CHIRALITY AND THE NATURE OF FOOD AUTHENTICITY OF AROMA

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Abstract. The phenomenon of chirality, common in nature, pertains also to food components. The effect of the chiral structure of chemical compounds is the occurrence of optical isomers, i.e. enantiomers. The only source of optically active substances are living organisms, which produce most frequently mostly one of isomers. Proteins and carbohydrates are chiral: amino acids are found in proteins only in the L form, whereas carbohydrates are formed of D-saccharides. Enantiomers may exhibit diverse behaviour in reactions with biologically active compounds of living organisms. Chiral structure of proteins turned out to be significant in the perception of taste perceptions as well as the perception of aroma. The most characteristic phenomenon is chirality among odorants. Numerous compounds essential for aroma are found in nature in the form of two isomers, with considerable predominance of one of them, while the ratio of these isomers is specific and stable. Enantiomers of odorants may differ in the intensity and character of their smell. The phenomenon of chirality has been known since mid-1800; however, it then constituted a serious analytical problem. Only the development of methods facilitating the separation of optical isomers created a possibility to investigate its universality and importance in living organisms. The application of more and more advanced analytical techniques in the control of chiral nature of food ingredients may be used to detect adulterations and especially to determine authenticity of fragrances.

Key words: chiral compounds, enantiomers, organic food, aroma, authenticity control

INTRODUCTION

There is a direct relationship between chirality and life [Brenna et al. 2003]. Chiral nature of life systems has a distinct effect on the interactions with biologically active compounds. Metabolic processes regulated by biological systems are sensitive to stereochemistry and different reactions are observed when the activity of pairs of enantiomers are compared [Maier et al. 2001].

Enantiomers, i.e. optical isomers are known to have identical chemical and physical properties with two exceptions:

– they cause rotary polarization of light in opposite directions, but by the same angle, the value of which is a characteristic feature of the substance; a laevorotatory isomer rotates the polarization plane to the left and a dextrorotatory isomer to the right, whereas a mixture of equal proportions of both forms constitutes an optically inactive racemate,

– they react with other optically active compounds at differing rates.

The full name of an optically active compound includes the direction of rotary polarization and a configuration connected with the actual spatial arrangement of atoms in the optically active compound. Dextrorotatory isomers are denoted by (+), while laevorotatory with (-). In turn, a configuration established on the basis of the priority rule is denoted by R (from Latin *rectus* – right) or S (from Latin *sinister* – left) [Morrison and Boyd 1996, Wawrzeńczyk 1997, Solomons and Fryhle 2000].

A source of optically active substances are living organisms, which produce most frequently predominantly one of the isomers. Chiral determination of a substance as the ability to distinguish the structure of a molecule from its mirror image is one of the most essential and common rules of biological activity. In biological systems such stereochemical specificity is a rule rather than an exception, since enzymes, being the most important catalysts, are optically active. For example in the metabolism of living organisms an essential role is played by (+)-glucose; the hormone activity of (-)-adrenaline is many times higher. Numerous drugs are proof of differing biological activity of enantiomers [Delatour et al. 1994, Maier et al. 2001], the same trend is also observed for e.g. compounds playing a role in chemical communication of insects [Maier et al. 2001].

Chirality was observed for the first time in 1848 by Louis Pasteur, who found that crystals of tartaric acid occur in two forms. These two forms were later identified as mirror images. Such compounds, called optical or configuration isomers, or enantiomers have an identical chemical structure but opposite spatial organization, right and left "handedness" [Marchelli et al. 1996, Solomons and Fryhle 2000].

It is believed that natural macromolecules generally are "homochiral", i.e. they contain stereocenters with the same configurations. Thus, proteins are composed of L-amino acids, while carbohydrates of D-saccharides. The occurrence of other enantiomers in nature (D-amino acids or L-saccharides) is very rare or results from an atypical or artificial transformation. It seems that biological processes produce optically pure compounds, whereas processes of chemical synthesis generate a mixture of enantiomers called a racemate.

Identification of optical purity was possible in the past only through a measurement of optical activity using a polarimeter. Separation of enantiomers was a tremendous challenge for analysts due to their chemical similarity. Making enantioseparation possible was the most significant advance in the analysis of chemical compounds achieved in the course of the last twenty years and interest in chirality resulted in a considerable increase in the level of expectations both from the scientific and economical point of view [Maier et al. 2001]. The first reports on the possible application of gas chromatography to separate enantiomers date back to 1966 – however, nobody at that time believed in a sufficiently large difference in the interaction between enantiomers and another asymmetrical substance [Schurig 2001]. It took a long time before cyclodextrins, applied as stationary phases in gas chromatography, turned out to be such substances. This made possible chiral separations of compounds, presently documented in publications.

Enantioseparation was first made possible through gas chromatography (GC) and further expanded to high performance liquid chromatography (HPLC), thin layer chromatography (TLC) and capillary electrophoresis. In recent years enzymatic methods have also been developed, based on enzyme stereoselectivity [Marchelli et al. 1996].

Although similar chemically, enantiomers differ in biological activity, which is expressed in the diverse interaction with receptors, transport system and enzymes. For this reason drug producers have to be prepared to obtain optically pure compounds and chiral analysis is becoming a necessary tool in the control of this purity [Rouhi 2003].

CHIRALITY OF FOOD INGREDIENTS

Chirality in food turns out to be a truly intriguing phenomenon. Natural components of foodstuffs as such should be optically pure. For this reason the detection of another enantiomer may be essential in the assessment of product quality. For instance proteins may undergo racemization as a result of extreme technological processes such as intensive heating or irradiation, or when they are found in a medium with high pH. The occurrence of another enantiomer may indicate adulteration with the use of synthetic substitutes.

Protein – the most important food ingredient – is frequently applied in the processed form to satisfy various dietary requirements. The technological process of food processing as a rule leads to advantageous changes in the aroma, texture and solubility, as well as the removal of toxins. However, processing procedures may also result in reactions of cross-linking, browning and racemization. It was found that microwave heating of reconstituted infant formula may lead to the formation of D-proline; moreover, a dependence was also established between parameters of the roasting process in case of coffee or cocoa beans and the rate of amino acid racemization [cited after Marchelli et al. 1996]. D-amino acids are found in lactic acid bacteria, in which they are produced from L-enantiomers by racemases and epimerases. Contamination of raw milk with gastrointestinal bacteria, primarily anaerobic, results in the occurrence of a certain slight quantity of D-amino acids. An increase in its level to over 4% in relation to the enantiomer total may indicate increased bacterial growth [Gandolfi et al. 1992]. Similarly, the presence of D-amino acids in fruit juices may constitute a criterion of their bacterial contamination [Gandolfi et al. 1994]. In turn, the occurrence of D-amino acids is a perfectly natural phenomenon, although they are also formed as a result of microbial action, but in this case it is purposeful as in fermented products such as cheeses, yoghurt, wine or vinegar.

The occurrence of amino acids in a specific optical configuration is also essential for sensory quality of foodstuffs. Amino acids except for methionine, depending on their configuration, are neutral, sweet or bitter in taste. Four of them, i.e. asparagine, tryptophan, tyrosine and isoleucine are characterized by bitter taste in their L form and sweet in the D form. The characteristic taste of numerous food products depends among other things on the contents of free amino acids, including especially glutaminic acid. However, only the L form of glutaminic acid is the carrier of taste, defined as meat, brothy or umami taste. Both the D form of glutaminic acid and its racemate do not have such a taste [Prescott and Bell 1995].

Protein plays a significant role in the process of taste reception. It is believed that the perception of bitter and sweet taste is dependent on a receptor connected with a G--protein, gustducin [McLaughlin and Margolskee 1994]. According to some authors the umami taste is perceived in the same way [Smith and Margolskee 2001]. A chiral receptor such as protein may explain the diverse (enantioselective) perception of taste sensations for various configuration forms of amino acids.

Although it is believed that nature produces optically pure isomers, more frequently than it is assumed certain food ingredients, including primarily aromatic substances, are found not only in the form of pure enantiomers, but rather in their specific ratio, as a rule with a considerable predominance of one enantiomer. In recent years the determination of these characteristic ratios has become an issue of interest in the analysis of aromatic compounds.

THE PHENOMENON OF CHIRALITY AMONG FLAVOUR COMPOUNDS

Role, occurrence and chiral structure of flavour compounds

Chiral reception is the primary criterion in biological activity. It is probably most evident in case of perception of olfactory sensations. The ability of volatile compound enantioseparation has been detected in numerous organisms including bacteria, gametes, insects, fish, frogs, deer, as the previously found the ability of mammals to distinguish the taste of enantiomers [Bernreuther et al. 1997]. The basic law of chemistry says that only the chiral subject may distinguish a chiral object. The human organism is chiral, thus it is not surprising that it can distinguish enantiomers. The ability of such a recognition depends on the effectiveness of interactions between a molecule of a flavour compound and our chiral receptors [Brenna et al. 2003].

Flavour compounds are extreme manifestations of the occurrence and effect of the phenomenon of chirality on the quality of a food product. The natural aroma of food may be generated using a variety of ways. According to Mor [1992] we distinguish a primary and secondary natural aroma. Biosynthesis pathways specific for a given product are responsible for the development of a primary natural aroma, from which frequently a secondary natural aroma is developed as a result of thermal processes or as a consequence of the action of microflora in the fermentation process. The formation of aroma depends not only on the method of its generation through purely natural processes or any other, but also on the presence in the product of certain original substances called precursors. Knowledge on their subject may be used in the planned production of flavour substances through initiation of respective processes, for which these compounds are original substances, such as thiamine – a precursor of odorants generated in thermal reactions [Güntert et al. 1992], glycosides – precursors of black tea aroma [Kobayashi et al. 1993], esters of cinnamic acid – precursors of volatile phenols in wines [Dugeloy et al. 1993].

Nature, although so rich in flavour compounds, is not able to meet the increasing demand for such components. Thus, other ways are investigated to obtain them, including primarily chemical synthesis, high temperature thermal processing and the production of "bioaromas" with the application of enzymes and tissue cultures. Attention needs to be paid to biotransformation methods, implemented at present, in which through the

application of appropriate microorganisms it is possible to produce specific flavour compounds from other such components found in a given natural raw material [Adams et al. 2003]. The variety of ways in which flavour components may be obtained creates classification problems [Bauer et al. 1990, Mor 1992, Rutkowski et al. 1997, Góra 1998]. Irrespective of the adopted divisions, generally all legal regulations, however they may differ from country to country; mainly distinguish between natural and synthetic odorants [Emberger 1981]. The underlying cause of the problem is the control of this naturality.

Although progress is observed in studies on the determination of the dependence between the chemical structure of a molecule and its aroma, so far no uniform theory has been developed on the subject. Since all chemical, physical and biological properties of organic compounds are dependent on the chemical structure, aroma – being one of these properties also has to depend on it. This dependence is not a simple one and the prediction of smell on the basis of chemical structure is not always possible. It is caused by the following facts:

– high similarity of aromas between compounds with very dissimilar chemical structures,

– differing character of aroma between molecules of chemical compounds with very similar structures,

– the phenomenon of isomerism, occurring only in organic chemistry.

Flavour compounds represent almost all groups of chemical substances, i.e. aliphatic compounds, acyclic and cyclic terpens, aromatic compounds and phenols, and this diversity is further complicated by the above mentioned phenomenon of isomerism, especially optical isomerism. The determination of the tetrahedral structure of carbon led to the creation of the theory of osmoreceptors, who indicated the effect of the presence of certain functional groups – osmophores on the smell of a compound. However, undoubtedly the most surprising phenomena in the perception of smell are connected with optical isomerism, a condition of which is the occurrence of chiral carbon in the molecule of a compound. Chiral differentiation was also considered one of the primary principles of smell perception [Mosandl 1995]. Innovative studies of e.g. Richard Axel and Linda Buck [Schiffman and Pearce 2003] have contributed greatly to the explanation of numerous details of olfactory perception.

Enantiomers may differ in aroma. The character of aroma or its intensity may vary. It is generally known that the basis of the perception of olfactory sensations is the presence of olfactory receptors in the epithelium of the nasal cavity. Individual flavour substances are received by olfactory receptors sensitive to a given smell, which is connected with the structure of the molecule. In the perception of smell at the molecular level the first occurring process is the interaction of the flavour compound with the receptor. Since receptors were identified as proteins, i.e. chiral molecules, their reactions should be enantioselective [Laska and Teubner 1999]. This means that olfactory receptors should react differently with each of the optical forms of a given chiral compound. Isomers of numerous compounds have already been described as having qualitatively different aromas, such as e.g. carvone [Leitereg et al. 1971, Russell and Hills 1971, Hormann and Cowart 1993], or linalool [Sugawara et al. 2000]. Sometimes differences pertain only to the intensity as in case of enantiomers of camphor, borneol or menthol [Laska and Teubner 1999]. There are also reports which show that one of the enantiomers has a specific aroma, while the other is odorless, as e.g. 3-methylthiobutanal [Weber and Mosandl 1997]; drastic differences in the perception of optical isomers

pertain frequently to chiral compounds containing sulfur. Enantiomeric selectivity of the sense of smell as well as the dependence of aroma on the structure thus remain unsolved, similarly as most life processes involving chiral compounds [Laska and Teubner 1999].

Isomers of flavour compounds may also differ in their biological activity. An example in this respect is carvone, the main component of aroma in case of dill, caraway or "spearmint". Its positive form, (S)-(+)-carvone inhibits the growth of potato sprouts and has an inhibitory effect also on the development of fungi of *Fusarium* spp. [Oosterhaven et al. 1995, 1996]. There are attempts to use this phenomenon in extending shelf--life of potatoes. Carvone isomers also differ in toxicity. Studies conducted on mice and rats showed a much stronger toxic action of (R)-(-)-carvone than (S)-(+)-carvone [Stelmaszczyk-Kusz et al. 1998].

Numerous attempts have been made to synthesize optically active compounds; obtaining appropriate optical purity of such generated enantiomers may be a problem. Racemates are synthetically produced chiral compounds. They may be divided, by being subjected to a reaction with an appropriately selected, optically active substance, isolated from biological material. At a considerable difference in the rate of the reactions one of the enantiomers may be transformed into another compound, while the other will remain unchanged. In this way certain strains of bacteria, introduced to a vessel with a racemate, adopt only one optical form, not interacting with the other one. Thus, the main methods to separate racemates into optically active components are based on the application of other, previously produced optically active molecules.

Chiral flavour compounds in fruits

The first major chiral differentiations of chiral flavour compounds concerned sulfur compounds in passion fruits, playing a significant role in this delicate aroma, in spite of their occurrence in trace amounts [Weber et al. 1995]. Already at that time it was observed that the specific ratio of stereoisomers of these compounds is stable, irrespective of technological processes, which suggested that enantioselective analysis makes it possible to differentiate between naturally occurring aroma components and their synthetic racemates. Chiral analysis of lactones made it possible to accurately characterize aroma of numerous fruits, such as strawberries, apricots and peaches. Results of studies in this respect presented by several authors [Engel et al. 1995, Mosandl 1995, Haffner et al. 1997] explained a typical enzymatic biogenesis pathway of these compounds, which shows that characteristic enantiomer ratios, in this case lactones, are specific solely to the natural sources of these compounds. This leads us to the conclusion that the detection of e.g. a racemic γ-decalactone in fruit products shows that a nature identical synthetic compound was added. Examples may be found in literature of chiral separation of alcohols and aldehydes [Mosandl 1995], as well as specific separation of methylthiobutanal [Weber and Mosandl 1997].

Chirality of mushroom aroma

One of the most popular aromas in foodstuffs is the mushroom aroma. The specific aroma of mushrooms is formed by volatile compounds, investigated by various authors [Wąsowicz 1974, Maga 1981, Chen and Wu 1984, Chen et al. 1984, Fischer and Grosch

1987, Mau et al. 1992, 1997, Assaf et al. 1997, Lizárraga-Guerra et al. 1997, Venkateshwarlu et al. 1999]. It results from these studies that in the mushroom aroma the biggest role is played by compounds with eight atoms of carbon. Some of the most important include 1-octene-3-ol, 3-octanol, 3-oktanon, 1-octene-3-on, 2-octene-1-ol. It is believed that the most important in this respect is 1-octene-3-ol, which is formed via the enzymatic pathway through oxidative decomposition of linoleic acid [Mau et al. 1992, Assaf et al. 1997, Cruz et al. 1997]. The content of 1-octene-3-ol in mushroom may exceed 70% of the total content of all volatile compounds as in edible mushroom *Agaricus bisporus* [Wąsowicz 1974], or oyster mushroom *Pleurotus florida* [Venkateshwarlu et al. 1999], and even 80% as in edible boletus *Boletus edulis* [Maga 1981]. 1-octene-3-ol is also found, although in smaller amounts in species characterized by not so intrinsically mushroom aroma, such as truffles *Tuber aestivum* [Diaz et al. 2002], or the exotic shiitake *Lentinum edodes* [Chen et al. 1984]. As it was found, 1--octene-3-ol is naturally found in two optically active forms (R)-(-) and (S)-(+) [Mosandl et al. 1986, Bauer et al. 1990, Chambers et al. 1998]. Studies have shown that (R)-(-)-1-octene-3-ol exhibits the aroma of fresh mushrooms, whereas (S)-(+)-1-octene--3-ol has the musty and grassy aroma [Mosandl et al. 1986]. The laevorotatory isomer (R)-(-)-1-octene-3-ol is indicated as dominant in the mushroom aroma and as essential for this aroma [Mau et al. 1992, Assaf et al. 1997, Belitz and Grosch 1999]. As it was shown in the investigations by Zawirska-Wojtasiak [2004 a, b] the R form was found in various fungal species with high optical purity, ranging depending on the species from 82.1% in bay boletus to 99.3% in garden mushroom. It was found that the measurement of the ratio of 1-octene-3-ol isomers may be used to control the authenticity of mushroom aromas in food products.

Chiral compounds in plant essential oils

The natural aromas most commonly found in nature are essential oils of numerous plants, being complex mixtures of flavour compounds, primarily terpens and phenols. Most of them are chiral compounds, occurring in specific ratios of enantiomers. Several studies have been conducted in this respect [Blank and Grosch 1991, Bouwmeester et al. 1995, Faber et al. 1994, 1997, Juchelka and Mosandl 1996, Juchelka et al. 1996, Kaunzinger et al. 1997, Kreis and Mosandl 1992, Mosandl 1995, Mosandl and Kreis 1992]. They concerned various oils, such as dill, lawandula, rose, rosemary, mint, bergamot, vanilla, neroli and petit-grain oils.

For many years adulterations of lawandula oil (*Lawandula augustifolia* M.) were discovered by detection of synthesis by-products such as dihydrolinalool or dehydroli-nalool. However, this option fails when these non-natural products are not found. Chiral analysis of linalyl and linalool acetates introduced a new, essential criterion of authenticity of lawandula oil. This may be especially linalyl acetate, which in the natural lawandula oil has a high enantiomeric purity of the (R)-(-) form, irrespective of the variety, storage and growth conditions of plants, reaching 99% of the total of both forms, R and S [Mosandl and Kreis 1992].

(R)-(-)-linalyl acetate and (R)-(-)-linalool may also be indicators of authenticity of bergamot oil, obtained by cold pressing of skins of *Citrus bergamia* fruits and used to aromatize Earl Grey tea [Juchelka and Mosandl 1996]. In turn, linalool is found in the pure form of a dextrorotatory isomer (S)-(+)-linalool in leaves of *Lippia alba* plants [Siani et al. 2002] and in essential coriander oil (*Coriandum sativum* L.) [Oliver 2003].

Similarly, in rose oil (*Rosa damascena* M. and *Rosa centifolia* L.) chiral analysis made it possible to determine compounds indicating authenticity of oil, such as (S)-(-)- -citronellol and rose oxides (2S,4R)-(-)-cis and (2R,4R)-(-)-trans. Rose oil belongs to the most expensive and most demanded oils, thus adulterations may be frequent [Kreis and Mosandl 1992], although in spite of constant progress in chemical analytic methodology and chemical synthesis, synthetic reconstitution of rose oil still remains a challenge.

One of the best known and widely applied oils is the one obtained from *Mentha piperita* plants, popularly called mint oil. Only the application of three different chiral columns made possible the separation of enantiomers of the major oil components, i.e. menthan-3-one, isomentan-3-one, menthol and menthyl acetate [Askari et al. 1992]. Further studies [Faber et al. 1994] showed that natural mint oil contains pure enantiomerically (1R)-configured monoterpenoids. The presence of (1S) enantiomers: (+)- -methyl acetate and (+)-menthol in commercial oil may be considered as adulteration with compounds of foreign biological origin or produced by chemical synthesis.

Neroli and petit-grain oils are obtained from the bitter orange tree *Citrus aurantium* L. ssp. *amara*. Ten components of aroma were detected giving two optical forms. High optical purity was observed for (R)-(-)-linalyl acetate and (S)-(-)-β-pinene [Juchelka et al. 1996]. Also other chiral compounds in these oils such as linalool, α-terpineol, α-pinene, β-pinene, limonene, terpinen-4-ol and diastereomers: (Z)-nerolidol and (E)-nerolidol may constitute a supplementation of their authenticity profile.

Monoterpens are basic components of oils produced by plants belonging to families *Labiatae*, *Pinaceae*, *Cupressaceae*, *Umbelliferae* and *Rutaceae*. Enantiomers of terpens in juniper [*Juniperus communis*] have been the subject of studies in terms of the effect of origin and cultivation site of the plant on the composition of monoterpens, including also their enantiomer ratio, which as results from these studies have not always been stable [Ochocka et al. 1997]. Similar studies were presented for different varieties of pine oil *Pinus sylvestris* [Sadof and Grant 1997] and no significant dependence was established for the enantiomer ratio of monoterpens (α-pinene, β-pinene, β-phellandrene, limonene) on the variety.

Some of the most typical and popular oil plants are caraway (*Carum carvi* L.) and dill (*Anethum graveolens* L.). Oils obtained from caraway and dill seeds are almost identical in composition. Studies of volatile components of these oils are presented in literature [Blank and Grosch 1991, Huopalahti 1986]. Main components of dill oil are limonene and carvone, the total content of which constitutes over 90% of all compounds. Contents of these compounds in dill fruits may depend on numerous factors connected with cultivation such as soil, temperature [Haelval et al. 1993], sowing and harvest dates [Singh et al. 1987, Pino et al. 1995], or variety [Zawirska-Wojtasiak et al. 1998]. Two major components are found in two optical isomer forms, but in dill fruits predominant compounds are (R)-(+)-limonene and (S)-(+)-carvone with high optical purity of over 99% [Blank and Grosch 1991, Bouwmeester et al. 1995, Lawrence 1996, Zawirska-Wojtasiak and Wąsowicz 2000, 2002]. (R)-(+)-limonene has lemon aroma, while (S)-(-)-limonene orange, whereas (S)-(+)-carvone has the intrinsic caraway aroma and is responsible for the aroma of both caraway and dill, while (R)-(-)-carvone is characterized by mint aroma. The latter is found with high optical purity in spearmint *Mentha spicata* [Bauer et al. 1990, Rawid et al. 1992]. Essential oils from plants such as spearmint *Mentha spicata*, *Mentha longifolia* or *Mentha villoso-nervata* are rich sources of carvone [Kokkini et al. 1995]. The enantiomer ratio in relation with the composition

of oil at various stages of plant development has made it possible to draw important conclusions concerning the biosynthesis of monoterpens in dill [Faber et al. 1997], both in fruits and in herbs. Herbs of dill also produce essential oil, which aroma depends to a larger extent on other components than it is the case in fruits. They are α-phellandrene and anethofuran (3,6 dimethyl 2,3,3a,4,5,7a-hexahydrobenzofuran) also called dill ether [Huopalahti 1986, Blank and Grosch 1991], which however as chiral compounds are also found in optically active forms, in this case as (4S)-(+)-phellandrene and (3R,4S,8S)-(+)-anethofuran [Faber et al. 1997]. Only this optic form of anethofuran, out of four possible, has the intrinsic aroma of dill herb [Reichert et al. 1998, Reichert and Mosandl 1999].

Rosemary (*Rosmarinus officinalis*) is becoming increasing popular as herb spice in Poland, although it is a plant of the Mediterranean climate. As spice it is used in the form of dried leaves, sometimes leaves and flowers. It is used primarily to cure meats, since rosemary oil gives specific aroma and promotes lipid digestion [Jaroniewski, 1994]. Antioxidative properties of rosemary are commonly known and used [Cuvelier et al. 1996, Korczak et al. 1999, Nakatani and Inatani 1984, Seňorans et al. 2000]. A whole book could be written on advantages of rosemary as is believed by Spaniards [Salido et al. 2003]. Rosemary oil contains several compounds, the most important of which are α-pinene, β-pinene, camphene, myrcene, limonene, eucalyptol, linalool, camphor, borneol, α-terpineol and verbenon [Bicchi et al. 2000 a, b, Flamini et al. 2002, Kaloustian et al. 2002, Mosandl 1995, Serrano et al. 2002]. Contents and ratios of these components vary considerably depending on the origin and cultivation of the plant and harvest time [Bauer et al. 1990, Flamini et al. 2002, Salido et al. 2003, Serrano 2002]. Apart from eucalyptol found in rosemary oil in significant amounts, the primary components of this aroma are chiral compounds. Enantioselective analysis showed the presence of optical forms of α-pinene, β-pinene, camphene, limonene, linalool, camphor, borneol and α-terpineol [Mosandl 1995]. This author indicated borneol as a compound which may be used as a criterion of authenticity of rosemary aroma. This compound is found in this case in the (S)-(-) form with high optical purity. Also other authors investigated enantiomers of α- and β-pinene, borneol, linalool and camphor in rosemary oil and decided that it is borneol which may be an indicator of origin for this oil [Marchelli et al. 1996, Zawirska-Wojtasiak 2004 a].

Chiral analysis of flavour compounds – authenticity control

Increasing knowledge on the stereoisomerism of flavour compounds has considerably accelerated progress achieved in enantioselective analysis [Mosandl 1995]. The invention of enantioselective stationary phases in gas chromatography with the application of cyclodextrins and their implementation into practice in 1988 resulted in a breakthrough in enantioselective analysis. The application of modified cyclodextrins has been effected in the trial and error manner and the mechanism of chiral identification is still being investigated [König et al. 1990]. Chirospecific differentiation of optically and sensory active components of aroma creates new possibilities in the determination of the connection between the structure and function as well as biogenesis of chiral volatile compounds. For many years now the total content of characteristic components of aroma and their relative percentage determined with the use of precise and repetitive methods were an accepted criterion in the assessment of aromas. At present, however,

they are of limited use at the legalization of flavour substances and in the assessment of their origin [Mosandl 1995].

However, not all chiral compounds are found in a characteristic and stable ratio of both optical forms. As the criterion of authenticity of a natural odorant only those volatile compounds may be taken into consideration, which are characterized by high enantiomeric purity, which means a high predominance of one optical form over the other and slight fluctuations in this ratio. Finally, only such a compound may be applied as a criterion of authenticity of a flavour substance, which has a high odour activity value (OAV) [Mosandl and Kreis 1992, Grosch 1993, Weber et al. 1995]. This value is expressed as a ratio of the concentration of a given substance in the material to its threshold value. The application of chiral analysis of active components of a flavour substance may be applied in their quality control.

Irrespective of huge opportunities created by chiral analysis in authenticity control, it also has some limitations, resulting in it not always being applicable in the control of flavour substances as well as other food ingredients [Engel et al. 1995, Mosandl 1995, Marchelli et al. 1996]. These limitations include the following facts:

– chiral compounds may occur naturally at varying enantiomer ratios,

– during storage or technological processing total or partial racemization may occur if structural properties of these chiral compounds are very susceptible,

– there may be racemates of natural origin generated by non-enzymatic reactions (self-oxidation, photooxidation),

– mixing chiral odorants in the production process of natural and synthetic flavour substances.

In these cases new possibilities are created by stable isotope ratio mass spectrometry (IRMS), making it possible to determine isotope ratios [Juchelka et al. 1998]. Substances separated in a gas chromatograph are transferred from the chromatograph column to the oven where they are combusted to carbon dioxide and afterwards analyzed in an isotope mass spectrometer on the basis of measurements of carbon isotope ^{13}C. The profile of such an isotope is characteristic for the composition of a given flavour substance. This method has been applied in the control of natural vanilla flavouring [Kaunzinger et al. 1997] and in combination with chiral analysis in authenticity control of citrus oils [Mosandl and Juchelka 1997]. It may be used when for the reasons mentioned above chiral analysis turns out to be insufficient or unsuitable in case of such flavour substances, in which components other than optically active compounds are decisive. Constant improvement of the IRMS method facilitates at present an increasingly thorough analysis of authenticity through the determination of the ratios of hydrogen and even oxygen isotopes [Schreier et al. 2003].

A limitation of the common application of chiral analysis in flavour substance control results also from the difficulty in obtaining chiral chromatographic separations in spite of the constant progress in this field. Increasingly effective chiral columns are produced based on specifically modified cyclodextrins; their selectivity, however, is not always sufficient [Engel et al. 1995, Mosandl 1995]. The mechanism of chiral separation and molecular inclusion has not been fully clarified, frequent atypical chromatographic behaviour and reversed elution order are characteristic. In consequence, neither the suitability of a given chiral phase nor elution order may be considered predictable. Optimum chiral separation and appropriate interpretation of behaviour in case of optical isomers are the primary goal in chirospecific analysis. In numerous cases the procedure of preliminary separation is required to achieve appropriate resolution. The best results are obtained at the application of multidimensional gas chromatography,

a combination of a non-chiral preliminary column with a chiral main column. Such a state-of-the-art solution was applied by Mosandl [1995] in his numerous studies concerning chiral odorants. However, this method requires specific, very expensive and frequently unavailable equipment, i.e. a double oven chromatograph with separate detection and temperature control.

CONCLUSIONS

In spite of the above mentioned limitations of chirospecific analysis, monitoring of optical purity of food components is becoming increasingly popular, primarily in flavour substance control. This trend is further strengthened by the fact that it turns out with increasing frequency that enantiomers despite identical physico-chemical properties may differ in sensory attributes and biological activity [Marchelli et al. 1996]. Availability of sensitive and specific chromatographic procedures for chiral differentiation makes it possible to assay most enantiomers in natural raw materials and in food. The development of modern analytical techniques applying enantioselective sensors and biosensors may in the future facilitate measurement of chirality and quality assessment of food products. Already at present biosensors are made available to assay D-alanine and L-lactic acid, thus reducing the time of analysis to several minutes. The application of modern solid phase extraction (SPME) also makes it possible to accelerate and simplify chiral analysis of flavour substances [Zawirska-Wojtasiak 2002, 2004 a, b].

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CHIRALNOŚĆ A NATURA ŻYWNOŚCI
AUTENTYCZNOŚĆ ZAPACHU

Streszczenie. Zjawisko chiralności, które jest powszechne w przyrodzie, dotyczy także składników żywności. Wynikiem chiralnej struktury związków chemicznych jest występowanie izomerów optycznych, czyli enancjomerów. Źródłem optycznie czynnych substancji są wyłącznie organizmy żywe, które wytwarzają najczęściej w znacznej przewadze jeden z izomerów. Chiralne są białka i węglowodany: aminokwasy występują w białkach tylko w formie L, podczas gdy weglowodany zbudowane są z D-sacharydów. Enancjomery mogą wykazywać zróżnicowane zachowanie w reakcjach z biologicznie aktywnymi związkami organizmów żywych. Chiralna struktura białek okazała się istotna zarówno w odbiorze wrażeń smakowych, jak i w percepcji zapachu. Najbardziej charakterystyczne jest zjawisko chiralności wśród związków zapachowych. Wiele istotnych dla aromatu związków występuje w naturze w formie dwóch izomerów, ze znaczną przewagą jednego z nich, przy czym stosunek tych izomerów jest specyficzny i stały. Enancjomery związków zapachowych mogą różnić się intensywnością i charakterem zapachu. Zjawisko chiralności było znane od połowy XIX wieku, stanowiło jednak poważny problem analityczny. Dopiero rozwój metod pozwalających na rozdział izomerów optycznych stworzył możliwość poznania jego powszechności i znaczenia w organizmach żywych. Wykorzystanie coraz bardziej udoskonalonych technik analitycznych w kontroli chiralnej natury składników żywności może służyć do wykrywania zafałszowań, a w szczególności do ustalania autentyczności aromatów.

Słowa kluczowe: związki chiralne, enancjomery, żywność naturalna, zapach, kontrola autentyczności