

Aspects of Functional Groups and Flavor

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Taste sensation, basic taste, and odors are constituents of the flavor complex which are greatly dependent on chemicals and their structural variations. The performance of such typical

flavor chemicals and the influence of structural changes on their physiological actions are demonstrated.

Flavor, an important part of our food, is due to a combination of odor, basic taste, and usually one or more of the following: taste sensation, texture, temperature, and psychological factor (appearance, etc.).

Among these flavor contributors, taste sensation, basic taste, and odor are greatly dependent on chemicals and their structural variations. This paper is concerned with these three groups.

Taste Sensation

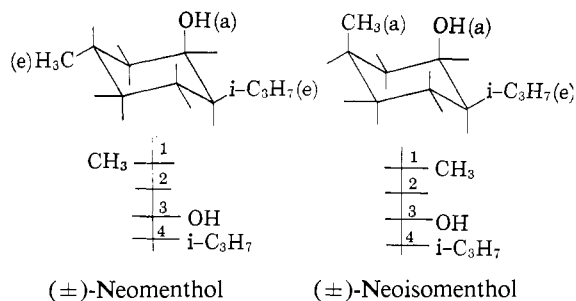
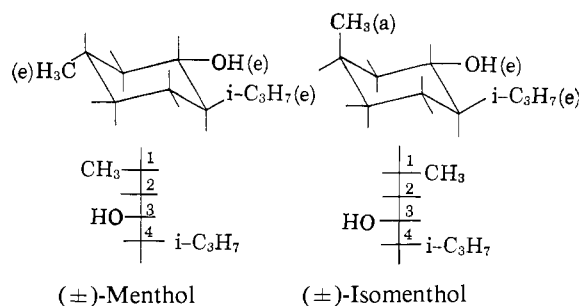
This terminology is used to differentiate between a true or basic taste—i.e., sweet, bitter, sour, or salty—and a specific sensation related to taste—i.e., a cooling, burning, pungent, or biting effect.

Chemicals exerting a taste sensation are the part pertaining to flavor of the complex of chemicals irritating to the chemical sense receptors as described by Moncrieff (19).

An example of a chemical having a taste sensation is (–)-menthol, which is an essential part of all mint flavors and a contributing factor to this complex of taste sensation, odor, and taste.

The various forms of menthol have been used many times to demonstrate stereoisomerism. Since menthol causes a taste sensation, it can be used to show the possible influence of different molecular configurations.

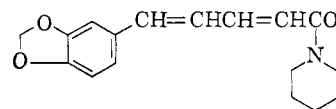
Applying the modern view of conformation, the four racemates of menthol would be the following:



Only (–)-menthol and (+)-menthol have the typical cooling effect. The (–)-form exhibits this property to a greater extent than the (+)-form.

These examples demonstrate the possible influence of isomerism on the existence or absence and the degree or quality of a taste sensation.

Another important example is piperine,



which is largely responsible for the “bite” of black pepper.

Because black pepper is the most popular and most widely used spice, piperine has been investigated, particularly when black pepper was in short supply, to find a commercially feasible synthesis or a replacement.

Staudinger and Schneider (31) reported that to give the desired bite, the molecule must consist of a phenyl group and a side chain of at least four carbons. The acid amide group derived from piperidine is the other prerequisite.

The two double bonds which are present in the side chain of the piperine are unnecessary; a saturated straight side chain of four carbons will give practically the same effect as an unsaturated straight side chain of four carbons.

The methylenedioxy group, present in the natural product, is also unnecessary with regard to bite.

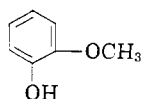
On the basis of these findings, it became possible to synthesize several chemicals, which give taste sensations similar to those of piperine.

Piperine, a solid having a melting point of 128–29° C.,

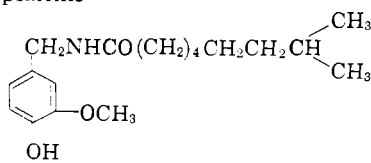
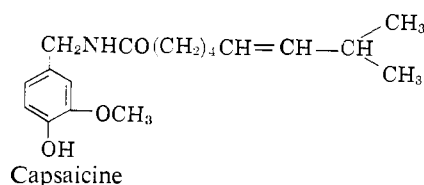
Fritzsche Brothers, Inc., New York, N.Y.

has the trans-trans configuration. Its isomeric cis-cis compound, chavicine, also having a bite, is a liquid and also part of the black pepper spice. Unfortunately, no data are available, comparing the bite intensities of these two compounds and thus the influence exerted by geometrical isomerism in this instance. The same applies to piperittin, another isolate from black pepper, which differs from piperine by having an additional vinyl group and, thus, three conjugated ethylene linkages in its side chain.

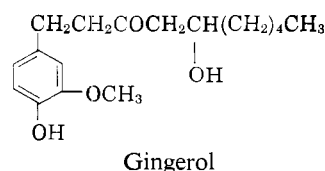
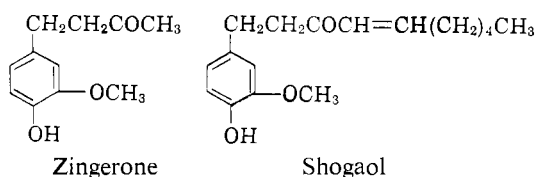
Several pungent compounds found in nature are derivatives of *o*-methoxyphenol,



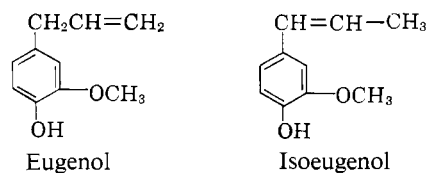
Examples of this group are capsaicine and dihydrocapsaicine:



which are constituents of the red pepper spice, zingerone shagaol, and gingerol,



which are constituents of the ginger root, and eugenol,



found in cloves, and isoeugenol, found in nutmeg and various essential oils.

The degree of pungency and the character of this taste sensation vary markedly among these chemicals.

Capsaicine, and dihydrocapsaicine, which was until recently assumed to be a synthetic prepared by the hy-

drogenation of capsaicine, are extremely pungent and hot. The quality and character of this sensation are experienced more immediately than those of the other compounds mentioned.

The red pepper spice, which has been the topic of intense research, was recently investigated with fruitful results. It was established (14) that the pungent principle of red pepper consists not of one chemical but actually of the unsaturated and saturated amides—i.e., capsaicine and dihydrocapsaicine. The mixture of these two amides was named capsaicinoid.

Thus, with regard to pungency of this group of compounds it can be stated that:

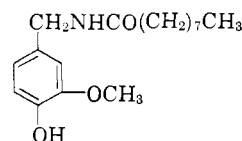
An aromatic ring, having a phenolic hydroxyl group and an ether group such as methoxy, in ortho position to each other, is a basic prerequisite.

A side chain is also necessary. The length and composition of this side chain are important. This becomes evident if we compare any of the pungent compounds mentioned with vanillin or ethylvanillin, which have no pungency.

The degree of the contributing effect of the side chain is shown by the increase in pungency: gingerol > shogaol > zingerone.

The pungency is greatly enhanced by an acid amide group, in this instance vanillylamide, as found in the capsaicinoid molecule.

Based on these observations, the synthetic compound nonoylvanyllamide,



was prepared. This has considerable pungency and heat.

In certain cases, chemicals having a taste sensation are also odor contributors. Eugenol, besides its familiar burning sensation, also has odor, which stimulates the odor preceptors in a positive manner. In contrast, piperine and capsaicinoid are odorless.

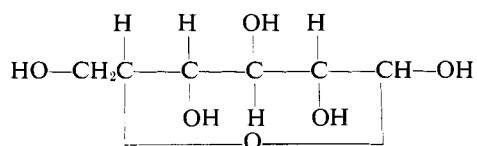
In recent decades important strides were made in the development of separation and identification procedures for chemicals, such as those found in natural products. Many novel and valuable synthetic methods were invented, and several classical procedures could be markedly improved. However, our approach to the architecture of chemicals, intended to have specific properties, has not changed basically. With a few exceptions, we still rely upon knowledge acquired in the past, observation, imitation, speculation, followed by experimentation, and eventually testing, to find out whether synthetics will perform in the way anticipated. Thus, the synthetic duplication of natural chemicals having odor or taste value is high on the list.

Sweetness

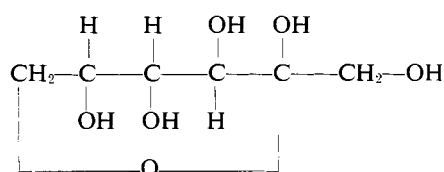
Among the four basic tastes—sweet, bitter, sour, and salty—sweetness occupies a prime position. It is the first taste the newly born experience and appreciate. Other tastes develop only gradually.

Among the various sweetening agents, the sugars or saccharides (monosaccharides and disaccharides) are the most important. We associate sweetness with sugars, and sucrose, commonly known as sugar, is the standard for sweetness.

Examples of monosaccharides are glucose and fructose.



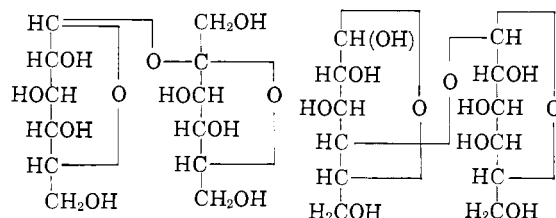
Glucose (D-Glucose)



Fructose (D-Fructose)

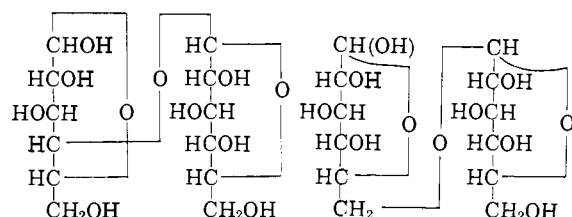
Glucose, the central compound of this group of chemicals, occurs naturally in fruits and other parts of plants. Fructose is present in a large number of fruits.

Examples of disaccharides are sucrose, lactose, maltose, and gentiobiose.



Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)

Lactose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)



Maltose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)

Gentiobiose (Amygdalose) ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$)

Sucrose is the standard sweetening agent in food. Lactose is present in the milk of all mammals. Maltose can be obtained by the enzymatic degradation of starch. Gentiobiose can be prepared by an enzymatic synthesis from glucose and emulsin.

Disaccharides exhibit marked taste variations. Thus, while lactose and maltose are sweet, but less so than sucrose, gentiobiose has a bitter taste.

From a chemical point of view, sugars are fascinating, and they were, and are, the topic of intense and fruitful research.

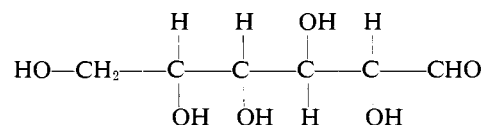
Recent studies of taste are concerned with configura-

tion, conformation, and sweetness of hexose anomers, as discussed by Shallenberger *et al.* (27) and the influence of hydrogen bonding on this taste of sugars. Shallenberger (26) pointed out that sweetness appears to be restricted when hydroxyl groups which elicit sweet taste are hydrogen-bonded. These observations were based upon molecular configuration, hydrogen-bonding measurements, and taste tests.

In this study, various sugars in the solid state (to prevent mutarotation) exhibited the following degree of sweetness:

| Sugar | Relative Sweetness |
|---------------------|--------------------|
| β -Fructose | 180 |
| Sucrose | 100 |
| β -Glucose | 82 |
| α -Glucose | 74 |
| α -Galactose | 32 |
| α -Mannose | 32 |
| β -Lactose | 32 |
| α -Lactose | 16 |
| Raffinose | 1 |

If a simple sugar molecule is written in the Kiliani structure—for example, D-glucose,



several functional groups which are generally associated with odoriferous properties of chemicals can be recognized. Such groups are typical of aldehydes, ketones, alcohols, lactones, etc.

In contrast, the significant property of sugars is that they are odorless, but have taste, and are nonvolatile. Thus, volatility is a prerequisite for human odor perception but not for taste. This statement can be substantiated by many other examples.

Several attempts have been made to correlate sweet taste with molecular configuration.

Cohn (5) in 1914 advanced the theory of the so-called "sapophoric" groups, which postulated that a multiplicity of hydroxyl groups and also α -amino groups gives sweetness. The hydroxyl groups often occur in pairs.

Probably influenced by Witt's theory for dyes (35), Oertly and Myers (20) in 1919 theorized that in order to produce sweetness a molecule must have two groups: a glucophore and an auxogluc.

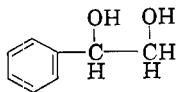
The interplay of these two groups can be observed in the following examples:

| Product | Glucophore | Auxogluc |
|--------------------------|---|-------------------------|
| Ethylene glycol: | | |
| $\text{HO}-\text{CH}_2-$ | | |
| CH_2-OH | $\text{HO}-\text{CH}_2-\text{CH}-\text{OH}$ | H |
| Glycerol: | | |
| $\text{HO}-\text{CH}_2-$ | | |
| $\text{CH}-\text{OH}-$ | | |
| CH_2-OH | $\text{HO}-\text{CH}_2-\text{CH}-\text{OH}$ | CH_2-OH |

However, while these theories are applicable to certain instances, there are many exceptions.

The main purpose in mentioning these theories here is to illustrate the fact that by 1914 scientific thinking and organized efforts existed, aiming at the correlation of taste and chemical structure.

Two alcoholic hydroxyl groups next to each other have an odor-depressing influence, and this phenomenon will decrease if the two hydroxyl groups are farther apart. This hypothesis gains ground by looking at the structure of styrene glycol,

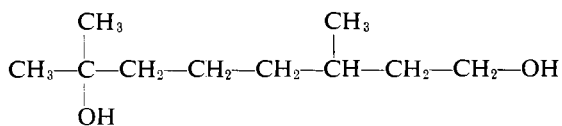


as another example.

We can assume that, because of the vicinal configuration of the two hydroxyl groups, this chemical is odorless, in spite of the presence of the aromatic ring, which—for example, in the case of benzyl alcohol—contributes to a rather faint but decidedly aromatic odor. This property of styrene glycol is drastically changed if one or both of the hydroxyl groups react to form derivatives such as mono- or diesters, or a cyclic acetal, all of which are highly odoriferous.

The influence of the aromatic ring on taste is also interesting; styrene glycol has a bitter taste.

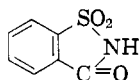
Another example of the significance of the position of the hydroxyl groups with regard to odor is the glycol hydroxycitronellol,



which is odoriferous. In this case the two hydroxyl groups are removed from each other and are on the 2 and 8 carbons. However, in this example the odor-intensifying influence of the tertiary alcohol group should be acknowledged.

In many instances, specific odor or taste characteristics are not the sole property of one compound or a family of compounds but are shared by other chemicals or groups of chemicals, completely unrelated to each other. Several theories were advanced in the past to explain such phenomena, particularly pertaining to odor.

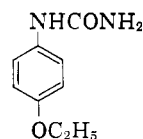
We are well aware of such chemicals as saccharin,



which is said to be 300 to 550 times as sweet as sucrose. Saccharin was prepared in 1879 (21) and is probably the oldest known synthetic sweetening agent. It is remarkable that this product has kept its predominant position. It is understandable that it was the topic of many types of research approaches—for example, to find the influence of molecular modifications. One such recent study, published in 1961 by Hamor (9), reported on the correlation of chemical structure and taste in the saccharin series. The results of experiments with approxi-

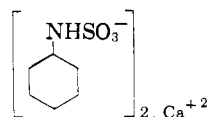
mately 80 saccharin derivatives showed that substitution in the No. 2 or 3 position gives tasteless products. Substitution in the benzene ring with electron-withdrawing groups such as the nitro group resulted in bitter-tasting substances. In contrast, substitution with electron-donating groups resulted in sweet-tasting compounds.

Runti and Colautti (24) recently reported their observation with nucleus-substituted derivatives of dulcin,



While this aromatic urea derivative, which was reported in 1883 (4) is about 250 times as sweet as sucrose, the four possible *C,C*-dimethyldulcins did not have a sweet taste.

A number of other sweet-tasting substances are known. Among them the relative newcomer (2, 32) cyclamate (calcium or sodium)



gained prominence and finds extensive use in sweetening many products, such as soft drinks.

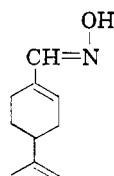
The corresponding acid, cyclohexanesulfamic acid,



having a melting point of 169–70° C., has a sweet-sour taste.

The synergistic effect of some of these synthetic sweeteners is remarkable. Thus, mixtures of saccharin and cyclamate are today often preferred over either one alone.

Occupying a place by itself is (–)-perillic aldehyde. The *syn*-oxime of this aldehyde has no sweetness, but its *anti*-isomer, (–)-perillic aldehyde α -*anti*-oxime,



was found in experiments conducted in 1920 by Furu-kawa and Tomizawa (7) to be 3000 times sweeter than sugar.

This demonstrates how simple isomerism can change a taste profoundly.

Certain glycols, such as D-sorbitol (C₆H₁₄O₆), which is about 60% as sweet as sucrose, and to a lesser degree, D-mannitol (C₆H₁₄O₆), which has about half the sweetening power of sucrose, are today in common use.

The following compilation of synthetic sweetening agents (23) does not exhaust all the possibilities.

Synthetic Sweetening Agents

| Chemical Family | Examples |
|-------------------------------|---|
| Sulfimides | Saccharin |
| Ureas | <i>p</i> -Ethoxyphenylurea |
| Sulfamic acid | Cyclamate (Na and Ca) |
| <i>m</i> -Nitroanilines | 2-Propoxy-5-nitroaniline |
| Oximes | Perillaldehyde oxime |
| Amides | 2-Hexyl-2-chloromalondiamide |
| Hydrazine | Succinic acid dihydrazide |
| Imine nitriles | β -(<i>p</i> -Tolyl)- β -amino- β -propionitrile |
| Aromatic keto-carboxylic acid | 2-(<i>p</i> -Methoxybenzoyl)benzoic acid |
| Triazine derivatives | Glucin |
| Benzimidazole derivatives | 2-Benzimidazolepropionic acid |

2-Propoxy-5-nitroaniline has a sweetening power 4000 times that of saccharin and thus is one of the sweetest chemicals known. However, because of its toxicity it is barred from human consumption.

Bitterness

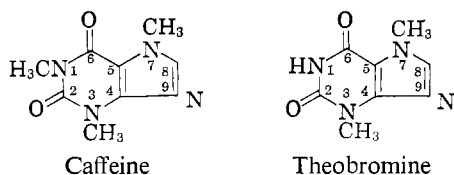
The bitter taste is widely distributed throughout the plant kingdom. Bitter principles are in many instances accompanied by odoriferous substances.

By itself the bitter taste is disagreeable. Even the coffee connoisseur drinks his coffee black and unsweetened merely to perceive better and not to change the aroma of this beverage. However, in conjunction with sweet, or sweet and sour, the bitter taste can contribute markedly to consumer acceptance of many food products.

Among the bitter substances are two chemical families, the alkaloids and the glycosides.

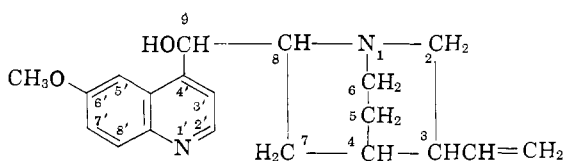
Alkaloids are basic organic nitrogenous chemicals and mainly derivatives of such ring systems as pyridine, pyrrolidine, quinoline and isoquinoline, and purine. One of their pronounced properties is the ability to form water-soluble addition salts with mineral acids and many organic acids.

The purine derivatives, caffeine and theobromine,



are the most important alkaloids from the point of view of volume and consumption in food products, particularly beverages.

More recently quinine,



was added to a soft drink (quinine water), which is usually consumed as a mixer. In this case the bitter taste becomes a contributing factor in the over-all flavor of an alcoholic drink.

Glycosides are the reaction products of sugars with another chemical, specified as an aglycone. The reactive part of the aglycone is a hydroxyl group, resulting in a hemiacetal-type linkage characteristic of glycosides. Such combinations are known to be loosely bound and prone to hydrolysis.

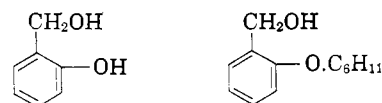
This group of bitter principles can be classified, in chemical terms, according to the sugar moiety of the molecule (glucose will give glucosides) or according to the aglycone part of the glycoside molecule, such as ethylene derivatives, benzene derivatives, styrolene derivatives, flavone derivatives, and saponins.

EXAMPLE OF ETHYLENE DERIVATIVE



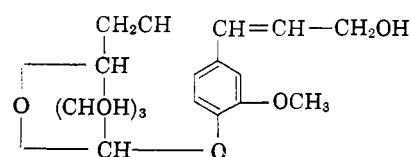
Allyl isothiocyanate is the aglycone of the sinigrin glycoside. Sinigrin is part of the black mustard seed and horseradish. When cleaved, allyl isothiocyanate (mustard oil), D-glucose, and potassium bisulfate (KHSO₄) are obtained.

EXAMPLE OF BENZENE DERIVATIVE



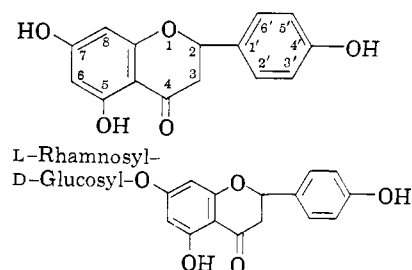
Salicyl alcohol is the aglycone of the salicyl glycoside, which is found in several flowers, barks, and roots.

EXAMPLE OF STYROLENE DERIVATIVE



Coniferin is the aglycone of the principal glycoside of the conifers. It is also present in sugar beets and asparagus. The structural relationship of this glycoside to vanillin is obvious. By oxidation with potassium bichromate and sulfuric acid, vanillin is produced.

EXAMPLE OF FLAVONE DERIVATIVE

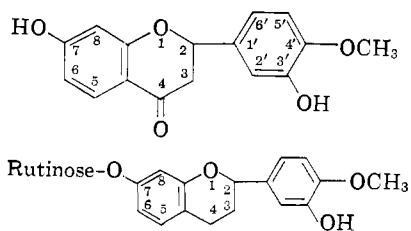


Naringenin is the aglycone of the naringin glycoside. The sugar part is attached to the No. 7 carbon. On hy-

drolysis of this glycoside, naringenin, glucose, and rhamnose are obtained.

Naringin is found most abundantly in the immature grapefruit but also in the ripe fruit and rind (13).

ANOTHER EXAMPLE OF FLAVONE DERIVATIVE

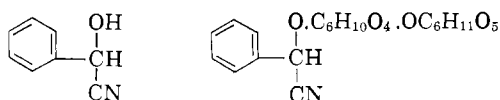


Hesperetin is the aglycone of the hesperidin glycoside. The sugar part—i.e., rutinose, a disaccharide—is attached to the No. 7 carbon.

This glycoside is found in most varieties of citrus plants, especially in the unripe, green fruits. While only traces are found in grapefruit, dried orange peels contain as much as 8% of this compound.

However, hesperidin has no bitter taste; in fact, it is tasteless. Thus, the findings of Horowitz and Gentili (10), that there is a relationship between bitterness of certain 7-rhamnoglycosides found in citrus and the structure of the disaccharide portion of these compounds, are of great importance. More specifically, the point of attachment of rhamnose to glucose is the important factor in determining bitterness or tastelessness in this group of glycosides. An example is neohesperidin, which is bitter. Its structure differs from the tasteless hesperidin only in the position of attachment of rhamnose to glucose.

EXAMPLE OF CYANOGEN DERIVATIVE



Mandelonitrile is the aglycone of the amygdalin glycoside. The sugar part of this glycoside is gentiobiose. On enzymatic decomposition, 2 moles of D-glucose, HCN, and benzaldehyde are obtained.

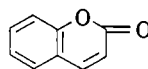
Saponins (18). The aglycone parts of these glycosides are triterpenes or steroids, identified as saponinins.

Saponins are widely distributed throughout the plant kingdom. A common property of these glycosides is to foam strongly when mixed with water. They have a bitter taste and are nontoxic when taken orally, but when injected into the blood stream they are powerful hemolytics.

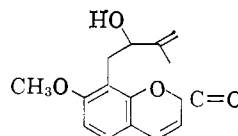
The above are only a few of the many glycosides and their main constituents, which are important flavor contributors.

Alkaloids and glycosides are not the only chemical families having a bitter taste. There are many other chemicals and groups of chemicals in this category. Among them, coumarins, terpene hydrocarbons, and terpenoids are of importance.

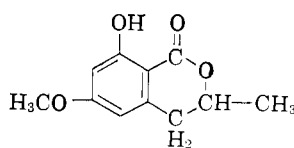
Examples of coumarins and related compounds belonging to this category are coumarin,



which is widely distributed throughout the plant kingdom and has a slightly burning, bitter taste, and auraptenol (7-methoxy-8-hydroxy-3-methyl-3-butenyl)coumarin,



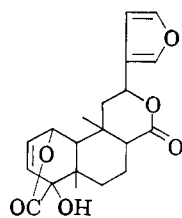
which was identified (30) in bitter orange oil of the Seville type. Another example is 3-methyl-6-methoxy-8-hydroxy-3,4-dihydroisocoumarin,



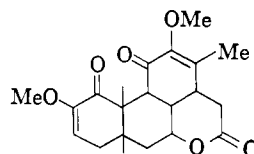
a bitter principle found in carrots (29).

Only a few bitter terpenoids are used in flavor compositions, because many of them have also more far-reaching physiological activities. Thus, while not suitable in food, some of them are of interest in other fields—for example, as pharmaceuticals.

Among bitter principles useful in food are those of the colombo root. This natural product contains three neutral, isomeric bitter principles: columbin ($C_{20}H_{22}O_6$), chasmanin, and palmarin. The most important is columbin (3),

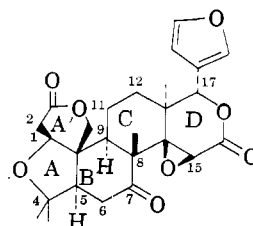


Another bitter substance, important in flavors, and belonging to this class of chemicals is quassin (33),



which is a constituent of quassia wood and quassia bark.

Among the natural bitter principles, the citrus bitter substance limonin,



occupies a special place. Its rather complicated structure was elucidated by four groups of scientists (1, 22). An extensive literature gives witness to the interest in this compound and its many derivatives (6).

The family of the bitter taste and its many members demonstrate that not one group of chemicals was privileged by nature to be the sole distributor of a single taste. As a result it becomes difficult to correlate chemical structure with taste, or even bring to logical order the many chemical structural possibilities.

While the sweet and bitter tastes are complex from a chemical point of view, the salty and acid tastes show some uniformity.

Saltiness

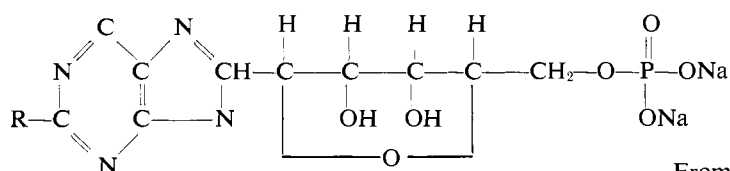
Salts are well described chemical families and result from the reaction of an organic or inorganic acid with a base. The classical example of a salt is sodium chloride. When considering this chemical as a flavor contributor, the following observations can be made. The taste of salt by itself is unpleasant. However, in conjunction with a great many food products, its action is like that of a synergist or, as it is known in food technology, a flavor potentiator. A great number of examples demonstrate these actions of salt, reaching literally from soup to nuts.

The application of the salty taste, or those of salts of various kinds, is almost synonymous with flavor enhancement.

Besides sodium chloride, which is the oldest known flavor potentiator, monosodium glutamate, $\text{HOOC-CH}(\text{NH}_2)\text{-CH}_2\text{-CH}_2\text{-COONa}$, was for many years the only known other food additive having this action. However, only its (–)-form, which is a natural product obtained from protein, has value in flavor.

While monosodium glutamate was discovered in 1908 in Japan (11) and became available there shortly afterwards, only the scarcity of spices in this country during World War II made this product known and appreciated in the United States. This product is also credited today with increasing the aroma of certain food products (28).

The action of these well established products was supplemented and in certain instances even topped by the dramatic performance of disodium inosinate and disodium guanylate,

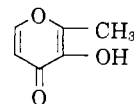


R=H. Disodium inosinate
R=NH₂. Disodium guanylate

Their enhancing effect in meaty and brothy tastes is today well known, and they are also credited with having synergistic action on monosodium glutamate.

Both compounds are chemically defined as derivatives of 5-nucleotides, which are the building blocks for nucleic acid. Several nucleotides are known to occur in nature. However, only 5'-inosine monophosphate and 5'-guanosine monophosphate supposedly have significant flavor activity (16).

Maltol,



has been known for many years but became commercially available only recently. It is today used in soft drinks, fruit drinks, baked goods, vanilla flavor, chocolate, etc., to enhance the sweetness rendered by sugar or other agents. Thus, these sweeteners can be used in markedly lower amounts. Maltol will also give a certain imitation of naturalness which is the wanted opposite of the undesired chemical note.

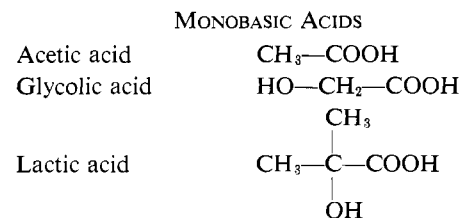
Acids

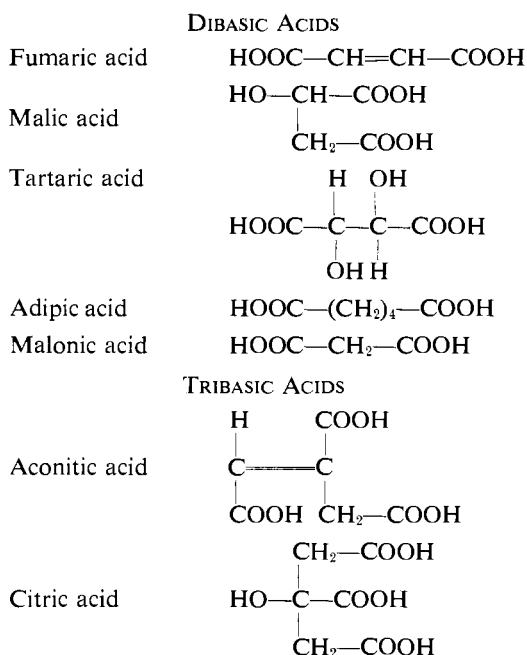
Many organic acids, free and esterified, are distributed throughout the plant kingdom. A great variety of these products are important to the aromatic industry because of their odor and taste. However, as we are at this point concerned with the sour or acid taste, the following is confined to acids which are primarily used as acidulants and not as odorants. As a prerequisite these chemicals have to be practically odorless. Acidulants are applied in a variety of products, such as soft drinks, ice creams, sherbets, hard candies, gelatin products, and effervescent agents releasing CO₂, to obscure unwanted flavors and enhance others.

The physical properties of these acids such as melting points and solubility in a variety of media, are important in the determination of their application. It is the task of the flavor chemist and the food technologist to choose the right acid or combination of acids for a specific job. Economic considerations—i.e., price—are often determining factors in their use.

One inorganic acid, phosphoric acid, has a specific application in a soft drink and is credited as giving a slight taste and mouth feel.

From a chemical point of view these organic acids can be divided into mono-, di-, and tribasic acids, such as:





Sourness is not identical to chemical acidity, which is a function of hydrogen ion concentration. A combination of pH and acid concentration will determine the actual degree of the sour taste. Any of the organic acids at the same pH will exhibit a far greater taste than, for example, hydrochloric acid.

The odoriferous part of natural flavors is generally composed of many chemicals which exhibit a variety of structural diversification.

Odor in this relationship is the total effect or the concerted impact on our odor receptors, of the combined odoriferous chemicals comprising this part of flavor.

Different individual odors are never alike, because only identical chemicals have identical odors. In the odoriferous part of a flavor as many different odors participate as there are individual chemical odorants present in this mixture. However, some of these chemical odorants resemble each other, more or less, in this respect, particularly if we apply such expressions as flowery, fruity, musty, ester-like, and aldehydic, which are common in perfumery.

Because of the relatively great number of different chemicals involved, they are present in a given flavor in various amounts. These chemicals can be classified as:

MAIN CONSTITUENTS, which represent the largest unit quantity or quantities of one or more of the odoriferous constituents. Examples are cinnamic aldehyde in cassia oils and cinnamon oils and methyl salicylate in oil of wintergreen.

MINOR CONSTITUENTS, which will be present in a flavor in smaller unit amounts, but probably in a greater number than the main constituents. An example is rose oxide, which is present in Bulgarian rose oil and in oil of geranium Bourbon.

TRACE SUBSTANCES, which are present only in trace unit quantities.

The value of certain trace substances in flavors can be easily recognized, because such components, present in the natural product or added in minute amounts to a

synthetic composition, will contribute markedly to the development of the full aroma. Such odor contributors are the C_{10} to C_{16} γ - and δ -lactones, identified recently (12) in butter. While present there only in parts per million, they contribute markedly to the flavor of butter-fat.

Hexenals and hexenols are among the important flavor contributors, and are found in small amounts in a relatively great variety of natural products. Recently *cis*-3-hexen-1-ol was detected in peach fruit aroma (25). Because of their potent odoriferous properties, these chemicals should be applied in flavor compositions only in minor or trace quantities.

The full merit of some other of these odor contributors will not always become immediately evident, particularly when examined by themselves. An example is methyl - β - methylthiolpropionate, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{COOCH}_3$, identified in 1945 (8) as a trace substance in pineapple. In some instances it is difficult to recognize the merit of trace substances and such compounds might be labeled as unimportant from the point of view of odor or taste. Great experimental skill and effort will be required to recognize the value of some of these products as odor contributors.

We might expect some of these products of biosynthesis to play an important part in other phases of plant life. It is doubtful that all compounds thus far isolated, or to be isolated in the future from plant materials, will have odor or taste value. Nature might have produced some of these materials for another purpose, unknown to us.

Because of the relatively large number of chemical participants in a flavor, they will have different physical properties, such as boiling points, evaporation rates, etc. While some might be similar, the majority will probably differ markedly in this respect.

To explain the perfect blend of natural odors we can assume that mixtures, such as we are dealing with, will be prone to exhibit the following phenomena:

Evaporation can be compared with distillation and azeotropic mixtures, which behave like a single substance, are likely to be formed.

The fixative influence of chemicals on others, which slows down the evaporation rate of lower boiling chemical constituents, also becomes a possibility.

We can distinguish among:

Top notes, which are the first odoriferous impression one will receive, comprising one or more of the low boiling constituents.

The main odoriferous body, which is composed of the bulk of the odoriferous participants.

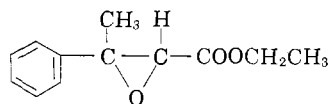
Dry out, which remains after the volatile components have evaporated.

The industrial flavor chemist or flavorist, in his creations, has to imitate a specific, organoleptically well known and accepted complex natural flavor. His work is confined to the duplication of natural effects. It is understandable that he will primarily favor natural products, such as essential oils, oleoresins, true fruit flavors, and specific materials which were isolated from these sources or their duplication in the chemical laboratory.

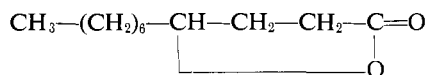
These products will offer, *a priori*, the probability of success. Such compounds are usually known constituents of those flavors, which are to be compounded and will give the finished flavor compound the desired natural aroma.

Modern instrumentation techniques, such as chromatographic separation methods, infrared, NMR, and mass spectrometry, are the main tools used by scientists to isolate such chemicals from their natural sources for identification of their chemical structures, also making possible in many instances their duplication in the chemical laboratory. The results of this endeavor not only constitute a needed contribution to flavor duplication and imitation, but are also appreciated as academic achievements contributing greatly to our understanding of flavor. However encouraging this work is, much remains to be done. Many constituents in natural products await identification. Instability of important flavor contributors, particularly those of certain fruits, makes their separation from their natural environment difficult, hence their identification problematic. In one instance, simple crushing of a fruit was sufficient to alter its chemical constituents; 2-hexanal, the main carbonyl constituent of crushed strawberries, does not exist in the undamaged fruit (34). There are also instances known where chemicals were changed in the course of their instrumental analyses, particularly by vapor-phase chromatography.

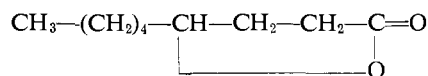
The value of many of the so-called artificial flavors is today well recognized. These are materials not found in nature thus far, but have distinctive odor or flavor value. This property was discovered originally by observation, and no valid prediction could have been made. Many flavor effects cannot be duplicated today by using only natural products. In certain instances the synthetics have stronger odors than the natural products and are indispensable as odor or flavor fortifiers. A typical example is ethyl methyl phenyl glycidate,



a synthetic material having a strong strawberry odor. It is extensively used in the compounding of such aroma. Undecalactone,

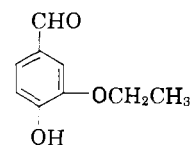


is another example. This chemical, known in the trade as peach aldehyde, is extremely useful in the imitation of the peach aroma. γ -Nonalactone,



has a strong coconut odor. It is widely used as the main constituent for the imitation of this flavor and as a minor constituent in many other flavor compositions.

In a place by itself is ethylvanillin,



which differs chemically from the natural product only by having an ethyl instead of a methyl group. This rather minor structural change makes ethyl vanillin three times as strong as vanillin. A similar situation is encountered with dulcin. The ethoxy group in the para position contributes markedly to the sweetness of this chemical, whereas a methoxy group reduces the taste. The position of the ether group in the ring is also of importance. The ortho isomer of dulcin is tasteless, whereas the meta isomer is bitter (17). Such structural changes are often the cause of similar experimental investigations with other chemicals. However, favorable results are not always obtained. For example, *p*-methoxybenzaldehyde has, by far, a stronger odor than *p*-ethoxybenzaldehyde (15).

Some chemicals which were considered to be strictly synthetics were recently identified in nature. An example is dihydrocapsaicin. It can be assumed that this trend will continue.

Conclusions

Flavor is a conglomeration of many contributing factors. Compared with yesterday, we know more about their many aspects; however, additional knowledge has to be acquired, and this is exactly what is being done by research scientists of various disciplines engaged in this complex field of flavor.

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