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Grażyna Bortnowska
West Pomeranian University of Technology in Szczecin
e-mail: Grazyna.Bortnowska@zut.edu.pl
ORCID: 0000-0003-0537-6800

CHARACTERISTICS OF AROMA COMPOUNDS AND SELECTED FACTORS SHAPING THEIR STABILITY IN FOOD WITH REDUCED FAT CONTENT

CHARAKTERYSTYKA SUBSTANCJI ZAPACHOWYCH ORAZ WYBRANE CZYNNIKI KSZTAŁTUJĄCE ICH STABILNOŚĆ W ŻYWNOŚCI O OBNIŻONEJ ZAWARTOŚCI TŁUSZCZU

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Summary: Shaping the quality of food aroma as an important factor in product selection and acceptance is still the current goal of the conducted scientific research. Many studies indicate that the quality of aroma in the hedonistic category depends on the volatility and concentration of odorants that can cause extremely desirable or undesirable sensory sensations. In turn, indicators for assessing the impact of selected factors affecting the quality of food aroma are retention and the odor activity value (OAV). Food flavorings are preferred because of their standardized quality, strength of aroma and sterility, while super-spices due to their multifunctionality. The attention is also drawn to the growing interest in food emulsions as universal carriers of aroma compounds, and the possibility of shaping their stability in foods, especially those with reduced fat content, by appropriate selection of natural emulsifiers and/or thickeners.

Keywords: low-fat foods, aroma compounds, flavorings, aroma quality.

Streszczenie: Kształtowanie jakości zapachu żywności, jako ważnego czynnika jej wyboru i akceptacji, jest wciąż aktualnym celem prowadzonych badań naukowych. W wielu opracowaniach wskazuje się, że jakość zapachu w kategorii hedonistycznej zależy od lotności i stężenia substancji zapachowych, które mogą wywoływać skrajnie pożądane lub niepożądane wrażenia sensoryczne. Wskaźnikami z kolei oceny wpływu wybranych czynników kształtujących jakość zapachu żywności są retencja oraz jednostka aktywności zapachu (OAV). Aromaty spożywcze preferowane są z uwagi na ich standaryzowaną jakość, moc zapachu i sterylność, natomiast superprzyprawy – za multifunkcjonalność. Zwraca się także uwagę na wzrastające zainteresowanie emulsjami spożywczymi jako uniwersalnymi nośnikami substancji zapachowych oraz możliwość kształtowania ich stabilności w żywności, szczególnie o obniżonej zawartości tłuszczu, poprzez odpowiedni dobór naturalnych emulgatorów i/lub zagęstników.

Słowa kluczowe: żywność niskotłuszczowa, substancje zapachowe, aromaty spożywcze, jakość zapachu.

1. Introduction

The aroma (smell, odor, fragrance) of food is one of the most important sensory impressions and in most cases determines the choice and acceptance of the product by the consumer, and also allows the distinction between different types of food such as: bread, apple, honey and others. The smell is a sensory impression caused by the stimulation of the olfactory receptors by some volatile substances (aroma compounds, odorants, aroma volatiles, odor molecules) released into the gas phase [Reineccius (ed.) 2006]. Most often it is associated by the consumer as a positive feeling, but it can also be perceived as a negative trait − off-odor. The smell felt orthonasally, i.e. inhaled by the nose with closed mouth, before the start of consumption provides the first impression of the product. The molecules of aroma compounds reaching the fragrance receptors during eating or drinking (retronasally) along with the taste and other sensations (touch, pain, etc.), creates a complex of sensations referred to as the flavor of the product. According to many authors, the aroma has a greater impact on the impression of flavor than taste [Taylor, Linforth 1996]. Taste and aroma are mutually overlapping impressions, therefore for experimental purposes they are very often assessed separately [Bortnowska 2008a; Genovese et al. 2015; Ployon et al. 2017]. Human reacts to more than 100,000 odorants, distinguishes around 10,000, and their theoretical possibilities in this range reach even one billion [Potargowicz 2008]. The mechanism of aroma sensation is based on the attachment of odor molecules to the binding proteins found in the nasal mucus, which induces a number of enzymatic reactions and causes that the chemical signal is converted into an electrical impulse transmitted to the brain. The perception of the aroma depends on the amount and properties of aroma molecules in the air that are capable to activate the odor receptors, their duration of exposure, as well as individual features of the consumer, such as: odor recognition, mood, remembered impressions and others [Reineccius (ed.) 2006].

Functional foods with pro-health effects, including those with reduced fat content, which consumers demand for their health, should have the same or similar sensory properties as a traditional product. The manufacturing of low-fat food products is a very difficult and complex task for a technologist, because fat plays an essential role in modifying the sensory and physicochemical properties of food, and is also an important precursor and carrier of aroma compounds, as well as a factor affecting the quantitative, qualitative and prolonged release of most odorants from the product, at the same time protecting them from reactions with other substances and limiting their hydrolytic degradation as a result of the impact of the water-acid environment [Reineccius (ed.) 2006; Bortnowska 2008a].

Therefore, the work was aimed to characterize the physicochemical properties of aroma compounds. Moreover, an attempt was made to assess the impact of selected factors on shaping the stability of odorants in foods, especially those with reduced fat content.

2. Characteristics of aroma compounds

Until 2017, over 10,000 odorants were identified in food (Figure 1) and the most dynamic growth was recorded in 2010-2017, which was related to the possibility of using modern analytical methods, especially gas chromatography, and the possibility of their identification with the application of mass spectrometry (gas chromatography – mass spectrometry, GC/MS) [Zawirska-Wojtasiak 2015; Bortnowska 2017].

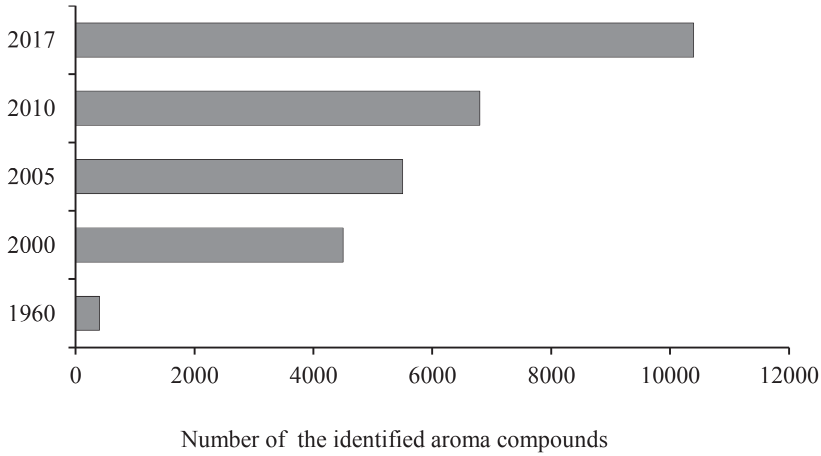

Fig. 1. Dynamics of the growth of the number of aroma compounds identified in the years 1960-2017

Source: [Reineccius (ed.) 2006; Zawirska-Wojtasiak 2015].

The source of natural aroma compounds created during the maturation process, e.g. herbs, fruits and vegetables (primary aroma) are, among others, essential oils, usually containing from several to several dozen chemical compounds, which depending on functional groups, are classified as: alcohols, aldehydes, ketones, esters, acids, ethers and others [Reineccius (ed.) 2006]. Some aroma compounds dominate the formation of the smell associated with a particular raw material (Table 1). It is assumed that the natural aroma of food is shaped by about 200 volatile substances [Yang et al. 2015; Pizzoni et al. 2015]. A significant amount of odorants, creating the so-called secondary odor, also arises as a result of thermal changes and the activity of microorganisms, as well as due to the use of technological processes during food production [Reineccius (ed.) 2006; Gao et al. 2014; Ahhmed et al. 2017]. Wang et al. [2017] for example, identified in red wine from grapes over seventy volatile substances belonging to: alcohols, esters, terpenic and phenolic compounds, lactones and others.

Coloretti et al. [2014] in turn showed that the addition of wine to fermented sausages reduced the amount of aroma compounds such as aldehydes and acids and increased the content of: alcohols, ketones and esters. It has been also found, that

Table 1. Essential oils and the main ingredient characterizing the smell of some spices

Essential oil name	Main components	Essential oil name	Main components
Anise	anethole	Clove	eugenol
Citron	limonene	Caraway	carvone
Cinnamon	cinnamaldehyde	Coriander	linalool
Eucalyptus	cineole	Thyme	thymol

Source: [Zawirska-Wojtasiak 2015].

aroma of roasted meat, roasted coffee, infusion of tea and chocolate is shaped by aroma components, the number of which can reach even several hundred [Reineccius (ed.) 2006; Baba and Kumazawa 2014; Yuan et al. 2016; Lee et al. 2017]. Despite many studies, the exact relationship between the type of aroma and the presence of functional groups is not known, although it has been noticed that some of them called osmophore groups can contribute to the characteristic odor of a chemical compound [Potargowicz 2008; Zawirska-Wojtasiak 2015]. It has been found that a pleasant aroma has volatiles containing the following groups: ester, hydroxyl, ketone, ether and aldehyde and unpleasant the ones: mercapto, thioformyl, amino, thioether and thiocarbonyl, which in relation to sensory sensations can be presumed that: acids will show acidic odor, aldehydes − fresh, ketones − fat, and esters − fruity. For example, diacetyl, which is a ketone, has a pleasant buttery aroma, and hexanal (aldehyde) − green grass, which confirms the above rule. At the same time, octanal (aldehyde) has a fruity aroma for which, it is suggested in the literature on the subject, rather esters are responsible. This suggests that the type of smell cannot be determined only on the basis of composition of the chemical compound, because it also depends on the spatial structure of the molecule and very often slight differences in the spherical structure of the compounds cause a completely different perception of their aroma. Reineccius (ed.) [2006] notes that there are odorants with similar structure and similar smell, different structure and similar smell, similar structure and different smell and stereoisomers with different aroma. For example, carvone occurs in two enantiomeric forms (colloquially referred to as mirror images), of which (S)-(+)-carvone smells like cumin, and (R)-(-)- carvone smells of garden mint. Similarly, 1-octenone 3-ol, in the optical form (R)-(-)-1-octen-3-ol is characterized by the smell of fresh mushrooms, and (S)-(+)-1-octen-3-ol – mold-grassy, while limonene: (R)-(+)-limonene has a lemon aroma, and (S)-(-)-limonene orange one [Zawirska-Wojtasiak 2015]. Aroma compounds also differ significantly in other physicochemical properties, while for a food technologist, information on their solubility in the hydrophilic (water) and lipophilic (oil) phases is important, on the basis of which the partition coefficient (P_{OW}) is calculated [Bortnowska 2011; Genovese et al. 2015]:

$$P_{OW} = C_O/C_W,$$

where: C_O and C_W, concentration of the odorant in oil and water, respectively.

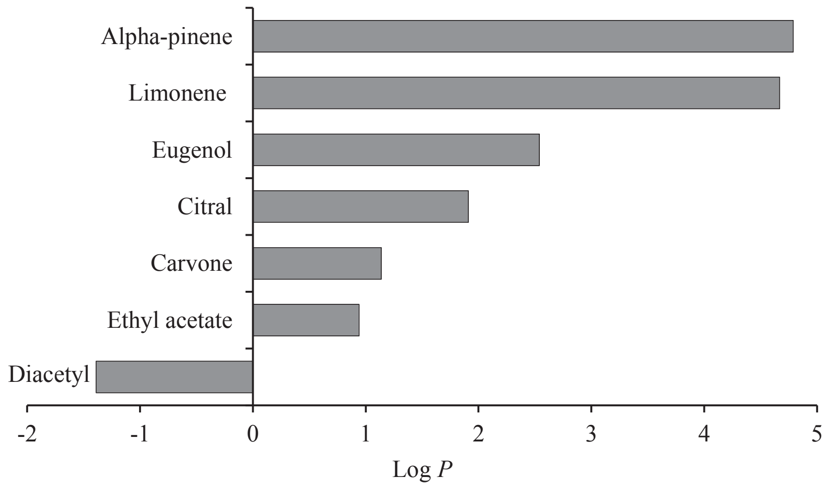

Fig. 2. Comparison of hydrophobicity (log P) of selected aroma compounds

Source: own researches (lipophilic phase − rapeseed oil).

The logarithm of this parameter (log P) is a measure of the hydrophobicity of the aroma compound and its values for selected aroma compounds are shown in Figure 2. A positive log P value means that the odorant exhibits lipophilic properties, whereas a negative one indicates its hydrophilic properties [Bortnowska 2008a].

3. Aroma quality shaping

3.1. Food flavorings and *super-spices*

The aroma of food can be modeled by the addition of flavor components. Most frequently are also used food flavorings, manufactured with the use of selected aroma compounds, which due to sterility and standardized strength and quality of the smell, have almost completely replaced typical spices obtained from different parts of plants and herbs, especially in the industrial production of highly processed foods, including functional ones with reduced fat content [Bortnowska 2002; Reineccius (ed.) 2006; Korczak 2015]. Food flavorings can be generally divided into natural and synthetic, in food technology they are used in the form of: liquid, semi-liquid or solid [Rutkowski 2007]. Particularly important in the manufacturing of flavorings is the choice of a carrier on which aroma compounds are introduced into food. For example, Bortnowska [2008b] showed that the released amount of carvone and limonene (the most important sensory caraway odorants) was twice smaller with the use a liquid aroma prepared on an oil carrier than propylene glycol or ethyl alcohol. There is also a growing interest in food emulsions as universal carriers of odorants that can be introduced into both low- and high-fat foods or sprayed onto the surface, for example in the aromatization process of products such as chips, crisps, nuts [Bortnowska, Goluch 2018]. Food emulsions containing aroma compounds can be also used as the carriers of functional enriching additives, for example: vitamins, minerals and other bioactive ingredients [Reineccius (ed.) 2006; Bortnowska (ed.) 2017]. Food flavorings containing microencapsulated aroma compounds (solid flavorings) are also very important. For their manufacturing mostly are used: maltodextrin, gum arabic, modified starch and proteins, usually whey proteins. The literature on the subject notes that improperly selected material of the walls of microcapsules can cause large losses of odorants as a result of their increased release or changes due to the oxidation [Sánchez-Cabrera et al. 2011]. Janiszewska et al. [2013] showed that in the microencapsulation of vanillin, the ratio of maltodextrin to gum arabic (GA) was of great importance, suggesting that with the increase of GA content, the aroma compound was more stable. At the same time, by fermenting selected plant raw materials, e.g. soy or rice, it is possible to manufacture flavorings belonging to pastes, with special sensory values, characteristic mainly for Asian cuisine [Inoue et al. 2016; Ahhmed et al. 2017].

One of the newest forms of aromatization of pro-health food is the use of the so-called *super-spices*, which are particularly valued by consumers for their multifunctionality, i.e. both high sensory, as well as technological and medicinal values. Gupta Jain et al. [2017] suggested for example that dietary supplementation with cinnamon caused the regulation of blood pressure in the examined group of patients and the content of total cholesterol, LDL (low density lipoproteins), HDL (high density lipoproteins) and triglycerides. Essential oils in turn, obtained from the flowers, leaves and rhizomes of turmeric contain a significant amount of terpenic and aromatic compounds exhibiting simultaneously: antioxidant, anti-inflammatory and antibacterial activities [Xiang et al. 2017; Zhang et al. 2017]. Current research results also provide numerous evidence of ginger's anti-diabetic and hypolipemic (lipid-lowering in blood) effects [Kulczyński, Gramza-Michałowska 2016]. Unfortunately, in the available literature did not find any scientific research indicating the possibility of using *super-spices*, including spice plants and herbs collected from natural stands, in the aromatization of functional foods, usually highly processed. However, the use of modern methods of spice hygienization, in particular ionizing radiation, already enables the production of durable and safe food for consumers [Chmielewski, Zimka 2017].

3.2. Aroma stability in food

Aroma compounds may interact with food ingredients (e.g. fats, proteins, carbohydrates), which affects their varied release from food [Bortnowska 2011; Lee et al. 2017]. A useful indicator in this regard is retention, defined as the amount of odorant retained in food to its initial quantity [Bortnowska, Goluch 2018]. Thus, the more aroma retained in the system, the higher the retention and the higher the sensory attractiveness of the food. Many scientific studies show that fat largely shapes the stability of aroma compounds in food products. For example, it was noted that with the increasing content of this ingredient in the system, the amount of hydrophilic (water-soluble) diacetyl (log P = –1.39) decreased, whereas the lipophilic (fat-soluble) odorants such as ethyl acetate (log P = 0.94), (+)-carvone (log P = 1.14) R-(+)-limonene (log P = 4.67) and (-)-a-pinene (log P = 4.79) demonstrated an ascending trend of retention (Figure 3).

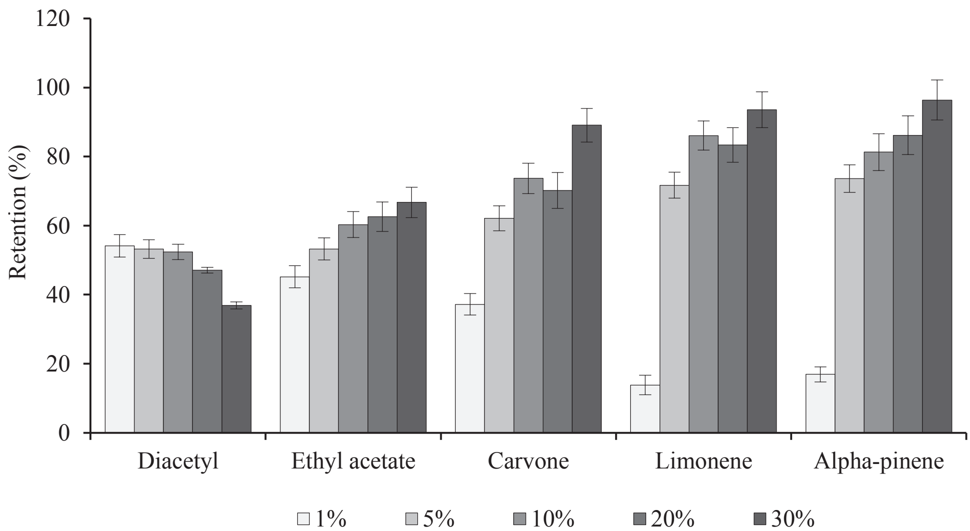

Fig. 3. Impact of fat concentration on the retention of selected aroma compounds

Source: [Bortnowska 2008a].

In assessing the level of the impact of the fat phase on aroma stability, other substances dissolved should also be taken into account. Genovese et al. [2015] reported, for example, that the addition of phenolic compounds (bioactive substances used in the production of functional foods) to olive oil, reduced the release (positive effect) of the odorants tested. To a much smaller extent, retention of aroma compounds in food systems is possible to model by the addition of proteins. Research of Bortnowska [2008a] showed that the addition of egg yolk reduced diacetyl retention and increased the values of this indicator in relation to (-)-a-pinene, especially in the concentration range of 1.4-2.6% (w/w). Partly opposite results obtained Chua et al. [2017], who reported that the increase in protein concentration in yogurt reduced the release of diacetyl, a substance that affects the sensory quality of this product. The observed differences, supposedly, could be due to the fact that egg yolk contains a significant amount of fat, which does not have a stabilizing effect on hydrophilic (water-soluble) aroma compounds [Bortnowska 2012]. Some polysaccharides (carbohydrates) may also have a stabilizing effect on odorants in food. Bortnowska

[2008a] for example demonstrated that the increase in concentration of modified starch used as an emulsifier contributed to the increase of both diacetyl and (-)-a-pinene retention. Similar results were reported by Yang et al. [2017] who proved that the increase in concentration (0-6 g/l) of xanthan gum in the system reduced the level of release of aroma compounds, such as: ethyl acetate, ethyl butyrate, (-)-a-pinene, D-limonene and hexenal. The research of Pizzoni et al. [2015] in turn shows that the use of gum arabic (GA) for the production of sweets, stabilized the fruit aroma to a greater extent than using pectin, which was probably associated with the relatively high content of protein in GA.

4. Sensory assessment of aroma quality

The quality of aroma in the hedonic category (liking and disliking) largely depends on the concentration of the odorant in the system. For example, concentrated ethyl-3-thiol propionate has a very oppressive smell − difficult to accept, while at 0.2 mg/dm^3 it changes to pleasant − fruity. Similar sensations are connected with with furfurylthiol, which at 0.005 mg/dm^3 has the aroma of freshly roasted coffee, in turn in the concentration range of 0.01-0.5 mg/dm^3, has a musty smell [Grabowska 2007]. The basic condition for sensing the aroma associated with a particular odorant is its volatility. Aroma compounds that are found naturally in food or introduced as food flavorings significantly differ in the concentration at which they are detected and recognized. In the literature, it is assumed that the detection threshold refers to the concentration of the odorant in the air at which there is a 50% probability of sensing the difference between smell, with and without the addition of a fragrance component. In turn, the recognition threshold defines the lowest concentration of odorant at which an aroma can be identified. Wollan et al. [2016] showed that the values of odorants (being found in wine) recognition threshold, for: hexanol, ethyl hexanoate, 2-phenylethyl alcohol are very diverse and are amounted to: 4; 0.005 and 10 mg/l, respectively. The value of the odor recognition threshold is always higher than its perceptibility threshold and does not increase linearly with raising odorant concentration in the system. At a certain concentration of aroma compounds, the so-called terminal threshold exists above which no further identification is possible [Chambers, Koppel 2013]. The potency of aroma is expressed as odor activity value (OAV), sometimes also called as flavor unit (FU) or aroma value (A) [Yonezawa, Fushiki 2002; Grabowska 2007; Belitz et al. 2009; Giungato et al. 2018] and calculated as the ratio of the concentration of aroma compound (C) in the food to its odor detection threshold (ODT):

$$OAV = C/ODT$$

Yonezawa and Fushiki [2002] believe that if the FU is greater than 2.0, the substance present in the system is highly aroma active, 1.0-2.0 means it is aroma active, 0.5-1.0, aroma can be only perceived by people with high sensory sensitivity, 0.2-0.5 FU possible aroma active, 0.2 FU and below unlikely to have impact on aroma.

5. Conclusion

The application of modern analytical techniques results in the amount of identified aroma compounds is constantly increasing. Therefore, it becomes necessary to systematically study their physicochemical properties, especially in terms of the possibility of use in food aromatization. A review of literature shows that the type of aroma perceived clearly depends on the chemical structure, including the spatial structure of the volatile component molecule and its concentration in the system. Based on the authoress own research, it has been proven that the quality of the aroma of functional foods, especially those with reduced fat content, is influenced by the type of flavoring including carrier used for the absorption of volatile components. Reference has also been made to the growing interest in food emulsions as universal carriers for aroma compounds of food flavorings useful for aromatization both low and high fat foods. It has also been pointed out that particularly useful in the aromatization of functional food are the so-called *super-spices*, but there is the need for application of modern methods regarding their hygienization. It has also been suggested that aroma stability in reduced fat foods can be increased by selecting appropriate natural thickeners and/ or emulsifiers including animal and milk proteins, as well as polysaccharides, such as food gums and starches.

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