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Abstract

The major output of milling process of wheat grains is flour, bran represents the most important fraction of all by-products. Its content in fibres and micro-nutrients makes its enrichment interesting in breads and cereals products if no unfavourable changes in the sensorial properties are induced. In this research, we proposed to compare the volatile components of flour, fine and coarse brans to evaluate the potential impact of addition of bran in flour. The three fractions were obtained by using a micro-mill and the aromatic profile was characterized by GC-MS after SPME extraction. Numerous compounds due to lipid oxidation such as hexanal, 1-octen-3ol, nonanal, 2-heptanone were found in the three fractions. Limonene, a terpenic compound, characterized by sweet, citrus and peely odour was identified in the three fractions. This unexpected compound was already identified in flour. Eugenol, a phenolic compound, with spicy, clove like, woody odour and phenolic savour was only identified in the brans fraction. This compound is formed via the general phenylpropanoid pathway, including the conversion of coniferyl alcohol and specific enzyme. It could provide a specific marker of bran addition in flour.

Keywords: aroma profile, bran, flour, marker, SPME, wheat

Introduction

Wheat grain is an indehiscent dry fruit consisting of a single seed intimately welded to different envelopes or layers. The seed was constituted of the starchy endosperm and the aleurone layer, embryonic axis and the scutellum and the nucellar epidermis and the testa. Each of these tissues has a particular structure and composition [1]. The milling process has for aim to recover the major part of the starchy endosperm into flour, a rich source of starch and proteins that is used to make cereal-based foods products. The flour extraction rate varies classically between 70 and 77%. Other fractions obtained by milling are coarse, fine brans and shorts. Wheat bran is composed with the pericarp, testa, hyaline and aleurone layer but also contains part of the peripheral starchy endosperm. Bran represents the most important fraction of overall by-products accounting for around 15-25% of the grain weight. It contains dietary fibres (45-55%), proteins (13-18%), minerals (ash 3.4-8%), lipids (3-4%) and micro-nutrients as antioxidant component and therefore its addition could improve breads and cereals products nutritional values if potential contaminants (heavy metals, pesticides, mycotoxins) are carefully checked and conform to the prevailing legislation limits [2]. However, bran addition in the consumable products can also induce changes in the sensorial properties such as texture of the dough or undesirable taste and flavour. In this research, we proposed to compare the volatile components of flour, fine and coarse brans to evaluate the potential impact of addition of bran in flour. Indeed, if the volatile compounds of flour have already been identified, few data exist about the volatile compounds present in the brans fractions after milling.

Experimental

Materials

Common wheat (*Triticum aestivum* L.) grown in organic conditions was purchased from Salvagnac Agribio Union (Salvagnac, France).

Milling

The wheat grains were tempered to reach 16.5 % (w/w) of moisture content. A micro-mill was used to simulate the industrial milling process. The process of milling is divided in four steps including two breaking stages, one sizing and one reduction stage leading to 4 fractions; flour, fine bran, coarse bran and shorts. Each step consisted of a size reduction phase and a sieving phase. For the last two phases, the flour obtained after milling was processed with a bran finisher (CHOPIN S.A) for 1.5 min. The total flour obtained corresponds to an extraction rate higher than 70%.

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Extraction and analysis

Headspace Solid Phase Micro-Extraction (HS-SPME) was used to analyse the different fractions obtained after milling. Samples of 0.5 g were deposited in 20 ml vial. For semi-quantification, 5 µl of internal standard solution was added (0.2 g/l of 2-heptanol in distilled water). Each sample was pre-incubated for 5 min at 50°C and extracted during 30 min at 50°C using fibre (30/50 µm DVB/CAR/PDMS, stableflex 2 cm 23 Ga).The desorption was carried out for 5 min at 250°C in the automatic Combipal injector. Between each measurement the fibre was baked-out for 30 min at 270°C.

GC-MS ISQ (ThermoScientific, Austin, Texas, USA) equipped with a DB-WAX polar capillary column (30 m, 0.25 mm i.d. x 0.25 µm of thickness) and a quadrupole detector was used for identification. Helium was used as carrier gas with a flow rate of 1.2 ml/min. The oven temperature was kept at 40°C for 5 min and programmed to 250 °C at a rate of 2°C/min. Spectra were obtained in the electron impact mode with 70 eV. The full scan mode was used, and the range of scans was between 40-500 amu. Compounds were identified by using different libraries (INRA, NIST, Wiley) and linear retention indices calculation.

Results and discussion

First, it is important to highlight that the HS-SPME method allowed to well extract the most volatile compounds compared to liquid-liquid extraction (data not shown).

Numerous compounds due to lipid oxidation such as 1-pentanol, hexanol, 1-octen-3-ol, 2-heptanone, hexanal and nonanal were present in the 3 fractions (Table 1) but in different rather high amounts.

Table 1: Aroma compounds of wheat grains milling fractions and their semi-quantification estimated using 2-heptanol as internal standard.

Aroma Compound (mg/kg dry basis)	**LRI**	**Flour**	**Fine bran**	**Coarse bran**	**Odour quality[a]**
Hexanal	1106	0.094± 0.003	0.057±0.009	0.093±0.009	Fresh green
2-Heptanone	1220	0.110±0.075	0.64±0.09	1.37±0.20	Cheese,fruity,
(*R*)-Limonene	1227	0.504±0.135	4.93±0.55	4.64±0.44	Citrus, peely
3-Methyl-1-Butanol	1254	ND	ND	0.127±0.004	Pleasant, fruity, brandy
2-Pentyl-furan	1263	ND	0.679±0.027	0.427±0.015	Beany, nut
1-Pentanol	1288	0.086±0.028	0.057±0.020	ND	Pungent, bready
1-Hexanol	1388	0.441±0.063	0.905±0.039	0.936±0.033	Pungent, fruity
Nonanal	1417	0.262±0.079	0.035±0.006	0.017±0.003	Aldehydic, citrus
Acetic Acid	1481	0.049±0.005	0.090±0.004	0.066±0.003	Sour, acetic
1-Octen-3-ol	1487	0.051±0.006	0.104±0.007	0.059±0.004	Earthy, fungal
2-Ethylhexanol	1525	0.089±0.012	ND	ND	Citrus fresh floral
Hexanoic Acid	1889	tr	0.156±0.009	0.087±0.005	Sour, fatty, cheese
Benzyl Alcohol	1919	0.052±0.009	0.051±0.007	ND	Sweet, floral, fruity
Eugenol	2229	ND	0.134±0.008	0.120±0.005	Spicy, clove like, wood
Total		**1.799±0.521**	**7.843±0.845**	**7.944±0.738**	

[a]All odour qualities collected at: http://www.thegoodscentscompany.com/. ND non detected

Quantitatively, the flour was less rich in volatile compounds (around to 2mg/kg dry basis) than fine and coarse brans (around 8mg/kg dry basis). As derived product of lipid represented the major part of volatiles components, it can be related to the lowest lipid content of flour compared to fine and coarse brans, 1.6, 5.3 and 4.7 %, respectively.

In the flour, the more represented compounds were limonene, 1-hexanol and nonanal followed by 2-heptanone. In the brans, limonene is clearly the major compound, but 1-hexanol and 2-heptanone were also identified. In general, the main contributors to the wheat flour aroma are the compounds derived from lipid peroxidation [3] and the amount of these compounds changed with the progress of reaction: the longer the time before analysis, the greater the risk of oxidation causing volatile profile modification. In their study Xu et al. [3] found that 1-hexanol was the major compound of the flour produced from common wheat grains followed by hexanal, and nonanal. Hexanol is produced by the action of alcohol dehydrogenase from hexanal. This latter is the main volatile product from the lipoxygenase activity and autoxidation degradation of linoleic acid. Nonanal is produced mostly from oleic acid and was strongly represented in flour. A high quantity of these compounds (aldehydes and alcohols) is an indication of major extend of lipid oxidation. In our fractions, their amounts remain relatively low suggesting a good preservation of the fractions.

2-Heptanone is formed by β-oxidation from octanoic acid in mitochondria of entire cell plants or by the action of fungi as Penicillium sp. Its higher presence in coarse brans could be due to the less intensive cell degradation. This hypothesis agrees with the presence of hexanoic acid, another product of β-oxidation of octanoic acid mainly in brans fractions.

2-Pentylfuran was only detected in brans but was not specific of these fractions because it has been already found in flour [3]; this component is formed via auto-oxidation of linoleic acid.

The strong amount of (R)-limonene specifically in the brans (50% of volatile compounds) was unexpected. However, limonene and other terpenes were evidenced in flour [3] and in derived product as bread. Their presence could be explained by the contamination by other plants which could be cropped with wheat grains. Limonene is also the major component of insecticide, fungicide and acaricide used in organic farming for vegetables. Then, a cross over contamination could be also evocated to explain the high amount of this compound in the flour and particularly in the bran fractions which are constituted to the more external layer of grains. It is important to highlight that the studied wheat was cultivated in organic conditions. Another hypothesis was the contamination by fungi able to produce terpene compounds.

In flour, three other compounds previously detected [3], were formed by other ways that lipid oxidation. Acetic acid can be a sign of natural grain contamination by acetic bacteria or other microorganisms. Benzyl-alcohol could occur from phenylalanine via benzaldehyde either by β-oxidative pathway and non-oxidative way. This compound was present in flour and in fine bran but not in coarse bran indicating potential difference in enzymes equipment or protein amount (e.g., more germ in fine than in coarse).

While the presence of 2-ethylhexanol has been already detected in flours, its origin requires further investigations. Indeed, it is known as an indoor air pollutant with human toxicity [4]. Its detection in flour only is surprising and could be problematic.

In bran fractions, two specific compounds were identified 3-methyl-1-butanol and eugenol. The former resulted from reduction of 3-methylbutanal which can be synthetized from leucine via Ehrlich pathway or Strecker degradation. The presence of alcohol indicates strong activity of alcohol-dehydrogenase [5]. The aldehyde and its corresponding alcohol were already identified in sourdough or bread and alcohol formation is considered as the result of yeast action.

Eugenol is a simple phenolic compound, formed via the general phenylpropanoid pathway, including the conversion of coniferyl alcohol and the action of specific enzymes [6]. The richness in lignin of bran suggested a possible deviation of the general way toward eugenol. It is possible that its formation is a defence mechanism due to pathogens attack. Other compounds like acetophenone and derived components have been found in brans (data not shown) with feruloyl-coA as a precursor and their presence was also described in a context of plant defence. The production of eugenol is positive because it shows antimicrobial activity against fungi (Fusarium, Penicillium or Aspergillus sp) contaminating wheat. Moreover, as this compound, is found only in bran, it can play the role of a marker of bran addition in flour.

Concerning the odour quality of compounds present in all fractions, the majority was characterized by green, vegetal aroma and are rather pleasant with the exception of acetic acid, 1-pentanol and 1-hexanol that are perceived as pungent. The presence of limonene can improve the sensorial attribute with citrus odour. The addition of bran in flour should not have a detrimental influence because numerous compounds are common to the flour and the two specific compounds have a pleasant odour. However, the oxidation reaction could be more important during storage in relation to the higher lipid content of brans and shelf life of product revaluated in functions of bran addition.

Conclusion

Numerous volatile compounds coming from lipid oxidation are present in all milling fractions. The amount of volatile components is higher in brans than in flour in relation to the strongest lipids content of bran. Limonene is found in great quantity, surpassing all the other components, in particular in brans. Its origin should be investigated. The specific bran compounds are pleasant and should positively impact flour sensory properties. Moreover, eugenol may provide a specific marker of bran addition into flour. Its presence or that of other phenylpropanoids need to be checked on a large number of samples.

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