21 Creation and Production of Liquid and Dry Flavours

Rainer Barnekow, Sylvia Muche, Jakob Ley, Christopher Sabater,
Jens-Michael Hilmer, Gerhard Krammer
Symrise GmbH & Co. KG,
Mühlenfeldstraße 1, 37603 Holzminden, Germany

21.1
Modern Flavour Creation

21.1.1
The Roots of Flavour Work

Among the oldest known and documented formulae, biblical anointment oils represent an interesting combination of spices such as cinnamon and fragrance materials, for example myrrh [1]. In those days, culinary developments and fragrance creations were heavily influenced by religious ceremonies. In the middle ages both the gastronomic and the fragrance aspects were influenced by new technologies like beer brewing or baking technology as well as the distillation of essential oils. The age of enlightenment and the curiosity of researchers led to the so-called great cycle of the aroma and fragrance industry, which generated numerous aroma chemical and fragrance materials which were all based on the combination of analytical identification of a chemical structure, synthesis, scale up and subsequent production.

In 1874 Wilhelm Haarmann started to produce the first synthetic aroma chemical, vanillin [2–4]. Since then the flavour, fragrance and aroma chemical industry has shown rapid progress. In the beginning, perfumers created the first flavour formula with synthetic aroma chemicals. Over the years many different parameters, like the availability of natural products, the development of food industry and changes in consumers' lifestyles, have led to a broad range of widely accepted flavourings.

In parallel, the fragrance industry has grown to meet consumer preferences with regard to the use of perfumes and also other aspects, such as personal identity, human odours, mood preferences, emotions and psychology [5].

The introduction and rapid development of highly effective analytical instrumentation like the combination of gas chromatography with mass spectrometry (GC-MS) facilitated a significant increase of known aroma chemicals from around 600 in the early 1960s to around 15,000 nowadays. In parallel, the flavourist work profile received strong impulses from the food industry with regard to flavour stability, dosage and flavour application, which finally initiated the development of a sophisticated flavour technology portfolio which comprises liquid and dry blending, plating, spray-drying, emulsions and various encapsulation techniques.

Additionally, in the last 5–10 years an emerging number of low-volatile taste-modifying molecules were found using sophisticated analytical methods based on liquid chromatography (LC), namely taste dilution analysis, LC-MS or LC-NMR methods.

21.1.2
Raw Materials—the Foundation of Every Creation

The world of aroma compounds is becoming more and more complex. In the early days people used aromatic products like fruit juices or fruit juice concentrates which were relatively weak and still close to the related foodstuff. Later, with more knowledge of separation techniques, infusions, extracts, oleoresins and absolutes ranging from weak to strong impact were used to impart aroma. Essential oils such as spice oils already had a very strong impact. Modern analytical technologies allowed the evaluation of the chemical compositions of extracts and essential oils, so that isolates either as powerful mixtures or even as single compounds could be obtained.

The route from cinnamon via the extract, the resin to the cinnamon bark oil and finally to cinnamic aldehyde stands only as one example of the increase in the number of natural aroma compounds. Later, the availability of nature-identical, synthetic aroma chemicals opened great opportunities for flavouristic creativity. In the future, with the completion of the EU positive list and based on the existing FEMA list, the modern raw material portfolio will provide a range of selected aroma chemicals with a defined safety standard. At the same time, well-established aroma chemicals such as estragol have to be omitted because of toxicological considerations. Another growing area a flavourist has to be aware of is the field of non-volatile taste compounds, since a modern flavour solution in the future will comprise the aroma and also a taste part or a taste-modifier part (i.e. umami enhancement, sweet enhancement, bitter masking).

The right choice of raw materials is crucial for creative development (Table 21.1). The final application, the market for which the flavouring will be developed, legislative and ethnic implications, and customer requirements all have to be considered by flavourists when choosing their starting materials.

21.1.2.1
Natural Raw Materials

The field of natural raw materials is dominated by plant derivatives. Important representatives of naturals are the botanical extracts. Extracts can be obtained by water or alcohol–water extraction. Onion extract, for example, is produced by squeezing the washed and ground onion bulbs in large filter presses. The resulting onion juice can then be concentrated to give a stable raw onion extract with superior flavour properties. A valuable by-product is the onion oil which

Table 21.1 Definitions and examples for common raw materials (not necessarily legal definitions)

Flavouring type	Definition/production	Example
Food with flavouring properties	Food or processed food with strong flavours	Vanilla beans, spices
Resins	Evaporated extracts	Pepper oleoresin
Essential oil	Steam distillation	Spearmint oil, lemon oil, pepper oil
Extracts	Alcoholic extracts	Vanilla extract
Natural aroma chemicals	Isolation and purification via physical processes	Citral from lemon grass oil, eugenol from cloves, menthol from *Mentha* species
Natural aroma chemicals	Production via fermentation or enzymatic treatment	Oxidation of 2-methylbutanol to 2-methylbutyric acid via *Acetobacter* species
Nature-identical aroma chemicals	Occur in nature and obtained via synthesis	Vanillin produced from lignin or catechol
Artificial	Do not occur in nature	Ethyl vanillin
Reaction flavours	Thermal treatment of amino acids and reducing carbohydrates based on Maillard reaction	Caramel and malt flavours
Smoke flavours	Preparation based on smoke, produced via defined processes	Smoky ham note

can be obtained via solvent extraction from the condensates of the concentration process.

These extracts are produced from a large variety of plants, like herbs and spices, with or without prior enzyme treatment for the hydrolysis of the cell walls. Extracts from plant or animal material can be generated by solvent extraction but also by complete enzyme hydrolysis of plant derivatives (wheat gluten, soy, etc.) or of real meat, filtration and subsequent concentration of the liquid extract (hydrolysed vegetable/animal protein). These hydrolysed vegetable proteins or hydrolysed animal proteins generate savoury-like notes and also contain a natural content of flavour enhancers such as monosodium glutamate (MSG), inosine 5′-monophosphate and guanosine 5′-monophosphate. The extracts can be used as such or can be further heat-treated as so-called thermally treated extracts or process flavours.

One of the most important and popular extracts from a market-potential perspective is certainly vanilla extract. North America is the largest market, followed by the European market, with ice cream being the largest single application. The predominant vanilla species is *Vanilla planifolia*, which is the basis for a large volume of available extracts. Madagascar is still the largest producer of high-quality vanilla extract, followed by Indonesia.

Vanilla is an excellent example in which a flavourist has to understand the market the flavour is to be created for. The Americans, for example, prefer the more prominent, phenolic and smoky notes, while French consumers are more interested in anisic notes.

In Germany buttery, creamy and balsamic profiles have a long tradition, while vanillin itself represents the key driver for Scandinavia.

The cured vanilla bean consists approximately of 98% of water, fats, waxes, sugar, cellulose, etc. Only some 2% is flavour compounds, the main constituent (approximately 90%) of these being vanillin. Roughly 9% are *p*-hydroxybenzaldehyde, vanillic acid and *p*-hydroxybenzoic acid, which do not contribute much to the overall flavour profile. The remaining approximately 1% of the constituents of the flavour compounds reveals the most significant flavour properties. This part itself comprises more than 400 chemicals giving an extract its specific sensorial "fingerprint" (Fig. 21.1). There are significant differences in the chemical compositions and therefore also in the sensory profiles of vanilla extracts as a result of the geographical origin, the soil, the climate and the processing conditions. Depending on the type of flavour that needs to be developed, a flavourist can start with a specific vanilla extract already supporting the desired flavour profile or with a more neutral extract which is typified with specific qualities.

Another important group is the essential oils which are manufactured mainly from herbs and spices mostly by steam distillation. The advantage of steam distillation is the fact that a clean and powerful oil can be isolated after the distillation step without waxes and other non-volatile compounds but with an odour

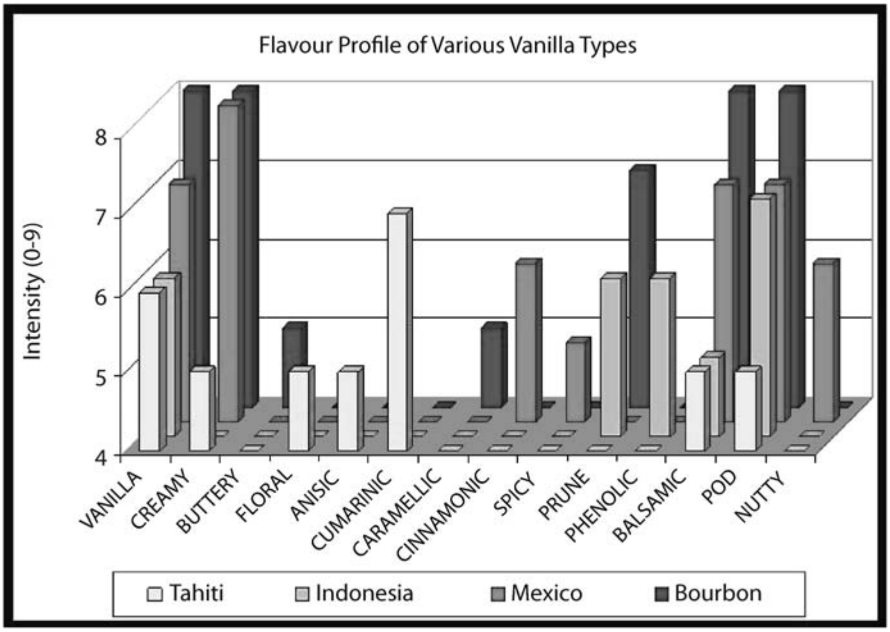


Fig. 21.1 Flavour profiles of different vanilla types

that strongly resembles the odour of the original spice or plant. The disadvantage of losses of highly volatile compounds and non-volatiles as well has to be taken into account. In addition possible chemical reactions and thermal degradation during the process affect the original flavour profile. In this way the essential oil loses some of the freshness and authenticity compared with the original material. Moreover, taste-sensation materials remain to a large extent in the botanical residue. While pepper extracts still have all the pungent spiciness of real pepper, the compounds actually responsible are not present in the pepper oil.

The essential oils from citrus fruits are often obtained through a cold-pressing step from the peel (e.g. orange peel oil). For this purpose several technologies are in use. The most prominent examples are *sfumatura* ("slow folding") with a superficial grazing or total abrasion of the whole fruit and the so-called *pelatrice speciale* method with a constant amount of water for the extraction of the oil. Both processes are very gentle and give very authentic essential oils. The problem of these citrus oils, mainly orange oils, is the presence of high amounts (80–95%) of the non-oxygenated terpenes, limonene being predominant. These terpenes, which do not contribute much to the aroma, can be oxidised when exposed to air and can generate off-flavours. The insolubility of these terpenes, for example, in clear beverage applications remains another disadvantage if citrus oils are used as such. A variety of processes like distillation, solvent extraction and washing can be used to remove the non-oxygenated terpenes to a large extent and to enrich the desired oxygenated terpenes. These processes lead to powerful multiconcentrated oils with a higher solubility in aqueous applications.

Other useful enriched natural materials such as paprika extract are predominantly produced through solvent-extraction methods using solvents or supercritical fluids like CO_2.

Single natural aroma compounds like natural vanillin are obtained through physical separation techniques from edible materials or through natural fermentative processes.

Natural raw materials are of high importance in flavour development. Natural isolates (Table 21.2) serve as a basis for most natural flavourings which can be blended with single natural aroma chemicals. The performance of nature-identical flavourings will be supported by using extracts and oils as they significantly enhance the complexity of flavourings and increase their authenticity.

21.1.2.2
Nature-Identical Raw Materials

Aroma chemicals which are found in natural sources or food preparations but are synthesised by normal chemical procedures are defined by the status "nature-identical". Most of them were discovered and developed during the nineteenth and twentieth centuries. The most important single aroma chemicals produced in very large amounts are vanillin, menthol, citral and anethol. They are used not only by flavour producers but also in large amounts in fragrance

Table 21.2 Important isolates from natural sources

Name	Lead compound(s)	Application
Anise oil	*trans*-Anethol	Alcoholic beverages, oral care
Bitter almond oil	Benzaldehyde	Pistachio flavours
Buchu	(+)-*trans*-8-Mercapto-*p*-menthan-3-one	Black currant flavours
Caraway oil	(+)-Carvone	Savoury flavours
Cardamom oil	1,8-Cineol, α-terpinyl acetate	Baked products
Cinnamon oil	*trans*-Cinnamic aldehyde	Flavours for confectionery products
Grapefruit oil	Nootkatone	Beverage flavours
Clove oil	Eugenol	Oral-care flavours, savoury flavours
Sweet fennel oil	Anethol	Beverage flavours
Ginger oil	β-Sesquiphellandrene	Beverage flavours
Ginger oleoresin	gingerols, shogaols	Hotness, savoury food, confectionery
Juniper berry oil	α-Pinene	Alcoholic drinks
Laurel leaf oil	1,8-Cineol	
Marjoram oils	1-Terpinen-4-ol, *cis*-sabinenhydrate	Savoury flavours
Cornmint	(-)-Menthol	Chewing gum, oral care
Spearmint	(-)-Carvone	Chewing gum, oral care
Origanum oils	γ-Terpinene, *p*-cymene, thymol, carvacrol	Savoury flavours
Star anise oil	*trans*-Anethol	Beverage and confectionery flavours
Thyme oil	Thymol	

applications. On the other hand, there are a lot of so-called high-impact flavour chemicals, which are produced only in very small amounts as a result of their low threshold levels, for example acetyl thiazoline and 1-menthen-3-thiol. Most of these materials are produced in high purity and therefore provide highly standardised sensorial properties for top note creation.

21.1.2.3
Ethical Requirements

Flavourings created for the US market or Israel normally have to follow requirements for kosher status, whereas markets as the Near and Middle East and parts of Asia (e.g. Indonesia, Philippines) have a strong need for halal flavourings. As the flavour market is becoming more and more global, even the European companies in the flavour industry have to be certified by the respective certifying authorities. In general these requirements result in a reduced number of raw materials and in specific cases also carrier materials (e.g. omission of ethanol for halal flavours) for the daily project work of a flavourist.

21.1.3
Process Flavours

Process flavours or process flavours play a key role in those food products which have been exposed thermal treatment during processing and final preparation, where heating steps during preparation are applied.

Since process flavours are generated by the interaction of raw materials like protein derivatives (amino acids) and reducing sugars (Maillard reaction), it is obvious that a large number of prepared food products are affected:

- Meat products, e.g. beef, chicken, pork, lamb
- Vegetables, e.g. onions, potatoes, garlic
- Roasted products, e.g. coffee, cocoa, roasted nuts, popcorn
- Cereal products, e.g. biscuits, bread, extrudates
- Beverages, e.g. beer, wine, whiskey

The generation of non-volatile components plays an important role because important attributes like umami, mouthfeel, texture, etc. can be given to the final products.

Besides the well-known Maillard reaction, additional reactions like sugar degradation, fat oxidation and interaction of Maillard intermediates are major sources for powerful flavour materials.

21.1.3.1
Process-Flavour Creation

For the production of process flavours, heat has to be applied to the raw materials for the thermal processing. This offers different possibilities for the production process:

- Heating in a (non-sealed) reactor (without pressure)
- Heating in an autoclave (with increased internal pressure)
- Heating in an extruder (continuous process)

All these methods provide different possibilities regarding throughput, temperature, pressure, etc. While non-sealed reactors have the simplest production setup, they are limited in the possible reaction temperature to the boiling point of the solvent, e.g. 100 °C for water. In contrast, autoclaves allow much higher reaction temperatures. An extruder system is especially useful for products with higher viscosity and provides all the advantages of a continuous production process rather than batchwise manufacturing.

The maximum permitted temperature for the production of process flavours is around 180 °C, as defined by legal regulations, but in general, the temperatures actually used are much lower in order to be able to reach a broad variety of different flavour profiles, such as cooked, boiled, fried, roasted and shallow-fried notes. The pressure during the reaction is usually below 10 bar (10,000 hPa).

21.1.3.2
Process-Flavour Stability

In order to achieve a long shelf life for the products, drying techniques like spray-drying, vacuum-drying or evaporation can be applied to produce dry powders or paste products. Conventional carrier materials are, for example, sugars (i.e. glucose or lactose) or high molecular weight products like gum arabic or maltodextrin.

Dry products can not only improve the microbiological stability but can also improve the sensorial stability, since chemical and physical interactions and degradations are limited to a minimum.

In the modern production of process flavours, the following topics are coming more and more into focus:

- Generation of inexpensive high-impact products (low dose)
- Generation of flavourful food preparations, based on the reaction of foodstuffs
- Generation of allergen-free products

21.1.4
Taste Modifiers

In the past the most common tastants used were sweet carbohydrates, inorganic salts (mainly sodium chloride, but also buffering salts), amino acids, especially MSG, fruit acids and phosphoric acid and to some extent bitter components such as caffeine, but also low-volatile chemosensates such as capsaicin and cooling compounds such as menthyl lactate. Most people are adapted to the classical ingredients which show a very high positive hedonic score and now are in several cases disfavoured for health-related reasons: the extensive consumption of (saturated) fats, sucrose, glucose and high-fructose corn syrup (HFCS) may cause obesity under certain circumstances, and as a consequence, some related diseases such as type II diabetes and cardiovascular disease and sodium chloride can cause hypertension, especially in persons who are prone to this effect [6]. MSG—one of the world's most important umami compounds—is found in many food preparations introduced by basic ingredients, for example vegetables such as tomatoes and various meat selections or seafood materials. At the same time, MSG is discussed in the context of adverse effects like the so-called Chinese restaurant syndrome. As a consequence, added MSG is disfavoured in some countries.

As a direct result of this so-called food-minus trend some of the ingredients have to replaced or reduced. Owing to their role as preference drivers in food consumption, it is important to retain the whole flavour and taste profile of the original product, which can be done in most cases using a mixture of flavours, tastants, taste modifiers and texturants.

Another problem arising from modern food trends is the off-taste generated by fortification. The fortification with healthy polyphenols, for example from grape seed or green tea, causes pronounced astringency or bitterness. The addition of selected fats such as fish oil causes strong metallic and rancid off-flavours. A very special problem arises in the growing use of soy products, which in several cases cause astringent, "beany" and bitter off-notes.

21.1.4.1
Masking Technologies

The challenge of masking is to suppress unpleasant tastes in functional or lightened-up products without negatively affecting the sensory profile, mouthfeel or the effectiveness of functional ingredients in a label-friendly way. Masking is a very complex challenge since there is no off-taste blocker system which can be applied in a universal way. In fact, rather a detailed analysis of the product formulation and a tailor-made application of appropriate masking strategies are required. There are several ways to fight against off-tastes:

- Identification and elimination of compounds causing off-tastes. Elimination is often process-optimisation oriented and in general not a matter of flavour development or optimisation.
- Retardation of release of functional ingredients. Since most of the biofunctionals express their functionality after passing the oral cavity, emulsion and encapsulation techniques are a perfect delivery system for food applications. Important aspects of this approach are stability and the beneficial combination with flavour systems.
- Masking via enhancing positive sensory drivers can lead to the suppression of negative sensory drivers. This can be done by addition of sweeteners/acidulants, congruent flavours with the ability of suppression and round-off, and real taste-masking and flavour-modifying components.

The masking topic is especially difficult. Off-taste generating ingredients can act very differently in the receptor landscape in the mouth. Especially for bitter taste, roughly 24–30 different receptors are known, which show a certain binding pattern to bitter molecules [7]. In addition, the transduction mechanisms of taste signals in bitter and sweet taste cells are very similar; therefore, it is difficult to develop a "universal" bitter blocker. Several molecules such as adenosine 5′-monophosphate (**1**) [8], neodiosmine (**2**) [9], homoeriodictyol (**3**) [10], γ-aminobutyric acid (**4**) [11] and some Maillard products originating from β-alanine or γ-aminobutyric acid (e.g. **5**) [12] were described as bitter-masking compounds (cf. Figure 21.2) and some of them were approved as generally recognised as safe (GRAS) (e.g. adenosine 5′-monophosphate) or Flavour and Extract Manufacturer's Association (FEMA) GRAS such as homoeriodictyol.

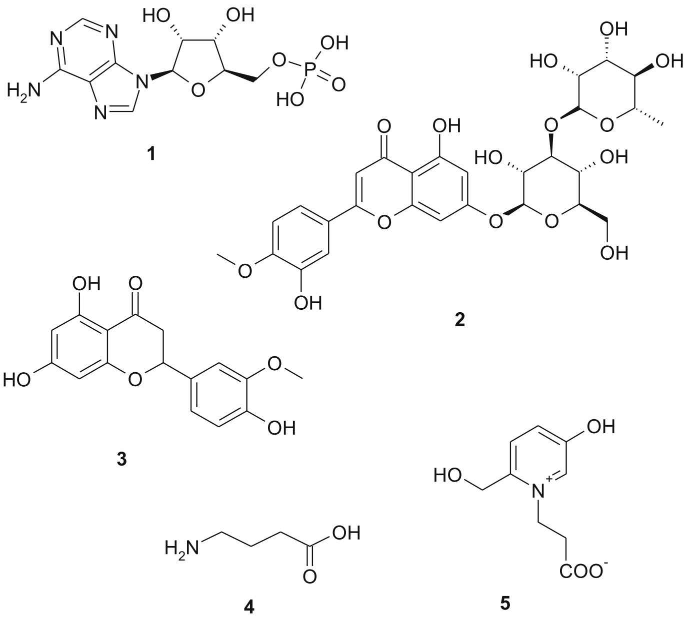


Fig. 21.2 Masking molecules towards bitter taste

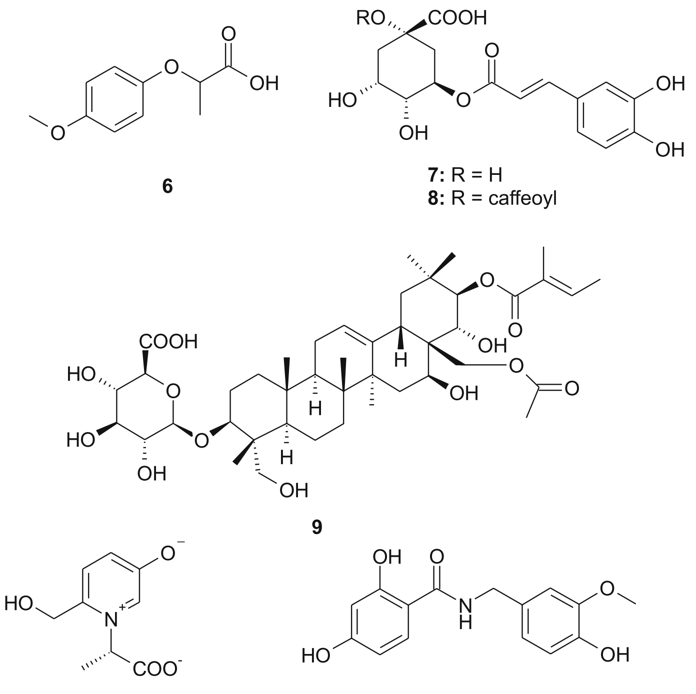
21.1.4.2
Sweet Optimisation

Foods which have a high sugar content (primarily sucrose, lactose, glucose or fructose or mixtures thereof) are usually strongly preferred by consumers owing to their sweetness. On the other hand, it is generally known that a high content of easily metabolised carbohydrates allows the blood sugar level to increase greatly. This leads to the formation of fatty deposits and can ultimately lead to health problems.

As a consequence, in most cases, mixtures of low-calorie sweeteners are used to address this issue. At the same time, numerous sensory and consumer tests have shown major differences between low-calorie sweeteners and sucrose or HFCS with regard to body and aftertaste.

In these cases, masking flavours can be used together with a rebalancing of the flavour profile to cover the changes in perception. The use of sweet inhibitors such as lactisol (**6**, Fig. 21.3) can help to reduce the lingering aftertaste in some cases.

An improvement in the taste properties, in particular the aftertaste problem of non-nutritive, highly intensive sweeteners, can be achieved by the use of tannic acid [13, 14].



6

7: R = H
8: R = caffeoyl

9

10

11

Fig. 21.3 Sweet-taste modifiers

Some other sweet taste modifiers have been described in the literature. Chlorogenic acid (7) and 1,5-dicaffeoyl quinic acid (cyanarin, **8**) from artichoke [15] can induce a sweet water taste, i.e. a sweet impression of water which is applied to the tongue after rinsing the mouth with the solution of the caffeic acid derivatives (Fig. 21.3). The proteins miraculin from miracle fruit [16] and neoculin and curculin occurring in the fruit of *Curculigo latifolia* [17] are able to induce sweet taste by using acidic solutions. Unfortunately, in both cases the effects are only perceived in the consecutive sequence and therefore the effects cannot really be used in food. Some triterpenoids such as gymnemic acids (e.g. **9**) occurring in *Gymnema sylvestre* are able to inhibit sweet perception similar to lactisol [18].

For some applications, it is of great interest to increase sweetness of sugar or HFCS-reduced products without using sweeteners. In several cases, it is possible to use supportive flavours [19] or to optimise the flavour to improve the overall profile [20–22] and to retain the preference. Significant importance is attributed to compounds which may increase the sweet sensation without showing significant intrinsic sweetness and strong flavour profile. Just recently, interesting compounds such as alapyraidine (**10**) [23], a general taste enhancer, were studied. In addition, sweetness-enhancing hydroxybenzoic acid amides of vanillylamine (e.g. **11**) were reported [20].

21.1.4.3
Savoury Enhancement

Owing to the unfavourable effects of high levels of ingested sodium ions on blood pressure, lowering the sodium content of food is one of the hottest topics in food development. On the other hand, salt taste, which is mainly caused by sodium chloride, is a main preference driver for most consumers. In liking tests, the sample containing higher amounts of sodium is often preferred. Additionally, sodium chloride or other sodium salts such as sodium gluconate have been used as maskers for bitter off-tastes [24] and as a common taste enhancer since ancient times. Therefore, the sodium problem is correlated not only to savoury products but also to sweet foods or beverages.

Reduction of the sodium chloride level can result in taste problems and flavour shifts. There are several approaches to maintain salt taste. Most often, potassium chloride is used, because it shows the most prominent salty taste of those applicable inorganic salts. Lithium chloride is the most salty salt but cannot be used for toxicological reasons. Most consumers, however, complain about the bitter, chalky taste of KCl-containing formulations. Development of sodium-reduced products using mineral salts is a challenge and the whole product formula has often to be adapted [25]. Therefore, the main focus of the research was the search for masking compounds or technologies to cover the bad taste of KCl, e.g. phenolic acids and derivatives [26] and lactisol [27].

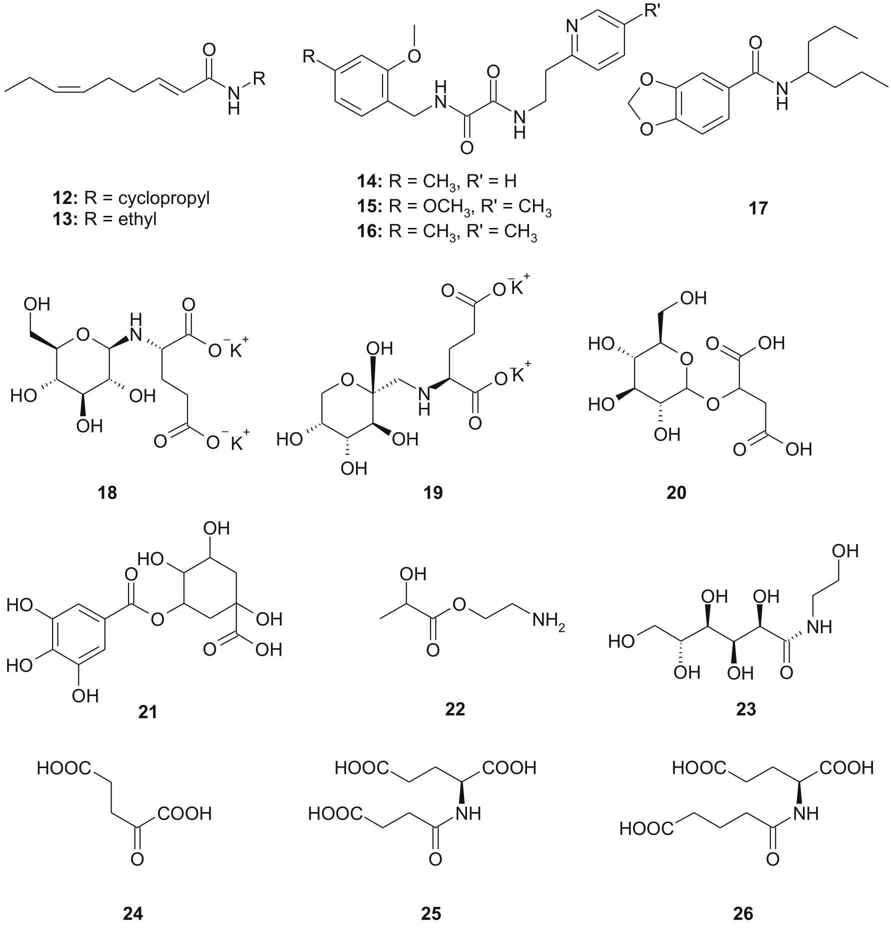
The salty and savoury character of salt-reduced food can be maintained by using glutamic acid salts, mainly MSG, but also the corresponding potassium and calcium salts [28, 29]. This strategy does not find wide acceptance because of the previously mentioned reasons.

In some cases, yeast preparations which contain a high amount of nucleotides can be used to increase saltiness in combination with masking off-notes of KCl [30]. Additionally, use of low amounts of fruit acids may reduce the bad taste of KCl-containing food preparations [31]. Usage of low amounts of sweeteners such as thaumatin [32] or neotame [33] was described to mask the off-taste of KCl.

Salty taste enhancing preparations or compounds besides KCl were described. For example, a mixture of certain amino acids based on L-lysine were used to increase the saltiness of a NaCl-reduced preparation [34]; *γ*-aminobutyric acid (**4**) was also used as a salty taste enhancer [35]. Some dipeptides such as *N*-L-ornithyl taurine hydrochloride or *N*-L-lysinyl taurine hydrochloride were described as very salty with a clean salt taste [36]. Additionally, choline chloride was suggested as a salt enhancer [37].

More recently, some new savoury-enhancing molecules have been described by Soldo and Hofmann [12] (alapyraidine **10**, Fig. 21.3). In addition, it was found that potentially pungent compounds such as midchain unsaturated alkamides **12** and **13** can enhance the salty or savoury taste [38, 39]. Most of the new savoury enhancers which were found via high-throughput screening based on the umami receptor [40] are not based on traditional natural product chemistry, e.g. oxalamides **14**–**16** and benzoic acid amide **17**. Combinations of pungent chemosensates such as cetylpyridinium chloride in combination with amino acids such as arginine were described as salt-taste enhancers [41].

Other components described in the literature which are able to enhance saltiness or umami taste are umami-tasting glutamate glycoconjugates (e.g. **18** or **19**) [42], (*S*)-malic acid 1-*O*-D-glucopyranoside (morelid **20**) [43], theogalline (**21**) [44], *N*-lactoyl ethanolamine (**22**) [45] and *N*-gluconyl ethanolamines (**23**) [46], *α*-keto acids derived from amino acids (e.g. **24**) [47] and some *N*-succinoyl derivatives of aspartic acid or glutamic acid (e.g. **25** and **26**) [48].



12: R = cyclopropyl
13: R = ethyl

14: R = CH_3, R' = H
15: R = OCH_3, R' = CH_3
16: R = CH_3, R' = CH_3

17

18 **19** **20**

21 **22** **23**

24 **25** **26**

Fig. 21.4 New savoury-taste enhancers

21.1.5
Chemosensates

Chemosensates play a tremendous role in flavour creation, especially for exotic and spicy foods or beverages. Chemosensates can be roughly classified into pungent/hot, tingling, cooling and astringent compounds. In contrast to the volatile flavours, which mainly act on the olfactory epithelium and bind to the olfactory receptors, and the tastants, which act on the taste buds and bind to the different taste receptors, the chemosensates act directly on the afferent nerve endings of the trigeminal ganglion in the face or mouth or on the afferent nerve endings of the dorsal root ganglions (DRG) in the skin. There are different types of trigeminal/DRG fibres: some are sensitive to heat, heat and mechanical stress, coldness, cold/heat and mechanical stress, etc. It is now known that temperature changes, the absolute temperature and mechanical stress can increase the signalling frequency of the neurons, which results in more or less severe pain feelings and reactions. The chemosensates are able to change the sensation threshold of the fibres or of the temperature-sensing receptors and can therefore initiate signalling at body temperature. As a consequence, chemosensates can induce a temperature feeling without changing the physical temperature [49]. Astringency is sometimes referred to as being a trigeminal sensation and is caused in most cases by precipitation of proline-rich proteins in the saliva by astringents such as catechins or gallated carbohydrates; there are indications that astringent polyphenols such as quercetin glycosides be directly act on the receptor level [50].

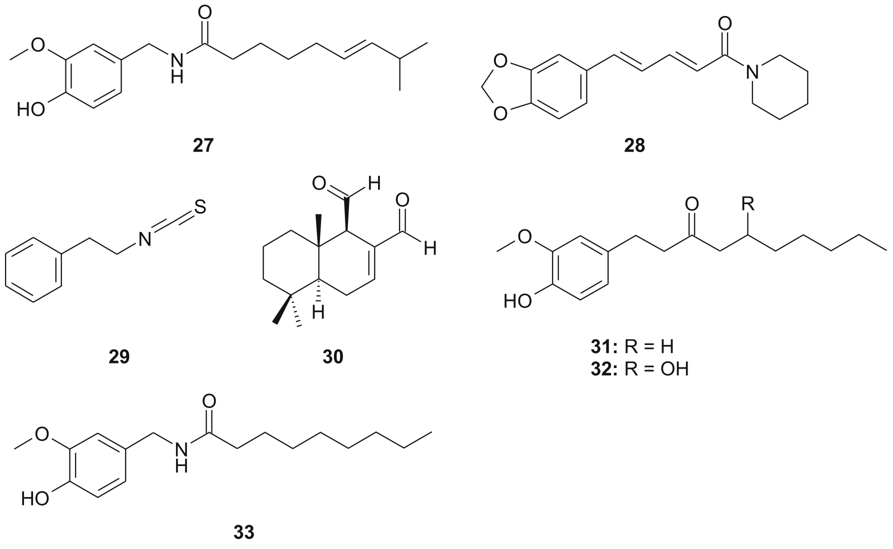


Fig. 21.5 Hot and pungent chemosensates

21.1.5.1
Pungent/Hot Compounds

A huge number of compounds causing a pungent or hot sensation are known from natural sources. In Fig. 21.5, some of the most important examples are illustrated: capsaicin (**27**) from chili pepper, piperine (**28**) from pepper, isothiocyanates (e.g. **29**) from Brassicaceae ssp., some dialdehydic drimanes (e.g. **30**) occurring in Tasmanian or water pepper, paradols (e.g. 6-paradol **31**) or gingerols (e.g. 6-gingerol **32**).

These compounds are all used in the form of ingredients occurring in the aforementioned oleoresins or extracts obtained from the corresponding plants. In some cases (like capsaicine and piperine) single compounds are used in flavourings. Capsaicine is restricted in the EU owing to its genotoxic potential [51]. Another capsaicinoid is nonivamide (**33**), which is characterised by a saturated side chain.

Pungent and hot compounds are used especially in savoury formulations and seasonings but can also be formulated in low amounts for other applications.

21.1.5.2
Tingling Compounds

Tingling sensation is an unusual and polarising sensation. The effect can be described by the perceived sensation after administering a 9-V battery to the tongue. There are assumptions that the effect is caused by a simultaneous activation of thermal and mechanosensitive fibres [52]. Important compounds inducing a tingling sensation are unsaturated medium-chain alkamides such as spilanthol (**34**) from *Spilanthes* ssp. or *Heliopsis longipes* [53], sanshools (e.g. *α*-hydroxysanshool, **35**) or pellitorine (**36**) from Roman pellitory root or *Piper* ssp. (Fig. 21.6).

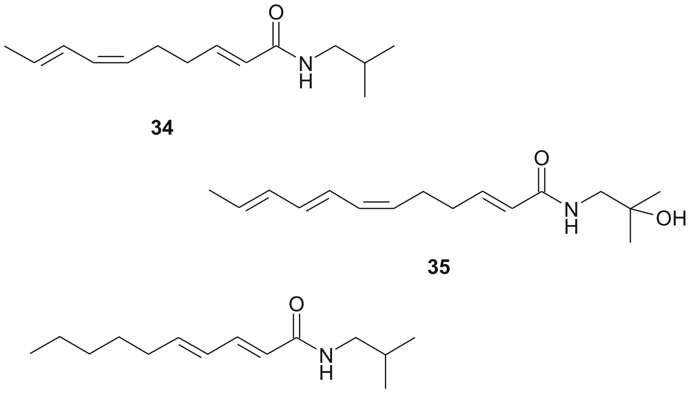


Fig. 21.6 Tingling chemosensates

Tingling compounds are mostly used in oral-care products and chewing gums. In low amounts, they can be used for spicy formulations. Most of the tingling compounds can trigger salivation to a certain extent [54].

21.1.5.3

Cooling Compounds

Besides the widespread usage in oral-care products and chewing gums, strongly cooling compounds are very rarely found in nature. Among the compounds which occur in nature, the odour-active L-menthol (**37**) and some direct derivatives such as the more or less tasteless L-menthyl succinate (**38**) and L-menthyl glutarate (**39**) [55] and the L-menthyl lactates (**40**) are known [56]. In addition, cubebol (**41**) was described as a moderately effective cooling compound [57]. On the other hand, a lot of artificial cooling compounds were developed in the past and the most important are shown in Fig. 21.7. The menthane carboxylic acid amides WS 3 (**42**) and WS 5 (**43**) are the most active cooling compounds known so far. Furthermore WS 23 (**44**), the l-menthone ketal of glycerol **45**, L-menthyl glyceryl ether **46**, and the L-menthyl carbonates of propylene glycol and ethylene glycol (**47** and **48**) are used as artificial compounds.

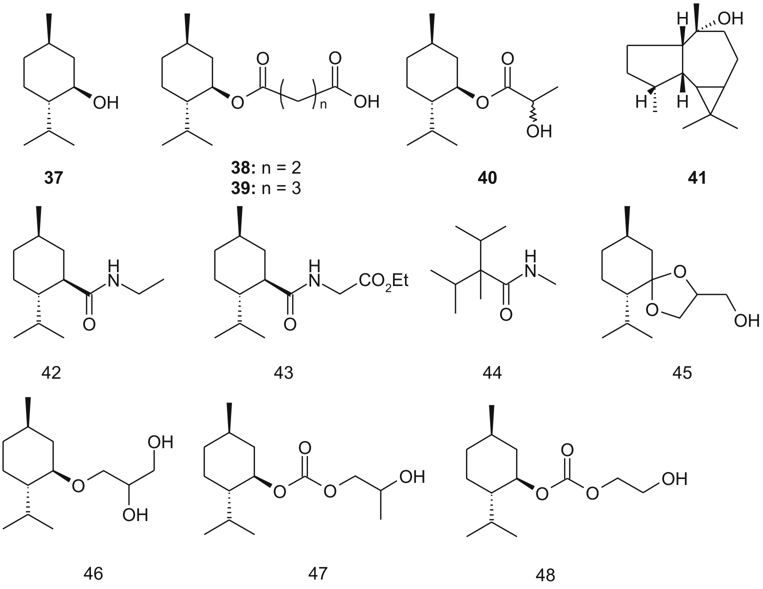


Fig. 21.7 Cooling chemosensates

21.1.6
Modern Tools for Flavour Development—Flavour Creation

Flavour work is characterised by basically two different views: the perspective of the application segment and the types of raw materials which are used. Complex raw materials like spices for seasoning blends and citrus oils for beverage flavours always bring advantages with regard to the body and the completeness of the final composition. Single molecules and purified fractions of, for example, essential oils usually offer the possibility to do a complete flavour design without any limitations arising from complex raw materials such as extracts and distillates from plants, roots, barks and fermented foodstuffs. The art of the flavour work comes into play when the flavourist starts to construct quantitative and qualitative skeletons for his composition. The main pillars of the first formula differ between the different application segments. In the field of non-alcoholic beverage development, juice, juice-derived materials, extracts, distillates and essential oils are of key importance. This is also true for a variety of vanilla flavourings. For many sweet and confectionery flavours, single aroma chemicals such as ethyl butyrate for fruity notes and sulphur compounds like methyl thioethyl propionate for tropical notes are essential for the final flavouring. In particular savoury flavours are based on important aroma chemicals such as 2-methyl furanthiol.

Young flavourists create the first formula in a trial-and-error approach. Experienced flavourists know how to create the first blueprint based on a qualitative and quantitative skeleton in a focussed and efficient way, because the roles and the interactions of single compounds have been learned over the years.

21.1.6.1
Modular Flavour Concept

A successful flavour is based on different elements. A very important part is the selection of the most potent volatile aroma compounds. All we eat, every fruit, every meal, every drink, every cup of fresh coffee contains a combination of various volatile flavour ingredients.

A strawberry, for example, has a total content of 10-ppm volatile flavour compounds. This amount of flavour is made up of at least 300 single raw materials. Each of these single ingredients has a special flavour character. Some of them are very strong, others are quite weak. It is very important to know the character and the strength of each individual ingredient. Only then is it possible to know the exact influence of a single ingredient in the total flavour. It is also important to know that all components have a more or less different flavour character. Some of them are more fruity, others are more floral and some of them have a very fresh leafy character, like freshly cut grass. Some of them are quite similar. It is possible to distinguish between all of these characters and select those which have a similar flavour impression. On the basis of this selection it is possible to develop a so-called building-block concept, which comprises different groups of important flavour characteristics. The example of modular strawberry flavour illustrates the blueprint and the strategy behind this flavour-creation concept.

A fresh strawberry flavour contains a group of flavour materials which are described as "green", like fresh leaves or similar to freshly cut grass. The main representatives are chemicals like (*E*)-2-hexenal or (*Z*)-3-hexenol. On the basis of a detailed description of all ingredients, it is possible to select all raw materials which are described as "green". Finally all those similar green components are put together into one basic mixture—a so-called green base.

Using the same approach, we can combine all other important volatile ingredients of a strawberry to form specific bases. All fruity esters like ethyl butyrate, ethyl caproate or ethyl isobutyrate can be combined to a "fruity base", and all caramel-like ingredients to a "caramel base", and so on. Finally, all major flavour characters of a strawberry can be obtained by appropriate combination of only a few bases.

With these building blocks it is possible to reassemble various types of strawberry flavours with fruity, spicy or ripe flavour character without dealing with the complexity of more than 300 single raw materials. This approach speeds up the combinatorial elements of the flavour work and provides an excellent learning platform for young flavourists.

21.1.6.2
Odour- and Taste-Activity Concept

Modern scientific tools like the so-called odour-activity value (OAV) concept were developed to unravel the quantitative and qualitative pattern of individual chemicals. Quantitation is achieved in an extremely accurate way by means of isotope dilution analysis.

In combination with the threshold of a flavour compound in a given matrix, it is possible to calculate the OAV value using the following formula:

$$\text{OAV} = \frac{\text{concentration of a flavour compound in a food}}{\text{threshold of a flavour compound in the corresponding food matrix}}$$

The complete OAV analysis of a food target is time-consuming and requires an excellent analytical setup. In many cases the well-established combination of GC combined with olfactometry provides an excellent insight with regard to the composition of aroma compounds in a mixture and the role of individual chemicals.

In recent years, non-volatile taste compounds have been becoming more important in the area of modern flavour development. Therefore, the principal approach of the OAV has been adapted for the taste side in the form of the so-called taste-activity value. In order to facilitate the search for taste-active materials and for a better understanding of the "taste dimension" of foodstuffs, a new instrumental setup called LC-Taste® has been developed [58].

Non-volatile ingredients play an important role in the overall flavour character of fruits and other foodstuffs. Many non-volatiles have a strong effect on the sensorial properties such as mouthfeel, creaminess and juiciness. Experienced flavourists know how to combine both the volatile and the non-volatile worlds of raw materials for delicious flavours.

21.1.6.3
The Sensorial Relevance of Ripening Effects

Apple flavour is an excellent example for chemical reactions which are responsible for the so-called ripening effect of juices, distillates and purees.

Starting from only one single ingredient, e.g. (*Z*)-3-hexenal, many other ingredients are formed during treatment and ageing of a fruit (Table 21.3). This effect has a strong contribution to the strength and character of the flavour.

During the production of recovery flavours, apple wines or brandies, the interaction with ethanol, acetaldehyde and acetic acid represents the next level of interactions. The reaction products contain compounds which result from esterification and acetal formation reactions, which are summarised in Table 21.4.

Table 21.3 Reaction products from isomerisation and degradation of (*Z*)-3-hexenal

Compound	Intensity
(*Z*)-3-Hexenal	Very strong
(*Z*)-3-Hexenol	Medium strong
(*E*)-2-Hexenal	Very strong
(*E*)-2-Hexenol	Medium strong
(*E*)-2-Hexenoic acid	Weak
3-Hydroxy hexanoic acid	Weak

Table 21.4 Reaction products originating from (*Z*)-3-hexenal, ethanol, acetaldehyde and acetic acid

Compound	Intensity
(*Z*)-3-Hexenyl acetate	Strong
(*E*)-2-Hexenal diethyl acetal	Medium strong
(*E*)-2-Hexenyl acetate	Strong
Ethyl-(*E*)-2-hexenoate	Medium strong
Ethyl 3-hydroxyhexanoate	Medium strong
(*E*)-2-Hexenal di-(*E*)-2-hexenyl acetal	Weak
(*E*)-2-Hexenyl-(*E*)-2-hexenoate	Weak
(*E*)-2-Hexenyl-3-hydroxyhexanoate	Weak

21.1.7
The Specifics of Flavour Application

The field of flavour application is basically driven by three main influencing factors. The market for flavoured foodstuffs and the technology which is needed for the flavour formulation have always played an important role in the flavour industry. In recent years, the relevance of the corresponding food technology has grown significantly. Among the most important fields of application, the beverage market represents a key area. Soft drinks, fruit-juice-containing beverages as well as alcoholic beverages and instant drinks are produced in an enormous variety of flavour and packaging materials. In the UK the market showed an increase of soft drinks and fruit juices of some 7% in 2003 over 2002. In the 10 years between 1993 and 2003 this same market grew from a consumption of around 9 billion litres to around 14 billion litres in a full year.

This growth rate is accompanied by an ever-increasing range of flavours and ingredients. Products are more and more being designed for lifestyle and for age groups. Meanwhile, a remarkable portfolio of product types has been established in the market (Table 21.5).

The aforementioned products are commercialised at different concentration levels, for example ready to drink or dilute to taste in the case of syrups.

The matrix for flavour applications in the beverage industry illustrates the tremendous variation for the required flavour systems with regard to sensory and

Table 21.5 The variety of product types of flavoured beverages (modified after Ashurst [65])

Soft drinks	Other drinks	Alcoholic beverages	Dry beverages
Definition	Tea	Flavoured beer	Instant beverages
Sweetened	Flavoured ice tea	Shandy-type products	Fruit beverages
Water-based			
Balancing acidity			
Juice and/or pulp content	Coffee-type Beverages	Wine coolers	Flavoured teas
No juice	With flavours	Low flavoured	Liquid flavour
Low juice	With dairy raw materials	High flavoured	Dry flavour
High juice			
Carbonation	Milk beverages	Liqueurs	Dry coffee type beverages
Carbonated	No juice	Flavoured	With creamer
Non-carbonated	Low juice	Non-flavoured	Without creamer
Alcohol content	Soy beverages	Spirits	Vending machines
Alcohol-free	Masking flavours	Extracts	Flavoured pads
Low alcohol content	Cream flavours	Distillates	

regulatory background. In addition, the wide range from liquid to dry applications emphasises the broad scope from emulsion technologies to spray-drying.

21.2
From Formula to Product

The formula of a liquid or dry flavouring represents the blueprint for a final product. At this stage various parameters of influence have to be considered. Besides the compounding or mixing instructions with impact on the solubility of compounds, the chemical interaction of formula constituents is one of the most important parameters.

The formula of a liquid flavouring usually comprises the list of ingredients and a short summary of the corresponding blending instructions. At this stage the solubility of the ingredients in the carrier system is of high importance. Additional criteria can be summarised under the headline of shelf-life stability.

21.2.1
Shelf-Life Stability

The modern food industry is confronted with the consumers' increased requirements concerning their final products. Apart from product safety, further crucial characteristics such as colour, flavour, texture and sensory stability are important issues for the evaluation by the consumer. Thus, the requirements for the flavour of the final product are increasing. This requires extensive knowledge in various fields.

- Processing properties of the flavour
- Behaviour of the flavour during the production of the food
- Behaviour of the flavour during the shelf-life of the food
- Interactions of flavour and foodstuff

Apart from simple handling and easy dosage, a constant high product quality and a guaranteed shelf life are absolutely essential. That means that the taste of the food products has to be constant during the entire product life [59].

The term "stability" in the following text will represent the sensorial quality of a food product during its whole life span under suitable and defined conditions. The stability of a food product is affected by a multiplicity of factors, like process temperature and time, residual moisture, degree of browning and the physical and chemical constitution of the ingredients. A further factor of crucial importance is the type and the quality of the packaging material [60]. The execution of real-time stability tests is essential for control purposes in the food industry. Storage conditions have to be adapted as realistically as possible: the products should be kept in their original packaging, temperature and light conditions should be realistically adjusted and varying conditions, e.g. during transportation, should also be included in the test parameters. During the development of food products real-time tests have a crucial disadvantage. They are very time-consuming.

21.2.2
Accelerated Shelf-Life Testing

There is considerable evidence in the literature that temperature plays a major role in causing changes in food quality during storage. Higher storage temperatures generally lead to increased quality deterioration. In the past, there have been several attempts to use mathematical techniques and models to describe changes in food quality as influenced by storage and temperature [61]. Not all ageing processes are influenced in the same way. So, for instance, a storage temperature increase of 10 °C will speed up Maillard reactions by a factor of 2.5 but will speed up oxidation reactions only by a factor of 1.5. This also depends on the total composition of a product. In the past, accelerated stability testing methodologies based on time, temperature and modified oxygen atmosphere were developed in order to accelerate shelf-life stability under defined conditions [62]. A new rapid method was developed which is even more adaptable to different food product types.

In general, a dry or liquid ingredient is brought into a high-pressure container without any sample preparation (Fig. 21.8). After closing this vessel, the product is exposed to oxygen pressure and heat. After a defined storage period, the sample can be used for further testing. In the subsequent sensory panel work, the samples are tested in a triangle test by comparing the nonstressed sample with the stressed one. If the panel is not able to detect a significant difference between the two samples, the sample can be considered as "stable" for the simulated time frame.

In case there is a significant difference between the stressed and the nonstressed sample, off-flavours or strong sensorial deviations are monitored. As a next step, further analytical evaluations, e.g. GC-MS, are performed for the identification of relevant degradation products.

Fig. 21.8 Principle of accelerated stability testing [63]

Figure 21.9 illustrates the correlation between temperature and testing time for real-time conditions and accelerated test conditions.

The kinetics of degradation processes in foodstuffs are not simulated by the accelerated shelf-life testing method in the same way. Different parameters like a_w value, pH value, acidity levels, sulphur compounds, etc. affect flavour degradation in the foodstuff very individually; therefore, a careful transfer of results is absolutely essential. The tested products have to be clustered depending on their ingredients and parameters for the accelerated testing have to be adapted (Fig. 21.10).

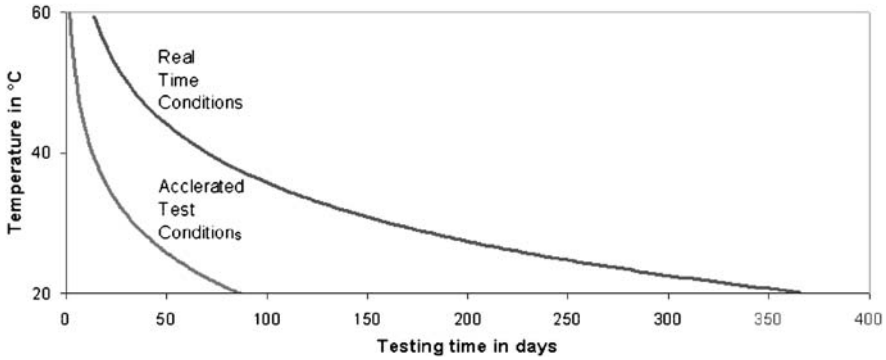
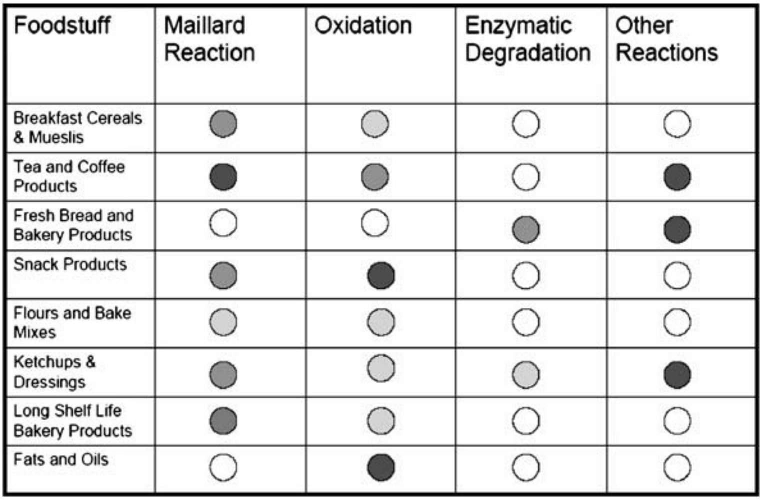


Fig. 21.9 Correlation of conditions in accelerated stability testing with real-time testing (1 year at room temperature) [63]



Foodstuff	Maillard Reaction	Oxidation	Enzymatic Degradation	Other Reactions
Breakfast Cereals & Mueslis	◑	◔	○	○
Tea and Coffee Products	●	◑	○	●
Fresh Bread and Bakery Products	○	○	◑	●
Snack Products	◑	●	○	○
Flours and Bake Mixes	◔	◔	○	○
Ketchups & Dressings	◑	◔	◔	●
Long Shelf Life Bakery Products	◑	◔	○	○
Fats and Oils	○	●	○	○

Fig. 21.10 Degradation hazards in different foodstuffs, white: low, black: high [63]

21.2.3
Chemical Interactions

The stability of the flavour in the food is an enormously complex issue. In order to come to a reliable prediction, the reactivity of flavour compounds and the embedding in the corresponding food matrix have to be considered. The interactions of flavours and foodstuff can be clustered into two main groups:

1. Degradation of flavour ingredients and subsequent flavour loss
2. Formation of new flavouring substances and, as a direct result, off-flavour formation

The typical flavour profile of many foodstuffs is not only characterised by so-called character-impact compounds like cinnamic aldehyde for cinnamon, vanillin for vanilla and eugenol for cloves. Flavour changes during processing and storage and the corresponding flavour stability are based on numerous chemical interactions which are directly linked to organoleptic properties. Table 21.6 summarises the main chemical reactions which are responsible for causing flavour changes.

Table 21.6 Overview of chemical interactions responsible for flavour changes

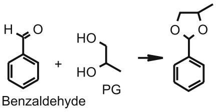
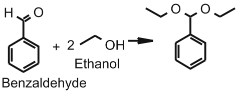
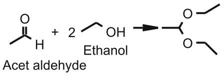
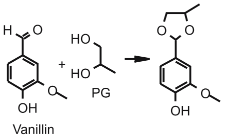
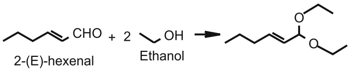
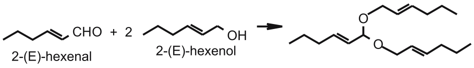
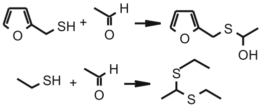
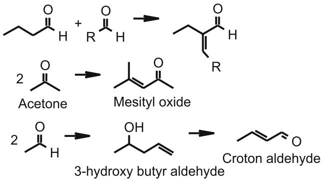
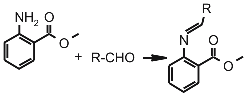
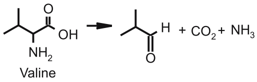
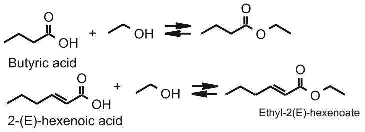
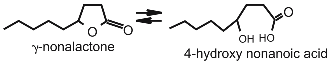
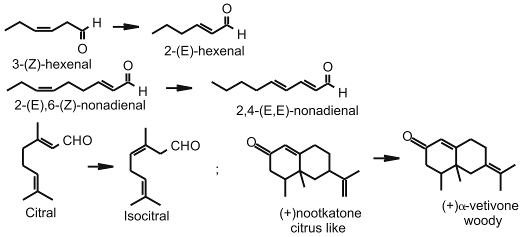
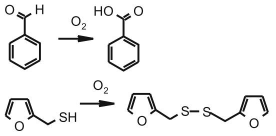
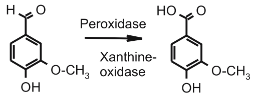
Reaction type	Main examples
Acetal formation	     

Table 21.6 (*Continued*) Overview of chemical interactions responsible for flavour changes

Reaction type	Main examples
Mercaptals and hemimercaptals	
Aldol formation	
Schiff base formation	
Decarboxylation and deamination	
Esterification	
Ring opening	
Isomerisation	
Oxidation	 

As soon as the cause of the instability is known, means can be found to improve the shelf-life of the product. So, in case of oxidation effects, antioxidants could be added, and the oxidative risk could be minimised by reducing oxidising substances, varying production parameters or optimising the packaging of a product.

21.3
Flavour Production

From its nature, a flavour is defined as a multicomponent blend of volatiles, non-volatiles and complex raw materials which is responsible for the final product properties. In flavour production, the volume-dominated operation units are mixing processes of liquids and dry blends.

Under technical production aspects, the manufacturing of flavourings can be divided into:

- The production of valuable aroma-active components
- The refining, blending and transformation of the flavour in the final physical, potentially encapsulated product

Properties such as viscosity are very important for the production process.

21.3.1
Liquid Flavours

Liquid flavours can be divided into low-viscous liquids, medium-viscous liquids, emulsions, pastes and suspensions. The main processing of liquid flavour production is basically liquid blending. The most popular carriers for flavours for aqueous systems are ethanol, propylene glycol or glycerol. For fat-soluble flavours, triacetin or vegetable oils are the most important carriers.

Long process times are required when single raw materials, compounds or natural extracts exhibit high viscosity. In general, in the flavour industry two approaches are used to reduce viscosity:

1. dilution of the highly viscous extract with a solvent
2. thermal treatment (heating) of the highly viscous extract

The disadvantage of the dilution of extracts is that the flavour concentration is lower and the flavour dose has to be increased. Significant heat treatment can influence the flavour stability in a negative way because oxidation and Maillard reactions are enhanced and the flavour might be less stable. Owing to the fact that flavours are mainly complex mixtures, their rheological properties, particularly in presence of hydrocolloids, fibres or other macromolecules, are often not Newtonian. This can cause problems in the production process. In order to simplify and optimise the dosage and the blending of micro components it is essential to work with pre-mixes. The mixing sequence is of elementary significance and determines product quality. In general, macro components, inert materials and low volatiles are added in the first production step. In a second step, this premix will incorporate the high volatiles or partly reacting components. For the production of liquid flavourings, a definition of flavour additives is needed such as antioxidants or preservatives in order to maintain the required shelf-life stability.

21.3.2
Dry Flavours

There are advantageous criteria for the application of dry flavours in food products. In numerous food products only dry flavours can be utilised owing to their physical properties. The physical form and the properties of a dry flavour are of fundamental importance for the successful processing of a food product. For instance, for a dry tea flavour blending and the filling process, the flavour has to fulfil several properties, e.g. defined particle size and shape, and a given hygroscopicity and flowing behaviour. Another reason for the application of dry flavours in the food industry is the beneficial application of encapsulated flavours in food products. The advantages of these flavour types are primarily an improved flavour stability and controlled flavour-release mechanisms. Meanwhile a broad range of technologies exist for flavour encapsulation. The most commonly used processes are spray-drying, spray-chilling, encapsulation, melt extrusion, coacervation, and β-cyclodextrin complexation. In order to select a suitable, specific encapsulation technology the final application of the flavour has to be known.

21.3.2.1
Plated Flavours

One of the oldest production methods for the production of dry flavours is the plating of a liquid flavour or extract onto a solid carrier. Carriers of main importance for the food industry are salt, lactose, starch and maltodextrin [64].

In the plating process it is essential to guarantee a homogenous blending besides homogenous addition/distribution of the liquid material. The liquid feeding can be carried out by inlet lances, injectors or nozzles, while agglomeration of the plated powder material has to be suppressed by a chopper or cutter.

Essential advantages of this flavour technology are the low production and investment costs. The fundamental disadvantage of this technology, however, is a far lower flavour stability owing to the fact that the specific surface of the flavour has been enlarged considerably and this results in a much higher sensitivity of the flavour towards oxidative degradation reactions.

21.3.2.2
Spray-Dried Flavours

The most common method to simultaneously dry and encapsulate flavours is the spray-drying technique (Fig. 21.11). For this technology, carrier materials like maltodextrin, starch and gum arabic are dissolved in water. As a next step, the liquid flavour raw material is emulsified in this slurry. Also non-volatile flavour components can be added. The slurry is "atomised" and dried in a spray-drying facility.

Spray-drying consists of four separate process steps:

1. Slurry preparation
2. "Atomisation" of a slurry
3. Drying and encapsulation of the flavour molecules
4. Separation of the dried flavour from the exhaust air

The typical flavour load of a spray-dried product amounts to 18–25%.

Besides the drying process, the flavour components are also encapsulated in the carrier matrix. After the slurry has been "atomised", all volatile components, including water, which are located at the surface of the droplet are immediately evaporated. Thereby the remaining carrier substance forms a membrane around the droplet. This membrane is semipermeable and inhibits further evaporation of flavour molecules. This production step is controlled by diffusion mechanisms. Water as a molecule with a small molecular size can pass through the membrane, while the larger flavour molecules are not able to permeate it.

An optimal dehumidified spray-dried product consists of small, round particles, whose size is almost similar to their former droplet size. They are hollow and the encapsulated flavour molecules are situated in the outer shell.

The advantages of spray-dried flavours are the high flavour load and the fast release. The process is very economical. A disadvantages of the flavour powder is the physical demixing in dry blends with sugar, tea, cereals or granulates.

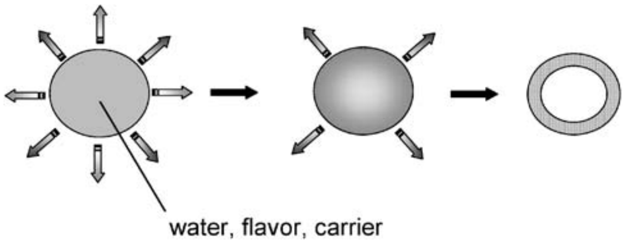


Fig. 21.11 The mechanism of encapsulation during spray-drying

21.3.2.3
Compacted Flavours

Compacted flavours are granules of size between 0.5 and 5 mm. The main application of the compacted flavour granules in the food industry is tea leaf flavouring for tea bags. Powdered flavours are not suitable because of demixing of the leaves and the powder during the blending process.

The spray-dried flavours or powder blends are processed by a roller compactor into lumps (Fig. 21.12). These lumps are crushed into granules. This process cannot be categorised as a direct encapsulating technique, since the flavour-encapsulating effect of compacted flavours is based on the use of spray-dried raw material.

A particular advantage of the compacted granules is the flexibility of the particle size. Each size between 0.5 and 5.0 mm is adjustable. A further advantage is shaped particles, colour and a combination of spray-dried flavour and additives (vitamins, minerals, functional food ingredients) can be combined in the granulated matrix.

In recent years, specific requirements with regard to shelf-life stability and tailor-made release behaviour led to the development of a range of specific encapsulation technologies such as glass-encapsulated flavours or seamless capsules with liquid cores.

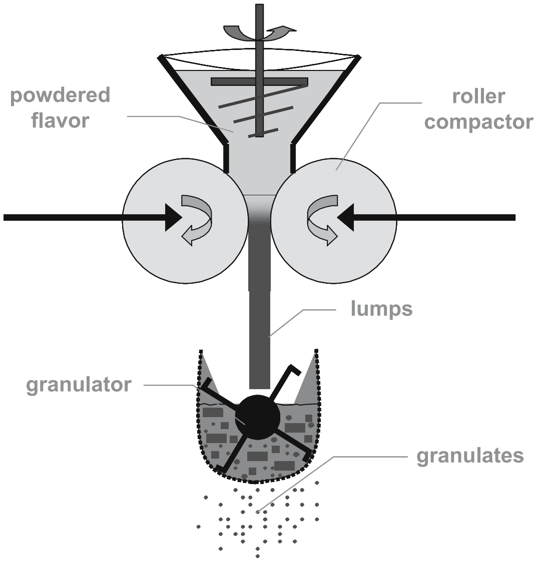


Fig. 21.12 Roller compaction

21.4
Conclusion

While in ancient times, the sensorial properties of a flavour for foodstuffs were of major importance, modern flavours have to perform like multifunctional systems. Physical form, chemical and mechanical stability and controlled release mechanisms are meanwhile essential criteria for the flavour quality. All these properties have to be addressed by a flavourist in close cooperation with technologists. Therefore, knowledge about food product properties must lead to a careful and intelligent evaluation of the flavour system as an important driver for the success of the final product.

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