Savor the Savory: Sulfur Aroma Chemicals

A chemist's view of savory flavor materials, both artificial and natural

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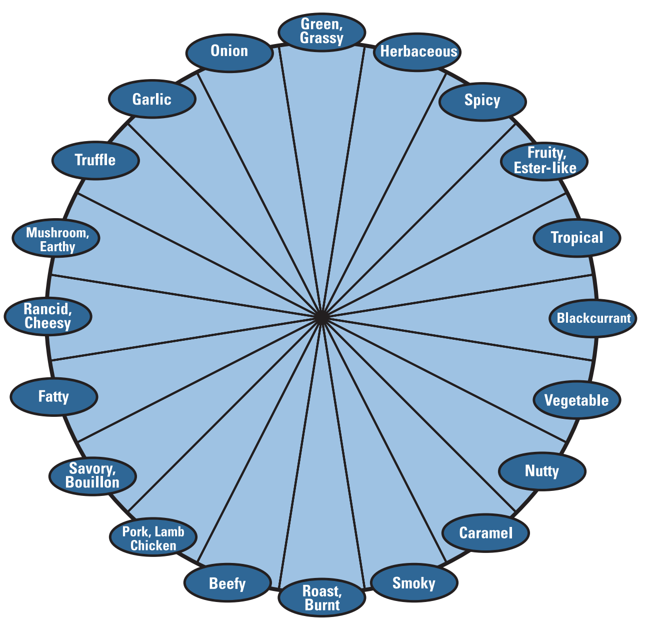
Flavorists are notoriously reluctant to describe the flavor creation process in any real detail, and companies are even more reluctant to tell mere mortals such as the author where an ingredient is used in consumer products. Being a simple chemist I've always believed that science would prevail, shining a bright light with the application of a little logic. "Fool," I hear all you flavorists cry, and you're all correct. However science does help us non-flavorists a little. The flavor wheel developed by Oxford Chemicals (now Frutarom, UK) and shown in **F-1** provides a correlation between chemical structure and odor profile, even if it doesn't describe where a specific aroma chemical can be used, and at what level in a formulation—for that we have to rely on black magic, and flavorists.

Focusing on high impact aroma chemicals (HIACs) should lead the flavorist to either a very interesting molecule for a top note or something that, when used at lower levels, could provide a particular nuance, turning the average into the extraordinary. So, where to begin? Clearly everything from "vegetable round" to "spicy" effects could be used in a savory flavor; however, this article will focus on sulfur molecules.

Sulfur Aroma Chemicals: Meat, Vegetable and Nontraditional Applications

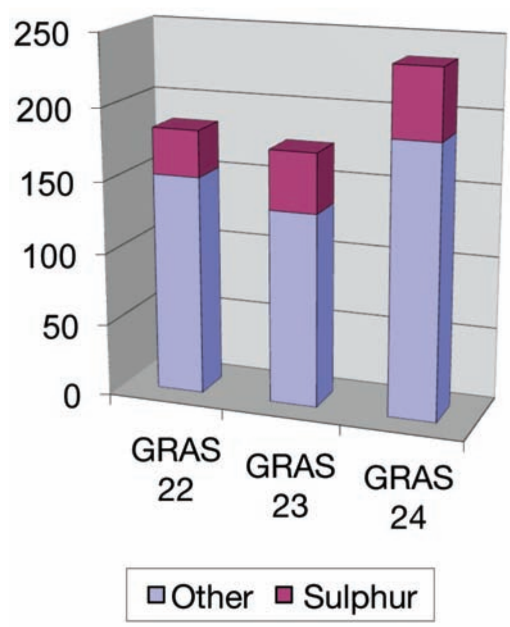
Some interesting analysis has been published on the rise of sulfur molecules obtaining FEMA GRAS status.[1] It appears that the use of sulfur molecules is becoming more prevalent—as evidenced by GRAS 22–24 (**F-2**)—and that flavorists themselves are becoming more familiar with these molecules. This is an achievement in itself, as HIACs are particularly difficult materials to formulate with, their powerful nature being both their big strength and weakness. Too much of an HIAC in a formulation and the note can either overpower the flavor or become altered. For example, methyl phenyl disulfide at the right levels imparts a nice roasted meat aroma; at too high a concentration,

Flavor wheel[a] **F-1**

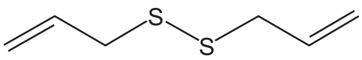


[a]Developed by Oxford, now Frutarom UK

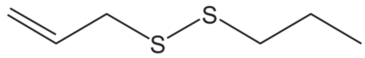
Sulfur molecules included in GRAS 22–24 **F-2**



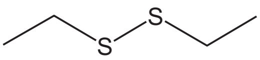
Typical sulfur compounds found in garlic **F-3**



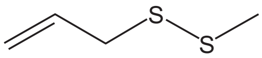
Allyl Disulfide; FEMA# 2028



Allyl Propyl Disulfide; FEMA# 4073

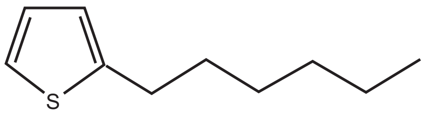


Diethyl Disulfide; FEMA# 4093

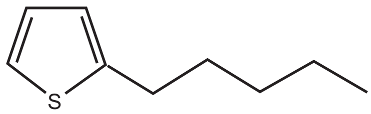


Allyl Methyl Disulfide; FEMA# 3127

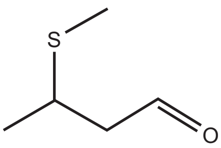
Sulfur molecules for use in vegetable applications **F-4**



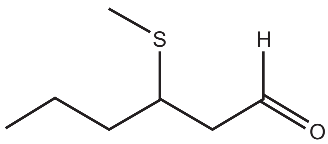
2-Hexyl Thiophene; FEMA# 4137



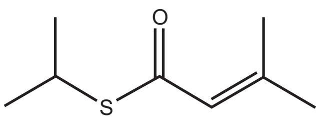
2-Pentyl Thiophene; FEMA# 4387



3-(Methylthio)butanal; FEMA# 3374



3-(Methylthio)hexanal; FEMA# 3877



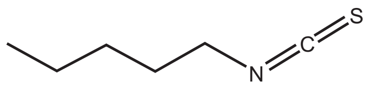
Isopropyl 3-Methylbutyl-2-enethioate; FEMA# 4260

it smells of burnt rubber. Meanwhile, formulate with too low of a dose and the effect is lost entirely.

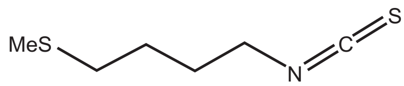
From an organoleptic and application point of view, it is interesting to return to the flavor wheel in **F-1** and look at some of the segments within that wheel. Garlic is rich in sulfur compounds (**F-3**). The major component of garlic oil is allyl disulfide (FEMA# 2028), which has typical alliaceous notes, whereas ally methyl disulfide (FEMA# 3127) has been observed on the breath of garlic eaters. Allyl propyl disulfide (FEMA# 4073), while still displaying a strong alliaceous odor, is a little greener and creamier than other disulfides. The material has use both in savory applications and, potentially, in tropical fruit flavors. Diethyl disulfide (FEMA# 4093), meanwhile, is a typically alliaceous sulfide, useful for garlic, onion, and, at low levels, in meat flavors.

Some of these materials find a range of applications in vegetable notes. (**See F-4**.) Despite that 2-hexylthiophene (FEMA# 4137) occurs naturally in turkey, mushroom and beef, the material has a green and slightly floral note that finds uses in summery green notes such as cucumber and celery applications. The homologue 2-pentylthiophene (FEMA# 4387) differs in that its odor profile is slightly meatier, while retaining an overall fresh, green and vegetable note. Other molecules in the vegetable area, including 3-(methylthio)butanal (FEMA# 3374), have an instantly recognizable note that is useful in mashed potato and other vegetable applications. 3-(Methylthio)hexanal (FEMA# 3877) has a greener note to it, retaining a strong winter vegetable character. At the other end of the spectrum, there are molecules such as isopropyl 3-methylbut-2-enethioate (FEMA# 4260),

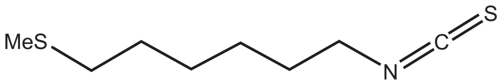
Isothiocyanate molecules from GRAS 23 — F-5



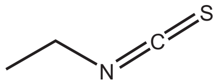
Pentyl Isothiocyanate; FEMA# 4417



4-(Methylthio)butyl Isothiocyanate; FEMA# 4414

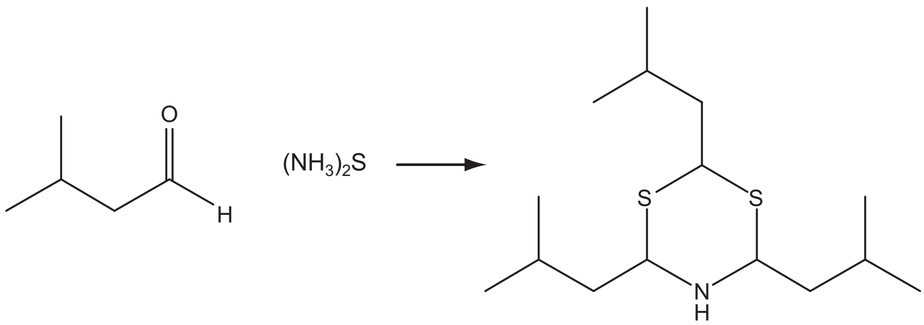


6-(Methylthio)hexy Isothiocyanate; FEMA# 4415

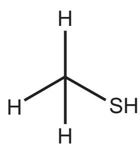


Ethyl Isothiocyanate, FEMA# 4417

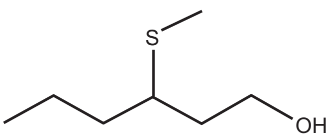
Synthesis of 2,4,6-triisobutyl-5,6-dihydro-1,3,5-dithiazine — F-6



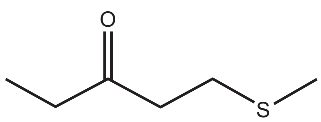
EU natural sulfur molecules — F-7



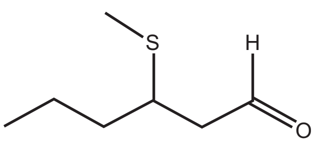
Methyl Mercaptan



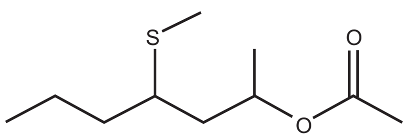
3-(Methylthio)hexanol



(1-Methylthio)-3-pentanone



3-(Methylthio)hexanal



3-(Methylthio)hexyl acetate

which have a green and galbanum note and can be useful in wide ranging applications such as jalapeno peppers and seafood.

For cheese and other dairy applications, versatile molecules such as isobutyl 3-methylthiobutyrate (FEMA# 4150) are prized for their cheesy and slightly fruity notes. Methyl thiopropionate (FEMA# 4172) has strong cheesy notes, but also hints of tomato and some seafood notes, and is quite different from its chemically similar "older brother," methyl thiobutyrate (FEMA# 3310). Sulfur molecules are also finding their way into areas where one previously wouldn't expect to see them. Molecules such as 3-mercapto-3-methyl-1-butyl acetate (FEMA# 4324) have powerful fruity and sweet notes, while methyl furfurylmercaptopropionate (FEMA# 4538) has earthy and fruity notes, and is excellent in mushroom, meat and coffee flavors.

It is interesting to see how flavorists use HIACs to create flavors to meet the changing and diversifying global flavor palate. This is clearly illustrated in GRAS 23, in which 14 molecules from the isothiocyanate family were added (**F-5**). These molecules track the trend and popularity, especially in the Far East, for flavors that exhibit mustard and radish notes. 6-(Methylthio)hexyl isothiocyanate (FEMA# 4415), for instance, exhibits a particularly nice note for use in horseradish and wasabi flavors.

A large portion of the flavor wheel is taken up by meat and meat-related materials, and this is where a large number of sulfur-containing molecules can be used to their best effect. Analysis of cooked beef reveals the complex nature of the flavor, with hundreds of aroma chemicals identified as occurring normally in beef, chicken and other meats. Regional variations in the consumer palate need to be taken into consideration, of course. In Europe there is a preference for roasted beef, which contains high amounts of roasted and nutty compounds such as pyrazines. Grilled beef is preferred in the United States, along with fried beef, which requires more fatty notes associated with unsaturated aldehydes. In Southeast Asia, a note more associated with boiled beef is preferred.

Looking more closely at the components of beef flavor (**T-1**), many meaty and sulfurous compounds have been identified, including materials such as 2-methyl-3-tetrahydrofuranthiol (FEMA# 3787), 3-methyl-2-butanethiol (FEMA# 3304) and methyl 2-methyl-3-furyldisulfide (FEMA# 3573).[2]

The components of beef flavor **T-1**

Area	Profile	Material
Buttery	Buttery	Diacetyl
	Buttery	Acetyl methyl carbinol
Burnt	Burnt	Pyridine
	Rubbery	Thiophenol
Candy	Candy, strawberry	Furaneol
	Candy	Maltol
	Candy	4-Acetoxy-2,5-dimethyl-3(2H)furanone
Cheesy	Cheesy	Butyric acid
	Cheesy, goaty	Hexanoic acid
	Goaty	Octanoic acid
	Soapy	Decanoic acid
Cooked	Caramel	5-Methyl furfural
	Caramel	Furfural
	Caramel	2-Acetyl furan
	Boiled	2-Methyl-3-furan thiol
	Bread	2-Methyl tetrahydrofuran-3-one
	Fenugreek	5-Ethyl-3-hydroxy-4-methyl 2(5H)-furanone
	Boiled	2-Methyltetrahydro furanthiol
	Boiled	2,5-Dimethylfuran-3-thiol
Creamy	Hay	γ-Hexalactone
	Hay, coconut	γ-Octalactone
	Creamy	γ-Decalactone
	Coconut	γ-Octalactone
	Creamy	γ-Dodecalactone
	Creamy	γ-Tetradecalactone
Fried	Fatty	*trans*-2-Nonenal
	Fried	*trans*-2, *trans*-4-Decadienal
Perfumed	Hair	4-Methyloctanoic acid
Roasted	Roasted	2,3,5-Trimethyl pyrazine
	Peanut	2,3-Diemethyl pyrazine
	Peanut	2,5-Dimethyl pyrazine
	Roasted, popcorn, peanut	2-Acetyl thiazole
Sulfurous	Potato	3-Methylmercaptopropional
	Eggy, meaty	5,6-Dihydro-2,3,6-trimethyl-1,3,5-dithiazine
Meaty	Meaty	2-Methyl butan-1-thiol
	Meaty	1,6-Hexanedithiol
	Meaty	2-Methyl-3-tetrahydroduranthiol
	Meaty, roasted	Methyl phenyl disulfide
	Meaty	Trithioacetone
	Coffee	Methyl-2-methyl-3-furyl disulfide
	Coffee	2-Furanmethane thiol

Natural Sulfur: The Holy Grail

Driven by consumer preference for health and wellness positioning, there continues to be a move away from artificial and towards natural. Rather than open the Pandora's box of naturals legislation, especially in view of the forthcoming changes to EU legislation, it would be fair to say that achieving EU natural sulfur molecules has always been something of a holy grail for suppliers of HIACs. The difference between EU and US legislation means that molecules such as 2,4,6-triisobutyl-5,6-dihydro-1,3,5-dithiazine (**F-6**), the synthesis of which has been previously reported, may meet the US designation, but not that of the EU.[3] A number of EU-designated natural sulfur molecules appear in **F-7**.

Due to this dichotomy, manufacturers of sulfur aroma chemicals have had to look to alternative sources to satisfy the need for natural sulfur. Such an endeavor requires the establishment of new industrial bioprocessing facilities applying novel biocatalytic routes to the production of validated natural flavor and fragrance HIACs from renewable and readily available resources. Some success has been achieved in this area at Frutarom's Hartlepool, United Kingdom site, where an industrial bioprocessing facility has been established. This facility will provide a platform to develop other chemistries and biocatalytic techniques which will be applicable to flavor and fragrance and other fine chemical applications.

Conclusion

It is clear that, as tastes diversify and choice increases, HIACs and particularly sulfur molecules will play an important role in the creation of savory flavors. In addition, with the continued move to natural flavors, the development of natural HIACs to meet both EU and US legislation is key to the growth of the industry.

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References

1. D Rowe, More Fizz for Your Buck: High-impact Aroma Chemicals. *Perfum Flav*, 25(5) 1–19 (2000)
2. J Wright, *Flavor Creation*. Allured Publishing, Carol Stream, IL (2004) 147-148
3. B Byrne, Reaction Flavors: The Next Generation. *Perfum Flav*, 30(5) 58–60 (2005)