EVALUATION OF FUNCTIONAL FOOD INGREDIENTS PRODUCED BY SPROUTING AND FERMENTATION OF DIFFERENT GRAINS IN TERMS OF BIOACTIVE AND NEUROACTIVE COMPOUNDS

FARKLI TAHILLARIN ÇİMLENDİRİLMESİ VE FERMANTASYONU İLE ÜRETİLEN FONKSİYONEL GIDA BİLEŞENLERİNİN BİYOAKTİF VE NÖROAKTİF BİLEŞİKLER AÇISINDAN DEĞERLENDİRİLMESİ

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ABSTRACT

EVALUATION OF FUNCTIONAL FOOD INGREDIENTS PRODUCED BY SPROUTING AND FERMENTATION OF DIFFERENT GRAINS IN TERMS OF BIOACTIVE AND NEUROACTIVE COMPOUNDS

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Sprouting takes place by keeping the grains at a certain temperature and relative humidity for a certain period after taking a certain amount of water into their structures. It is known that sugar and amino acid concentrations increase with the biochemical reactions occurring in the structure of grains during sprouting. Fermentation is also a metabolic biochemical process in which desired changes occur in the food environment via yeast and/or bacterial activity in order to increase flavor, protect food, and provide health benefits. The main purpose of this thesis is to understand the sprouting and various fermentation processes of grains and the change and/or formation of their bioactive and neuroactive components since the results of the combined sprouting and fermentation process are lacking in the literature.

In this study, six types of grains, namely wheat, barley, rye, oat, einkorn and buckwheat, were used as materials. Commercial yeast and sourdough fermentation were applied to selected grains at different temperatures (10-40 °C) and times (1-36 hours) after each sprouting for an appropriate time (36-72 hours). Thus, 6 sets of samples were created: native, sprouted, commercial yeast fermented, sourdough fermented, sprouted and commercial yeast fermented, and sprouted and sourdough fermented. Total phenolic compounds analysis, free phenolic compounds analysis, antioxidant capacity analysis, amino acid analysis, amino acid derivatives analysis and melatonin analysis were applied to these sample groups.

As a result of the analysis, no significant changes were observed in the phenolic acid concentration, antioxidant capacity, and melatonin concentration in general. It has been observed that the combination of sprouting and sourdough fermentation creates a synergistic effect for the generation of tyrosine derivatives. More tyramine, L-DOPA, and dopamine formation were observed during sourdough fermentation than yeast fermentation. It has made a significant difference especially in the formation of L-Dopa and dopamine. As a result of the combined sprouting and fermentation processes at 10 °C-36 hours, the L-DOPA concentration increased the most in einkorn, increasing 955 times and as a result of the combined sprouting and fermentation processes at 30 °C-36 hours, the dopamine concentration increased the most in einkorn, increasing 273 times. Tryptophan derivatives showed significant increases only in samples fermented with commercial yeast. The most increase is in kynurenic acid with the commercial yeast fermentation of wheat at 30 °C-3 hours with 28 times.

Keywords: Sprouted cereals, sprouted and fermented cereals, functional cereals, bioactive compounds, neuroactive compounds, antioxidant capacities of cereals.

ÖZET

FARKLI TAHILLARIN ÇİMLENDİRİLMESİ VE FERMANTASYONU İLE ÜRETİLEN FONKSİYONEL GIDA BİLEŞENLERİNİN BİYOAKTİF VE NÖROAKTİF BİLEŞİKLER AÇISINDAN DEĞERLENDİRİLMESİ

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Çimlendirme, tanelerin yapılarına belirli bir miktar su aldıktan sonra belirli bir sıcaklık ve bağıl nemde belirli bir süre tutulmasıyla gerçekleşir. Çimlendirme sırasında tanelerin yapısında meydana gelen biyokimyasal reaksiyonlarla şeker ve amino asit konsantrasyonlarının arttığı bilinmektedir. Fermentasyon lezzeti arttırmak, gıdaları korumak ve sağlık açısından fayda sağlamak amacıyla maya ve/veya bakteri aktivitesi yoluyla gıda ortamında istenilen değişikliklerin meydana geldiği metabolik bir biyokimyasal süreçtir. Bu tezin temel amacı, kombine çimlendirme ve fermantasyon işlemlerinin sonuçları literatürde eksik olduğundan, tahılların çimlendirme ve çeşitli fermantasyon süreçleri ile bunların biyoaktif ve nöroaktif bileşiklerinin değişimi ve/veya oluşumunu anlamaktır.

Bu çalışmada buğday, arpa, çavdar, yulaf, siyez ve karabuğday olmak üzere altı çeşit tahıl material olarak kullanılmıştır. Seçilen tahıllar; her biri uygun süre boyunca (36-72 saat) çimlendirildikten sonra farklı sıcaklık (10-40 °C) ve sürelerde (1-36 saat) ticari maya ve ekşi maya fermantasyonu uygulanmıştır. Böylece 6 örnek grubu oluşturulmuştur: işlem görmemiş, çimlendirilmiş , ticari mayalı fermente edilmiş, ekşi mayalı fermente edilmiş, çimlendirilmiş ve ticari mayalı fermente edilmiş ve çimlendirilmiş ve ekşi mayalı fermente edilmiş. Bu örnek gruplarına toplam fenolik madde analizi, serbest fenolik madde analizi, antioksidan kapasite analizi, amino asit analizi, amino asit türevleri analizi ve melatonin analizi uygulanmıştır.

Analiz sonucunda genel olarak fenolik asit konsantrasyonu, antioksidan kapasite ve melatonin konsantrasyonunda önemli bir değişiklik gözlenmemiştir. Filizlenme ve ekşi hamur fermentasyonu kombinasyonunun tirozin türevlerinin oluşumu için sinerjik bir etki yarattığı gözlemlenmiştir. Ekşi maya fermantasyonu sırasında maya fermentasyonuna göre daha fazla tiramin, L-DOPA ve dopamin oluşumu gözlenmiştir. Özellikle L-Dopa ve dopamin oluşumunda önemli fark yaratmıştır. 10 °C-36 saatte kombine filizleme ve fermantasyon işlemleri sonucunda L-DOPA konsantrasyonu en fazla siyezde 955 kat, 30 °C-36 saatte kombine filizleme ve fermantasyon işlemleri sonucunda dopamin konsantrasyonu en fazla siyezde 273 kat artmıştır. Triptofan türevleri sadece ticari maya ile fermente edilmiş örneklerde önemli artışlar göstermiştir. En fazla artış, buğdayın ticari maya fermantasyonu ile 30 °C-3 saatte 28 kez kinürenik asittedir.

Anahtar Kelimeler: Çimlendirilmiş tahıllar, çimlendirilmiş ve fermente edilmiş tahıllar, fonksiyonel tahıllar, biyoaktif bileşikler, nöroaktif bileşikler, tahılların antioksidan kapasiteleri.

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CONTENTS

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SYMBOLS AND ABBREVIATIONS

Symbols

T	Temperature
t	Time
h	Hour

Abbreviations

TAG	Triacylglycerol
GABA	Gamma-aminobutyric acid
5-HTP	5-hydroxy-L-tryptophan
OCD	Obsessive-compulsive disorder
ADHD	Attention deficit-hyperactivity disorde
HPLC	High pressure liquid chromatography
LC-MS/MS	Liquid Chromatography with tandem mass spectrometry
DPPH	2.2-diphenyl-1-picrylhydraz
TROLOX	6-hydroxy-2.5.7.8-tetramethylchromal-2-carboxylic acid
nd	Not detected
N	Native
S	Sprouted
SC FERM	*S.cerevisiae* fermented
SD FERM	Sourdough fermented
MRM	Multiple reaction monitoring
CE	Collision energy
Tyr	Tyrosine
Trp	Tryptophan

1. INTRODUCTION

The widely consumed grains in the world include wheat, barley, rye, and oats. The demand for einkorn is also growing due to its high nutritional value and multiple health benefits. In addition to these buckwheat, a pseudo-grain, has become popular in recent years with its very similar nutritional content to other grains. Buckwheat is gluten-free which makes it important in terms of the grain consumption of celiac patients.

Sprouting and fermentation are among the basic processes applied to grains. Many compounds are formed as a result of biochemical reactions that take place during sprouting and fermentation processes. Among these compounds, amino acid derivatives have an important place with both their beneficial or harmful effects on human health. These compounds are also referred to as neuroactive and bioactive compounds due to their effects on the nervous system. It is known that proteins are degraded to free amino acids by sprouting and these amino acids are converted into secondary metabolites some of which are neuroactive or bioactive compounds. There are also studies on the amount and formation of amino acid derivatives and their precursors in fermented products. According to them, the combination of sprouting and fermentation is interesting in terms of amino acid derivatives, but it is unclear how these compounds respond to the combination of both sprouting and fermentation processes.

In this thesis these 6 selected grains were subjected to both sprouting and fermentation processes independently and in combination to investigate the resultant content of amino acid derivatives.

The results reported in this thesis have been published in the following article;

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2. GENERAL INFORMATION

2.1. Grains

Grains are an important food source in terms of carbohydrates, proteins, and fats as macro components; iron, zinc, and calcium and provide phytochemicals as micro components [1-3]. According to the 2018/2019 data of the United Nations Food and Agriculture Organization (FAO), grain production in the world is 2652.6 million tons, consumption is 2681.0 million tons, and these numbers are increasing every year [3]. The increase in grain consumption has led to an increase in research on grains over the years. However, there are still points that need improvement including the effect of the combination of sprouting and fermentation.

2.1.1. Wheat (*Triticum aestivum*)

It has a large share as a food source in the world, as it is a major source of carbohydrates. It is a fertile seed if its water and nutrient supply is not restricted, and its quality is high when it matures in dry conditions [4]. Wheat germ consists of three parts: bran, endosperm, and germ. The bran is the outer layer of the whole grain. It contains high amounts of insoluble fiber (about 95% of its total) and small amounts (about 5%) of soluble fiber in the form of arabinoxylan, cellulose, and lignin [5]. Bread wheat is the most dominant source of dietary fibers and starch. It has positive effects on human health, especially by facilitating digestion [5]. A hundred g of wheat has an average of 14.2 g of protein, 3.3 g of fat, 64.2 g of carbohydrates, and 42.8 g of dietary fiber [3, 5].

2.1.2. Einkorn (*Triticum monococcum)*

It was cultivated 10000 years ago in the Karaca Mountains. located in the southeast of Turkey [6]. Compared to other polyploid kinds of wheat, it contains more protein, polyunsaturated fatty acids, fructans, and phytochemicals such as tocols, carotenoids, alkylresorcinols, phytosterols. However, its α- amylase, β-amylase, and lipoxygenase activities are less [7]. A hundred g of einkorn has an average of 18 g of protein, 4.2 g of fat, 70 g of carbohydrates, and 8.8 g of dietary fiber [8].

2.1.3. Rye *(Secale cereale)*

It is generally produced in Europe and can be used for bread and other bakery products [9]. A hundred g of rye contains an average of 8.2 g of protein, 2 g of fat, and 75.9 g of carbohydrates [3]. Besides its α-amylase activity, the presence of arabinoxylan is the most important factor in the use of rye in the production of bakery products [9]. Rye arabinoxylans, as a minor carbohydrate fraction, improves baking due to its water-binding capacity and viscosity-increasing properties [10].

2.1.4. Oats *(Avena sativa L.)*

Oat, which was used in animal nutrition before, has an important place in human nutrition today, due to its high nutritional content. In addition, oat shows health-promoting effects such as antioxidant activity, hypolipidemic effect, cardiovascular effect, anti-obesity effect, antidiabetic effect, and antimicrobial effect [11]. A hundred g of oats has an average of 11.2 g of protein, 9.2 g of fat, and 66 g of carbohydrates [3]. Starch is the most abundant component in oats, and its high content of amylase (approximately 25-30%) gives oats a typical gelling character. Oat, which is also rich in protein content, is the only cereal among cereals that has globulin or a legume-like protein, avenaline [11].

2.1.5. Barley (*Hordeum vulgare)*

Barley is used as a food source in many parts of the world. It can be used in breakfast cereals, soups, baby foods, and its main use is fermented foods. It is well known that it can be used to make malt in alcoholic beverages as well as its use in fermented baking products for increasing the soluble sugar, protein, and α-amylase in the dough [12]. A hundred grams of barley has an average of 13 g protein, 2 g or less fat, 73 g carbohydrates [13.14]. The principal non-starch polysaccharide β-glucans in barley have many beneficial health effects. The daily β-glucan intake recommended by the European Food Safety Board (EFSA) is 3 grams [13]. However, besides its beneficial effects, it reduces the water availability for the protein network in the dough and thus impairs its cooking properties [14]. Therefore, it should be added to the dough in certain proportions.

2.1.6. Buckwheat *(Fagopyrum esculentum)*

Buckwheat is not included in the cereal family, it is included in the pseudo-cereal (grain-like) group due to its similarities to cereals. A hundred grams of buckwheat has an average of 74 g of carbohydrates, 11.5 g of protein, 3 g of fat in 100 g of buckwheat. Apart from these, it also has a significant content of vitamins, minerals, and phenolic compounds. Although it is similar to other kinds of wheat in terms of carbohydrates, it is distinguished by its high polyunsaturated fat content such as linoleic acid, and high and balanced protein distribution [15]. Another important point is that while it is rich in albumin and globulin, it is poor in glutenin and gliadin. Buckwheat is gluten-free which makes it important in terms of the grain consumption of celiac patients [15.16]. The fact that it does not contain gluten in general causes problems because it changes the viscosity, elasticity, and cohesiveness of bakery products [16]. Buckwheat is the only cereal analog containing proanthocyanidins [17].

2.2. Sprouting

Sprouting is the first and key process in the development of plants and grains. The grains obtained as a result of the sprouting process, which takes about 2-3 days, and in which the sprout does not exceed the kernel size are called "sprouted grains". Sprouting includes 4 stages: water immersion, stretching of the cell, cell division, and transformation of cells into tissues [18]. These 4 phases take place in 3 steps: steeping. sprouting. and low-temperature roasting of the sprouted grains (kilning). In steeping, the seeds are kept in water with aeration for a certain period. Thus, the seeds are moistened before sprouting [19]. During sprouting, the seeds are kept in a dark environment at a certain temperature and humidity. As can be understood from the process; water, temperature, oxygen, light are environmental factors that affect the seed sprouting. Although the sprouting process is the same, different days are required for each grain to germinate.

With sprouting, changes occur in the chemical and physical structures of grains. Physical changes are visible, such as the emergence of sprouts from the grain. Chemical changes are mainly reflected in the nutritional value. Chemical changes can be examined in 5 categories as carbohydrates, proteins, lipids, phenolic acids, and antioxidants.

During sprouting, amylase breaks down starch into simpler sugars. The majority of these simple sugars are reducing sugars such as glucose and maltose, and the rest are non-reducing sugars such as sucrose. This provides better digestibility [20]. Although generally summarized as such, changes in carbohydrates vary by species. For example. Agu et al. (2012) found that glucose formation in buckwheat was higher than maltose formation, but they did not observe any sucrose at the end of sprouting [21]. On the other hand, Furbank et al. saw that sucrose was dominant in the early stages of sprouting of wheat, while glucose and maltose were dominant in the later stages [22]. Nutritional fibers are also structural carbohydrates, which are important for whole grains. Cellulose, hemicellulose, and lignans are insoluble in water; β-glucans and arabinoxylans are water-soluble dietary fibers. The change in dietary fiber after sprouting also depends on fiber fraction, sprouting time, and genotype [20]. For example, Koehler et al. saw that although the total dietary fiber in the wheat they sprouted decreased after 48 hours, it reached its maximum at the end of 192 hours. At the end of 192 hours, a decrease in water-insoluble fibers was observed, while an increase in water-soluble fibers led to an increase in the total [23]. Hübner et al. in a study they conducted, there was an increase in time-dependent water-insoluble dietary fibers in sprouted oats, while there was a decrease in water-soluble dietary fibers; total dietary fiber does not change. Although there was a decrease in water-soluble dietary fiber in sprouted barley, no change was observed in the ratio of water-insoluble and total dietary fiber [24].

Proteins are classified according to their solubility in whole grains as water-soluble (albumins), salt-soluble (globulins), alkali-soluble (glutelins), and alcohol-soluble (prolamins). During sprouting, storage proteins are hydrolyzed to peptides and amino acids. Thus, the bioavailability of proteins increases. Grain type and sprouting time are important in amino acid composition [20]. In a study of Tkachuk. he found that the free tryptophan and aspartic acid contents of wheat were increased after sprouting. He also observed that amino acid formation accelerates at high temperatures and slows down at low temperatures [25]. Globulin is the main protein source in oats. Likewise, in a study of Wu. concentrations of the main storage proteins in oats, globulin, and prolamin were observed to decrease after 8 days of sprouting. [26].

Lipids are abundant in whole grains. Also, they contain lipids in the form of triacylglycerols (TAGs). Mobilization of TAG, which begins with sprouting, leads to the conversion of fat into sugar. Lipases first cleave esterified fatty acids from TAG. Free fatty acids can then be broken down and converted to sugars via β-oxidation and glyoxylate cycles. The change in lipid content varies depending on the type of grain, sprouting time, and applications made before sprouting, as in other components [20]. Ozturk et al. saw that there was a decrease in saturated fatty acids such as 4:0, 10:0, 12:0 and unsaturated fatty acids such as cis-18:1, cis-18:2 in sprouted kinds of wheat compared to their unsprouted forms, while linolenic acid (18:3. n3) increased [27].

In addition to the well-known antioxidant effects of phenolic acids, they also have important roles as anticarcinogenic activity and important roles in the control of other diseases[28]. In a study of Kim et al (2018). it was observed that the free and total vanillic acid concentrations of sprouted wheat increased with increasing sprouting times for certain periods. The free *p*-coumaric acid and ferulic acid concentrations increased only with 72 hours of sprouting, while the total *p*-coumaric acid and ferulic acid concentrations increased with increasing sprouting times. Consistent with the results, it was also observed that antioxidant activity increased with sprouting [29]. In another study, it was observed that free phenolic acid concentrations of barley were increased during 36 hours of sprouting. [30]. Likewise, the free and total phenolic acids of rye and oats were also observed to be increased during sprouting [31], which in turn resulted in an increased antioxidant capacity. With increasing phenolic acid content. antioxidant activity also increased with sprouting [32].

2.3. Fermentation

Fermentation, by definition, is a metabolic process in which carbohydrates or sugars are converted into alcohol or acid either by yeasts, bacteria, molds, algae or fungi. Yeast fermentation converts sugar into alcohol (alcoholic beverages), while bacteria convert carbohydrates into lactic acid (sourdough bread). Fermentation is a process that has been used since ancient times, even though its metabolism is unknown. Not only the increase in aromatic elements like *iso*-butanol, *iso*-pentanol, ethyl acetate, and ethyl lactate [33] but also the increase in nutrient content makes fermentation interesting.

Saccharomyces cerevisiae is a eukaryotic microorganism that has been used by humans for centuries. It has various applications in the food industry in the production of beer, wine, spirits, bakery products and heterologous protein. Centuries of use have led to the specification of different strains for each process. This specificity has increased the desired flavors in the final product [34.35].

When the dough is formed, the α- and β- amylases in the flour are activated with the water added to the medium. As a result, starch is broken down. α-amylase randomly breaks starch into dextrins, starting at the α-1.4 bond, β-amylase also breaks down dextrins into maltose, starting at the non-reducing end and skipping one at a time. There are naturally occurring sugars in the flour itself: less than 0.5% glucose, fructose, and maltose, up to 1% sucrose and less than 0.5% raffinose. They are broken down into glucose and fructose by the invertase enzyme in yeast. During fermentation, the enzyme maltase in yeast converts maltose into glucose [36].

Sourdough fermentation is an old fermentation method. Compared to *S. cerevisiae* fermentation. the resulting product is not only more aromatic compounds but also has a longer shelf life. Another difference is that lactic acid is formed in sourdough fermentation, which makes it to be called lactic acid fermentation as well. However, lactic acid bacteria are not enough for sourdough fermentation. Yeast is still needed to create carbon dioxide and alcohol.

There are 3 types of sourdough fermentation. Type 1 is referred to as the traditional method. In this type, fermentation is restarted with a piece of dough leftover from the previous one. Type 2 and Type 3 are mostly used industrially. The desired bacteria mixture (together *with S. cerevisiae*) is used in the liquid form in type 2 and in the dried form in type 3. In Type 1 *S. cerevisiae* is not required. [37]. Type 1 sourdough fermentation was used in this study.

Sourdough is considered a unique food ecosystem as it can select adaptable lactic acid bacterial strains and hosts specific lactic acid bacterial communities for each sourdough. A mature sourdough can produce 50 different types of lactic acid bacteria and 25 different types of yeast. [38]. Lactic acid bacteria are divided into three subgroups according to their fermentation characteristics and types: obligate heterofermentative, facultative heterofermentative and obligate homofermentative. Lactobacillus brevis is an example of all three types. Lactobacillus brevis is obligate heterofermentative for all three species. Lactobacillus fermentum is suitable for Types 1 and 2, while Lactobacillus sanfranciscensis is the obligate heterofermentative species suitable only for Type 1. Lactobacillus plantarum is facultative heterofermentative for Types 1 and 2 and Pediococcus pentosaceus is for Types 3 [38].

Some factors affect sourdough fermentation. Dough yield is one of them. Dough yield is calculated by multiplying the sum of the dough and water amounts by 100 and dividing by the dough amount. (HV = (flour amount + water amount)*100/flour amount) Dough yield directly affects the aroma profile. In doughs with high dough yield, acidification will be faster and the amount of lactic acid and acetic acid will be higher. Temperature is one of the important factors. The temperature has a great influence on dough yield and microbial load. Lactobacilli grow best at 30 – 40°C, yeasts at 25 – 27°C. In general, high temperature increases acid production. The third parameter is the microflora used for fermentation. Acid production and flavor vary, depending on the type and strain used. Titration acidity and pH are also important factors. While both are stable in the initial stage of fermentation, titration acidity begins to increase with the effect of yeast in the later stages. Another factor is the substrate. The main substrate in fermentation is flour. The falling number of flour is an indicator of enzymatic activity. At lower values of falling number, amylase is more effective and releases more free sugars, which provides a favorable environment for the growth of microflora [37].

With fermentation, enzymes such as α-amylase are activated and starch is broken down into simple sugars like glucose. Even if the concentration of glucose increases ith fermentation [39] its levels are shown to decrease at the later stages due to its use by microorganisms as a substrate [40]. The change in proteins with fermentation is not as precise as carbohydrates. Some researchers have reported that the amount of proteins and/or amino acids, increases while others as a result of fermentation, while others report the opposite. Enzymes activated by fermentation can degrade proteins into peptides and amino acids. However, as with glucose, microorganisms can also use amino acids during fermentation [39].

2.4. Bioactive and Neuroactive Compounds

Neuroactive compounds are chemically synthesized compounds that can affect neurons and muscle cells. They are not only synthesized by humans but also by plants and microorganisms. They can be formed naturally or as a result of processing in foods. A neuroactive compound has important roles as a neurotransmitter, neuromodulator, and neurohormone [41].

2.4.1. Tryptophan Derivatives

Tryptophan is a precursor involved in protein and amino acid derivatives synthesis [42]. It can not be synthesized by animals and humans but can be synthesized from "phosphoenolpyruvate" by bacteria, fungi, and plants. 95% of tryptophan is catabolized metabolically, in the kynurenine pathway [42].

Besides being one of the essential amino acids, it is a precursor in the synthesis of important molecules like serotonin and melatonin. It is also involved in the synthesis of NAD+ in the case of niacin deficiency [42].

2.4.1.1. Melatonin

Melatonin, also called N-acetyl-5-methoxytryptamine, is a neurohormone. Synthesis of melatonin occurs mainly in the pineal gland of humans and its production occurs in several cells and tissues like retina and gastrointestinal tract [41]. It is an indolamine that offers many advantages in specificity for receptor binding [43].

Melatonin is known as a sleep hormone. It reduces sleep latency and increases the quality of sleep. Consequently, it eases the jet lag that occurs after long flights. Melatonin is known to reduce the risk for some neurodegenerative diseases, such as Alzheimer's, Parkinson's, Huntington's diseases [43.44].

Formation mechanisms of melatonin in humans, plants, and yeasts are described before [41.45]. In the human body, the reactions start with the formation of 5-hydroxy-L-tryptophan (5-HTP) from L-tryptophan by tryptophan-5-hydroxylase. This is followed by decarboxylation of 5-HTP by 5-hydroxytryptophan decarboxylase in which 5-HTP is transformed into serotonin. After serotonin is synthesized, N-acetyl-serotonin is formed by its acetylation with serotonin-N-acetyltransferase. Finally, N-acetyl-serotonin is methylated by hydroxy indole-O-methyltransferase to form melatonin [41].

In plants, due to the decarboxylation of tryptophan by tryptophan decarboxylase, tryptamine forms, which is transformed into serotonin by tryptamine-5-hydroxylase. There are two pathways for melatonin synthesis in plants and yeast. In the first one, serotonin is acetylated to N-acetylserotonin by serotonin N-acetyltransferase and then it is methylated to form melatonin by N-acetylserotonin methyltransferase. In the second one, serotonin is methylated to 5-methoxytryptamine by N-acetylserotonin methyltransferase and then it is acetylated to form melatonin by serotonin N-acetyltransferase [41].

2.4.1.2. Serotonin

In humans, serotonin synthesis occurs via the kynurenine pathway. Tryptophan is converted to 5-hydroxytryptophan by tryptophan 5-hydroxylase. It is then converted to serotonin by 5-hydroxytryptophan decarboxylase. The synthesis of serotonin in plants occurs by the conversion of tryptophan to tryptamine by tryptophan decarboxylase and it turns into serotonin by tryptamine 5-hydroxylase [41].

Many non-fermented foods like fruits and vegetables such as tomatoes, strawberries, onions, spinach, bananas, oranges, kiwis, pineapples, avocados, grapes, apples, watermelon, carrots, potatoes, many nuts such as almonds, hazelnuts, pistachios, and other food sources like chocolate (cocoa), green coffee, fish, etc. contain serotonin at ppm levels [41].

It is known to play a role in the treatment of many diseases such as depression, anxiety, schizophrenia, obsessive-compulsive disorder, Parkinson's disease, gastrointestinal and cardiovascular disorders, and hypertension [46].

2.4.1.3. Kynurenine

Tryptophan is approximately 95% catabolized by the kynurenine pathway in humans [47]. In the kynurenine pathway tryptophan is converted to N-formyl-L-kynurenine by tryptophan dioxygenase and/or indolamine dioxygenase and then N-formyl-L-kynurenine is converted to kynurenine by kynurenine formamidase [41].

Kynurenine is found in a variety of foods at different concentrations including: honey (0.1-5.5 μg/kg) [48]. The presence of kynurenine in various fermented foods was found as follows: bread (n.d-0.14 μg/g), beer(0.03-0.09 μg/g), cheese (0.03-0.32 μg/g) and yoghurt (0.29-0.75 μg/g) [49].

It has been found that compounds occurring in the kynurenine pathway, including the catabolism of tryptophan, affect nervous system diseases. Kynurenine has positive effects on schizophrenia [35] and Huntington's disease [37].

2.4.1.4. Kynurenic Acid

In humans, kynurenic acid occurs from kynurenine by kynurenine aminotransferase [41]. Kynurenic acid can also be found in many non-fermented foods such as fruits and vegetables, meat products, grains, and fresh spices [50], as well as in many fermented foods such as beer (0.02-0.05 μg/g), red wine (0.08-0.17 μg/g), cheese (0.03-0.08 μg/g), yoghurt (0.07-0.28 μg/g), cocoa powder (4.0-4.5 μg/g) [49].

Free radicals have many known harmful effects on health including immunological, neurological and urological disorders; eye, muscle, and skin disorders, diabetes, cancer and hypertension [38]. Kynurenic acid is able to scavenge free radicals which gives it antioxidant properties [39]. It also has positive health effects on Alzheimer's disease [36].

2.4.1.5. Picolinic Acid

Picolinic acid, which is tryptophan catabolite detected in the human body is formed in the kynurenine pathway. Kynurenine is converted to 3-hydroxy-L-kynurenine by kynurenine monooxygenase. 3-hydroxy-L-kynurenine is transformed to 3-hydroxyanthranilic acid by kynureninase. 3-hydroxyanthranilic acid is converted to 2-amino-3-carboxymuconate-semialdehyde and then finally transformed to picolinic acid in humans [41].

In literature, there is no information about its existence in non-fermented foods. However, it was shown to form in both red and white wine. [51].

Picolinic acid has antifungal, antiviral, antitumoral and cell growth regulatory activities [52]. Apart from these, its use as a dietary nutrient is known to reduce the risk of diabetes and it may have antimicrobial activity [53].

2.4.1.6. Quinolinic Acid

The formation of quinolinic acid is similar to that of picolinic acid. It is formed from 2-amino-3-carboxymuconate-semialdehyde from kynurenine in the kynurenine pathway [41].

According to Yılmaz and Gökmen (2021) fermentation of white wine with a mixture of *Torulaspora delbrueckii, Kluyveromyces thermotolerans* and *Saccharomyces cerevisiae* strains increase the concentration of quinolinic acid in the first 2 days [51]. Quinolinic acid may play a neuroprotective role at low concentrations. It has a positive health effect on various neurodegenerative diseases such as Alzheimer's disease and Huntington's disease [52].

2.4.1.7. Niacin

Niacin, also called nicotinic acid can be formed after quinolinic acid: Quinolinic acid is converted to nicotinic acid mononucleotide by quinolinate phosphoribosyltransferase and then nicotinic acid mononucleotide transforms to nicotinic acid by nicotinic acid phosphoribosyltransferase [54].

Niacin can be found in various concentrations in non-fermented foods such as peanuts, biscuits, fruit juice, green peas and tomatoes as well as in yeasts [55]. It is also found in a variety of fermented foods such as bread, beer, red wine, white cheese, yogurt, kefir, and cocoa [49].

Also known as vitamin B3, niacin has positive effects on health. Supraphysiological doses of niacin decrease total cholesterol, LDL cholesterol and triglycerides and increase HDL cholesterol [56]. It is also said to play a role in the treatment of migraine headaches [57].

2.4.2. Tyrosine Derivatives

Tyrosine is another important amino acid in terms of neuroactive compounds formation. Although it is not an essential amino acid, it has an important role in the formation of neuroactive such as L-DOPA, dopamine and biogenic amines such as tyramine. These compounds, which can also be called catecholamines, are known to have a positive effect on the cardiovascular system, metabolism, immune modulation and respiratory functions [58]. According to a study conducted by Nardil et al (2003). the average concentrations of tyrosine in grains harvested in certain periods are as follows: 24.2 mg / g protein in wheat, 15.8 mg / g protein in the rye, 16.2 mg / g protein in barley [59].

2.4.2.1. L-Dopa

L-DOPA is formed in humans and plants by hydroxylation of tyrosine by tyrosine hydroxylase [41]. In addition, L-DOPA, which is a non-protein amino acid, plays a role in the formation of many catecholamines like itself and alkaloids. It has functions as a prooxidant or antioxidant in plants [60].

In literature, there is limited information about L-DOPA in foods. According to Egounlety (2003). it is shown that raw bean has 6.36% L-Dopa content by weight. Also, Mucuna-based foods L-dopa content is increased in 12 hours and then decreased up to 48 hours with fermentation [61].

L-DOPA is one of the important neuroactive compounds used in the treatment of Parkinson's disease [41]. Today, improvements are still being made in the treatment of this disease using L-DOPA [62].

2.4.2.2. Dopamine

Dopamine is formed by carboxylation of L-DOPA by dopa carboxylase in humans, by dopa carboxylase or by hydroxylation of tyramine by monophenol hydroxylase in animals [41].

Dopamine is one of the main neuroactive compounds in the catecholamine group. Dopamine is known to be present in various foods such as bananas, fish, broad beans and cocoa [63-65].

Dopamine is known to affect movement and sensory stimuli, pleasure, and reward-seeking behaviors, addiction, emotion and perception, memory, attention and learning behaviors. It also plays a role in the treatment of diseases such as schizophrenia, obsessive-compulsive disorder (OCD), autism spectrum disorder, attention deficit-hyperactivity disorder (ADHD), substance abuse and Parkinson's disease [66.67].

2.4.3. GABA

GABA is formed by the decarboxylation of glutamic acid by glutamic acid decarboxylase [41].GABA is found in non-fermented foods such as oats, barley, soybeans, mung beans, black beans, sesame, wheat germ and bran, spinach, potato, broccoli, carrot, onion, apple, cabbage, tea types, chocolate [68-75], and fermented foods such as cocoa, red wine, beer and cheese [76-79]. It has been observed that beverages containing GABA reduce psychological and physical fatigue and increase the ability to solve in humans [80]. In addition. chocolates enriched with GABA were observed to decrease psychological stress

[81]. It has also been observed that intake of GABA reduces stress [82] and sleep delay [83].

2.4.4. Biogenic Amines

Biogenic amines are low molecular weight compounds containing nitrogen groups formed by decarboxylation of certain amino acids. Tyramine, histamine and phenylethylamine are common biogenic amines.

They can be found in many foods such as fish, various vegetables, meat and cheese, sausage, wine, fermented vegetables. The presence of biogenic amines in food can be interpreted as food spoilage or fermentation. Biogenic amines can cause allergic reactions such as difficulty in breathing, itching, rash, vomiting, fever and hypertension [84. 85]. They are also considered carcinogens due to their ability to react with nitrites [86].

2.4.4.1. Tyramine

Tyramine is formed by decarboxylation of tyrosine by aromatic amino acid decarboxylase in humans and by decarboxylation of tyrosine by tyrosine decarboxylase in plants [41].Tyramine is known to be contained in many non-fermented foods such as fruits and vegetables: tomatoes, paprika, strawberries, green onions, lettuce, cabbage, spinach, bananas, oranges, potatoes, raw coffee beans, fish, hazelnut, chocolate, salami [65.66.87-90] and many fermented foods such as red wine, white wine, beer, kefir, yogurt, sausage and various types of cheese contain tyramine [91-103].

Hypertensive crises and migraines are among the most well-known side effects of tyramine intoxication [104]. In addition, 600-2000 mg tyramine minimally increases systolic blood pressure in healthy individuals [105].

2.4.4.2. Histamine

Histamine is formed by the decarboxylation of histidine by histidine decarboxylase [41]. It is found in non-fermented foods such as spinach, chocolate, raw coffee bean, fish and salami [65.87-89.106], besides fermented foods such as red wine, white wine, beer, sausage and various types of cheese [91.95-103].Histamine poisoning causes increased heart contraction, dilation of peripheral blood vessels, causing hypotension, flushing and headache and abdominal cramps, diarrhea, and vomiting due to the contraction of the intestinal muscle [107].

2.4.4.3. Phenylethylamine

Phenylethylamine is formed by the decarboxylation of phenylalanine by the aromatic amino acid decarboxylase [41]. Like other biogenic amines, it is found in a variety of foods including non-fermented chocolate, fish, salami [65.87.88] and fermented red wine, white wine, beer and sausages [91.95.103]. It is known that high doses of phenylethylamine can cause hypertension, headache, vomiting, and perspiration [104].

3. MATERIALS AND METHODS

3.1. Chemicals and Consumables

Rye, buckwheat, oat and barley were supplied from ETİ A.Ş. (Eskişehir. Turkey). Wheat, einkorn, sugar, salt, and commercial yeast (*S. cerevisiae*) were supplied from a local market in Ankara, Turkey. Formic acid (98%), acetonitrile (LC gradient grade) and methanol (LC gradient grade) were purchased from J.T. Baker (Deventer. Holland). Calcium hypochlorite was purchased from Klortab (Ankara. Turkey). .2'-diphenyl-1-picrylhydraz (DPPH) and 6-hydroxy-2.5.7.8-tetramethylchroman-2-carboxylic acid (Trolox) were obtained from Sigma-Aldrich (Steinheim. Germany).

3.2. Sample Preparation

Wheat, einkorn, oat, rye, barley and buckwheat were subjected to sprouting. Both native and sprouted whole grain flours were then subjected to commercial yeast and sourdough fermentations. By doing so, 6 types of samples were obtained for each cereal. These were whole grain flours of native (N), sprouted (S), *Saccharomyces cerevisiae* fermented (SC Ferm), sourdough fermented (SD Ferm), sprouted *S. cerevisiae* fermented (sprouted SC Ferm) and sprouted sourdough fermented (sprouted SD Ferm).

3.3. Sprouting

Wheat, buckwheat and rye were obtained without husks, while einkorn, barley and oat were obtained with husks. In preliminary trials, it was observed that grains with husks were not able to sprout when their husks were mechanically separated. Therefore, husks of einkorn were manually removed, while barley and oat were sprouted with their husks.

Before sprouting, damaged and different colored grains were sorted out. The remaining intact grains were washed under tap water and immersed in 2% calcium hypochlorite solution for 10 minutes for disinfection. The grains were washed again under tap water till pH 7.5 (tap water pH) was reached to remove calcium hypochlorite residues. Steeping was carried out in air-conditioned cabinets (Nüve TK 120. Ankara) by soaking 1 kg of grain in 2 L of water for 7 hours at 20 °C. Sprouting was carried out in 5 L PET bottles with holes that allow air passage over 2 kg of each grain in the same cabinets at 95%

relative humidity and 20 °C in dark. During sprouting, grains were washed under tap water every 12 hours. Sprouting times were determined as the times in which the sprout/size ratios of grains reach approximately 1. These were 36 hours for buckwheat; 48 hours for wheat, barley, rye and einkorn; and 72 hours for oat. After sprouting, grains were freeze-dried, ground, and kept under 4 °C until extraction.

3.4. Commercial Yeast (*S. cerevisiae)* Fermentation

The dough was prepared by mixing the flour, yeast (5% on flour basis) and water (70% on flour basis) for 4 minutes with a kitchen type mixer (KitchenAid. Whirlpool Co. and Meyer Co. USA). The doughs were prepared in bulk and then were divided into 50 mL containers in 10 g pieces and left to fermentation. The fermentation process was carried out in air-conditioned cabinets at 20, 30 and 40 °C for 1, 2 and 3 h at 95% relative humidity. Fermented samples were freeze-dried, ground and kept at 4 °C until extraction.

3.5. Sourdough Fermentation

The sourdough was produced spontaneously according to the method described previously with some modifications (Minervini. De Angelis. Di Cagno. & Gobbetti. 2014). In this regard, only the flour: water ratio specified in the procedure has been changed to 100:70 (w:w). The dough was prepared by mixing flour, water (70% on flour basis) and sourdough starter (20% of the flour) for 4 minutes with a kitchen type mixer (KitchenAid. Whirlpool Co. and Meyer Co. USA). All doughs were prepared from the same batch of sourdough starters. The doughs were prepared in bulk for each cereal and then were divided into 50 mL containers in 10 g pieces and left to fermentation at different time-temperature combinations. The fermentation process was carried out in air-conditioned cabinets at 10, 20 and 30 °C for 12, 24 and 36 hours at 95% relative humidity. Fermented samples were freeze-dried, ground and kept at 4 °C until extraction.

3.6. Analysis of Free and Total Phenolic Acids

Free phenol analysis was carried out as previously performed by Žilic et al.[108]. A quantity of 1 g ground sample was extracted with 10 mL of acetone, methanol, water (7:7:6. v/v) in three stages (5-2.5-2.5 mL). Test tubes were vortexed for 10 minutes in each stage and then centrifuged at 7500 rpm for 5 minutes. The supernatants obtained were collected in a test tube. The clear supernatant was filtered through a 0.45 µm nylon filter and collected in an autosampler vial.

Total phenol analysis was carried out as previously performed by Antoine et al. [109]. A quantity of 75 mg ground sample was released by alkaline hydrolysis for 4 h at room temperature using 4 M NaOH. After the pH was reached 2.0 by 6 M HCl. all the hydrolyzates were extracted with 2 mL of ethyl acetate and diethyl ether (1:1. v/v) in four stages (0.5-0.5-0.5-0.5 mL). Three milliliters of combined extracts were evaporated under N_2 stream at 30 °C to dryness. Final residues were redissolved in 0.9 ml of methanol. The clear sample was filtered through a 0.45 µm nylon filter and collected in an autosampler vial.

Chromatographic analyses were performed on an Agilent 1200 HPLC system consisting of a photodiode array detector, quaternary pump, autosampler and column oven for both analyses. Phenolic acids were separated on a Waters Atlantis C18 column (250 mm × 4.6 mm. 5 µm) using a linear gradient elution program with a mobile phase containing solvent A (formic acid/H2O. 1:99. v/v) and solvent B (pure methanol) at a flow rate of 0.8 mL/min. The solvent gradient was programmed as described elsewhere [109].

3.7. Analysis of Antioxidant Capacity

Antioxidant capacity analysis was carried out as previously performed by Gökmen et al (2009) according to the QUENCHER procedure [110]. DPPH• radical solution was prepared according to the method described elsewhere [111]. Ethanol: water (1:1. v/v) mixture was used for the preparation of the radical solution. Samples were diluted 10 times with cellulose. The reaction was started by mixing 10 mg of the sample with 10 mL of a radical solution. The reaction mixture was shaked in an orbital shaker at 350 rpm for 27 min in dark at room temperature. Then. it was centrifuged at 6080 g for 2 min. The optically clear supernatant obtained was transferred into a cuvette and the absorbance of the reaction solution was measured at 525 nm using a Shimadzu model 2100 variable-wavelength UV–visible spectrophotometer (Shimadzu Corp.. Kyoto. Japan). The total antioxidant capacity of the samples were expressed in terms of Trolox equivalents (mmol Trolox/kg sample) by using the calibration curves constructed within the range between 10 – 250 mmol Trolox/L

3.8. Analysis of Amino Acids

A quantity of 0.5 g ground sample was extracted with 10 mL of 0.1% formic acid in water in three stages (5-2.5-2.5 mL). Test tubes were vortexed for 10 minutes in each stage and then centrifuged at 7500 rpm for 5 minutes. The supernatants obtained were collected in a test tube and stored at -20 °C until analysis. A quantity of 200 µL extract was first mixed with 800 µL of acetonitrile to precipitate coextracted colloids and centrifugated at 10000 rpm for 5 min. The clear supernatant was filtered through a 0.45 µm nylon filter and collected in an autosampler vial. Amino acids were analyzed by an Agilent 1260 HPLC coupled to an Agilent Ultivo Triple Quadrupole MS in positive electrospray mode. Chromatographic separation was performed in SeQuant-ZIC-HILIC (150 mm × 4.6 mm i.d.. 3.5 µm) column at 30 °C using a gradient mixture of 0.1% formic acid in water (A) and 0.1% of formic acid in acetonitrile (B) as mobile phases at a flow rate of 1 mL/min. The gradient mixture was started with 80% B, held for 3 min and decreased to 40% B in 2 min. After being held at 40% B for 3 min, it was decreased to 20% B in 1 min and held for 6 min. The total chromatographic run was completed in 15 min. The injection volume was 2 µL. The electrospray source in positive ionization mode had the following settings: gas temperature 300 °C; gas flow 10 L/min; nebulizer 40 psi; capillary voltage 1.5 kV; sheath gas temperature 375°C; sheath gas flow 12 L/min; nozzle voltage 500 V. Tyrosine was identified by multiple reaction monitoring (MRM) of two channels. The quantifier MRM was 182.1→136.1 (collision energy (CE): 4 V) and the qualifier MRM was 182.1→91 (CE: 24 V). both transitions at a fragmentor voltage of 80 V. Quantitation was performed using an external calibration curve in a range between 1 and 100 µmol/L.

3.9. Analysis of Amino Acid Derivatives

Ground sample of 0.1 g was extracted with deionized water in three stages (1-0.5-0.5 mL) by vortexing for 5 min in each stage. After centrifugation at 10000 rpm for 5 min, clear supernatants were collected in a test tube. The clear supernatant was filtered through a 0.45 µm nylon filter and collected in an autosampler vial. Amino acid derivatives were analyzed with an Agilent 1260 HPLC coupled to an Agilent Ultivo Triple Quadrupole MS in positive electrospray mode. Chromatographic separation was performed on Accucore phenyl hexyl (150 mm × 4.6 mm i.d.. 2.6 µm) column at 25 °C using a gradient mixture of 0.2% formic acid in water (A) and 0.1% formic acid in methanol (B) as mobile phases at a flow rate of 0.7 mL/min. The gradient mixture was started with 10% B, held for 3 min. and increased to 90% B in 10 min. After being held at 90% B for 1 min, it was decreased to 10% B in 1 min and held for 3 min. The total chromatographic run was completed in 15 min. The electrospray source in positive ionization mode had the following settings: gas temperature 250 °C; gas flow 7 L/min; nebulizer 40 psi; capillary voltage 1.5 kV; sheath gas (N_2) temperature 375 °C; sheath gas flow 12 L/min; nozzle voltage 500 V. MRM transitions were as follows: L-DOPA 198.1→152 (CE: 2 V. quantifier) and 198.1→181 (CE: 2 V. qualifier); dopamine 154.1→137 (CE: 2 V. quantifier) and 154.1→91 (CE: 16 V. qualifier); tyramine 138.1→121 (CE: 2 V. quantifier) and 138.1→77 (CE: 16 V. qualifier), 3-hydroxykynurenine 225.1 -> 208.1 (CE: 2 V, quantifier) and 225.1 -> 110.1 (CE: 8 V, qualifier); 5-hydroxytryptophan 221 -> 204 (CE: 2 V, quantifier) and 221 -> 162 (CE: 10 V, qualifier); kynurenine 209 -> 192.1 (CE: 2 V, quantifier) and 209 -> 146 (CE: 12 V, qualifier); kynurenic acid 190 -> 144 (CE: 16 V, quantifier) and 190 -> 162 (CE: 10 V, qualifier); N-acetylserotonin 219.1 -> 160 (CE: 4 V, quantifier) and 219.1 -> 114.9 (CE: 30 V, qualifier); niacin 124.1 -> 53.1 (CE: 4 V, quantifier) and 124.1 -> 78 (CE: 14 V, qualifier); picolinic acid 124.1 -> 106.1 (CE: 2 V, quantifier) and 124.1 -> 78 (CE: 14 V, qualifier); quinolinic acid 168 -> 78 (CE: 18 V, quantifier) and 168 -> 150 (CE: 2 V, qualifier); serotonin 177.1 -> 160 (CE:2 V, quantifier) and 177.1 -> 132 (CE: 14 V, qualifier). Quantification was performed through external calibration curves built for all tyrosine derivatives in a range between 2 and 5000 µg/L.

3.10. Melatonin Analysis

Ground samples of 0.2 gram and 100 µl of 3 ppb melatonin-d4 as internal standard were extracted with acetonitrile in three stages (1.0-0.5-0.5 ml) by vortexing for 5 min in each stage. After centrifugation at 10000 rpm for 5 min, clear supernatants were collected in a test tube. The clear supernatant was filtered through a 0.45 µm nylon filter and 1400 µl of clear filtered supernatant evaporated to dryness under a gentle stream of nitrogen. The final residue was re-dissolved in 300 µl of the mixture of acetonitrile-water (50:50. v/v). After centrifugation at 10000 rpm for 5 min, 100 µl of the sample was collected in an autosampler vial. LC-MS/MS conditions were chosen as in the previous study by Kocadagli et al [112].

3.11. Statistical Analysis

Mean values are from fermentation or sprouting duplicates. Statistically significant differences between the mean values of fermented samples ($p > 0.05$) were evaluated by Duncan's post hoc test after the analysis of variance (ANOVA) by using IBM SPSS Statistics version 24. The student's paired t-test was performed in Excel version 2016 (Microsoft Corporation. Washington. USA) to compare sprouted grain flour to native grain flour ($p > 0.05$).

4. RESULTS AND DISCUSSION

In the presented thesis, the results of the analyzes of 6 different grains applied to 6 different groups that native, sprouted, fermented with commercial yeast, fermented with sourdough, sprouted and fermented with commercial yeast, sprouted and fermented with sourdough were examined.

4.1. Changes in Total and Free Phenolic Compounds Content and Antioxidant Capacity

Changes in the concentrations of total and free phenolic compounds of native and sprouted cereal flour samples were given in Tables 1 and 2, while changes in their antioxidant capacities were given in Table 3.

While a general decrease was observed in total *p*_coumaric acid concentration with the sprouting of grains, total *p*_coumaric acid concentration increased with sprouting oats. After sprouting, vanillic acid was not observed in most cereals, but increased in einkorn and rye and decreased in barley. Ferulic acid was not observed with the sprouting of wheat. barley and buckwheat, but increased with the sprouting of other grains. In parallel with the total phenolic acid results, the free *p*_coumaric acid concentration decreased in general and the ferulic acid concentration increased with the sprouting of the grains. Exceptionally sprouting of rye increased the *p*_coumaric acid concentration, sprouting of buckwheat decreased the ferulic acid concentration. While the vanillic acid concentration decreased with the sprouting of barley and einkorn, it increased with the sprouting of rye and buckwheat. Antioxidant capacity results are generally in line with total phenolic substance concentrations. However, while a decrease was observed in the total *p*_coumaric acid concentration of wheat, the antioxidant capacity increased and no difference was observed in the antioxidant capacity of oats.

Sprouting can lead to an increase in the production of polyphenolic compounds by causing the enzymatic breakdown of carbohydrates [113]. On the other hand, it is thought that the sprouting process may have some negative effects on the water-soluble free phenolic content, which was associated with the consumption of soluble phenolic compounds by the increased moisture content during sprouting [114].

Table 1. Total phenolic acid concentrations (mg/kg) of native and sprouted grains

Grains	Phenolic Acids	Native	Sprouted
Wheat	Vanillic Acid	9.4±0.1	9.3±2.3
	p-coumaric Acid	15.8±1.1*	12.4±1.1
	Ferulic Acid	392.4±62.9	491.9±38.5
Barley	Vanillic Acid	17.6±5.8*	8±0.3
	p-coumaric Acid	152.2±8.8*	101.4±4.8
	Ferulic Acid	335.6±34.4	295.9±5.1
Einkorn	Vanillic Acid	10±2.3*	20.4±5
	p-coumaric Acid	45.1±2.7*	37.4±2.4
	Ferulic Acid	523.2±37.9*	611.6±28.6
Oats	Vanillic Acid	44.3±0.6	47.4±2.6
	p-coumaric Acid	1139.3±79.4*	2014.1±45.7
	Ferulic Acid	866.1±20.1*	1364.2±4.3
Rye	Vanillic Acid	19.2±0.2*	30.7±1.8
	p-coumaric Acid	57.4±33.6	95.7±12.8
	Ferulic Acid	520.3±302.1*	1130.4±44.7
Buckwheat	*p*-coumaric Acid	77.2±1.5*	2.7±1.5

The asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Table 2. Free phenolic acid concentrations (mg/kg) of native and sprouted grains

Grains	Phenolic Acids	Native	Sprouted
Wheat	*p*-coumaric Acid	2.2±0	nd
	Ferulic Acid	4.9±0.6*	8.5±0.2
Barley	Vanillic Acid	13.1±1.5*	7.4±0.4
	p-coumaric Acid	29.8±1.2*	2.2±0.1
Einkorn	Ferulic Acid	0.4±0	0.4±0
	Vanillic Acid	19.1±0	nd
Oats	*p*-coumaric Acid	13.8±0.6*	3.4±0.1
	Ferulic Acid	2.9±0*	3.4±0.4
Rye	Vanillic Acid	4.2±0*	48.7±6.4
	p-coumaric Acid	3.9±0*	4.6±0.1
	Ferulic Acid	5.4±0.2*	7±0.5
Buckwheat	Vanillic Acid	30±0.7*	38.8±0.4
	p-coumaric Acid	28.3±1.3*	2.6±0.1
	Ferulic Acid	5.4±0.1*	0.4±0

The asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Table 3. Antioxidant capacity (mmol Trolox/kg) of native and sprouted grains:

Grains	Native	Sprouted
Wheat	19±1.6*	26.5±2
Barley	60.1±0*	57.7±0.2
Einkorn	24.1±1.4*	29.1±2.6
Oats	40.9±8.5	36.8±5.7
Rye	26.1±2.1*	34.3±1.2
Buckwheat	59.8±0.9*	42.8±1.5

The asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Changes in the total phenolic acid concentrations of commercial yeast fermented native and sprouted grains were given in Table 4. According to this table, there is no change in total phenolic acid concentrations in general for neither native nor sprouted grains. As an exception vanillic acid concentration decreased with the commercial yeast fermentation of native wheat at 20 °C, 1 and 2 hours, while it increased with commercial yeast fermentation of native and sprouted barley at 20-30-40 °C, of native oat at 20 °C – 3 hours and of sprouted oat at 30-40 °C, of native einkorn at 20 °C, of sprouted buckwheat at 20 °C-3 hours. *p*-coumaric acid concentration decreased with commercial yeast fermentation of native wheat at 20-30 °C, of native wheat at 40 °C- 1 and 2 hours, of native oat at 20 °C-1 hour and increased with commercial yeast fermentation of native oat at 30 °C-3 hours, of sprouted oats at 30-40 °C. It is an interesting result that both a decrease and an increase in *p*_coumaric acid are observed with the process applied to oats. Ferulic acid concentrations decreased with commercial yeast fermentation of native wheat at 20-30-40 °C in different times, of native barley at 40 °C, of native rye at 20 °C-2 hours, of oats at 20 °C-1 hour, of native buckwheat at 20-40 °C and sprouted buckwheat at 30 °C-2 hours and increased with commercial yeast fermentation of sprouted rye at 30-40 °C, of native oats at 30 °C-3 hours and sprouted oats at 30-40 °C. There is an also interesting result that both decrease and increase in ferulic acid are observed with the process applied to oats.

Changes in the free phenolic acid concentrations of commercial yeast fermented native and sprouted grains were given in Table 5. Vanillic acid was not observed with commercial yeast fermentation of sprouted grains except rye. An increase in vanillic acid concentration is observed at 30 – 40 °C with commercial yeast fermentation of sprouted rye. In addition, besides the decrease observed in vanillic acid concentration with commercial yeast fermentation of buckwheat, the vanillic acid concentration increased in general with commercial yeast fermentation of other grains. Similarly, the concentration of *p*_coumaric acid was generally increased by commercial yeast fermentation of both native and sprouted grains. As an exception, a decrease in *p*_coumaric acid concentration was observed with commercial yeast fermentation of native einkorn wheat and buckwheat at 40 °C. Apart from that. ferulic acid concentration generally increased with commercial yeast fermentation of both native and sprouted forms of whole grains.

Changes in the total phenolic acid concentrations of sourdough fermented native and sprouted grains were given in Table 6. According to this table, there is no change in total phenolic acid concentrations in general for neither native nor sprouted grains. As an exception, vanillic acid was not observed in sprouted rye and buckwheat. In addition, it is seen that there is no vanillic acid in native rye before sourdough fermentation, but it is formed later. It was observed that vanillic acid decreased with sourdough fermentation of native wheat and increased with sourdough fermentation of sprouted einkorn. *p*-coumaric acid increased in sourdough fermentation of native barley at 20 °C, sourdough fermentation of native rye at 10-20 °C and sprouted rye at 20 -30 °C, sourdough fermentation of sprouted oats at 30 °C and with sourdough fermentation of sprouted einkorn at 40 °C – 36 hours. Exceptions in ferulic acid are less common than others. Ferulic acid concentration increased with sourdough fermentation of native rye at 10-20 °C, sourdough fermentation of sprouted oats at 30 °C - 36 hours and sourdough fermentation of sprouted buckwheat at 10-20 °C for 36 hours.

Changes in the free phenolic acid concentrations of sourdough fermented native and sprouted grains were given in Table 7. Sourdough fermentation did not have a standardized effect on the free phenolic acid concentration of cereals. Vanillic acid was not observed with sourdough fermentation of sprouted wheat at 10 °C and initial stage before fermentation, sourdough fermentation of sprouted rye and einkorn, sourdough fermentation of native and sprouted buckwheat. Apart from these, although it generally showed an increasing trend with sourdough fermentation of cereals, it decreased with sourdough fermentation of sprouted oats. *p*-coumaric acid was not observed with the fermentation of native wheat, barley, einkorn and buckwheat at 30 °C for variable times. Apart from this, although the concentration of *p*-coumaric acid also showed an increasing trend in general with sourdough fermentation of grains, it decreased with sourdough fermentation of sprouted barley at 10-30 °C and sprouted oats at 10-20-30 °C. Ferulic acid was also not observed with sourdough fermentation of native wheat, barley and oats at 30 °C for 24-36 hours. Ferulic acid concentration also generally increased with sourdough fermentation of grains, although sprouted wheat at 20 °C, sprouted barley at 30 °C, native rye at 10-20 °C and sprouted rye at 30 °C, sourdough fermentation of oat at 20 °C and sprouted einkorn at 20 °C caused an increased first and then decreased. It also showed a decrease with the sourdough fermentation of sprouted wheat at 30 °C, native oats at 20 °C and native einkorn at 30 °C.

The reason why there is no regular change in the amount of total phenolic acids in both fermentation applications is due to the fact that these substances are in a dynamic system where they are hydrolyzed and decomposed on the one hand and released as a result of yeast activity on the other [115]. However, the increase in the amount of free phenolic acids as a result of both commercial yeast and sourdough fermentations are associated with the structural breakdown of grain cell walls during fermentation, which leads to and the release of bound phenolic compounds [116].

Changes in the antioxidant activity capacity of fermented (commercial yeast and sourdough) and sprouted-fermented samples were given in Table 8 and Table 9. According to this table, there is no change in antioxidant capacity in general for neither native nor sprouted grains. However, there are some exceptions. Antioxidant capacity increased with the commercial yeast fermentation of native wheat at 30-40 °C, of sprouted wheat at 40 °C, of native barley at 20 °C – 1 hour, of sprouted barley at 30 °C, of native rye at 40 °C-2 hours, of sprouted rye at 30-40 °C, of sprouted oats at 20-40 °C, of sprouted einkorn at 30-40 °C, of sprouted buckwheat at 40 °C. Antioxidant capacity decreased with commercial yeast fermentation of sprouted wheat at 20 °C, native oats at 30 °C-1 hour, of sprouted buckwheat at 40 °C. Also with the sourdough fermentation of native wheat at 20 °C, of sprouted wheat at 20-30 °C, of sprouted rye at 10 °C-36 hours, of sprouted oats at 20-30 °C caused a decrease in antioxidant capacity. There are exceptions to the increased antioxidant capacity in sourdough fermentation. It increased with sourdough fermentation of native barley at 10-20-30 °C, of native rye at 30 °C, of sprouted rye at 20-30 °C-24 hours, of sprouted buckwheat at 30 °C-36 hours.

It has been reported that the increase in the number of compounds that contribute to the antioxidant capacity may occur as a result of a sprouting process that lasts for days [117].

Table 4. Total phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation

T (°C)			20				30				40			
t (h)			0	1	2	3	0	1	2	3	0	1	2	3
Wheat	Vanillic acid	N	18.5±2.3^{a}	12.9±1.1^{bA}	11.7±0^{bB}	14.6±0.2^{abB}	18.5±2.3^{a}	15±1.1^{aA}	12.8±1.2^{aB}	15±1.1^{aB}	18.5±2.3^{a}	17.3±1.1^{aA}	18±0.7^{aA}	21.4±1.5^{aA}
		S	10.7±5.1^{a}	12.1±0^{aA}	17±1.3^{aA}	15.7±3.8^{aA}	10.7±5.1^{a}	12.2±1^{aA}	18±5.3^{aA}	16.3±2.4^{aA}	10.7±5.1^{a}	15.9±1.9^{aA}	16.7±2.8^{aA}	14±5.7^{aA}
	p-Coumaric acid	N	24.1±0.4^{a}	19.4±0.9^{bcA}	17.9±0.4^{cA}	21.8±0.8^{abA}	24.1±0.4^{a}	25.2±0.9^{aA}	19±1.2^{bA}	24.4±0.8^{aA}	24.1±0.4^{a}	21.9±1.9^{aA}	20.6±1.5^{aA}	21.4±0.3^{aA}
		S	57.7±3.2^{a}	56.7±3.7^{aA}	57.6±2.7^{aA}	47.7±7.4^{aA}	57.7±3.2^{a}	44.5±8.2^{aA}	50.1±10.6^{aA}	48.5±8.9^{aA}	57.7±3.2^{a}	49.2±8.5^{aA}	51.5±8.3^{aA}	48.2±8.5^{aA}
	Ferulic acid	N	611.2±2.5^{a}	515.6±8.1^{bB}	495.3±2^{bA}	570.4±44^{abcA}	611.2±2.5^{a}	630.1±19.2^{aA}	497.9±20.5^{bA}	606.4±7^{aA}	611.2±2.5^{a}	557.5±25.8^{abAB}	551±28.5^{abA}	520.3±11.3^{bA}
		S	490.6±31.5^{a}	499.3±4.7^{aA}	497±23^{aA}	422.8±59^{aA}	490.6±31.5^{a}	383.9±75.4^{aA}	434.4±89.7^{aA}	432±55^{aA}	490.6±31.5^{a}	410.1±64^{aA}	460.3±76.5^{aA}	427.9±74^{aA}
Barley	Vanillic acid	N	6.2±0.3^{b}	19.8±1.1^{aB}	22.9±0.7^{aA}	19.8±1.1^{aA}	6.2±0.3^{c}	27±0.7^{aA}	21.8±1^{bA}	21.5±1.8^{bA}	6.2±0.3^{c}	15.9±1.9^{bB}	22.8±0.4^{aA}	22.3±0.1^{aA}
		S	37.3±5.1^{a}	38.5±5.1^{aA}	40.8±6.2^{aA}	33.3±1.6^{aA}	37.3±5.1^{a}	37.7±2.7^{aA}	40.5±2.8^{aA}	37.8±5.2^{aA}	37.3±5.1^{a}	39.4±1.6^{aA}	30±3.3^{aA}	43.4±5.7^{aA}
	p-Coumaric acid	N	58.2±1.3^{a}	52.9±0.3^{aAB}	49±0.2^{aA}	49.1±5.3^{aA}	58.2±1.3^{a}	61±6.3^{aA}	30.3±14.7^{aA}	57.1±4.5^{aA}	58.2±1.3^{a}	40.4±0.6^{cB}	49.1±3.2^{bA}	53±0.8^{abA}
		S	29.3±3.5^{a}	33.2±4.8^{aA}	39.6±1.1^{aAB}	31.3±1.2^{aA}	29.3±3.5^{a}	36.1±7.1^{aA}	33.5±2.1^{aB}	41.9±2.6^{aA}	29.3±3.5^{a}	40.8±2.4^{aA}	41.8±1.6^{aA}	41.1±4.3^{aA}
	Ferulic acid	N	319±0.3^{ab}	316±3^{bAB}	319.2±1.7^{abA}	325.6±2.7^{aA}	319±0.3^{a}	368.7±39^{aA}	197.6±92.3^{aA}	328.1±26.7^{aA}	319±0.3^{a}	262.6±6.6^{bB}	300±21.4^{abA}	287±8.6^{abA}
		S	349±61.1^{a}	357.7±53.2^{aA}	388.9±30.1^{aA}	325.3±19.3^{aA}	349±61.1^{a}	382.3±65.9^{aA}	402.2±53.1^{aA}	412.9±64.9^{aA}	349±61.1^{a}	408.8±33.7^{aA}	438.1±23.7^{aA}	401.6±57^{aA}
Rye	Vanillic acid	N	26.3±3^{ab}	31.8±0.1^{aA}	20.9±0.6^{bB}	32.2±4.3^{aA}	26.3±3^{c}	34.1±2.3^{bcA}	39±0^{abA}	44.3±3^{aA}	26.3±3^{b}	31.6±4^{abA}	37.6±0.3^{aA}	34.7±2.1^{abA}
		S	881±45.1^{b}	974.4±20.6^{abA}	1013.2±35.8^{aA}	975.8±6^{abA}	881±45.1^{b}	852.5±12.3^{bB}	1006.7±23.6^{aA}	986.7±8.5^{aA}	881±45.1^{b}	945.1±7.5^{abA}	1021.7±1.3^{aA}	973.6±7.1^{abA}

Table 4. Total phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation **(continue)**

Rye	***p*-Coumaric acid**	**N**	92.2±9.4^{a}	98.1±0.3^{aA}	69.1±19.2^{aB}	98.2±6.7^{aB}	92.2±9.4^{b}	126.7±14.1^{aA}	141.5±4^{aA}	149.5±1.3^{aA}	92.2±9.4^{b}	128.3±1.4^{aA}	129.3±6.9^{aA}	116.2±1.4^{aB}
		S	53.6±11^{a}	66.3±3.5^{aA}	70.2±2.1^{aA}	65.2±1.4^{abA}	53.6±11^{a}	57.6±4.7^{aA}	71±1.7^{aA}	67.1±0.2^{aA}	53.6±11^{a}	66.6±0.9^{aA}	70.6±1.1^{aA}	65.6±1.4^{aA}
	Ferulic acid	**N**	1153.1±117.7^{a}	895.3±15^{abA}	578.2±157^{bB}	877.5±109.7^{abB}	1153.1±117.7^{a}	1028.2±83.4^{aA}	1144±17.7^{aA}	1264.4±48.6^{aA}	1153.1±117.7^{a}	1044.3±32.5^{aA}	1074.8±17.3^{aA}	925.1±16.2^{aB}
		S	496.4±28.2^{a}	552.4±3.5^{aA}	558.6±23.1^{aA}	532.3±8^{aB}	496.4±28.2^{b}	506.9±0.8^{bC}	576.3±0.2^{aA}	546.2±1.6^{abAB}	496.4±28.2^{c}	525.4±2.3^{bcB}	596.9±0.8^{aA}	558.6±5.3^{abA}
Oat	**Vanillic acid**	**N**	42.7±2.5^{a}	21.1±10.3^{aA}	46.6±3.9^{aB}	38.3±7.6^{aA}	42.7±2.5^{b}	47.6±3^{bA}	44±1.2^{bB}	81.5±2.3^{aA}	42.7±2.5^{a}	50.1±9.9^{aA}	57.4±0.1^{aA}	69.7±15^{aA}
		S	29.9±7.7^{a}	45.5±9^{aA}	43.4±10^{aA}	49.8±6.1^{aA}	29.9±7.7^{b}	62.2±10.8^{aA}	60.6±10.3^{aA}	63.5±7.5^{aA}	29.9±7.7^{b}	51.1±7.3^{aA}	59±8.4^{aA}	61.6±11.2^{aA}
	***p*-Coumaric acid**	**N**	471.1±38.4^{a}	268.8±46^{bB}	401.3±34.1^{aA}	396.2±42.4^{abA}	471.1±38.4^{b}	534±44.1^{bA}	473.1±19.9^{bA}	733.7±46.5^{aA}	471.1±38.4^{a}	459±37.9^{aAB}	525.9±50.6^{aA}	585.7±134.3^{aA}
		S	340.2±80^{a}	485.3±95.9^{aA}	500.5±87.8^{aA}	584.3±92.1^{aA}	340.2±80^{b}	683.8±87.4^{aA}	657.6±47.2^{aA}	686.4±55.3^{aA}	340.2±80^{b}	553.9±78.7^{aAb}	647.3±53.6^{aA}	704.8±155.5^{aA}
	Ferulic acid	**N**	474±18.5^{a}	277.1±59.6^{bB}	419.8±24.2^{abA}	367.6±38.3^{abB}	474±18.5^{b}	501.7±32^{bA}	455.4±21.8^{bA}	676.5±11.4^{aA}	474±18.5^{a}	414.4±35.5^{aAB}	458.7±35.5^{aA}	491.6±94.6^{aAB}
		S	279.9±79.5^{a}	401.3±81.1^{aA}	468.4±76^{aA}	559.6±79.4^{aA}	279.9±79.5^{b}	599.5±76.1^{aA}	609.9±56^{aA}	630±68^{aA}	279.9±79.5^{b}	501.3±76.5^{abA}	570±49^{aA}	593.4±118.9^{aA}
Einkorn	**Vanillic acid**	**N**	12.2±1.1^{b}	21.1±1.1^{aA}	15.5±2.2^{abA}	19.3±0.7^{aA}	12.2±1.1^{a}	20.5±5^{aA}	20.6±1.5^{aA}	17.6±4.5^{aA}	12.2±1.1^{a}	11.1±4.4^{aA}	25±2.7^{aA}	15.6±4.6^{aA}
		S	18.8±8.9^{a}	27.2±4.5^{aA}	28.3±1.5^{aA}	18.5±2.7^{aA}	18.8±8.9^{a}	29.3±8^{aA}	31.6±6.8^{aA}	34.2±4.3^{aA}	18.8±8.9^{a}	29.9±2.9^{aA}	30.1±6^{aA}	36.5±6.6^{aA}
	***p*-Coumaric acid**	**N**	380.7±5^{a}	365±5.2^{aA}	356±20.2^{aA}	343.4±15.3^{aA}	380.7±5^{a}	364.3±12.2^{aA}	361.8±5.2^{aA}	401.9±14.6^{aA}	380.7±5^{a}	306.3±144.7^{aA}	471.8±62.2^{aA}	427.6±42.3^{aA}
		S	38±7^{a}	43.7±7.9^{aA}	49.7±6.3^{aA}	42.9±0.7^{aA}	38±7^{a}	47.1±10.5^{aA}	52.6±10.7^{aA}	58.5±2.3^{aA}	38±7^{a}	42.3±1.3^{aA}	50.2±11.1^{aA}	55.6±10.9^{aA}
	Ferulic acid	**N**	533.5±6.1^{a}	524.2±12.6^{aA}	500.1±21.6^{aA}	491.7±25.6^{aA}	533.5±6.1^{a}	519.7±16.2^{aA}	518.4±33.7^{aA}	554±11.3^{aA}	533.5±6.1^{a}	425.1±203.8^{aA}	636.9±75.7^{aA}	513.1±38.5^{aA}
		S	492.2±92.9^{a}	542.1±89.9^{aA}	589.1±69.3^{aA}	532.7±7.6^{aA}	492.2±92.9^{a}	593.8±117.7^{aA}	643.2±109.3^{aA}	645.9±62.4^{aA}	492.2±92.9^{a}	566±31.9^{aA}	570.3±102.3^{aA}	624.4±91.6^{aA}

Table 4. Total phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation **(continue)**

Buckwheat	**Vanillic acid**	**N**	$3.6±2.3^{a}$	$4.8±1.2^{aA}$	$6.4±2.8^{aA}$	$4.7±1.1^{aA}$	$3.6±2.3^{a}$	$4.7±1.1^{aA}$	$5.9±2.2^{aA}$	$3±0.5^{aA}$	$3.6±2.3^{a}$	$5.3±0.5^{aA}$	$7±1.2^{aA}$	$4.2±0.5^{aA}$
		S	$12.9±1.8^{b}$	$17.3±0.9^{abB}$	$17.4±0.4^{abC}$	$20±0.8^{aC}$	$12.9±1.8^{c}$	$24.9±0.1^{bA}$	$24.7±0^{bB}$	$31.7±1.3^{aB}$	$12.9±1.8^{c}$	$29.1±1.5^{bA}$	$29.6±0.8^{bA}$	$36±0^{aA}$
	***p*-Coumaric acid**	**N**	$9.9±0.5^{a}$	$9.1±1.7^{aA}$	$9.9±0.5^{aA}$	$9.4±3.1^{aA}$	$9.9±0.5^{a}$	$9.8±0.5^{aA}$	$9.4±1^{aA}$	$8.8±1.5^{aA}$	$9.9±0.5^{a}$	$9.1±0.4^{aA}$	$8.9±0.4^{aA}$	$11.9±1.4^{aA}$
		S	$16.3±2.1^{a}$	$15±1.3^{aB}$	$15±0.7^{aA}$	$13.9±0.9^{aB}$	$16.3±2.1^{a}$	$19.4±0.4^{aA}$	$21.3±4.5^{aA}$	$18.6±0.2^{aA}$	$16.3±2.1^{a}$	$17.6±0.5^{aAB}$	$16.3±1.1^{aA}$	$18.2±0.8^{aA}$
	Ferulic acid	**N**	$10.8±0.1^{a}$	$5.9±0.1^{cA}$	$8.8±0.3^{bA}$	$7.6±0.8^{bA}$	$10.8±0.1^{a}$	$7.6±0.8^{aA}$	$7.2±2.1^{aA}$	$7.2±0.4^{aA}$	$10.8±0.1^{a}$	$8.1±0.4^{bA}$	$7.6±0.8^{bA}$	$8.9±0.5^{abA}$
		S	$9.2±2^{a}$	$5.9±0.9^{aA}$	$7.9±0.5^{aA}$	$5±0^{aA}$	$9.2±2^{a}$	$5.4±0.4^{abA}$	$4.5±0.4^{bB}$	$5.4±0.4^{abA}$	$9.2±2^{a}$	$6.2±0.4^{aA}$	$5.4±0.4^{aB}$	$5.8±0.8^{aA}$

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of total phenolic acids (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of total phenolic acids (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 5. Free phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation

T (°C)			20				30				40			
t (h)			**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**
Wheat	**Vanillic acid**	**N**	nd	nd	nd	nd	nd	nd	3.4±0.2^{aA}	3.7±0.2^{aA}	nd	2.9±0.3^{cA}	3.3±0.2^{abA}	3.9±0.2^{aA}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	nd	nd	nd	nd	nd	Nd	2±2^{abA}	4.4±0.3^{aA}	nd	1.7±1.7^{abA}	4.2±0.1^{aA}	4.8±0.1^{aA}
		S	3.3±0.1^{b}	5.4±0.2^{aA}	5.9±0.3^{aA}	6±0.1^{aB}	3.3±0.1^{b}	5.7±0.2^{aA}	6.2±0.2^{aA}	5.9±0^{aB}	3.3±0.1^{c}	5.7±0.2^{bA}	6.8±0.1^{aA}	6.8±0.1^{aA}
	Ferulic acid	**N**	7.4±0.4^{d}	10.1±0.1^{cC}	11.5±0.2^{bC}	13.3±0^{aC}	7.4±0.4^{d}	12.4±0.3^{cB}	15.5±0.4^{bB}	17.4±0.5^{aB}	7.4±0.4^{d}	14.1±0.1^{cA}	17.9±0.4^{bA}	21.7±0.1^{aA}
		S	5.7±0.7^{b}	9.3±1.2^{aA}	9±0.5^{aB}	9.8±0.4^{aB}	5.7±0.7^{b}	9.6±0.1^{aA}	11.7±1^{aAB}	11±0^{aB}	5.7±0.7^{d}	10.5±0^{cA}	14.3±0.3^{bA}	16.1±0.5^{aA}
Barley	**Vanillic acid**	**N**	6.5±0.7^{b}	10±0.7^{aA}	7.6±0.6^{abA}	6.9±1.2^{abAB}	6.5±0.7^{b}	11±0.7^{aA}	6±0.2^{bA}	6.2±0.3^{bB}	6.5±0.7^{b}	5.3±0.2^{bB}	5.6±0.7^{bA}	9.7±0.4^{aA}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	1.8±0.1^{b}	2.3±0.1^{aA}	2.1±0.1^{abB}	2.5±0.1^{aA}	1.8±0.1^{a}	2.3±0.2^{aA}	2.4±0^{aA}	2.4±0.2^{aA}	1.8±0.1^{b}	2.3±0.2^{aA}	2.5±0^{aA}	2.7±0.1^{aA}
		S	5.1±0^{b}	9.3±0.2^{aA}	9.9±0.1^{aA}	9.4±0.3^{aB}	5.1±0^{c}	9.6±0.1^{bA}	10.4±0^{aA}	10.4±0.3^{aA}	5.1±0^{c}	9.8±0.1^{bA}	10.4±0.1^{aA}	10.7±0^{aA}
	Ferulic acid	**N**	3.7±0.4^{d}	5.2±0.1^{cB}	7.1±0^{bC}	8.9±0.3^{aC}	3.7±0.4^{c}	8.6±1^{bA}	9.8±0.2^{bB}	12.6±0.3^{aB}	3.7±0.4^{d}	8.2±0.1^{cA}	11.4±0.3^{bA}	14.1±0.3^{aA}
		S	7.8±0.1^{c}	11.6±0.4^{bC}	13±0^{aC}	13.4±0.2^{aC}	7.8±0.1^{d}	13.2±0.2^{cB}	16.5±0.1^{bB}	17.6±0.4^{aB}	7.8±0.1^{d}	15.1±0^{cA}	17.9±0.3^{bA}	20±0.1^{aA}
Rye	**Vanillic acid**	**N**	4.5±0.1^{ab}	4.1±0.3^{bB}	4.8±0.2^{abB}	5.4±0.3^{aC}	4.5±0.1^{b}	4.9±0.2^{bB}	4.8±0.4^{bB}	6.7±0^{aB}	4.5±0.1^{c}	6.6±0.1^{bA}	7.1±0.4^{bA}	8±0.1^{aA}
		S	4.1±0.2^{a}	4.7±0.2^{aA}	5±0.3^{aA}	4.9±0.3^{aA}	4.1±0.2^{b}	4.7±0.4^{abA}	5.7±0.4^{aA}	6±0.3^{aA}	4.1±0.2^{b}	5.3±0.1^{aA}	0	0

Table 5. Free phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation **(continue)**

Rye	***p*-Coumaric acid**	**N**	5.2±0.2^{c}	6.9±0^{bA}	7.5±0.2^{aB}	7.7±0.1^{aB}	5.2±0.2^{c}	6.8±0.3^{bB}	8±0.7^{bB}	9.9±0.1^{aA}	5.2±0.2^{c}	9.6±0^{bB}	11.3±0.5^{aA}	11.4±0.6^{aA}
		S	5.4±0.1^{c}	7.1±0^{bB}	7.6±0.1^{aB}	8.1±0.2^{aB}	5.4±0.1^{d}	7.4±0.1^{cB}	8.5±0.3^{bAB}	9.6±0.3^{aA}	5.4±0.1^{c}	8.5±0.2^{bA}	9.2±0.2^{abA}	9.8±0.3^{aA}
	Ferulic acid	**N**	8.2±0.4^{c}	17.1±0.2^{abA}	17.4±1.1^{bC}	19.6±0.2^{aC}	8.2±0.4^{d}	17.7±0.1^{cA}	25.4±1.4^{bB}	34.9±0.3^{aB}	8.2±0.4^{d}	27.4±0.2^{cB}	38±1.4^{bA}	44.3±0.2^{aA}
		S	13.5±0.3^{d}	20±0.1^{cC}	22.7±0.6^{bC}	24.6±0.3^{aB}	13.5±0.3^{c}	22.8±0.5^{bB}	29.8±0.7^{aB}	32.9±2.5^{aA}	13.5±0.3^{d}	27.6±0.3^{cA}	33±0^{bA}	39.6±1^{aA}
Oats	**Vanillic acid**	**N**	12.1±0.1^{b}	12.8±0.3^{bA}	14.1±0.4^{aB}	15.3±0.4^{aC}	12.1±0.1^{c}	14.8±1.1^{bcA}	17.7±1.2^{abAB}	18.5±0.7^{aB}	12.1±0.1^{c}	17.1±2^{bA}	19.5±0.7^{abA}	22.2±0.2^{aA}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	10.3±0.2^{a}	10.3±1^{aA}	10.2±0.4^{aA}	10.5±0.3^{aA}	10.3±0.2^{a}	10.8±1^{aA}	11.5±0.4^{aA}	11.2±0.1^{aA}	10.3±0.2^{b}	10.7±0.4^{abA}	10.8±0^{abA}	11.4±0.3^{aA}
		S	8.8±0.1^{b}	8.8±0.2^{bA}	10.4±0.2^{aA}	10.3±0.4^{aA}	8.8±0.1^{b}	8.7±0.4^{bA}	9.9±0.2^{aA}	9.1±0.1^{abA}	8.8±0.1^{a}	8.7±0.1^{aA}	8.6±0.8^{aA}	9.1±0.5^{aA}
	Ferulic acid	**N**	6.9±0^{c}	9±0.1^{bA}	10.4±0.7^{abB}	10.9±0.3^{aC}	6.9±0^{c}	10±0.8^{bA}	12.7±0.3^{aA}	13.9±0.1^{aB}	6.9±0^{d}	10.9±0.5^{cA}	13.4±0.2^{bA}	16.1±0.7^{aA}
		S	7.7±0^{c}	9.7±0.7^{bA}	11.3±0.1^{abA}	12±0.6^{aA}	7.7±0^{c}	11.3±0.1^{bA}	12.6±0.1^{aA}	11.5±0.1^{bA}	7.7±0^{c}	9.8±0.1^{bA}	12.1±0.8^{aA}	12.3±0.1^{aA}
Einkorn	**Vanillic acid**	**N**	2.8±0.1^{c}	3.5±0.4^{cC}	4.7±0.1^{bC}	5.9±0.4^{aC}	2.8±0.1^{d}	6.3±0.4^{cB}	10±0.2^{bB}	12.8±0.5^{aB}	2.8±0.1^{d}	10.2±0^{cA}	17.3±0^{bA}	19.2±0.2^{aA}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	27.5±1.2^{a}	25.9±1.7^{aA}	25.6±0.7^{aA}	27.2±1.5^{aA}	27.5±1.2^{a}	26.3±0.4^{aA}	24.4±0.3^{aA}	19.4±5.8^{aA}	27.5±1.2^{a}	26.4±0.6^{abA}	25.5±0.5^{abA}	24.3±0.7^{bA}
		S	4.5±0.1^{c}	7.3±0.2^{bB}	8.7±0.1^{aC}	8.4±0.2^{aB}	4.5±0.1^{c}	9.2±0.5^{bA}	9.4±0.1^{bB}	10.4±0.1^{aA}	4.5±0.1^{d}	9.1±0.1^{cA}	10.2±0.1^{bA}	10.9±0.2^{aA}
	Ferulic acid	**N**	1.6±0.1^{a}	1.7±0.3^{aA}	1.6±0.1^{aB}	1.8±0.2^{aB}	1.6±0.1^{b}	1.5±0^{bA}	1.6±0.1^{bB}	2.2±0.3^{aB}	1.6±0.1^{b}	2.4±0.4^{abA}	2.7±0.3^{aA}	3.3±0.3^{aA}
		S	7±0.1^{c}	13.5±0.1^{bC}	17.3±0.1^{aC}	17.3±0.4^{aC}	7±0.1^{d}	17.6±0.2^{cB}	21±0.1^{bB}	25.5±0.2^{aB}	7±0.1^{d}	20.9±0^{cA}	26.6±0.2^{bA}	32.7±0.1^{aA}

Table 5. Free phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation **(continue)**

Buckwheat	**Vanillic acid**	**N**	24.8±0.2^{a}	22.2±0.7^{bA}	5.4±0.1^{cC}	21±0.2^{bA}	24.8±0.2^{a}	22.2±0.7^{bA}	19.7±0.4^{cB}	21.2±0.4^{bcA}	24.8±0.2^{a}	19.7±0.4^{cA}	22.4±0.2^{bA}	22.2±0.7^{bA}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	25.7±0.7^{a}	25.2±1.4^{aA}	25±0.7^{aA}	26.6±0.7^{aA}	25.7±0.7^{a}	25±1.1^{aA}	23.9±0.7^{aA}	24.1±0.7^{aAB}	25.7±0.7^{a}	25.4±0^{abA}	23.9±0.2^{bcA}	23.3±0.6^{cB}
		S	0	3.2±0^{bC}	3.9±0.1^{aC}	3.8±0.2^{aC}	0	4.1±0^{cB}	4.8±0^{bB}	5.7±0.1^{aB}	0	5.2±0.2^{bA}	6.5±0.2^{aA}	6.9±0.3^{aA}
	Ferulic acid	**N**	4±0.5^{a}	3.5±0.2^{aA}	4±0.5^{aA}	4.3±0.3^{aA}	4±0.5^{a}	4.2±0.1^{aA}	4.1±0.3^{aA}	3.8±0.3^{aA}	4±0.5^{a}	4.5±0.5^{aA}	3.9±0.4^{aA}	3.6±0.1^{aA}
		S	4.4±0^{a}	4.3±0.1^{aB}	4.3±0.1^{aC}	4.5±0.1^{aB}	4.4±0^{b}	4.3±0.1^{bB}	5±0.1^{aB}	5.3±0.1^{aB}	4.4±0^{d}	6.3±0.2^{cA}	7.7±0.2^{bA}	11±0.3^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of free phenolic acids (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of free phenolic acids (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 6. Total phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after sourdough fermentation

T (°C)			10				20				30			
t (h)			**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**
Wheat	**Vanillic acid**	**N**	27.1±8.9^{a}	9.7±0.4^{abA}	4.4±0.4^{bA}	4.5±0.5^{bA}	27.1±8.9^{a}	4.3±0.3^{bB}	4.6±0.5^{bA}	5.6±1^{bA}	27.1±8.9^{a}	5.1±0.5^{bB}	4.4±0.4^{bA}	6±1^{bA}
		S	15.4±3.1^{a}	16.1±2.3^{aA}	15.7±0.9^{aA}	14.3±0.5^{aA}	15.4±3.1^{a}	12±2.7^{aA}	16.5±3.6^{aA}	19.2±0.9^{aA}	15.4±3.1^{a}	17.4±2.6^{aA}	19.2±0.9^{aA}	18.3±3.6^{aA}
	***p*-Coumaric acid**	**N**	29.7±3^{a}	22.4±4.3^{aA}	24.6±4.6^{aA}	20.2±2.9^{aA}	29.7±3^{a}	16.8±4.3^{aA}	18.2±3.4^{aA}	22.3±5.6^{aA}	29.7±3^{a}	18±5.6^{aA}	14.5±0.3^{aA}	19±5.9^{aA}
		S	28±8.7^{a}	26.3±2.7^{aA}	25.9±4.5^{aA}	29.2±0.4^{aA}	28±8.7^{a}	23.2±10.1^{aA}	31.5±5.6^{aA}	29.9±1.9^{aA}	28±8.7^{a}	26.5±2.9^{aA}	28±5.2^{aA}	26.1±3.3^{aA}
	Ferulic acid	**N**	562.2±48.3^{a}	480.6±84.1^{aA}	465.9±86^{aA}	525.2±78^{aA}	562.2±48.3^{a}	523.5±94.5^{aA}	503.4±47^{aA}	621.9±108.7^{aA}	562.2±48.3^{a}	521.4±97.5^{aA}	476.4±5.3^{aA}	559.7±110.6^{aA}
		S	452.7±96.5^{a}	518.5±45.9^{aA}	456.5±51.2^{aA}	540.7±11.8^{aA}	452.7±96.5^{a}	395.2±144.3^{aA}	553.8±97.5^{aA}	562.9±33.5^{aA}	452.7±96.5^{a}	512.7±63.2^{aA}	566.7±105.3^{aA}	536.7±73.6^{aA}
Barley	**Vanillic acid**	**N**	12±7.4^{a}	27.5±6.8^{aA}	26.2±11.2^{aA}	26.3±8.2^{aA}	12±7.4^{a}	27.5±10.7^{aA}	16.4±21.7^{aA}	28.9±1.4^{aA}	12±7.4^{a}	25.5±4.7^{aA}	31.7±6^{aA}	24.6±7.7^{aA}
		S	79.5±1.9^{a}	88.2±1.4^{aA}	111.6±26.4^{aA}	102.1±16.9^{aA}	79.5±1.9^{a}	110.9±21.2^{aA}	105.4±18.2^{aA}	111.5±8.3^{aA}	79.5±1.9^{a}	106.2±19^{aA}	113.7±18.4^{aA}	119.8±16.2^{aA}
	***p*-Coumaric acid**	**N**	27.9±10.9^{b}	50.6±11.4^{aA}	50.4±13.8^{aA}	50.9±10.1^{aaA}	27.9±10.9^{b}	80.2±4.8^{aA}	60.7±4.4^{abA}	63.5±11^{aA}	27.9±10.9^{a}	49.6±9.6^{aA}	59.7±11.8^{aA}	48.6±10.4^{aA}
		S	66.5±0.8^{a}	73.7±4.2^{aA}	96.6±0.6^{aA}	75.4±18.5^{aA}	66.5±0.8^{a}	81.8±13.6^{aA}	76.9±14.1^{aA}	74.7±6.5^{aA}	66.5±0.8^{a}	68.4±13.6^{aA}	93.9±25.6^{aA}	80.8±9.4^{aA}
	Ferulic acid	**N**	250.9±71.4^{a}	398.2±70.3^{aA}	419.6±78.2^{aA}	387.2±52.2^{aA}	250.9±71.4^{a}	403±63.8^{aA}	460.6±42.4^{aA}	412±61.7^{aA}	250.9±71.4^{a}	395±53^{aA}	426.4±62.9^{aA}	390.3±83^{aA}
		S	922.9±0.5^{a}	1074.2±121.2^{aA}	1343.9±5.5^{aA}	1030.2±192.5^{aA}	922.9±0.5^{a}	1096.5±188.3^{aA}	1070.9±178.2^{aA}	1129.7±81.4^{aA}	922.9±0.5^{a}	988.7±189.3^{aA}	1168.1±216.3^{aA}	1235.9±173^{aA}
Rye	**Vanillic acid**	**N**	nd	25.8±3.4^{aA}	30.2±4.9^{aA}	27.1±3.6^{aA}	nd	26.5±4.8^{aA}	23.2±0.3^{aA}	29.8±4.5^{aA}	nd	23.6±0.2^{aA}	19±1.1^{aA}	25.7±3.8^{aA}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table 6. Total phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after sourdough fermentation **(continue)**

Rye	***p*-Coumaric acid**	**N**	31.1±10.9^{b}	56.6±7.2^{aA}	66.9±12^{aA}	53.8±9.3^{aA}	31.1±10.9^{b}	66±16.3^{aA}	61.4±9.3^{aA}	58.3±7.2^{aA}	31.1±10.9^{a}	57.2±8.2^{aA}	47.2±5.2^{abA}	55.4±3^{aA}
		S	20.2±8.5^{a}	28.7±1.6^{aA}	27.6±1.8^{aB}	44.2±8.5^{aA}	20.2±8.5^{b}	48.4±8.1^{aA}	48.5±1.9^{aA}	55±3.9^{aA}	20.2±8.5^{b}	49.6±9.3^{abA}	36.2±7.4^{abcAB}	56.6±3.1^{aA}
	Ferulic acid	**N**	266.2±105.6^{b}	513.8±94.3^{abA}	655.5±92.6^{aA}	469.1±85.8^{abA}	266.2±105.6^{b}	625.3±162.4^{aA}	558.9±101.4^{aA}	523.2±91^{aA}	266.2±105.6^{a}	538.4±102.6^{aA}	381.5±62^{aA}	514.8±59.6^{aA}
		S	254±92.7^{a}	340±10.6^{aA}	375.8±8.3^{aAB}	483.3±79.8^{aA}	254±92.7^{a}	532.8±82.7^{aA}	530.8±22.7^{aA}	518.9±64^{aA}	254±92.7^{a}	490.1±74.3^{aA}	356.9±57.8^{aB}	495.1±41.4^{aA}
Oats	**Vanillic acid**	**N**	40.7±4.4^{a}	40.1±14.2^{aA}	34.7±6.4^{aA}	33.1±3.7^{aA}	40.7±4.4^{a}	33.2±6.5^{aA}	35.8±3^{aA}	41.1±2.9^{aA}	40.7±4.4^{a}	36.3±4.4^{aA}	24.9±6.7^{aA}	27.9±4.1^{aA}
		S	25.3±5.3^{a}	32.5±5.1^{aA}	33.7±4.6^{aA}	30.5±8.9^{aA}	25.3±5.3^{a}	35±7^{aA}	32.2±6.6^{aA}	34.2±8.1^{aA}	25.3±5.3^{a}	38.6±7.2^{aA}	32.4±6.9^{aA}	34.5±3.7^{aA}
	***p*-Coumaric acid**	**N**	479.6±71.4^{a}	398.9±79.3^{aA}	319.4±56.2^{aA}	330.3±47.2^{aA}	479.6±71.4^{a}	339.5±52.6^{aA}	377±53.7^{aA}	395.4±13.9^{aA}	479.6±71.4^{a}	312.6±69.8^{aA}	276.9±42^{aA}	324.6±43.2^{aA}
		S	211.6±76.7^{a}	326.3±29.1^{aA}	466.2±94.9^{aA}	449.1±73.3^{aA}	211.6±76.7^{a}	464.7±49.7^{aA}	576±61.1^{aA}	519.1±106.8^{aA}	211.6±76.7^{b}	397.9±1.1^{abA}	586.8±63.9^{aA}	455±8.7^{aA}
	Ferulic acid	**N**	422.6±60.8^{a}	348.3±61.5^{aA}	310.6±60.5^{aA}	338.7±39.9^{aA}	422.6±60.8^{a}	316.7±60.5^{aA}	363.9±56^{aA}	351.4±10.7^{aA}	422.6±60.8^{a}	324.5±58.1^{aA}	273.2±24.5^{aA}	314.1±49^{aA}
		S	203.2±83.5^{a}	317.8±40.6^{aB}	409.4±83.7^{aA}	399.4±75.8^{aA}	203.2±83.5^{a}	460±8.1^{aA}	480.4±62.7^{aA}	422±96.2^{aA}	203.2±83.5^{b}	319±4^{abB}	437.6±44.5^{aA}	457±65.7^{aA}
Einkorn	**Vanillic acid**	**N**	26.7±3.8^{a}	26±2.6^{aA}	32.2±2.9^{aA}	30.3±6.9^{aA}	26.7±3.8^{a}	32.8±3.7^{aA}	36.5±4.4^{aA}	36.3±5.7^{aA}	26.7±3.8^{a}	19.9±11.7^{aA}	29.5±3.9^{aA}	31.3±2.9^{aA}
		S	17.6±0.2^{b}	20.7±2.8^{bA}	32±3.5^{aA}	19.1±0.3^{bB}	17.6±0.2^{b}	24.6±0.8^{abA}	26.3±2.7^{aA}	30.2±2.8^{aA}	17.6±0.2^{b}	28.2±2.8^{aA}	27.8±4.2^{aA}	30.3±0.5^{aA}
	***p*-Coumaric acid**	**N**	360.1±25.7^{a}	347.2±34.3^{aA}	371.6±49^{aA}	320.4±61.7^{aA}	360.1±25.7^{a}	357.7±25.6^{aA}	401.7±63^{aA}	390.2±56.1^{aA}	360.1±25.7^{a}	370.8±57.7^{aA}	359.9±25.8^{aA}	388.5±66^{aA}
		S	28.4±0.3^{a}	34.9±6.6^{aA}	41±3.3^{aA}	32.5±4.9^{aA}	28.4±0.3^{a}	39.6±7.3^{aA}	38.3±3.3^{aA}	42.8±5.6^{aA}	28.4±0.3^{b}	42.1±3.5^{abA}	42±7.3^{abA}	46±3.2^{aA}
	Ferulic acid	**N**	483.2±53.6^{a}	482.5±54.6^{aA}	517.6±61.6^{aA}	468.5±98^{aA}	483.2±53.6^{a}	485.4±65.8^{aA}	533.7±59^{aA}	542.1±74.6^{aA}	483.2±53.6^{a}	475.6±100.1^{aA}	448.5±47.1^{aA}	508.4±75.6^{aA}
		S	438±0.5^{a}	563.6±96.4^{aA}	614.3±62.6^{aA}	518.1±83.8^{aA}	438±0.5^{a}	559.1±72.2^{aA}	612±57.5^{aA}	644.5±102.4^{aA}	438±0.5^{a}	609.6±48.8^{aA}	599.6±101^{aA}	641.1±74.8^{aA}

Table 6. Total phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after sourdough fermentation **(continue)**

Buckwheat	**Vanillic acid**	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	14.2±2.6^{a}	13.5±2.3^{aA}	16.4±2.5^{aA}	15.5±2.7^{aA}	14.2±2.6^{a}	16.5±2.3^{aA}	16.9±2^{aA}	15.5±1.3^{aA}	14.2±2.6^{a}	14.2±2.3^{aA}	15±1.6^{aA}	15.5±3.1^{aA}
		S	8.5±0.8^{a}	7.9±1^{aA}	9.3±1.4^{aA}	10±0.8^{aA}	8.5±0.8^{a}	11.2±1.3^{aA}	11.9±1.9^{aA}	9.9±0.5^{aA}	8.5±0.8^{a}	10.5±0.5^{aA}	7.7±2.2^{aA}	8.9±1.3^{aA}
	Ferulic acid	**N**	50.5±8.9^{a}	50.3±10.2^{aA}	63.1±13.8^{aA}	65.6±12.3^{aA}	50.5±8.9^{a}	64.3±9^{aA}	55.5±6.5^{aA}	57±3.3^{aA}	50.5±8.9^{a}	56.3±8.2^{aA}	58.7±11.4^{aA}	68±8^{aA}
		S	21.2±2^{b}	21±7.9^{bA}	29.5±7.9^{abA}	47.4±1.2^{aA}	21.2±2^{b}	33.9±5^{abA}	32.1±5.5^{abA}	38.1±0.6^{aA}	21.2±2^{a}	35±0^{aA}	29.5±12.6^{aA}	36.1±7.3^{aA}

***** Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of total phenolic acids (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of total phenolic acids (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 7. Free phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after sourdough fermentation

T (°C)			10				20				30			
t (h)			0	12	24	36	0	12	24	36	0	12	24	36
Wheat	**Vanillic acid**	**N**	5±0^{b}	9±0.3^{aA}	9.8±0.8^{aA}	10.4±0.2^{aA}	5±0^{c}	8.9±0.3^{bA}	10.2±0.1^{aA}	9.6±0.1^{aA}	5±0^{c}	9.6±0.3^{aA}	7.6±0.1^{bB}	7.1±0.2^{bB}
		S	nd	nd	nd	nd	nd	5.4±0.1^{aA}	4.5±0.1^{bA}	3.2±0^{cA}	nd	1.8±0.1^{aB}	1.5±0.1^{bB}	2±0.1^{aB}
	***p*-Coumaric acid**	**N**	1.6±0.1^{a}	2±0.2^{aAB}	1.8±0.2^{aB}	1.7±0^{aB}	1.6±0.1^{c}	2.6±0.2^{aA}	2.8±0.1^{bA}	2.1±0^{bA}	1.6±0.1^{a}	1.7±0.2^{aB}	nd	nd
		S	3.5±0.1^{b}	4.9±0.1^{aA}	4.7±0.1^{aA}	4.5±0.1^{aA}	3.5±0.1^{ba}	nd	nd	nd	3.5±0.1^{a}	nd	nd	nd
	Ferulic acid	**N**	8.9±0.4^{d}	18.3±0.4^{cB}	23.6±1.4^{bA}	27.2±0.4^{aA}	8.9±0.4^{c}	22.2±0^{aA}	22±0.3^{aA}	12.9±0.4^{bB}	8.9±0.4^{a}	8.9±0^{aC}	nd	nd
		S	7.9±0.2^{d}	11.6±0^{cB}	14.1±0.3^{bA}	15.6±0.1^{aA}	7.9±0.2^{b}	14.2±0.1^{aA}	9.5±0.4^{cB}	5.6±0.1^{dB}	7.9±0.2^{a}	3.3±0.2^{bC}	3.1±0^{bC}	2.6±0^{cC}
Barley	**Vanillic acid**	**N**	7.1±0.3^{b}	11.9±0.9^{aA}	13±0.3^{aB}	14.5±0.9^{aA}	7.1±0.3^{c}	13.2±0.4^{bA}	14.4±0.2^{aA}	15±0^{aA}	7.1±0.3^{b}	13.2±0.1^{aA}	13.2±0.2^{aB}	13.7±0.9^{aA}
		S	2.7±0.1^{d}	3.2±0.1^{cB}	4.6±0.1^{bB}	5.7±0.1^{aA}	2.7±0.1^{c}	4.2±0.2^{bA}	6.1±0.1^{aA}	6.4±0.3^{aA}	2.7±0.1^{c}	3.8±0.2^{bAB}	4.7±0.2^{aB}	3.5±0^{aB}
	***p*-Coumaric acid**	**N**	2.6±0.1^{a}	3±0^{aB}	3.3±0.3^{aA}	3±0.2^{aA}	2.6±0.1^{b}	3.9±0.1^{aA}	3.7±0.1^{aA}	3.8±0.3^{aA}	2.6±0.1^{a}	2.8±0.1^{aB}	nd	nd
		S	9.6±0.4^{a}	9.7±0.2^{aA}	7.9±0.1^{bB}	7.3±0.2^{bB}	9.6±0.4^{a}	9.3±0.3^{aAB}	9.1±0.1^{aA}	8.9±0.1^{aA}	9.6±0.4^{a}	8±0.2^{bB}	5.9±0.1^{cC}	2.9±0.1^{dC}
	Ferulic acid	**N**	7.1±0.3^{c}	16.7±0.5^{bB}	25.8±1.7^{aA}	26.6±0.5^{aA}	7.1±0.3^{b}	20.5±0.2^{aA}	21.7±0.6^{aA}	21.9±1^{aB}	7.1±0.3^{b}	11±0.1^{aC}	nd	nd
		S	12.7±0.5^{d}	17.8±0.2^{cB}	21.5±0.1^{bB}	23.4±0.3^{aA}	12.7±0.5^{c}	20.7±0.6^{bA}	23.5±0.1^{aA}	24.2±0.1^{aA}	12.7±0.5^{b}	15±0^{aC}	10.2±0.1^{cC}	5.8±0.7^{dB}
Rye	**Vanillic acid**	**N**	4.8±0^{b}	10.1±0.6^{aC}	11±0.3^{aB}	11.5±0.4^{aB}	4.8±0^{c}	11.9±0^{bB}	15.1±0.9^{aA}	16.4±1^{aA}	4.8±0^{c}	15.7±0.2^{aA}	13.9±0.4^{bA}	13.3±0.2^{bB}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	4.7±0.2^{b}	6.1±0.4^{aB}	5.7±0.3^{abB}	5.8±0.2^{abB}	4.7±0.2^{b}	8.3±0.6^{aA}	8.9±0.1^{aA}	8.8±0.4^{aA}	4.7±0.2^{c}	8.4±0.1^{aA}	6.4±0.1^{bB}	2.7±0.2^{dC}
		S	5.6±0.2^{b}	7±0.2^{abB}	8.9±1^{aA}	7.1±0.3^{abA}	5.6±0.2^{b}	9.2±0.3^{aA}	9.9±0.4^{aA}	10.9±1.7^{aA}	5.6±0.2^{c}	9.7±0.2^{aA}	8.8±0.2^{bA}	8±0.3^{bA}

Table 7. Free phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after sourdough fermentation **(continue)**

Rye	**Ferulic acid**	**N**	15.1±0.3^{d}	38±0.7^{cB}	48.2±1.3^{bB}	60.4±2.2^{aA}	15.1±0.3^{c}	50.6±0.4^{abA}	53.6±0.7^{aA}	49.2±1.8^{bB}	15.1±0.3^{b}	40.3±0.5^{aB}	12.4±1.1^{bC}	3.9±0.9^{cC}
		S	15.9±0.7^{c}	26.3±0^{bB}	38.7±0.7^{aB}	41.2±1.7^{aAB}	15.9±0.7^{b}	39.5±0.5^{aA}	45.3±0.8^{aA}	50.6±8.9^{aA}	15.9±0.7^{d}	39.5±1.5^{aA}	35±0.5^{bC}	25.2±0.9^{cB}
Oats	**Vanillic acid**	**N**	6.8±0.7^{b}	6.7±0.2^{bB}	17.7±0^{aA}	17.6±0.5^{aB}	6.8±0.7^{b}	18.3±0^{aA}	18.7±0.5^{aA}	19.4±0.2^{aA}	6.8±0.7^{c}	19.5±2.2^{aA}	13.8±0.2^{bB}	11.8±0.3^{bC}
		S	16.6±0.8^{a}	18.4±0.4^{aA}	5.6±0^{bB}	6.3±0.2^{bAB}	16.6±0.8^{a}	6.1±0.1^{bB}	7.2±0.1^{bA}	6.8±0.3^{bA}	16.6±0.8^{a}	7.2±1.1^{bB}	5.2±0.4^{bB}	5.4±0.2^{bB}
	***p*-Coumaric acid**	**N**	6.6±0.1^{c}	7.2±0.1^{bB}	10.8±0^{aA}	10.8±0.2^{aA}	6.6±0.1^{d}	11.4±0.1^{aA}	10.7±0.1^{bA}	10±0.2^{cA}	6.6±0.1^{b}	10.6±1^{aA}	5.6±0.2^{bB}	5.5±0.1^{bB}
		S	11.5±0.3^{a}	11.5±0.3^{aA}	7.5±0^{bA}	7.3±0.2^{bA}	11.5±0.3^{a}	7.8±0.3^{bB}	7.9±0^{bA}	6.6±0.1^{cB}	11.5±0.3^{a}	6.9±0.9^{bB}	5.2±0.6^{bB}	4.9±0.1^{bC}
	Ferulic acid	**N**	8.3±0.2^{d}	10.1±0.4^{cB}	23±0.1^{bA}	25.9±0.5^{aA}	8.3±0.2^{d}	22.6±0.4^{aA}	20.8±0.1^{bB}	17.2±0.4^{cB}	8.3±0.2^{b}	11.4±1.1^{aB}	nd	nd
		S	13.1±0.1^{b}	19.8±0.4^{aA}	12.5±0.1^{bA}	13.4±0.4^{bA}	13.1±0.1^{a}	12.5±0.1^{aB}	10.4±0.1^{bB}	6.2±0.7^{cB}	13.1±0.1^{a}	nd	nd	nd
Einkorn	**Vanillic acid**	**N**	9.2±0^{c}	13.1±0.4^{bC}	14.1±0^{aB}	14.6±0.1^{aB}	9.2±0^{c}	15.9±0.1^{bA}	17.3±0.5^{aA}	18.5±0.3^{aA}	9.2±0^{c}	16.9±0.1^{aB}	16.9±0.1^{aA}	14.7±0.4^{bB}
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	4.8±0^{b}	5.3±0.2^{aB}	5.4±0.1^{aB}	5.6±0.1^{aB}	4.8±0^{c}	7.3±0^{bA}	7.8±0.1^{bA}	8.3±0.3^{aA}	4.8±0^{b}	4.9±0.1^{aA}	4.9±0.1^{bC}	nd
		S	5.7±0.3^{b}	7.1±0.1^{aB}	6.8±0.1^{abB}	6.1±0.6^{abA}	5.7±0.3^{b}	8.9±0.2^{aA}	8.6±0.1^{aA}	8.7±0.1^{aB}	5.7±0.3^{c}	7.8±0.5^{abAB}	6.3±0.6^{bcB}	8.3±0.1^{aB}
	Ferulic acid	**N**	11.1±0.3^{d}	32.3±0.8^{cB}	43.2±0.8^{bA}	52.2±0.3^{aA}	11.1±0.3^{b}	40.3±0.1^{aA}	40±0.5^{aB}	40.6±0.1^{aB}	11.1±0.3^{b}	9.7±0.7^{aC}	9.7±0.7^{bC}	nd
		S	11.9±0.6^{d}	20.6±0.1^{cB}	28.8±0.4^{bA}	31.6±0.3^{aA}	11.9±0.6^{c}	27.1±0.4^{aA}	25.9±0.4^{aB}	22.1±0.1^{bB}	11.9±0.6^{b}	19.9±1.4^{aB}	nd	nd
Buckwheat	**Vanillic acid**	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	***p*-Coumaric acid**	**N**	2±0.1^{b}	3.3±0.2^{aB}	3±0^{aB}	3±0.1^{aB}	2±0.1^{c}	4.6±0.1^{bA}	5.8±0.2^{aA}	4.7±0.4^{bA}	2±0.1^{a}	nd	nd	nd
		S	3.9±0.2^{b}	5.1±0.2^{aB}	5.6±0.1^{aB}	5.8±0.2^{aA}	3.9±0.2^{c}	7.6±0^{aA}	7.6±0.5^{aA}	5.7±0.1^{bA}	3.9±0.2^{b}	3.4±0.5^{bCB}	3.3±0.2^{bC}	4.4±0.2^{aB}

Table 7. Free phenolic acid concentrations (mg/kg) of native (N) and sprouted (S) grains after sourdough fermentation **(continue)**

Buckwheat	**Ferulic acid**	**N**	3.5±0.5^{a}	3.9±0.3^{aA}	4±0^{aA}	4.3±0.2^{aA}	3.5±0.5^{a}	4.4±0.1^{aA}	4.7±0.4^{aA}	4.6±0.1^{aA}	3.5±0.5^{a}	3.8±0.2^{aA}	4.2±0.4^{aA}	4.5±0^{aA}
		S	3±0.2^{a}	3.2±0.5^{aC}	3.8±0.1^{aC}	4±0.2^{aB}	3±0.2^{b}	4.2±0.2^{aB}	4.1±0.1^{aB}	4.3±0.1^{aB}	3±0.2^{d}	5.6±0.3^{cA}	6.7±0.2^{bA}	7.2±0^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of free phenolic acids (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of free phenolic acids (either for sprouted or native grains), according to the fermentation temperature at a certain time

Table 8. Antioxidant capacity (mmol Trolox/kg) of native (N) and sprouted (S) grains after Commercial yeast fermentation

T (°C)		20				30				40			
t (h)		**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**
Wheat	**N**	25.1±2.3^{a}	28.8±2.5^{aA}	29.9±0.4^{aB}	27.7±0^{aB}	25.1±2.3^{b}	26.3±0.7^{bA}	29.7±1.6^{abB}	34.5±0.4^{aA}	25.1±2.3^{b}	27.4±2.1^{abA}	34.7±0.2^{aA}	35.9±3.2^{aA}
	S	47.6±3.4^{a}	39.2±2.7^{aB}	42.1±4^{aB}	32.7±1.9^{bC}	47.6±3.4^{a}	45.8±1.5^{aA}	42.1±4.8^{aB}	47±2.5^{aB}	47.6±3.4^{c}	38.5±1.4^{dB}	55.3±2.9^{bA}	71.1±3.9^{aA}
Barley	**N**	50.4±3.8^{b}	69.1±6^{aA}	60±2.9^{abA}	52.7±3.8^{abA}	50.4±3.8^{a}	60.7±1^{aB}	58±4.2^{aA}	52.8±0.7^{aA}	50.4±3.8^{a}	53.3±1.3^{aC}	57.4±2.7^{aA}	56.2±0.2^{aA}
	S	76.7±2^{a}	73±3.7^{aC}	78.1±3.4^{aB}	75.3±1.8^{aC}	76.7±2^{b}	86.6±2.1^{aB}	80.6±2.7^{aB}	93.1±6.2^{aA}	76.7±2^{d}	93.5±5.8^{bA}	106.6±1.7^{aA}	82.3±2.1^{cB}
Rye	**N**	24.1±1.9^{a}	31.7±1.6^{a}	29.3±4^{a}	28.5±0.7^{a}	24.1±1.9^{a}	29±3.3^{a}	28.5±0.7^{a}	27.5±2.3^{a}	24.1±1.9^{b}	32.2±0^{ab}	35.5±1.9^{a}	31.5±3.3^{ab}
	S	49.8±0.4^{a}	57.3±2.6^{aA}	50.3±2.1^{aC}	57.7±5.2^{aA}	49.8±0.4^{b}	59.6±5.6^{aA}	60.9±3.9^{aB}	55.5±4.3^{aA}	49.8±0.4^{b}	64.7±5.6^{aA}	69.1±3^{aA}	69.9±5.6^{aA}
Oats	**N**	51.5±3.6^{a}	46.5±6.3^{a}	60.2±7.4^{a}	45.7±0.6^{a}	51.5±3.6^{a}	29.8±3.1^{b}	54.8±4.7^{a}	49.9±2.2^{a}	51.5±3.6^{ab}	40.7±3.7^{b}	53.6±1.8^{a}	55.5±2.4^{a}
	S	46.4±6.9^{b}	36.7±1.4^{cC}	47.2±1.2^{bB}	55.5±1^{aB}	46.4±6.9^{a}	55.4±0.5^{aB}	52±4.2^{aB}	50.3±1.2^{aC}	46.4±6.9^{b}	60±2.6^{aA}	63.2±4.2^{aA}	68.3±5.1^{aA}
Einkorn	**N**	30.7±0.3^{ab}	29.2±0.9^{b}	29.7±0^{ab}	32.8±1.4^{a}	30.7±0.3^{a}	30.3±0.9^{a}	33.9±2.4^{a}	29.7±2.9^{a}	30.7±0.3^{a}	32.6±4.5^{a}	33.8±1.2^{a}	31±2.4^{a}
	S	60.1±0.2^{a}	66.3±1.8^{aA}	60.6±0.4^{aB}	60.3±5.4^{aB}	60.1±0.2^{b}	61.2±2.7^{bB}	71.1±1.4^{aA}	60.5±4.1^{bB}	60.1±0.2^{c}	61.2±0.2^{cB}	73.2±1.4^{bA}	84±6.1^{aA}
Buckwheat	**N**	65.9±4.8^{a}	64.6±3.1^{a}	69.9±7.7^{a}	72.3±2.2^{a}	65.9±4.8^{a}	73.2±7.3^{a}	68±3.1^{a}	69.8±1.3^{a}	65.9±4.8^{a}	76.2±2.2^{a}	67.8±8.8^{a}	81.3±2.6^{a}
	S	61.7±5.2^{a}	63.5±3.7^{aA}	66.7±0.2^{aB}	55.8±0.4^{aB}	61.7±5.2^{a}	61.2±0.6^{aA}	58.8±0.4^{aC}	52.7±2.6^{bB}	61.7±5.2^{b}	64.4±2.4^{bA}	76.6±3.4^{aA}	85.2±3.8^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the antioxidant capacity (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the antioxidant capacity (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 9. Antioxidant capacity (mmol Trolox/kg) of native (N) and sprouted (S) grains after sourdough fermentation

T (°C)		10				20				30			
t (h)		0	12	24	36	0	12	24	36	0	12	24	36
Wheat	N	23.1±3.3^{a}	19.7±0.2^{aA}	17.8±1.1^{aB}	23.3±3.8^{aA}	23.1±3.3^{a}	20.3±0.2^{aA}	15.7±0.9^{bC}	15.5±0.9^{bB}	23.1±3.3^{a}	18.3±0.9^{aA}	21.4±1.1^{aA}	21.2±0.3^{aA}
	S	32.8±0.2^{a}	38±2^{aA}	39.3±3.3^{aA}	30±0.9^{aA}	32.8±0.2^{a}	26.5±3.4^{bC}	23.9±4.5^{bB}	25.3±2.1^{bB}	32.8±0.2^{a}	30.9±2.8^{abB}	23.2±1.1^{bB}	30.2±1.3^{aA}
Barley	N	40±0.3^{b}	39.7±1.5^{bC}	38.9±0.8^{bB}	53.6±3.5^{aA}	40±0.3^{b}	51.6±0.6^{aA}	49.8±1.8^{aA}	47.5±2.5^{aA}	40±0.3^{c}	48±0.9^{bB}	46±1.2^{bA}	60.9±4.4^{aA}
	S	48±1.9^{a}	40.9±0.2^{aB}	45.1±3.3^{aB}	47.9±2.9^{aA}	48±1.9^{c}	41.9±2.7^{cB}	64.6±2.9^{aA}	55.9±5.8^{bA}	48±1.9^{a}	47.6±1.4^{aA}	47.6±0.6^{aB}	55.6±4.7^{aA}
Rye	N	19.3±0.6^{a}	15.8±0.5^{aC}	19±0.9^{aB}	16.9±1.2^{aA}	19.3±0.6^{a}	17±0.2^{aB}	19.3±2.8^{aB}	22.5±5.5^{aA}	19.3±0.6^{b}	23.9±0.2^{abA}	22.9±0.2^{abA}	26.9±1.1^{aA}
	S	43.3±3.5^{a}	40.2±0.4^{aA}	38.2±2^{abA}	33.2±0.4^{bB}	43.3±3.5^{a}	43.2±2.6^{aA}	43.2±2.6^{aA}	43.2±2.6^{aA}	43.3±3.5^{a}	42.2±3.7^{aA}	40.9±2^{aA}	47.2±2^{aA}
Oats	N	14.3±2^{a}	13.8±0.9^{aA}	14.4±0.3^{aA}	12.7±0.2^{aA}	14.3±2^{a}	15.3±0.5^{aA}	15.4±0.6^{aA}	14.7±0.8^{aA}	14.3±2^{a}	13.9±0.3^{aA}	17.9±1.1^{aA}	14.9±0.9^{aA}
	S	28.2±4.1^{a}	23.5±2.4^{aA}	26.1±0.6^{aA}	21.5±1.1^{aA}	28.2±4.1^{a}	20±1.5^{bA}	20.2±0.6^{bC}	21.7±0.6^{bA}	28.2±4.1^{a}	22.8±0.6^{bA}	22.2±0.6^{bB}	24.8±1.3^{abA}
Einkorn	N	23.2±3.5^{a}	22.8±2.5^{aA}	21.4±2.3^{aA}	23.6±3.2^{aA}	23.2±3.5^{a}	19.8±0.3^{aA}	20.1±2.2^{aA}	20.3±2^{aA}	23.2±3.5^{a}	17.5±0.2^{aA}	24.5±2.2^{aA}	23.7±1.7^{aA}
	S	30.2±3.1^{a}	37.6±5.4^{aA}	36.7±3^{aA}	32.3±5.2^{aA}	30.2±3.1^{b}	29±0.4^{bA}	35.7±1.1^{aA}	30.7±3.9^{abA}	30.2±3.1^{b}	29.2±3.2^{bA}	43.7±6.3^{aA}	38.3±4.7^{abA}
Buckwheat	N	57±2.2^{a}	53.6±3.1^{aA}	56.6±4.5^{aA}	62.6±4.4^{aA}	57±2.2^{a}	62±3.4^{aA}	52.6±3.4^{aA}	55.5±1.9^{aA}	57±2.2^{a}	60.8±0.3^{aA}	64.4±4.4^{aA}	57.2±3.7^{aA}
	S	29.2±3.4^{a}	29.4±0.7^{aA}	27.2±4.3^{aA}	27.9±2^{aC}	29.2±3.4^{a}	26.1±0.2^{aA}	30.8±4.9^{aAB}	32.5±0.4^{aB}	29.2±3.4^{b}	30±5.1^{bA}	34.9±1.3^{bA}	39.1±0.7^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the antioxidant capacity (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the antioxidant capacity (either for sprouted or native grains), according to the fermentation temperature at a certain time

4.2. Changes in Glutamic Acid and GABA Concentrations

Changes in the concentrations of glutamic acid and GABA with the sprouting of grains are given in Table 28. According to this table, glutamic acid concentration increased with the sprouting of all grains except einkorn. It did not differ with the sprouting of einkorn ($p>0.05$). The highest increase of glutamic acid is 3.8 fold with the sprouting of rye. GABA concentration increased with the sprouting of all grains without an exception. The highest increase of GABA is 12.7 fold with the sprouting of oats. It is known in the literature that the GABA concentration increases with the sprouting of various grains and seeds [118].

Table 10. Concentrations of glutamic acid and GABA (mg/kg) for native and sprouted grains

Grains	Glutamic Acid and GABA(mg/kg d.w.)	Native	Sprouted
Wheat	Glutamic Acid	162 ± 0*	528 ± 37
	GABA	22 ± 2*	72 ± 1
Barley	Glutamic Acid	250 ± 38*	547 ± 51
	GABA	78 ± 5*	323 ± 24
Rye	Glutamic Acid	224 ± 3*	847 ± 7
	GABA	36 ± 3*	152 ± 13
Oats	Glutamic Acid	259 ± 13*	462 ± 33
	GABA	35 ± 1*	443 ± 34
Einkorn	Glutamic Acid	547 ± 19	520 ± 15
	GABA	37 ± 2*	347 ± 25
Buckwheat	Glutamic Acid	511 ± 24*	628 ± 15
	GABA	104 ± 2*	226 ± 11

$^{\alpha}$The asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Table 11. Changes of glutamic acid concentrations (mg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains

T (°C)		20 °C				30 °C				40 °C			
T (h)		**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**
Wheat	**N**	724 ± 62^{a}	420 ± 10^{bB}	353 ± 21^{cC}	344 ± 31^{cC}	724 ± 62^{a}	414 ± 14^{bB}	483 ± 34^{bB}	437 ± 13^{bB}	724 ± 62^{a}	557 ± 19^{bA}	588 ± 33^{bA}	673 ± 22^{aA}
	S	1266 ± 114^{a}	589 ± 37^{cC}	677 ± 14^{bC}	687 ± 39^{bC}	1266 ± 114^{a}	848 ± 19^{bcB}	805 ± 11^{cB}	914 ± 26^{bB}	1266 ± 114^{a}	915 ± 15^{cA}	1000 ± 11^{bcA}	1076 ± 4^{bA}
Barley	**N**	804 ± 16^{a}	332 ± 10^{bC}	314 ± 26^{bC}	283 ± 7^{bC}	804 ± 16^{a}	438 ± 72^{bB}	370 ± 10^{bcB}	356 ± 3^{cB}	804 ± 16^{a}	511 ± 28^{bA}	513 ± 24^{bA}	474 ± 9^{cA}
	S	1215 ± 81^{a}	575 ± 74^{bC}	454 ± 42^{bC}	520 ± 19^{bC}	1215 ± 81^{a}	683 ± 8^{bB}	693 ± 6^{bB}	753 ± 44^{bB}	1215 ± 81^{a}	766 ± 65^{bA}	889 ± 60^{bA}	922 ± 174^{bA}
Rye	**N**	943 ± 70^{a}	387 ± 40^{bB}	417 ± 6^{bB}	443 ± 47^{bB}	943 ± 70^{a}	738 ± 80^{bA}	541 ± 12^{cA}	435 ± 17^{dB}	943 ± 70^{a}	630 ± 54^{cA}	609 ± 64^{cA}	827^{b} A
	S	909 ^{a}	458 ± 37^{bC}	475 ± 5^{bB}	470 ± 1^{bC}	909 ^{a}	631 ± 26^{cB}	783 ± 52^{bA}	866 ± 65^{bB}	909 ^{b}	760 ± 13^{cA}	767 ± 65^{cA}	1005 ± 64^{aA}
Oats	**N**	1353 ± 38^{a}	875 ± 5^{bB}	832 ± 48^{bA}	705 ± 9^{cC}	1353 ± 38^{a}	877 ± 43^{bB}	945 ± 106^{bA}	915 ± 20^{bB}	1353 ± 38^{a}	1008 ± 35^{bcA}	1025 ± 10^{bA}	1031 ± 8^{bA}
	S	1594 ± 125^{a}	987 ± 56^{bC}	1031 ± 39^{bB}	1023 ± 22^{bC}	1594 ± 125^{a}	1133 ± 96^{bB}	1195 ± 97^{bB}	1193 ± 27^{bB}	1594 ± 125^{a}	1305 ± 48^{bA}	1488 ± 94^{aA}	1711 ± 213^{aA}
Einkorn	**N**	667 ± 2^{a}	404 ± 20^{cC}	441 ± 0^{cC}	502 ± 31^{bB}	667 ± 2^{a}	530 ± 2^{bB}	536 ± 11^{bB}	487 ± 63^{bB}	667 ± 2^{a}	663 ± 4^{aA}	659 ± 26^{aA}	695 ± 24^{aA}
	S	1321 ± 42^{a}	710 ± 64^{aB}	653 ± 16^{aB}	530 ± 21^{aB}	1321 ± 42^{a}	720 ± 28^{aB}	1068 ± 303^{aA}	984 ± 18^{aA}	1321 ± 42^{a}	969 ± 3^{aA}	1279 ± 46^{aA}	2186 ± 1047^{aA}
Buckwheat	**N**	1076 ± 12^{a}	809 ± 3^{bB}	669 ± 43^{cC}	602 ± 67^{cC}	1076 ± 12^{a}	767 ± 65^{bB}	872 ± 25^{bB}	947 ± 43^{bB}	1076 ± 12^{b}	977 ± 34^{bA}	1124 ± 52^{abA}	1280 ± 210^{aA}
	S	1561 ± 68^{a}	1160 ± 70^{bC}	1147 ± 57^{bC}	1262 ± 200^{bB}	1561 ± 68^{a}	1284 ± 15^{bB}	1475 ± 23^{aB}	1254 ± 84^{aB}	1561 ± 68^{a}	1490 ± 61^{aA}	1618 ± 28^{aA}	1647 ± 76^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of glutamic acid derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of glutamic acid derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 12. Changes of glutamic acid concentrations (mg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains

T (°C)		10 °C				20 °C				30 °C			
T (h)		**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**
Wheat	**N**	100 ± 7^{c}	77^{dC}	148 ± 4^{bC}	172 ± 7^{aC}	100 ± 7^{d}	192 ± 12^{cB}	323 ± 19^{bB}	447 ± 7^{aB}	100 ± 7^{d}	321 ± 16^{cA}	635 ± 21^{bA}	774 ± 8^{aA}
	S	505 ± 36^{a}	341 ± 106^{bC}	320 ± 4^{bC}	461 ± 23^{bC}	505 ± 36^{d}	642 ± 41^{cB}	1040 ± 41^{bB}	1371 ± 177^{aB}	505 ± 36^{d}	1114 ± 10^{cA}	1544 ± 1^{bA}	1971 ± 25^{aA}
Barley	**N**	147 ± 10^{a}	109 ± 4^{bC}	100 ± 4^{bC}	121 ± 8^{aC}	147 ± 10^{c}	171 ± 1^{cB}	240 ± 36^{bB}	355 ± 4^{aB}	147 ± 10^{d}	279 ± 4^{cA}	521 ± 0^{bA}	642 ± 10^{aA}
	S	597 ± 97^{a}	327 ± 29^{cC}	376 ± 51^{cC}	463 ± 7^{bC}	597 ± 9^{c}	559 ± 113^{cB}	1008 ± 50^{bB}	1245 ± 17^{aB}	597 ± 97^{d}	1104 ± 45^{cA}	1759 ± 46^{bA}	2237 ± 232^{aA}
Rye	**N**	282 ± 8^{a}	136 ± 20^{cC}	170 ± 14^{bC}	253 ± 19^{aC}	282 ± 8^{d}	358 ± 49^{cB}	561 ± 5^{bB}	766 ± 65^{aB}	282 ± 8^{d}	762 ± 84^{cA}	1172 ± 148^{bA}	1444 ± 24^{aA}
	S	495 ± 9^{b}	355 ± 23^{dC}	427 ± 16^{cC}	588 ± 16^{aC}	495 ± 9^{d}	898 ± 38^{cB}	1204 ± 20^{bB}	1499 ± 80^{aB}	495 ± 9^{c}	1602 ± 25^{bA}	1941 ± 366^{aA}	2127 ± 165^{aA}
Oats	**N**	803 ± 39^{a}	664 ± 15^{bB}	388 ± 12^{dC}	456 ± 6^{cC}	803 ± 39^{a}	604 ± 4^{cB}	724 ± 17^{bB}	864 ± 4^{aB}	803 ± 39^{d}	905 ± 20^{cA}	1224 ± 77^{bA}	1395 ± 21^{aA}
	S	565 ± 12^{b}	401 ± 4^{cC}	717 ± 19^{aC}	719 ± 45^{aC}	565 ± 12^{d}	917 ± 14^{cB}	1076 ± 16^{bB}	1322 ± 116^{aB}	565 ± 12^{d}	1196 ± 16^{cA}	1536 ± 34^{bA}	1781 ± 63^{aA}
Einkorn	**N**	294 ± 15^{a}	188 ± 25^{bC}	226 ± 18^{bC}	278 ± 14^{aC}	294 ± 15^{d}	343 ± 5^{cB}	518 ± 4^{bB}	667 ± 2^{aB}	294 ± 15^{d}	621 ± 54^{cA}	978 ± 30^{bA}	1220 ± 156^{aA}
	S	589 ± 2^{a}	482 ± 9^{bC}	684 ± 110^{aC}	780 ± 58^{aC}	589 ± 2^{d}	1059 ± 107^{cB}	1605 ± 34^{bB}	1888 ± 190^{aB}	589 ± 2^{d}	1868 ± 73^{cA}	2879 ± 10^{bA}	3251 ± 116^{aA}
Buckwheat	**N**	334 ± 8^{a}	193 ± 5^{dC}	252 ± 7^{cC}	297 ± 13^{bC}	334 ± 8^{d}	439 ± 5^{cB}	720 ± 13^{bB}	961 ± 94^{aB}	334 ± 8^{d}	844 ± 4^{cA}	1317 ± 91^{bA}	1715 ± 37^{aA}
	S	745 ± 20^{c}	745 ± 27^{cC}	838 ± 8^{bC}	1086 ± 86^{aC}	745 ± 20^{d}	1342 ± 80^{cB}	1768 ± 12^{bB}	2068 ± 136^{aB}	745 ± 20^{c}	1956 ± 3^{bA}	3029 ± 173^{aA}	3304 ± 93^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of glutamic acid derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of glutamic acid derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 13. Changes of GABA concentrations (mg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains

T (°C)		20 °C				30 °C				40 °C			
T (h)		**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**
Wheat	**N**	153 ± 10^{a}	175 ± 8^{aB}	158 ± 20^{aB}	159 ± 13^{aB}	153 ± 10^{a}	160 ± 3^{aB}	166 ± 17^{aB}	148 ± 10^{aB}	153 ± 10^{b}	210 ± 7^{aA}	210 ± 9^{aA}	236 ± 16^{aA}
	S	138 ± 5^{d}	252 ± 16^{cB}	304 ± 17^{bB}	346 ± 7^{aB}	138 ± 5^{d}	311 ± 6^{cA}	348 ± 16^{bA}	372 ± 4^{aA}	138 ± 5^{d}	334 ± 13^{cA}	366 ± 10^{bA}	381 ± 1^{aA}
Barley	**N**	209 ± 23^{b}	276 ± 6^{aA}	262 ± 10^{aC}	288 ± 11^{aB}	209 ± 23^{b}	310 ± 34^{aA}	287 ± 2^{aB}	277 ± 5^{aB}	209 ± 23^{d}	299 ± 2^{cA}	339 ± 11^{bA}	363 ± 0^{aA}
	S	243 ± 38^{b}	463 ± 56^{aA}	468 ± 28^{aB}	524 ± 14^{aA}	243 ± 38^{c}	514 ± 16^{bA}	490 ± 21^{bB}	567 ± 22^{aA}	243 ± 38^{b}	597 ± 62^{aA}	600 ± 68^{aA}	547 ± 99^{aA}
Rye	**N**	250 ± 7^{c}	321 ± 10^{bB}	343 ± 3^{aB}	348 ± 22^{aC}	250 ± 7^{b}	455 ± 14^{aA}	465 ± 8^{aA}	447 ± 11^{aB}	250 ± 7^{c}	450 ± 21^{bA}	454 ± 1^{bA}	560^{aA}
	S	$270\ ^{c}$	376 ± 21^{bB}	451 ± 12^{aB}	473 ± 7^{aB}	$270\ ^{c}$	496 ± 8^{bA}	542 ± 17^{aA}	577 ± 20^{aA}	$270\ ^{b}$	492 ± 28^{aA}	532 ± 15^{aA}	555 ± 52^{aA}
Oats	**N**	140 ± 16^{c}	256 ± 4^{bC}	304 ± 16^{aB}	300 ± 7^{aC}	140 ± 16^{c}	295 ± 7^{bB}	376 ± 38^{aA}	404 ± 11^{aB}	140 ± 16^{d}	349 ± 4^{cA}	399 ± 23^{bA}	442 ± 14^{aA}
	S	355 ± 17^{b}	415 ± 82^{bA}	502 ± 31^{bB}	614 ± 19^{aB}	355 ± 17^{b}	567 ± 48^{aA}	654 ± 59^{aA}	662 ± 3^{aA}	355 ± 17^{b}	607 ± 17^{aA}	633 ± 26^{aA}	612 ± 14^{aB}
Einkorn	**N**	269 ± 18^{b}	288 ± 3^{bC}	337 ± 12^{aC}	360 ± 21^{aB}	269 ± 18^{b}	367 ± 4^{aB}	381 ± 1^{aB}	378 ± 31^{aB}	269 ± 18^{c}	400 ± 9^{bA}	428 ± 8^{abA}	433 ± 7^{aA}
	S	289 ± 4^{b}	476 ± 27^{aA}	481 ± 26^{aA}	437 ± 38^{aB}	289 ± 4^{b}	462 ± 20^{aA}	588 ± 119^{aA}	543 ± 8^{aA}	289 ± 4^{b}	526 ± 17^{aA}	535 ± 30^{aA}	657 ± 104^{aA}
Buckwheat	**N**	203 ± 8^{b}	302 ± 4^{aA}	329 ± 11^{aB}	345 ± 15^{aA}	203 ± 8^{c}	304 ± 13^{bA}	358 ± 4^{aA}	372 ± 22^{aA}	203 ± 8^{b}	313 ± 6^{aA}	312 ± 0^{aB}	307 ± 34^{aA}
	S	104 ± 6^{c}	188 ± 8^{bB}	215 ± 6^{aB}	236 ± 18^{aB}	104 ± 6^{c}	219 ± 6^{bA}	253 ± 1^{aA}	243 ± 1^{aB}	104 ± 6^{d}	225 ± 1^{cA}	256 ± 3^{bA}	293 ± 7^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of GABA derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of GABA derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 14. Changes of GABA concentrations (mg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains

T (°C)		10				20				30			
T (h)		**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**
Wheat	**N**	101 ± 3^{d}	168^{cB}	283 ± 14^{bB}	306 ± 3^{aA}	101 ± 3^{d}	317 ± 9^{cA}	350 ± 7^{aA}	333 ± 9^{bA}	101 ± 3^{b}	333 ± 11^{aA}	334 ± 10^{aA}	321 ± 3^{aA}
	S	270 ± 8^{b}	458 ± 65^{aA}	445 ± 6^{aB}	489 ± 31^{aA}	270 ± 8^{d}	438 ± 23^{cA}	470 ± 1^{bA}	513 ± 48^{aA}	270 ± 8^{d}	456 ± 2^{cA}	473 ± 9^{bA}	516 ± 10^{aA}
Barley	**N**	295 ± 7^{b}	464 ± 56^{aA}	444 ± 30^{aB}	503 ± 12^{aB}	295 ± 7^{c}	497 ± 17^{bA}	549 ± 45^{abA}	532 ± 20^{aB}	295 ± 7^{b}	558 ± 13^{aA}	577 ± 2^{aA}	589 ± 1^{aA}
	S	373 ± 19^{b}	427 ± 23^{aA}	466 ± 29^{aA}	486 ± 7^{aA}	373 ± 19^{c}	451 ± 25^{bA}	531 ± 35^{aA}	518 ± 22^{aA}	373 ± 19^{b}	483 ± 4^{aA}	497 ± 17^{aA}	503 ± 26^{aA}
Rye	**N**	402 ± 12^{c}	461 ± 34^{bB}	491 ± 12^{abB}	536 ± 13^{aA}	402 ± 12^{b}	533 ± 29^{aB}	551 ± 5^{aA}	562 ± 28^{aA}	402 ± 12^{b}	599 ± 22^{aA}	583 ± 34^{aA}	585 ± 10^{aA}
	S	415 ± 1^{b}	499 ± 35^{aA}	537 ± 14^{aA}	546 ± 9^{aA}	415 ± 1^{d}	513 ± 2^{cA}	533 ± 4^{bA}	560 ± 27^{aA}	415 ± 1^{b}	523 ± 5^{aA}	514 ± 30^{aA}	514 ± 17^{aB}
Oats	**N**	384 ± 12^{b}	484 ± 6^{aA}	368 ± 9^{bC}	394 ± 16^{bC}	384 ± 12^{d}	411 ± 4^{cC}	435 ± 6^{bA}	453 ± 4^{aA}	384 ± 12^{d}	444 ± 6^{aB}	419 ± 4^{cB}	422 ± 10^{bcB}
	S	222 ± 1^{d}	316 ± 4^{cB}	507 ± 1^{bB}	526 ± 3^{aB}	222 ± 1^{c}	528 ± 10^{bcA}	553 ± 3^{aA}	585 ± 29^{aA}	222 ± 1^{b}	510 ± 10^{aA}	509 ± 8^{aB}	527 ± 6^{aB}
Einkorn	**N**	265 ± 10^{b}	433 ± 39^{aA}	462 ± 36^{aB}	477 ± 12^{aB}	265 ± 10^{b}	475 ± 13^{aA}	503 ± 1^{aB}	496 ± 13^{aB}	265 ± 10^{b}	527 ± 40^{aA}	552 ± 18^{aA}	577 ± 49^{aA}
	S	299 ± 12^{c}	378 ± 3^{bB}	445 ± 32^{aA}	460 ± 2^{aA}	299 ± 12^{b}	437 ± 19^{aA}	461 ± 8^{aA}	468 ± 13^{aA}	299 ± 12^{b}	440 ± 7^{aA}	451 ± 5^{aA}	445 ± 7^{aA}
Buckwheat	**N**	421 ± 1^{c}	498 ± 10^{bC}	568 ± 7^{aB}	570 ± 18^{aB}	421 ± 1^{b}	620 ± 1^{aB}	609 ± 1^{aA}	632 ± 37^{aA}	421 ± 1^{c}	656 ± 3^{aA}	608 ± 27^{bA}	674 ± 31^{aA}
	S	177 ± 13^{b}	248 ± 0^{bB}	252 ± 3^{bB}	285 ± 15^{aB}	177 ± 13^{b}	303 ± 14^{aA}	297 ± 7^{aA}	294 ± 1^{aB}	177 ± 13^{c}	287 ± 6^{bA}	312 ± 13^{aA}	314 ± 2^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of GABA derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of GABA derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time

Changes in the concentrations of glutamic acid during commercial yeast and sourdough fermentation of native and sprouted grains are given in Table 29 and Table 30, respectively. Glutamic acid generally decreased with commercial yeast fermentation of grains. Exceptionally, it did not differ with commercial yeast fermentation of sprouted rye, of native einkorn, of sprouted buckwheat at 40 °C ($p>0.05$). Also, it decreased first and then increased with commercial yeast fermentation of sprouted rye at 40 °C and increased with commercial yeast fermentation of native buckwheat at 40 °C. Glutamic acid generally increased with sourdough fermentation of grains, unlike commercial yeast fermentation. As an exception, it decreased with sourdough fermentation of sprouted wheat at 10 °C, of native and sprouted barley at 10 °C, of native oats at 10 °C, of native einkorn at 10 °C-12 and 24 hours, of sprouted einkorn at 10 °C-12 hours. Also, it first decreased and then increased with sourdough fermentation of native rye, native oats and native buckwheat at 10°C.

Changes in the concentrations of GABA during commercial yeast and sourdough fermentation of native and sprouted grains are given in Table 31 and Table 32, respectively. According to this, GABA generally increased with commercial yeast fermentation of all grains. As an exception, it did not differ with commercial yeast fermentation of native wheat at 20-30 °C. GABA generally increased also with sourdough fermentation of all grains. Exceptionally, it first increased and then decreased with sourdough fermentation of native oats and buckwheat at 30 °C.

4.3. Formation of Tyrosine and Its derivatives with Sprouting and Fermentation

Changes in the concentrations of tyrosine and its derivatives for native and sprouted samples were given in Table 10. Accordingly, a significant increase was observed in the concentrations of tyrosine and tyramine for all-grain samples. The increase in the tyrosine concentration as a result of sprouting was attributed to the increased proteolytic activity during this period, which lead to the hydrolysis of proteins to amino acids as mentioned before. Among native grains, the highest concentration of tyrosine was observed in buckwheat as 108.2±1.9 mg/kg, while the lowest concentration was observed in wheat as 47.9±1.9 mg/kg. The highest increase was seen for rye as 14.6 times which rised to 910.6±33.4 from 62.4±1.0. In a study of Van Hung et al (2012). the tyrosine level of waxy wheat after sprouting at 30 °C, 48 hours was observed to increase 2.9 times [119].

Likewise, in a study of Ohm et al (2016). an immediate formation and a dramatic increase (49.3 mg/kg) for tyrosine was observed for wheat during 5 days of sprouting at 30 °C [120]. In addition, it was observed that the tyrosine concentration started to increase after 24 hours of sprouting of barley at 15 °C [121].

For tyramine, the highest concentration in native grains was detected in barley as 1733.5±43.2 mg/g, while the lowest concentration was detected in the rye as 0. After sprouting, significant increases were observed, the highest being for einkorn as130.5 times from 3.6±1.7 to 469.9±6.2. According to the results. it is considered that the tyrosine decarboxylase enzyme increased with sprouting and it is explained in the literature with the presence of tyrosine decarboxylase in plants [122]. In rice tyramine was reported to be formed after 72 hours of sprouting and increased 2 folds at the end of 96 hours. [123].

For L-Dopa, a significant increase was observed in einkorn, buckwheat, and rye, no change was observed in oats and a significant decrease (to 0 mg/kg) was observed in wheat and barley. Among native grains, the highest concentration of L-Dopa was detected in barley as 313.0±3.4 and the lowest value was detected in wheat as 9.2±2. The highest increase was observed for einkorn as 9.3 times from 69.6±6.2 to 644.8±36.6.

Dopamine concentration increased for rye and buckwheat and decreased for wheat, barley, oats and einkorn after sprouting. Among native grains, the highest dopamine concentration was detected in buckwheat as 114.9±3.4 and the lowest concentration was detected in wheat as 9.5±0. The most dramatic decrease was observed in barley by %9.4 from 96.2±4.9 to 9±0.2.

Although there is also no information about L-Dopa and dopamine formation of these grains in literature dopamine. L-Dopa concentration of Vicia faba L. Seed was reported to increase after sprouting in daylight [124] and decreased after sprouting in dark [125]. This shows the importance of sprouting conditions on the formation of tyrosine derivatives. A general overview of the results reveals that transformation of tyrosine to tyramine was the most dominant reaction among others in the tyrosine pathway.

Table 15. Concentrations of tyrosine (mg/kg) and tyrosine derivatives (μg/kg) for native and sprouted grains

Grains	Tyr Derivatives(μg/kg d.w.)	Native	Sprouted
Wheat	Tyrosine	47.9±1.9*	342.2±55.9
	Tyramine	8.5±1.2*	165.7±11.3
	L-DOPA	9.2±2	nd
	Dopamine	9.5±0*	3.1±0.1
Barley	Tyrosine	54.9±5.2*	597.4±24.1
	Tyramine	1733.5±43.2*	21548.1±839.4
	L-DOPA	313±3.4*	nd
	Dopamine	96.2±4.9*	9±0,2
Rye	Tyrosine	62.4±1*	910.6±33.4
	Tyramine	nd	11.1±0.1
	L-DOPA	140.3±16.5*	623,4±31,3
	Dopamine	36.1±0.1*	55.5±7.5
Oats	Tyrosine	58.1±2.8*	265.9±21.4
	Tyramine	94.8±6.4*	183,5±177,1
	L-DOPA	59.7±4.8	51,3±11,3
	Dopamine	45.8±1.5*	13,5±0,1
Einkorn	Tyrosine	92.9±6.4*	622.2±2.8
	Tyramine	3.6±1.7*	469,9±6,2
	L-DOPA	69.6±6,2*	644,8±36,6
	Dopamine	48.4±0,3*	14,8±0,2
Buckwheat	Tyrosine	108.2±1.9*	323.3±3.2
	Tyramine	1015.6±3.4*	2201,5±28,5
	L-DOPA	35.7±0*	58,7±5,3
	Dopamine	114.9±3.4*	133,1±6,1

The asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Changes in the concentrations of tyrosine during commercial yeast fermentation and sourdough fermentation of native and sprouted grains are given in Table 11 and Table 12, respectively. According to these tables, tyrosine concentration increased with commercial yeast fermentation at 40 °C generally for all native grains except wheat and decreased with commercial yeast fermentation at 20-30 °C generally for all native grains except oats and buckwheat. Also, it increased with commercial yeast fermentation at 40 °C for all sprouted grains. Tyrosine concentration decreased with commercial yeast fermentation of sprouted wheat and einkorn at 20 °C, increased with commercial yeast fermentation of sprouted wheat, barley and buckwheat at 30 °C. Additionally, tyrosine concentration increased with sourdough fermentation at 10 °C for all native grains and first increased then decreased with sourdough fermentation at 20 °C generally for all native grains except oats and buckwheat. It decreased with sourdough fermentation of native barley at 30 °C, of native oats at 20 °C, of native buckwheat at 20-30 °C; increased with sourdough fermentation of native oats and einkorn at 30 °C. With sourdough fermentation of sprouted grains, tyrosine concentration increased at 10 °C. It also increased at 30 °C with sourdough fermentation of sprouted oats and buckwheat. As opposed to these, it decreased at 20 °C with sourdough fermentation of sprouted wheat, oats, and buckwheat. An interestingly, tyrosine concentration is first increased and then decreased with sourdough fermentation of sprouted rye at 20 °C, of sprouted einkorn at 20-30 °C.

Changes in the tyrosine derivatives concentrations of commercial yeast fermented native and sprouted grains were given in Table 13. According to this, dopamine concentrations did not show a significant difference with commercial yeast fermentation of all grains for general. Exceptionally, it decreased with commercial yeast fermentation of native wheat at 20-40 °C, of native barley at 40 °C, of sprouted barley at 30-40 °C, of native oats at 40 °C of native buckwheat at 30-40 °C, of sprouted buckwheat at 40 °C. Also, it first increased and then decreased with commercial yeast fermentation of sprouted einkorn at 30 °C. Also, it is seen that L-DOPA concentrations increased with commercial yeast fermentation of all grains generally. As an exception, commercial yeast fermentation of native rye and neither native nor sprouted buckwheat at any temperature made any difference in L-DOPA concentration ($p>0.05$). Tyramine concentration did not exhibit common behavior for all grains. There is no change in tyramine with commercial yeast fermentation of neither native nor sprouted wheat. Nevertheless, according to Rizello et al (2010). it was reported that the tyramine level of wheat germ fermented with sourdough was 700 ppm [126]. It decreased with commercial yeast fermentation of both native and sprouted barley except the native form at 20 °C. While it was not observed with commercial yeast fermentation of native rye, it decreased with the fermentation of sprouted rye at 30-40 °C. Tyramine increased with commercial yeast fermentation of both native and sprouted oats at every temperature and time conditions and it also increased with commercial yeast fermentation of sprouted einkorn at every temperature. Although it decreased with commercial yeast fermentation of native buckwheat at 20 °C and 40 °C-1 hour, it increased with the fermentation of sprouted buckwheat at 40 °C -3 hours.

Changes in the concentrations of tyrosine derivatives during sourdough fermentation of native and sprouted grains are given in Table 14. According to this table, generally all tyrosine derivatives increased with sourdough fermentation of both native and sprouted forms of all grains. Exceptionally, dopamine did not differ with sourdough fermentation of sprouted barley at 10 °C ($p>0.05$). it first increased and then decreased with sourdough fermentation of native rye at 10 °C, it did not differ with sourdough fermentation of neither native nor sprouted oats at 10 °C ($p>0.05$), it decreased with sourdough fermentation of native buckwheat at every temperature with different fermentation times. Also, there are some exceptions for L-DOPA. It did not differ with sourdough fermentation of native rye at 10-30 °C ($p>0.05$), it first increased and then decreased with sourdough fermentation of sprouted einkorn at 20 °C, like dopamine results it decreased with sourdough fermentation of native buckwheat at every temperature with different fermentation times. Furthermore. there are some exceptions for tyramine. It decreased with sourdough fermentation of sprouted wheat at 10 °C, it did not differ with sourdough fermentation of neither native nor sprouted rye at 10 °C ($p>0.05$), it first increased and then decreased with sourdough fermentation of sprouted oats at 30 °C, it did not differ with sourdough fermentation of sprouted einkorn at 10 °C ($p>0.05$).

According to these results, the concentration of L-DOPA in the native form of the grains is higher than that of dopamine. While tyrosine concentration increased with sprouting, L-DOPA and dopamine concentrations generally decreased. When the grains were sprouted, L-DOPA concentration was higher in half, while dopamine concentration was higher in the other half. Tyramine, on the other hand, showed higher concentration even in the native grains, while it reached even higher concentrations in sprouted grains. It is seen that tyramine formation is more dominant with sprouting.

The formation of L-DOPA and degredation of tyramine seems to be dominant with commercial yeast fermentation. This works for both native and sprouted grains. With the sourdough fermentation of cereals, the formation of all tyrosine derivatives seems to be dominant. Contrary to the situation in commercial yeast, the tyramine concentration also increased. While hydroxylase enzymes are more active with commercial yeast fermentation, both hydroxylase and decarboxylase enzymes may be working more actively with sourdough fermentation. According to the results of both commercial yeast and sourdough fermentation. the highest increases were observed in einkorn. There was a 198.9 fold increase in L-DOPA with the commercial yeast fermentation of native einkorn at 40 °C-3 hours, also the highest concentrastion of L-DOPA is in einkorn with 10481.6±2009.1. Sourdough fermentation of sprouted einkorn wheat at 30 °C-36 hours increased dopamine 272.9 times and the highest concentration of dopamine is in einkorn with 45224.4±5256.2, sourdough fermentation of sprouted einkorn at 10 °C-36 hours increased L-DOPA 954.9 times but the highest concentration of L-DOPA is in sprouted rye with 56189.5±11676.6, sourdough fermentation of sprouted einkorn at 30 °C-36 hours increased 245.4 times in tyramine and sourdough fermentation of sprouted barley at 10 °C-36 hours decreased %18. The proteolytic activity was promoted by fermentation and the tyrosine concentration was generally higher than in both the native and sprouted form.

These results do not include buckwheat. While commercial yeast fermentation of buckwheat does not seem to be effective in the formation of tyrosine derivatives, sourdough fermentation seems to be effective only in the formation of tyramine.

4.4. Formation of Tryptophan and Its derivatives with Sprouting and Fermentation

Changes in the tryptophan and its derivatives concentrations of native and sprouted samples were given in Table 15. Accordingly, sprouting increased tryptophan in all grains but decreased almost all tryptophan derivatives. The highest increase was observed for tryptophan as 3.5 times. The increase in the tryptophan concentration as a result of sprouting was attributed to the increased proteolytic activity during this period, which lead to the hydrolysis of proteins to amino acids as mentioned before. In a study of Lorenz et al. (2009) tryptophan concentration increased with the sprouting of the wheat, barley, rye, and oats[127]. 5-hydroxytryptophan did not show a specific trend for all grains. It did not appear with the sprouting of wheat and barley, did not differ with the sprouting of rye and oats ($p>0.05$), decreased with the sprouting of einkorn and increased with the sprouting of buckwheat. The highest increase in 5-hydroxytryptophan was observed for buckwheat 1.3 times and the most dramatic decrease was observed for einkorn by 41%. Serotonin did not differ with the sprouting of most grains ($p>0.05$). Exceptionally, it decreased with the sprouting of barley and einkorn, increased with the sprouting of buckwheat. The only increase in serotonin was observed for buckwheat 2.4 times and the most dramatic decrease was observed for barley by 95%. N-acetylserotonin decreased with the sprouting of most grains. As an exception, it did not appear with the sprouting of wheat and barley, did not differ with the sprouting of einkorn ($p>0.05$). The most dramatic decrease was observed for buckwheat by 19%. Kynurenine decreased with the sprouting of most grains except the increase with einkorn and buckwheat. The highest increase in kynurenine was observed for buckwheat as 1.9 times and the most dramatic decrease was observed for rye by 81%. On the contrary, kynurenic acid decreased with the sprouting of all grains. The most dramatic decrease was observed for wheat by 75%. 3-hydroxykynurenine did not appear with the sprouting of wheat, did not differ with the sprouting of einkorn ($p>0.05$) and increased with the sprouting of buckwheat. But it decreased with the sprouting of other grains. The only increase in 3-hydroxykynurenine was observed for buckwheat 1.3 times and the most dramatic decrease was observed for barley by 90%. Picolinic acid decreased with the sprouting of most grains except the increase with buckwheat. The highest increase in picolinic acid was observed for buckwheat as 1.2 times and the most dramatic decrease was observed for oats by 70%. Similarly quinolinic acid decreased with the sprouting of most grains except the increase with einkorn and buckwheat. The highest increase in quinolinic acid was observed for buckwheat 4.3 times and the most dramatic decrease was observed for oats by 97%. Despite decreases in other tryptophan derivatives, niacin increased with the sprouting of most grains except that there was no change with the sprouting of barley. The highest increase was observed for niacin as 3.8 times. A general overview of the results reveals that transformation of tryptophan to niacin was the most dominant reaction among others in the tryptophan pathway and the cereal with the highest increase in tryptophan derivatives is buckwheat.

Changes in the concentrations of tryptophan during commercial yeast fermentation and sourdough fermentation of native and sprouted grains are given in Table 16 and Table 17, respectively. According to these tables tryptophan generally decreased with commercial yeast fermentation of native grains at 20-30 °C except buckwheat and increased with commercial yeast fermentation of sprouted grains at 40 °C except einkorn. Also, there is an exception that it first decreased and then increased with commercial yeast fermentation of native rye at 40 °C and it first increased and then decreased with commercial yeast fermentation of sprouted rye at 30 °C. It generally increased with sourdough fermentation of both native and sprouted forms of grains. As an exception, it decreased with sourdough fermentation of sprouted wheat at 20-30 °C, with sourdough fermentation of sprouted rye at 20 °C. In a study of Heo et al. (2020) tryptophan concentration increased about 3.2 fold with sourdough fermentation of mix-grains. Heo et al. attribute this to the fact that fermentation improves protein quality and therefore increases essential amino acid concentration [128]. In another study of Collar et al. (1992) tryptophan concentration increased with lactic acid fermentation and decreased with commercial yeast fermentation [129], in line with our results.

Table 16. Changes in the tyrosine concentrations (mg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains

T (°C)		20				30				40			
t (h)		0	1	2	3	0	1	2	3	0	1	2	3
Wheat	**N**	185 ± 8^{a}	138 ± 6^{bA}	106 ± 4^{cB}	102 ± 7^{cB}	185 ± 8^{a}	91 ± 1^{bB}	101 ± 14^{bB}	94 ± 9^{bB}	185 ± 8^{a}	135 ± 3^{bA}	144 ± 9^{bA}	189 ± 13^{aA}
	S	356 ± 30^{a}	296 ± 11^{bB}	326 ± 9^{abB}	334 ± 6^{abC}	356 ± 30^{ab}	322 ± 0^{bB}	331 ± 4^{bB}	390 ± 8^{aB}	356 ± 30^{d}	423 ± 14^{cA}	541 ± 6^{bA}	619 ± 6^{aA}
Barley	**N**	133 ± 5^{a}	123 ± 5^{aA}	104 ± 3^{bB}	109 ± 2^{bB}	133 ± 5^{a}	123 ± 17^{abA}	100 ± 3^{bB}	98 ± 1^{bB}	133 ± 5^{bc}	135 ± 3^{cA}	198 ± 1^{abA}	247 ± 6^{aA}
	S	599 ± 110^{a}	724 ± 133^{aA}	675 ± 64^{aB}	757 ± 13^{aA}	599 ± 110^{b}	744 ± 14^{abA}	690 ± 16^{abB}	832 ± 54^{aA}	599 ± 110^{b}	973 ± 137^{abA}	1098 ± 119^{aA}	1025 ± 248^{abA}
Rye	**N**	261 ± 16^{a}	203 ± 4^{bA}	179 ± 6^{cB}	163 ± 2^{cB}	261 ± 16^{a}	227 ± 22^{aA}	165 ± 4^{bB}	146 ± 2^{cC}	261 ± 16^{b}	222 ± 17^{bA}	241 ± 16^{bA}	378^{aA}
	S	753 ± 0 ^{a}	713 ± 98^{aB}	837 ± 3^{aA}	808 ± 19^{aB}	753 ± 0 ^{a}	852 ± 5^{aAB}	840 ± 57^{aA}	857 ± 53^{aB}	753 ± 0 ^{b}	946 ± 28^{abA}	999 ± 80^{abA}	1284 ± 123^{aA}
Oats	**N**	181 ± 12^{a}	173 ± 17^{aC}	207 ± 9^{aB}	191 ± 9^{aC}	181 ± 12^{b}	208 ± 4^{bB}	303 ± 35^{aA}	340 ± 11^{aB}	181 ± 12^{d}	283 ± 7^{cA}	373 ± 13^{bA}	463 ± 8^{aA}
	S	305 ± 22^{a}	229 ± 52^{aB}	252 ± 16^{aB}	292 ± 8^{aB}	305 ± 22^{a}	292 ± 26^{aAB}	331 ± 44^{aB}	345 ± 9^{aB}	305 ± 22^{c}	391 ± 23^{bA}	491 ± 30^{aA}	549 ± 34^{aA}
Einkorn	**N**	307 ± 22^{a}	235 ± 1^{bB}	256 ± 16^{abB}	255 ± 30^{abB}	307 ± 22^{a}	256 ± 12^{bB}	258 ± 0^{bB}	259 ± 2^{bB}	307 ± 22^{b}	288 ± 5^{bA}	327 ± 22^{abA}	368 ± 13^{aA}
	S	764 ± 21^{ab}	834 ± 54^{aB}	862 ± 70^{aB}	662 ± 16^{bB}	764 ± 21^{a}	769 ± 60^{aB}	1018 ± 268^{aAB}	987 ± 11^{aAB}	764 ± 21^{b}	1089 ± 40^{bA}	1379 ± 40^{abA}	2108 ± 641^{aA}
Buckwheat	**N**	213 ± 11^{a}	208 ± 2^{aB}	193 ± 15^{aC}	203 ± 25^{aB}	213 ± 11^{c}	201 ± 19^{cB}	282 ± 1^{bB}	335 ± 24^{aAB}	213 ± 11^{c}	253 ± 3^{bcA}	346 ± 19^{abA}	397 ± 67^{aA}
	S	219 ± 16^{a}	218 ± 13^{aC}	239 ± 12^{aC}	286 ± 55^{aB}	219 ± 16^{c}	262 ± 4^{bB}	324 ± 3^{aB}	285 ± 20^{bB}	219 ± 16^{d}	337 ± 3^{cA}	440 ± 5^{bA}	512±38^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of tyrosine (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of tyrosine (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 17. Changes in the tyrosine concentrations (mg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains

T (°C)		10				20				30			
t (h)		**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**
Wheat	**N**	11 ± 5^{c}	15^{cC}	284 ± 29^{bA}	371 ± 8^{aA}	11 ± 5^{c}	251 ± 14^{aA}	89 ± 14^{bC}	76 ± 3^{bC}	11 ± 5^{a}	166 ± 2^{aB}	186 ± 2^{aB}	166 ± 36^{aB}
	S	998 ± 90^{b}	1473 ± 306^{abA}	1463 ± 5^{abA}	1687 ± 151^{aA}	998 ± 90^{a}	740 ± 78^{bB}	586 ± 4^{bC}	590 ± 73^{bC}	998 ± 90^{a}	967 ± 2^{aAB}	897 ± 1^{aB}	988 ± 24^{aB}
Barley	**N**	174 ± 16^{c}	377 ± 69^{abA}	369 ± 19^{bA}	486 ± 31^{aA}	174 ± 16^{b}	288 ± 46^{aAB}	103 ± 10^{cB}	57 ± 1^{cC}	174 ± 16^{a}	144 ± 7^{abB}	118 ± 7^{bB}	158 ± 27^{abB}
	S	1343 ± 114^{c}	1652 ± 173^{cA}	2132 ± 175^{bA}	2599 ± 32^{aA}	1343 ± 114^{a}	1290 ± 168^{aA}	712 ± 49^{bC}	671 ± 75^{bC}	1343 ± 114^{ab}	1266 ± 30^{bA}	1390 ± 31^{abB}	1484 ± 81^{aBd}
Rye	**N**	515 ± 36^{c}	703 ± 168^{bcA}	800 ± 29^{abA}	1035 ± 68^{aA}	515 ± 36^{b}	811 ± 71^{aA}	399 ± 11^{bcC}	351 ± 28^{cC}	515 ± 36^{a}	557 ± 52^{aA}	542 ± 51^{aB}	515 ± 4^{aB}
	S	1623 ± 15^{c}	1817 ± 107^{cB}	2106 ± 101^{bA}	2394 ± 37^{aA}	1623 ± 15^{b}	2254 ± 0^{aA}	1401 ± 8^{cB}	1284 ± 134^{cB}	1623 ± 15^{a}	1877 ± 35^{aB}	1949 ± 308^{aAB}	2071 ± 129^{aA}
Oats	**N**	307 ± 17^{c}	436 ± 0^{bA}	507 ± 39^{bA}	597 ± 37^{aA}	307 ± 17^{a}	192 ± 13^{bC}	147 ± 0^{cB}	176 ± 1^{bcB}	307 ± 17^{c}	312 ± 1^{cB}	480 ± 12^{bA}	616 ± 13^{aA}
	S	245 ± 4^{c}	407 ± 10^{bA}	574 ± 18^{aA}	598 ± 5^{aB}	245 ± 4^{a}	195 ± 4^{bcC}	171 ± 6^{cB}	215 ± 20^{abC}	245 ± 4^{d}	313 ± 26^{cB}	573 ± 11^{bA}	808 ± 35^{aA}
Einkorn	**N**	361 ± 16^{b}	727 ± 110^{aA}	840 ± 85^{aA}	877 ± 33^{aA}	361 ± 16^{b}	512 ± 9^{aA}	268 ± 11^{cB}	288 ± 38^{cB}	361 ± 16^{c}	565 ± 62^{bA}	696 ± 63^{abA}	766 ± 55^{aA}
	S	1412 ± 82^{c}	1764 ± 54^{bcA}	2420 ± 449^{abA}	2668 ± 176^{aA}	1412 ± 82^{b}	1847 ± 150^{aA}	1388 ± 52^{bB}	1020 ± 61^{cC}	1412 ± 82^{c}	2054 ± 21^{aA}	1670 ± 6^{bAB}	1437 ± 71^{cB}
Buckwheat	**N**	747 ± 40^{c}	925 ± 80^{bA}	1240 ± 9^{aA}	1178 ± 83^{aA}	747 ± 40^{a}	495 ± 10^{bB}	206 ± 5^{cC}	189 ± 26^{cC}	747 ± 40^{a}	464 ± 1^{bB}	403 ± 13^{cB}	372 ± 8^{cB}
	S	283 ± 24^{c}	436 ± 13^{bA}	532 ± 29^{bA}	692 ± 78^{aA}	283 ± 24^{a}	187 ± 23^{bB}	199 ± 12^{bB}	186 ± 5^{bB}	283 ± 24^{c}	405 ± 12^{bA}	585 ± 29^{aA}	646 ± 33^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of tyrosine (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of tyrosine (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 18. Changes in the concentrations of tyrosine derivatives (μg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains.

T (°C)			20				30				40			
t (h)			0	1	2	3	0	1	2	3	0	1	2	3
Wheat	**Dopamine**	**N**	21,4±0,2^{a}	20,9±0,6^{aA}	22,6±0,5^{aA}	21,7±0,2^{aAB}	21,4±0,2^{a}	23,2±0,2^{aA}	21,1±0,3^{aA}	22,1±0^{aA}	21,4±0,2^{a}	21,6±0,5^{aA}	20,4±0,6^{aA}	20,7±0,4^{aB}
		S	26,4±0,7^{a}	22,4±0,6^{bA}	23±0,6^{bA}	24,3±0,4^{abA}	26,4±0,7^{a}	23,7±1,1^{aA}	23,6±1,6^{aA}	23±1,1^{aA}	26,4±0,7^{a}	20,9±0,1^{bA}	21,4±0^{bA}	21,4±0,5^{bA}
	L-DOPA	**N**	16,2±6,2^{a}	41±16,5^{aAB}	61±19,9^{aA}	57,4±1,6^{aB}	16,2±6,2^{c}	24,6±2^{cB}	50,4±0,8^{bA}	66,2±0,1^{aB}	16,2±6,2^{c}	70,1±0,1^{bA}	98,5±12^{bA}	148±3,6^{aA}
		S	10,4±5,7^{c}	82,1±9,1^{bC}	168,5±12,3^{aB}	193,9±7,6^{aC}	10,4±5,7^{c}	157,6±9,3^{bB}	224,1±56,5^{bB}	397,1±17,3^{aB}	10,4±5,7^{d}	252,4±5,5^{cA}	461,7±10,4^{bA}	611±28,3^{aA}
	Tyramine	**N**	13±2,1^{a}	13±1^{aA}	16,2±1,4^{aA}	13,3±0,2^{aA}	13±2,1^{a}	12,2±0,4^{aA}	13,6±0,4^{aA}	12,6±0,6^{aA}	13,2±2,1^{a}	14,4±0,1^{aA}	15,7±0,5^{aA}	17,2±3,2^{aA}
		S	108,6±11,4^{a}	106,8±10,6^{aA}	116,5±11,1^{aA}	109,6±4,3^{aAB}	108,6±11,4^{a}	108,7±11,2^{aA}	57,6±51,1^{aA}	106,9±4,6^{aB}	108,6±11,4^{a}	113,1±5,3^{aA}	120,9±5,7^{aA}	130,2±5,3^{aA}
Barley	**Dopamine**	**N**	105,1±6,2^{a}	105,8±1,2^{aA}	107,4±5,9^{aAB}	110,6±4,1^{aAB}	105,1±6,2^{a}	107,5±2,3^{aA}	117,2±7,8^{aA}	116,4±8,3^{aA}	105,1±6,2^{a}	95,2±0,4^{abB}	88,1±0,7^{bB}	87,2±1,3^{bB}
		S	81,5±3,6^{a}	70,4±0^{aA}	74,6±4,5^{aA}	70,1±3,9^{aA}	81,5±3,6^{a}	66,6±1,4^{bAB}	66,9±0,2^{bA}	67,6±2,5^{bA}	81,5±3,6^{a}	63,6±1,2^{bB}	62,7±1,7^{bA}	62,5±1,3^{bA}
	L-DOPA	**N**	349±67,9^{a}	414,8±92,4^{aA}	551,9±0,6^{aB}	550,9±48,9^{aB}	349±67,9^{a}	517,9±50,9^{aA}	531,2±51,9^{aB}	537,4±36,6^{aB}	349±67,9^{b}	685,8±66,2^{aA}	767,9±56,8^{aA}	769,5±29,6^{aA}
		S	247,9±4,8^{c}	362,4±1,4^{bA}	450,4±5,5^{aA}	408,8±41,8^{abA}	247,9±4,8^{b}	352,8±32^{aA}	378,5±6,9^{aB}	363,3±8,6^{aA}	247,9±4,8^{a}	312,5±25,6^{aA}	295,9±13^{aC}	305,2±24,4^{aA}
	Tyramine	**N**	2453,1±8,1^{a}	2430,6±80,2^{aA}	2332,7±12^{aA}	2394,2±28,8^{aA}	2453,1±8,1^{a}	2336,1±21,5^{abAB}	2349,9±43,7^{abA}	2325±32,9^{bA}	2453,1±8,1^{a}	2152±54,9^{bB}	2196±4,3^{bB}	2020,6±98,8^{bB}
		S	22595,7±48,4^{a}	22339,6±779,4^{abA}	21652,4±318,1^{abA}	20747,3±261,3^{bA}	22595,7±48,4^{a}	22008,5±122,3^{abA}	20704,6±559,9^{bcA}	20403,7±467,9^{cA}	22595,7±48,4^{a}	20241,7±871,2^{bA}	19904,9±375,5^{bA}	19780,2±391,2^{bA}
Rye	**Dopamine**	**N**	73,1±0,4^{a}	73,1±0,3^{aA}	72,9±0,2^{aA}	73,7±0,6^{aA}	73,1±0,4^{a}	73,4±0,5^{aA}	73,4±0,1^{aA}	73,5±0,5^{aA}	73,1±0,4^{a}	73,2±0,3^{aA}	73,3±0^{aA}	73,1±0,2^{aA}
		S	153,5±0,6^{a}	153,9±1^{aA}	154,9±1,3^{aA}	155,7±0,4^{aA}	153,5±0,6^{a}	155,8±1^{aA}	156,3±0,3^{aA}	157±2,5^{aA}	153,5±0,6^{a}	155,8±0,6^{aA}	153,9±0,7^{aA}	153,7±1,1^{aA}

Table 18. Changes in the concentrations of tyrosine derivatives (μg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Rye	**L-DOPA**	**N**	614,3±451,8^{a}	466,2±281,5^{aA}	431,7±279,4^{aA}	322±117,2^{aB}	614,3±451,8^{a}	557,1±374,9^{aA}	688,5±338,6^{aA}	449,8±15,2^{aB}	614,3±451,8^{a}	1183,6±619,3^{aA}	1139,9±93,5^{aA}	1548,8±44,4^{aA}
		S	212,1±23,3^{d}	655,6±147^{cA}	1424,8±259,7^{bC}	3080,2±515,4^{aA}	212,1±23,3^{d}	1941,9±477^{cA}	6055,4±17,3^{aA}	3691,3±289,9^{bA}	212,1±23,3^{c}	1199,8±68^{bA}	4321,7±165,8^{aB}	5463±1012^{aA}
	Tyramine	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	234,1±13,4^{a}	215,9±3,8^{aA}	231±4,5^{aB}	235,7±18,4^{aA}	234,1±13,4^{a}	215,3±8,3^{abA}	247,7±1,5^{aA}	187,4±9,9^{bA}	234,1±13,4^{a}	152,7±2,6^{cB}	179,3±0,5^{bcC}	194±14,5^{bA}
Oats	**Dopamine**	**N**	90,2±1,1^{a}	90,2±0,3^{aA}	89,2±1,3^{aA}	89,4±0,3^{aA}	90,2±1,1^{a}	88,8±0,2^{aA}	89,3±0,2^{aA}	88±0,6^{aA}	90,2±1,1^{a}	87,1±0,6^{bB}	86,2±0,1^{bA}	88,2±0,3^{abA}
		S	87,2±1,5^{a}	89±1,4^{aA}	89,5±0,7^{aAB}	91,3±1,9^{aA}	87,2±1,5^{a}	88,6±1^{aA}	90,8±0,2^{aA}	90,4±1,9^{aA}	87,2±1,5^{a}	90,8±2,4^{aA}	87,9±0,4^{aB}	87,7±0,1^{aA}
	L-DOPA	**N**	127,3±10,6^{c}	240,9±2,6^{bA}	236,5±5,5^{bA}	311,3±16,8^{aB}	127,3±10,6^{c}	267±8^{bcA}	438,3±49,9^{abA}	520,4±84,6^{aAB}	127,3±10,6^{b}	348,5±76,4^{abA}	447,4±80,1^{aA}	597,2±62,7^{aA}
		S	80,4±50,4^{a}	31,8±6,5^{aA}	31,8±11^{aC}	77,1±56,5^{aB}	80,4±50,4^{a}	160,7±36,8^{aA}	126,1±10,7^{aB}	334,7±178,2^{aAB}	80,4±50,4^{c}	128,8±82,9^{cA}	460,3±11,2^{bA}	748,6±27,2^{aA}
	Tyramine	**N**	109±0,8^{c}	145,4±13,3^{bB}	193,3±8,8^{aB}	227,9±8,4^{aB}	109±0,8^{b}	246±5,8^{aA}	247,3±1,7^{aA}	251,3±3,8^{aAB}	109±0,8^{b}	248,4±9,4^{aA}	239,2±1,2^{aA}	259,8±6^{aA}
		S	188,8±23^{b}	331±25,8^{aB}	352,3±16,3^{aC}	399,6±38,9^{aB}	188,8±23^{c}	430,6±38,1^{bAB}	501,3±16,4^{abB}	619,7±44,4^{aB}	188,8±23^{d}	525,2±38,3^{cA}	808,2±37,9^{bA}	1360,5±76,8^{aA}
Einkorn	**Dopamine**	**N**	99,6±1,7^{a}	99,2±0,4^{aA}	101,3±1,7^{aA}	100,8±0,4^{aA}	99,6±1,7^{a}	99,8±0,6^{aA}	100,1±0,8^{aA}	100±0,3^{aA}	99,6±1,7^{a}	99,4±2,2^{aA}	101±2,3^{aA}	99,9±2,6^{aA}
		S	98,6±0,3^{a}	101,1±2^{aA}	102,5±1,5^{aA}	99,4±0,8^{aA}	98,6±0,3^{b}	100,2±0,6^{aA}	100,4±0,3^{aAB}	96,9±0,1^{cB}	98,6±0,3^{a}	98,7±0,9^{aA}	97,3±0,5^{aB}	96,8±0,5^{aB}
	L-DOPA	**N**	52,7±6,4^{b}	508,1±334,2^{bB}	1483,2±49,6^{aC}	1303±6,1^{aB}	52,7±6,4^{d}	2520,1±530,4^{cA}	4501,1±147,5^{bB}	6003,3±136,3^{aAB}	52,7±6,4^{c}	2852,9±166,3^{bcA}	5978,5±327,4^{bA}	10481,6±2009,1^{aA}
		S	50±0,7^{ab}	70,7±3,8^{aA}	43,7±18,1^{abA}	31,4±4,5^{bA}	50±0,7^{a}	35,5±3,9^{aB}	17,7±2^{aA}	525,3±495,7^{aA}	50±0,7^{a}	26,3±0,3^{aB}	36,8±2,9^{aA}	629,8±555,1^{aA}
	Tyramine	**N**	37,8±3,6^{a}	20,1±6^{bA}	15,9±0,5^{bA}	14,1±0,5^{bA}	37,8±3,6^{a}	10,2±3^{bA}	6,1±0,5^{bB}	9,1±0,2^{bB}	37,8±3,6^{a}	11±2,1^{bA}	7,4±1,1^{bB}	5±0^{bC}
		S	282,8±30,1^{a}	258,3±2,1^{aA}	284,9±7^{aA}	230,1±31,6^{aA}	282,8±30,1^{a}	252,8±12,2^{aA}	224,6±24,3^{aA}	198±48,7^{aA}	282,8±30,1^{a}	261,1±11,3^{aA}	271,7±1,3^{aA}	224,1±28,1^{aA}

Table 18. Changes in the concentrations of tyrosine derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Buckwheat	**Dopamine**	**N**	203,1±3,5^{a}	204,5±6,2^{aA}	202,8±2,4^{aA}	202,6±2,3^{aA}	203,1±3,5^{a}	193±3,2^{abA}	198,7±4,2^{abAB}	189,2±2,1^{bA}	203,1±3,5^{a}	197±0,1^{abA}	188,2±1,6^{abB}	183,8±6,7^{bA}
		S	216,1±8,8^{a}	186,4±13,2^{aA}	212±10^{aA}	205,7±2,7^{aA}	216,1±8,8^{a}	207,1±7,8^{aA}	198,3±0,3^{aA}	200,3±9,4^{aA}	216,1±8,8^{a}	214,4±6,5^{aA}	207±2,8^{abA}	181,1±7,1^{bA}
	L-DOPA	**N**	97±20,3^{a}	71,8±13^{aA}	82,9±11^{aA}	87,7±2,7^{aA}	97±20,3^{a}	74,2±0,4^{aA}	105,2±15,8^{aA}	78,7±27,7^{aA}	97±20,3^{a}	67,6±10,7^{aA}	87,7±11,4^{aA}	82,4±3,3^{aA}
		S	168,4±11,4^{a}	201,4±0,7^{aA}	203,5±8,8^{aA}	191,2±25,5^{aA}	168,4±11,4^{a}	312,1±90,9^{aA}	175,4±14,6^{aA}	237,4±18,7^{aA}	168,4±11,4^{a}	173,8±7,1^{aA}	182,2±7,9^{aA}	153,2±21,3^{aA}
	Tyramine	**N**	1072,4±2,8^{a}	1056,2±22,4^{aA}	990,4±4,9^{cA}	1021±17,2^{abA}	1072,4±2,8^{a}	1016,6±41^{aA}	1023,4±16,6^{aA}	1043,8±5,2^{aA}	1072,4±2,8^{a}	995,1±25,1^{bA}	1023,4±6,2^{abA}	1045,7±3,1^{abA}
		S	1598±20,2^{a}	1566±4,6^{aA}	1599,1±31,4^{aAB}	1653,3±42,3^{aB}	1598±20,2^{a}	1583,4±17,1^{aA}	1653,6±5^{aA}	1657,3±59,7^{aB}	1598±20,2^{b}	1504,8±2,1^{bB}	1536,2±3^{bB}	1999,6±80,9^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of tyrosine derivatives (either for sprouted or native grains), according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of tyrosine derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 19. Changes in tyrosine derivatives concentrations (μg/kg d.w.) by sourdough fermentation of native and sprouted grains (N/S)

T (°C)			10				20				30			
t (h)			0	12	24	36	0	12	24	36	0	12	24	36
Wheat	Dopamine	N	89,5±43,1^{c}	97,2±6,5^{cC}	187,6±4,9^{bC}	389,2±4,7^{aB}	89,5±43,1^{d}	351,9±63,4^{cB}	1008,3±13,6^{bB}	1443,6±14,9^{aA}	89,5±43,1^{b}	736,8±11,2^{bA}	1418,7±106,7^{abA}	5834,3±2332,6^{aA}
		S	27,8±0,8^{c}	27,2±0,1^{cC}	145,2±23,1^{bC}	618,7±26^{aA}	27,8±0,8^{d}	1222,3±4,3^{cB}	2417,9±45,7^{bB}	3476,9±263,1^{aA}	27,8±0,8^{c}	1514,4±29,3^{bcA}	2665,1±53^{abA}	3763,1±857,6^{aA}
	L-DOPA	N	84±13,4^{d}	397,3±26,7^{cC}	892,9±76,6^{bB}	1494,7±130^{aA}	84±13,4^{d}	742,4±9^{cA}	960,9±62,2^{bA}	1111,5±40,7^{aA}	84±13,4^{b}	822,8±44,8^{bB}	1259,7±52,7^{abA}	3615,1±1209,4^{aA}
		S	8±0,9^{c}	21,6±3,6^{cB}	1534,3±181,9^{bB}	5709,8±105,6^{aA}	8±0,9^{c}	2324,8±164,4^{bA}	2524,3±42,8^{bB}	3029,2±59,8^{aA}	8±0,9^{c}	1540,9±1,6^{bcA}	2994,3±77,5^{abA}	5050,1±1057,7^{aA}
	Tyramine	N	5965,5±459,3^{b}	6612,8±248,7^{abC}	6715,9±327,2^{abC}	7706,6±172^{aB}	5965,5±459,3^{c}	12672±4177,2^{cB}	66138,6±28,1^{bB}	86755±367,8^{aA}	5965,5±459,3^{d}	65769,8±589,9^{cA}	92141,2±9025,1^{bA}	113819,3±3301,4^{aA}
		S	4453,6±507,6^{c}	6230,8±134,4^{bB}	7163,5±218^{abC}	7834,9±288,1^{aC}	4453,6±507,6^{c}	69674,2±1572,1^{bB}	88798,8±13,1^{aB}	91869,8±545,4^{aB}	4453,6±507,6^{b}	87403,1±117,3^{aA}	92056,5±524,6^{aA}	91453,8±6239,2^{aA}
Barley	Dopamine	N	589,1±106,1^{b}	659,6±31,7^{abB}	822,3±79,4^{abC}	898,7±3,5^{aC}	589,1±106,1^{c}	741,2±1,4^{cB}	1691,4±3,7^{bB}	2747,3±13,2^{aB}	589,1±106,1^{d}	1388,8±64,2^{cA}	2973±55,2^{bA}	6140,5±92,6^{aA}
		S	310±121,9^{a}	492,8±206,9^{aB}	534,3±101^{aC}	620,6±59^{aC}	310±121,9^{d}	830±39,5^{cB}	2203,3±70,4^{bB}	3656,3±63,7^{aB}	310±121,9^{d}	1531,2±49,6^{cA}	3834,9±255,1^{bA}	4956,9±277,4^{aA}
	L-DOPA	N	1168,2±158,7^{c}	2202,8±68,3^{bA}	3148,8±330,6^{aA}	3392±90^{aB}	1168,2±158,7^{c}	1530±9,7^{bB}	1919,3±33,2^{aB}	2098,5±13,6^{aC}	1168,2±158,7^{c}	1340,2±98,9^{cB}	2223,7±54,1^{bB}	4213,3±117,5^{aA}
		S	871,4±158^{b}	1451,9±247^{bA}	3018,9±339,2^{aAB}	3743,8±615,1^{aAB}	871,4±158^{c}	1726,4±161,2^{bA}	2236,3±32,9^{aB}	2578,8±105,6^{aB}	871,4±158^{c}	1519±76,5^{cA}	3691,6±347,3^{bA}	5189,9±282,9^{aA}
	Tyramine	N	14777,8±1387^{b}	17392,4±953,6^{abC}	15397±404,2^{bC}	19823,5±603,1^{aC}	14777,8±1387^{d}	38984,2±2503,9^{cB}	83066,9±4387,8^{bB}	99963,6±2735,6^{aB}	14777,8±1387^{c}	90560,7±2984,5^{bA}	113222,2±2540,5^{aA}	119081,3±4147,1^{aA}
		S	30888,3±1007,4^{a}	28428,3±384,4^{bC}	26778,4±67,8^{bcC}	25332,9±314,2^{cC}	30888,3±1007,4^{c}	105016±1598,4^{bB}	136731,4±2108,6^{aB}	139659,6±2105,1^{aA}	30888,3±1007,4^{c}	123258,3±1064,6^{bA}	116542,6±1742,3^{aA}	121620,7±412,9^{aB}

Table 19. Changes in tyrosine derivatives concentrations (μg/kg d.w.) by sourdough fermentation of native and sprouted grains (N/S) **(continue)**

Rye	**Dopamine**	**N**	332,8±52,4^{c}	671,6±60,2^{abB}	750,5±41^{aB}	542,3±25,9^{bC}	332,8±52,4^{c}	776,3±54^{cB}	3855,2±789,8^{bB}	8051,7±541,4^{aB}	332,8±52,4^{c}	4327,1±52,4^{cA}	11053,9±1411,3^{bA}	25038,8±2743,5^{aA}
		S	504,9±18,7^{c}	728,6±55,9^{bC}	1587,8±1,5^{aC}	1683,5±19,4^{aB}	504,9±18,7^{c}	2773,9±156^{cB}	9187,6±1260,5^{bB}	15419,1±1259,3^{aA}	504,9±18,7^{c}	9724,3±366^{bcA}	17922±1035,3^{abA}	27119,8±4816,8^{aA}
	L-DOPA	**N**	4456,3±1275,4^{a}	5146,3±1695,1^{aA}	10240,3±2086,9^{aB}	7988,5±1775,3^{aA}	4456,3±1275,4^{c}	6086,2±515,7^{bcA}	11011,7±1061,7^{aAB}	9662,7±632^{abA}	4456,3±1275,4^{a}	11625,7±3516,1^{aA}	24309,1±4813,9^{aA}	20326,8±14870,4^{aA}
		S	7500,2±525,6^{b}	28444,4±14038,1^{abA}	56189,5±11676,6^{aA}	46563±14937,2^{abA}	7500,2±525,6^{b}	29051±1176,3^{aA}	28239,5±4627,6^{aA}	26207,4±7481,3^{aA}	7500,2±525,6^{c}	25113,1±5793,9^{bA}	30524,3±2603,1^{bA}	49882,6±1,6^{aA}
	Tyramine	**N**	1311,7±832,3^{a}	2975,2±1179,3^{aB}	5665,2±1576,9^{aB}	17402,7±10465,2^{aA}	1311,7±832,3^{b}	74029,6±46048,9^{abAB}	134130,9±13698,8^{aA}	141919,8±6423^{aA}	1311,7±832,3^{a}	149860,8±16599^{aA}	171556,1±4580,9^{aA}	88084,6±84471,6^{aA}
		S	3575,9±585,1^{a}	5513,5±2003,8^{aB}	6377,8±57,2^{aB}	28225,7±21698,6^{aB}	3575,9±585,1^{b}	82133,4±33103,7^{aAB}	122148,8±10587,5^{aA}	127507,8±4525,3^{aA}	3575,9±585,1^{b}	126759,4±2900,4^{aA}	133753,9±8077,2^{aA}	135888,4±1,6^{aA}
Oats	**Dopamine**	**N**	97,7±1,4^{a}	97,8±1,6^{aC}	100,3±1,1^{aC}	104±11,6^{aC}	97,7±1,4^{c}	275,2±3^{bcB}	802,2±39,6^{bB}	1466,2±321,4^{aB}	97,7±1,4^{d}	511,3±22,3^{cA}	1373,1±53,1^{bA}	4450,9±136^{aA}
		S	131±6,7^{ab}	102,4±9,6^{bB}	132,2±9,1^{abB}	170,7±17,9^{aB}	131±6,7^{d}	310,5±18,2^{cB}	1271,6±11^{bA}	2110,4±309,3^{aA}	131±6,7^{d}	745,1±79,9^{cA}	1077,5±112,5^{bA}	1359,6±4,1^{aA}
	L-DOPA	**N**	349,8±39,5^{c}	406,5±25,5^{cC}	846,5±29,1^{bC}	1494,9±3,8^{aB}	349,8±39,5^{b}	987,1±6,1^{abB}	1305,5±55,1^{aB}	1739,4±411,3^{aB}	349,8±39,5^{d}	1073,3±14,5^{cA}	1915±102,7^{bA}	6187,5±126,6^{aA}
		S	437,4±7,7^{c}	629,9±46,9^{cB}	1987,5±319,4^{bA}	3602,4±150,9^{aA}	437,4±7,7^{d}	1931,6±45,1^{cA}	2678,3±50,2^{bA}	2925,9±69,9^{aB}	437,4±7,7^{d}	2020,7±9,4^{cA}	2157,8±49,1^{bA}	2556,9±35,7^{aB}
	Tyramine	**N**	9660,2±35,3^{d}	12286±234,4^{cC}	15901±217,6^{bB}	22978,6±635,3^{aC}	9660,2±35,3^{d}	94187,2±297,3^{cB}	114050,7±1014,1^{bA}	123176,1±440,7^{aB}	9660,2±35,3^{b}	108114,8±392,4^{aA}	110096,3±1425,1^{aA}	109992,6±1515,3^{aA}
		S	10165,5±514,1^{d}	12396,7±643,3^{cC}	15275±70,2^{bC}	22634,7±368,6^{aC}	10165,5±514,1^{c}	95338,6±1096^{bB}	112548,8±404,3^{aB}	113444,5±1841,5^{aB}	10165,5±514,1^{c}	100823,5±806^{aA}	99341,4±550^{abA}	95556,8±1720,9^{bA}

Table 19. Changes in tyrosine derivatives concentrations (µg/kg d.w.) by sourdough fermentation of native and sprouted grains (N/S) **(continue)**

Einkorn	**Dopamine**	**N**	344,6±8,6^{d}	846,4±46,1^{cB}	1924,7±57,8^{bB}	2510,3±68,1^{aB}	344,6±8,6^{d}	10146,5±109,2^{cA}	14748,2±381,3^{bA}	17152±329,3^{aAB}	344,6±8,6^{b}	10862,9±420,1^{abA}	16839,9±1507,8^{abA}	29790,2±9794,9^{aA}
		S	165,7±6^{c}	121,7±2,4^{cC}	744,8±95,6^{bB}	1973,6±83,7^{aB}	165,7±6^{d}	19460±243,1^{cB}	28805±164,4^{bA}	34212,6±981^{aA}	165,7±6^{c}	23291,1±654,2^{bA}	30119,2±654,1^{bA}	45224,4±5256,2^{aA}
	L-DOPA	**N**	1975,2±67,4^{d}	4617,5±201,9^{cC}	13729,2±304,6^{bB}	34051,1±433,5^{aA}	1975,2±67,4^{d}	26465,4±574,8^{aB}	18993,2±149,3^{bA}	16111,9±413,1^{cB}	1975,2±67,4^{d}	16494,5±359^{cA}	19030±667,2^{bA}	27208,4±6004,4^{aAB}
		S	37,8±6,5^{d}	105,5±31,7^{cC}	4293,4±652,2^{bC}	36098,3±6462,5^{aA}	37,8±6,5^{c}	18199,5±225,8^{bB}	21748,4±149,6^{aB}	21200±153^{aA}	37,8±6,5^{d}	14234,1±72,1^{cA}	18405,2±249,2^{bA}	24645,5±1948,4^{aA}
	Tyramine	**N**	414,6±28,9^{d}	1071,8±62,5^{cC}	2679,6±41,7^{bB}	5613,2±109,6^{aB}	414,6±28,9^{d}	50658,5±114,2^{cB}	91996,6±1299,5^{bA}	99234,2±522,4^{aA}	414,6±28,9^{c}	75228,8±505^{bA}	93996,6±1097,2^{aA}	101757,9±4916,7^{aA}
		S	5021,4±355,7^{a}	4209,9±351,2^{aC}	4163,6±113,9^{aC}	5396±628,4^{aC}	5021,4±355,7^{d}	92219,1±602,7^{cB}	117374,3±454,1^{bB}	120436,3±608,8^{aA}	5021,4±355,7^{c}	109116,9±522^{aA}	105468,7±639,2^{bA}	110357,4±193,1^{aB}
Buckwheat	**Dopamine**	**N**	1160,9±157,2^{a}	1305,6±69,7^{aA}	1271,5±87^{aAB}	616,6±21,7 ^{bB}	1160,9±157,2^{a}	949,1±33,5^{bcB}	1313,6±44^{aA}	1145,2±75,7^{aA}	1160,9±157,2^{a}	843,7±3,5^{bB}	1025,9±6,5^{aB}	1004,1±71,8^{aA}
		S	928,7±14,8d	1635,5±112,5cA	2390,9±50,1bA	3886±261,7aA	928,7±14,8c	2090,6±248,8bcA	3013,5±292,8abA	3583,1±466,9aA	928,7±14,8b	1447±40,7bA	3965,1±977,7aA	5345,4±1523aA
	L-DOPA	**N**	425,1±57,6^{a}	478,1±25,5^{aA}	465,6±31,9^{aA}	225,8±7,9^{bA}	425,1±57,6^{a}	347,6±12,3^{bB}	481±16,1^{aB}	419,4±27,7^{aB}	425,1±57,6^{a}	309±1,3^{bB}	375,7±2,4^{aB}	367,7±26,3^{aB}
		S	340,1±5,4^{d}	598,9±41,2^{cA}	875,5±18,4^{bA}	1423±95,8^{aA}	340,1±5,4^{c}	765,6±91,1^{bB}	1103,6±107,2^{aB}	1312,1±171^{aB}	340,1±5,4^{c}	529,9±14,9^{bC}	1452±358^{aB}	1957,5±557,7^{aAB}
	Tyramine	**N**	7406,7±195,1^{d}	9468±3,2^{cC}	12359,7±691,8^{bC}	20710,2±436,3^{aC}	7406,7±195,1^{d}	73392,6±1576,4^{cB}	108430,7±175,7^{bB}	126102,7±660,6^{aB}	7406,7±195,1^{b}	96932,7±854,1^{aA}	124490,5±48,1^{aA}	143707,2±3259,4^{aA}
		S	7049±274,3^{d}	8680,8±98,4^{cC}	11383,6±427,1^{bC}	24307,4±389,4^{aC}	7049±274,3^{d}	99756±1524,9^{cB}	116769,8±140,5^{bA}	125584,3±2557,8^{aB}	7049±274,3^{b}	107201,9±0,9^{aA}	105766,1±744,9^{aB}	105203±2634,8^{aA}

Changes in the concentrations of tryptophan derivatives during commercial yeast fermentation of native and sprouted grains are given in Table 18. According to the table, 5-hydroxytryptophan did not appear with commercial yeast fermentation of neither native nor sprouted wheat and barley. Although it showed different changes in other grains, it was very low in concentration. Serotonin generally decreased with commercial yeast fermentation of both native and sprouted grains. As an exception, it did not differ with commercial yeast fermentation of both native and sprouted wheat and sprouted oats ($p>0.05$), first increased and then decreased with commercial yeast fermentation of sprouted rye at 30-40 °C, increased with commercial yeast fermentation of native einkorn at every temperature and sprouted einkorn at 40 °C. N-acetylserotonin generally did not appear or did not differ with commercial yeast fermentation of both native and sprouted grains ($p>0.05$) except the increase with native oats at 30 °C, native einkorn at every temperature, both native and sprouted einkorn at every temperature. Kynurenine showed a different trend for different grains. It increased with commercial yeast fermentation of native wheat at 20-40 °C, first increased and then decreased with commercial yeast fermentation of native wheat at 30 °C and did not differ with commercial yeast fermentation of sprouted wheat ($p>0.05$). There is no change with commercial yeast fermentation of neither native nor sprouted barley ($p>0.05$) except that it decreased with commercial yeast fermentation of native barley at 40 °C-3 hours. Also, there is no change with commercial yeast fermentation of sprouted rye but it decreased with native rye at every temperature. Kynurenine increased with commercial yeast fermentation of both native and sprouted oats and einkorn. While it is also increased with commercial yeast fermentation of native buckwheat, it decreased with sprouted buckwheat at 40 °C. Despite this complex distribution in kynurenine, kynurenic acid generally increased with commercial yeast fermentation of both native and sprouted grains. Exceptionally, it did not differ with commercial yeast fermentation of native oats at any temperature. In a study of Nakov et al. (2016), varying concentrations of kynurenine, kynurenic acid, and niacin were also seen in beer [8]. 3-hydroxykynurenine did not appear with commercial yeast fermentation of neither native nor sprouted wheat, did not differ with commercial yeast fermentation of sprouted barley, sprouted rye, sprouted einkorn, native buckwheat, and sprouted buckwheat ($p>0.05$). Also similarly to 5-hydroxytryptophan, it showed different changes in other grains but it was very low in concentration. Picolinic acid did not differ generally with commercial yeast fermentation of neither native nor sprouted grains ($p>0.05$). Exceptionally, it decreased with commercial yeast fermentation of sprouted wheat at 30 °C, of sprouted barley at every temperature, of sprouted rye at 40 °C, of both native and sprouted einkorn at 40 °C. It increased with commercial yeast fermentation of native barley at 30 °C, of native oats at 20 °C, of native buckwheat at 30 °C-3 hours, of sprouted buckwheat at 20 °C. Lastly, as an exception, it first increased and then decreased with commercial yeast fermentation of native oats at 30-40 °C. Quinolinic acid also decreased generally with commercial yeast fermentation of native grains at 40 °C, except buckwheat, and sprouted grains at every temperature. Exceptionally, it increased with commercial yeast fermentation of native wheat at 30 °C, of native barley at 20-30 °C, of native einkorn at 30 °C. Niacin, without exception, decreased with commercial yeast fermentation of both native and sprouted forms of all grains. In a study of Yılmaz et al. (2017), kynurenic acid was not found in wheat bread, but niacin concentration was observed at varying concentrations [47].

Changes in the concentrations of tryptophan derivatives during sourdough fermentation of native and sprouted grains are given in Table 19. According to this table, 5-hydroxytryptophan did not appear with sourdough fermentation of neither native nor sprouted wheat and did not differ with sprouted oats. Although there was an increase in the remaining grains, concentrations were low. Serotonin generally decreased with sourdough fermentation of grains. Exceptionally, it increased with sourdough fermentation of sprouted wheat, oat, einkorn at 10 °C and of sprouted buckwheat at 20 °C. Also for an exception, it is first increased and then decreased with sourdough fermentation of sprouted wheat, oat, einkorn at 20-30 °C and of sprouted buckwheat at 30 °C. N-acetylserotonin generally did not differ with sourdough fermentation of grains. It did not appear with sourdough fermentation of neither native nor sprouted wheat. Exceptionally it decreased with sourdough fermentation of native barley at 20 °C, of sprouted barley at 30 °C, of sprouted oats and sprouted einkorn at 30°C; it increased with sourdough fermentation of native oats at 10 °C, of native oats at 30 °C-12 hours, of sprouted einkorn at 10 °C, of native buckwheat at 20-30 °C and sprouted buckwheat at 10-30 °C. Kynurenine generally increased with sourdough fermentation of grains. Exceptionally it decreased with sourdough fermentation of native rye at 10 °C, of sprouted einkorn, and sprouted buckwheat at 10-20 °C; it did not differ with sourdough fermentation of native barley, of sprouted rye. Kynurenic acid generally did not differ with sourdough fermentation of grains. Exceptionally, it decreased with sourdough fermentation of sprouted wheat at 20-30 °C, of native rye at 10 °C, of sprouted rye at 20 °C, of sprouted oats, of native buckwheat at 20-30 °C, of sprouted buckwheat at 30 °C; it increased with sourdough fermentation of native oats at 10 °C, of native oats at 20 °C-12 hours, of sprouted einkorn at 20-30 °C, of sprouted buckwheat at 10 °C. 3-hydroxykynurenine did not appear with sourdough fermentation of neither native nor sprouted wheat and did not differ with sprouted rye. Although there were increases and decreases in the remaining grains, concentrations were low similarly to 5-hydroxytryptophan. Picolinic acid also did not differ with sourdough fermentation of grains, generally. As an exception, it increased with sourdough fermentation of native wheat at 30 °C, of sprouted rye at 10 °C-24 hours, of native oats; it decreased with sourdough fermentation of sprouted wheat at 30 °C, of sprouted oats, of native einkorn at 30 °C, of native buckwheat at 10 °C-12 hours and native buckwheat at 30 °C-24 hours. Quinolinic acid also did not differ with sourdough fermentation of grains, generally. In the remaining grains, it decreased generally like sourdough fermentation of native wheat at 10 °C, of sprouted wheat and barley at 20-30 °C, of sprouted oats, of native einkorn at 10-20 °C-12 hours. As an exception, it increased with sourdough fermentation of native oats at 10-30 °C; it first increased and then decreased with sourdough fermentation of native oats at 20 °C. Niacin decreased with sourdough fermentation of most grains, like commercial yeast fermentation. Exceptionally, it increased with sourdough fermentation of sprouted oats at 10 °C, of native einkorn at 10 °C.

According to these results, the formation of kynurenic acid in the kynurenine pathway via tryptophan is dominant for commercial yeast fermentation. The highest increase in kynurenic acid was observed for native wheat 28 times but the highest kynurenic acid concentration is in native buckwheat with 1588.9±2.8. In general, it was observed that sourdough fermentation did not dominate the formation of any tryptophan derivatives. Nevertheless, sourdough fermentation of oats, especially the native form, seems important for the formation of tryptophan derivatives. Nevertheless, quinolinic acid concentration increased about 6.7 fold with sourdough fermentation of native oats at 20 °C-12 hours and serotonin increased about 13.8 fold withsourdough fermentation of sprouted einkorn at 10 °C-36 hours . In addition, it is an interesting result that niacin concentration decreases with fermentation in contrast to the increase in niacin with sprouting. It was observed that decarboxylase activity increased with germination. Therefore, tryptophan derivatives did not increase with germination, nor did they show changes with fermentations compared to other amino acid derivatives.

Considering that the fermentation conditions were the same, more tryptophan derivatives were predicted to form since the initial tryptophan concentration was higher than the tyrosine concentration. However, the chemical structure of tryptophan, containing more carbon and nitrogen than tyrosine, may have been a better substrate source for bacteria and yeasts. Thus, the source of amino acids that can be converted may be depleted. Also it may be concluded that enzymes forming tryptophan derivatives are more sensitive to pH than enzymes forming tyrosine derivatives.

Table 20. Concentrations of tryptophan and its derivatives (µg/kg) for native and sprouted grains

Grains	Trp Derivatives(µg/kg d.w.)	Native	Sprouted
Wheat	3-hydroxykynurenine	nd	nd
	5-hydroxytryptophan	nd	nd

	Kynurenic Acid	18.1±3.9*	4.6±2
	Kynurenine	100.4±5.5*	54±7
	N-acetylserotonin	nd	nd
	Niacin	1697.6±116.9*	2174.5±320.3
	Picolinic Acid	14.9±0.3*	5.7±0.2
	Quinolinic Acid	5.7±0.4*	3.8±0.6
	Serotonin	4.2±3	7.9±1.1
	Tryptophan	168000 ± 3000*	226000 ± 28000
Barley	3-hydroxykynurenine	2.1±0.7*	0.2±0.1
	5-hydroxytryptophan	nd	nd
	Kynurenic Acid	46.8±1.2*	25.9±0.1
	Kynurenine	387.1±15.8*	136.3±6
	N-acetylserotonin	nd	nd
	Niacin	1646.3±206.2	1350.3±115.4
	Picolinic Acid	14.4±0.7*	4.9±0.2
	Quinolinic Acid	8.8±0.6*	5.5±0.2
	Serotonin	297.1±24.3*	14.6±9
	Tryptophan	148000 ± 5000*	253000 ± 3000
Rye	3-hydroxykynurenine	6.3±0.1*	4.6±0
	5-hydroxytryptophan	17.3±0.2	17.7±0.8
	Kynurenic Acid	168.9±4.3*	59.2±1.7
	Kynurenine	903.5±35.6*	173.3±21
	N-acetylserotonin	11.8±0.1*	10.5±0.1
	Niacin	784.7±0.9*	2991.3±814.3
	Picolinic Acid	23±2*	16.4±0.9
	Quinolinic Acid	83.7±4.8	60.2±20.5
	Serotonin	32±1.5	30.5±2.3
	Tryptophan	51000 ± 0*	161000 ± 0
Oats	3-hydroxykynurenine	4.8±0.1*	3.8±0.2
	5-hydroxytryptophan	7.7±0.4	7.7±0.6
	Kynurenic Acid	260.3±64.6*	113.8±0.9
	Kynurenine	573.9±173.1*	169±8.2
	N-acetylserotonin	10.4±0.2*	8.7±0
	Niacin	1464.1±80.7*	2954±35.9
	Picolinic Acid	94.1±2.2*	28.1±0.4
	Quinolinic Acid	1713.8±48.6*	51.6±4.7
	Serotonin	143.3±18.3	153.5±19.8
	Tryptophan	47000 ± 1000*	91000 ± 7000
Einkorn	3-hydroxykynurenine	4.3±0.1	4.4±0.1
	5-hydroxytryptophan	12.4±0*	7.3±0.3
	Kynurenic Acid	27.2±1*	16.5±1.3
	Kynurenine	115.3±0.3*	171.2±5.8
	N-acetylserotonin	9.1±0.1	9.4±0
	Niacin	8198.4±260.7*	8626.9±86.8
	Picolinic Acid	30.8±8.4*	18±1.1
	Quinolinic Acid	33.3±1.2*	40.8±1.6
	Serotonin	6±0.2*	4±0
	Tryptophan	101000 ± 1000*	161000 ± 2000
Buckwheat	3-hydroxykynurenine	22.6±0.7*	28.7±2.3
	5-hydroxytryptophan	298.1±4.2*	380.3±3.5
	Kynurenic Acid	1378.8±65.7*	868.3±51.1
	Kynurenine	355.8±6.9*	675±9.7
	N-acetylserotonin	10.3±0.2*	8.3±0
	Niacin	2936.5±24.9*	3903.1±15.6
	Picolinic Acid	12.5±0.4*	15±0.7
	Quinolinic Acid	20.9±0.1*	90.1±37.4
	Serotonin	1126.8±0.6*	2648.4±35.3
	Tryptophan	40000 ± 2000*	139000 ± 2000

The asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Table 21. Changes in the concentrations of tryptophan (mg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains.

T (°C)		20				30				40			
t (h)		**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**
Wheat	**N**	292 ± 19^{a}	222 ± 16^{bA}	186 ± 40^{bcA}	183 ± 28^{bcB}	292 ± 19^{a}	189 ± 7^{bcA}	143 ± 17^{cA}	92 ± 1^{dC}	292 ± 19^{a}	218 ± 7^{bA}	209 ± 10^{bA}	231 ± 17^{bA}
	S	357 ± 16^{a}	293 ± 19^{bA}	293 ± 15^{bB}	302 ± 14^{bB}	357 ± 16^{a}	287 ± 7^{bA}	274 ± 9^{bB}	281 ± 3^{bB}	357 ± 16^{b}	312 ± 7^{cA}	353 ± 2^{bA}	384 ± 0^{aA}
Barley	**N**	256 ± 18^{a}	196 ± 2^{bA}	176 ± 12^{cB}	181 ± 1^{cB}	256 ± 18^{a}	196 ± 23^{bA}	157 ± 4^{cC}	140 ± 3^{dC}	256 ± 18^{a}	174 ± 4^{dB}	199 ± 2^{cA}	222 ± 4^{bA}
	S	289 ± 59^{a}	320 ± 59^{aA}	287 ± 24^{aB}	323 ± 29^{aB}	289 ± 59^{a}	314 ± 6^{aA}	257 ± 19^{aB}	335 ± 10^{aB}	289 ± 59^{b}	391 ± 50^{aA}	430 ± 33^{aA}	411 ± 65^{aA}
Rye	**N**	112 ± 10^{a}	86 ± 3^{bA}	59 ± 0^{cB}	46 ± 1^{dB}	112 ± 1^{a}	68 ± 4^{bB}	46 ± 0^{cC}	40 ± 1^{dC}	112 ± 10^{b}	78 ± 5^{dA}	90 ± 3^{cA}	146^{aA}
	S	$202^{\ b}$	208 ± 26^{abC}	235 ± 1^{aB}	229 ± 2^{aB}	$202^{\ c}$	245 ± 4^{aB}	219 ± 15^{bB}	215 ± 8^{bB}	$202^{\ c}$	265 ± 8^{bA}	268 ± 10^{bA}	316 ± 34^{aA}
Oats	**N**	88 ± 6^{a}	81 ± 5^{aB}	86 ± 8^{abC}	77 ± 2^{bC}	88 ± 6^{b}	83 ± 0^{bB}	111 ± 11^{aB}	118 ± 1^{aB}	88 ± 6^{d}	117 ± 0^{cA}	149 ± 2^{bA}	180 ± 3^{aA}
	S	129 ± 5^{a}	95 ± 26^{bcB}	97 ± 7^{cB}	110 ± 2^{bB}	129 ± 5^{a}	111 ± 11^{bB}	111 ± 9^{bB}	116 ± 1^{bB}	129 ± 5^{d}	149 ± 13^{cA}	181 ± 7^{bA}	206 ± 25^{aA}
Einkorn	**N**	156 ± 14^{a}	118 ± 3^{bB}	126 ± 5^{bB}	125 ± 14^{bB}	156 ± 14^{a}	125 ± 6^{bB}	125 ± 1^{bB}	124 ± 2^{bB}	156 ± 14^{ab}	144 ± 3^{bA}	161 ± 10^{aA}	175 ± 1^{aA}
	S	304 ± 4^{a}	308 ± 15^{aA}	292 ± 13^{aB}	209 ± 10^{bC}	304 ± 4^{a}	249 ± 11^{bB}	288 ± 64^{abB}	267 ± 5^{bB}	304 ± 4^{a}	318 ± 8^{aA}	359 ± 32^{aA}	524 ± 117^{aA}
Buckwheat	**N**	99 ± 1^{a}	110 ± 3^{aB}	108 ± 9^{aC}	108 ± 10^{aC}	99 ± 1^{c}	106 ± 11^{cB}	139 ± 3^{bB}	159 ± 15^{aB}	99 ± 1^{c}	125 ± 3^{bA}	168 ± 12^{aA}	183 ± 31^{aA}
	S	109 ± 5^{a}	106 ± 6^{aC}	113 ± 2^{aC}	121 ± 15^{aB}	109 ± 5^{c}	119 ± 3^{bB}	138 ± 1^{aB}	124 ± 5^{bB}	109 ± 5^{d}	147 ± 3^{cA}	182 ± 1^{bA}	512 ± 23^{aA}

Table 22. Changes in the concentrations of tryptophan (mg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains.

T (°C)		10				20				30			
t (h)		0	12	24	36	0	12	24	36	0	12	24	36
Wheat	N	97 ± 7^{c}	102^{cC}	339 ± 2^{aB}	326 ± 1^{bC}	97 ± 7^{c}	316 ± 5^{bB}	342 ± 10^{aB}	342 ± 10^{aB}	97 ± 7^{c}	345 ± 10^{bA}	427 ± 15^{aA}	444 ± 8^{aA}
	S	404 ± 16^{a}	497 ± 99^{aA}	417 ± 0^{aA}	397 ± 17^{aA}	404 ± 16^{a}	325 ± 9^{bC}	305 ± 3^{bC}	321 ± 32^{bB}	404 ± 16^{a}	357 ± 7^{bB}	365 ± 1^{bB}	402 ± 4^{aA}
Barley	N	241 ± 4^{c}	296 ± 33^{aA}	255 ± 3^{bB}	259 ± 6^{abB}	241 ± 4^{a}	260 ± 4^{aA}	260 ± 25^{aB}	263 ± 8^{aB}	241 ± 4^{d}	292 ± 5^{cA}	335 ± 8^{bA}	361 ± 8^{aA}
	S	492 ± 39^{a}	484 ± 32^{aA}	498 ± 30^{aA}	483 ± 6^{aB}	492 ± 39^{a}	413 ± 32^{bB}	429 ± 12^{bB}	411 ± 11^{bC}	492 ± 39^{b}	484 ± 2^{bA}	506 ± 4^{bA}	542 ± 20^{aA}
Rye	N	139 ± 8^{b}	150 ± 24^{abB}	161 ± 11^{aB}	167 ± 8^{aB}	139 ± 8^{c}	147 ± 12^{cB}	162 ± 2^{bB}	181 ± 10^{aB}	139 ± 8^{c}	220 ± 13^{bA}	256 ± 17^{aA}	274 ± 1^{aA}
	S	291 ± 11^{b}	330 ± 42^{abA}	352 ± 19^{aA}	325 ± 3^{abB}	291 ± 11^{a}	272 ± 0^{bB}	255 ± 1^{cB}	274 ± 15^{bC}	291 ± 11^{b}	341 ± 3^{abA}	330 ± 26^{abA}	356 ± 13^{aA}
Oats	N	164 ± 6^{b}	181 ± 4^{aB}	186 ± 7^{aB}	188 ± 6^{aC}	164 ± 6^{c}	186 ± 6^{bB}	189 ± 0^{bB}	202 ± 3^{aB}	164 ± 6^{d}	256 ± 1^{cA}	296 ± 14^{bA}	332 ± 5^{aA}
	S	155 ± 2^{c}	184 ± 3^{bC}	192 ± 2^{aB}	185 ± 5^{abC}	155 ± 2^{c}	192 ± 0^{bB}	193 ± 4^{bB}	220 ± 17^{aB}	155 ± 2^{d}	233 ± 9^{cA}	278 ± 1^{bA}	323 ± 9^{aA}
Einkorn	N	179 ± 7^{b}	261 ± 33^{aA}	253 ± 25^{aB}	223 ± 10^{aB}	179 ± 7^{c}	191 ± 6^{bcB}	195 ± 5^{bC}	214 ± 1^{aB}	179 ± 7^{c}	249 ± 19^{bA}	302 ± 14^{aA}	332 ± 26^{aA}
	S	320 ± 11^{d}	360 ± 2^{cB}	406 ± 39^{aA}	376 ± 10^{abB}	320 ± 11^{a}	357 ± 26^{aB}	343 ± 7^{aB}	328 ± 7^{aC}	320 ± 11^{b}	429 ± 9^{aA}	432 ± 3^{aA}	436 ± 8^{aA}
Buckwheat	N	149 ± 2^{c}	168 ± 1^{bC}	187 ± 1^{aC}	181 ± 8^{aC}	149 ± 2^{d}	190 ± 2^{cB}	209 ± 2^{bB}	232 ± 8^{aB}	149 ± 2^{d}	256 ± 0^{cA}	303 ± 7^{bA}	366 ± 5^{aA}
	S	153 ± 7^{d}	190 ± 3^{cC}	204 ± 7^{abB}	226 ± 14^{aB}	153 ± 7^{b}	221 ± 18^{aB}	204 ± 1^{aB}	151 ± 86^{abB}	153 ± 7^{d}	274 ± 4^{cA}	338 ± 7^{bA}	368 ± 7^{aA}

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains.

T (°C)			20				30				40			
t (h)			0	1	2	3	0	1	2	3	0	1	2	3
Wheat	**3-hydroxykynurenine**	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	5-hydroxytryptophan	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Kynurenic Acid	**N**	23,4±2,5^{b}	29,5±0,4^{bB}	30,8±3,5^{bC}	50,4±2^{aC}	23,4±2,5^{c}	77,4±4,1^{cA}	329,3±11,7^{bA}	657,4±37,3^{aA}	23,4±2,5^{d}	85,1±5,6^{cA}	147,3±7,3^{bB}	186,4±1,7^{aB}
		S	16,1±3,9^{a}	11,8±2^{aA}	14,8±1,2^{aA}	13,8±0,5^{aC}	16,1±3,9^{a}	15,3±2,8^{aA}	11,6±9,7^{aA}	30,7±0,3^{aA}	16,1±3,9^{b}	19,4±0,5^{bA}	23±0,9^{abA}	28,1±0,1^{aB}
	Kynurenine	**N**	171,3±4,6^{c}	189,7±3,7^{bB}	202,7±1,8^{abA}	206,2±5,1^{aA}	171,3±4,6^{c}	238,7±4,2^{aA}	209,2±5^{bA}	149±4,6^{dB}	171,3±4,6^{c}	233,7±2,5^{aA}	200,9±0,1^{bA}	200,3±1,6^{bA}
		S	139,4±4^{a}	135,5±7,4^{aA}	143,1±5,2^{aA}	149,2±4,3^{aA}	139,4±4^{a}	145,3±3,2^{aA}	85,4±60,8^{aA}	149,4±2,8^{aA}	139,4±4^{a}	134,3±4,7^{aA}	121,8±5,7^{aA}	122,8±2,5^{aB}
	N-acetylserotonin	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Niacin	**N**	7715,1±421,5^{a}	5763,4±731,4^{aA}	5736,8±731,4^{aA}	5349,8±651,9^{aA}	7715,1±421,5^{a}	5793,1±663,4^{abA}	5502,4±717,7^{abA}	5191,6±475,4^{bA}	7715,1±421,5^{a}	4850,9±717,1^{bA}	4508,2±860,5^{bA}	5207,5±573,6^{abA}
		S	6866,3±638,6^{a}	4690,7±575,9^{bA}	3802,5±478^{bA}	3428,6±371^{bA}	6866,3±638,6^{a}	3411,5±357^{bA}	2060,4±1192,2^{bA}	2882±264,7^{bA}	6866,3±638,6^{a}	2894,8±393,7^{bA}	2722,4±319,4^{bA}	2592±221,3^{bA}
	Picolinic Acid	**N**	37,4±3,6^{a}	37,2±1,7^{aA}	36,3±0,8^{aA}	33,2±1,8^{aAB}	37,4±3,6^{a}	31,7±1,7^{aA}	34,7±1,9^{aA}	38,8±0,4^{aA}	37,4±3,6^{a}	32,2±1,9^{aA}	34,7±0,5^{aA}	30,3±1,1^{aB}
		S	18,4±2,3^{a}	20,2±2,6^{aA}	18,5±0,2^{aAB}	19,6±1,5^{aA}	18,4±2,3^{ab}	23,8±0,2^{aA}	16,7±1,3^{bB}	22±1^{abA}	18,4±2,3^{a}	19,7±1,1^{aA}	20,9±0,7^{aA}	21,6±0,2^{aA}

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Wheat	**Quinolinic Acid**	**N**	74,1±0,4^{a}	62,3±1,7^{aAB}	60±0,4^{aB}	59,5±7,4^{aB}	74,1±0,4^{b}	74,1±2,7^{bA}	82,2±6,3^{bA}	106,6±7^{aA}	74,1±0,4^{a}	52,6±5,6^{bB}	49,4±5,5^{bB}	44,3±1,5^{bB}
		S	67,1±3^{a}	58,5±1,2^{bA}	54,8±0,5^{bA}	54,6±0,7^{bA}	67,1±3^{a}	42,6±1,8^{abB}	28,3±15,4^{bA}	43±1,2^{abB}	67,1±3^{a}	37,5±1,2^{bB}	31±0,4^{cA}	28,6±0,6^{cC}
	Serotonin	**N**	16,4±3,1^{a}	17,1±3,3^{aA}	19,1±2,6^{aA}	18,7±3,9^{aA}	16,4±3,1^{a}	17,8±2,4^{aA}	19±2,9^{aA}	21,2±1,6^{aA}	16,4±3,1^{a}	20,3±2,8^{aA}	20,3±1,1^{aA}	21,2±0,9^{aA}
		S	20,2±2,7^{a}	23,6±1,6^{aA}	25,4±2,3^{aA}	26,1±2,9^{aA}	20,2±2,7^{a}	23,6±1,7^{aA}	16,7±12,1^{aA}	25,4±1,7^{aA}	20,2±2,7^{a}	22,8±1,2^{aA}	22±0,3^{aA}	21±0,7^{aA}
Barley	**3-hydroxykynurenine**	**N**	1,6±0,2^{a}	2,1±0,2^{aB}	3,5±0,9^{aB}	3±0,2^{aB}	1,6±0,2^{b}	4,2±0,4^{bA}	8,8±1,6^{aA}	10,5±0,8^{aA}	1,6±0,2^{b}	3,3±0,2^{aAB}	4±0,4^{aAB}	4,1±0,4^{aB}
		S	1,3±0,5^{a}	0,7±0,2^{aA}	0,8±0,1^{aB}	0,6±0,3^{aA}	1,3±0,5^{a}	1±0,1^{aA}	1,6±0,1^{aA}	1,4±0,2^{aA}	1,3±0,5^{a}	1±0^{aA}	1,1±0,2^{aAB}	1±0,1^{aA}
	5-hydroxytryptophan	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Kynurenic Acid	**N**	43±1,7^{b}	48,5±1,4^{bA}	47,8±2,8^{bB}	62,3±4,2^{aB}	43±1,7^{c}	55,1±2,3^{cA}	184,4±10^{bA}	362±39,4^{aA}	43±1,7^{c}	60,3±4,6^{bA}	74±4,9^{aB}	75±0,6^{aB}
		S	31,4±1,4^{a}	27,6±1,1^{aA}	31,1±0,1^{aB}	28,9±4,5^{aA}	31,4±1,4^{b}	29,7±1,6^{bA}	37,4±2,9^{abAB}	43,2±4,5^{aA}	31,4±1,4^{a}	36,9±3,6^{aA}	41,3±2^{aA}	41,3±3,1^{aA}
	Kynurenine	**N**	1011±24,6^{a}	1003,8±25,8^{aA}	957,4±8,5^{aA}	996,9±18,8^{aA}	1011±24,6^{a}	1014,6±18,8^{aA}	1002,3±6,9^{aA}	966,6±15,8^{aA}	1011±24,6^{a}	966,2±35,9^{aA}	1010,8±18,8^{aA}	859,9±72,2^{bA}
		S	382,3±14,6^{a}	345,8±5,8^{aA}	358,7±13^{aA}	370,4±10,9^{aA}	382,3±14,6^{a}	371,7±0,9^{aA}	395,4±6,3^{aA}	383,2±8,8^{aA}	382,3±14,6^{a}	367,4±11,4^{aA}	377,2±2,2^{aA}	366±1,7^{aA}
	N-acetylserotonin	**N**	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	Niacin	**N**	7626,2±506,5^{a}	6092,2±505^{abA}	5522,2±476,9^{bA}	5576,9±385,6^{bA}	7626,2±506,5^{a}	5582,7±587,8^{aA}	5664,6±602,4^{aA}	6081,9±646,1^{aA}	7626,2±506,5^{a}	5170,2±497,6^{bA}	5730±297,1^{bA}	5592,9±214,8^{bA}
		S	6758,6±595,4^{a}	4047,9±483,6^{bA}	3581,5±383,7^{bA}	3525,7±471,7^{bA}	6758,6±595,4^{a}	3524,8±287,8^{bA}	3685,6±252,6^{bA}	3371,4±436^{bA}	6758,6±595,4^{a}	3260±130,1^{bA}	3204,9±283,2^{bA}	2898,5±297,8^{bA}

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Barley	**Picolinic Acid**	**N**	40,5±2,4[a]	42,7±4,9[aA]	39,7±0,1[aA]	46,9±0,3[aB]	40,5±2,4[c]	46,6±1,3[bcA]	53±2,9[bA]	61,7±1[aA]	40,5±2,4[a]	48,2±1,6[aA]	23,2±19,9[aA]	40,5±3,2[aB]
		S	41,6±1,2[a]	31,2±1,8[bA]	27,7±0,7[bA]	28,9±1,3[bA]	41,6±1,2[a]	27,7±2,9[bA]	25,8±1[bA]	23,3±0,7[bB]	41,6±1,2[a]	24,2±0,4[bA]	20,7±0,6[cB]	19,7±0,5[cB]
	Quinolinic Acid	**N**	106±2,3[b]	92±3,4[bA]	100±4,5[bB]	128,8±7,4[aB]	106±2,3[c]	99,6±4,3[cA]	135,6±2,4[bA]	176,3±11,7[aA]	106±2,3[a]	70±2,9[bB]	60,5±4,4[bC]	57,2±3,6[bC]
		S	46,1±0,3[a]	41,3±1,6[abA]	32,8±5,1[bcA]	23,3±3,6[cA]	46,1±0,3[a]	16±1,6[bcB]	18,5±1,2[bB]	12,3±0,8[cB]	46,1±0,3[a]	16,9±3[bB]	8,2±0,4[cB]	9,4±1,3[cB]
	Serotonin	**N**	311±15,3[a]	292,1±3,8[aA]	274,3±24[aA]	276,5±1,5[aA]	311±15,3[a]	267,3±3[bA]	244,1±5[bAB]	243,6±8,7[bB]	311±15,3[a]	209,3±17,3[bB]	193,1±11,8[bB]	160,5±5,1[bC]
		S	140,4±2,8[a]	138,8±5,3[aAB]	140±3,5[aA]	110,1±18,5[aA]	140,4±2,8[a]	144,1±4,3[aA]	125,9±9,7[aAB]	117,9±10,4[aA]	140,4±2,8[a]	103,2±13,5[bB]	95,3±6,9[bB]	87±3,3[bA]
Rye	**3-hydroxykynurenine**	**N**	9,5±0,3[a]	5,8±1,1[bA]	6,6±0,9[abA]	6±1[abC]	9,5±0,3[a]	6,2±1,1[bA]	8,6±0,1[aA]	10,2±0,1[aB]	9,5±0,3[c]	8,7±0,1[cA]	13,1±0,3[bA]	17,4±0,3[aA]
		S	9,5±0[a]	8,7±0,5[aAB]	8,2±1[aA]	11,3±1,5[aA]	9,5±0[a]	9,6±0,3[aA]	12±1,7[aA]	9,5±1,4[aA]	9,5±0[a]	7,8±0,1[aB]	9,6±1,2[aA]	9,2±0,2[aA]
	5-hydroxytryptophan	**N**	14,8±1,9[aa]	15,5±0,7[aAB]	14,8±0,2[aA]	13,3±0,7[aA]	14,8±1,9[a]	14,5±0,2[aB]	15,3±0,6[aA]	16,7±2,6[aA]	14,8±1,9[a]	17,5±0[aA]	14,7±0,1[aA]	18,1±1,6[aA]
		S	24,6±1,9[a]	27,2±3,2[aA]	32,1±0,6[aA]	31±3,5[aA]	24,6±1,9[b]	30,2±3,5[abA]	36,3±0,5[aA]	31±0,9[abA]	24,6±1,9[b]	28,8±0,7[abA]	26,7±1,9[abB]	31,7±1,9[aA]
	Kynurenic Acid	**N**	111±2,8[a]	114,2±4,5[aA]	120,2±3,2[aA]	120,9±1,9[aC]	111±2,8[d]	130,3±2,1[cA]	143,2±1,7[bA]	173,8±5[aA]	111±2,8[b]	138,3±8,1[abA]	145,2±11,2[aA]	149,9±1,3[aB]
		S	54,2±0,4[b]	57,4±1,3[abA]	65,7±2,7[aB]	60,6±2,9[abA]	54,2±0,4[b]	57,5±4[bA]	75±1,8[aA]	58±6,6[bA]	54,2±0,4[ab]	60,2±0,9[aA]	53±0,6[bC]	48,9±3,1[bA]
	Kynurenine	**N**	1839,2±40,4[a]	1850,7±13,9[aA]	1896,4±12,3[aA]	1686,2±9,4[bA]	1839,2±40,4[a]	1739,8±16,3[abB]	1725,4±19[bB]	1515,1±23,3[cB]	1839,2±40,4[a]	1760,7±23[abB]	1671,5±18[bcB]	1538,9±50,5[cB]
		S	259,2±178,3[a]	463±76,1[aA]	511,3±6,9[aA]	459,1±74,7[aA]	259,2±178,3[a]	430,2±39,5[aA]	509,6±2[aA]	416,5±21,9[aA]	259,2±178,3[a]	450,6±19,3[aA]	347,7±14,1[aB]	345,1±23,9[aA]

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Rye	**N-acetylserotonin**	**N**	11,9±1,3^{a}	11,6±0,8^{aA}	12,6±1^{aA}	11,8±0,5^{aA}	11,9±1,3^{a}	12,1±1^{aA}	12±0,6^{aA}	13,4±1,6^{aA}	11,9±1,3^{a}	12±0,8^{aA}	12,1±0,8^{aA}	12,5±1,9^{aA}
		S	20,5±0^{ab}	20,3±0,1^{abA}	20,8±0,2^{aA}	20,1±0,2^{bA}	20,5±0^{a}	20,5±0,3^{aA}	20,9±0,1^{aA}	21,2±0,6^{aA}	20,5±0^{ab}	20,3±0,1^{bA}	20,9±0,1^{abA}	21,1±0,3^{aA}
	Niacin	**N**	10055,7±263,2^{a}	7595,6±556^{bA}	7651,8±246,1^{bA}	7907,2±398,4^{bA}	10055,7±263,2^{a}	6894,4±458,5^{bA}	7354,1±448^{bA}	6923,6±310,5^{bA}	10055,7±263,2^{a}	6610,6±294^{bA}	5559,2±77,8^{bcB}	5070,9±425,9^{cB}
		S	34365,6±1021,2^{a}	31478,5±2697,2^{aA}	32462,3±612^{aA}	29181,5±4148^{aA}	34365,6±1021,2^{a}	26999,4±1295^{bAB}	27529,5±176,3^{bB}	22984,5±542,5^{cA}	34365,6±1021,2^{a}	20064,5±58^{bB}	12763,8±52,3^{cC}	10620,2±784,3^{cB}
	Picolinic Acid	**N**	43±10,9^{a}	51,5±5,3^{aA}	49,4±5,2^{aA}	60,5±7,9^{aA}	43±10,9^{a}	63,8±3,5^{aA}	52,5±6,7^{aA}	65,2±1,7^{aA}	43±10,9^{a}	48,9±8,9^{aA}	49,7±13,4^{aA}	47,4±1,4^{aA}
		S	95,7±2,8^{a}	84,5±5,8^{aA}	90±12,1^{aA}	91,9±1^{aA}	95,7±2,8^{a}	81,5±12,2^{aA}	86,1±4,6^{aAB}	63,9±9,6^{aB}	95,7±2,8^{a}	64,7±10,6^{bA}	54±3,3^{bB}	47,3±1,4^{bB}
	Quinolinic Acid	**N**	366,7±3,5^{a}	270,9±8,5^{abA}	230,1±29,7^{bA}	186,8±51,9^{bA}	366,7±3,5^{a}	197,7±63,8^{bA}	267,1±9,1^{abA}	202,2±47,6^{bA}	366,7±3,5^{a}	142,2±27,8^{bA}	105,9±34^{bB}	61±15,4^{bA}
		S	325,8±11,2^{a}	291,1±23,8^{abA}	296,1±14,9^{abA}	252,7±19,9^{bA}	325,8±11,2^{a}	264,8±7^{bAB}	258,5±10,1^{bA}	175,9±2,9^{cB}	325,8±11,2^{a}	186,1±18,2^{bB}	139,8±6,3^{bcB}	121,6±12,4^{cB}
	Serotonin	**N**	24,9±3,7^{aa}	26,1±0,3^{aA}	26,9±0,7^{aA}	23,1±0^{aA}	24,9±3,7^{a}	21±1,8^{aB}	22±1,2^{aB}	20,5±2,2^{aA}	24,9±3,7^{a}	17,7±0,1^{abB}	15,5±0,3^{bC}	18,5±1,5^{abA}
		S	27,9±0,1^{c}	30,8±1,2^{bcB}	33,8±1,6^{abA}	35,2±0,7^{aA}	27,9±0,1^{b}	35,4±0,2^{aA}	36,2±1,6^{aA}	14,4±0,3^{cC}	27,9±0,1^{b}	29±0^{aB}	29,3±0,4^{aB}	27,7±0,1^{bB}
Oat	**3-hydroxykynurenine**	**N**	5,7±0,2^{c}	7,3±0,8^{bcA}	9±0,1^{abA}	10,7±1,1^{aA}	5,7±0,2^{a}	13,9±2,9^{aA}	19,2±6,1^{aA}	19,7±8,2^{aA}	5,7±0,2^{b}	9,8±0,9^{abA}	10,9±0,3^{aA}	11,7±2,3^{aA}
		S	4,4±0,2^{a}	4,1±0,3^{aA}	4,3±0^{aB}	4±0,2^{aB}	4,4±0,2^{a}	4±0^{aA}	4,3±0,2^{aB}	4,8±0,5^{aB}	4,4±0,2^{b}	4,3±0,4^{bA}	5,4±0,2^{bA}	7,8±1^{aA}
	5-hydroxytryptophan	**N**	31,7±0,9^{a}	32,3±0,1^{aB}	34,3±1^{aC}	35,1±2,3^{aB}	31,7±0,9^{b}	34,6±2,7^{bB}	43,1±1,9^{aB}	49,5±2,3^{aA}	31,7±0,9^{d}	41,7±0,3^{cA}	50,2±0,4^{bA}	54,1±0,1^{aA}
		S	21,4±4,7^{a}	18,2±1,7^{aB}	18,6±0,2^{aB}	23,1±0,8^{aB}	21,4±4,7^{a}	21,8±0,4^{aAB}	25,3±1,5^{aA}	26,9±0,6^{aA}	21,4±4,7^{a}	23,9±1^{aA}	28±1,4^{aA}	27,5±0,1^{aA}

Table 23. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Oat	**Kynurenic Acid**	**N**	118,6±10^{a}	122,3±1,6^{aA}	121±4,8^{aB}	123,3±0,5^{aA}	118,6±10^{a}	128±0,9^{aA}	136,6±2,3^{aAB}	148,1±3,6^{aA}	118,6±10^{a}	128±9,5^{aA}	142,2±5,4^{aA}	142,1±10,7^{aA}
		S	88,2±1,6^{b}	89,8±1^{bA}	99,7±2,8^{aB}	99,6±3,3^{aB}	88,2±1,6^{c}	107,3±3,6^{bA}	114,8±0,9^{bA}	134,8±4^{aA}	88,2±1,6^{a}	108,9±11,5^{aA}	107,6±2,8^{aAB}	108,9±2,5^{aB}
	Kynurenine	**N**	366,4±4,8^{c}	389,7±0^{bB}	403,3±6,9^{abC}	412,9±6,6^{aB}	366,4±4,8^{c}	474,3±11,3^{bA}	564,5±1,4^{aA}	579,8±7,4^{aA}	366,4±4,8^{c}	496,5±8,3^{bA}	519,9±12,4^{abB}	563,8±25,2^{aA}
		S	388,7±1^{a}	366,3±6,6^{aB}	389,1±16,7^{aC}	393±13,1^{aB}	388,7±1^{d}	489,7±6,9^{cA}	573,7±10,5^{bA}	619,4±12,9^{aA}	388,7±1^{b}	503,1±6,2^{aA}	466,1±1^{aB}	459,4±21,7^{aB}
	N-acetylserotonin	**N**	13,7±0,3^{a}	14±1,1^{aA}	14,5±1,1^{aA}	13,7±0,8^{aA}	13,7±0,3^{b}	15,3±0,2^{abA}	15,1±0,5^{abA}	16,6±0,7^{aA}	13,7±0,3^{a}	13,4±0,6^{aA}	16,1±0,6^{aA}	14,1±1,3^{aA}
		S	10,2±1,3^{a}	10,1±0,8^{aA}	9±0,1^{aB}	9,9±0,8^{aA}	10,2±1,3^{a}	10,7±0,3^{aA}	11,4±0,3^{aA}	11,7±0,1^{aA}	10,2±1,3^{a}	11,5±0,6^{aA}	11,9±0,1^{aA}	12±0,5^{aA}
	Niacin	**N**	13592,5±688^{a}	10059,9±302,4^{bA}	9408,8±208,8^{bcA}	8173,7±276^{cA}	13592,5±688^{a}	9126,8±363,2^{bA}	7372,3±463,8^{bcB}	6785,9±334,3^{cAB}	13592,5±688^{a}	6926,7±198^{bB}	5622,6±26,9^{bC}	5390,8±423,1^{bB}
		S	20104,9±195,2^{a}	17600±403^{bA}	18116,9±142^{bA}	18221,8±254,1^{bA}	20104,9±195,2^{a}	14720,6±281^{bB}	16212,7±40,8^{bB}	16084,4±1267,6^{bA}	20104,9±195,2^{a}	11214,8±87,4^{bC}	9174,6±471,1^{bcC}	8205±963,5^{cB}
	Picolinic Acid	**N**	82,2±1,6^{c}	99,8±6,6^{bcAB}	116,6±5,9^{abA}	127,1±5,3^{aA}	82,2±1,6^{c}	120,4±5,9^{aA}	101,9±6,2^{bAB}	99,5±0,8^{bB}	82,2±1,6^{c}	92,6±0,4^{aB}	85,6±0,9^{bcB}	86,7±0,4^{bB}
		S	65,8±1,9^{a}	64,6±2,7^{aA}	77,5±7,1^{aA}	82±4,7^{aA}	65,8±1,9^{a}	83,9±3,2^{aA}	81,3±10,9^{aA}	86,8±6,2^{aA}	65,8±1,9^{a}	75,8±2,2^{aAB}	63,2±3,6^{aA}	56,9±9,4^{aA}
	Quinolinic Acid	**N**	720,9±104,7^{a}	579±113,3^{aA}	549,9±111,3^{aA}	685,7±0,1^{aA}	720,9±104,7^{a}	478,6±80^{baA}	493,5±4,3^{baA}	475,2±16,9^{aB}	720,9±104,7^{a}	462,3±2,4^{bA}	415,2±25,3^{bA}	357,6±6^{bC}
		S	362,7±8,5^{a}	314,3±10^{bA}	332,8±9,2^{abA}	324,4±15,1^{abA}	362,7±8,5^{a}	270±22,6^{bA}	274,2±1,3^{bA}	245,7±22,6^{bB}	362,7±8,5^{a}	190,3±0,1^{bB}	137,7±29,7^{bB}	135,5±1,1^{bC}
	Serotonin	**N**	520,9±1,9^{a}	472±9,9^{bAB}	496,5±17,4^{abA}	485,7±6,1^{abA}	520,9±1,9^{a}	517,4±23^{abA}	473,3±1,8^{bA}	417,1±3^{cB}	520,9±1,9^{a}	425±1,6^{bB}	375±3,1^{cB}	362,6±13,4^{cC}
		S	330,4±192,1^{a}	300,3±24,6^{aB}	278,6±55,5^{aB}	435,2±66,2^{aA}	330,4±192,1^{a}	442,1±26,5^{aAB}	561±32,3^{aA}	589,4±7,5^{aA}	330,4±192,1^{a}	564,5±67,3^{aA}	589,6±6,5^{aA}	507,8±11,9^{aA}

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Einkorn	3-hydroxykynurenine	N	5±0,4^{b}	6,5±0,5^{aA}	6,4±0^{aB}	5,9±0,1^{abB}	5±0,4^{c}	6±0,4^{bcA}	7,1±0,2^{bB}	10,6±0,6^{aA}	5±0,4^{b}	7,4±0,2^{abA}	8,6±0,4^{aA}	9,1±1,1^{aAB}
		S	5±0,2^{a}	4,6±0,2^{aA}	4,6±0,1^{aB}	4,5±0,1^{aA}	5±0,2^{a}	4,6±0,1^{aA}	4,4±0,2^{aB}	5,4±0,7^{aA}	5±0,2^{ab}	4,7±0,2^{bA}	5,4±0,1^{abA}	7,1±1^{aA}
	5-hydroxytryptophan	N	11,5±0,9^{b}	16,5±0,7^{aA}	15±0,2^{aA}	15,7±0,5^{aA}	11,5±0,9^{b}	15,2±1,1^{aA}	15,3±0,7^{aA}	15±0,7^{aA}	11,5±0,9^{b}	14,8±0,7^{aA}	15,6±0,4^{aA}	15,7±0,1^{aA}
		S	6,8±0,2^{a}	7,2±0,1^{aA}	7,3±0,2^{aA}	10±2,3^{aA}	6,8±0,2^{b}	7,2±0,1^{abA}	9,3±1,8^{abA}	11,7±1,5^{aA}	6,8±0,2^{b}	7,2±0,2^{bA}	9,9±1,8^{abA}	12,9±1,2^{aA}
	Kynurenic Acid	N	63,5±2,4^{a}	60±1,5^{aA}	58±2,4^{aC}	58,1±1,8^{aB}	63,5±2,4^{c}	62,6±0,4^{cA}	74,2±0,2^{bA}	94,5±4,1^{aB}	63,5±2,4^{a}	62,8±0,6^{aA}	65,3±0,2^{aB}	69,7±4,4^{aA}
		S	24,2±0,8^{a}	22,4±2,7^{aA}	24,3±2,7^{aA}	23,9±3,3^{aA}	24,2±0,8^{b}	23,1±1,7^{bA}	25,8±2,3^{bA}	33±2,1^{aA}	24,2±0,8^{c}	26,6±0,3^{bcA}	33,3±2,5^{aA}	30,7±0,8^{abA}
	Kynurenine	N	253±4,1^{a}	277,2±5,3^{aA}	271,7±16,3^{aB}	271,7±0,5^{aB}	253±4,1^{c}	321,6±2^{bB}	364,7±3,7^{aA}	376,1±10^{aA}	253±4,1^{c}	309,3±3,5^{bB}	355,9±6,3^{aA}	390,6±21,9^{aA}
		S	265,4±11,7^{a}	294,5±14^{aB}	309,4±24^{aB}	322,1±15,4^{aB}	265,4±11,7^{b}	286,9±3,8^{bB}	391,9±27,9^{aAB}	403,4±1,7^{aA}	265,4±11,7^{c}	346,5±6,9^{bA}	434,6±8,9^{aA}	337,3±1,3^{bB}
	N-acetylserotonin	N	9,7±0,1^{b}	13,4±0,1^{aB}	14±0,8^{aA}	14,6±0,6^{aA}	9,7±0,1^{c}	13±0,2^{bB}	15,4±0,8^{aA}	14,2±0,3^{bcA}	9,7±0,1^{b}	14,1±0,1^{aA}	15±0,7^{aA}	15,4±0,3^{aA}
		S	9,1±0,1^{a}	9,1±0^{aA}	9±0,1^{aA}	9,2±0^{aA}	9,1±0,1^{a}	9,1±0,1^{aA}	9,2±0^{aA}	9,4±0,3^{aA}	9,1±0,1^{a}	9±0,1^{aA}	9,1±0,1^{aA}	9,2±0^{aA}
	Niacin	N	33514,7±502,5^{a}	28234,8±817,8^{bA}	25203±1155,3^{cA}	24616,3±145,9^{cA}	33514,7±502,5^{a}	25993,6±208,3^{bA}	23519,4±90,3^{cA}	23185,6±216,9^{cA}	33514,7±502,5^{a}	18932,7±1190,7^{bB}	15624,9±255,9^{cB}	16748,2±888,5^{bcB}
		S	29712,6±605,9^{a}	26027,5±657,5^{bA}	25705,9±646,8^{bA}	24820,6±83,8^{bA}	29712,6±605,9^{a}	22162,6±437,4^{bcB}	23669,1±478,1^{bA}	20855,1±266,5^{cB}	29712,6±605,9^{a}	15204,2±86,9^{bC}	13232,8±437,8^{cB}	12129,6±133,7^{cC}
	Picolinic Acid	N	97,9±7,9^{a}	100,1±8,8^{aA}	92,8±5,8^{aA}	88,3±3,3^{aAB}	97,9±7,9^{a}	95,9±0,8^{aA}	93,9±1,4^{aA}	102,5±6^{aA}	97,9±7,9^{a}	81,2±2,7^{abA}	79,9±2,7^{abA}	75,8±3,5^{bB}
		S	71,6±5,9^{a}	73,6±3,7^{aA}	66,3±5,3^{aA}	75,6±1,7^{aA}	71,6±5,9^{a}	66,7±6,6^{aA}	67,7±2,9^{aA}	57,5±3,9^{aB}	71,6±5,9^{a}	60,6±0,1^{abA}	53,1±1,7^{cA}	46,5±0,1^{dB}

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Einkorn	**Quinolinic Acid**	**N**	308,4±7,2^{a}	283,3±13,3^{aA}	304,2±12,6^{aA}	302±8^{aB}	308,4±7,2^{b}	320,8±3,5^{bA}	343,9±18,9^{abA}	367,7±0,6^{aA}	308,4±7,2^{a}	205,3±16,8^{bB}	194,8±7,7^{bB}	188,9±5,2^{bC}
		S	219,7±4,3^{a}	194,5±5^{abA}	181,4±13,9^{bA}	188,5±4,3^{abA}	219,7±4,3^{a}	169,9±5,7^{bB}	164,9±8,4^{bAB}	163,4±7,6^{bA}	219,7±4,3^{a}	154,9±4,7^{bB}	130,7±1,9^{cB}	100,4±7,7^{dB}
	Serotonin	**N**	9,8±0,7^{b}	24,7±0^{aB}	27,2±1,3^{aC}	26,7±0,1^{aC}	9,8±0,7^{d}	28,6±2^{cB}	36±2,6^{bB}	47,3±0,2^{aB}	9,8±0,7^{d}	45,2±2,5^{cA}	63,4±0,8^{bA}	74,4±2,8^{aA}
		S	4±0,1^{a}	27,2±20,3^{aA}	4,8±0,7^{aA}	50,4±45,3^{aA}	4±0,1^{a}	5,3±0,2^{aA}	39±31^{aA}	85,7±64^{aA}	4±0,1^{b}	5,1±0,6^{bA}	19,4±13,7^{abA}	63,8±20,7^{aA}
Buckwheat	**3-hydroxykynurenine**	**N**	4,9±0,4^{a}	5,1±0,6^{aA}	5,2±0,1^{aA}	5±0,6^{aA}	4,9±0,4^{a}	5,3±0,5^{aA}	4,4±0^{aB}	4,5±0,3^{aA}	4,9±0,4^{a}	4,4±0,2^{aA}	4,3±0,1^{aB}	4,6±0^{aA}
		S	4,5±0,2^{a}	4,1±0,1^{aA}	4,4±0,1^{aA}	4,3±0^{aA}	4,5±0,2^{a}	4,9±0,4^{aA}	4,2±0,2^{aA}	4,2±0,3^{aA}	4,5±0,2^{a}	4,3±0,2^{aA}	5±0,5^{aA}	4,4±0,1^{aA}
	5-hydroxytryptophan	**N**	460,8±2,9^{a}	338,5±13,6^{bA}	328,7±8,4^{bA}	287,5±6,2^{cA}	460,8±2,9^{a}	321,3±27,5^{bA}	275,8±7,1^{bcB}	241,7±0,2^{cB}	460,8±2,9^{a}	280,7±9,5^{bA}	229±7,2^{cC}	174,7±5,3^{dC}
		S	155,7±7^{a}	118,8±3,3^{bA}	103,9±6,9^{bcA}	83,8±3,6^{cB}	155,7±7^{a}	111,2±5,6^{bA}	106,7±4,5^{bA}	104±0,7^{bA}	155,7±7^{a}	126,7±5,3^{bA}	93,9±4,2^{cA}	65,8±3,2^{dC}
	Kynurenic Acid	**N**	1289,4±40,6^{a}	1348±29,8^{aA}	1354,3±47,1^{aA}	1366,9±28,9^{aB}	1289,4±40,6^{b}	1350,2±51,6^{abA}	1406,7±45,7^{abA}	1469,9±38,8^{aAB}	1289,4±40,6^{c}	1426,5±16,4^{bA}	1476,1±4,2^{bA}	1588,9±2,8^{aA}
		S	1009,8±11^{a}	1047,4±12^{aA}	1043,7±15,6^{aA}	1134,7±60,6^{aA}	1009,8±11^{a}	1017,3±1,5^{aAB}	928,4±72,4^{aA}	1069,5±0,7^{aA}	1009,8±11^{b}	1010,2±0,4^{bB}	1084,2±12,9^{aA}	1139,7±31,5^{aA}
	Kynurenine	**N**	694,6±2,1^{b}	725,9±11,6^{aA}	710,1±1,4^{abB}	730,4±4,1^{aB}	694,6±2,1^{d}	742,3±7,7^{cA}	779,5±9^{bA}	817,5±1,9^{aA}	694,6±2,1^{b}	717,7±8,2^{aA}	704,5±0,7^{abB}	703,2±3,8^{abC}
		S	872,8±11,4^{a}	867,7±3,1^{aA}	857,3±22,9^{aAB}	892,7±0^{aA}	872,8±11,4^{a}	878,4±16,7^{aA}	888,2±11,7^{aA}	908,4±15,1^{aA}	872,8±11,4^{a}	878,5±7,1^{aA}	799,2±4,4^{bB}	829,7±6,7^{cbB}
	N-acetylserotonin	**N**	11,2±0^{b}	13,8±0,3^{aA}	14,1±0,7^{aA}	15,3±0,2^{aB}	11,2±0^{d}	13,9±0,1^{cA}	17,1±0,6^{bA}	19,7±0,2^{aA}	11,2±0^{b}	14,2±1^{aA}	15,7±0,8^{aA}	13,7±0,3^{abC}
		S	10,6±0,6^{b}	16,5±1,6^{aA}	17±1,6^{aA}	22,1±1,7^{aA}	10,6±0,6^{b}	19±1,6^{aA}	17,3±0,1^{aA}	20,5±1,4^{aA}	10,6±0,6^{c}	17,4±0,3^{bA}	17,5±0,9^{bA}	23,6±2,3^{aA}

Table 23. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Buckwheat	**Niacin**	**N**	15579,3±249^{a}	11584,8±540^{bA}	11410,5±13^{bA}	10877,7±14^{bA}	15579,3±249^{a}	9936,4±386,6^{bA}	8476,1±9,1^{cB}	8360,8±176,6^{cB}	15579,3±249^{a}	6851,8±59,5^{bB}	6236,4±29,3^{bC}	6079,6±332,5^{bC}
		S	15236,6±669,6^{a}	12582,8±744,1^{abA}	12208,9±459,9^{bA}	12148,2±800,5^{bA}	15236,6±669,6^{a}	11782,7±556,1^{bA}	12184,8±539,5^{bA}	12454,7±364,6^{bA}	15236,6±669,6^{a}	6541,1±56,4^{bB}	5464,6±70,5^{bcB}	4955,7±371,1^{cB}
	Picolinic Acid	**N**	61,9±6,8^{a}	65±2,9^{aA}	59±0,9^{aA}	64,3±1,8^{aA}	61,9±6,8^{b}	56±1,7^{bA}	63±0,6^{bA}	78,9±1,2^{aB}	61,9±6,8^{a}	55,4±2^{aA}	61±7,8^{aA}	54,6±1,3^{aC}
		S	46,1±2,1^{c}	50,2±3,3^{bcA}	72,3±6,5^{aAB}	70,8±7,3^{abA}	46,1±2,1^{a}	60,9±5,3^{aA}	73,8±2^{aA}	66,5±13^{aA}	46,1±2,1^{a}	57,7±4,6^{aA}	54,6±2,5^{aB}	55,5±5,7^{aA}
	Quinolinic Acid	**N**	267,6±114,5^{a}	121,6±11,3^{aB}	278,1±12,4^{aA}	296,8±7^{aB}	267,6±114,5^{a}	255,7±3,2^{aA}	286,8±50,9^{aA}	367,8±25,5^{aA}	267,6±114,5^{a}	240,6±3,9^{aA}	198,1±17,2^{aA}	194,5±1,1^{aC}
		S	255,3±3,1^{b}	242,8±6,4^{bA}	259±19^{bA}	368±5,5^{aA}	255,3±3,1^{b}	267,4±5,2^{bA}	311,6±8,5^{abA}	349,4±28,2^{aA}	255,3±3,1^{a}	182,7±6,9^{bB}	162,5±3,5^{bB}	173,3±5,9^{bB}
	Serotonin	**N**	1828,8±30,4^{a}	1433±33,8^{bA}	1281,1±38,2^{cA}	1144,4±33,8^{dA}	1828,8±30,4^{a}	999±129,7^{bA}	999,4±110,6^{bA}	969,3±67,7^{bAB}	1828,8±30,4^{a}	1070,2±161,4^{bA}	974,1±97,4^{bA}	851,3±19,5^{bB}
		S	1685±7,3^{a}	1613,6±19^{aA}	1635,5±55,8^{aA}	1590,6±97,5^{aA}	1685±7,3^{a}	1594±4,9^{bA}	1525,7±19^{bA}	1599,2±30,7^{bA}	1685±7,3^{a}	1416,9±10,2^{bB}	1288,9±5,5^{cB}	1235,2±4,2^{dB}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of tryptophan derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of tryptophan derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 24. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains.

T (°C)			10				20				30			
t (h)			0	12	24	36	0	12	24	36	0	12	24	36
Wheat	3-hydroxykynurenine	N	0,2±0,2	0,3±0	0,1±0,1	nd	0,2±0,2	nd	nd	nd	0,2±0,2	nd	nd	nd
Wheat	3-hydroxykynurenine	S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Wheat	5-hydroxytryptophan	N	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Wheat	5-hydroxytryptophan	S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Wheat	Kynurenic Acid	N	15,3±0,6^{a}	15±0,9^{aA}	13,6±1^{aA}	12,3±3,2^{aA}	15,3±0,6^{a}	8,4±3^{aA}	6,4±6,4^{aA}	7,2±3,1^{aA}	15,3±0,6^{a}	9±3,7^{aA}	7,2±5,9^{aA}	11,4±5,4^{aA}
Wheat	Kynurenic Acid	S	4,2±0,9^{a}	3,7±0,5^{aA}	2,9±0,4^{aA}	2,6±0,1^{aA}	4,2±0,9^{a}	0,9±0,9^{bAB}	0,6±0,6^{bA}	0,1±0,1^{bB}	4,2±0,9^{a}	0,5±0,5^{bB}	1,2±1,2^{abA}	0,2±0,2^{bB}
Wheat	Kynurenine	N	132,9±6,3^{a}	136,7±7,4^{aB}	138,5±1,2^{aC}	138,1±0,4^{aB}	132,9±6,3^{d}	151,4±0,3^{cB}	198,2±4,1^{bB}	245,5±5,5^{aA}	132,9±6,3^{b}	219,2±0,2^{aA}	244,2±5,8^{aA}	227,2±15^{aA}
Wheat	Kynurenine	S	49,6±1,3^{b}	53,4±2,7^{bC}	56,8±1^{abC}	65,5±3,1^{aB}	49,6±1,3^{d}	81±0,7^{cB}	105,7±1,6^{bB}	110±0,1^{aA}	49,6±1,3^{b}	114,6±2^{aA}	117,9±1,7^{aA}	112,5±1,5^{aA}
Wheat	N-acetylserotonin	N	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Wheat	N-acetylserotonin	S	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Wheat	Niacin	N	6760,4±368,2^{a}	7703,5±653,1^{aA}	8224,6±248,9^{aA}	8150,6±116^{aA}	6760,4±368,2^{a}	6428,8±83,7^{aB}	3576,8±77,4^{bB}	2508,8±141,5^{cB}	6760,4±368,2^{a}	2895,3±141^{bC}	2006,1±487,7^{bcC}	1222,4±86,8^{cB}
Wheat	Niacin	S	5718±387,6^{a}	6358,1±188,8^{aA}	6281,8±79,6^{aA}	6239±250,7^{aA}	5718±387,6^{a}	4037,7±137,8^{bA}	2084,8±57^{cB}	1330,9±22,3^{cB}	5718±387,6^{a}	1807,7±93,5^{bB}	636,8±20,1^{cC}	692,7±296,6^{cC}
Wheat	Picolinic Acid	N	9,5±0^{a}	7,6±0,2^{aA}	8±0,8^{aA}	9,4±0,4^{aB}	9,5±0^{a}	9,7±1,3^{aA}	9±0,8^{aA}	9,7±0,4^{aAB}	9,5±0^{b}	11,2±0,9^{abA}	10,7±0,5^{abA}	12,4±0,9^{aA}
Wheat	Picolinic Acid	S	6,5±0,6^{a}	7,1±0,5^{aA}	6,8±0,4^{aA}	7,8±0,6^{aA}	6,5±0,6^{a}	7,1±0,2^{aA}	6,2±1,8^{aA}	5±0,1^{aB}	6,5±0,6^{a}	4,4±0,1^{bB}	4,8±0^{bA}	4,6±0,1^{bB}
Wheat	Quinolinic Acid	N	6,6±0^{a}	7±0,1^{aA}	7,1±0,1^{aA}	6,2±0,2^{bB}	6,6±0^{a}	9,7±1,7^{aA}	8,5±0,2^{aA}	9,1±0,6^{aA}	6,6±0^{a}	9,7±1,3^{aA}	4,8±3,8^{aA}	8,8±0,6^{aA}
Wheat	Quinolinic Acid	S	4,9±0,5^{a}	3,3±0,5^{aA}	3,4±0^{aA}	3,3±1^{aA}	4,9±0,5^{a}	3±0,5^{abA}	2,3±0,6^{bA}	2,4±0,6^{bA}	4,9±0,5^{a}	1,7±0,1^{bA}	2,9±0^{cA}	0,6±0,1^{dA}

Table 24. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Wheat	**Serotonin**	**N**	24,9±2,7^{a}	27,8±2,7^{aA}	28,3±0,6^{aA}	24,3±0,5^{aA}	24,9±2,7^{a}	22,3±2,9^{abA}	17,6±0,1^{abB}	15,4±0,8^{bB}	24,9±2,7^{a}	17,9±1,3^{abA}	17,7±2,3^{abB}	15,7±1,3^{bB}
		S	6,9±0,9^{b}	7,2±0,1^{bC}	19,3±0,3^{aA}	19,5±0,1^{aA}	6,9±0,9^{d}	19,8±0,2^{aA}	16,6±0,3^{bB}	13,9±0,5^{cB}	6,9±0,9^{d}	15,1±0,2^{aB}	12,8±0^{bC}	10,1±0,5^{cC}
Barley	**3-hydroxykynurenine**	**N**	15,6±1,8^{a}	15,9±0,2^{aA}	12,6±1,1^{aA}	10,9±1,8^{aA}	15,6±1,8^{a}	10,8±1,2^{abA}	9,6±0,6^{bA}	11,7±0,9^{abA}	15,6±1,8^{a}	10,8±2,1^{aA}	10,8±0,1^{aA}	12,8±0,7^{aA}
		S	3,6±0,1^{a}	3,1±0,3^{aC}	6,3±2,5^{aA}	5,7±2,1^{aA}	3,6±0,1^{d}	5±0,4^{cB}	6,2±0,3^{bA}	8,3±0^{aA}	3,6±0,1^{c}	8,9±0,3^{bA}	8,9±0,2^{bA}	10,2±0,1^{aA}
	5-hydroxytryptophan	**N**	18,1±2^{a}	21,1±1,5^{aA}	19,5±0,5^{aA}	23,7±2,1^{aA}	18,1±2^{a}	24,6±3,3^{aA}	26,7±3^{aA}	26,5±1,9^{aA}	18,1±2^{b}	24,9±1,6^{abA}	27,6±3^{aA}	20,8±1,9^{abA}
		S	13,5±0,3^{a}	12,8±0,2^{aA}	13,9±1,2^{aA}	14,4±0,2^{aB}	13,5±0,3^{a}	15,7±1,5^{aA}	15,9±1,4^{aA}	13,5±0,5^{aB}	13,5±0,3^{d}	15,5±0,2^{cA}	18,1±0^{bA}	21,7±0,6^{aA}
	Kynurenic Acid	**N**	51,1±8,5^{a}	51,9±7,4^{aA}	48,9±0,4^{aA}	41,6±8,5^{aA}	51,1±8,5^{a}	31,3±9,8^{aA}	29,1±12,4^{aA}	24,3±7,7^{aA}	51,1±8,5^{a}	24,9±9,2^{aA}	24,2±7,3^{aA}	22,1±8,1^{aA}
		S	28,4±2,9^{a}	29,8±3,3^{aA}	28,6±3,2^{aA}	24,2±6,7^{aA}	28,4±2,9^{a}	17,9±2,8^{aA}	15,4±3,6^{aA}	15,4±4,2^{aA}	28,4±2,9^{a}	15,5±4,8^{aA}	18,6±4^{aA}	19,4±4^{aA}
	Kynurenine	**N**	822,5±140,7^{a}	896,4±65,1^{aA}	670,6±51,7^{aB}	868,1±41,6^{aB}	822,5±140,7^{a}	849,3±76,7^{aA}	877,9±74,6^{aAB}	989,8±50,5^{aAB}	822,5±140,7^{a}	853,2±40^{aA}	1156,8±67,6^{aA}	1142,1±74^{aA}
		S	222±11,1^{a}	222,4±6,4^{aA}	243,8±13^{aB}	241±7^{aC}	222±11,1^{a}	254,6±27,7^{aA}	264,3±3,5^{aB}	280,8±8,9^{aB}	222±11,1^{b}	271,6±1,2^{bA}	360,8±33^{aA}	396,7±3,3^{aA}
	N-acetylserotonin	**N**	3±0,1^{a}	3,4±1,2^{aA}	2,3±0,1^{aA}	2,9±0^{aA}	3±0,1^{a}	2,4±0,2^{bA}	2,3±0,2^{bA}	2,3±0,1^{bA}	3±0,1^{a}	2,9±0,5^{aA}	2,6±0,5^{aA}	2,7±0,5^{aA}
		S	2,5±0^{a}	2,4±0^{aA}	2,3±0,1^{aA}	2,5±0,2^{aA}	2,5±0^{a}	2,3±0,2^{aA}	3±0,9^{aA}	2,3±0^{aA}	2,5±0^{ab}	3±0,3^{aA}	2,4±0,1^{bA}	2,2±0,1^{bA}
	Niacin	**N**	14326,5±725,6^{a}	14390,2±549,8^{aA}	11113,2±94,3^{bC}	11939,4±187,4^{bA}	14326,5±725,6^{a}	9958,9±171,7^{bB}	7999,2±487,3^{cB}	7086,3±298,4^{cB}	14326,5±725,6^{a}	5630,1±672,7^{bC}	4757,7±77,8^{bA}	5884±64,3^{bC}
		S	7381,8±311,1^{a}	6205,3±150,2^{bA}	5128,9±211,5^{cA}	3918,4±44,7^{dA}	7381,8±311,1^{a}	2512,6±350,9^{bB}	1017,6±12,4^{cB}	633±87^{cB}	7381,8±311,1^{a}	846,1±92,9^{bC}	356,6±45,4^{bC}	439,4±27,4^{bB}

Table 24. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Barley	**Picolinic Acid**	**N**	27,4±9,8^{a}	29±8,3^{aA}	26,4±5,1^{aA}	29,2±0,2^{aA}	27,4±9,8^{a}	21,4±0,8^{aA}	23,3±2,2^{aA}	22,9±2,7^{aA}	27,4±9,8^{a}	26,4±1,2^{aA}	25,6±2^{aA}	24,3±0,3^{aA}
		S	23,3±5,5^{a}	21,3±2,9^{aA}	23,6±3^{aA}	16,6±4,4^{aA}	23,3±5,5^{a}	16,4±1,8^{aA}	17,1±2,2^{aA}	15,3±5,6^{aA}	23,3±5,5^{a}	18,9±0,1^{aA}	14,6±1,2^{aA}	13±4,9^{aA}
	Quinolinic Acid	**N**	55,1±5,5^{ab}	66,4±3,3^{aA}	47,7±6,4^{bA}	52,2±1,3^{abA}	55,1±5,5^{a}	51,3±1,7^{aB}	45,6±5,9^{aA}	50,7±1,1^{aA}	55,1±5,5^{a}	49,4±1,4^{aB}	51,9±5,1^{aA}	48±5,6^{aA}
		S	32,8±1,3^{a}	33,2±0,9^{aA}	33,7±0,3^{aA}	31,5±0,4^{aA}	32,8±1,3^{a}	25,2±1,5^{bB}	24,1±0,5^{bB}	24,9±0^{bB}	32,8±1,3^{a}	26,8±1,4^{bB}	21,9±1,5^{bB}	25,2±0,9^{bB}
	Serotonin	**N**	658,6±83^{a}	633±40,2^{aA}	498,1±4,3^{aA}	533,7±38,2^{aA}	658,6±83^{a}	562,5±25,2^{abAB}	513,6±21,6^{abA}	467,2±14,8^{bAB}	658,6±83^{a}	488,1±21,3^{abB}	418,6±7,6^{bB}	367,9±14,5^{cB}
		S	238,3±11,3^{a}	192,8±5,8^{bA}	187,9±2,1^{bA}	179,5±2,8^{bA}	238,3±11,3^{a}	186,2±8,6^{bA}	165,4±4,5^{cbB}	153,8±11,4^{bAB}	238,3±11,3^{a}	152,6±6,1^{bB}	128,4±5,6^{bC}	128,8±3,5^{bB}
Rye	**3-hydroxykynurenine**	**N**	16,5±0,1^{b}	16±1,2^{bB}	19,2±1^{abB}	20,4±0,2^{aC}	16,5±0,1^{c}	27,7±2,1^{bA}	27,8±1,2^{bA}	33,2±1^{aA}	16,5±0,1^{c}	32,7±2^{aA}	26±2^{bA}	26,6±0,6^{bB}
		S	7,9±0,3^{a}	8,9±0,2^{aA}	7,7±0,6^{aA}	8±0,3^{aA}	7,9±0,3^{a}	9,3±0,8^{aA}	8,6±0,4^{aA}	9,1±0,3^{aA}	7,9±0,3^{a}	9±0,9^{aA}	10,1±0,6^{aA}	8,6±0,6^{aA}
	5-hydroxytryptophan	**N**	12,1±0,6^{b}	13,2±0,3^{bC}	13,7±0,5^{bC}	16,3±0,5^{aB}	12,1±0,6^{d}	19,7±1,7^{cB}	24,8±0,8^{bB}	31,2±1,2^{aA}	12,1±0,6^{c}	25,9±1,4^{bA}	35,2±1,2^{aA}	31,3±1,5^{aA}
		S	16,1±0,3^{b}	16±1^{bB}	20,3±0,1^{aA}	19,9±0^{aB}	16,1±0,3^{b}	23±0,1^{aA}	24,2±1^{aA}	24,2±1,9^{aAB}	16,1±0,3^{b}	25,3±0,3^{aA}	24,7±1,6^{aA}	25,3±0,1^{aA}
	Kynurenic Acid	**N**	83,4±3,4^{a}	66,5±2,1^{abA}	70,8±0,6^{abA}	59,8±7,9^{bA}	83,4±3,4^{a}	59,4±10,8^{aA}	64,6±9,8^{aA}	67±4,4^{aA}	83,4±3,4^{a}	69,1±5,2^{aA}	62,6±1,2^{aA}	63±14,8^{aA}
		S	43,5±0,8^{a}	46,1±1,7^{aAB}	44,4±2,6^{aA}	37,3±3,2^{aAB}	43,5±0,8^{a}	35,1±2,3^{bB}	33,6±0,2^{bA}	35,6±1,6^{bB}	43,5±0,8^{a}	40,7±0,9^{aA}	44±3,2^{aA}	46,7±1,7^{aA}
	Kynurenine	**N**	1664,1±48,6^{a}	1251,2±11,5^{cC}	1491,2±43,1^{bA}	1344,7±20,2^{cA}	1664,1±48,6^{b}	1596,9±25,9^{bB}	1778,3±9^{aA}	1815,8±12,1^{aA}	1664,1±48,6^{a}	1767,7±55,9^{aA}	1582±142,4^{aA}	869,4±651,7^{aA}
		S	203,4±19,1^{a}	206,2±18,5^{aA}	211,7±1,5^{aA}	194±1,8^{aB}	203,4±19,1^{a}	199,5±18,7^{aA}	194,5±14,9^{aA}	205,9±1,6^{aA}	203,4±19,1^{a}	201,1±11,8^{aA}	187,2±7,1^{aA}	199,4±0,6^{aB}

Table 24. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Rye	**N-acetylserotonin**	**N**	21±0,4^{a}	20,5±0,2^{aA}	21,1±0,2^{aA}	21,7±0,7^{aA}	21±0,4^{a}	20,9±0,5^{aA}	22,1±0,2^{aA}	21,2±0,4^{aA}	21±0,4^{a}	22±0,1^{aA}	22,1±0,3^{aA}	20,9±0,5^{aA}
		S	20,2±0,2^{ab}	20,7±0,1^{aA}	20,3±0,2^{abA}	19,9±0^{bA}	20,2±0,2^{a}	20,3±0,1^{aB}	20,3±0^{aA}	19,9±0^{aA}	20,2±0,2^{a}	20,2±0,1^{aB}	20,4±0,2^{aA}	20±0^{aA}
	Niacin	**N**	7668,5±267,4^{a}	5849,6±254,9^{aA}	8791,9±108^{aA}	5926,7±1937,6^{aA}	7668,5±267,4^{a}	3528,1±1916,1^{bAB}	1523,5±355,6^{bB}	1072,9±149,2^{bA}	7668,5±267,4^{a}	554±309^{aB}	344,4±64^{aC}	6066±5473,9^{aA}
		S	10656,3±642,3^{a}	10709,2±4,6^{aA}	9105,5±651^{aA}	6096,3±2103,2^{aA}	10656,3±642,3^{a}	2573,6±874,3^{bB}	1549,5±136,3^{bB}	1475,9±239,6^{bA}	10656,3±642,3^{a}	1140±326,8^{bB}	862,5±116,9^{bB}	892,3±2,3^{bA}
	Picolinic Acid	**N**	36,3±0,1^{a}	41,3±0,5^{aA}	43±3,6^{aA}	35,6±4,4^{aA}	36,3±0,1^{a}	37,2±2^{aA}	40,1±3,1^{aA}	39,4±2,5^{aA}	36,3±0,1^{a}	37,9±4,6^{aA}	38,4±2,2^{aA}	32,6±2,5^{aA}
		S	28,3±2,9^{b}	34,7±4,4^{abA}	45,3±2,5^{aA}	35,6±3,5^{abA}	28,3±2,9^{a}	30,6±4,9^{aA}	24,7±0,5^{aB}	21,2±1,3^{aB}	28,3±2,9^{a}	18,3±5,1^{aA}	25,9±4,7^{aB}	15,6±0,6^{aB}
	Quinolinic Acid	**N**	36,3±4,2^{ab}	32±1,9^{bA}	45,6±3,6^{aA}	40±1^{abA}	36,3±4,2^{a}	49,2±8,4^{aA}	36,9±5,7^{aA}	39,5±3,4^{aA}	36,3±4,2^{a}	48,2±11,1^{aA}	40,3±4,1^{aA}	57±20,7^{aA}
		S	39,5±3,2^{a}	43,8±0,5^{aA}	63,3±11,8^{aA}	42,8±4,1^{aA}	39,5±3,2^{a}	34,1±1,2^{aA}	33,9±1^{aA}	37,5±1,9^{aA}	39,5±3,2^{a}	38,2±5,7^{aA}	38,1±4,5^{aA}	35,9±0,9^{aA}
	Serotonin	**N**	40,1±0,2^{a}	38,2±0,4^{bB}	39,6±0,2^{aB}	40,5±0,4^{aA}	40,1±0,2^{b}	44,2±0,7^{aA}	42,6±0,1^{aA}	43,6±0,4^{aA}	40,1±0,2^{a}	45,7±0^{aA}	42,2±1^{aA}	32,8±10,2^{aA}
		S	23,7±1,2^{a}	25±0,3^{aA}	25,6±0^{aA}	25±0,9^{aA}	23,7±1,2^{a}	24,6±0,4^{aA}	23±0,9^{aAB}	23,5±0,3^{aAB}	23,7±1,2^{a}	23,4±0,4^{aA}	21,7±0,9^{aB}	20,6±0,6^{aB}
Oat	**3-hydroxykynurenine**	**N**	4,9±0,3^{b}	3,9±0,2^{bC}	10,9±0,8^{aA}	9,5±1,1^{aB}	4,9±0,3^{c}	13±0,5^{aB}	13,4±0,7^{aA}	11±0,1^{bB}	4,9±0,3^{c}	15,1±0,3^{aA}	9,1±1,4^{bA}	14,6±0,2^{aA}
		S	10,5±1,2^{a}	10,2±0,3^{aA}	4,5±0,1^{bB}	4,6±0,1^{bB}	10,5±1,2^{a}	6,8±0,1^{bB}	8±0,2^{abA}	7,5±0,9^{abAB}	10,5±1,2^{a}	9,2±1^{aAB}	6,8±0,5^{aA}	8,8±0,8^{aA}

Table 24. Changes in the concentrations of tryptophan derivatives (µg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Oat	**5-hydroxytryptophan**	**N**	18,9±0^{c}	17,8±0,4^{cB}	26,6±0,3^{bB}	28,4±0,6^{aA}	18,9±0^{b}	31±1,2^{aA}	26,1±2,2^{aB}	28,1±0,8^{aA}	18,9±0^{c}	30,8±1,5^{bA}	35±1,3^{aA}	27,5±0,3^{bA}
		S	23,4±0,5^{a}	23,3±0,4^{aA}	19±0^{aB}	11,8±7,4^{aA}	23,4±0,5^{ab}	23,9±0,2^{abA}	26±0,8^{aA}	21,2±1^{bA}	23,4±0,5^{a}	25,1±2^{aA}	26,5±0,3a^{aA}	24,2±1,6^{aA}
	Kynurenic Acid	**N**	75±1,5^{b}	71,4±0,3^{bB}	91,9±1,6^{aA}	92,9±1,2^{aA}	75±1,5^{b}	89,8±1,3^{aA}	83,8±3,1^{abA}	73,4±4,9^{bB}	75±1,5^{b}	90,8±1,2^{aA}	73,5±1,3^{bB}	65,3±1,6^{cB}
		S	96,9±0,3^{a}	97,1±1,1^{aA}	70,3±2,1^{bA}	67,1±1,5^{bA}	96,9±0,3^{a}	68,4±2,3^{bB}	61,5±4,4^{bAB}	61,2±4,8^{bA}	96,9±0,3^{a}	49,3±9,9^{bB}	48,9±0,3^{bB}	44,2±0,7^{bB}
	Kynurenine	**N**	225,4±11,7^{b}	231,2±0,2^{abC}	243,7±2,5^{abC}	256±4,5^{aB}	225,4±11,7^{c}	292,4±6,7^{bB}	371,1±9,3^{aB}	383,7±4,7^{aA}	225,4±11,7^{c}	429,2±4,6^{aA}	444,9±12,4^{aA}	365,2±5^{bA}
		S	226,8±1,2^{b}	221,9±2,5^{bC}	239,6±1,2^{aC}	246±1,4^{aB}	226,8±1,2^{c}	285,8±4,9^{bB}	393,8±0,3^{aB}	397,7±14,8^{aA}	226,8±1,2^{c}	393,3±22,2^{abA}	433,4±9,5^{aA}	361,9±17,3^{bA}
	N-acetylserotonin	**N**	9,7±0,2^{b}	9±0,3^{bB}	12,6±0,5^{aA}	12,7±0,2^{aA}	9,7±0,2^{a}	12,2±0,9^{aAB}	11,1±0,7^{aA}	13,2±1,9^{aA}	9,7±0,2^{b}	13±0,8^{aA}	11±0,3^{bA}	11,4±0,1^{abA}
		S	13±0,1^{a}	11,8±0,4^{abA}	9,4±0^{cB}	10,3±0,8^{bcA}	13±0,1^{a}	9,2±0,1^{cB}	10,3±0,1^{bA}	9,3±0,1^{cA}	13±0,1^{a}	9,7±0,2^{bB}	8,9±0,1^{bC}	9,3±0,5^{bA}
	Niacin	**N**	9155,3±105,6^{a}	9136,4±135,2^{aA}	7537±136,5^{bA}	7069,2±259,3^{bA}	9155,3±105,6^{a}	4839,2±91,3^{bB}	2135,8±8,3^{cB}	1469,1±15,1^{dB}	9155,3±105,6^{a}	748,9±22,1^{bC}	292,4±132,4^{cC}	721,6±80,3^{bC}
		S	7735,2±15,2^{c}	7632,3±161,2^{cA}	9594,6±68,4^{aA}	8561,5±8^{bA}	7735,2±15,2^{a}	6678±134,3^{bB}	3234,4±49,3^{cB}	2443,6±124,2^{dB}	7735,2±15,2^{a}	1293,4±32,2^{bC}	584,8±28,1^{dC}	1000,1±63,4^{cC}
	Picolinic Acid	**N**	27,3±2,2^{c}	48,6±1^{bB}	67,2±2,8^{aA}	69,9±8,1^{aA}	27,3±2,2^{b}	58,5±0,3^{aA}	67,5±1,7^{aA}	57,6±5,6^{aA}	27,3±2,2^{b}	50,5±1,2^{aB}	50,3±0,4^{aB}	47,6±2,7^{aA}
		S	64,8±3,3^{a}	68,8±1,5^{aA}	34,3±4^{bA}	34,6±1,5^{bA}	64,8±3,3^{a}	26,4±1,8^{bB}	29,2±0,9^{bA}	33±0,6^{bA}	64,8±3,3^{a}	30,7±4,3^{bB}	31,6±0,1^{bA}	35±4,8^{bA}
	Quinolinic Acid	**N**	95,4±3,1^{b}	72,3±11,5^{bC}	494±17,5^{aB}	513,9±5,8^{aA}	95,4±3,1^{d}	641,3±12,4^{aA}	594,3±10,4^{bA}	545,3±10,8^{cA}	95,4±3,1^{d}	535±10,7^{cB}	408,7±0,5^{bC}	229,1±0,9^{aB}
		S	557,1±4,9^{a}	502,8±9,8^{bA}	84±0,2^{cA}	94,7±9,2^{cA}	557,1±4,9^{a}	105,6±3,6^{bB}	105±1,4^{bA}	100,2±0,6^{bA}	557,1±4,9^{a}	76,6±11,7^{bB}	62±17,6^{bA}	75,4±2,8^{bA}

Table 24. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Oat	**Serotonin**	**N**	761,2±11,4^{a}	575,2±2,2^{bB}	587,4±4,5^{bA}	600,4±11^{bA}	761,2±11,4^{a}	692,6±20,5^{abA}	515,8±69,5^{bA}	570,3±50,2^{bA}	761,2±11,4^{a}	599,2±5,4^{bB}	506,1±8^{cA}	471,5±8,4^{dA}
		S	572,7±6,9^{b}	587,9±7,7^{bC}	645,8±4,1^{aB}	679,7±16^{aA}	572,7±6,9^{c}	849,5±12,3^{aA}	847,3±7,9^{aA}	727,5±10,4^{bA}	572,7±6,9^{b}	757,5±18,2^{aB}	511,8±4^{bC}	385±41,9^{cB}
Einkorn	**3-hydroxykynurenine**	**N**	9,8±0,6^{a}	7,7±0,5^{aC}	8,6±1,1^{aB}	9,8±1,4^{aB}	9,8±0,6^{c}	14,7±0,2^{bA}	19,2±1,1^{aA}	14,1±0,1^{bA}	9,8±0,6^{a}	12,5±0,4^{aB}	11,5±2,1^{aB}	13±0,4^{aAB}
		S	4,5±0,1^{a}	4,4±0^{aB}	4,5±0,3^{aB}	4,4±0,1^{aC}	4,5±0,1^{b}	5,2±0,8^{bAB}	8±0,5^{aA}	8,3±0,4^{aB}	4,5±0,1^{c}	7±0,4^{bA}	9,5±0,6^{aA}	10,2±0,5^{aA}
	5-hydroxytryptophan	**N**	11,3±0,1^{b}	12±0,1^{bC}	12,2±0,9^{bB}	15,4±1^{aC}	11,3±0,1^{c}	23,9±0,6^{bB}	41,1±1,4^{aA}	41,9±0,3^{aA}	11,3±0,1^{c}	40,3±0,6^{aA}	36,3±3^{aA}	28,8±1,4^{bB}
		S	7,3±1^{b}	8,3±0,7^{bB}	9,5±0,2^{abB}	11,1±0,2^{aB}	7,3±1^{b}	12,9±1,1^{aA}	15,1±0,1^{aA}	15,3±0,2^{aA}	7,3±1^{b}	13,9±0,5^{aA}	14±0,5^{aA}	15,1±0,9^{aA}
	Kynurenic Acid	**N**	47,5±0,4^{a}	42,3±2,2^{aA}	45,4±3,9^{aA}	43,9±2,4^{aA}	47,5±0,4^{a}	38,8±6,8^{aA}	35,5±5,4^{aA}	39,2±6,5^{aA}	47,5±0,4^{a}	41,8±6^{aA}	44,9±0,5^{aA}	41,6±1,2^{aA}
		S	17,1±0,4^{a}	17,7±1,5^{aA}	19,1±0,2^{aB}	17,8±0,5^{aC}	17,1±0,4^{b}	19,8±1,6^{abA}	18,6±0,6^{abB}	22±0,2^{aB}	17,1±0,4^{d}	22±0,4^{cA}	24,9±0,1^{bA}	28,7±1^{aA}
	Kynurenine	**N**	179,1±9^{b}	204,6±6,6^{aC}	202,1±4,8^{abC}	214±1^{aB}	179,1±9^{c}	235,1±2,6^{bB}	332,9±2,6^{aB}	357,4±8,5^{aA}	179,1±9^{c}	354±5,4^{bA}	405,2±3,5^{aA}	356,8±9,3^{bA}
		S	168,4±0,1^{a}	162,3±8^{aA}	140,9±1^{bA}	139,4±0,4^{bA}	168,4±0,1^{a}	145,7±6,4^{bA}	140,6±0,9^{bA}	152,9±4,8^{abA}	168,4±0,1^{a}	143,2±0,1^{cbA}	145,2±2,6^{cbA}	139,3±2,1^{bA}
	N-acetylserotonin	**N**	13,7±0,8^{a}	12,2±0,1^{aA}	13±0,5^{aAB}	12,7±0,2^{aA}	13,7±0,8^{a}	13,9±1,3^{aA}	14±0,1^{aA}	12,6±0,1^{aA}	13,7±0,8^{a}	13,1±0,7^{aA}	12,7±0,1^{aB}	11,5±0,3^{aB}
		S	9,5±0,1^{b}	9,1±0,1^{bA}	9,2±0,1^{bA}	9,9±0,1^{aA}	9,5±0,1^{a}	9,3±0,3^{aA}	9,3±0,4^{aA}	9,2±0,2^{aB}	9,5±0,1^{a}	9±0^{bA}	9,1±0,1^{abA}	9,2±0,1^{abB}
	Niacin	**N**	16021,7±687,8^{b}	17907,3±191,9^{aA}	18195,9±60,5^{aA}	18990,5±213,2^{aA}	16021,7±687,8^{a}	16693,2±131,3^{aB}	11282,2±247^{bB}	10166,5±190,3^{bB}	16021,7±687,8^{a}	8106,2±282,5^{bC}	6273,2±190,2^{cC}	5933,4±368,3^{cC}
		S	12860,1±178^{a}	12575,6±196,8^{aA}	10277,9±157,1^{bA}	8170,1±188,2^{cA}	12860,1±178^{a}	3758,2±172,2^{bB}	1555,2±42,4^{cB}	993,7±32,8^{dB}	12860,1±178^{a}	1320,5±120,3^{bC}	658,1±13,7^{cC}	605,8±47,1^{cB}

Table 24. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Einkorn	Picolinic Acid	N	48±0,9^{a}	39,7±8,2^{aA}	41,4±9^{aA}	32±1^{aA}	48±0,9^{a}	30,9±8,6^{aA}	30,9±12,7^{aA}	19,3±3,4^{aB}	48±0,9^{a}	23,8±0,8^{cA}	33,1±0,4^{bA}	22,7±0,9^{cAB}
		S	25,3±8,4^{a}	24,9±5,9^{aA}	30,2±0,7^{aA}	25,2±0,7^{aA}	25,3±8,4^{a}	24,3±0,9^{aA}	15,3±2,4^{aB}	15,8±0,6^{aB}	25,3±8,4^{a}	9,4±1,2^{aA}	12,6±1,2^{aB}	14,7±0,8^{baB}
	Quinolinic Acid	N	41,9±3,9^{a}	26,4±3,5^{bA}	40,2±5,3^{abA}	38,5±0,6^{abA}	41,9±3,9^{a}	26,8±3,1^{bA}	36±2,6^{abA}	35,7±3,4^{abA}	41,9±3,9^{a}	36±1,9^{aA}	35,6±5,7^{aA}	40,9±2,4^{aA}
		S	37,1±4,9^{a}	35±4,1^{aA}	27,4±2,2^{aA}	36,2±1,1^{aA}	37,1±4,9^{a}	34,3±0,6^{aA}	27,5±5,2^{aA}	29,5±2,5^{aAB}	37,1±4,9^{a}	32,5±0,1^{aA}	27,5±2,6^{aA}	27,3±0,6^{aB}
	Serotonin	N	39,1±2,4^{a}	40,9±0,2^{aB}	42,9±1,6^{aB}	43,7±1^{aB}	39,1±2,4^{c}	62,5±0^{aA}	51,4±1^{bA}	47,6±1,5^{bAB}	39,1±2,4^{c}	63,5±1,3^{aA}	54±2,1^{bA}	50,3±0,3^{bA}
		S	8,4±3,9^{c}	25±2,9^{cC}	94,1±3,8^{bB}	115,7±6,6^{aA}	8,4±3,9^{d}	136,7±0,2^{aA}	111,4±2,7^{bA}	101,6±1^{cAB}	8,4±3,9^{c}	111,4±0,9^{aB}	90±1,2^{bB}	85,2±0,1^{bB}
Buckwheat	3-hydroxykynurenine	N	155,8±1,4^{a}	140,5±0,1^{bB}	132±1,5^{bA}	129,9±6,4^{bA}	155,8±1,4^{a}	148,5±2,1^{aA}	139,4±3,9^{bA}	129,1±0,2^{cA}	155,8±1,4^{a}	127,7±1,8^{bC}	100,4±0,8^{cB}	86,9±2,6^{dB}
		S	27,2±2,9^{a}	22,3±0,6^{abC}	15±0,7^{bcB}	17,1±0,6^{cA}	27,2±2,9^{a}	27,2±0,4^{aA}	25,9±0,2^{aA}	24,7±2^{aA}	27,2±2,9^{a}	25,2±0^{aB}	24,1±1,2^{aA}	21,4±2,3^{aA}
	5-hydroxytryptophan	N	141,2±2,6^{b}	142,5±3,9^{bB}	152,1±0,5^{abB}	178,4±12,6^{aA}	141,2±2,6^{c}	247,2±10,5^{aA}	220,6±0,5^{bA}	213,3±1,2^{bA}	141,2±2,6^{bc}	225,5±4,9^{aA}	160,3±7,4^{bB}	129,8±5,6^{cB}
		S	76,8±0,2^{a}	65,9±1,3^{bC}	59,4±0,8^{cB}	66,6±2,9^{bB}	76,8±0,2^{d}	107,8±0,1^{aA}	99,3±0,9^{bA}	83,9±1,4^{cA}	76,8±0,2^{b}	98,6±1,2^{aB}	61,9±0,6^{cB}	38,3±0,5^{dC}
	Kynurenic Acid	N	1188,4±33,2^{ab}	1230,2±9,1^{aA}	1164,6±33,8^{abA}	1104,1±31,8^{bA}	1188,4±33,2^{a}	1131,9±44,7^{abAB}	944,4±121,9^{abA}	900,3±31,7^{bB}	1188,4±33,2^{a}	961,3±58^{bB}	878,3±27,6^{bcA}	773,6±39,1^{cB}
		S	818,3±12,6^{b}	877,1±29,3^{abA}	873,2±23,3^{abA}	899,1±3,1^{aA}	818,3±12,6^{a}	799,1±87,7^{aA}	769,1±22,5^{aB}	718,5±13,2^{aB}	818,3±12,6^{a}	749,3±8,6^{bA}	622±21,2^{cC}	604,5±8,4^{cC}

Table 24. Changes in the concentrations of tryptophan derivatives (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains. **(continue)**

Buckwheat	Kynurenine	N	561±18,8^{a}	574,5±0,5^{aA}	563,2±17,2^{aA}	553,1±21,3^{aB}	561±18,8^{a}	570,3±10,1^{aA}	565,2±2,3^{aA}	576,2±3,8^{aB}	561±18,8^{b}	573,7±9,9^{bA}	595,6±4,2^{bA}	664±4,2^{aA}
		S	558,1±4,2^{a}	506,6±3,8^{bA}	486,7±1,8^{cA}	509,1±3,5^{cbB}	558,1±4,2^{a}	508,8±6,1^{bA}	503,9±5,9^{bA}	491,9±9,2^{bB}	558,1±4,2^{b}	513,9±0,7^{cA}	493,2±10,8^{cA}	599,8±11,5^{aA}
	N-acetylserotonin	N	9,5±0,1^{a}	9,4±0,4^{aA}	9,8±0,3^{aB}	9,5±0,5^{aA}	9,5±0,1^{b}	9,3±0^{bA}	10,1±0^{aB}	10,5±0,1^{aA}	9,5±0,1^{b}	10,4±0,4^{abA}	11,1±0,1^{aA}	11,1±0,6^{aA}
		S	8,3±0,2^{b}	8,3±0,1^{bA}	8,5±0,1^{bA}	9,3±0,1^{aA}	8,3±0,2^{a}	8,8±0^{aA}	8,6±0,6^{aA}	9,4±0,9^{aA}	8,3±0,2^{b}	9±0,3^{abA}	9,3±0,2^{aA}	9,1±0^{aA}
	Niacin	N	10958,2±177,9^{a}	11038,1±18,7^{bA}	11211,3±170,1^{aA}	11973,6±183,6^{abA}	10958,2±177,9^{a}	10051,2±260,1^{bB}	5211,1±16,9^{dB}	5713,6±228^{cB}	10958,2±177,9^{a}	3859,9±161,7^{bC}	2900±42,6^{cC}	2547±211,4^{cC}
		S	12992,3±130,4^{a}	11633,5±118,7^{bA}	13164,1±377,3^{aA}	12176,6±311,2^{abA}	12992,3±130,4^{a}	8993,9±45,6^{bB}	5500,5±72^{cB}	4957,6±70,5^{dB}	12992,3±130,4^{a}	3982,6±25,8^{bC}	2539,2±43^{cC}	2261,9±176,3^{cC}
	Picolinic Acid	N	19,7±0,3^{a}	14,1±2,2^{bA}	17,6±0,9^{abA}	16±0,7^{abA}	19,7±0,3^{a}	14,4±2,4^{aA}	13,2±3,9^{aA}	13,9±1,3^{aA}	19,7±0,3^{a}	13,9±1,7^{abA}	11,1±1,2^{bA}	15,4±2,9^{abA}
		S	15,4±2,2^{a}	16,7±2,2^{aA}	17,2±3,1^{aA}	23,5±0,9^{aA}	15,4±2,2^{a}	12,7±1^{aA}	16,6±0,5^{aA}	17,6±4,6^{aA}	15,4±2,2^{a}	13,7±3^{aA}	15,4±0,1^{aA}	11,2±2,3^{aA}
	Quinolinic Acid	N	20,6±3,2^{a}	22,9±0,2^{aA}	21,2±1,3^{aA}	19,3±0,6^{aA}	20,6±3,2^{a}	25,3±6,4^{aA}	19,3±2,4^{aA}	21±0,3^{aA}	20,6±3,2^{a}	21,9±2^{aA}	19,7±2,2^{aA}	20,2±4,1^{aA}
		S	46,7±3,5^{a}	35,9±6,2^{aA}	51,1±2,9^{aA}	51,1±7,7^{aA}	46,7±3,5^{a}	48,3±1,2^{aA}	34,4±6,4^{aA}	39,9±9,5^{aA}	46,7±3,5^{a}	30,7±4,2^{aA}	35,6±11,6^{aA}	28,7±2,3^{aA}
	Serotonin	N	666,7±0,2^{a}	588,7±3,9^{bA}	526,3±9,5^{cA}	503,5±19,8^{cA}	666,7±0,2^{a}	560,9±0,3^{bA}	545,9±0,7^{bcA}	523,1±15^{cA}	666,7±0,2^{a}	507,4±14,1^{bB}	472,9±15,7^{bB}	403,7±12,7^{cB}
		S	789,5±26^{a}	849,8±34,2^{aB}	795,1±7,3^{aC}	844,8±9,8^{aB}	789,5±26^{b}	975,1±16,5^{aA}	961,8±1,2^{aA}	960,9±20,8^{aA}	789,5±26^{bc}	928,7±5,8^{aAB}	830,4±7,9^{bB}	739,1±1,1^{cC}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of tryptophan derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of tryptophan derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

4.5. Changes in Melatonin Concentrations

According to Table 25, the sprouting process did not change the melatonin concentration in any grain ($p>0.05$).

Changes in the concentrations of melatonin during commercial yeast and sourdough fermentation of native and sprouted grains are given in Table 26 and Table 27, respectively.

Commercial yeast fermentation of sprouted wheat at 20 °C, 3 hours and 30 °C, 1 and 3 hours decreased the melatonin concentration. In a study of Yılmaz et al (2014), wheat was fermented with commercial yeast, the concentration of melatonin measured at different times did not show a certain trend, but after 2 hours, it was observed that melatonin increased approximately 2 folds and reached the maximum level [130]. Sourdough fermentation of native oats at 20 °C and 30 °C increased the melatonin concentration. Commercial yeast fermentation of native einkorn increased melatonin concentration, while commercial yeast fermentation of sprouted einkorn decreased melatonin concentration. Sourdough fermentation of native oats at 20 °C - 1 hour, 30 ° C and 40 ° C decreased the melatonin concentration. Commercial yeast fermentation of native buckwheat at 30 °C - 2 hours, 40 °C - 1 hour, and sprouted buckwheat at 20 °C - 3 hours increased the melatonin concentration.

Standard deviation values are very high for melatonin for whole grains. Therefore, without the exceptions mentioned above, it was observed that there was no change in general.

Table 25. Concentrations of melatonin (*p*g/kg) for native and sprouted grains

Melatonine	Native	Sprouted
Wheat	77±44	47±19
Barley	4±2	7±4
Rye	20±22	30±19
Oats	76±65	34±9
Einkorn	87±27*	37±20
Buckwheat	11±6	4±0

αThe asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Table 26. Changes of melatonin concentrations (*p*g/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains

T (°C)		**20 °C**				**30 °C**				**40 °C**			
T (h)		**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**	**0**	**1**	**2**	**3**
Wheat	**N**	106±49^{a}	499±246^{a}	112±82^{a}	148±124^{a}	106±49^{a}	90±42^{a}	89±33^{a}	71±42^{a}	106±49^{a}	68±37^{a}	93±42^{a}	51±37^{a}
	S	214±125^{a}	827±660^{a}	293±234^{a}	22±15^{b}	214±125^{a}	23±15^{b}	383±302^{a}	23±24^{b}	214±125^{a}	123±61^{a}	42±43^{a}	24±5^{a}
Barley	**N**	115±104^{a}	79±44^{a}	10±6^{a}	5±1^{a}	115±104^{a}	8±3^{a}	5±1^{a}	6±0^{a}	115±104^{a}	8±3^{a}	3±0^{a}	5±1^{a}
	S	8±7^{a}	6±0^{a}	5±0^{a}	6±4^{a}	8±7^{a}	9±6^{a}	6±1^{a}	6±3^{a}	8±7^{a}	4±0^{a}	12±2^{a}	3±1^{a}
Rye	**N**	212±220^{a}	33±18^{a}	13±5^{a}	37±32^{a}	212±220^{a}	88±95^{a}	30±27^{a}	47±26^{a}	212±220^{a}	51±41^{a}	19±4^{a}	61±73^{a}
	S	6±2^{a}	20±21^{a}	4±3^{a}	7±7^{a}	6±2^{a}	5±4^{a}	33±24^{a}	14±15^{a}	6±2^{a}	125±208^{a}	3±1^{a}	8±4^{a}
Oats	**N**	42±5^{a}	38±15^{a}	27±2^{a}	31±8^{a}	42±5^{a}	19±2^{a}	128±103^{a}	29±4^{a}	42±5^{a}	30±11^{a}	27±3^{a}	25±8^{a}
	S	63±57^{a}	8±0^{a}	13±3^{a}	14±0^{a}	63±57^{a}	20±3^{a}	10±5^{a}	15±3^{a}	63±57^{a}	10±4^{a}	9±2^{a}	19±2^{a}
Einkorn	**N**	27±1^{b}	41±4^{a}	38±5^{a}	36±5^{a}	27±1^{b}	35±5^{a}	89±50^{a}	39±7^{a}	27±1^{b}	36±3^{a}	31±2^{a}	39±7^{a}
	S	333±17^{a}	14±11^{b}	4±0^{b}	8±2^{b}	333±17^{a}	5±0^{b}	10±4^{b}	12±2^{b}	333±17^{a}	3±2^{b}	6±0^{b}	5±1^{b}
Buckwheat	**N**	5±1^{a}	4±0^{a}	5±0^{a}	39±32^{a}	5±1^{b}	6±1^{b}	68±32^{a}	4±0^{b}	5±1^{b}	21±15^{a}	5±1^{b}	5±2^{b}
	S	19±16^{b}	2±0^{b}	2±0^{b}	82±49^{a}	19±16^{a}	3±0^{a}	4±2^{a}	4±1^{a}	19±16^{a}	11±3^{a}	5±1^{a}	4±0^{a}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of melatonin derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of melatonin derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 27. Changes of melatonin concentrations (*p*g/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains

T (°C)		**10 °C**				**20 °C**				**30 °C**			
T (h)		**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**	**0**	**12**	**24**	**36**
Wheat	**N**	77±92^{a}	53±70^{a}	12±5^{a}	49±65^{a}	77±92^{a}	44±52^{a}	20±14^{a}	39±18^{a}	77±92^{a}	19±9^{a}	36±38^{a}	60±45^{a}
	S	6±2^{a}	31±30^{a}	18±26^{a}	51±67^{a}	6±2^{a}	10±8^{a}	9±7^{a}	12±8^{a}	6±2^{a}	3±0^{a}	7±3^{a}	173±281^{a}
Barley	**N**	12±9^{a}	6±1^{a}	7±2^{a}	6±1^{a}	12±9^{a}	6±1^{a}	5±0^{a}	7±1^{a}	12±9^{a}	8±3^{a}	8±2^{a}	8±1^{a}
	S	11±6^{a}	8±4^{a}	5±1^{a}	5±1^{a}	11±6^{a}	7±4^{a}	5±2^{a}	6±0^{a}	11±6^{a}	11±2^{a}	9±0^{a}	9±1^{a}
Rye	**N**	2±0^{a}	1±1^{a}	1±1^{a}	1±0^{a}	2±0^{a}	5±4^{a}	4±0^{a}	9±2^{a}	2±0^{a}	3±0^{a}	5±1^{a}	6±3^{a}
	S	1±0^{a}	7±5^{a}	10±10^{a}	0±0^{a}	1±0^{a}	3±3^{a}	2±1^{a}	3±2^{a}	1±0^{a}	22±6^{a}	13±9^{a}	5±2^{a}
Oats	**N**	4±1^{a}	5±1^{a}	8±1^{a}	7±0^{a}	4±1^{b}	8±1^{b}	10±1^{a}	14±4^{a}	4±1^{b}	8±1^{b}	19±4^{a}	17±2^{a}
	S	8±3^{a}	11±3^{a}	15±2^{a}	6±1^{a}	8±3^{a}	20±12^{a}	9±5^{a}	11±6^{a}	8±3^{a}	5±2^{a}	13±3^{a}	13±2^{a}
Einkorn	**N**	38±11^{a}	8±6^{b}	29±1^{a}	29±7^{a}	38±11^{a}	18±3^{b}	17±2^{b}	18±1^{b}	38±11^{a}	14±3^{b}	21±1^{b}	24±1^{b}
	S	5±1^{a}	17±6^{a}	7±1^{a}	69±56^{a}	5±1^{a}	7±0^{a}	13±2^{a}	15±1^{a}	5±1^{a}	15±9^{a}	12±2^{a}	10±1^{a}
Buckwheat	**N**	14±5^{a}	15±9^{a}	7±1^{a}	6±0^{a}	14±5^{a}	56±37^{a}	13±4^{a}	10±2^{a}	14±5^{a}	8±1^{a}	8±1^{a}	8±1^{a}
	S	4±0^{a}	4±0^{a}	4±1^{a}	4±0^{a}	4±0^{a}	6±2^{a}	24±20^{a}	4±0^{a}	4±0^{a}	3±1^{a}	5±0^{a}	3±0^{a}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of melatonin derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of melatonin derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time

4.6. Formation of Biogenic Amines with Sprouting and Fermentation

Changes in the concentrations of histidine, phenylalanine, histamine, and phenylethylamine with the sprouting of grains are given in Table 20. According to this table, histidine generally increased with the sprouting of all grains except the decrease with einkorn. The highest increase was 4.7 fold with the sprouting of rye. Phenylalanine increased with the sprouting of all grains without exception. The highest increase was 6.6 fold with the sprouting of rye. Histamine increased generally with the sprouting of grains. Exceptionally, it did not differ with the sprouting of oats ($p>0.05$) and decreased with the sprouting of buckwheat about %1,2. Unlike histamine, phenylethylamine decreased generally with the sprouting of grains. The most decrease was about %70.5 with the sprouting of oats. As an exception, it did not differ with the sprouting of wheat ($p>0.05$) and increased with the sprouting of barley and buckwheat. The highest increase was 17.1 fold for phenylethylamine with the sprouting of buckwheat.

Changes in the concentrations of histidine and phenylalanine during commercial yeast and sourdough fermentation of native and sprouted grains are given in Table 21 and Table 22, respectively. Histidine generally increased with commercial yeast fermentation of grains. Exceptionally, it decreased with commercial yeast fermentation of sprouted wheat at 30 °C, of native barley and rye at 20-30 °C, of native oats at 20 °C, os sprouted oats at 30 °C, of native einkorn at 30 °C and did not differ with commercial yeast fermentation of native wheat at 20-30 °C, of sprouted barley at 20-30 °C, of sprouted rye, of sprouted oats at 20 °C, of native einkorn at 20 °C, of sprouted einkorn at 20-30 °C, of sprouted buckwheat at 20 °C ($p>0.05$). Also, phenylalanine generally increased with commercial yeast fermentation of grains. As an exception, it decreased with commercial yeast fermentation of native wheat at 20-30 °C, of sprouted wheat at 20 °C-1 hour, of native barley and rye at 20-30 °C. Sourdough fermentation of grains generally increased the histidine and phenylalanine concentrations. Although there was no exception for phenylalanine, histidine did not differ with commercial yeast fermentation of sprouted wheat at 10 °C, of sprouted barley at 10-20 °C, of sprouted rye at 30 °C, of native oats at 10-20 °C.

Changes in the concentrations of histamine and phenylethylamine during commercial yeast and sourdough fermentation of native and sprouted grains are given in Table 23 and Table 24, respectively. Commercial yeast fermentation of grains generally did not differ the histamine and phenylethylamine concentrations. Exceptionally histamine decreased with commercial yeast fermentation of sprouted wheat at 40 °C, of sprouted rye at 30-40 °C, of sprouted einkorn at 40 °C, of sprouted buckwheat. Also, it increased with commercial yeast fermentation of native einkorn at 40 °C-2 hours and it first increased and then decreased with commercial yeast fermentation of native barley at 20 °C. Phenylethylamine increased with commercial yeast fermentation of native wheat at 40 °C, of sprouted wheat at 20-40 °C, of native barley at 40 °C, of native rye at 40 °C, of sprouted rye at 30 °C, of native oats, of sprouted oats at 40 °C, of native einkorn at 30-40 °C, of sprouted einkorn and decreased with commercial yeast fermentation of native rye at 30 °C, of native buckwheat at 40 °C, exceptionally. Histamine generally decreased with sourdough fermentation of grains. As an exception, it did not differ with sourdough fermentation of native wheat, of native barley at 30 °C, of sprouted barley at 10-20 °C, of native and sprouted rye at 30 °C, of native einkorn at 30 °C, of sprouted einkorn at 10 °C, of native buckwheat at 30 °C, of sprouted buckwheat ($p>0.05$) and increased with sourdough fermentation of sprouted oats. Phenylethylamine generally increased with sourdough fermentation of grains. Exceptionally, it first increased and then decreased with sourdough fermentation of sprouted wheat and einkorn at 30 °C and of sprouted oats at 10 °C. Also, it did not differ with sourdough fermentation of native buckwheat at 10 °C, of native rye at 10-30 °C while it decreased with sourdough fermentation of native buckwheat at 10 °C-12 hours. In one study, it was observed that histamine, phenylethylamine, tryptamine, and tyramine were formed during the malting of barley [128]. According to these results, commercial yeast fermentation of grains generally did not differentiate the histamine and phenylethylamine concentrations, while sourdough fermentation generally increased the phenylethylamine concentrations and decreased the histamine concentrations. Because of these amino acid derivatives are biogenic amines, sourdough appears to be more optimal for histamine than commercial yeast. For phenylethylamine, it seems better to be no difference rather than increase, so commercial yeast is more optimal. Both histidine and phenylalanine concentrations were increased by sprouting. With both commercial yeast and sourdough fermentations, the initial conditions of histidine and phenylalanine concentrations were generally higher with sprouted ones. However, the initial conditions of histamine and phenylethylamine concentrations were generally higher with native ones with both commercial yeast and sourdough fermentation.

According to some studies, the level of histamine with no side effects is 50 mg/kg. Up to 200 mg/kg of histamine can be observed in fresh fish [131]. In addition, phenylethylamine was observed up to 182 mg/kg in fermented meat products, up to 180 mg/kg in fish products, and up to 61 mg/kg in fermented milk products [132]. There is no problem in consuming the biogenic amines observed with the applications made to grains, since they do not even reach the permissible levels, as they are far below the levels of biogenic amines observed in other foods.

Table 28. Concentrations of biogenic amines and their precursors (μg/kg) for native and sprouted grains

	(μg/kg d.w.)	Native	Sprouted
Wheat	Histidin	34000 ± 0*	122000 ± 38
	Phenylalanine	44000 ± 1*	187000 ± 20
	Histamine	8995,1±2934	20474,6±8782,6
	Phenylethylamine	51,7±32,6	41,3±5,7
Barley	Histidin	56000 ± 3*	185000 ± 1
	Phenylalanine	58000 ± 3*	295000 ± 1
	Histamine	1205,6±0,2*	1256±1,3
	Phenylethylamine	9,6±0,1*	54,3±10,2
Rye	Histidin	46000 ± 0*	218000 ± 12
	Phenylalanine	71000 ± 2*	472000 ± 0
	Histamine	373,3±0,2*	2598,6±8,6
	Phenylethylamine	46,7±2,3*	38±1,4
Oats	Histidin	77000 ± 1*	155000 ± 9
	Phenylalanine	53000 ± 1*	168000 ± 14
	Histamine	421,4±4,5	413,7±5,7
	Phenylethylamine	153,5±11,9*	45,3±5,2
Einkorn	Histidin	168000 ± 14*	129000 ± 3
	Phenylalanine	74000 ± 5*	357000 ± 11
	Histamine	469,9±0,8*	496,4±3
	Phenylethylamine	130±116,5	39,2±0,9
Buckwheat	Histidin	56000 ± 1*	149000 ± 6
	Phenylalanine	53000 ± 2*	176000 ± 4
	Histamine	464,5±2,7*	458,9±0,9
	Phenylethylamine	52,5±5,5*	900,7±55,7

αThe asterisk (*) indicates that there is a statistical difference between the two data according to the t-test.

Table 29. Changes in the histidine and phenylalanine concentrations (mg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains

T (°C)			20				30				40			
t (h)			0	1	2	3	0	1	2	3	0	1	2	3
Wheat	**Histidin**	**N**	48 ± 7^{a}	50 ± 1^{aA}	41 ± 1^{aB}	43 ± 1^{aB}	48 ± 7^{a}	40 ± 0^{aB}	44 ± 7^{aAB}	45 ± 4^{aB}	48 ± 7^{b}	50 ± 2^{bA}	57 ± 4^{bA}	80 ± 5^{aA}
		S	137 ± 3^{a}	131 ± 1^{aB}	135 ± 2^{aB}	141 ± 9^{aB}	137 ± 3^{a}	130 ± 0^{abB}	116 ± 1^{cC}	128 ± 5^{bB}	137 ± 3^{d}	157 ± 3^{cA}	178 ± 7^{bA}	198 ± 9^{aA}
	Phenylalanine	**N**	104 ± 2^{a}	81 ± 1^{bA}	75 ± 6^{bB}	73 ± 1^{bB}	104 ± 2^{a}	70 ± 2^{bB}	80 ± 2^{cAB}	73 ± 3^{cB}	104 ± 2^{b}	80 ± 2^{dA}	89 ± 2^{cA}	119 ± 3^{aA}
		S	323 ± 12^{ab}	307 ± 4^{bB}	351 ± 16^{aB}	343 ± 15^{aB}	323 ± 12^{b}	300 ± 5^{abB}	293 ± 10^{bC}	359 ± 9^{aB}	323 ± 12^{d}	369 ± 5^{cA}	479 ± 1^{bA}	554 ± 9^{aA}
Barley	**Histidin**	**N**	72 ± 0^{a}	65 ± 1^{bA}	56 ± 3^{cB}	54 ± 1^{cB}	72 ± 0^{a}	57 ± 10^{bA}	56 ± 2^{bB}	55 ± 1^{bB}	72 ± 0^{c}	69 ± 1^{cA}	87 ± 1^{bA}	103 ± 0^{aA}
		S	196 ± 38^{a}	244 ± 29^{aAB}	210 ± 10^{aB}	229 ± 5^{aA}	196 ± 38^{a}	225 ± 1^{aB}	181 ± 8^{aC}	219 ± 11^{aA}	196 ± 38^{b}	307 ± 27^{abA}	324 ± 5^{aA}	304 ± 71^{abA}
	Phenylalanine	**N**	100 ± 3^{a}	94 ± 4^{aA}	77 ± 4^{bB}	78 ± 3^{bB}	100 ± 3^{a}	86 ± 13^{abA}	76 ± 3^{bB}	82 ± 2^{bB}	100 ± 3^{d}	106 ± 0^{cA}	165 ± 6^{bA}	206 ± 2^{aA}
		S	495 ± 25^{b}	606 ± 62^{aA}	599 ± 33^{abB}	660 ± 15^{aA}	495 ± 25^{c}	622 ± 3^{bA}	713 ± 15^{aB}	732 ± 8^{aA}	495 ± 25^{b}	817 ± 101^{abA}	1020 ± 58^{aA}	1066 ± 239^{aA}
Rye	**Histidin**	**N**	81 ± 2^{a}	65 ± 0^{bB}	58 ± 2^{bB}	54 ± 8^{bB}	81 ± 2^{a}	85 ± 2^{aA}	69 ± 5^{bB}	58 ± 3^{cB}	81 ± 2^{b}	78 ± 7^{bAB}	87 ± 7^{bA}	150 ± 0^{aA}
		S	250 ± 0^{a}	239 ± 13^{aC}	249 ± 1^{aA}	274 ± 14^{aB}	250 ± 0^{a}	276 ± 6^{aB}	272 ± 12^{aA}	264 ± 1^{aB}	250 ± 0^{a}	307 ± 2^{aA}	287 ± 37^{aA}	362 ± 38^{aA}
	Phenylalanine	**N**	160 ± 4^{a}	143 ± 2^{abA}	135 ± 11^{bAB}	132 ± 7^{bB}	160 ± 4^{a}	149 ± 17^{aA}	116 ± 5^{bB}	113 ± 4^{bC}	160 ± 4^{bc}	142 ± 3^{cA}	170 ± 16^{bA}	275 ± 0^{aA}
		S	605 ± 0^{b}	627 ± 58^{aB}	743 ± 7^{aB}	709 ± 25^{aB}	605 ± 0^{b}	689 ± 15^{aAB}	712 ± 23^{aB}	721 ± 38^{aB}	605 ± 0^{b}	779 ± 19^{abA}	873 ± 39^{abA}	1131 ± 34^{aA}

Table 29. Changes in the histidine and phenylalanine concentrations (mg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains **(continue)**

Oat	**Histidin**	**N**	101 ± 4^{a}	94 ± 4^{abB}	97 ± 4^{aB}	84 ± 1^{bC}	101 ± 4^{a}	94 ± 6^{aB}	110 ± 13^{aB}	114 ± 1^{aB}	101 ± 4^{d}	125 ± 7^{cA}	160 ± 2^{bA}	183 ± 3^{aA}
		S	153 ± 12^{a}	118 ± 25^{aB}	125 ± 7^{aB}	131 ± 1^{aB}	153 ± 12^{a}	131 ± 10^{abAB}	125 ± 8^{bB}	120 ± 1^{bB}	153 ± 12^{c}	170 ± 6^{bcA}	195 ± 10^{abA}	216 ± 19^{aA}
	Phenylalanine	**N**	144 ± 5^{c}	161 ± 10^{bcC}	191 ± 6^{aC}	176 ± 4^{abC}	144 ± 5^{c}	196 ± 3^{bB}	272 ± 22^{aB}	301 ± 7^{aB}	144 ± 5^{d}	266 ± 9^{cA}	365 ± 2^{bA}	428 ± 12^{aA}
		S	251 ± 21^{a}	232 ± 1^{aB}	258 ± 14^{aB}	258 ± 9^{aB}	251 ± 21^{a}	237 ± 18^{aB}	261 ± 26^{aB}	287 ± 0^{aB}	251 ± 21^{c}	337 ± 29^{bcA}	450 ± 25^{abA}	598 ± 99^{aA}
Einkorn	**Histidin**	**N**	87 ± 2^{a}	79 ± 2^{aB}	79 ± 6^{aB}	84 ± 6^{aB}	87 ± 2^{a}	74 ± 3^{bB}	77 ± 4^{bB}	77 ± 3^{bB}	87 ± 2^{c}	90 ± 1^{cA}	108 ± 1^{bA}	125 ± 3^{aA}
		S	183 ± 11^{a}	217 ± 29^{aAB}	199 ± 11^{aA}	170 ± 2^{aA}	183 ± 11^{a}	183 ± 14^{aB}	244 ± 80^{aA}	197 ± 5^{aA}	183 ± 11^{b}	252 ± 7^{aA}	281 ± 8^{aA}	470 ± 260^{aA}
	Phenylalanine	**N**	197 ± 5^{ab}	194 ± 7^{abAB}	188 ± 12^{bB}	209 ± 1^{aB}	197 ± 5^{ab}	181 ± 4^{bB}	193 ± 1^{abB}	200 ± 9^{aB}	197 ± 5^{c}	206 ± 5^{cA}	250 ± 5^{bA}	306 ± 3^{aA}
		S	660 ± 12^{b}	775 ± 40^{aB}	814 ± 32^{aB}	710 ± 59^{abB}	660 ± 12^{c}	707 ± 37^{bcB}	916 ± 167^{abB}	980 ± 24^{aB}	660 ± 12^{c}	972 ± 5^{bcA}	1440 ± 89^{abA}	1970 ± 448^{aA}
Buckwheat	**Histidin**	**N**	64 ± 1^{b}	91 ± 1^{aA}	73 ± 7^{abC}	71 ± 15^{abA}	64 ± 1^{d}	78 ± 4^{cB}	110 ± 4^{bB}	127 ± 8^{aA}	64 ± 1^{b}	92 ± 2^{abA}	127 ± 4^{aA}	146 ± 42^{aA}
		S	157 ± 7^{a}	150 ± 7^{aB}	153 ± 6^{aC}	156 ± 19^{aB}	157 ± 7^{b}	160 ± 3^{bB}	181 ± 2^{aB}	161 ± 3^{bB}	157 ± 7^{c}	181 ± 7^{bA}	201 ± 2^{aA}	219 ± 9^{aA}
	Phenylalanine	**N**	124 ± 3^{b}	157 ± 6^{aB}	160 ± 12^{aC}	167 ± 14^{aB}	124 ± 3^{d}	168 ± 1^{cB}	232 ± 1^{bB}	257 ± 18^{aB}	124 ± 3^{c}	217 ± 4^{bA}	300 ± 1^{aA}	368 ± 51^{aA}
		S	205 ± 11^{a}	212 ± 16^{aC}	230 ± 9^{aC}	272 ± 48^{aB}	205 ± 11^{c}	255 ± 3^{bB}	323 ± 6^{aB}	284 ± 26^{abB}	205 ± 11^{d}	357 ± 10^{cA}	459 ± 22^{bA}	520 ± 1^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of histidine and phenylalanine derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of histidine and phenylalanine derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 30. Changes in the histidine and phenylalanine concentrations (mg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains

T (°C)			10 °C				20 °C				30 °C			
t (h)			0	12	24	36	0	12	24	36	0	12	24	36
Wheat	**Histidin**	**N**	36 ± 2^{b}	41 ± 0^{bB}	111 ± 11^{aB}	107 ± 2^{aB}	36 ± 2^{c}	107 ± 0^{bA}	105 ± 6^{bB}	125 ± 3^{aAB}	36 ± 2^{c}	110 ± 10^{bA}	141 ± 4^{abA}	163 ± 23^{aA}
		S	127 ± 10^{a}	182 ± 64^{aA}	159 ± 0^{aC}	181 ± 20^{aB}	127 ± 10^{c}	163 ± 15^{bcA}	205 ± 13^{abB}	243 ± 40^{aB}	127 ± 10^{d}	199 ± 7^{cA}	240 ± 7^{bA}	337 ± 9^{aA}
	Phenylalanine	**N**	41 ± 3^{c}	52 ± 0^{cC}	180 ± 6^{bC}	206 ± 6^{aC}	41 ± 3^{d}	210 ± 4^{cB}	322 ± 11^{bB}	411 ± 8^{aB}	41 ± 3^{d}	366 ± 8^{cA}	635 ± 12^{bA}	733 ± 42^{aA}
		S	337 ± 27^{b}	458 ± 89^{abB}	462 ± 0^{abC}	552 ± 13^{aC}	337 ± 27^{d}	574 ± 35^{cB}	801 ± 18^{bB}	1020 ± 81^{aA}	337 ± 27^{d}	794 ± 28^{cA}	1053 ± 1^{bA}	1325 ± 7^{aB}
Barley	**Histidin**	**N**	106 ± 3^{b}	130 ± 13^{aA}	122 ± 6^{abA}	128 ± 6^{abB}	106 ± 3^{b}	140 ± 19^{aA}	122 ± 2^{abA}	123 ± 2^{abB}	106 ± 3^{c}	124 ± 1^{bcA}	139 ± 9^{bA}	166 ± 16^{aA}
		S	236 ± 35^{a}	235 ± 11^{aA}	263 ± 29^{aA}	259 ± 2^{aB}	236 ± 35^{a}	198 ± 60^{aA}	266 ± 12^{aA}	271 ± 9^{aB}	236 ± 35^{c}	262 ± 9^{bcA}	330 ± 30^{bA}	419 ± 25^{aA}
	Phenylalanine	**N**	147 ± 3^{b}	209 ± 26^{aB}	194 ± 6^{aC}	233 ± 7^{aC}	147 ± 3^{d}	239 ± 4^{cB}	289 ± 29^{bB}	341 ± 8^{aB}	147 ± 3^{d}	361 ± 5^{cA}	495 ± 1^{bA}	611 ± 20^{aA}
		S	742 ± 58^{c}	857 ± 47^{bcC}	1006 ± 67^{abC}	1153 ± 89^{aB}	742 ± 58^{c}	1020 ± 74^{bB}	1276 ± 58^{aA}	1301 ± 38^{aB}	742 ± 58^{d}	1291 ± 1^{cA}	1534 ± 19^{bB}	1739 ± 94^{aA}
Rye	**Histidin**	**N**	69 ± 5^{b}	65 ± 0^{bB}	71 ± 1^{bB}	88 ± 8^{aB}	69 ± 5^{b}	89 ± 16^{abAB}	94 ± 8^{abB}	111 ± 14^{aB}	69 ± 5^{d}	121 ± 14^{cA}	173 ± 30^{bA}	230 ± 1^{aA}
		S	215 ± 7^{b}	252 ± 15^{abA}	273 ± 19^{aA}	299 ± 24^{aA}	215 ± 7^{b}	274 ± 20^{aA}	271 ± 0^{aA}	297 ± 19^{aA}	215 ± 7^{a}	286 ± 44^{aA}	324 ± 76^{aA}	337 ± 43^{aA}
	Phenylalanine	**N**	185 ± 11^{c}	217 ± 30^{bcC}	252 ± 9^{bC}	315 ± 6^{aC}	185 ± 11^{d}	321 ± 21^{cB}	431 ± 8^{bB}	533 ± 40^{aB}	185 ± 11^{d}	525 ± 36^{cA}	761 ± 60^{bA}	870 ± 14^{aA}
		S	875 ± 1^{c}	962 ± 74^{bcC}	1072 ± 35^{abC}	1162 ± 27^{aC}	875 ± 1^{d}	1213 ± 8^{cB}	1332 ± 29^{bB}	1440 ± 53^{aB}	875 ± 1^{c}	1560 ± 10^{bA}	1649 ± 123^{abA}	1809 ± 57^{aA}

Table 30. Changes in the histidine and phenylalanine concentrations (mg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains **(continue)**

Oat	**Histidin**	**N**	143 ± 10^{a}	160 ± 0^{aA}	143 ± 8^{aB}	157 ± 5^{aB}	143 ± 10^{a}	138 ± 4^{aB}	141 ± 4^{aB}	147 ± 0^{aB}	143 ± 10^{c}	168 ± 9^{bcA}	192 ± 16^{bA}	237 ± 15^{aA}
		S	100 ± 0^{c}	126 ± 0^{bB}	163 ± 3^{aB}	161 ± 18^{aB}	100 ± 0^{b}	173 ± 4^{aA}	162 ± 7^{aB}	177 ± 12^{aB}	100 ± 0^{d}	181 ± 5^{cA}	212 ± 3^{bA}	245 ± 7^{aA}
	Phenylalanine	**N**	310 ± 12^{c}	375 ± 0^{bC}	424 ± 28^{bC}	483 ± 18^{aC}	310 ± 12^{d}	495 ± 11^{cB}	594 ± 1^{bB}	729 ± 4^{aB}	310 ± 12^{d}	742 ± 25^{cA}	1038 ± 53^{bA}	1288 ± 18^{aA}
		S	273 ± 6^{d}	379 ± 4^{cC}	452 ± 2^{bC}	471 ± 9^{aC}	273 ± 6^{d}	499 ± 3^{cB}	602 ± 12^{bB}	741 ± 51^{aB}	273 ± 6^{d}	680 ± 22^{cA}	921 ± 4^{bA}	1154 ± 43^{aA}
Einkorn	**Histidin**	**N**	54 ± 1^{b}	77 ± 9^{aA}	89 ± 7^{aB}	94 ± 3^{aB}	54 ± 1^{c}	75 ± 6^{bA}	80 ± 5^{bB}	100 ± 6^{aB}	54 ± 1^{c}	98 ± 10^{bcA}	142 ± 7^{abA}	187 ± 36^{aA}
		S	179 ± 3^{b}	205 ± 15^{bB}	260 ± 21^{aB}	256 ± 12^{aB}	179 ± 3^{c}	239 ± 13^{bB}	261 ± 15^{abB}	302 ± 30^{aB}	179 ± 3^{c}	296 ± 2^{bA}	436 ± 33^{aA}	433 ± 20^{aA}
	Phenylalanine	**N**	148 ± 3^{c}	264 ± 32^{bB}	315 ± 31^{abC}	347 ± 11^{a}	148 ± 3^{dC}	329 ± 0^{cB}	441 ± 13^{bB}	534 ± 8^{a}	148 ± 3^{cB}	531 ± 48^{bA}	752 ± 33^{aA}	885 ± 88^{aA}
		S	814 ± 15^{c}	976 ± 15^{cC}	1287 ± 114^{bC}	1491 ± 57^{aC}	814 ± 15^{c}	1705 ± 93^{bB}	2052 ± 45^{aB}	2102 ± 54^{aB}	814 ± 15^{d}	2248 ± 51^{cA}	2513 ± 44^{bA}	2647 ± 6^{aA}
Buckwheat	**Histidin**	**N**	74 ± 1^{b}	91 ± 1^{bC}	110 ± 9^{aB}	122 ± 10^{aB}	74 ± 1^{c}	108 ± 5^{bB}	138 ± 9^{abAB}	154 ± 21^{aB}	74 ± 1^{c}	166 ± 1^{bA}	183 ± 24^{bA}	223 ± 12^{aA}
		S	154 ± 5^{c}	190 ± 15^{bA}	197 ± 3^{abB}	219 ± 12^{aB}	154 ± 5^{c}	212 ± 0^{aA}	201 ± 3^{bB}	199 ± 2^{bB}	154 ± 5^{c}	216 ± 18^{bA}	266 ± 14^{aA}	260 ± 17^{aA}
	Phenylalanine	**N**	191 ± 10^{d}	254 ± 9^{cC}	317 ± 17^{bC}	361 ± 18^{aC}	191 ± 10^{d}	391 ± 5^{cB}	519 ± 7^{bB}	616 ± 40^{aB}	191 ± 10^{d}	609 ± 6^{cA}	869 ± 36^{bA}	1092 ± 7^{aA}
		S	294 ± 11^{d}	413 ± 7^{cC}	473 ± 6^{bC}	574 ± 37^{aC}	294 ± 11^{d}	598 ± 19^{cB}	727 ± 7^{bB}	804 ± 12^{aB}	294 ± 11^{d}	820 ± 20^{cA}	1128 ± 24^{bA}	1285 ± 27^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of histidine and phenylalanine derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of histidine and phenylalanine derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 31. Changes in the biogenic amines concentrations (µg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains

T (°C)			20				30				40			
t (h)			0	1	2	3	0	1	2	3	0	1	2	3
Wheat	**Histamine**	**N**	10618,5 ±1420,5^{a}	9080,2 ±1752,9^{aA}	7636,1 ±2971,6^{aA}	8465,5 ±1213,7^{aA}	10618,5 ±1420,5^{a}	9472,6 ±386^{aA}	6862,9 ±1686,9^{aA}	7533,3 ±1627,7^{aA}	10618,5 ±1420,5^{a}	9414,1 ±489,1^{aA}	6221,9 ±2586,5^{aA}	9613,9 ±516,5^{aA}
		S	40013,3± 105,6^{a}	44146,3± 4625,3^{aA}	38081,1± 491,7^{aA}	36470,4± 392,9^{aA}	40013,3± 105,6^{a}	36739± 515,9^{aA}	21241,3± 9322,1^{aA}	34998,9± 633,8^{aA}	40013,3± 105,6^{a}	36587,7 ± 392,8^{bA}	33923,2 ± 1276,2^{bA}	29023,2± 618^{cB}
	Phenylethyl amine	**N**	36,6±0,4^{a}	41±3,4^{aA}	40,5±2,7^{aA}	44,2±2,6^{aA}	36,6±0,4^{a}	38,4±3,4^{aA}	36,3±2,6^{aA}	37,9±2,8^{aA}	36,6±0,4^{b}	38,7±0,3^{abA}	41,9±4,2^{abA}	46,3±0,9^{aA}
		S	10,1±0,9^{b}	14,3±1,4^{abA}	15,5±0,2^{aA}	16,6±1,6^{aB}	10,1±0,9^{a}	17±0,9^{aA}	10,4±8^{aA}	17,2±2,4^{aAB}	10,1±0,9^{d}	17,1±1,1^{cA}	21±0,4^{bA}	24,5±0,4^{aA}
Barley	**Histamine**	**N**	1213,5± 0,5^{b}	1216,5± 0,5^{aA}	1212± 1,1^{bcA}	1210,2± 0,6^{cA}	1213,5 ± 0,5^{a}	1216,4± 0,6^{aA}	1215± 1,6^{aA}	1213,6± 0,8^{aA}	1213,5 ± 0,5^{a}	1213,9± 1,7^{aA}	1215± 3,5^{aaA}	1210,5±3,1^{aA}
		S	1227,3±2,5^{a}	1225,3± 0,3^{aA}	1230,3± 0,1^{aA}	1217,9± 7,9^{aA}	1227,3 ± 2,5^{ab}	1229,4± 0,1^{aA}	1222,9± 1,4^{bB}	1226,1 ±0,3^{abA}	1227,3 ± 2,5^{a}	1224,2± 2,2^{aA}	1225,6± 1,7^{aAB}	1228,4±4,8^{aA}
	Phenylethyl amine	**N**	11±0,5^{a}	11,2±0,4^{aA}	11±0,1^{aB}	10,7±0,3^{aA}	11±0,5^{a}	11±0,2^{aA}	11,2±0,1^{aB}	11,1±0,4^{aA}	11±0,5^{b}	11,8±0,2^{bA}	14,2±0,1^{aA}	12,8±0,8^{abA}
		S	34±1,4^{a}	35,7±0,9^{aA}	32±1^{aA}	34,6±2^{aA}	34±1,4^{a}	33,8±0,9^{aA}	30,8±0,7^{aA}	30,2±0,8^{aA}	34±1,4^{a}	31,4±2,2^{aA}	31,3±0,7^{aA}	30,9±0^{aA}
Rye	**Histamine**	**N**	379,2± 34,2^{a}	348,8±5,4^{aA}	445,4± 116,4^{aA}	336,3± 11,1^{aA}	379,2± 34,2^{a}	329,5±6,2^{aA}	2139,3± 1811,2^{aA}	335,5± 16,2^{aA}	379,2± 34,2^{a}	356,8± 18,6^{aA}	419,6± 89,7^{aA}	365,8± 41,6^{aA}
		S	9779± 222,5^{a}	9862,7± 138,8^{aA}	10266,9± 55,3^{aA}	9656,1± 564,5^{aA}	9779± 222,5^{a}	9604,8± 340,1^{aA}	9367,6± 70,4^{aB}	6609,1± 43,7^{bB}	9779± 222,5^{a}	7256,7± 125,9^{bB}	6338,9± 3,1^{cC}	6056,5± 161,9^{cB}
	Phenylethyl amine	**N**	49,5±1,3^{a}	43±0,9^{aB}	49,6±3,1^{aB}	44±0,5^{aB}	49,5±1,3^{a}	47,4±0,6^{abA}	48,1±0,8^{abB}	43,1±2,3^{bB}	49,5±1,3^{b}	50,8±1,1^{bA}	70,8±0,6^{aA}	52,8±0,4^{bA}
		S	75,4±2,5^{a}	119,7±9,6^{aA}	178,2±57,9^{aA}	136,3±18,4^{aA}	75,4±2,5^{b}	98,1±12,5^{abA}	111,4±0,9^{aA}	105,6±3,4^{aAB}	75,4±2,5^{a}	79,4±5^{aA}	66,1±1,5^{aA}	72,2±4,4^{aB}

Table 31. Changes in the biogenic amines concentrations (μg/kg dw) during commercial yeast fermentation of native (N) and sprouted (S) grains. **(continue)**

Oat	**Histamine**	**N**	417,1±3,9^{a}	412,9±2,1^{aA}	413,8±0,3^{aA}	413,1±4,8^{aA}	417,1±3,9^{a}	414,3±0,2^{aA}	413±3,8^{aA}	416,6±0,6^{aA}	417,1±3,9^{a}	414±5,7^{aA}	418,4±3^{aA}	734,6±318,7^{aA}
		S	447,1±6,6^{a}	438,8±11,2^{aA}	440,2±6,6^{aA}	447,1±3,9^{aA}	447,1±6,6^{a}	431,4±7,9^{aA}	430,1±17,5^{aA}	445±1,2^{aA}	447,1±6,6^{a}	443,1±0,1^{aA}	440,6±2,6^{aA}	441,3±0,8^{aA}
	Phenylethyl amine	**N**	112±0,1^{c}	127,4±3^{bA}	141±2,5^{aA}	145,7±2,9^{aA}	112±0,1^{b}	139,8±1,2^{aA}	140,3±0,7^{aA}	152,1±6,4^{aA}	112±0,1^{b}	145,4±10,8^{aA}	145±0,9^{aA}	149±1,9^{aA}
		S	10,1±0,2^{a}	11±1^{aA}	10,7±1^{aB}	12,3±0^{aB}	10,1±0,2^{a}	13,8±1,4^{aA}	13,2±2^{aB}	16,2±3,1^{aB}	10,1±0,2^{c}	15,6±0,6^{bcA}	25,2±3,1^{abA}	37±5,7^{aA}
Einkorn	**Histamine**	**N**	504,8±0,6^{a}	502,2±1,2^{aB}	503,7±0,9^{aB}	503±0,3^{aA}	504,8±0,6^{a}	503,9±0,1^{aAB}	504,7±0,8^{aB}	503,1±2,6^{a}	504,8±0,6^{b}	508±1,4^{abA}	509,2±0,3^{aA}	508,5±1,2^{abA}
		S	541,8±0,9^{a}	542,6±3,9^{aA}	541,4±1,5^{aA}	537,4±0,8^{aA}	541,8±0,9^{a}	538,7±1,4^{aA}	539,3±0,1^{aA}	540,8±3^{aA}	541,8±0,9^{a}	537,8±1,8^{abA}	536,2±1,4^{bA}	533,6±0^{bA}
	Phenylethyl amine	**N**	363,1±31,5^{a}	347,1±7,5^{aB}	353,1±32,4^{aB}	341,5±1,2^{aB}	363,1±31,5^{b}	342,9±14,7^{bB}	387,2±8,2^{abB}	439,4±2,4^{aB}	363,1±31,5^{b}	484,6±29,8^{abA}	551,7±10,4^{aA}	619,7±61,3^{aA}
		S	31,5±4,4^{b}	45,3±6,6^{abA}	45,8±2,7^{abB}	52,6±5,9^{aB}	31,5±4,4^{b}	41,4±1,1^{abA}	52,5±9,7^{abB}	60,8±0,1^{aB}	31,5±4,4^{c}	57±1,2^{bA}	82,8±1,3^{aA}	80,4±1,5^{aA}
Buckwheat	**Histamine**	**N**	461,5±0,6^{a}	465,1±5,5^{aA}	463,3±3,7^{aA}	459,9±0,9^{aA}	461,5±0,6^{a}	459,8±1,3^{aA}	459,7±0,8^{aA}	459±0,3^{aA}	461,5±0,6^{a}	468,4±8,8^{aA}	459,6±0^{aA}	460,7±1,6^{aA}
		S	469±2,4^{a}	461,5±1,8^{bA}	460±1,2^{bA}	460,9±0,7^{bA}	469±2,4^{a}	459,6±0,9^{bA}	460,1±0,2^{bA}	462,9±3,4^{abA}	469±2,4^{a}	459,9±1,4^{bA}	460±0,1^{bA}	458,4±0,5^{bA}
	Phenylethyla mine	**N**	136±1,5^{a}	141,8±13,4^{aA}	151±7,5^{aA}	148,6±3,8^{aA}	136±1,5^{a}	121,3±9,7^{aA}	136,7±19,8^{aA}	126,5±2,7^{aB}	136±1,5^{a}	106,2±9,5^{bA}	110,5±7,6^{bA}	100,4±3,3^{bC}
		S	80,2±1,1^{a}	87,3±0,1^{aA}	78,7±5^{aA}	89,4±2,4^{aA}	80,2±1,1^{a}	83,5±2,9^{aA}	86,9±1,3^{aA}	85,7±0,6^{aA}	80,2±1,1^{a}	77,6±3,1^{aA}	73,2±1,6^{aA}	78,9±0,2^{aB}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of biogenic amines derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of biogenic amines derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time.

Table 32. Changes in the biogenic amines concentrations (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains

T (°C)			10				20				30			
t (h)			0	12	24	36	0	12	24	36	0	12	24	36
Wheat	Histamine	N	8242,7± 3735,9^{a}	8668,9± 935,6^{aA}	8545,9± 247,3^{aA}	6248,1± 403,6^{aA}	8242,7± 3735,9^{a}	6112± 1004,5^{aA}	6535,3± 250,2^{aB}	5716,9± 252,1^{aA}	8242,7± 3735,9^{a}	6158,3± 710,1^{aA}	5669,6± 434,2^{aB}	5907,4± 1092,8^{aA}
		S	32364,2 ± 1094,5^{a}	23857,6 ± 1257,3^{bA}	21948,9 ± 1271,4^{bA}	22443,6 ± 57^{bA}	32364,2 ± 1094,5^{a}	22382,5 ± 288,8^{bA}	22516,6 ± 914,9^{bA}	20742,6 ± 722,7^{bAB}	32364,2 ± 1094,5^{a}	21739,8 ± 509,3^{bA}	20069,8 ± 261,1^{bA}	19382,6 ± 797,6^{bB}
	Phenylethyl amine	N	98,8± 3,1^{c}	149,5± 1,7^{bC}	179,8± 3,9^{aC}	187,9± 4,2^{aC}	98,8± 3,1^{d}	183,7± 2,1^{cB}	531,1± 9,3^{bB}	931± 5,1^{aB}	98,8± 3,1^{d}	592,2± 11,9^{cA}	1205,7± 42^{bA}	1713,4± 30,5^{aA}
		S	78,4± 1,8^{c}	88,1± 0,4^{bcC}	94,8± 4,5^{abC}	102,6± 1,9^{aC}	78,4± 1,8^{d}	493,9± 4,1^{cB}	973± 6,6^{bB}	1050,9± 0,4^{aA}	78,4± 1,8^{d}	1274± 10,6^{aA}	1216,6± 12,2^{bA}	661,2± 13,4^{cB}
Barley	Histamine	N	351,8± 2,3^{a}	348,3± 0,5^{abA}	345,6± 0,8^{bcA}	342,4± 1,4^{cA}	351,8± 2,3^{a}	346,2± 1,6^{abA}	345,6± 0,9^{abA}	343,1± 1,9^{bA}	351,8± 2,3^{a}	348,2± 4^{aA}	343,6± 0,3^{aA}	344,6± 1,8^{aA}
		S	355,6± 3,7^{a}	348,7± 0,4^{aB}	348,2± 1,1^{aA}	370,9± 15^{aA}	355,6± 3,7^{a}	355,1± 1,5^{aA}	351,8± 1,5^{aA}	351,3± 0,3^{aA}	355,6± 3,7^{a}	350± 0,4^{abB}	351,3± 0,9^{abA}	347,8± 0,3^{bA}
	Phenylethyl amine	N	103,4± 16,8^{a}	112,2± 5,9^{aC}	99,6± 7^{aC}	120,4± 0,9^{aC}	103,4± 16,8^{c}	162,1± 6,7^{cB}	629,7± 42,2^{bB}	1064,8± 25^{aB}	103,4± 16,8^{d}	1095,4± 15,7^{cA}	2051,5± 47,3^{bA}	2515,5± 189,6^{aA}
		S	112,4± 6,8^{b}	127,7± 6^{abC}	132,4± 2,9^{abC}	137,5± 6^{aC}	112,4± 6,8^{d}	652± 56^{cB}	2480,9± 52,7^{bB}	3503± 92,8^{aB}	112,4± 6,8^{c}	2974,7± 29^{bA}	3291,2± 290,5^{abA}	3857,2± 2,2^{aA}
Rye	Histamine	N	199,3± 8,3^{a}	170,3± 3,9^{bA}	180± 2,5^{bA}	173,2± 0,3^{bA}	199,3± 8,3^{a}	181,6± 1,9^{abA}	179,5± 3,6^{bA}	177,9± 2,6^{bA}	199,3± 8,3^{a}	176,5± 4^{aA}	173 ±2,2^{aA}	2957,6± 2790^{aA}
		S	5665,1± 362,6^{a}	5588,2± 35,8^{aA}	5314,7± 130,8^{aA}	5152,5± 15,1^{aA}	5665,1± 362,6^{a}	4879,1± 134,5^{bB}	4467,3± 40,5^{bB}	4463,7± 59,3^{bB}	5665,1± 362,6^{a}	4436± 198,6^{bB}	3972,9± 134,7^{bB}	4051± 1^{bC}
	Phenylethyl amine	N	103,2± 7^{a}	92,6± 3,6^{aB}	121,1± 6,2^{aB}	128,6± 15,9^{aA}	103,2± 7^{c}	357,3± 199,5^{bcAB}	767,6± 191,6^{abB}	1026,4± 85^{aA}	103,2± 7^{a}	1593± 526,1^{aA}	2389,3± 229,9^{aA}	1470,6± 1295,5^{aA}
		S	138,6± 6,8^{b}	164,5± 22,4^{abB}	193,9± 2,2^{abC}	260,1± 54,7^{aC}	138,6± 6,8^{b}	634,7± 346^{abB}	1156,6± 310,1^{aB}	1590± 145,4^{aB}	138,6± 6,8^{b}	2041,6± 255,8^{aA}	2245,4± 20^{aA}	2209,1± 0,9^{aA}

Table 32. Changes in the biogenic amines concentrations (μg/kg dw) during sourdough fermentation of native (N) and sprouted (S) grains **(continue)**

Oat	**Histamine**	**N**	448,1±1,4^{a}	436,5±8,5^{abA}	422,2±0,5^{bA}	424,1±1,7^{bA}	448,1±1,4^{a}	421,2±4,9^{bA}	423,9±2,7^{bA}	421,8±1,2^{bA}	448,1±1,4^{a}	425,3±1^{bA}	424,3±1,7^{bA}	422,6±0,9^{bA}
		S	417±2,3^{b}	416,5±5,5^{bB}	443,9±3,9^{aA}	439±8,8^{abA}	417±2,3^{b}	454±5,3^{aA}	447,8±2,3^{aA}	444,2±0,4^{aA}	417±2,3^{b}	448±1^{aA}	441,5±6^{aA}	444,7±0,3^{aA}
	Phenylethylamine	**N**	63,2±3,9^{c}	77,7±0,2^{cC}	358±9,1^{bC}	410,8±3,2^{aB}	63,2±3,9^{d}	655,3±10,6^{cB}	1206,8±10,6^{bB}	1442,2±118,6^{aA}	63,2±3,9^{c}	1382,6±3,3^{bA}	1528,2±47^{abA}	1628,6±61,4^{aA}
		S	184±1,5^{b}	275,3±8^{aC}	111,7±3,6^{dC}	144,3±2^{cB}	184±1,5^{d}	445,2±2,3^{cB}	870±0,6^{bB}	1058±48,9^{aA}	184±1,5^{b}	1114,9±25,5^{aA}	1225,6±34,2^{aA}	1105,1±161,8^{aA}
Einkorn	**Histamine**	**N**	502,2±0,4^{a}	500,1±1,5^{abA}	497,4±0,4^{bAB}	497,3±0^{bA}	502,2±0,4^{a}	494,2±0,8^{bB}	495,3±1^{bB}	496,4±2,7^{abA}	502,2±0,4^{a}	496,6±1^{aAB}	499,2±0,3^{aA}	496,7±3,3^{aA}
		S	525,2±1,4^{a}	526,6±3,8^{aA}	522±0,9^{aA}	519±0,9^{aA}	525,2±1,4^{a}	517,6±2,9^{bAB}	513±0,8^{bcB}	508,6±1,4^{cB}	525,2±1,4^{a}	512,4±0,2^{bB}	503,9±1,8^{cC}	501,9±0,3^{cC}
	Phenylethylamine	**N**	216,6±8,8^{c}	428±34,3^{bB}	478,1±18,1^{abC}	525,1±13,4^{aC}	216,6±8,8^{d}	548,5±18,4^{cB}	1041,6±14,6^{bB}	1369,4±2,4^{aB}	216,6±8,8^{d}	1085±45,8^{cA}	1558,6±3,7^{bA}	1770,3±9,3^{aA}
		S	109,7±1,2^{b}	124,3±7,8^{bC}	147,4±2,8^{aC}	164,4±2,5^{aC}	109,7±1,2^{d}	665,9±2,8^{cB}	1610,8±17^{bA}	1891,4±4,4^{aA}	109,7±1,2^{d}	1869,8±3,1^{aA}	1429,5±6,2^{bB}	1390,9±13,9^{cB}
Buckwheat	**Histamine**	**N**	461,8±0,5^{a}	459,4±0,8^{bA}	458,5±0,6^{bA}	458,4±0,1^{bA}	461,8±0,5^{a}	458,3±0,8^{abA}	457,4±1,1^{bA}	457±0,6^{bA}	461,8±0,5^{a}	464,3±6^{aA}	457,8±0,9^{aA}	457,8±0,5^{aA}
		S	478,9±17,5^{a}	461,6±1,5^{aA}	460,4±0,4^{aA}	461,1±1,8^{aA}	478,9±17,5^{a}	459,1±0,4^{aA}	459,1±0,9^{aA}	459,2±0,5^{aA}	478,9±17,5^{a}	458±0,3^{aA}	459,3±1^{aA}	458,7±0,1^{aA}
	Phenylethylamine	**N**	110±2,3^{a}	129,1±2,4^{bcC}	145,9±2,3^{abC}	159,3±9^{aC}	110±2,3^{d}	393,2±2,4^{cB}	1212,6±0,2^{bB}	2292±32,7^{aB}	110±2,3^{d}	1243,2±47^{cA}	2206,3±26,2^{bA}	3133,7±161,6^{aA}
		S	110,3±6,4^{b}	111,2±0,5^{bC}	125,1±1^{bC}	154,3±4,4^{aC}	110,3±6,4^{d}	591,8±1,5^{cB}	1000,5±7,5^{bB}	1353,4±72,5^{aB}	110,3±6,4^{d}	1440,1±19,1^{cA}	1572±40,3^{bA}	1675,5±22,6^{aA}

* Lower case letters in superscripts indicate the statistical significance of the difference in the concentrations of biogenic amines derivatives (either for sprouted or native grains) according to the fermentation time at a certain temperature. Upper case letters in superscripts indicate the statistical significance of the difference in the concentrations of biogenic amines derivatives (either for sprouted or native grains), according to the fermentation temperature at a certain time

5. CONCLUSION

In this study, it was observed that the concentration of total phenolic compounds generally did not change with the combination of sprouting and fermentation, while the concentration of free phenolic substances increased. As mentioned in the results part, although the applications caused the cell wall of the grains to be destroyed and thus the free phenolic substances to increase, there was not much difference in the total amount since the phenolic compounds, which are in a dynamic system, are degraded on the one hand and formed on the other. For the same reason, no difference was observed in antioxidant activity in general.

From the results obtained in this study, it has been observed that amino acid concentrations generally increased with sprouting due to the increased proteolytic activity. It has been understood that tyrosine, one of the amino acids whose amount increases due to the increased proteolytic activity during sprouting, is metabolized by microorganisms participating in fermentation. In this context, it has been observed for the first time that the combined application of sprouting and sourdough fermentation on cereals has a synergetic effect in terms of the formation of tyrosine derivative compounds. The results showed that sourdough fermentation along with sprouting significantly increased the formation of tyramine, L-DOPA, and dopamine. The amount of dopamine in native barley, native wheat, and sprouted buckwheat with sourdough fermentation at 30 °C in 36 hours are 6.1, 5.8, and 5.3 mg/kg, respectively, comparable to the dopamine level in bananas (6.4 mg/kg) [1]. This increase is valuable to the industry, as the amount of L-DOPA and dopamine naturally found in grains is limited. Because the positive health effects mentioned in the literature will come directly thanks to the increase obtained without extra supplements. It can be recommended to be consumed by experts with its positive effect on some diseases and positive effects on mood control. In future studies, the mechanism behind the synergistic effect of sprouting and sourdough fermentation can be investigated. Thus, increasing concentrations can be carried to even higher points.

Bioactive compounds occurred from tyrosine become significant with the combined application of sprouting and sourdough fermentation, while bioactive compounds occurred from tryptophan become especially significant without sprouting. The reason for this is thought to be the decarboxylase activity that occurs with sprouting. In addition, it was observed that commercial yeast fermentation played an important role in increasing the concentration of kynurenic acid, rather than sourdough fermentation. Because of the yeast activity, kynurenine and kynurenic acid (compounds containing carboxyl groups) occurred from tryptophan are not formed by fermentation after sprouting and the amount of biogenic amines increases. Due to thier known antioxidant activity, consuming cereals fermented with commercial yeast will also be beneficial for health, as the concentration of kynurenic acid will increase. In this part of the study, sprouted grains were freeze-dried. Based on the difference in the production of diastatic and non-diastatic malt flour, it has been predicted that tryptophan derivatives can be obtained from sprouted flours by fermentation when the sprouted grains are subjected to commercial drying by heat treatment and enzymes are deactivated.

When the native and sprouted wholemeals and the initial conditions of fermentations were compared, it was seen that commercial yeast and sourdough contain biogenic amines. The biogenic amine concentration in the structure of yeasts may be due to the presence of too many precursors in their structures. Precursors can rapidly convert to biogenic amines when exposed to favorable environmental conditions. However, no difference was observed during the commercial yeast fermentation. In addition, although a decrease was observed especially in histamine concentration during sourdough fermentation, the concentration of phenylethylamine increased.

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