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Volatile organic compounds and their generation in sourdough

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Abstract. Sourdough technology is involved in bread making process for improving the sensory, rheological, nutritional and shelf life characteristics of bakery products. More than 540 volatile organic compounds (VOCs) and other flavour precursors belonging to the chemical classes, such as aldehydes, ketones, esters, acids, alcohols, terpenes and others, have been identified in sourdoughs and sourdough breads. The synthesis of VOCs is microbial species-specific, originating mainly from fermentation process. VOCs can be used as indicators to characterize microbial processes. Other additional sources of VOCs in sourdoughs are lipid oxidation and browning reactions, the latter of which occurs during the production of dried starter cultures. The purpose of this article is to provide an overview of the composition of VOCs and their effect on the sensory properties of sourdough bread, and to describe the most common extraction methods of VOCs used in the studies of sourdough and bread aroma profile. Long-term propagated sourdough VOCs have been less studied compared to volatiles found in bread crust and crumb or sourdoughs started with defined starter culture(s) due to their complexity and diversity in metabolic pathways, including sophistication of the analytical methodology of VOCs. The relation between sourdough microbiota and its volatile profile is not fully understood and therefore, their variability and precise role as a bread flavour enhancer is not yet known in detail.

Key words: lipid oxidation, proteolysis, sourdough fermentation, volatile profile.

INTRODUCTION

The use of sourdough in food fermentation as a leavening agent for bread making is one of the oldest biotechnological processes in cereal food production (Röcken & Voysey, 1995). Sourdough is a mixture of cereal flour and water, which is fermented mainly by facultative and obligate heterofermentative lactic acid bacteria (LAB) and yeasts. Sourdough fermentation can be started spontaneously or initiated by the addition of mother sourdough or defined starter culture (s), including constantly refreshed sourdough with the mixture of flour and water. Metabolic processes of sourdough microbiota are mainly associated with the fermentation of bread dough (by LAB), the formation of aromatic compounds of bread (by LAB and yeasts) and the proofing of bread dough (by yeasts and heterofermentative LAB) (Hammes & Gänzel, 1998; De Vuyst et al., 2009, 2016).

All food products contain hundreds of volatile organic compounds (VOCs) (Maarse, 1991). VOCs in wheat and rye bread crumb and crust have been extensively studied, however much less is known about their variability and concentration in long-term propagated sourdoughs, especially in rye sourdoughs. Several studies (Schieberle & Grosch, 1994; Kirchoff & Schieberle, 2001; Pico et al., 2018) have been indicating that the flavour compounds of the bread crumb are significantly different from those of the bread crust due to the process parameters in sourdough fermentation and baking. Flavour components occurring in the bread crumb are mainly produced during sourdough fermentation while the baking process has the greater effect on the flavour of the bread crust (Heiniö, 2003; Pico et al., 2015). Although main bread aroma compounds are produced upon baking, the importance of fermentation should not be neglected since fermentation is a source of several precursor VOCs that only react at baking temperatures. Studies by Hansen (1994a, 1994b), Gobbetti et al. (1995), Ravyts & De Vuyst (2011), Settanni et al. (2013), Ventimiglia et al. (2015), Ripari et al. (2016) and Warburton et al. (2022) have demonstrated that the volatile fractions of wheat and rye sourdoughs are very complex and consist of numerous compounds with a variety of functional groups. The range of research on VOCs in sourdough has been relatively limited in terms of the diversity of microbial cultures, including regional differences in sourdough fermentation and propagation technology, and the variety of generated VOCs. Overall, the detailed knowledge of the microbial and enzymatic processes involved in sourdough fermentation, especially the evolution of aroma volatiles at the early stages of sourdough preparation, is limited and undervalued. In order to understand the impact of microbiota, raw material and technological parameters on the sensory properties of bread, it is important to know which VOCs are produced by the sourdough microbiota during its several metabolic pathways. Due to the multiplicity and complexity of metabolic pathways, including the species diversity of microbial cultures in sourdoughs, it is difficult to identify the sources of various volatile compounds more precisely. This article provides a systematic overview of the VOCs associated with sourdough and their effect on bread flavour and aroma, including a brief overview of commonly used methods for detecting these aroma compounds.

VOCs, VOLATILE ORGANIC COMPOUNDS

VOCs have a significant impact on the formation of organoleptic properties (aroma and flavour) of different fermented food products (Pinu & Villas-Boas, 2017). These are defined as a class of low-molecular-weight (< 300 g mol^{-1}), carbon-containing aliphatic and aromatic compounds characterized by their high volatility, low vapor pressure (≥ 0.01kPa at 20 °C), and low water solubility (Schulz & Dickschat, 2007; Herrmann, 2010). VOCs are comprised of hydrocarbons, acids, alcohols, aldehydes, aromatics, ketones, terpenes, thiols, and their derivatives (Pennerman et al., 2016). Their concentration varies between ng L^{-1} to g L^{-1} depending on the various metabolic processes occurring in food (Pinu & Villas-Boas, 2017). These compounds exist in the initial raw material, but can be also produced by different microorganisms (e.g. LAB, yeasts, fungi) as metabolites and by-products through catabolic pathways, including glycolysis, proteolysis, and lipolysis (Schulz & Dickschat, 2007; Pinu & Villas-Boas, 2017).

Analytical methods for detecting VOCs in sourdough

Assessment of the VOCs profile requires sample preparation, extraction of VOCs from matrix to be examined and their identification and quantification using relevant analytical instrumental method. There are several approaches for isolating and concentrating VOCs from the cereal-based products such as steam distillation/extraction, supercritical CO_2 extraction or solid phase microextraction (Chambers & Koppel, 2013; Maarse, 1991). The oldest and most common technique of VOCs characterization and measurement involves the use of analytical techniques such as gas-chromatography (GC) coupled with mass-spectrometry (MS) and GC-MS with an olfactometric port or a sniff port (Lawless & Heymann, 2010). In recent years, several online tools based on MS, such as membrane inlet MS, selected ion flow tube MS (SIFT-MS), proton-transfer-reaction MS (PTR-MS), and PTR-time-of-flight MS (PTR-ToF-MS), are being studied and applied for the assessment of VOCs. The high time resolution brought by PTR-MS is one of the direction-injection MS technologies which allows non-invasive VOC fingerprinting (Farneti et al., 2015). The coupling of PTR-MS with ToF mass analyzers has improved time and mass resolution, allowing the monitoring of VOCs during food fermentation process (Romano et al., 2015). Due to its advantages of rapid response, absolute quantification, and high sensitivity, PTR-MS has been successfully applied to detect VOCs in the field of food research (flavour studies, assessment of food quality) (Wang et al., 2012) including breadmaking process (Makhoul et al., 2014, 2015; Pico et al., 2018, 2020). While the sourdough fermentation process has been successfully examined by SIFT-MS (Van Kerrebroeck et al., 2015; Van Kerrebroeck et al., 2018) due to its simple use and direct quantification, PTR-ToF-MS has proved to be a fast high-throughput tool for the study of interactions between microbes (LAB, yeasts) and flour. Thereby manufacturers have the opportunity to choose the combination of ingredients able to yield the production of preferred volatiles serving as flavour precursors in the final baked product (Makhoul et al., 2015).

Various methods have been used to extract flavour compounds from bread and sourdoughs, but the main ones are solvent extraction methods and headspace analysis (HS) followed by identification by GC-MS (Pico et al., 2015; Petel et al., 2017). However, dynamic headspace (DHS), especially in-tube extraction (HS-ITEX), has been proposed as an alternative to optimize HS. DHS method provides better sensitivity and has fewer problems related to the selectivity of the extraction to matrix effects, but so far, only one study has investigated the optimization of DHS extractions based on sourdough (Fuchsmann et al., 2019; Dias et al., 2022).

Solvent extraction process followed by concentration under nitrogen or in a rotary evaporator was one of the first extraction methods for the separation of VOCs from foods (Zhou et al., 1999). Yet, the solvent extraction method by Soxhlet apparatus allows the extraction of a large number of volatile compounds (Sides et al., 2000) which yet may introduce potential qualitative or quantitative errors in the results (Heiniö, 2003). For instance, the solvent may limit the identification of volatile compounds (poor selectivity) and its removal requires heating that could cause thermal degradation of organic compounds (Sides et al., 2000), also flavour components may become contaminated by unwanted material such as lipids and non-aroma hydrocarbons (Zhou et al., 1999).

Nowadays the solvent-based extraction is less used due to the above-mentioned disadvantages, e.g. volatile compounds elute solvent-specifically and therefore some of the odour active compounds may disappear (Heiniö, 2003). The most preferred option for extracting volatiles from bread and sourdough is the headspace (HS) method (Ravyts & De Vuyst, 2011; Aponte et al., 2013; Settanni et al., 2013; Ripari et al., 2016). More precisely, solid phase micro-extraction (HS-SPME) coupled to GC-MS has been preferred because it is a rapid, convenient and solvent-free technique (Thompson-Witrick et al., 2015). In HS-SPME the samples are generally cleaner, containing fewer compounds than samples pre-treated with organic solvents (Grosch, 2007; Prost et al., 2012) and it may happen that important volatile substances present in sourdough in low concentrations give no electrical signal. Therefore, in order to achieve reproducibility, this method requires the precise control of many parameters (like sample volume, extraction temperature, equilibrium time, fibre coating etc.) which differ according to the food matrix (Thomsen et al., 2014; Pico et al., 2015).

In addition to above-mentioned methods, it is also conceivable to use supercritical fluid extraction (SFE) which is generally used as an alternative primary method for Soxhlet type extractions (Doane-Weideman & Liescheski, 2004). So far there is no overview of the application efficiency of the SFE method for analysing VOCs in bread or sourdough, but it has found a use in determining polycyclic aromatic hydrocarbons in toasted breads (Kayali-Sayadi et al., 2000). The main advantages of SFE for the extraction of odorant compounds from food matrices compared to conventional extraction methods are its safety (GRAS solvent in comparison to many organic solvents), higher selectivity, shorter extraction times and the possibility of its direct coupling with analytical chromatographic methods (Doane-Weideman & Liescheski, 2004; Herrero et al., 2006).

Qualitative and quantitative methods for the analysis of flavour compounds in various fermented food products have developed a lot, but the synergistic effect of several flavour substances is still difficult to evaluate due to the complexity of LAB and yeasts metabolism. Different sampling techniques offer a number of individual advantages but also suffer from specific limitations, e.g. the potential destruction of aroma components and/or production of flavour artifacts. It has been shown that the choice of analysis method for volatile compounds from cereals has a significant influence on the compounds recovered, and therefore the results obtained by using different methods should be considered carefully (Heiniö, 2003; Boyacı et al., 2015). While there are several approaches to the analysis of VOCs, there is a constant demand for a method that prevents oxidation, thermal degradation, and other chemical and biochemical changes in the sample. Currently, there is no standard method for the determination of volatile compounds in sourdough, which would enable an adequate comparison of the results of different studies, which is why there are no accurate profiles of volatile organic compounds for sourdoughs. Among the existing ones, the HS-SPME and HS-ITEX could be the most suitable methods to develop a standard extraction method for the analysis of VOCs in sourdough and sourdough bread.

Common VOCs in sourdough

Aromatic compounds in food are commonly formed in four ways such as biosynthesis, enzymatic action, oxidative decomposition and pyrolysis. The biosynthesis of VOCs mainly depends on the citric acid and amino acid metabolism pathway. The volatile profile of sourdough is rather complicated and difficult to describe thoroughly due to the variety of LAB and yeasts, fermentation substrates and flavour substances produced. (Wang et al., 2021) Sourdough VOCs are mainly produced by microbiological and enzymatic processes during fermentation (Petel et al., 2017), which depend on interactions between LAB and yeasts (Zhang et al., 2021; Fang et al., 2023). The aroma compounds produced by the sourdough microbiota can be divided into two groups: first, non-volatile compounds, including non-volatile organic acids (lactic and pyruvic acid) which acidify and contribute to the aroma of bread (Gobbetti et al., 1995) and second, VOCs such as alcohols, aldehydes, ketones, esters and sulphur, as well as volatile acids like butyric and acetic acid (Pan et al., 2014; Fang et al., 2023). The study of VOCs has mostly relied on the formation of volatile compounds in sourdough using specific microbial cultures (Kaseleht et al., 2011; Yang et al., 2020; Luca et al., 2021; Warburton et al., 2022), natural starters from local bakeries (Bianchi et al., 2008), or by creating spontaneous starters (Ripari et al., 2016; Siepmann et al., 2019; Katsi et al., 2021).

Organic acids, alcohols, esters, ether and furan derivatives, lactones, pyrazines, pyrrole derivatives, sulphur compounds and carbonyls mostly affect the sensory properties of bakery products (Hofmann & Schieberle, 2000; Czerny & Schieberle, 2002; Kirchhoff & Schieberle, 2002; Pacyński et al., 2015; Giannone et al., 2018; Gancarz et al., 2021). The metabolism of VOCs during sourdough fermentation is influenced by the interaction between LAB or/and yeasts, and the type of fermentation pattern where the activity is mainly attributed by endogenous or non-controllable parameters (e.g. nutrient composition) and, exogenous or technological parameters (e.g. fermentation time and back-slopping, temperature), affecting the amount of formed metabolites (Vrancken et al., 2011). Petel et al. (2017), Liu et al. (2020) and Wu et al. (2022) have reported that many VOCs begin to accumulate after 12 h of fermentation. According to Hansen & Hansen (1996), Decock & Cappelle (2005) and Catzeddu (2019), sourdough bread have more VOCs compared to yeast leavened bread.

Hydrocarbons (e.g. benzene, propane) have been the most abundant chemical class detected in sourdough fermentation followed by esters, alcohols, ketones, aldehydes, and sulphur compounds. Origins of hydrocarbons are not yet clearly identified in the literature but their occurrence is more common in studies that employed HS extraction (Seitz et al., 1998; Bianchi et al., 2008) compared to solvent extraction (Kirchhoff & Schieberle, 2001; Czerny & Schieberle, 2002; Pizarro & Franco, 2017). The most frequent VOCs detected in bread crust and sourdough are 2- methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-1-propanol, phenylethyl alcohol, hexanal, benzaldehyde, 3-methylbutanal, ethyl acetate, ethyl octanoate, acetic acid and butanoic acid. These compounds originate from the fermentation process, lipid oxidation, and Maillard reactions (Birch et al., 2014; Pico et al., 2015; Pizarro & Franco, 2017).

Isoalcohols, e.g. 2-methyl-1-propanol, 2,3-methyl-1-butanol, with their respective aldehydes and ethyl acetate, are synthesized inside the yeast cell due to the degradation of the flour amino acids (Damiani et al., 1996; Birch et al., 2014). According to Hansen & Schieberle (2005), the different amount of alcohol production may be related to the distinct degradation reaction of amino acids occurring during sourdough fermentation via the Ehrlich pathway, leading to formation of aldehydes or the corresponding alcohols. Alcohol formation involve the initial transamination of an amino acid producing an α-keto acid, irreversible decarboxylation of the acid to the fusel aldehyde, and reduction by alcohol dehydrogenase to fusel alcohol (Birch et al., 2014).

Generation of VOCs in bread and sourdough is also influenced by both raw material and technological parameters (Hansen et al., 1989; Saa et al., 2019; Kirchoff & Schieberle, 2002). The formation of principal VOCs are mainly induced by the sourdough fermentation process, lipid oxidation and Maillard reaction, while volatile compounds from raw materials have only a minor effect on the amount of VOCs in the sourdoughs (Pozo-Bayon et al., 2006; Prost et al., 2012). Due to the lack of studies, precise data on the effect of the interaction of microbial communities, technological parameters and raw materials on the concentration of VOCs is not available. From few studies (Lund et al., 1989; Kirchhoff & Schieberle, 2002; Kaseleht et al., 2011) it appears that the most abundant amounts of ethanol, iso-alcohol, hexanol, acetic acid, hexanoic acid, dimethyl sulfide, ethyl acetate, ethyl lactate, ethyl hexanoate, pentanone and 2,3-butanedione are present in rye sourdoughs. Extruded rye sourdough has been reported to contain high levels of furfural, ethyl acetate, 3-methylbutanol, 3-methylbutanal and 2-methylbutanol (Heiniö et al., 2003). The characteristic strong flavour of rye bread is induced by the alcohols, 2-phenylethanol (phenolic, plastic), 2-methylbutanol (roasted, fruity) and benzyl alcohol (vinegar) and acetone (essential, fruity, acidic) (Hansen et al., 1989). Esters in sourdough and bread are associated with a pleasant fruity (apple, banana) and sweet aroma (Reale et al., 2016; Pizarro & Fransco, 2017) although their concentration declines due to their hydrolysis by the heat during dough baking (Hanis-Syazwani et al., 2018). Ethyl esters originate from the reaction of alcohols and acetyl coenzyme A derivatives of fatty acids, but fatty acid esters may be a product of free fatty acids from further oxidation of aldehydes, reacting with some alcohols (Pico et al., 2015). Hexadecanoic acid and 1-(hydroxymethyl)-1,2-ethanediyl ester have been identified as the most common esters in rice bran sourdough. Other esters found in the rice sourdough are 9-octadecenoic acid, (2-phenyl-1,3-dioxolan-4-yl) methyl ester, methoxyacetic acid, 3-tridecyl ester, and pentanoic acid, 4-methylethyl ester (Bolarinwa et al., 2019; Özgül-Yücel & Türkay, 2002). A study by Özgül-Yücel & Türkay (2002) and Bolarinwa et al. (2019) indicate that the types and amounts of esters are influenced by the temperature and time of fermentation. Reale's et al. (2016) data showed that the production of ethyl acetate, isoamyl acetate and ethyl hexanoate was improved when the yeast was co-cultured with *L. casei* N87 grown under respiratory conditions. In the evaluation of volatile organic compounds, it was observed that the respiratory metabolism of *L. casei* N87 significantly affected the flavour of the sourdough, demonstrating that the type of cultivation of microbial starter can have an important factor in the formation of the profile of volatile compounds in sourdough. Low concentrations of hexyl acetate and isoamyl lactate were found only in dough inoculated with *L. casei* N87. The increase in their content can be facilitated by the use of heterofermentative LAB in wheat/rye firm sourdoughs. Moreover, Lanciotti et al. (2003) proved that hexyl acetate, hexanal and (*E*)-2-hexanal have significant inhibitory effects against pathogenic microorganisms.

FORMATION AND ORIGIN OF VOCs IN SOURDOUGH

Raw material as a source of VOCs

In addition to chemical and microbiological generation of volatile compounds, some of the flavour-active compounds are also detected naturally in the cereal flours, which, based on their flavour activity values (ratio of concentration to flavour threshold), have an impact on both the overall aroma of sourdough and the bread itself. The flour in the sourdough is a substrate for microorganisms with its heterogeneous nutritional composition. Most of the sourdoughs are made of wheat and/or rye flour (Meroth et al., 2004; Valcheva et al., 2005; De Vuyst et al., 2009), but corn, cassava, barley, emmer, oat, rice and teff flours and flours based on legumes (fava bean, pea, chickpea) and pseudo-cereals, such as buckwheat, amaranth and quinoa, have also found application in the sourdough fermentation. Some investigations refer to using teff flour in sourdough fermentation which has a great influence on the aroma profile of the baked products due to its high contents of unsaturated fatty acids and phenolic compounds (Kirchhoff & Schieberle, 2001; Gänzle, 2015; Campo et al., 2016). In general, scarce information is available on the VOC profile of fava bean (*Vicia faba* L.), although it has been subjected to several studies in last decade for increasing cereal food nutritional quality (Rizzello et al., 2014; Coda et al., 2017; Verni et al., 2019). Fava beans are characterized by off-flavours resulting from non-VOCs that cause bitterness and unpleasant odours, which are mainly promoted by auto- and enzymatic oxidation of free fatty acids and degradation of free amino acids during seed processing. Its off-flavours are defined for instance as dried or fresh pea, mouldy, rancid and yeast (Karolkowski et al., 2021, 2022; Tuccillo et al., 2022). Although beans have off-flavours and their addition can compromise the gluten network, they are still considered sustainable and highly nutritious gluten-free alternatives to cereal flours. Huang et al. (2023) have shown that using the exopolysaccharide-producing strain *Weisella confusa* QS813 in red bean (*Vigna angularis*) sourdough fermentation can improve the rheo-fermentation and viscoelastic properties of red bean dough, as well as the aroma profile of bread made from it. Wheat-red bean sourdough bread was enriched with new aroma compounds, such as acetic acid and a higher content of 3-methyl-1-butanol and 2,3-butanediol. Their findings were consistent with other studies (Cho & Peterson, 2010; Pico et al., 2015), which observed that the use of sourdough in breadmaking reduces the total content of aroma compounds, but increases other types of aroma compounds in the bread crumbs. Perri et al. (2021) also identified the positive effect of using dextran producing LAB (e.g *W. confusa* SLA4) and sprouted lentil sourdough on the sensory (synthesis of bread key-aroma compounds) and nutritional quality (high fiber content) of white sourdough bread.

Insect flour (house cricket *Acheta domesticus* L.) is also a new promising and sustainable raw material for the production of sourdough due to its nutrient richness and suitability to support the growth of the *Lactiplantibacillus plantarum* strain. Beldean et al. (2022) study highlighted that during controlled insect flour sourdough fermentation with *L. plantarum* ATCC 8014 strain, higher level of benzaldehyde, 2-methyl-5-propan-2-ylcyclohex-2-en-1-one, p-cymene and β-myrcene were produced; meanwhile, the spontaneous fermentation enhanced the formation of benzoic acid and disulphide dimethyl, with a faint and unpleasant odour perception. Among these, the odour of 2-methyl-5-proparn-2-ylcyclohex-2-en-1-one is associated with spicy, minty, caraway, bread, and rye bread. The formation of benzaldehyde and 3-methyl-1-butanol could be the result of degradation of phenylalanine and leucine, respectively (Pico et al., 2015; Fang et al., 2023). In a recent study, Bartkiene et al. (2023) found that non-fermented cricket flour contained higher concentrations of acetic acid, hexanal and decane, but their content decreased after fermentation by *L. plantarum* no. 122. After 48 hours of fermentation, hexanal was not detected in the fermented samples. Furthermore, the content of several other compounds, including 1-octen-3-ol, 2-pentylfuran, 4-methyldecane, 3,6-dimethyldecane, 3-methylundecane, ethyl octanoate, and dodecane, decreased during fermentation. Meanwhile, the concentration of various VOCs such as acetoin, 2,3-butanediol, butanoic acid, 3-methylbutanoic acid, 2-methylbutanoic acid, 1-hexanol, 2,6-dimethylpyrazine, 2,2-dimethyl-3-heptanone, 2,6-dimethyl-4-heptanol, 2-hydroxy-

3-methylpentanoic acid methyl ester, benzaldehyde, phenol, benzeneacetaldehyde, 3-ethyl-2,5-dimethylpyrazine, nonanal, and phenylethyl alcohol, increased due to the metabolic activity of LAB. Nissen et al. (2020) concluded in their study that insect flour gives bread a unique bouquet of volatile compounds consisting of nonanoic acid, 2,4-nonadienal (*E,E*), 1-hexanol, 1-heptanol and 3-octene-2-one. The most interesting results were those obtained from sourdough fermentation, where the amount of acetoin in the cricket sourdough samples (24.42 ± 0.23 mg kg^{-1}) was twice that of the control sourdough samples (13.74 ± 0.35 mg kg^{-1}). Similarly, higher concentrations of acetoin, ethyl acetate and acetic acid have been noticed in breads made with teff sourdough compared to breads made with LAB-initiated wheat sourdough. It can be associated with the high content of unsaturated fatty acids and phenolic compounds in teff flour, which could influence the formation of VOCs (Campo et al., 2016). The high content of acetic acid has a positive effect on the aroma of the bread and an antimicrobial effect against molds and rope-forming bacilli (Rosenquist & Hansen, 1998).

The first studies on the composition of VOCs in rye flour were carried out by Markova et al. (1970), Hougen et al. (1971), Prince & Mackey (1972). Several studies indicate that the concentrations of aroma compounds vary widely in straight-grade, low-grade, and wholemeal flours, and therefore the choice of flour type affects the aroma quality of sourdough bread (Hansen & Hansen, 1994a; Czerny & Schieberle, 2002; Kirchhoff & Schieberle, 2002; Galoburda et al., 2020).

When bakery products are made from flour rich in phenolic acids, such as wholemeal flour, the ability of LAB and yeasts to reduce or decarboxylate phenolic acids is significantly altered (De las Rivas et al., 2009). Some LAB have strain-specific properties to decarboxylate and/or reduce phenolic acid. The use of free phenolic acids increases the bioavailability of phenols as antioxidants. In addition, the reduction of phenolic acids is important for the elimination of bitter taste compounds in bread (Gänzle, 2014). A study by Kirchhoff & Schieberle (2002) suggested that many compounds already present in flour belong to the important odorants in sourdough, such as methional or (*E,E*)-2,4-decadienal. Some aldehydes that are already present in the flour and undoubtedly resulting from the peroxidation of flour lipids, for example, hexanal or (*E*)-2-nonenal, are clearly degraded during the fermentation process. Czerny & Schieberle (2002) identified fatty-smelling odorants (*E,Z*)- and (*E,E*)-2,4-decadienal, (*E*)-2-nonenal, (*E, Z*)-2,6-nonadienal, and (*E,Z*)-2,6-nonadienol, 2- and 3-methylbutanal, 2- and 3-methylbutanoic acid, phenylacetaldehyde, phenylacetic acid, 3-(methylthio) propanal, acetic acid, pentanoic acid, and vanillin to be present in whole wheat flour in higher concentrations compared to wheat flour type 550. It can be seen in Table 1 that the concentrations of acetic acid, 3-methylbutanol or 2,3-butanedione in sourdough increased compared to these concentrations in flour. Although these three compounds have also been found in flour, they are mainly produced by LAB metabolism during fermentation. Since Czerny & Schieberle (2002) used commercial starter in their laboratory sourdough fermentation, resident microbiota remained unidentified and no association between volatile profile and starter species could be established.

The main chemical classes of volatile compounds identified in flour and flour blends are alcohols, carboxylic acids, terpenes, aliphatic aldehydes (e.g. pentanal and hexanal, formed as fatty acid oxidation products), alkanes and esters (Hansen, 1995; Galoburda et al., 2020), including derivatives of pyrazines and pyridines, which are also often found as a result of heat treatment (Heiniö, 2003). The following volatile compounds have been detected mainly in rye flour: alcohols (ethanol, n-propanol, 2-methyl-1-propanol, 2-butanol, acetone), a homologous series of n-alkanals (from propanal to heptanal) as well as (E)-2-hexanal, benzaldehyde, 2-heptanone, 2-pentylfuran, and 2-furaldehyde, esters ethyl acetate and methyl formate (Markova et al., 1970; Lund et al., 1989, Kirchhoff & Schieberle, 2002). The listed VOCs above are produced through technological processes from flavour precursors present in cereal grains, such as amino acids, fatty acids and phenolic compounds (Galoburda et al., 2020). Major phenolic compounds in wheat and rye grains are phenolic acids (e.g. ferulic acid, caffeic acid, dihydrobenzoic acid and sinapic acid) and alkylresorcinols (Shewry et al., 2010). Microorganisms may decompose the phenolic acids into chemical compounds with a strong flavour; for example, ferulic acid is the source of 2-methyl-4-vinylphenol, which is described as having a burnt or tar-like flavour (Hansen, 1995). Saccharomyces cerevisiae have two enzymes (phenylacrylic acid decarboxylase and ferulic acid decarboxylase) responsible for the decarboxylation of hydroxycinnamic acids (Dzialo et al., 2017). Several additional methods can be used to improve the taste characteristics of cereals, e.g. germination, extrusion and grinding. Germinated cereal grains are a good source of amino acids, peptides and sugars that act as flavour precursors for odour-active compounds. Germinated, extruded rye is characterized by grainy and fresh taste and hard texture related to the concentration of dimethyl sulphide and 2-methylbutanal (Heiniö et al., 2003).

The chemical characteristics of flour, such as ash content and falling number, also have a significant impact on the fermentation of sourdough. The falling number of flours is an indicator of the enzymatic activity of the flour - the lower it is, the higher the amylase activity of the flour and the more free sugars are available for microorganisms. The ash content of flours varies depending on the extent of flour extraction. The higher the flour extraction, the higher the ash content in the flour. The bran fraction contains more minerals and micronutrients that are essential for the growth of LAB. (Spicher & Stephan, 1999) Thus, the use of a higher extraction flour prolongs the fermentation time of the sourdough and more lactic acid and VOCs are produced. The higher nutrient content in higher-grade flours stimulates the microbial growth and their biochemical activity, resulting in the production of more flavour and aroma compounds (Hansen & Hansen, 1994a).

The chemical composition and quality of flour determine the dynamics of the microbial communities in the fermentation process and the kinetics of their metabolites (De Vuyst et al., 2014). The amount of fermented carbohydrates in the flour varies depending on the cereal, but above all on the activity of endogenous enzymes. These enzymes may originate from the cereal flour, from the microbial strains (e.g. yeast or LAB) or additives used. The activity of flour enzymes (amylases, xylanases and peptidases) is important in the release low molecular weight carbohydrates and amino acids (Hellemann et al., 1988; Hansen, 2012). LAB do not normally degrade starch, and the content of fermented mono- and disaccharides is less than 3% in wheat sourdoughs and 1% in rye sourdoughs. Rye has a higher arabinoxylan content (9–12%) compared to wheat. During sourdough fermentation, flour enzymes can degrade arabinoxylans into xyloses and arabinoses which affect the consistency of the sourdough (Hansen, 2004). It has been observed that the fermentation of sourdough with *Leuconostoc mesenteroides* increases the maltose content from 1.5%–2.4% and the fructose content from 0.05–0.45%. The glucose content remains unchanged at 0.17% due to the balance between enzymatic and microbiological processes (Lefebvre et al., 2002).

Table 1. Comparison of the amount of odour-active compounds in flours and sourdoughs made from wholemeal wheat flour (WWF), white wheat flour (WF) and rye flour (RF) (Kirchhoff & Schieberle, 2002; Czerny & Schieberle, 2002)

VOCs	Odour description	Amount in flour (µg per kg of dry weight)			Amount in sourdough (µg per kg of wet weight)*		Amount in sourdough (µg per kg of dry weight)
Aldehydes		WF	WWF	RF	WF-S	WWF-S	RF-S
3-methylbutanal	malty	97	153	265	105	452	899
2-methylbutanal	malty	30	74	205	54	96	180
hexanal	fresh, green, fatty	11,000	112,00	3,080	5,600	5,900	503
phenylacetaldehyde	honey-like	183	508	121	144	325	170
(*E,Z*)-2,4-decadienal	fatty	389	1,810	n.d	65	148	n.d
(*E,E*)-2,4-decadienal	deep fat fried	355	1,690	80	82	136	78
vanillin	vanilla-like	583	2,910	1,270	265	823	2,790
3-(methylthio)propanal	cooked-potato-like	25	127	n.d	12	41	n.d
Ketones							
2,3-butanedione	buttery	n.d	n.d	55	n.d	n.d	744
Alcohols							
3-methylbutanol	malty	n.d	n.d	76	n.d	n.d	15,200
2-phenylethanol	flowery	n.d	n.d	416	n.d	n.d	9,100
Organic acids							
2- and 3-methylbutanoic acid	sweaty	342	629	1412	524	1,030	3,519
acetic acid	vinegar	134,000	218,000	50,000	601,000	1,220,000	3,100,000
butanoic acid	sweaty	5,900	6,980	5,100	13,900	13,,400	21,800
pentanoic acid	sweaty	6,900	11,600	n.d	12,100	13700	n.d
2-phenylacetic acid	honey-like	142	418	2,260	327	852	4,990

*sourdoughs contained 40% water; n.d – no data; WF – wheat flour (type 550), WWF – wholemeal wheat flour, RF – rye flour, -S – sourdough.

A comparison of the key odorants identified in wheat and rye flour has shown significant differences in the qualitative and quantitative composition. For instance, compounds such as (*E,E*)-2,4-nonadienal (deep fat fried), (*E,Z*)-2,6-nonadienol (cucumber-like), hexanoic acid (sweaty), γ-nonalactone (coconut-like), and 4-methylphenol (faecal), are not associated with the aroma of rye flour, whereas 2,3-butanedione (buttery), octanal (fruity), (E)-2-octenal (fatty), 4-vinyl-2-methoxyphenol (apple, spicy) and 3-hydroxy-5-ethyl-4-methyl-2(5H)-furanone (sweet, fruity) have been characterized in rye flour but not in wheat flour (Czerny & Schieberle, 2002). The origin of the mild, cereal-like aroma of native rye flour is still unclear and complex.

Another aspect beside the type of cereal flour is the grain milling procedure used. Although nowadays the stone milling procedure has been almost completely replaced by the roller milling method, the main advantages of slow and low-temperature stone milling are the minimal oxidation of numerous compounds and the reduction of components (e.g amino acids as a precursors of aromatic substances) which are essential nutrients for microbes. Cardinali et al. (2022) study is currently the only one where stone-ground soft wheat flour was analyzed for its aromatic profile. The most characteristic compounds belonged to classes of aldehydes and alcohols. Within aldehydes, pentanal (strong acid, pungent) and hexanal (green, grassy, tallow) were found in appreciable amounts. Ethanol (alcoholic), 1-hexanol (green grass, flowery, woody) and isoamyl alcohol (pungent, cognac, fruity) were the most represented alcohols in stone-ground soft wheat flour. The results of the study confirmed that flour already contains many important substances contributing to the aroma of baked bread, and the choice of flour type is also one major factor affecting the quality of the aroma of bread.

In addition to the impact of flour, the effects of a natural pre-ferment aroma mixture, purified exogenous enzyme preparations and cell-free enzyme extract on the formation of VOCs have also been investigated (Niçin et al., 2022). In the biotechnology of bakery products, exogenous enzymes are used more as technological aids to replace additives, such as oxidants and emulsifiers, because in addition to the aroma formation, they increase the dough volume, improve crust and crumb colour, and have antiaging effects (Gänzle, 2008). Cavallo et al. (2017) found higher levels of alcohols in bread samples prepared with cell-free enzyme extract (CFE) of *Fructilactobacillus sanfranciscensis*, *Hafnia alvei* and *Debaryomyces hansenii* compared to bread samples without enzyme extracts. Some alcohols (e.g. acetaldehyde, propanal, 3-methylbutanal) were found at the highest levels in the bread produced with *F. sanfranciscensis* and especially *H. alvei* CFEs. The level of ketones, mainly 2,3-butanedione (or diacetyl), was not affected by the addition of CFEs in the sourdoughs. 2,3-butanedione is characterized by buttery odour and according to Pico et al. (2015) it may be produced by both lactic acid bacteria and yeasts from the glycolysis intermediate pyruvic acid or during baking upon oxidative decarboxylation of acetohydroxyacids (Pico et al., 2015). The addition of CFE of *D. hansenii* affected negatively the levels of five ester compounds in sourdough breads. While CFE of *F. sanfranciscensis* improved the synthesis of ethyl acetate; and CFEs from *H. alvei* and *D. hansenii* showed the ability to increase the level of heterocyclic compounds (e.g., pyrrole and pyrazine containing molecules) in sourdough breads. This study showed that microbial CFEs combined with sourdough fermentation could be an effective biotechnological tool to improve the sensory properties of sourdough bread (Cavallo et al., 2017).

The production of volatile compounds can be further influenced by the addition of nonconventional ingredients such as milk, fruits, by-products of beer and wine (e.g brewers' spent grain, cava lees), additional carbohydrates (including fibers) and other chemical compounds (e.g. citrate, glutamate) that stimulate the growth of certain microbial communities. The use of an additional source of fructose as an electron acceptor in sourdough increases the activity of mannitol dehydrogenase and acetate kinase and decreases the activity of lactate dehydrogenase, resulting in an increase in acetate production and a decrease in lactic acid production (Gobbetti et al., 1995). Similarly, naturally occurring citrate in milk acts as a substrate for microbial activity, resulting in production of 4-carbon flavour compounds such as acetoin and diacetyl (nutty and buttery aromatic notes) via citrate metabolism in LAB (Laëtitia et al., 2014). Since citrate metabolism affects the aroma of sourdough and sourdough bread, Comasio et al. (2019) investigated the effect of citrate addition on acetoin and diacetyl production by the citrate-positive *Companilactobacillus crustorum* strain LMG 23699 during wheat sourdough fermentation. Butter flavour compounds were detected both sourdough and bread, but compared to other studies (Kang et al., 2013; Gänzle, 2015) that have found an increase in growth rate or cell yield of LAB (e.g. *Limosilactobacillus panis*, strains of *Lactococcus lactis* and *Leuconostoc* spp) when citrate was added to sourdough, no growth stimulation of the *C. crustorum* strain was observed.

Previously, studies conducted by Hernández-Macias et al. (2021) and Martín-Garcia et al. (2022a) reported that Cava lees have a growth-promoting effect on some LAB species (mainly *L. sakei*, *L. curvatus*, *L. fermentum*, *L. casei*) both *in vitro* and in sourdough. Cava lees are a good source of soluble and insoluble fibers (β-glucans and mannan-oligosaccharides) derived from the yeast cell wall (Alonso et al., 2002). Their prebiotic effect and ability to support the growth and survival of LAB has been well recognized by several studies (Shi et al., 2018; Liu et al., 2021). Martín-Garcia et al. (2022b) study referred that Cava lees increased the concentration of 1-hexanol, acetic acid, hexanal, and ethyl decanoate in wheat sourdough. Compounds characteristic of sparkling wine, such as 1-butanol, octanoic acid, benzaldehyde, and ethyl hexanoate, were also detected in sourdoughs. This indicates that Cava lees not only support the production of volatile compounds in sourdough but also provide VOCs found in sparkling wines. Additionally, many studies have focused on the use of flaxseed (*Linum usitatissimum* L.) and its by-products, mainly seed cake, as a functional ingredient in bread making (Ozkoc & Seyhun, 2015; De Lamo & Gómez, 2018; Sanmartin et al., 2020). Sourdough bread fortified with flaxseed cake flour has been characterized by a more complex VOC composition compared to bread not containing flaxseed cake flour. Specifically, increasing the content of flaxseed cake flour increased the levels of esters (e.g. ethyl acetate), 2-butanone and isobutyl alcohol. The bread had a higher acetic acid content even when flaxseed cake flour was not added to the dough (Sanmartin et al., 2020).

Formation of VOCs during sourdough fermentation

The predominant LAB in sourdough are a group of gram-positive bacteria which are catalase-negative, non-motile, non-spore-forming rods or cocci that produce lactic acid mainly through lactic acid fermentation (Hammes & Vogel, 1995; Gänzle et al., 1998). The main genera of LAB identified in sourdoughs are *Lactobacillus*, *Leuconostoc*, *Pediococcus* and *Streptococcus* (Hansen & Schieberle, 2005). The primary function of the LAB in sourdoughs is to ferment cereal carbohydrate substrates (e.g. maltose, sucrose, fructose and glucose) into organic acids (mainly lactic acid) and many other metabolites that affect the nutritional, sensory, and technological properties of fermented foods (Chiş et al., 2020).

According to whether the enzyme aldolase is used in the production of lactic acid, LAB are divided into homolactic and heterolactic fermentation types. Homofermentative LAB generally produce diacetyl, acetaldehyde and hexanal, while heterofermentative LAB are responsible for the production of ethyl acetate, alcohols, and aldehydes. (Wang et al., 2021) Studies conducted between 1987–2017 in Europe (mainly Italy, France, Germany and Belgium), U.S. and Canada show that 95% of the sourdoughs contain heterofermentative LAB alone or in combination with homofermentative lactobacilli. The most frequently detected species were (taking into account the revised taxonomy of the genus *Lactobacillus*) *Fructilactobacillus sanfranciscensis*, *L. plantarum* and *Levilactobacillus brevis*, species in the *Companilactobacillus alimentarius* group (*C. paralimentarius*, *C. crustorum*, *C. mindensis* and *C. nantensis*), *Leuconostoc* spp. and *Weissella* spp. (Gänzle & Zheng, 2019) All homofermentative lactobacilli produce 2,3-butanedione (particularly *Lacticaseibacillus casei*), which is not seen in heterofermentative species. Probably, the heterofermentative bacteria lack the diacetyl synthesis pathway or/and the redox potential is too high to allow acetoin oxidation (Kaseleht et al., 2011). Homofermentative LAB (*Lactobacillus (Lb.) delbrueckii*, *Lb. acidophilus*, *C. farciminis*, *Lb. amylovorus*, *C. mindensis*) convert almost all hexose into lactic acid via the Embden-Meyerhof pathway (EMP). This metabolism is characterized by the breakdown of 1,6-diphosphate fructose into two triose phosphates, which are converted into lactate. Other hexoses, such as mannose, fructose, and galactose, enter the EMP after different stages of isomerization and phosphorylation of glucose-6-phosphate or fructose-6-phosphate. Heterofermentative LAB (*Fr. sanfranciscensis*, *Furfurilactobacillus rossiae*, *Le. brevis*, *Limosilactobacillus pontis*, *Li. fermentum*) decompose degrade hexose into lactic acid, acetic acid, ethanol and carbon dioxide via the phosphoketolase pathway (Axelsson, 1998; Hansen & Schieberle, 2005).

Specifically, monosaccharides are used in glycolysis to produce pyruvic acid, which is the basis for fermentation by LAB and yeasts. Several compounds are produced from pyruvic acid, such as e.g. lactic acid, propionic acid, propanol, ethyl lactate, ethanol, acetic acid, 2,3-butanedione, 2-butanone or butanol. Therefore, the production of VOCs is highly dependent on the sourdough microbiota, including fermentation time. The fermentation time required to produce a sufficient amount of VOCs is at least 12 h (Petel et al., 2017; Wu et al., 2022). When *Saccharomyces cerevisiae* is used, the fermentation of the sourdough takes place within a few hours and the resulting bread is therefore less aromatic (Hansen & Schieberle, 2005), despite the higher concentration of volatiles compared to single LAB starters (Hansen & Hansen, 1994b; Meignen et al., 2001; Annan et al., 2003).

Moreover, LAB release precursors of aromatic compounds, such as free amino acids, which are degraded to aldehydes or alcohols as a result of metabolic processes (Hansen & Schieberle, 2005). The main amino acid conversion pathways of LAB cells include decarboxylation, transamination (such as the conversion of glutamine to glutamate), and deamidation (various α-carboxylic acids) (Fernandez et al., 2006; Gänzel et al., 2007; Wang et al., 2021). Sourdough fermentation with LAB has been shown to increase amino acid content, while dough fermentation with yeasts decreases free amino acid concentration. The enhancement of proteolysis during sourdough fermentation can be attributed to the proteolytic activity of sourdough LAB or to enhanced proteolysis by cereal enzymes (Thiele et al., 2002). Amino acid metabolism has also a crucial role in the adaptation of LAB to the acidic environmental conditions prevailing in sourdough (Wang et al., 2021).

Ketones, aldehydes, carboxylic acids and alcohols are synthesized in catabolic (e.g. deamination, decarboxylation, transamination) pathways, which have a significant impact on the sensory properties of bakery products (Kieronczyk et al., 2001). For example, expression of the arginine deiminase pathway promotes ornithine production (LAB metabolism), which in turn enhances the formation of 2-actetyl-1-pyrroline, that is responsible for the roasty note of bread crumbs (Gänzle et al., 2007). Peptides and free amino acids are substrates for microbial conversion or are converted into volatile compounds (e.g. methylbutanol, acetaldehyde, methionic acid) during baking. The catabolism of free amino acids in sourdough by LAB not only has a sensory effect, but also improves the acid tolerance of LAB and promotes microbial development in poor nutrient conditions (Su et al., 2011; Gänzle & Gobbetti, 2013).

During spontaneous sourdough fermentation, butyric acid and acetic acid, butyl formate, butanol and 4-methyl propanol are the main volatile compounds produced (Kam et al., 2011). Although lactate is the end-product of lactic acid fermentation, under aerobic conditions it can be catabolised by lactate oxidase or NAD+ (nicotinamide adenine dinucleotide) -independent LDH (lactate dehydrogenase) of some LAB (e.g. *Latilactobacillus curvatus*, *Lat. sakei*, *L. casei*, *La. plantarum*) to produce pyruvate, which is further catabolised by pyruvate oxidase into acetate and carbon dioxide. Under anaerobic conditions, some LAB (e.g. *Le. brevis*, *Lentilactobacillus buchneri*, *La. plantarum*) can via NAD+-independent LDH catabolise lactate into acetate and formate. (Liu, 2003) A study by Damiani et al. (1996) concluded that in laboratory-produced sourdoughs containing single-strains of *Le. brevis* subsp. *linderi* and *La. plantarum*, had most complex VOCs profiles. In addition, they also determined that sourdoughs initiated by microbial starter cultures produce an even greater amount of volatiles.

Studies in the past decade (Minervini et al., 2012; Zhang & He, 2013; Lhomme et al., 2015; Li et al., 2016; Ripari et al., 2016; Comasio et al., 2019) have reported the occasional occurrence of acetic acid bacteria (AAB) in spontaneous wheat, rye and maize sourdoughs. AAB are not considered typical members of sourdough microbiota probably because of their growth is highly dependent on the availability of molecular oxygen. However, some studies indicate that a number of AAB can still grow despite anaerobic conditions during sourdough fermentation. Their oxygen requirement cannot be fulfilled through aeration, as this would also enhance mold growth and oxidation of flour compounds. Further, AAB oxidation of ethanol and lactic acid would increase the flavour-impacting concentrations of acetic acid and acetoin to a great extent and hence result in variations in VOC compositions. Finally, they may have a retarded impact on the dough rise (De Vuyst et al., 2021).

The ratio of lactic acid to acetic acid, defined as the percentage of fermentation, is also an important parameter that may affect the flavour profile of bread, as well as play an important role in the structure of the final product (Lorenz, 1983). To give the bread a balanced flavour and aroma, the ratio of lactic to acetic acid should be about 4:1. If the concentration of acetic acid is low, the bread has too weak taste and no characteristic odour. However, if the relative amount of acetic acid is too high, the taste and aroma may be excessively sharp (Spicher & Stephan, 1999). AAB are obligate aerobic bacteria with a unique oxidative fermentation pattern. Their membrane-bound aldehyde dehydrogenases oxidize a variety of sugars and sugar alcohols, ethanol, organic acids, and then release the oxidized products (aldehydes, ketones and organic acids). The presence of AAB in the sourdough may induce oxidative stress in LAB and yeasts, which is why the latter are able to produce various volatile compounds in sourdough (Saichana et al., 2015; Li et al., 2021).

Yeasts, mainly *S. cerevisiae* strains, occur naturally or in added form in sourdough, contributing to the formation VOCs. The extensive variation in the number of yeast species and strains depends on several factors, e.g. degree of sourdough hydration, type of cereal, fermentation temperature and storage temperature of the sourdough (Corsetti et al., 2007). VOCs synthesis is also influenced by microbial interactions. Yeasts are often associated with LAB in the sourdough, and the ratio of yeasts to LAB is usually 1:100 (Guerzoni et al., 2013). Yeasts identified in sourdough belong to more than 20 species, including *Kazachstania exigua*, *Candida humilis* and *Issatchenkia orientalis* (Corsetti et al., 2007). Sourdough fermentation which has been initiated by *Fr. sanfranciscensis* and other homo- and heterofermentative LAB and/or *K. exigua* communities are characterized by a balanced aroma profile. Sourdough based on the combination of *Fr. sanfranciscensis* and *S. cerevisiae*, contain a higher concentration of metabolites produced by yeast fermentation (1-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol) and a lower concentration of bacterial compounds (Meignen et al., 2001). However, the presence of *S. cerevisiae* does not significantly affect the formation of VOCs by *Fr. sanfranciscensis* during sourdough fermentation. In a study by Liu et al. (2022), the content of 1-butanol and 1-penten-3-ol decreased as the fermentation progressed, which are known to be novel findings in sourdough fermentation by *Fr. sanfranciscensis*. This may mean that *Fr. sanfranciscensis* S1 strain can utilize these two alcohols. It is evident that LAB, including *Fr. sanfranciscensis* and *L. plantarum* species, contribute to a higher and broader spectrum of VOCs than baker's yeast (Arora et al., 2021).

Yeast fermentation mainly produces carbon dioxide and ethanol, the concentration of which depends on the microbial strain (Hansen & Hansen, 1994a, 1994b). Moreover, the formation of metabolites depends on the concentration of fermentable carbohydrates (mainly maltose) in the sourdough, which in turn is due to the activity of microbial amylase, which breaks down starch into simple sugars (De Vuyst et al., 2016). The carbon dioxide produced by yeasts causes the proofing of bread dough. Although ethanol has an impact on the properties of bread, most of it evaporates during baking. Furthermore, yeasts produce a small amounts of organic acids (acetic and succinic acid), which lower the pH of the bread dough and thus contribute to the taste of the bread (Jayaram et al., 2013, 2014).

In addition to ethanol and carbon dioxide, yeasts produce a variety of metabolites, such as higher alcohols with branched chain amino acids via the Ehrlich metabolic pathway (Fig. 1) and derived esters, that have an effect on the aroma of bread (Hazelwood et al., 2008; Pico et al., 2015). For instance, higher alcohol 3-methyl-1-butanol (acidic, fruity odour) originates from the conversion of the L-leucine amino acid via α-ketoisocaproic acid and already at very low concentrations has a significant effect on the development of bread aroma (Rehman et al., 2006; Birch et al., 2013; Pico et al., 2015). Xu et al. (2020) and Fang et al. (2023) have also obtained similar results regarding the alcohol content of yeast-containing sourdoughs. The study of Fang et al. (2023) indicates that phenylethyl alcohol content increases in mixed fermentation of yeasts and LAB due to the promotion of the Ehrlich pathways of yeasts.

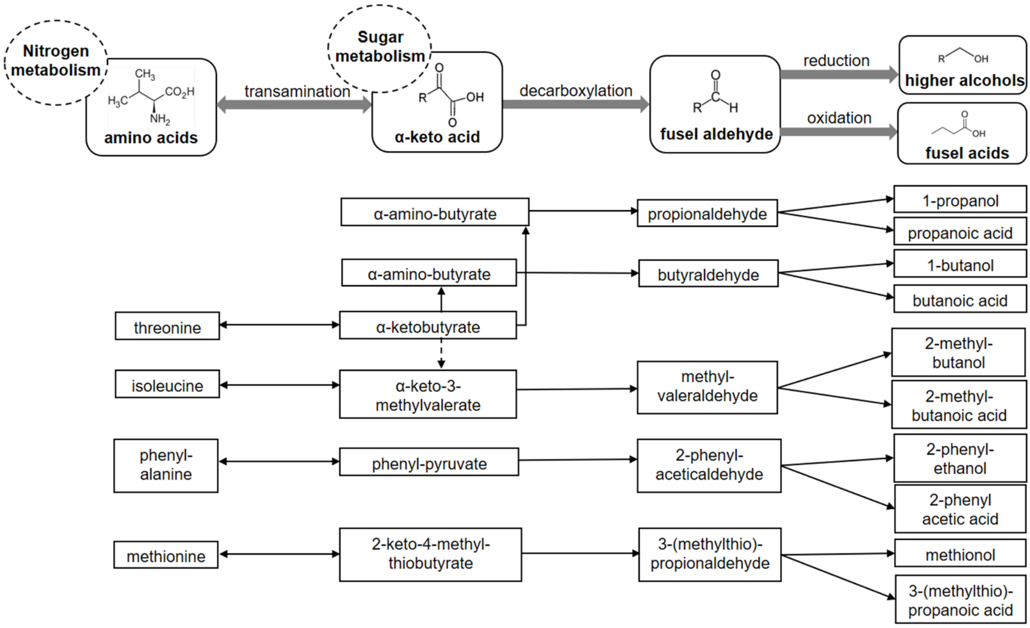

Figure 1. The three step Ehrlich pathway: catabolism of amino acids into fuse acids and fusel alcohols (Hazelwood et al., 2008; Dzialo et al., 2017).

Although *S. cerevisiae* prefers maltose as an energy source, specific yeasts such as *C. humilis* and *K. exigua* are maltose-negative (i.e. do not ferment maltose) and form a trophic relationship (mutualism) with the heterofermentative lactic acid bacterium *Fr. sanfranciscensis*, hydrolysing sucrose and glucofructan, and consuming glucose during the process (Gobbetti et al., 1994; Gobbetti, 1998). 2,3-butandione (diacetyl) produced by both LAB and yeasts (via pyruvate catabolism or Ehrlich metabolic pathway) supports the formation of a characteristic aroma (buttery flavour) of bread, while this compound is also formed by Strecker degradation (α-amino acid conversion to aldehydes) during bread baking, yielding pyrazines, for example (Hansen & Schieberle, 2005; Cho & Peterson, 2010; Birch et al., 2013; Pico et al., 2015). It has been observed that when yeast strains are added to the sourdough, the yeasts use the available oxygen for growth, thereby increasing the metabolite content. At low concentration of yeasts, oxygen is available for flour lipoxygenase, which oxidizes flour lipids to aldehydes (Pico et al., 2015).

Of the compounds produced by LAB and yeast fermentation, 36 are characteristic of both wheat and rye sourdough. These are for example hexanal (fresh, fatty, sweaty), acetylaldehyde (sharp, pungent), hexanoic acid (sour, fatty), 1-hexanol (ethereal, alcohol), 1-pentanol (oily, sweet), 2- and 3-methyl butanol (oily, alcohol, sweet, roasted), 2-pentylfuran (fruity, metallic) and dimethylsulfide (sulphur, fresh), associated with

LAB fermentation (Gobbetti et al., 1995; Kaseleht et al., 2011). 2,3-butanedione (strong, buttery, sour, caramel) is mainly produced by homofermentative LAB (Damiani et al., 1996; Liu et al., 2020), while the production of acetic acid and esters is specific to heterofermentative LAB and their compounds (ethyl acetate, ethyl lactate (sharp, caramel) (Hansen et al., 1989; Petel et al., 2017). Homo- and heterofermentative LAB can produce the same volatile compounds, but their content varies. The study by Kaseleht et al. (2011) shows that heterofermentative LAB has greater activity in reducing aldehyde (2- and 3-methylbut-anal, 2-hexenal, (*E*)-2-heptenal, hexanal, heptanal and 2-octenal) content than homofermentative LAB.

Thermally induced generation of VOCs

Volatile compounds formed during baking of dough or drying the sourdough (production of dry sourdough, Type III sourdoughs) are directly dependent on the precursors - aldehydes (usually reduced sugars) and amines (amino acids or proteins) (Parker et al., 2000; Nursten, 2002). The colour of the bread crust and its roasted aroma are caused by non-enzymatic reactions, e.g. compounds obtained by the Maillard reaction. The Maillard reaction is mainly induced by high temperatures (roasting, baking, extruding), while the free amino groups of lysine, peptides or proteins react with the carbonyl groups of reducing sugars (Silván et al., 2006). Nowadays, the Maillard reaction is one of the most important reactions in terms of food quality. Its importance lies in the formation of compounds that affect the organoleptic quality and preservation of food (Somoza & Fogliano, 2013). Since the chemical structures of the aldehydes generated during the Ehrlich pathway and the Strecker reaction are identical, it is a challenge to quantitatively distinguish the amounts of compounds formed from the respective pathways (Chavan & Chavan, 2011).

According to Hodge (1953) and Martins et al. (2001), the Maillard reaction consists of three main stages: initial, intermediate and final. At each stage, the special chemical structures are formed. The initial stage is related to sugar-amine condensation and Amador rearrangement. In the following intermediate stage, sugar dehydration and fragmentation, and amino acid degradation takes place, which continues in the final stage with aldol condensation, aldehyde-amine condensation and the formation of heterocyclic nitrogen compounds. The final step of Maillard reaction itself is under-explored, but it is known that the reaction consists of polymerization and condensation reactions of carbonyl compounds with the participation of amino compounds. As a result of the reactions, a mixture of cyclic compounds containing nitrogen is formed: pyrazines, pyrroles, furans and sulphur-containing compounds that are insoluble in water and have a brown colour, and lipid degradation products, e.g. alkanal, 2-alkene, 2,4-alkadenane (Parker et al., 2000). Pyrazines are nitrogenous cyclic compounds with very strong odour properties (Ji & Berhard, 1992). Zhou et al. (2022) detected pyrazine compounds (e.g 2,5-dimethyl pyrazine, 2,6-diethylpyrazine, 2-methylpyrazine, 2,3-dimethyl-5-ethylpyrazine) as the dominant volatile compounds in Tatary buckwheat sourdoughs. The study also found a significant negative correlation between most pyrazines and microbial diversity.

Individual Maillard reaction and Strecker degradation compounds, for instance 2-methylbutane (fruity), 3-methylbutanal (sweet, roasted) and 2,3-butanedione (buttery) and furfural (almond) have been identified in wheat and rye bread (Heinio et al., 2003). These compounds may be derived from fermentation associated with LAB and *K. exigua* yeasts (Kratochivil & Holas, 1983; Gobbetti et al., 1995) and most of them contribute to the desired roasted (or toasted), caramelized and sweet flavour. In addition to the Maillard reaction, caramelization of sugars occurs during dough baking (above 140 °C), while VOCs produced during fermentation (Hadiyanto et al., 2008; Bianchi et al., 2008) and low molecular weight components, e.g. ethanol, smaller esters (ethyl acetate (ethereal, floral) and ethyl 3-methylbutanoate (sweet)) and acids, evaporate (Birch et al., 2013). In sourdough, the Maillard reaction affects gluten proteolysis, resulting in free amino acids (Gobbetti et al., 1995). The addition of enzymes (e.g., amylase and glycosidase) to sourdough during fermentation increases the concentration of sugars, thereby contributing to the Maillard reaction. Some compounds, e.g. methylpropanol (isobutanol), 2- and 3-methylbutanol (iso-pentanols), ethyl acetate and ethyl lactate identified in bread have been shown to be related to their respective concentrations in sourdough (Chavan & Chavan, 2011). The formation of these compounds can be attributed to Maillard reactions, influenced by the amount of free amino acids. An increase in free amino acid content has also been observed in sourdough fermentation (Hansen et al., 1989).

Free amino acids can also be a source of nitrogen for both yeast growth and metabolism, resulting in higher alcohols such as 3-methylbutanol (Heiniö, 2003), or are converted to flavour compounds during steaming (production of steamed bread). Cereal protein hydrolysates, including amino acids and peptides, are important precursors for VOCs (Gänzle, 2008), but degradation and depolymerisation of cereal proteins are complicated to achieve due to the low and limited activity of cereal and microbial enzymes in sourdoughs. According to Gänzle (2008) proteolysis in both wheat and rye sourdough is less than 5% of cereal proteins and malt or fungal enzymes are required to increase protein degradation. Liu et al. (2015) have demonstrated that the addition of 1% Hyd-SPI (hydrolysed soy protein isolate) promotes the growth and fermentation of the selected starter due to its content of peptides and amino acids (especially phenylalanine, tyrosine, arginine, leucine and glutamic acid). Higher concentrations of volatile compounds such as 3-methyl-1-butanol (apple, banana), 2-pentylfuran (fruity), phenylethyl alcohol (floral) and variety of esters responsible for the flavour of steamed bread were detected due to the presence of Hyd-SPI. Moreover, the activity of cereal proteinases depends on the pH of the nutritional environment. A drop in pH during sourdough fermentation is known to activate aspartic proteases, which are the major proteinases in resting grains of wheat and rye (Bleukx et al., 1998).

VOCs originating from enzymatic processes

Lipids are a minor component of flours, but they have a great impact on the bread quality (Castello et al., 1998). Lipid oxidation is a complex of reactions involving several molecular mechanisms such as the generation of reactive oxygen precursors, free radicals and peroxides (Ahmed et al., 2016). Oxidation of lipids in sourdough is caused by the presence of active enzymes (e.g. lipoxygenase), the addition and type of fatty substances (e.g. shortenings and margarines), and mixing (aeration) of the sourdough (Maire et al., 2013). Lipid oxidation is not sourdough or process specific, but it creates precursors that become a source for volatile compounds (Petel et al., 2017). Lipoxygenase oxidizes polyunsaturated fatty acids to free radicals, peroxides, and hydroperoxides, which are common VOCs during bread baking. Hydroxyperoxy acids are decomposition products of linoleic acid oxidation. In the presence of cysteine, hydroxyl-fatty acids are also produced, which may have a bitter taste (Shahzadi, 2011). Lipoxygenase of wheat origin is capable of forming 9 hydroperoxy linoleic acids in contrast to lipoxygenase of rye, whose lipolysis produces 13 hydroperoxy isomers (Belitz et al., 2004). Oxidation of lipids in sourdough and breadcrumbs mainly produces aldehydes (hexanal, heptanal, octanal (fresh, fatty, aldehydic)), ketones (2-octanone (grass, woody)), alcohols and esters, depending on the primary material of the fatty acids (Martínez-Anaya, 1996; Birch et al., 2013; Maire et al., 2013). Studies by Waraho et al. (2011) and Frankel (2005) have shown that free fatty acids are more prone to oxidation than esterified fatty acids. The effect of vegetable oils on sourdough fermentation is still little studied. Wu et al. (2022) determined that addition of corn oil to sourdough had a positive effect on the concentrations of aldehydes, ketones and furans. Important odour-active compounds including (*E,E*)-2,4-decadienal, 2-pentylfuran, 1-octen-3-ol, 3-methylthio-1-propanol, and (*E*)-2-nonenal were produced by *Lb. lactis*, corn oil, and lipase individually or via their interactions.

Vermeulen et al. (2007) have reported that the metabolic reactions of LAB in sourdough can favor lipid oxidation during fermentation. Lipid oxidation is enhanced by homofermentative LAB, meanwhile obligate heterofermentative LAB (*Li. reuteri*, *Fr. sanfranciscensis*) decrease the oxidation-reduction potential of sourdoughs and accumulate glutathione or thiol compounds and convert decadienal and nonenal rapidly to the corresponding unsaturated alcohols. The activity of lipoxygenase can be affected by yeasts activity. While yeast content is reduced, there appears to be an increase in the amount of oxygen available for lipid oxidation (Czerny & Schieberle, 2002; Gänzle et al., 2007; Poinot et al., 2007). Some LAB can convert lipid oxidation compounds into alcohols (Vermeulen, 2006). For example, 3-methylbutanoic acid (cheesy, sweaty) is produced by the oxidation of 3-methylbutanal with aldehyde dehydrogenase (Guerzoni et al., 2007). The following volatile compounds from lipid oxidation have been identified from wheat and rye sourdoughs: hexanal (fresh, fruity, fatty), acetaldehyde (ethereal, aldehydic), benzaldehyde (strong, sharp, bitter, almond), nonanal (citrus), (E)-2-octenal (fresh, nutty, roasted), (E)-2-heptenal (sour, fatty), (E)-2-nonenal (fatty, citrus), 1-pentanol (oily, sweet), 1-hexanol (essential), 1-heptanol (musty, sweet) and 2-pentylfuran (green, fruity) (Martínez-Anaya, 1996; Birch et al., 2013; Maire et al., 2013; Liu et al., 2020). According to Fernández Murga et al. (1999), the ability of lactic acid bacteria to convert fatty acids is probably related to their membrane homeostasis.

Research on the lipolytic activity of sourdough lactic acid bacteria has been limited to studies of the esterase and lipase activities of several strains of *Lb. sanfranciscensis*, *Lb. plantarum*, *Pd. pentosaceus*, *T. delbrueckii* and *S. cerevisiae* (De Angelis et al., 1999; Paramithiotis et al., 2010). In a study conducted by Wang et al. (2020), it was found that *Lactobacillus* spp, *Kazachstania* spp and *Candida* spp had close linkages with lipid metabolism, suggesting these microbes genera exhibited higher metabolic capacity of lipid metabolism; and thus during lipid metabolism they can produce a variety of organic acids with different carbon chain lengths.

Proteolysis during sourdough fermentation has been poorly investigated, despite the fact that protein content and its degradation can noticeably affect flavour and odour development. It is unclear whether the proteolysis during sourdough fermentation is attributed to the proteolytic activity of starter cultures (LAB, yeasts) or cereal enzymes, e.g. aminopeptidase, carboxypeptidase, and endopeptidase (Thiele et al., 2002; Di Cagno et al., 2014). Thiele et al. (2002) results indicate that the amino acid levels in wheat dough mainly depends on the pH level of the dough, the fermentation time, and the consumption of amino acids by the microbiota. Proteolysis has been studied indirectly by determining the content of free amino acids and peptides after the fermentation process (Gobbetti et al., 1994; Thiele et al., 2002). Free amino acids and peptides produced during microbial and enzymatic reactions are important growth substrates for microbes or are converted into flavour precursors or flavour compounds during baking. LAB proteolysis involves three main processes. First, degradation of extracellular proteins into oligopeptides by proteinases associated with the cell wall. Next, the transport of peptides into the cell by peptide transporters and finally the degradation of peptides into shorter peptides and amino acids by several intracellular peptidases (Rizzello et al., 2016; Chiș et al., 2020). The proteolytic activity of sourdough LAB has been studied most thoroughly, although extracellular proteinase activity has not been detected in most sourdough lactobacilli (Gerez et al., 2006; Zotta et al., 2007; Paramithiotis et al., 2010), but the peptidase activity of sourdough LAB significantly contributes to the hydrolysis of peptides (Gänzle, 2008).

The effect of microbiota on proteolysis and peptide hydrolysis during fermentation is well known, but the contribution of the metabolic activity of microbes involved in the formation of flavour-active peptide derivatives remains unknown. Flavour-active amino acids and their derivatives and peptides are thought to be catalyzed by lactoyl-transferase, succinyl transferase, pyroglutamyl cyclase or γ-glutamyl-transferase (Zhao et al., 2016). Zhao & Gänzle study (2016) demonstrated that *Limosilactobacillus reuteri* 100-23 and *L. reuteri* 100-23Δ*gadB* produce γ-glutamyl dipeptides during growth in sourdough and suggested that these peptides influence the flavour of bread. Zhao & Gänzle (2016) and Zhao et al. (2016) studies refer to the formation of flavour-active peptides, such as glutathione and some γ-glutamyl dipeptides and tripeptides, through proteolysis, which give rise to kokumi taste (described as a sensation of enhancement of sweet, salty and umami tastes). The addition of vital wheat gluten, proteolysis, and fermentation time were the most relevant indicators contributing to γ-glutamyl peptide synthesis, but the supplement of microbial transglutaminase did not support production of γ-glutamyl peptides. It is worth highlighting and further investigation that flavour-active peptides may be a new innovative tool for improving several flavour characteristics. Although kokumi-active compounds are not classified as flavour-active compounds, these compounds have the ability to increase the flavour intensity of other compounds. For instance, Zhao & Gänzle (2016) observed that the taste of bread with higher kokum peptides was rated as more balanced than the taste of bread with lower content of kokum peptides, which was rated as saltier.

The extent of proteolysis in sourdoughs fermented with LAB (exhibit proteinase and peptidase activities, which are mainly bound to the cell wall) has been found to be higher, while sourdough fermentation with yeasts produces less free amino acids (Gobbetti et al., 1994; Thiele et al., 2002). Sourdough fermentation has been shown to significantly increase levels of the branched-chain amino acids leucine and isoleucine, branched-chain amino acid metabolites, as well as several small peptides containing branched-chain amino acids. This effect is more prominent in rye than in wheat sourdough most likely due to intensive proteolysis in acidic rye sourdough (Koistinen et al., 2018). Amino acids, e.g. glutamate, improve the taste of sourdough bread, while other amino acids (incl. ornithine, leucine and phenylalanine) are flavour precursors, which are converted to 2-acetyl-pyrroline, 3-methyl-butanol and 2-phenylethanol (Hansen & Schieberle, 2005; Gänzle, 2014).

The content of amino acids, e.g. ornithine, methionine, phenylalanine, leucine, isoleucine, and valine in the dough is essential for the development of bread flavour. Ornithine, a precursor compound of 2-acetyl-1-pyrroline (roasty note of the crust odour), is derived from the yeast biomass or arginine metabolism of LAB. *Lb. amylolyticus*, *Le. brevis*, *Li. fermentum*, *Li. frumenti*, *Li. pontis*, *Li. reuteri*, *Lat. sakei*, and few strains of *Fr. sanfranciscensis* convert arginine to ornithine via the arginine-deiminase (ADI) pathway. (Vermeulen, 2006) Ornithine is not a proteinogenic amino acid and therefore its presence in dough is the consequence of microbial metabolism (Thiele et al., 2002). In addition to LAB, the addition of baker's yeast has been observed to increase the level of ornithine in wheat doughs and corresponding levels of 2-acetylpyrroline in wheat bread crust (Schieberle, 1990). Moreover, ornithine can react with the carbonyl compound 2-oxopropanal during Maillard reactions in the bread baking process, to form 2-acetyl-1-pyrroline, which is responsible for the aroma of bread crust (Gänzle, 2014; Pico et al., 2015).

CONCLUSIONS

An abundant literature shows the various functional properties of sourdough fermentation that contribute to the production of VOCs. The formation of VOCs in sourdough and sourdough bread is therefore mainly related to the sourdough microbiota and their metabolic activity, raw materials and technological parameters of fermentation and proofing. The aroma profile of sourdough bread is mainly influenced by the breakdown of carbohydrates and amino acids during sourdough fermentation, as well as by thermal reactions occurring during baking of the dough, such as caramelization of sugars and nonenzymatic Maillard reactions. Improvements in VOC analysis methods, diversity of starter cultures and novel ingredients as microbial growth substrate have expanded and created new directions in VOC research, enabling a better understanding of the complex and versatile metabolism of sourdough. VOCs not only play a role in developing flavour or preventing the growth of spoilage microorganisms, but are also gaining popularity for their potential health-promoting role in human health. Principally, the scientific literature on VOCs in sourdough bread is more focused on sensory descriptive analysis, and less research has been done using an analytical approach to determine the VOC content in sourdough and sourdough bread. In-depth knowledge of microbial and enzymatic metabolism increases the understanding of the effect of VOCs on the sensory and nutritional properties of sourdough bread and thus enables the bakery industry to more effectively control and optimize technological processes. In the future, more detailed and systematic studies are needed to evaluate the influence of sourdough fermentation on the formation of non-volatile flavour-active compounds, which has so far been little studied.

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