothing New Under the Sun?

The resurgence of naturals and ongoing innovations in organic chemistry

Brian Byrne, Natural Advantage Inc., and David Rowe, Riverside Aromatics Ltd.

Let the title be considered a rather downbeat opening, it should be noted that its purpose is simply to ground natural aroma chemicals where they belong, i.e. in organic chemistry. (All life is made with chemicals, after all.) Amongst the first organic chemicals to be purified and characterized were some of the most important natural aroma chemicals, beginning with menthol in 1771 (see **T-1**). The fundamental difference between now and then, of course, is that in the early days of organic chemistry it was believed that life was essential to the creation of complex molecules, the so-called “vital force” or “vitalism.” We understand now that the reverse is true, i.e. it’s the complexity of organic chemistry that is the mechanism of life. The 19th and 20th centuries saw the development of chemistry to the level that most organic molecules can now be made *in vitro*; despite this, recent years have seen continually growing interest in natural materials.

## Naturals and the foundations of organic chemistry—a timeline

### T-1

**~ 4th Century BC:** Vitalism: Hippocrates, Aristotle and others posit that the spark of life creates what we now know as the complexity of organic chemistry

**1771:** Menthol

**1828:** Friedrich Wöhler and the beginning of the end of vitalism—preparation of urea from ammonium isocyanate, described by him in a letter to Jöns Jakob Berzelius as “the slaying of a beautiful hypothesis by an ugly fact”

**1834:** Cinnamaldehyde

**1837:** Benzaldehyde

**1845:** Adolph Wilhelm Hermann Kolbe, the supposed inventor of the modern term “synthesis”: Synthesis of acetic acid from carbon—the complexity of organic chemistry creates life

**1858:** Vanillin

**2006:** Doctor Who: “What’s life? Nothing. A quirk of matter. Nature’s way of keeping meat fresh.”\*

“The thing that hath been, it is that which shall be; and that which is done is that which shall be done: and there is no new thing under the sun.”

-Ecclesiastes 1, Authorized Version  
 (“King James” Bible)

*Plus ça change, plus c’est la même chose.*

“The more things change, the more they stay the same.”

-Jean-Baptiste Alphonse Karr  
 (1808–1890)

## Naturals in the 21st Century

The rising demand for natural aroma chemicals has been driven by several factors, all pushing in the same direction. The largest factor is simply the marketing value of the term “natural,” evoking—theoretically—a simple, rustic past that most of the developed world has moved away from. To the general public, this natural concept is synonymous with health benefits and the whole green/sustainability package. Above all, it means there are no “chemicals” involved! This expectation, as we stated earlier, is unrealistic.

“There’s a natural mystic flowing through the air/If you listen carefully now you will hear...”

-“Natural Mystic,” Bob Marley and the Wailers (*Exodus*, Island Records, 1977)

A second factor is that in recent years there have been many more approaches to natural aroma chemicals development, adding a much greater range of materials to the flavorist’s palette. These changes are the main focus of this article; if one compares the situation of natural aroma chemicals with synthetic or nature-identical materials, there are still some key differences. Nature-identicals are well-defined in terms of identity, quality, markets

\**Doctor Who*, “The Doctor Dances,” BBC TV (2006)

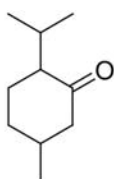
and sources; naturals are largely well-defined in terms of identity, but there are still quality issues; often it is more difficult to define a “standard” material. In addition, markets are still evolving, as are sources. It is to the latter that we can now turn.

## Sources

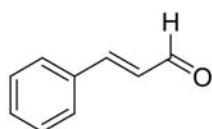
All the materials mentioned in the first section of this article had, de facto, the same source—essential oils—from which some components could be isolated by simple physical methods; e.g. menthol (1) crystallizes out of mint oils on cooling and can be filtered off, and cinnamaldehyde (2) is readily distilled out of cinnamon and cassia oils, to which it contributes ca. 80% of the total (see **F-1**). As isolation techniques improved, especially those of fractional distillation at reduced pressure, many more materials that are present at lower levels in their sources became available. For example, *cis*-3-hexenol (3) is now isolated from mint oils by fractionation, despite being present at only a few percent, at most, in the oil. Until recently, dimethyl sulfide (DMS) (4) was also isolated from peppermint, via the so-called “peppermint heads,” the most volatile fraction, but here we can see the impact of new sources (**F-1**). Off-gasses from cane sugar molasses, which contain DMS, can be trapped onto charcoal and then liberated by heating, re-trapping, and then distilled to give DMS at much higher purity (>99% compared to ca. 95% ex mint). DMS from this new source has a much better and more consistent odor; i.e. it has the characteristic sweet corn/asparagus note even on dry-out. Formerly, the main, or even sole, organoleptic criterion was that it didn't smell of mint! This leads to another issue, which will be addressed later in this article—that of the comparison of natural aroma chemicals with their synthetic counterparts. Meanwhile, this process highlights “new sources” for natural aroma chemicals—waste streams and off-gasses. Here there is a commercial advantage; the price of natural DMS obtained via this route is only a fraction of the price of material ex peppermint.

### Natural isolates

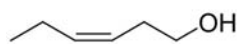
**F-1**



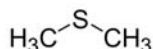
(1)



(2)



(3)



(4)

## “New lamps for old!” Aladdin (Middle Eastern folktale)

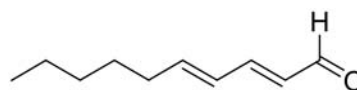
### Natural Aroma Chemicals from “Waste Streams”

Obtaining valuable materials from “wastes,” i.e. materials that would otherwise be disposed of, incurring further costs, comprises a modern-day search for the Philosopher's Stone. It is also a factor in the issue of sustainability, which is already affecting the supply of some essential oils such as sandalwood. Trapping the off-gasses from fermentation has already been mentioned as a new source of DMS; in a similar manner, the off-gasses from vegetable oil deodorization are a source of *trans,trans*-2,4-decadienal (5), the powerful fatty note of which is essential for adding character to another modern phenomenon, the low-fat food or beverage (see **F-2**). In turn, *trans,trans*-2,4-decadienal can be used to make natural pear ester, ethyl *trans*-2,*cis*-4-decadienoate (6) (**F-2**).

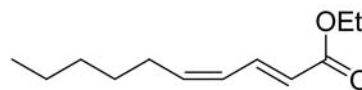
## “Where there's muck there's brass.” English proverb

### Decadienal and pear ester

**F-2**



(5)



(6)

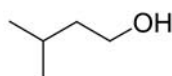
The ultimate use of a waste stream is perhaps fusel oils, the by-product of the distillation of whisky, other liquors and fuel ethanol. The oils' main components are isoamyl alcohols (7) and (8), followed by other alcohols such as 1-butanol and 1-hexanol (see **F-3**). Natural pyrazines such as 2,3,5-trimethylpyrazine (9) and—at even lower levels that are “down in the noise” of GC traces—β-damascenone (10) can be obtained from the residues remaining after this distillation (**F-3**).

Waste from tomatoes, processed by the ton for the Western market, supplies 2-isobutylthiazole (11); this in turn, provides the aroma chemical market the option of “from the named fruit” natural aroma chemicals (see **F-4**). Similarly, 1-octen-3-ol (12) can be obtained from mushroom waste (**F-4**). In the latter case, one is confronted

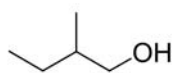
with an example in which the natural aroma chemical is very different from its synthetic counterpart; because the natural version has the characteristic enantiomeric ratio and impurity profile of mushroom, it has a more obvious mushroom character, making it a much more “realistic” note—more “natural,” one might say.

Fusel oil derivatives

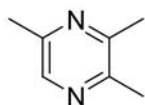
F-3



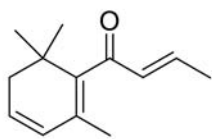
(7)



(8)



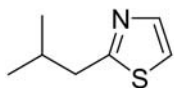
(9)



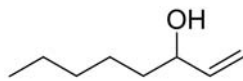
(10)

Food by-products

F-4



(11)



(12)

Biotechnology

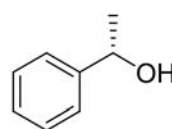
Here is a nice example of the power of language; “biotechnology” evokes scientists in white laboratory coats—scientists, as one knows from the movies, being, at best, naive and bit barmy (*The Nutty Professor*, for example)—whereas the terms “fermentation” and “brewing” are more universally familiar and thus acceptable. Brewing and the baking of bread, both using yeast, are amongst man’s oldest technologies; if one adds the making of cheese, soy sauce and various fermented fish sauces, one can see that humans have enjoyed the products of biotechnology across the globe since the start of recorded history. In the 21st century, biotechnology affords two approaches—the use of whole cells, most commonly yeast and other fungi, and the use of isolated enzymes.

The use of yeast is such a common practice in the field of natural aroma materials that standard processes appear in “cookbook” form. In 1985, Seebach and co-workers published such a process in *Organic Syntheses* for the

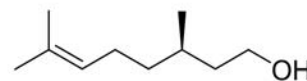
bio-reduction of ketones to optically active alcohols.<sup>1</sup> It has proven to be a very general and reliable way to produce high S-isomer natural alcohols. In a similar manner, the authors of this current work have obtained natural (S)-styralyl alcohol (**13**) from natural acetophenone (see **F-5**). Primary alcohols are also accessible through this process via their parent aldehydes, for example l-citronellol (**14**) from l-citronellal ex citronella oil (**F-5**). Anaerobic fermentation, although much more difficult than aerobic fermentation, is an effective tool for producing natural succinic acid (**15**), a rather general savory flavor enhancer (**F-5**).

Naturals from biotechnology

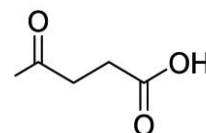
F-5



(13)



(14)



(15)

Chirality

This is one of the most misunderstood, yet potentially most valuable, areas concerning natural aroma chemicals. Chirality, or optical isomerism, is a feature of many molecules used as aroma chemicals.<sup>\*\*</sup> As the human sensory system is based on biomolecules that are chiral, people can often differentiate enantiomers by their odor. The best-known and perhaps most extreme case comes in the enantiomers of carvone; the R-isomer (**16**) is spearmint and the S-isomer (**17**) caraway (see **F-6**). However, these extremes are rare, and more commonly both enantiomers have some shared character, with one of the enantiomers being more powerful and more “typical” than the other. In addition, and most importantly, most aroma chemicals are found as mixtures of both isomers, i.e. even if one enantiomer dominates, the other is usually found at a lower level; very few, if any, aroma chemicals are found in nature in “homochiral” form (corresponding to an enantiomeric excess of 100%). Similarly, they are rarely found to be truly “racemic,” i.e. an enantiomeric excess of zero. This can be illustrated with the enantiomers of hazeltone (5-methyl-2-hepten-4-one) (**18**; **19**) (**F-6**). Both enantiomers have the nutty, buttery, metallic character implied by the name, with the d-isomer (**18**) (which has

<sup>\*\*</sup>For an excellent and regularly updated online review of chirality and odor perception, see [www.leffingwell.com/chirality/chirality.htm](http://www.leffingwell.com/chirality/chirality.htm)

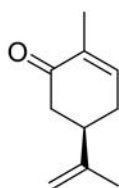
the S-configuration) having the lower odor threshold; both are found in nature—ca. 80:20 (S:R) in raw hazelnuts and 70:30 in roasted hazelnuts.

“Perhaps Looking-glass milk isn’t good to drink ...”

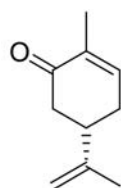
*Through the Looking-Glass and What Alice Found There*  
—Lewis Carroll (1832–1898)

### Carvones and the hazeltones

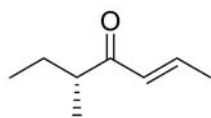
## F-6



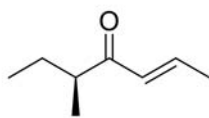
(16)



(17)



(18)



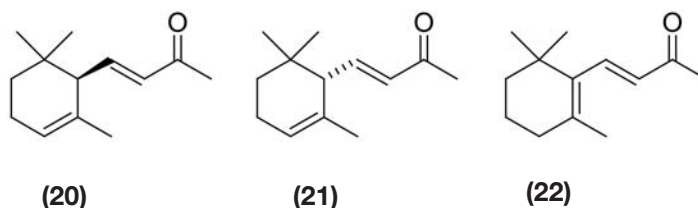
(17)

With this in mind, it is important to dispel the concept that only chiral—or more strictly, homochiral—natural aroma chemicals are truly natural. The reality is both more complex and more interesting. An area where this has become something of a *cause célèbre* is  $\alpha$ -ionone (**20**; **21**) (see **F-7**). It has been known for many years that the  $\alpha$ -ionone found in raspberry extract does approach homochirality, with an enantiomeric excess of at least

99.9% R-isomer (**20**) (by headspace analysis). However, in a simplification that rivals author George Orwell’s “two legs good, four legs bad,” this fact has been converted into: 100% R-isomer = natural; <100% R-isomer = synthetic. This wretched dictum is even being used to promote chiral GC systems to enable people to “prove” whether their raspberry flavors are natural or not. Yet it is not based on scientific fact. Both isomers are found in nature; work by the former Haarmann & Reimer (now Symrise) on a variety of foodstuffs found that while the R-isomer predominates, the S-isomer (**21**) is found at a level of 5% in Darjeeling tea (by solvent extraction), 3% in vanilla pods and 5% in carrots (both by headspace analysis).<sup>2</sup> Boronia absolute has been found to have 9% S-isomer. Even in raspberry there was some S-isomer, if only 0.1%. In addition, work by Firmenich and the University of Hamburg found that the S-isomer, not the R-isomer, was the main isomer in black tea.<sup>3</sup> This is a particular problem as the ionones can be obtained by air oxidation of carotenes; the elevated temperature and purification by distillation leads to a loss of chirality as the chiral center has an active proton  $\alpha$ - to two double bonds, one of which is also conjugated to a carbonyl group. This loss of chirality is shown in **F-8**, in this case via a carbanion mechanism; as a result, the  $\alpha$ -ionone thus obtained has little enantiomeric excess, typically R:S = 60:40. We have seen above that both enantiomers are found in nature; the techniques used fulfill all the criteria of EC 1334/2008 and US 21 CFR 101.22, yet due to the “two legs good, four legs bad” manner of thinking—the present paradigm of naturalness in the ionones—there is resistance to use of what is potentially a very important natural aroma chemical. This absurdity has even spilled over into issues with  $\beta$ -ionone (**22**), which itself is not and cannot be chiral (**F-7**). Distillation of  $\beta$ -ionone leads to formation of  $\alpha$ -ionone, an energetically unfavorable transformation as this takes a double bond out of conjugation, but since the  $\alpha$ - form has the lower boiling point of the two, the equilibrium is always shifted in its favor as the distillation proceeds (**F-8**). Hence, distilled  $\beta$ -ionone always contains traces of  $\alpha$ -ionone, and since  $\beta$ -ionone is achiral, the resulting  $\alpha$ -ionone has zero enantiomeric excess, leading, once again, to accusations of unnaturalness when the material is analyzed on a chiral GC column (**F-8**).

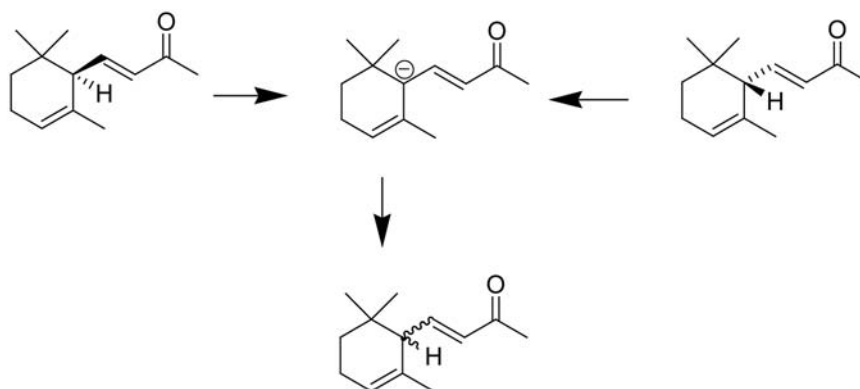
The ionones

F-7



Loss of chirality in  $\alpha$ -ionone

F-8



Issues surrounding chirality can be illustrated well with the lactones, especially the widespread  $\gamma$ -lactones. All of the  $\gamma$ -lactones (**23**)—except the simplest,  $\gamma$ -butyrolactone, R=H—have a chiral center  $\alpha$ - to the ring oxygen (see **F-9**). Another piece of received “wisdom” is that all naturally occurring  $\gamma$ -lactones are found exclusively in the R-configuration. **T-2** shows that while in most—though not all—sources, the R-form predominates. Yet, with the possible exception of  $\gamma$ -dodecalactone, both forms are found in nature—and in the case of the wonderfully named *lulo del choco*, things are the reverse, with the S-forms dominating.

By using different culture media, both high-R and low enantiomeric excess  $\gamma$ -lactones can be obtained by fermentation of natural long-chain carboxylic acids—essentially, enzymatic oxidation at position 3 followed by cyclization. The organoleptic properties of the high-R forms are subtly different from that of the R/S mixture, giving the flavorist an extra opportunity to influence the flavor.

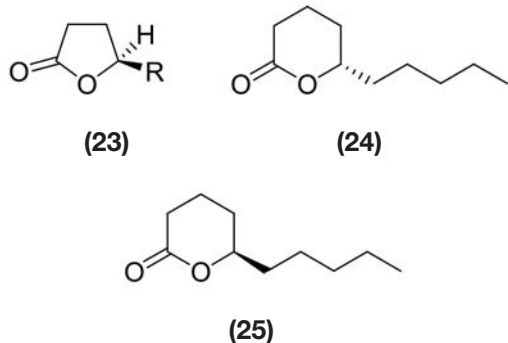
We have a similar situation with the six-membered  $\delta$ -lactones. For example, the  $\delta$ -decalactone in raspberries is 98% S-isomer (**24**), whereas in peach the situation is reversed at 97% R-isomer (**25**), while in cheddar cheese there is a 72:28 mixture (**F-9**).

Enantiomeric ratios (R/S) in some fruits\*\*\*

T-2

Source	C8	C9	C10	C12
Apricot <sup>4,5</sup>	89/11	84/16	94/6	100/0
	85/15	-	100/0	100/0
Mango <sup>4</sup>	53/47	73/27	66/34	100/0
Peach <sup>4</sup>	87/13	85/15	87/13	96/4
Passionfruit <sup>6</sup>	55/45-78/22	50/50-56/44	87/13-93/7	99/1-100/0
Raspberry <sup>6</sup>	44/56	28/72	49/51	50/50
Lulo del choco ( <i>Solanum tojiro</i> ) <sup>7</sup>	23/77	-	20/80	-

\*\*\*The contents of T-2 and the references herein are adapted from: RC Brown,  $\gamma$ -Lactones in wine: Synthesis, quantification and sensory studies. PhD Thesis, Flinders University of South Australia (2007)



### High Impact Naturals

This is a potentially difficult area in that direct isolation can be very difficult; by their very nature, high impact aroma chemicals are detectable at very low levels, and hence the concentration in natural foodstuffs is low, in turn making isolation difficult and commercially unviable; one would need to distill a herd of cows to isolate 2-methyl-3-furanthiol (**26**) from roast beef. However, there are several approaches available (see **F-10**).

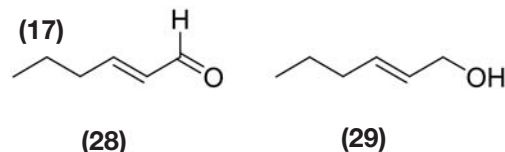
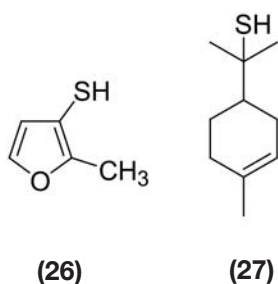
*Odorato rectus ergo sum.*

“I stink therefore I am (naturally).”

(With apologies to Rene Descartes)

Looking at isolation, there are exceptions that prove the rule. The wide availability of citrus oils and their downstream derivatives such as terpeneless oils means that the intensely odorous p-menthen-8-thiol (**27**) (grapefruit mercaptan) can be isolated commercially from grapefruit oil (**F-10**). There is also the waste-streams option, which provides the fatty *trans*, *trans*-2,4-decadienal from vegetable oil and the herbaceous green 2-isobutylthiazole from tomato.

Considering biotechnology, enzymatic degradation of lineolic acid ex vegetable oil produces the extremely important green material *trans*-2-hexenal (**28**), and yeast reduction leads to *trans*-2-hexenol (**29**) (see **F-11**).



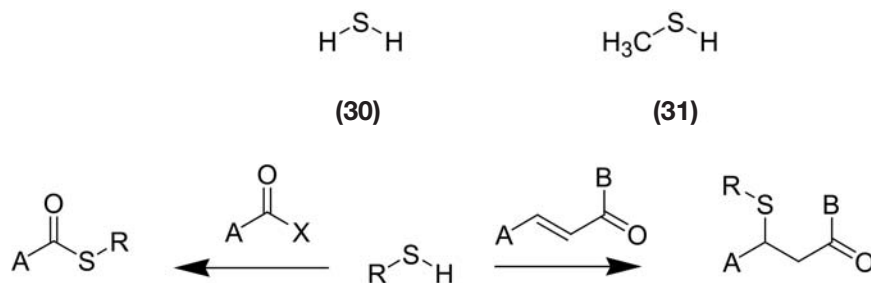
Next up is “cooking chemistry.” Sulfur compounds are perhaps the most important and typical high impact aroma chemicals, and two key materials are available that provide access to a number of interesting and essential natural compounds: natural hydrogen sulfide (**30**) ex vegetable protein and natural methyl mercaptan (**31**) ex fermentation of broccoli (see **F-12**). Combined with the remarkable nucleophilicity of the mercaptan moiety—leading to ready reaction without the use of inorganic catalysts with carbonyl functions (formation of thioesters) and double bonds  $\alpha$ -,  $\beta$ - to carbonyl functions (Michael addition)—this provides access to a wide range of interesting natural high impact aroma chemicals. Both methyl mercaptan and hydrogen sulfide are themselves, of course, very important aroma chemicals; the former, a gas at room temperature, is a ubiquitous roasted note in meaty and savory materials, and can be supplied as solution in organic solvents such as propylene glycol. Hydrogen sulfide, on the other hand, is much more volatile, but can be combined with natural ammonia to give ammonium sulfide, which is stable in aqueous solution.

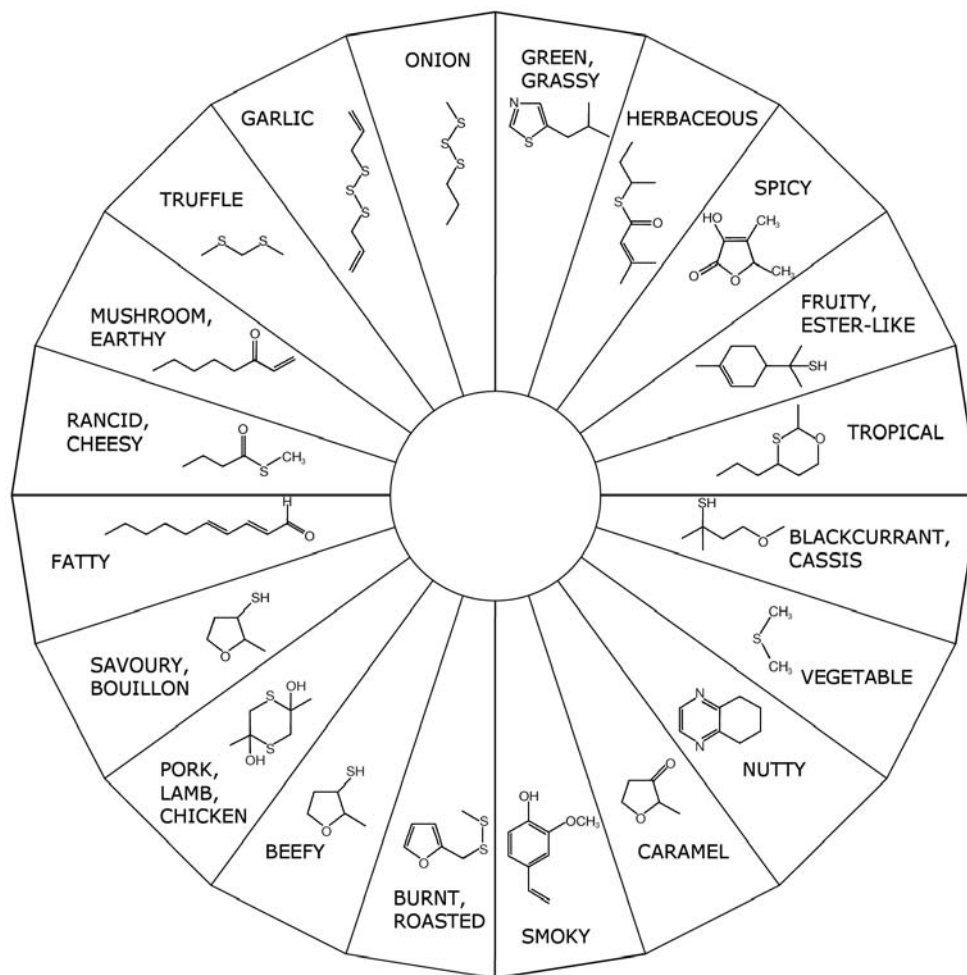
### Around the Flavor Wheel

Thanks to the approaches discussed above, combined with perhaps a slightly less rigorous approach compared to the criteria used for nature identical, the industry can have natural access to the original high impact aroma chemical flavor wheel (see **F-13**).

**Green, grassy:** Here one will find the classic *trans*-2-hexenal (**28**), *cis*-3-hexenol (**3**) as well as the herbal green 2-isobutylthiazole (**11**) (see **F-14**).

**Herbaceous:** This is a more difficult area for natural aroma chemicals. The availability of herb extracts (oils





and absolutes) means there is less demand for individual chemicals; flavorists can make use of the extracts themselves.

**Spicy:** As with the herbaceous category, spice extracts are more readily available than individual aroma chemicals. Fenugreek lactone (sotolon) (**32**) is, in theory, available ex fenugreek absolute, but the level makes it economically difficult (see **F-15**).

**Tropical:** This is an area in which there is a good range of sulfur compounds available, obtained using natural methyl mercaptan and natural hydrogen sulfide. These include trophathiane (**33**) (2-methyl-4-propyl-1,3-oxathiane), ethyl 3-methylthiopropionate (**34**) and 3-methylthiohexanol (**35**) (see **F-16**).

**Fruity, esterlike:** The availability of natural alcohols and natural acids means that esters are amongst the most readily available naturals; however, most interesting is the über-odorant p-menthen-8-thiol (**27**), the grapefruit mercaptan (see **F-17**). Fermentation of lemongrass oil imparts 2,6-dimethylheptenal (**36**), which possesses a powerful melon tonality (**F-17**).

**Blackcurrant, cassis:** This segment houses the classic thiomenthone (**37**), available from reaction of natural hydrogen sulfide with pulegone from pennyroyal oil, and

4-mercapto-4-methyl-2-pentanone (**38**), the cat ketone, which, one might say “does what it says on the tin” (see **F-18**).

**Vegetable:** The best example in this category is the previously mentioned dimethyl sulfide (**4**), with its sweet corn-asparagus aroma (see **F-19**). Dimethyl disulfide (**39**) has brassica notes, best described as “old cabbage” when in high concentration (**F-19**). There is also the potato-like methional (**40**), prepared from natural methyl mercaptan; yeast reduction of this gives the corresponding alcohol, methionol (**41**) (**F-19**). Also commercially available is natural *trans*-2-dodecenal (**42**), with its characteristic cilantro/coriander taste (**F-19**).

**Nutty:** Unfortunately, the nuttiest of pyrazines, 5,6,7,8-tetrahydroquinoxaline (**43**), is not yet available as a natural; however, fusel oils provide a selection of simple alkyl pyrazines such as the isomers of dimethylpyrazine (**44**), 2,3,5-trimethylpyrazine (**45**) and the isomers of ethyldimethylpyrazine (**46**)—but not tetramethylpyrazine (**47**), which is only present at a very low level in fusel oils, rendering its isolation economically unviable (see **F-20**). And if one seeks nuttiness of the hazel variety, there is hazeltone (**48**) (**F-20**).

**Caramel:** This is a contentious area, as the standard is, or was, diacetyl (49), which is available in natural form via fermentation (see F-21). However, safety concerns are restricting the use and availability of this material. Acetyl propionyl (50) (2,3-pentandione) is available as a natural alternative, and even though it is more expensive per kilo, its lower volatility leads to less loss of material in handling (F-21). Also available in this category is 2-methyltetrahydro-3-furanone (51) (coffee furanone), using coffee roaster and grinder gasses as a source (F-21).

**Smoky:** This segment encompasses the guaiacols—guaiacol (52); 2-methoxy-4-vinylphenol (53) (MVP), with its smoky-clove odor; and the smoky-medicinal 4-methylguaiacol (54) (creosol), popular for its vanilla beanlike notes (see F-22).

**Burnt, roasted:** Reaction of natural hydrogen sulfide with natural furfural ex bran yields natural furfuryl mercaptan (55), which can be oxidized with air to produce disulfide (56) or reacted with methyl mercaptan to give its disulfide (57) (see F-23).

**Beefy:** Natural 2,4-undecadienal (58), with its beefy, brothy, fatty taste, is a new natural on the scene (see F-24). Natural *trans*-2-decenal (59), with its distinctive tallow, T-bone steak flavor, is also included in this category.

**Pork, chicken, lamb:** Presently, this area is best covered by nature identical materials, with the notable exception of natural 2,4-decadienal (5), with its distinctive chicken fat flavor (see F-25). Also available is the roasted chickenlike 2,5-dimethyl-3-furanthiol (60) (F-24).

**Savory, bouillon:** This category, generally described as savory and meaty, is the weakest area for natural aroma chemicals. Isolation is rarely an option, and the more complex chemistry precludes the simple heating and mixing-type approach. Biotechnology is perhaps the most hopeful approach here, which has produced methyl mercaptan (31), a simple but very valuable savory aroma chemical (see F-24).

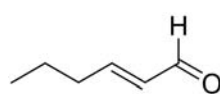
**Fatty:** The previously mentioned *trans,trans*-2,4-decadienal (5) falls under this category. Here there is also 3-methylthiobutanal (61), a fattier homologue of methional that has a powerful fried potato aroma (F-25).

**Rancid, cheesy:** The availability of methyl mercaptan and natural acids provides access to thioesters, including the strawberry cheese-cake chemical methyl thiobutyrate (62) and the cheesier methyl thioisovalerate (63), which has powerful blue cheese notes (F-25).

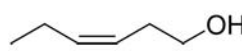
**Mushroom, earthy:** As noted earlier, chemists can isolate 1-octen-3-ol (12) from mushroom processing; the more powerful 1-octen-3-one (64) can be obtained from the same source, the latter having an odor threshold some 20 times lower than the alcohol (see F-26).

## Natural greens

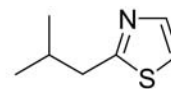
# F-14



(28)



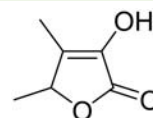
(3)



(11)

## Fenugreek

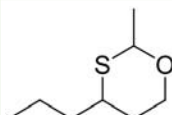
# F-15



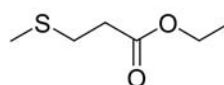
(32)

## Natural tropicals

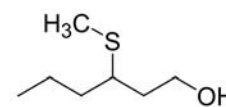
# F-16



(33)



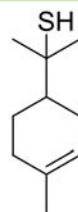
(34)



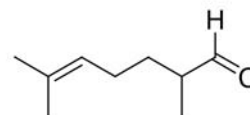
(35)

## Fruity naturals

# F-17



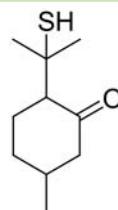
(27)



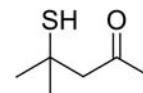
(36)

## Catty, cassis naturals

# F-18



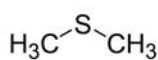
(37)



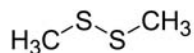
(38)



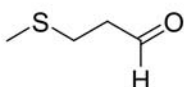
Natural vegetable aroma chemicals **F-19**



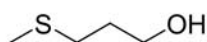
(4)



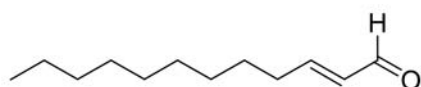
(39)



(40)



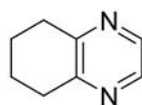
(41)



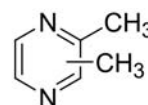
(42)

Nutty materials

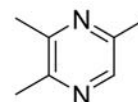
**F-20**



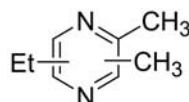
(43)



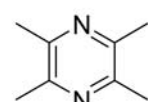
(44)



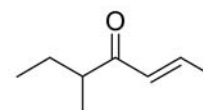
(45)



(46)



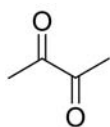
(47)



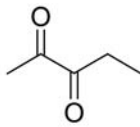
(48)

Natural caramel notes

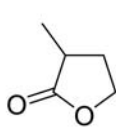
**F-21**



(49)



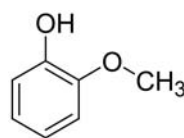
(50)



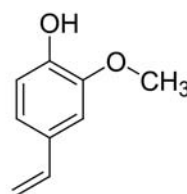
(51)

Smoky naturals

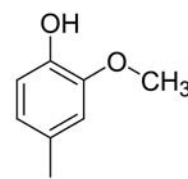
**F-22**



(52)



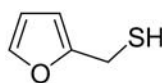
(53)



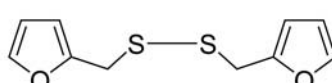
(54)

Naturals for roasted and coffee aromas

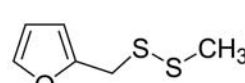
**F-23**



(55)



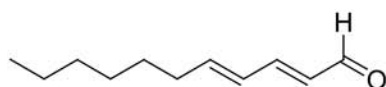
(56)



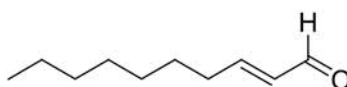
(57)

Meaty and savory naturals

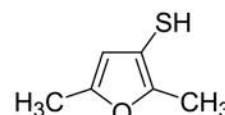
**F-24**



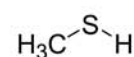
(58)



(59)



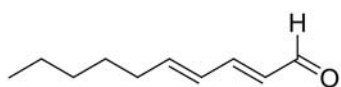
(60)



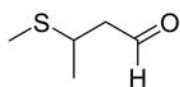
(31)

Fatty and cheesy naturals

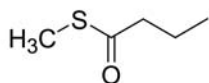
F-25



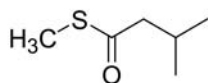
(5)



(61)



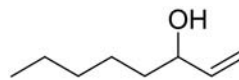
(62)



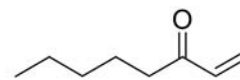
(63)

Fungal aroma chemicals

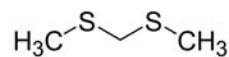
F-26



(12)



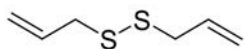
(64)



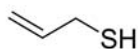
(65)

Alliaceous issues

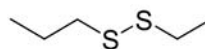
F-27



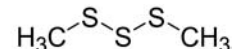
(66)



(67)



(68)

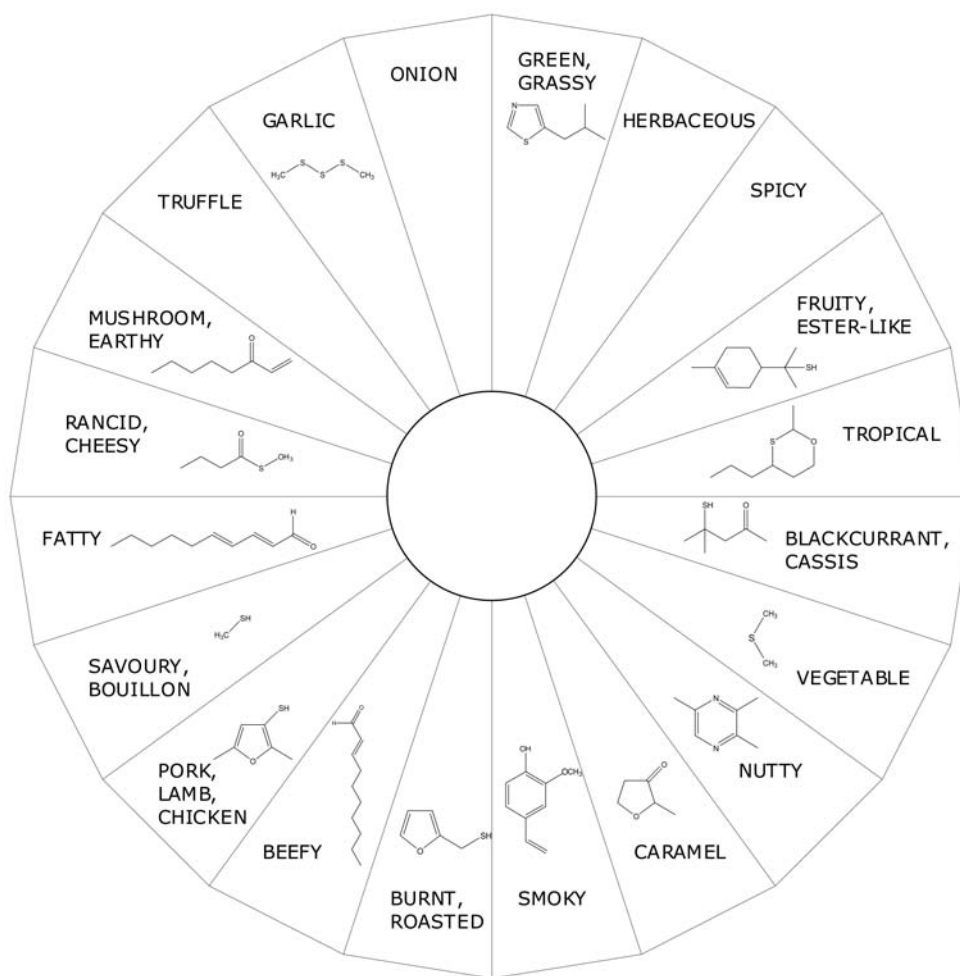


(69)

45

A flavor wheel for natural high impact aroma chemicals<sup>8,9</sup>

F-28



**Truffle:** At the moment, one draws a blank on this category. Isolation of bis(methylthio)methane (**65**) from black truffles is unlikely to be a commercially successful approach (**F-26**).

**Garlic:** Although natural allyl disulphide (**66**) and allyl mercaptan (**67**) are commercially available, it is difficult for them to compete with natural garlic oil (see **F-27**).

**Onion:** This is the other “alliaceous” sector. The availability and low cost of onion oil means that there is little demand for natural propyl disulfide (**68**) and its derivatives (**F-27**). On the other hand, natural methyl trisulfide (**69**), which has strong alliaceous character, is available (**F-27**).

With these materials in mind, one can do a remarkably good job of populating the sectors of the flavor wheel (see **F-28**).

### Naturals and the Future

Although there has been remarkable growth in the use of natural aroma chemicals, the death of synthetics/nature identicals has, in the words of Mark Twain, been greatly exaggerated. Price and lack of availability of natural materials such as 2-acetylpyrazine (**70**) and 2-acetylthiazole (**71**) have kept the need for synthetics high (see **F-29**).


In the case of institutional food and restaurant/fast food, natural claims have not been important. Similarly, oral care, chewing gum and confection have enjoyed a strong market using artificial aroma chemicals. Similarly, the current recession is acting as a brake on the growth of natural flavors. Despite this, it remains visibly true that, overall, natural aroma chemicals are growing at the expense of synthetic/nature identical aroma chemicals. A natural mystic (or should it be mystique?) is definitely blowing in the air.

Address correspondence David Rowe, Riverside Aromatics Ltd., 16 The Aztec Centre, 34 Nuffield Road, Poole, Dorset, BH17 0RT, United Kingdom; david.rowe@riversidearomatics.com

#### References

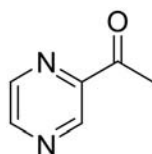
1. D Seebach, MA Sutter, RH Weber and MF Züger, Yeast Reduction of Ethyl Acetoacetate: (S)-(+)-Ethyl 3-Hydroxybutanoate. *Organic Syntheses* 1, **63** (1985); *Collected Volume VII*, 215–220 (1990)
2. P Werkhoff, W Bretschneider, M Güntert, R Hopp and H Surburg, Chiroscopic analysis in flavor and essential oil chemistry Part B. Direct enantiomer resolution of *trans*- $\alpha$ -ionone and *trans*- $\alpha$ -damascone by inclusion gas chromatography. *Zeitschrift für Lebensmitteluntersuchung und -Forschung A*, 1431–4630, 192 (1991)

3. WA König, P Evers, R Krebber, S Schulz, C Fehr and G Ohloff, Determination of the absolute configuration of  $\alpha$ -damascone and  $\alpha$ -ionone from black tea by enantioselective capillary gas chromatography. *Tetrahedron*, 7003–7006, 45 (1989)
4. A Bernreuther, N Christoph, and P Schreier, Determination of the enantiomeric composition of  $\gamma$ -lactones in complex natural matrices using multidimensional capillary gas chromatography. *Journal of Chromatography A*, 363–367, 481 (1989)
5. V Greger and P Schieberle, Characterization of the key aroma compounds in apricots (*Prunus armeniaca*) by application of the molecular sensory science concept. *Journal of Agricultural and Food Chemistry*, 5221–5228, **55** (2007)
6. S Nitz, H Kollmannsberger, B Weinreich and FJ Drawert, Enantiomeric distribution and  $^{13}\text{C}/^{12}\text{C}$  isotope ratio determination of  $\gamma$ -lactones—appropriate methods for the differentiation between natural and non-natural flavours? *Journal of Chromatography*, 187–197, 557 (1991)
7. AL Morales, C Duque and EJ Bautista, Identification of Free and Glycosidically Bound Volatiles and Glycosides by Capillary GC and Capillary GC-MS in Lulo del Chocó (*Solanum topiro*). *Journal of High Resolution Chromatography*, 23, 379–385 (2000)
8. DJ Rowe, More Fizz for Your Buck: High-impact Aroma Chemicals. *Perfum Flavor*, 25(5), 1–8 (2000)
9. DJ Rowe, High Impact Aroma Chemicals Part 2: the Good, the Bad, and the Ugly. *Perfum Flavor*, 27(4), 24–33 (2002); DJ Rowe, High Impact Aroma Chemicals. In: *Advances in Flavours and Fragrances: From the Sensation to the Synthesis*. Edit: KAD Swift, Royal Society of Chemistry, Cambridge, 202 (2002)

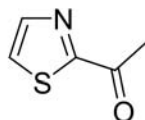
To purchase a copy of this article or others, visit [www.PerfumerFlavorist.com/magazine](http://www.PerfumerFlavorist.com/magazine). 

### A wish list for natural aroma chemicals

## F-29



(70)



(71)