Naturally Does It

The flavorist's job has been complicated by legislative discrepancies between the United States and the European Union—what are the solutions and opportunities?

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When I was growing up my grandfather used to tell me a particularly bad joke: "When is a door not a door? When it's ajar." I used to think this joke was pretty funny as I imagined our front door becoming a large jar, usually full of jelly, rather than contemplating the play on words the joke actually represented. Today, when I talk to friends about the F&F industry, I use a similar line: "When is a strawberry not a strawberry? When it's a strawberry flavor." After some simple explanation on how flavors are created, their normal reply to this is: "What? Even when it's a natural flavor?" And here the can of worms opens. Just what *is* natural? How does legislation affect the flavorist and what he or she is trying to achieve? How can material suppliers help—or in fact hinder—this process?

Let's start things off simply, with a nice, easy definition of natural. From the *Oxford English Dictionary*:

In accordance with nature; Relating to, or concerning nature. Existing in or produced by nature. Not artificial or imitation.

I particularly like the last two sentences, especially when applied to the F&F industry. If we take the first half of "Existing in or produced by nature" on its own, then the problem is solved. If we can identify a material in nature and then somehow produce it, then surely it's natural. Not quite, for if we take the last part of this sentence, unless nature has produced a material, surely it is artificial. If only the world was as black and white as this.

In the consumer's mind, natural products have a positive image and are healthy and safe when compared to those nasty artificial products. This is despite the fact that, from the view of the simple chemist, a molecule is a molecule, with a distinct structure and, in some cases, specific stereochemical properties—what does it matter who, what or how it was produced? The consumer, however, often thinks that natural fruit flavors, for example, are derived solely from the named fruit, and that the ingredients, being natural, are strictly controlled. What the consumer doesn't know is that natural materials derived from a cultivated (i.e., it has been grown rather than synthesized) source can be poorly specified in terms of chemical constituents, have sometimes not been assessed for safety, and often contain substances that, when added as individual chemical components, can be classed as toxins or carcinogens.

Legislation

Legislation tries to help in this area. However, in most cases it simply confuses those of us who aren't lawyers or politicians. Take the US Flavor Definitions, for example (21 CFR. Chapter 1. Parts 101.22(a).1 and 3), or the EEC Council Directive on flavorings and source materials for their production (88/388/EEC).* While these definitions are meant to clarify the natural situation, differences in their wording mean that different materials can be classified as natural depending on where their final use is, geographically.

For example, taking the US definitions first:

(21.CFR. Chapter 1. Part 101.22(a).3)
The term natural flavor or natural flavoring means the essential oil, oleoresin, essence or extractive, protein hydrolysate, distillate, or any product of roasting, heating or enzymolysis, which contains the flavoring constituents derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or similar plant material, meat, seafood, poultry, eggs, dairy products, or fermentation products thereof, whose significant function in food is flavoring rather than nutritional. Natural flavors include the natural essence or extractives obtained from plants listed in Secs. 182.10, 182.20, 182.40, 182.50 and part 184 of this chapter and the substances listed in Sec. 172.510 of this chapter.

(21.CFR. Chapter 1. Part 101.22(a).1)
The term artificial flavor or artificial flavoring means any substance, the function of which is to impart flavor, which is not derived from a spice, fruit or fruit juice, vegetable or vegetable juice, edible yeast, herb, bark, bud, root, leaf or similar plant material, meat, seafood, poultry, eggs, dairy products, or fermentation products thereof. Artificial flavor includes the substances listed in Secs. 172.515(b) and 182.60 of this chapter except where these are derived from natural sources.

This definition means that process and smoke flavors can be deemed natural, providing their source materials are natural. It also means that, from an aroma chemical manufacturer's point of view, as long as the starting

*www.accessdata.fda.gov/SCRIPTs/cdrh/cfdocs/cfcfr/CFRSearch.cfm
http://ec.europa.eu/food/fs/sfp/flav_index_en.html

materials are natural, the same chemical reaction and conditions can be applied as would be used to manufacture the artificial equivalent, i.e. catalyst, elevated temperatures over a prolonged period, high pressures, etc.

The European definition provides us with a little more "guidance":

Natural flavouring substance (Article 1.2(b)(i)):
Means a defined chemical substance with flavouring properties which is obtained by appropriate physical processes (including distillation and solvent extraction) or enzymatic or microbiological processes from material of vegetable or animal origin either in the raw state or after processing for human consumption by traditional food preparation processes (including drying, torrefaction and fermentation).

Flavouring preparation (Article 1.2(c)):
Means a product, other than a defined chemical substance, whether concentrated or not, with flavouring properties, which is obtained by appropriate physical processes (including distillation and solvent extraction) or enzymatic or microbiological processes from material of vegetable or animal origin either in the raw state or after processing for human consumption by traditional food preparation processes (including drying, torrefaction and fermentation).

Natural flavourings labelling (Article 9.2):
The word 'natural' or any other word having substantially the same meaning may be used only for flavourings in which the flavouring component contains exclusively flavouring preparations and/or natural flavouring substances. If the sales description of the flavouring contains a reference to a foodstuff or flavouring source, the word 'natural' or any other word having substantially the same meaning, may not be used unless the flavouring component has been isolated by appropriate physical, enzymatic or microbiological processes or traditional food preparation processes solely or almost solely from the foodstuff or flavouring source concerned.

So, this definition effectively includes essential oils, oleoresins, extracts, absolutes and juices used for their flavoring properties, but there is no definition of appropriate physical processes. This means that smoke flavorings and process flavors cannot be classed as natural. For chemical manufacturers it means that inorganic catalysts can't be used, elevated temperatures for extended periods are out, and high pressures are a no-go area.

The European waters, however, get muddied further with the proposed EU legislation on natural:[**]

Natural flavouring substance (Chapter I Article 3.2 (c))
shall mean a flavouring substance obtained by appropriate physical, enzymatic or microbiological processes from material of vegetable, animal or microbiological origin either in the raw state or after processing for human consumption by one or more of the traditional food preparation processes listed in Annex II. Natural flavouring substances correspond to substances that are naturally present and have been identified in nature.

Flavouring preparation (Chapter I Article 3.2 (d))
shall mean a product other than a flavouring substance obtained from: food, by appropriate physical, enzymatic or microbiological processes, either in the raw state of the material or after processing for human consumption by one or more of the traditional food preparation processes listed in Annex II.

and/or

(ii) Material of vegetable, animal or microbiological origin, other than food, by appropriate physical, enzymatic or microbiological processes, the material being taken as such or prepared by one or more of the traditional food preparation processes listed in Annex II.

When is a strawberry not a strawberry? When it's a strawberry flavor.

Specific requirements for the use of the term "natural" (Chapter IV Labelling Article 16)
The term "natural" for the description of a flavoring may only be used if the flavoring component comprises only flavoring preparations and/or natural flavoring substances.

The term "natural" may only be used in combination with a reference to a food, food category or a vegetable or animal flavoring source if the flavoring component has been obtained exclusively or by at least 95% by w/w from the source material referred to. The maximum of 5% (w/w) of the flavoring component derived from other source materials shall not reproduce the flavor of the source material referred to.

This last part refers to the 95/5 rule, which has been talked about in hushed circles—and, depending on your point of view, praised or derided—for some time. In all probability, the only thing this is likely to achieve is the use of more vague descriptions on products and a more confused consumer.

Having waded through all this legalese, one may now choose to take an aspirin. Now, take a moment to consider the plight of the poor ingredients supplier, who not only has to figure out whether it is manufacturing its ingredients in a manner which meets this legislation, but also has to figure out if it can be used by the flavor manufacturer in a way that also conforms to "natural" standards. From there, the supplier has to choose which legislative outline (or both) it intends to comply with. If the supplier chooses both, it must ensure that it has separate processes, leading to separate products, and the internal procedures to make sure the two don't cross over.

Most ingredient manufacturers will stick to one set of legislation or the other, based on history and geography.

[**]The European Flavour & Fragrance Association has issued a guidance document on the subject here: *www.effa.be/guidance/EFFA%20Guidance%20Document%20on%20the%20new%20EC%20Flavouring%20Regulation.pdf*

Some will derive manufacturing methods that meet the demands of both legislations, in order to keep things simple, but in the main, most European manufacturers will stick to the EU legislation (which also complies with the US guidelines), and US manufacturers will comply with the US legislation (which doesn't always comply with the EU guidelines).

Flavorists will also continue to solve this riddle in their own way, and there exist some geographical generalizations. There is a tendency for those based in the United States, for example, to use natural extracts and distillates to assist with creation, and to limit the involvement of a natural aroma chemical. Flavorists in Europe, however, tend to prefer creating a top note using chemicals, which can in some cases add limitations to the scope of their formulations.

Natural Essential Oils, Oleoresins and Extracts

The easiest sources available to the flavorist for natural building blocks are natural essential oils, extracts and oleoresins. There exist a huge variety of sources of extracts and essential oils; for natural extracts, theoretically anything that is from a crop can become a good source of material from which to make a natural extract. Obviously, there are commercial constraints to consider, but these usually are traded off against market trends and potential.

Using natural extracts, oleoresins and essential oils does circumvent some of the issues faced by aroma chemical manufacturers; however, it still presents other challenges. The isolation of these materials can often satisfy the legislative requirements that the flavorist needs to meet. The challenge comes in other areas. By their very nature, extracts and essential oils are a complex mixture of a multitude of different components. This can cause problems with consistency of products, which can itself lead to differing organoleptic properties. Additionally, crop variation and seasonality can create organoleptic and extractive problems. However, by understanding fully the extraction process and controlling the incoming crude materials, these properties can be controlled and standardized from company to company. The flip side to using mixtures like extracts and essential oils is that, by their very nature, the mixture is multifaceted and can benefit the flavorist greatly.

Extracts and essential oils can be used in a flavorist's formulation as the main material to impart flavor, which can be of great benefit as these extracts/oils add a variety of organoleptic nuances to a flavor profile due to the various components contained within. Materials such as fenugreek, for example, with its brown, roasted and caramel notes, can be used in a huge variety of different applications from baked goods to beverages, and from confectionary to wines (aperitifs) and spirits. Other materials such as chamomile are equally as multifunctional. With a sweet, coumarinlike floral odor, the material easily finds use in beverage and confectionary formulations,

Natural and artificial chicken fat flavor (with salt) **F-1**

NAT & ART CHICKEN FAT KEY W.S. FC-07048

INGREDIENTS	FORMULA %
PROPYLENE GLYCOL	84.20%
ETHYL ALCOHOL	12.00%
METHYL MERCAPTAN 1% PG	0.10%
SULFUROL	0.60%
2,4 UNDECADIENAL	0.50%
2,4 DECADIENAL	1.00%
2,4 HEPTADIENAL	0.20%
DIMETHYL SULFIDE	0.10%
2-METHYL TETRAHYDROPHEN 3 ONE	0.20%
T-2 OCTENAL	0.10%
MERCAPTOPROPANONE	0.10%
2-ACETYL PYRIDINE	0.60%
METHYL NONYL KETONE	0.10%
4 METHYL NONANOIC ACID	0.05%
METHIONAL @ 10% PG	0.05%
INDOLE @ 10% PG	0.10%
	100.00%

Procedure:

Dissolve solids in solvent first. Heat gently if necessary. Allow to cool before adding additional ingredients. Filter clear if necessary. Materials are very potent in odor. Work under a ventilated hood if possible. May be easier to work with materials in dilutions.

Natural and artificial chicken fat key (with salt) **F-2**

NAT & ART CHICKEN FAT FLAVOR W.S. FC-07054

INGREDIENTS	CODE#	FORMULA
PROPYLENE GLYCOL		84.00%
ETHYL ALCOHOL		9.00%
N&A CHICKEN FAT KEY FL W.S.	FC-07048	5.00%
SE GENTIAN ROOT FR	27-3-156-0	2.00%
		100.00%

Procedure:

MIX WELL UNTIL UNIFORM. FILTER IF NECESSARY

Low-fat/low-salt chicken broth demo **F-3**

LOW FAT/LOW SALT CHICKEN BROTH DEMO

INGREDIENTS	CODE#	FORMULA %
LOW FAT/LOW SALT CHICKEN BROTH		99.94%
N&A CHICKEN FAT FLAVOR W.S.	FC-07054	0.06%
		100.00%

Chrysanthemum-yerba mate tea **F-4**

INGREDIENTS

SE CHRYSANTHEMUM FR 3327307501.33	0.80 GRAMS
SE YERBA MATE 3337300081.00	0.10 GRAMS
HONEY	4.00 GRAMS
SUGAR	3.00 GRAMS
WATER (HOT)	QS TO 100.00
	100.00 GRAMS

PROCEDURE:

ADD EXTRACTS AND QS WITH HOT WATER TO 100.00 GRAMS.
MIX WELL UNTIL EXTRACTS ARE DISSOLVED.
SERVED HOT OR COLD.

as it does in dairy and savory flavors. To replicate these using aroma chemicals alone could potentially require tens of materials, dosed at different levels, causing extra development work for the flavorist.

Extracts, oleoresins and essential oils add other properties and secondary benefits that cannot be obtained using single-component systems like aroma chemicals. In addition to their use in imparting flavor or aroma, they can bring other benefits such as enhanced mouthfeel, nutritional benefits, health or wellness value, or even fixative action in the flavor system. Some extracts contain properties that increase salivation, which creates flavor potentiation aspects, as in the case of lovage root and gentian root. This is particularly useful when creating formulations for low salt or reduced salt applications. In **F-1** it can be observed that the use of a natural gentian extract imparts not only a multitude of organoleptic properties, but also compliments the low salt effect in the final broth. One can also see that formulation of the key in **F-2** requires a number of aroma chemicals to obtain the required taste and odor properties. However, by adding the natural extract, which itself already contains a complex blend of constituents, the flavorist has produced a more sophisticated creation. A small amount of this added to a low-fat, low-salt chicken broth (**F-3**) therefore has the desired effect of creating something that is not only highly desirable for the palette, but also offers the further benefit of being "low in."

These additional properties can be very desirable, especially with consumers focusing not only on taste, but also seeking to gain a perceived benefit of healthy eating or potential health gains from the food they eat. Materials such as ginseng and guarana are known to increase energy and alertness, but others such as valerian can aid relaxation, while ginger can assist cardiovascular health and boost the immune system. These materials are increasingly important tools to the flavorist, as the consumer perception of all things natural becomes increasingly popular.

It would seem, then, that naturals must be better overall. The flavorist has more flexibility and a stronger comfort zone working with natural materials. But wait—what if that material is not GRAS (generally recognized as safe)? The flavorist will most likely not be comfortable working with a non-GRAS material, or may have been told by his/her company that working with such ingredients is not in line with its policy. This is the case with chrysanthemum extract. The fact that it is not GRAS must certainly mean that it is unsafe—despite that it has been consumed by markedly healthy Far Eastern populations for centuries—doesn't it?

F-4 displays a surprising chrysanthemum application. Combining this material with a yerba mate solid extract, along with honey, sugar and hot water, creates a multilayered, calming tea flavor, without the presence of a tea leaf. This can only be achieved because of the complex nature of natural extracts.

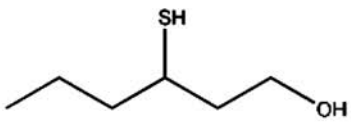
Natural Aroma Chemicals

In an attempt to capitalize on the naturals craze, aroma chemical manufacturers have developed an increasing number of natural aroma chemicals in recent years. Molecules such as ethyl butyrate, ethyl hexanoate, propyl acetate and a whole host of other ester molecules are quite simple to make, with synthetic methods on both sides of the Atlantic easy to derive—all that changes is the cost, as the use of catalysts, and other physical methods give a better yield. Where life becomes more complicated, however, is in the search for those molecules of more significant interest to the flavorist. The rise in demand for natural savory flavors has driven a call for molecules which, in their synthetic form, give the exact organoleptic properties that the flavorist desires. These flavors are generally derived from sulfur and heterocyclic molecules that are more difficult to prepare, and depending on which side of the Atlantic one is on, can even be impossible.

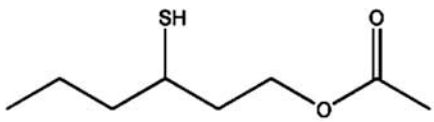
High impact aroma chemicals (HIAC) would generally have an odor threshold of parts per million (ppm), or in some cases parts per billion (ppb), yet impart a desired nuance or odor profile that allows the flavorist to create the perfect top note. To illustrate with a borrowed comparison, 1 ppm of 1 kg of salt would be 1 grain of salt. Parts per billion are an all together different matter; if one took the world's biggest role of toilet paper and unfurled it between New York and London, 1 ppb would equate to one single sheet in that entire roll. Obviously, given the proportions involved, these molecules are very powerful and complex; consequently, even in their synthetic form, they are difficult to generate. Add in the constraints of natural legislation and the difficulty becomes multiplied to virtual impossibility.

Postulated methods of obtaining natural sulfur molecules include trapping the gaseous decomposition products of a variety of vegetables and fruit, or even harvesting the gaseous "byproducts" of masticating cattle—a pleasant thought! Alternative methods include the isolation of aroma chemicals from the waste streams of processes such as fermentation. While there remain doubts about the practicality and sustainability of some

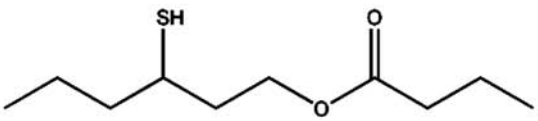
3-Mercaptohexan-1-ol and its derivatives identified in purple passion fruit **F-5**



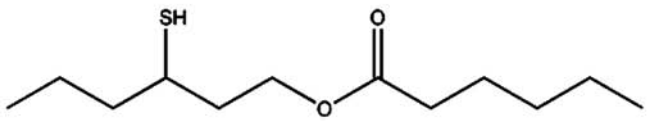
3-Mercaptohexan-1-ol (FEMA 3850)



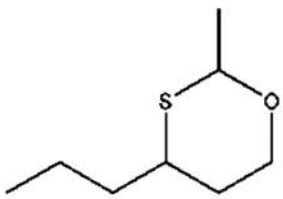
3-Mercaptohexyl Acetate (FEMA 3851)



3-Mercaptohexyl Butyrate (FEMA 3852)



3-Mercaptohexyl Hexanoate (FEMA 3853)



Tropathiane (FEMA 3578)

of these processes, HIAC manufacturers will continue to investigate these and other methods of manufacturing and obtaining these molecules.

Another area that is being investigated is the use of an enzymatic process that, in principle, would mimic the process in which the desired HIAC is formed in nature—or at least meet the stringent requirements of EU legislation. There have been a variety of reports in the literature that outline potential methods for the production of HIACs such as alkyl pyrazines.[1–3]

On reviewing these observations of in vivo synthesis of natural alkyl pyrazines, one can rationalize that a reaction of amino acetone with a suitable enzyme would form these much sought-after natural compounds.[2–4] However, moving from the theoretical arena to the commercial world presents a large technical gap, which has yet to be bridged. Other examples of sought-after aroma chemicals can be found in purple passion fruit (**F-5**). 3-Mercaptohexan-1-ol and its derivatives provide the characteristic tropical notes found in this material. Recently, the identification of a conjugate of 3-mercaptohexanol in passion fruit has suggested a biosynthetic route for the generation of such compounds. [4,5]

Conclusion

While work continues to find synthetic routes to some of the more interesting aroma chemicals—while meeting both EU and US natural legislation—the flavorist's work will continue to be difficult. In the meantime, natural extracts, oleoresins and distillates offer a viable, cost-effective alternative. Despite the issues over some extracts not having GRAS status, these materials are derived from nature and clearly represent the flavorist's best chance of meeting the ever evolving demands of an expanding market, while staying within the complex arena of natural legislation.

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