Advances in Natural Flavors and Materials

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The demand for natural flavorings in foods and beverages has increased worldwide, and this has imposed an ever-challenging problem to the flavor industry as good marketing strategists take advantage of this trend.

The toxicological properties of approved *artificial* ingredients are well documented, possible health hazards have been assessed and the products cleared for use, either with no restrictions or with specific use levels and applications. Equivalent chemicals in *natural* form have the same toxicological properties and limitations. Any change from artificial to natural ingredients has to be commercially justified, since natural ingredients are normally less cost effective.

Naturals Defined

Current legislation[1] in the *Code of Federal Regulations* (CFR) governing natural flavors or natural flavorings in the United States defines naturals in 21 CFR 101.22 (a) (3) as isolates from both plant and animal sources, fermentation products and commonly called "process flavor products" which are flavors derived from thermal reaction and enzymatic treatment. Source materials, processing conditions and isolation techniques are stated, but further work is needed to resolve specific cases.

Furthermore, within the body of regulations, 21 CFR 101.22 (J) (iii) allows a "natural flavor" which contains both a characterizing flavor from the product whose flavor is being simulated and other natural flavors which simulate, resemble or reinforce the characterizing flavor to be labeled as a "natural flavor WONF (With Other Natural Flavors)." This regulation enables the use of the materials cited in 21 CFR 101.22 (a) (3) by the flavor industry to create flavors of excellent fidelity and efficacy.

The techniques to produce natural flavors or flavorings by biotechnological routes have pushed back the boundaries of food science, but FDA regulations require some interpretation on how they impact on the commercialization of new food products. The flavor industry has drawn up its set of guidelines based on the principles outlined in the CFR. Principles applicable to the production of nature materials are the following:

- Source materials must occur in nature. Water and atmospheric air can be used during production.
- When considering a process, the resultant material must be found in nature or as an artifact in traditional foods.
- In biotechnological processes, the substrate must be natural, but nutrients can be used regardless of source.
- Processing conditions are allowed so long as they meet the criteria of traditional or in-home preparation techniques.

The classic problems associated with traditional natural flavoring materials are the following:

- Quality and supply can be variable, as production is affected by natural catastrophes, political unrest and socioeconomic changes within the countries of origin.
- Products with restrictive stability are limited in both range and form.
- Naturals are normally weak in strength when first extracted and are therefore expensive in use.

Traditional Technologies Surveyed

In the past, natural flavor components were derived from fruit, flowers, roots, leaves, animal glands and tissue. Dependent upon the manner of production, they were either botanical particulates or in oil or water-soluble liquid form. Examples are the essential oils, fruit juices, vegetable

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juices and meat and fish broth concentrates. Fruit flavorings were some of the earliest products available and single-fold fruit juices were normally a major component, especially in beverages, where they were fortified with water-solubilized synthetics or essential oils.

Early attempts to use juices, normally in unconcentrated form, resulted in fermented products such as wines and cider. Commercial production only became possible when it was found that heat treatment stabilized them.

Fruit processing factories are normally set up to handle one type of fruit. Several of the major juices which are produced in large volume are derived from the fleshy fruits and can be categorized as:

- Fruits that require specialized processing and incidentally have the highest commercial value (such as the citrus fruits and pineapple).
- Fruits that can be pulped, then extracted (such as apples and berries).
- Fruits requiring some cooking before extraction (tomato is the best-known example).

To make storage and handling economical, juices are concentrated to minimize volume. Typically, soft fruit juices are flash heated to boiling point and 10-15% of the volume distilled off. The vapor is condensed and collected, as it contains much of the flavor volatiles of the juice. This aromatic material is fractionated to produce approximately a 1% yield of the 100-fold essence oil. The balance of the juice is then further reduced to 12-15% of its original volume and the essence oil collected can either be blended back into the concentrated juice to standarize quality or used as a raw material for natural flavors. For labeling purposes, concentrated juices, whether from fruits or vegetables, play an important role in today's natural flavors.

Juices after heat treatment require fortifying with juice volatiles or flavor compositions which mimic the flavor of the juice. This is because many of the taste components change during processing or are driven off. Crucial to the development of natural flavors have been the evolution of the use of essential oils, and the analytical research leading to the understanding of their makeup with the subsequent production of discrete components, through advances in technology.

Early essential oil processing was very crude; a few were obtained by expression, a form of direct physical squeezing.

One of the oldest extraction techniques still in use today is distillation. Originally, the process involved the use of very rudimentary stills, normally heated by direct fire to boil the water which was added in with the plant material. Steam carried the aromatics over to be condensed and separated as the essential oil and scented waters. Simple processing equipment of this type can still be found in underdeveloped countries around the world.

Large-scale commercial equipment design was improved in southern France during the 1800s, in Grasse; steam produced in a separate boiler was blown through the plant material. This was a far less risky procedure, because there was little chance of the plant material being burnt.

Another traditional technique, extraction with hot or cold deodorized animal fat with subsequent extraction of the aromatics with alcohol washes, has been superseded by the use of organic solvents, mainly for cost reasons.

Solvent extraction involves soaking natural raw materials in a solvent. The temperature of the extraction, the length of the process and the number of successive extractions are dependent upon the solvent being used and the material being processed.

After maceration the saturated solvent is filtered and then pumped into a still where most of the solvent is evaporated. The final concentration is carried out in a high-vacuum still to yield a concrete. Concretes are normally solid waxy masses, containing all the hydrocarbon soluble and odorous matter of the plant. Alcohol washing at low temperatures precipitates the waxes which are then filtered off, and subsequent removal of the alcohol at low pressure leads to the highly concentrated product called an absolute. Solvent extraction is also used extensively to process herbs and spices yielding the oleoresins which are normally used as such.

The processes discussed give the flavorist the odorous constituent of each plant in the most concentrated form practical. However, it is sometimes necessary to remove undesirable parts of the oil such as impurities, waxes, colors and certain terpene fractions, or to increase the overall percentage of a given component or components. This purification by high vacuum distillation is known as rectification. This process, a more sophisticated form of distillation, leaves behind in the still a residue which is the dark coloring material found in many oils. An old method of rectification consisted of blowing steam through the oil to effect the separation, but the more modern method of dry distillation in a high vacuum allows rectification at much lower temperatures.

Further modification to the simple "straight over" still by the inclusion of a packed column enables greater efficiency in separating volatile components. This procedure is known as fractional distillation and enables the isolation of the main constituents of essential oils; some examples are citral from lemongrass, eugenol from clove leaf and linalool from rosewood.

Advances

Historically, until the advent of modern analytical techniques and synthetic chemistry, our ancestors had to be content with natural products when developing flavors.

Catalyzed by the trend for healthy natural foods during the late 1970s, intense research, aided by advances in analytical techniques and equipment, gave insight into the way nature generates the materials responsible for the taste and aroma of more complex flavors such as meats, chocolate and dairy products.

New and novel technologies evolved to supply the flavorist with natural building blocks, which were necessary to improve the quality of flavors. Some of the most innova-

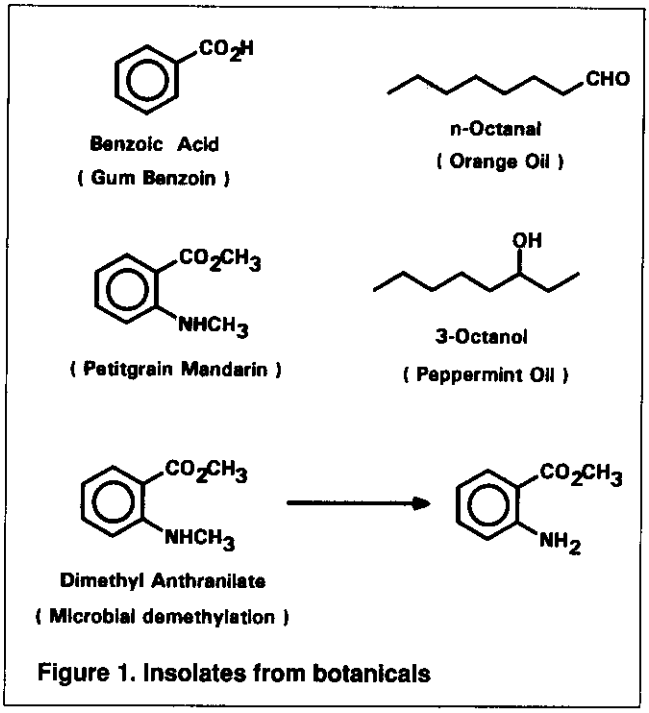

Figure 1. Isolates from botanicals

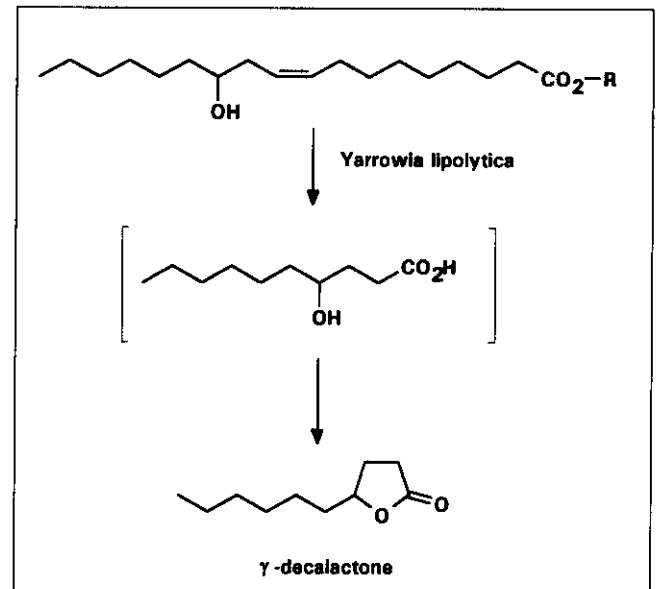

Figure 2. Microbial transformation of castor oil
(from US Patent 4,560,656)

tive research has led to the production of flavors and flavor components by process flavor and biotechnological routes. Currently, the major sources of accepted natural flavoring materials can be grouped into three main categories:

- Those materials that are formed during normal plant or animal metabolism. The material is used in the dry form or aromatics are extracted and refined using techniques already discussed.
- Aromatic components formed during enzymatic or microbial action.
- Discrete components and flavor bases formed during heat processing of natural ingredients.

Advances using plant or animal metabolism: Essential oils and juices still remain the largest source of natural flavor components, but dry plant and animal materials still find use as ingredients for inclusion into food stuffs.

As mentioned earlier, during the concentration of vegetable and fruit juices, volatile organics are steam distilled over with the waste waters. Modern extraction techniques are capable of economically collecting these minute quantities of flavor components produced by the food industry, and they can be utilized either as a total extractive or as discrete chemicals.

Constituents of normal plant metabolism can be isolated as single components. Sophisticated analytical techniques have been modified to enable the extraction and investigation of concentrated fractions that are of interest using fractional distillation of the concentrate, or isolated using solvent extraction techniques. Similar techniques can be utilized when investigating other flavor sources such as cooked meat and fish protein.

By-product streams, such as the light and residual fractions generated during rectification of essential oils or alcoholic spirits (whiskey, brandy, etc.), are interesting sources of natural chemicals that would otherwise be wastefully utilized. These are just some of the approaches used to supply flavorists with naturals of high quality and in commercially viable quantities.

Natural isolates can also be obtained from specific botanical sources (Figure 1). Dimethyl anthranilate (Figure 1) is an interesting example because further processing by microbial demethylation yields methyl anthranilate, the characterizing component of concord grape flavor.

Advances using enzymatic or microbial action: Biotechnology is an area of research being heavily emphasized by the world's leading flavor houses for current and future natural material demands. Biotechnology, broadly defined, includes any technique that uses live organisms (or parts of organisms) to make or modify products. Biotechnology can accomplish reactions that are not easily carried out by classical chemistry, and the added bonus is that the materials produced are legally natural.

A process, patented in 1985 by Fritzsche, Dodge and Olcott, demonstrated how castor oil can be hydrolyzed, then beta-oxidized by the cultured fungi *Yarrowia lipolytica* under mild pH and temperature conditions to form γ-hydroxydecanoic acid which can then be lactonized in situi (Figure 2). This novel natural chemical finds use in a whole range of WONF flavors, encompassing fruit, dairy, nuts and meats.

These processes are commercially viable, because of the extraction methods utilized to remove the small quantities of product from the cultured medium. The methods include filtration, centrifuging, distillation, reverse osmosis and chromatographic techniques.

(Continued on page 18)

Meat Flavors from Heat Processing

The flavor of cooked meat is attributed to a complex mixture of compounds produced by heating to give a heterogeneous system comprising:

- Volatile compounds with odor properties.
- Non-volatile compounds with taste properties.
- Potentiators and synergists.

During the last three decades, the chemistry of the compounds responsible for the flavor of cooked meat has been the subject of considerable research. Significant facts about cooked meats are:

- The flavor depends on the preparation method, such as boiling, frying, broiling and roasting.
- Each meat has its own characteristic flavor after cooking.

Because it is necessary to heat the meat to produce its characteristic flavor profile, it follows that meat must contain substances which interact or degrade during the cooking process to produce flavor compounds responsible for the taste.

Differing meat sources contain similar types of components, such as proteins, amino compounds (some containing sulphur sources), lipids, carbohydrates and mineral salts. It is apparent that these components interact uniquely or are in significantly different proportions in varying meat protein sources. The differences in flavor profile due to cooking technique are a function of temperature, processing time and moisture content in the meat.

Many meat aroma precursors were identified in the early 1970s and development of simple model systems has led to the process meat flavor technology of today.

The Maillard reaction (amino acids reacting with reducing sugars via Strecker's degradation) is one route for producing meat aroma components. It has been used for many years (Figure 3).

Pyrolysis products of amino acids, sugars and peptides along with thermal degradation of vitamins such as

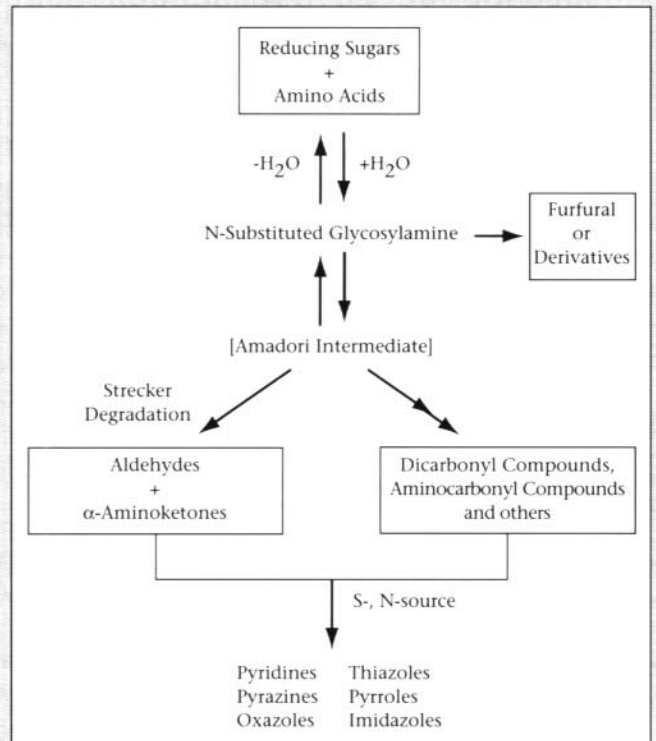

Figure 3. Maillard reaction and flavor production—a simplified illustration

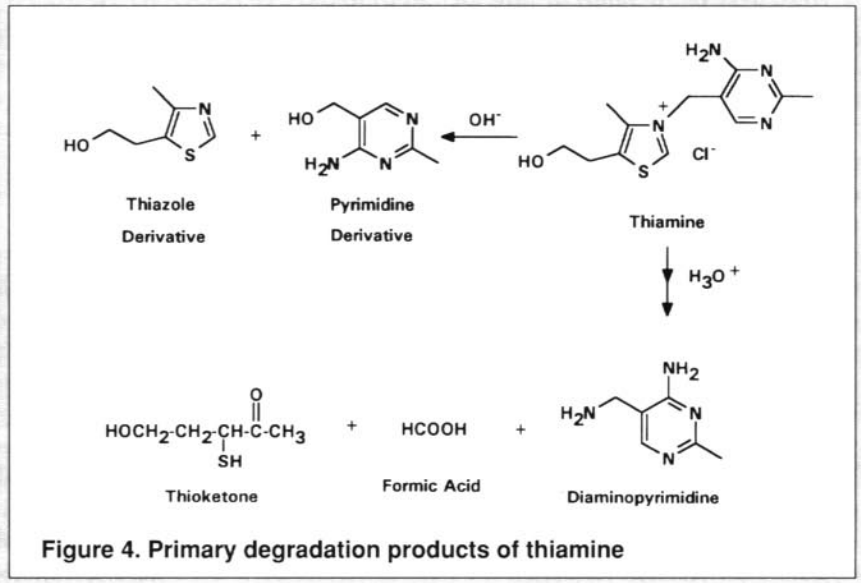

Figure 4. Primary degradation products of thiamine

thiamine (vitamin B_1) can produce strong meaty character (Figure 4). These reactions along with the aroma chemicals produced from controlled oxidation of lipids and fatty acids (Figure 5) all interact to give characteristic meat aroma similar to the organoleptic profiles developed during normal home cooking.

An appreciation of the distinctive flavors resulting from preservation techniques or the addition of typical processing aids can be directly used by the flavorist when creating specific profiles. Preservation of meat has been practiced for centuries as a means of storing foodstuffs. In the past, drying, salting and smoking were the most common and simplest methods used to preserve meats. Meats treated in these ways have traditional aroma and taste, and a flavorist must use this knowledge by emphasizing those characteristics when developing a specific flavor.

Flavorists have a wealth of information at their disposal when developing meat flavors for a specific food product (Table I).

One can attempt to duplicate the flavor chemicals produced during cooking by heating mixtures of specific amino acids, fats and sugars, and the resultant flavors is then added to the foodstuff. Or, one can create precursor flavors which develop the meat character within the foodstuff while it is being prepared, heated or cooked.

Herb and spice extracts can be blended together to create a concentrated form of traditional flavorings, which would normally be added as leaves, berries or buds of aromatic plants.

As the flavor chemists confirm the presence of more and more flavor chemicals in cooked meat and develop processes for their production, components become available for the flavorists to create synthetic meat aroma. Flavorists also use their traditional creative skills by utilizing other non-meat ingredients that have meat-like flavor characteristics.

In recent years, fears about the toxicological safety of certain raw materials and pressures of marketing trends on the industry have required a modification of the approach to creating meat flavors. Animal protein and fat sources are increasingly used to enable the development of the rich flavor character of meat, especially when hydrolyzed vegetable protein, MSG and the ribonucleotides are not permitted. This situation causes other dilemmas for the flavor industry, since such flavor compositions generally require USDA approval of the formula and inspection while being produced in a USDA-approved plant.

Table I. Typical components of natural process flavors

Beef type	Chicken type
Beef extract	Hydrolyzed chicken meat
Beef tallow	*l*-Leucine
Yeast extract	*l*-Cysteine
l-Cysteine	Glucose
l-Glutamic acid	Arabinose
Glucose	Onion powder
Ribose	Egg powder
Onion powder	Carrot powder
Garlic powder	Water
Water	Chicken fat
Black pepper oil	

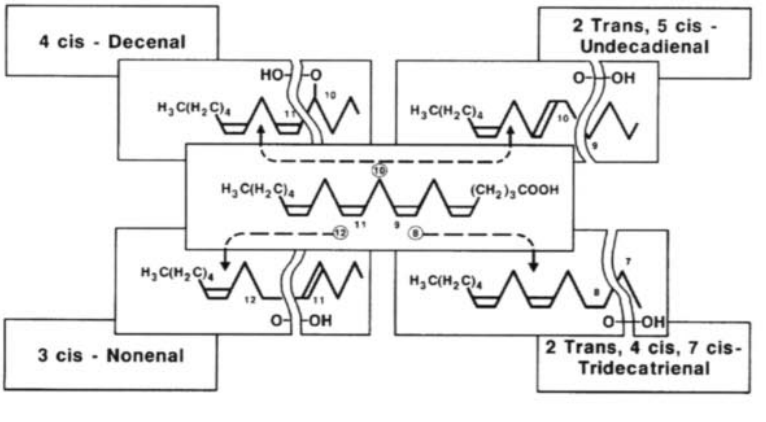

Figure 5. Flavors from controlled oxidation of fatty acids

Table II. Typical botanical components in benedictine

Nutmeg	Coriander
Clove bud	Orange peel
Cassia	Peppermint leaf
Cardamom seed	Mugwort
Musk seed	Lemon balm herb
Arnica blossom	Anglica root
Thyme	Camomile Roman
Hyssop leaf	Gentian root
Hyssop root	Mace
Calamus root	

Research continues in the enzymatic biotransformations that produce aromatics, but the complex interaction between substrate enzymes and metabolites makes R&D lengthy and capital expenses very high. Examples of the commercially successful use of this technology include the enhancement of total cheese and butter flavors by enzyme modification, and the production of many of the novel natural chemicals that continue to appear on the market.

The processes in other biochemical technology areas like plant cell cultures and recombinant DNA are still in their infancy for flavor use. More work and capital investment will be required.

Advances using heat processing of natural ingredients: The third most important means of natural flavor and flavor chemical production is the thermal processing of natural precursor systems. Scientific research into natural chemical formation in cooked foodstuffs gave rise to the process flavoring technology used to produce such flavors as cocoa, bread, coffee and meat from naturally sourced precursors. (See previous pages for a detailed examination of meat flavor development.)

Thermal processing can also be used to produce discrete chemicals and as long as the starting materials are natural and processing guidelines are adhered to, resultant chemicals are accepted as natural here in America.

Consider, for example, a process developed by Fritzsche, Dodge and Olcott for the controlled thermal reaction of specific sugars with selected amino acids to form Enhansol (4-hydroxy-2,5-dimethyl-3(2H)-furanone). First found in beef and subsequently in strawberries, pineapples and many other fruits, Enhansol has flavor application across the entire food product range.

Examples Using Botanicals and Essential Oil Blends

I would now like to give a few examples of traditional materials used in some natural flavor compositions employing botanicals or essential oil blends. I will then move on to more recent developments, which have enabled today's formulations to be created more effectively.

Numerous novel flavor creations evolved in alcoholic beverages, many of which had been developed and utilized for medicinal purposes. Benedictine (Table II) is a typical example of a flavored spirit incorporating herbs and spices gathered locally, and exotic spices brought in from the Orient. Complex processing, involving alcoholic extraction of the botanicals and eventual distillation to yield the flavored liquor, is still a closely guarded secret.

Table III. Typical traditional components of a cherry-type WONF fortifier

Almond bitter oil	Ethyl alcohol
Cinnamon bark oil	Geranium oil bourbon
Cognac green oil	Neroli oil
Coriander oil	Rose oil
Clove bud oil	

Table IV. Typical botanical components in chicken spice

Clove buds	Pepper
Ginger	Pimento berries
Mace	Sage
Majoram	Savory
Nutmeg	Thyme

A good example of the traditional flavorist's art is in the use of essential oils and isolates to create flavor fortifiers to enhance flavor character lost or damaged during fruit processing.

Typically, a cherry fortifier (Table III) would exhibit a benzaldehyde character from the bitter almond oil, modified with sweet floral/spice notes. Alcohol is used as a solvent for water-soluble products in this example, but could easily be altered to give different functional solubility for end use of the fortifier.

Blends such as chicken spice (Table IV), used to enhance the flavor of meat and savory foods, evolved as Oriental spices became available. The botanicals were ground into a powder for use directly on the meat or in stuffings. For biological stability in modern factory production, it is more effective to formulate such spice blends using oils and oleoresins which have been functionalized to perform under specific process conditions.

Examples Using Naturals WONF

Flavor ingredients were originally limited in number and consisted of essential oils and other natural extractives. Flavor fidelity was lacking and attempts to reformulate aromas were limited to the creative skills of the flavorist. During the 19th century, coumarin, vanillin and heliotropine were synthesized. By the beginning of this century, research chemists were busily studying the composition and structures of the components found in essential oils.

Table V. Typical components of a natural black cherry WONF

Acetaldehyde	Coffee essence
Acetic acid	Davana oil
Iso amyl acetate	Ethyl acetate
Benzaldehyde	Ethyl alcohol
Benzyl acetate	Ethyl benzoate
Benzyl alcohol	Ethyl butyrate
Butyric acid	cis-3-Hexenal
Caproic acid	cis-3-Hexenol
Capric acid	Maltol
Cherry essence concentrate	

Table VI. Typical components of a natural peach WONF

Acetaldehyde	cis-3-Hexenol
Benzaldehyde	cis-3-Hexenyl acetate
Benzyl acetate	Hexyl acetate
Buchu oil	Jasmin absolute
Iso butyl iso valerate	Linalool ex bois de rose oil
Caproic acid	*l*-Menthyl acetate
γ-Decalactone	*l*-Menthone
Dimethyl sulfide	*n*-Octyl acetate
γ-Octalactone	Orange oil
Ethyl alcohol	Peach essence concentrate
Ethyl acetate	Phenyl ethyl acetate
Ethyl benzoate	Phenyl ethyl alcohol

Table VII. Typical components of a natural strawberry WONF

Acetic acid	cis-3-Hexenol
Iso amyl butyrate	cis-3-Hexenyl acetate
Apple essence folded	4-Hydroxy-2,5-dimethyl-3(2H)-furanone
Caproic acid	2-Methyl butyric acid
Diacetyl	Methyl cinnamate
γ-Decalactone	Orange oil
Ethyl alcohol	Strawberry essence folded
Ethyl butyrate	Vanilla extract
Ethyl caproate	
Ethyl iso valerate	

Table VIII. Typical components of a natural dairy WONF

Acetaldehyde	Enzyme modified dairy products – butter, cheese, cream, etc.
Acetic acid	cis-3-Hexenol
Acetyl methyl carbinol	Lactones
Acetyl propionyl	γ-Decalactone
Butyric acid	γ-Octalactone
Capric acid	Lactic acid
Caproic acid	Lauric acid
Caprylic acid	2-Methyl butyric acid
Corylone - methyl cyclopentenalone	Methyl ketones
Diacetyl	Methyl amyl ketone
Dimethyl sulfide	Methyl hexyl ketone
Enhansol (4-Hydroxy-2,5-dimethyl-3(2H)-furanone)	Methyl nonyl ketone
	Palmitic acid
	Solvent system

Table IX. Typical components of a natural cocoa/chocolate WONF

Acetic acid	Phenylacetic acid
Benzaldehyde	Pyrazines
Isobutraldehyde	Tetramethyl pyrazine
Cocoa extract	Trimethyl pyrazine
Corylone - Methyl cyclopentenalone	2,5-Dimethyl pyrazine
Diacetyl	Smoke extract
Enhansol (4-Hydroxy-2,5-dimethyl-3(2H)-furanone)	Isovaleraldehyde
Maltol	Vanilla oleoresin
	Vanillin
	Solvent system

Analytical methods were improved and new techniques invented to assist in this research. Infrared and ultraviolet spectroscopy, gas chromatography, mass spectroscopy, high field nuclear magnetic resonance spectroscopy, high performance liquid chromatography—all are routinely used today to further elucidate qualitative and quantitative components in naturally occurring flavor systems.

While the analyst confirmed the structure of the aromatics, the organic chemists were busily synthesizing the most useful molecules.

Using these raw materials, flavors were created with truer-to-life character, improved strength and greater stability for the new food systems that were being developed.

The inexperienced eye sees a bewildering amount of information from modern instrumentation. But to the trained researcher, main constituents, trace components and artifacts all point to how a flavor can be formulated in order to duplicate the original flavor. From such detailed observations flavorists were able to fabricate flavors with excellent fidelity.

Compare the formulation of a modern cherry (Table V) to the traditional flavor composition shown earlier (Table III). The flavor is a natural interpretation of an artificial cherry utilizing raw materials developed by current technologies.

The components of a natural peach flavor (Table VI) are all found in nature but not necessarily in peach. Analytical

data is still not found to be enough to totally duplicate the subtle nuances of the fruit flavor, and the flavorist's creative skills must be called upon to fine tune the blend.

Today's state-of-the art natural WONF formulations (Table VII) result in products that more closely resemble the taste found in nature and are much more effective in food products than traditional compositions, especially when they are adequately functionalized. These strawberry, cherry and peach formulas are composed mostly of discrete isolates obtained by the processes we previously discussed, and look more like a list of components found in the analysis of a natural extract. Such compounds find use in fortification of juice-based flavors, improving both the overall taste and the in-use strength of the WONFs.

All dairy flavors (such as cheese, butter, yogurt and cream) contain similar ingredients since they are based on a common source—mammalian milk. What differentiates the flavors are the levels of the components which are generated during the processing of the milk. A range of materials can be used for creating specific types (Table VIII).

Diacetyl and acetoin were some of the earliest natural components to be commercially offered in the form of starter distillate, but more sophisticated materials such as the lactones, γ-decalactone and the furanone Enhansol have been around for over ten years. Most of these chemicals are available to the flavorist, but the cost can be high.

My last example, a natural cocoa/chocolate (Table IX), gives some idea of the range of the more esoteric products that until recently were not available to the flavorist, but now make it possible to create the nuts, coffee, bread, meat and so-called "brown note" flavors. The pyrazines are now commercially available, being produced from waste materials generated by the food industry or natural thermal process techniques. Natural vanillin necessary for a chocolate flavor is now commercially sold, as are the well-known components Maltol, Enhansol and Corylone. Flavors developed using these materials can be used to top-note cocoa and chocolate extracts, giving us much stronger WONFs with commercial viability and excellent efficacy.

Conclusion

The flavor industry has a wealth of excellent formulary as a basis to fabricate natural flavors. Dependent upon the availability of viable materials that future technologies can generate, and the development of new delivery systems to successfully incorporate them, natural flavors will continue to improve the quality of tomorrow's food products.

References

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1. *The Code of Federal Regulations 21 Food and Drugs*, Parts 100-169, revised April 1, 1993, Washington, DC: National Archives and Records Administration (1993)