

Aroma Chemicals for Savory Flavors

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The term "savory" is one that is readily understood, but difficult to define. It incorporates both positive and negative features; *Chambers Concise 20th Century Dictionary* defines it as "of good savour or relish; appetizing, salty, piquant or spiced (opp. to sweet)". This introduces some key aspects, especially the implication of a strong, pleasant aroma, and the idea of being opposite to sweet, but this still does not tell the full story.

In an attempt to discover more about people's perceptions of "savory," a number of people at or associated with Oxford Chemicals were asked to complete a simple questionnaire assessing the suitability of 146 odor descriptors against the term "savory". According to the questionnaire, the ten most appropriate descriptors, in descending order, were the following:

- Fried chicken
- Meaty (cooked)
- Seasoning
- Garlic, onion
- Spicy
- Warm
- Black pepper
- Smoky
- Cheesy
- Kippery (smoked fish)

From this it can be gleaned that the key notes are:

- Fried, fatty and roasted notes
- Meaty aromas
- "Allium" odors - onion and garlic
- Spicy / smoky / cheesy notes

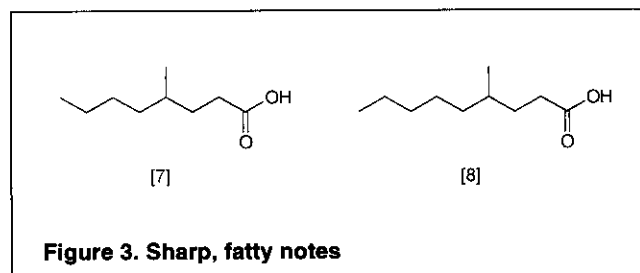
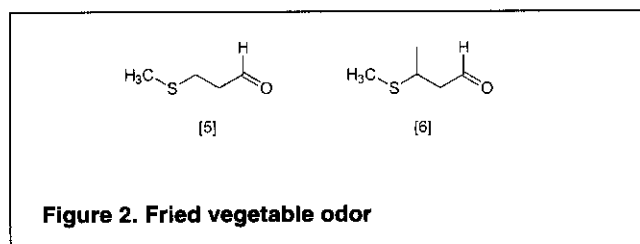
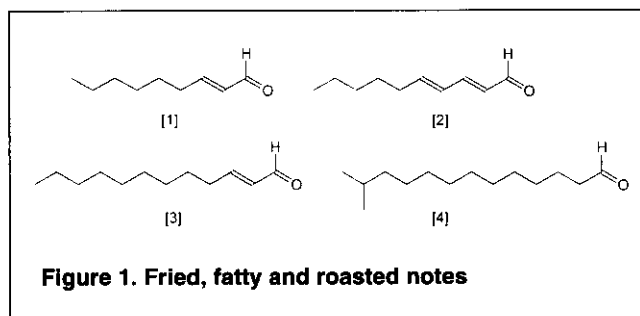
Fried, Fatty and Roasted Notes

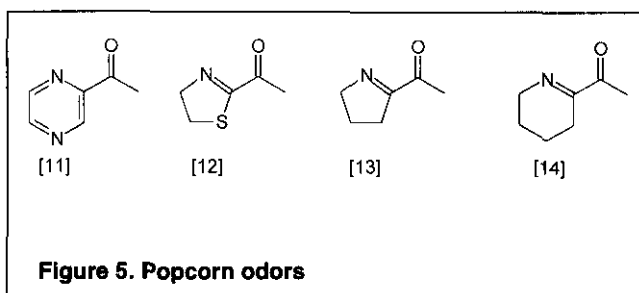
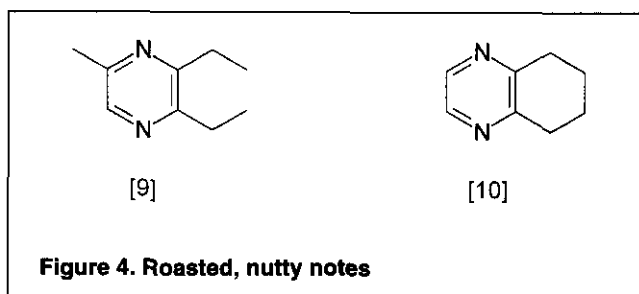
Here, the important aroma chemicals derive from the thermalolysis of fats, carbohydrates and amino acids. Long-chain unsaturated aldehydes such as trans-2-nonenal [1] and trans-2-trans-4-decadienal [2] have characteristic fatty odors and low odor thresholds of 0.08 and 0.07 ppb, respectively.¹ From C₆ to C₁₂ the odor of alkenals becomes less citrus and more fat-like, and the odor threshold falls; [2] is characteristic of chicken fat and fried chicken; and trans-2-dodecenal [3] has an intense fatty, herbaceous odor characteristic of coriander.² The saturated aldehyde 12-methyltridecanal [4] is found in beef where it contributes a meaty, tallow odor.³

The sulfur-containing aldehydes 3-methylthiopropenal (methional) [5] and 3-methylthiobutanal [6] have a more pronounced fried vegetable odor,⁴ especially fried potatoes/french fries.

The fat from meat often has a sharper aroma associated with carboxylic acids. 4-Methyloctanoic acid [7] and its homologue [8] are found in lamb fat and impart some of that sharpness; they also have an inherently fatty odor. These can be used with high levels of acetic and lactic acids, thereby creating a "juicy" and "rounded" flavor.

Pyrolysis of amino acids, especially in the presence of carbohydrates, gives rise to pyrazines that contribute to the "roasted" aromas of meats and vegetables. The formation of pyrazines in the Maillard reaction⁵ has been extensively studied and the impact of pyrazines on the savory nature of





hydrolyzed vegetable proteins (HVP) has been examined.⁶ The more highly substituted pyrazines such as 5-methyl-2,3-diethylpyrazine [9] and 5,6,7,8-tetrahydroquinoxaline [10] have "nutty" odors that associate well with furfural and its derivatives to give roasted aromas.

A number of acetyl compounds have roasted popcorn odors and low odor thresholds.⁷ These include 2-acetylpyrazine (0.4 ng/l) [11], 2-acetyl-2-thiazoline [12] (0.05 ng/l), 2-acetyl-2-pyrroline [13] (0.02 ng/l) and 6-acetyltetrahydropyridine [14] (0.02 ng/l).

Structure-odor relationships in pyrazines and other nitrogen heterocyclics have been studied.⁸

Thermolysis and Maillard-type reactions also generate furans. 4-Hydroxy-2,5-dimethyl-3[H]-furanone (furanol) [15] is well-known for its sweet, cotton-candy aroma, but it also enhances the savory flavor of the pyrazines described above. Furfuryl mercaptan [16] has a pronounced roasted, almost burnt aroma, as do its disulfide derivatives [17] and [18]. First isolated from roasted coffee beans (it is not believed to be present in the unroasted bean), it has a low odor threshold of 5×10^{-3} ppb.

Meaty Aromas

Meaty aromas are frequently associated with sulfur compounds, many of which are present only in trace quantities but have very low odor thresholds and hence are of vital importance to the meat aroma.

The use of aroma extract dilution analysis and gas chromatography-olfactometry of headspace samples has led to the identification of key odorants at very low concentrations but with high odor activity values due to their extremely low odor thresholds. 2-Methyl-3-furanthiol (MFT) [19] has been found to be a key odorant in a number of meats, especially pork and beef, and in Maillard reaction mixes.⁹ It is intensely odorous, as is its disulfide [20], which

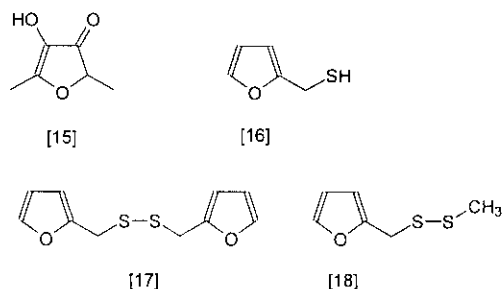


Figure 6. Furans for sweet and roasted notes

is reported to have an extremely low odor threshold in water of 2×10^{-6} ppb. This oxidation-reduction system will profoundly affect the organoleptic properties of formulations. MFT also forms disulfides with other thiols and with sulphhydryl-containing foods.^{10,11} At high dilutions MFT has a beef aroma, especially when enhanced with 4-hydroxy-2,5-dimethyl-3[H]-furanone [15]. Its acetate [21], methyl ether [22], methyl disulfide [23] and tetrahydroderivative [24] all exhibit variations on the theme of meaty, savory aromas.

The series of α -mercaptoketones [25], [26] and [27] all have meat-like odors. Mercaptopropanone [25] (which exists as a solid dimer) has a pork or chicken broth aroma, with the butanone [26] having a "beefier" odor and the pentanone [27] a more raw-meat "bloody" note.

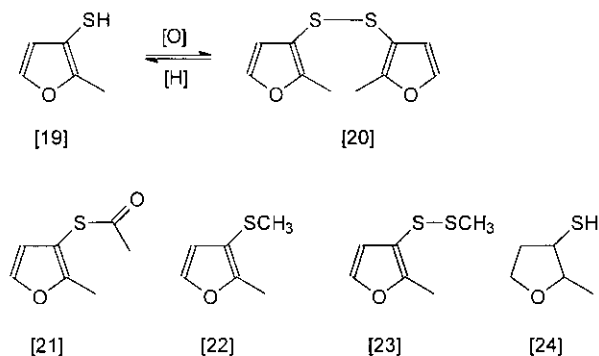


Figure 7. Meaty notes

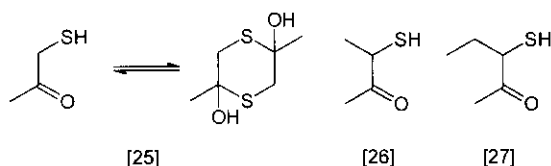


Figure 8. Raw meat, bloody notes

Simple mercaptans are more associated with unpleasant, "burnt rubber" aromas, but at high dilution a number of these have a savory character, especially methyl mercaptan [28], which has been identified as a key odorant in several meats, 2-methyl-3-butanethiol [29] and "fattier" compounds such as 1,9-nonanedithiol [30].

The heterocyclic thiols 2-pyridinemethanethiol [31] and pyrazineethanethiol [32] have odors characteristic of lamb and pork, respectively.

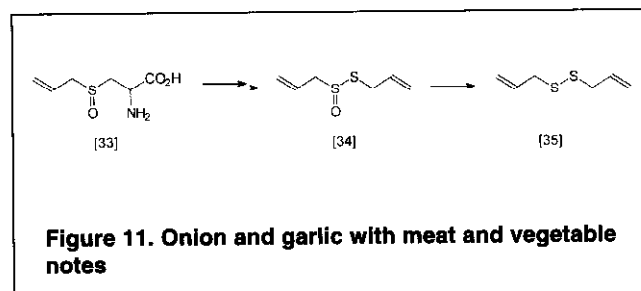
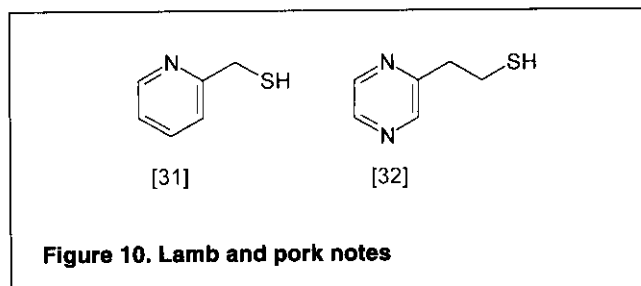
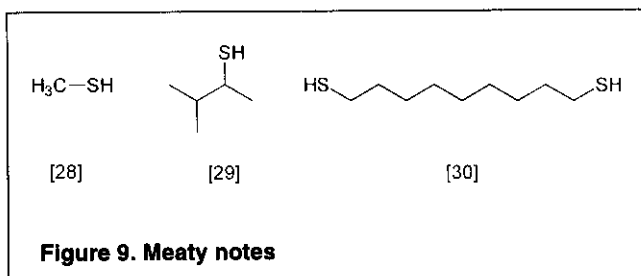
Garlic and Onion

"For this is every cook's opinion, no savoury dish without an onion."

Jonathon Swift (1667-1745)

The powerful aroma of onion and garlic, often fried or heated together with meat and other vegetables, is perhaps the most familiar savory odor. It is recognized as such in cultures across the globe. The origins of these aromas are sulfur compounds such as allyl disulfide [35], which constitutes 90% of garlic oil and derives from the amino acid derivative allin [33] via the sulfoxide allicin [34].¹²

The *Allium* species contain many hundreds of sulfur compounds and only a brief summary can be given here. In general it may be said that the allyl sulfides are intensely garlic-like in odor, with the propyl compounds being sweeter



and more associated with onions and leeks, as illustrated in Table 1. A sweet, roasted character can be obtained by formulating these compounds with 3-hydroxy-2,5-dimethyl-4[H]-furanone.

Table 1. Sweet propyl compounds associated with onions and leeks

Family	Garlic character	Onion/Sweet character
Mercaptans	allyl	
Sulfides	diallyl	dipropyl
	allyl methyl	methyl propyl
	allyl propyl	
Disulfides	diallyl	dipropyl
	allyl methyl	methyl propyl
	allyl propyl	1-propenyl (cis- and trans-)
Trisulfides	diallyl	dipropyl
	allyl methyl	methyl propyl
	allyl propyl	
	dimethyl	

An increase in sulfur content also seems to increase the savory notes in the methyl sulfide series, as shown in Table 2.

Di- and higher sulfides are themselves reactive species, and react with nucleophilic species, especially thiols, lead-

Table 2. An increase in sulfur increases the savory notes in the methyl sulfide series

Methyl sulfide	Savory note
H_3CSCH_3	vegetable/sweetcorn
$H_3CS.SCH_3$	vegetable/cabbage
$H_3CS.S.S.CH_3$	garlic/onion
$H_3C.S.S.S.SCH_3$	meaty/onion

ing to disproportionation and rearrangement (Figure 12). Hence, new disulfides can be formed in a foodstuff or formulation by reaction of mercaptans with disulfides, a factor that must be born in mind by the flavorist. This may be the origin of allyl methyl disulfide [36] found in the breath of garlic eaters!¹³

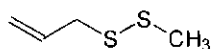
Trisulfides can undergo disproportionation with the formation of di- and tetrasulfides. For example, at high pH allyl trisulfide [37] disproportionates readily to a statistical mixture of di-, tri- and tetrasulfides.¹⁴ This may lead to unexpected problems in formulations.

Smoky/Spicy/Cheesy Notes

Our questionnaire results showed that compared to meaty, onion and garlic descriptors, the smoky, spicy and cheesy descriptors were less frequently associated with

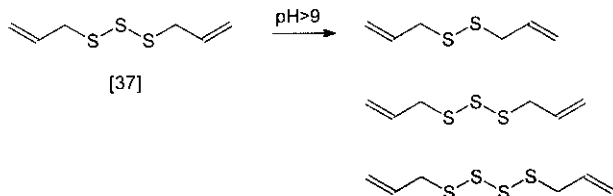


Figure 12. Disproportionation and rearrangement of disulfides



[36]

Figure 13. Allyl methyl disulfide (garlic breath)



[37]

Figure 14. Disproportionation of trisulfides

perceptions of “savory,” and might be called optional rather than essential.

Smoke flavors derive from phenols, which in turn derive from pyrolysis of lignins. The particular wood used to generate the smoke will influence the odor, hence the existence of “oak-smoked,” “hickory-smoked” and so on. The most important aroma chemicals are guaiacol [38] derivatives such as creosol (4-methylguaiacol) [39] and 4-ethylguaiacol [40]. The vinyl compound [41] also has a spicy odor reminiscent of cloves.

The term “spice” covers so many ingredients, and the components of spices are so varied, that a detailed description cannot be entered into here. However, mention may be made of zingerone [42] (the key component of ginger) and 3-hydroxy-4,5-dimethyl-2[5H]-furanone [43] (sotolone) with its spicy, curry, fenugreek aroma. When speaking of spices, one should also mention capsaicin [44], the “hot principle” of chili peppers.

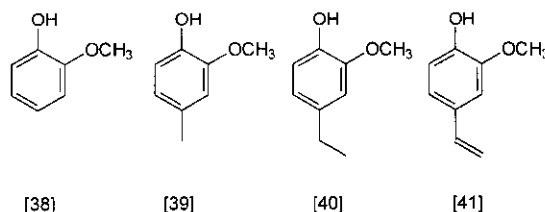


Figure 15. Smoky notes

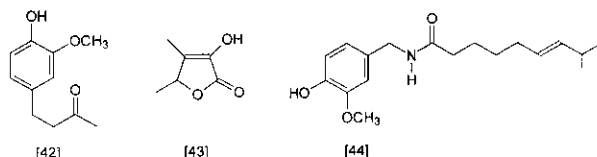


Figure 16. Spicy notes

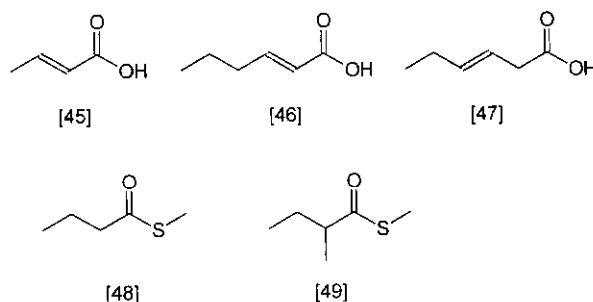


Figure 17. Cheesy notes

Like "spice," the word "cheese" is a broad term that covers a variety of flavors. Mid-length carboxylic acids, especially unsaturated acids such as [45], [46] and [47], confer an intense, slightly acrid note, and the thioesters [48] and [49] have the ripeness, bordering on rancidness, of strong, mature cheeses.

Conclusions

The market in savory flavors for foodstuffs is wide and varied — from snacks to ethnic foods. This will no doubt continue to expand as microwave cooking increases in popularity. The temperatures generated are close to 100°C, as opposed to approximately 230°C in traditional roasting, and this slows the Maillard reaction,¹⁶ and hence lowers the "savor" of the food.

New molecules of savory character are still being identified, and with the wide range of aroma chemicals already available, the creation of savory flavors will challenge the chemist's science and the flavorist's art for many years to come.

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