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Relationship between volatile profile and sensory development of an oat-based biscuit

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ABSTRACT

The shelf-life of plain oatcakes and oatcakes containing a natural antioxidant (rosemary extract) was studied for 28 weeks. The biscuits were evaluated using several chemical analyses to determine oxidation (headspace analysis, free fatty acids profile, peroxide value and anisidine value), in addition to sensory testing. A selection of volatiles, including hexanal, were found to be positively correlated to three sensory parameters (aroma, flavour and aftertaste). These volatiles, responsible for the perception of off-flavour in oat biscuits, were predominantly secondary lipid breakdown products, primarily from the unsaturated fatty acids C18:1 and C18:2. The peroxide value was also found to be a useful tool to assess oxidation in oatcakes. The impact of the antioxidant was insufficient at the concentration tested to be used as a solution to prevent the development of off-flavour; however the antioxidant did appear to slow down the rancidity process.

1. Introduction

Rancidity is the development of characteristic, unpalatable odours and flavours following oxidative or hydrolytic oxidation of edible fats and oils. This process includes the oxidation of lipids, a common and undesirable chemical group of reactions that may impact upon flavour, aroma, nutritional and health beneficial properties, and in some cases the texture of a product (Zhou, Robards, Glennie-Holmes, & Helliwell, 1999). The key reactions involved in the mechanism of rancidity are the peroxidation of unsaturated fatty acids to form intermediate hydroperoxides from which more stable secondary products are subsequently derived (Heiniö, Oksman-Caldentey, Latva-Kala, Lehtinen, & Poutanen, 2001). Such compounds include alkanes, aldehydes, alkenes, alcohols, ketones and furans. Among these secondary products, hexanal is generally considered as a major volatile compound associated with rancidity (Zhou, Robards, Glennie-Holmes, & Helliwell, 2000) and measurement of its abundance can therefore be used to assess the extent of rancidity (García-Llatas, Lagarda, Romero, Abellán, & Farré, 2007).

Oat (*Avena sativa* L.), that has had no treatment following harvesting, does not have an appealing or satisfying flavour, it has an unpleasant, slightly bitter taste which can be overcome by an appropriate thermal process (Klensporf & Jeleń, 2008). In order to be deemed desirable for human consumption, this heat processing method includes stabilisation at high temperature to inactivate most of the enzymes, especially lipases, followed by kiln-drying for flavour development (Kent & Evers, 1994). It is when the grain is milled that the lipases, located in the pericarp of the oat, and the lipids, found in the starchy endosperm, come into contact, and that the hydrolysis of the triglycerides takes place to produce secondary products which can lead to detrimental aroma and flavour in oat-based products (Welch & McConnell, 2001).

One well-known product derived from oat is oatcake, which is a traditional Scottish food made of oatmeal and fat. In the product studied, the added fat was a mixture of palm oil and sunflower oil. In the presence of oxygen, with light and heat, the lipid components of these added oils can be a major source of off-flavours. Oat also contains lipids which can contribute to oxidation; indeed, between 3.1% and 11.6% of the total composition of oat grain is oil, depending on the variety (Leonova et al., 2008), and can be up to 18% in exceptional cases (Frey & Holland, 1999). During the storage of oat products, oxidation of unsaturated fatty acids, including oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids, is strongly related to rancid flavour development (Lehtinen & Kaukovirta-Norja, 2011). Oat lipids contain a high proportion of these specific fatty acids. Several solutions are available to prevent the development of rancidity, including careful processing, storage, selection of suitable packaging and the control of moisture content and the

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presence of transition metal (Robards, Kerr, & Patsalides, 1988). However these solutions can be commercially expensive to put in place on an industrial scale.

Moreover, perceived health benefits associated with oat have increased the interest of food manufacturers in developing and commercialising a wide range of oat-based products (for instance, in Europe, porridge, snack bars, oatcakes and muesli) while overcoming the problems of rancidity. For oatcake manufacturers, it is essential to understand the origin of rancidity and the role of saturated and unsaturated fats in the rancidity process, so as to estimate and improve shelf-life, thereby opening up global export markets.

Because of the variability of oat material (seasonal and varietal) and the unpredictable progress of rancidity, it is essential to closely monitor off-flavour/odour development from production to the current end of shelf-life (28 weeks). The most well-established methods for the evaluation of rancidity are based on sensory evaluation and chemical analyses, such as peroxide value, anisidine value, or volatile analysis. In a previous study, we compared two methods of volatile analysis to assess rancidity in plain oat biscuits (Cognat, Shepherd, Verrall, & Stewart, 2012). The headspace trapping system, employing the porous polymer Tenax TA, was revealed to be a rapid and efficient technique to analyse volatile flavour compounds from oatcakes at fresh through to rancid stages. This technique does not involve sample preparation or any solvent extraction which could potentially lead to contamination; as a consequence it results in a clean, fast and unbiased measurement process.

In this work we report the study of the chemical transformation of plain oatcakes from production to the end of the shelf-life (i.e. 28 weeks). Several chemical analyses were used for this purpose, including volatile analysis using Tenax TA, fatty acids analysis of ingredients susceptible to oxidation, peroxide value and anisidine value of oil extracted from oatcakes. A sensory analysis was run in parallel in order to relate instrumental results to human perception. The present paper also investigates the effect of adding a naturally-occurring commercial food antioxidant, a rosemary extract (*Rosmarinus officialis*), on the stability of the product, from both a chemical and a sensory point of view. This antioxidant is widely used in the food industry and its efficacy is reported to be derived from the high content of carnosic acid and carnosol (Jensen, Ostdal, Skibsted, & Thybo, 2011).

2. Materials and methods

A batch of plain oatcakes, as well as oatcakes containing a rosemary extract used as an antioxidant, were produced by a local manufacturer, using a traditional recipe, and packaged in sachets made of polypropylene (seven biscuits per sachet), as described by Cognat et al. (2012). The sachets were kept in cardboard boxes, away from direct sunlight and at a constant temperature of 20 °C. The product was made of oatmeal (87.9% of the dry mix), salt (1.6%), water and added palm (4.7%) and sunflower (5.7%) oils. These two products were studied over a 28-week period, the current producer-defined shelf-life. The oatcakes with antioxidant utilised a commercially available rosemary extract (Inolens 12; Vitiva d.d.o., Markovci, Slovenia) at a concentration of 0.03% (w/w) of the dry mix. The natural rosemary extract is a hydrophobic powder soluble in oil and alcohol. The main active compound found in the extract was carnosic acid, with its content being $\geqslant$12% (according to the manufacturer's specification). Carnosol and rosmarinic acid were also two active compounds found in the rosemary extract (content non-specified).

Several timed analyses were carried out over 28 weeks on these two products and are summarised in the following paragraphs.

2.1. Chemical analyses

2.1.1. Headspace analysis

Headspace analysis was carried out over 28 weeks on the two oat-based products every two weeks from the production day, with volatiles collected in tubes containing Tenax TA (2.6-diphenylene oxide polymer resin, 60–80 mesh, surface area 35 sq m/g; Markes International Ltd, Llantrisant, UK). Three technical replicates per type of oat products were collected at each time point. More details on the method for volatile collection and analysis using automated thermal desorption–gas chromatography–mass spectrometry (ATD–GC–MS), as well as data analysis of volatile compounds, can be found in our previous publication (Cognat et al., 2012). In brief, a Tenax tube was attached vertically to a punctured sachet of biscuits. This tube was connected *via* a ¼ inch stainless steel union coupling (SS-400-6, Swagelok, UK) to a flow metre and then *via* a flow control manifold to a vacuum pump. Adsorbent tubes were then loaded onto an automated thermal desorption (ATD) autosampler prior to analysis by GC–MS. All analyses were performed in triplicate. The analysis of volatiles was performed using a unity thermal desorber with an UltrA TD autosampler (Markes International) coupled to an Agilent 5975B GC–MS system (Agilent Technologies, Santa Clara, CA). The thermal desorption of the sampling tubes was carried out at 240 °C for 5 min, during which time the eluted compounds were transferred from the Tenax tube to a cryofocusing trap, also containing Tenax, maintained at −10 °C. After this primary desorption, the cold trap was rapidly heated up from −10 °C to 240 °C. During this secondary desorption, the compounds were rapidly transferred onto a DB-1701 GC column (60.0 m × 0.25 mm × 1.00 μm; J&W, Folsom, CA) *via* a transfer line heated at 150 °C. The oven temperature was initially 40 °C, increasing to 240 °C at a rate of 5 °C min^{-1} and was then maintained at 240 °C for 20 min. Helium was the carrier gas at a flow rate of approximately 0.5 mL min^{-1}. After a 2.0-min solvent delay, EI (70.0 eV) mass spectra were acquired at 1.33 scans s^{-1} over the mass range 20–300 amu with a source temperature of 230 °C. Data were acquired using MSD Chemstation software (G1710DA, Rev. D.03.00).

2.1.2. Peroxide and anisidine values

Lipid oxidation was also determined using peroxide value and anisidine value on oil extracted from oatcakes and was performed by an independent accredited laboratory (Mylnfield Lipid Analysis, Dundee, UK) for specialist analysis of oils and fats. To extract the oil from the oat biscuits, a procedure based on the IUPAC method 1.122 (IUPAC, 1992) was used. In summary, 10 g of ground oatcakes were extracted twice using isohexane (Fisher Scientific, Loughborough, UK) in an automated extraction apparatus (Buchi extraction system B-811 LSV, Büchi, Flawil, Switzerland). After extraction, any remaining solvent was removed under a flow of nitrogen while the sample was kept at 100 °C for 30 min. The operation was repeated until a consistent weight was obtained. On average, the oat biscuits contained 16% (w/w) of extractable oil.

The extraction procedure for oatmeal was different due to the nature of this ingredient. Approximately 20 g of oatmeal were extracted using 20 mL cyclohexane, 40 mL 2-propanol and 16 mL of water. Samples were homogenised for 2 min; then 20 mL of cyclohexane and 20 mL of water were added. After each addition, samples were homogenised for 30 s. After centrifugation (1800 rpm, 10 min) at room temperature, the supernatants were collected, pooled and evaporated under nitrogen. Three technical replicates were extracted each time.

Peroxide value (milliequivalent O_2/kg lipids) was determined using the American Oil Chemists' Society (AOCS) Recommended Official Method Cd 8–53 (Anon, 2009) and the European Pharmacopoeia 7.0 Method 2.5.5 (Anon, 2010a). In summary, approximately