Food Chemistry 141 (2013) 896–899

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Non-destructive flavour evaluation of red onion (*Allium cepa* L.) Ecotypes: An electronic-nose-based approach

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ARTICLE INFO

Article history:
Received 4 October 2012
Received in revised form 9 March 2013
Accepted 14 March 2013
Available online 22 March 2013

Keywords:
Alliums cepa L.
"Tropea" red onion
Artificial olfactory system
Electronic nose
Metal oxide semiconductor
Pyruvic acid

ABSTRACT

This work reports preliminary results on the potential of a metal oxide sensor (MOS)-based electronic nose, as a non-destructive method to discriminate three "Tropea Red Onion" PGI ecotypes (TrT, TrMC and TrA) from each other and the common red onion (RO), which is usually used to counterfeit. The signals from the sensor array were processed using a canonical discriminant function analysis (DFA) pattern recognition technique. The DFA on onion samples showed a clear separation among the four onion groups with an overall correct classification rate (CR) of 97.5%.

Onion flavour is closely linked to pungency and thus to the pyruvic acid content. The e-nose analysis results are in good agreement with pyruvic acid analysis. This work demonstrated that artificial olfactory systems have potential for use as an innovative, rapid and specific non-destructive technique, and may provide a method to protect food products against counterfeiting.

1. Introduction

Onion (*Allium cepa* L.) is a species of great economic importance, which is widely cultivated all over the world. The health benefits of onion consumption include protection against cancer, coronary heart disease, diabetes and ageing. These effects have been mainly attributed to flavonoids, vitamins and organosulphur compounds (Goldman, Kopelberg, Debaene, & Schwartz, 1996; Kumari, Mathew, & Augusti, 1995). Although they possess significant nutritional value, onions are primarily consumed for their unique flavour and for their ability to enhance the taste of foods (Kopsell & Randle, 1997; Rodrigues et al., 2003).

Onions are widely cultivated throughout the Mediterranean basin and in Italy. The "Tropea Red Onion" (TrO), a sweet red onion characterised by its elongated bulb and almost white flesh, is cultivated, in three different ecotypes, only in the Tyrrhenian coastal areas of Calabria region (Southern Italy). In March 2008, the European Union registered the Protected Geographical Indication (PGI) certification for the onions produced in this particular area (Commission Regulation (EC) No. 284/2008). The 'Cipolla Rossa di Tropea – Calabria' PGI denotes bulbs of the species *A. cepa* exclusively from the local ecotypes. These have a characteristic shape according to time of production: 'Tonda Piatta', the early crop; 'Mezza Campana', the mid to early crop; 'Allungata', the late crop. TrO, for its tenderness, crispness and sweetness is a highly regarded Italian horticultural product and one of the most counterfeited.

Sensory evaluation of onion flavour is closely linked to its pungency, which shows a close correlation with its pyruvate content (Schwimmer & Weston, 1961). The pungent flavour of onions is produced by hydrolysis of precursor compounds, such as *S*-alk(e-n)yl-L-cysteine sulfoxides (Lancaster, Shaw, Joyce, McCallum, & McManus, 2000), when the cells are mechanically ruptured. The hydrolysis reaction is catalysed by allinase and is completed within 6 min (Schwimmer & Weston, 1961). This reaction produces thiopropanol *S*-oxide (a lacrymator), ammonia, sulfur volatiles and pyruvic acid (Fig. 1; Block, 1992). Pyruvic acid concentration (μmol/g FW) in macerated onion tissue is used as a quality assurance indicator of pungency (Abayomi, Terry, White, & Warner, 2006; Pineda, Lué- Merù, Rivas, et al., 2004). Pyruvic acid exists universally in the plant tissues as part of an intermediate metabolism (Goodwin & Mercer, 1983). For this reason, the background levels of pyruvic acid or control (P_C) need to be subtracted from the total pyruvic acid (P_T) concentrations to calculate the enzymatically produced pyruvate (P_E). Background pyruvic acid can be measured after the alliinase is deactivated. The deactivation of alliinase has been achieved by heating onion tissues in a

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http://dx.doi.org/10.1016/j.foodchem.2013.03.052

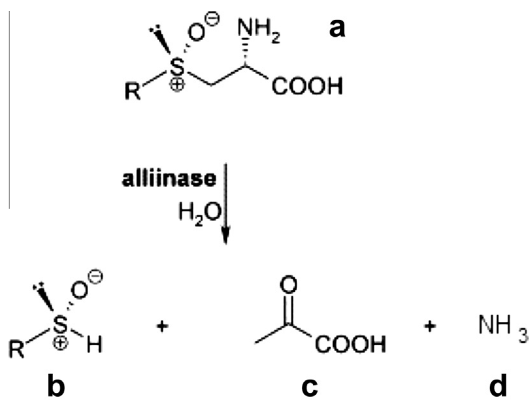

Fig. 1. Schematic of the compounds formed in onion from the hydrolysis of flavour precursors (a: *S*-alk(en)yl-cysteinsulfoxide; b: alk(en)yl-sulfenic acid; c: pyruvic acid; d: ammonia).

microwave oven (Schwimmer & Weston, 1961; Yoo, Pike, & Hamilton, 1995) or by homogenising with trichloroacetic acid (Randle & Bussard, 1993). Since the P_C level can substantially change the P_E concentration, its accurate measurement is critical in measuring onion pungency (Boyhan, Schmidt, Woods, Himelrick, & Randle, 1999; Thomas, Parkin, & Simon, 1992; Yoo & Pike, 2001).

Pyruvic acid content determination and organoleptic tests are used for assessing the eating characteristics of onions. The accumulation of organosulfur compounds in onions and pyruvic acid content depends upon many factors, especially sulfur-based fertilisation and environmental growing conditions, although genotype the most important factor (Chope, Terry, & White, 2007; Yoo, Pike, Crosby, Jones, & Leskovar, 2006). The genetic background seems to be directly related to the different abilities to control sulfur uptake and assimilation in the biosynthetic pathway that results in the onion's flavour (Randle, 1992; Randle, Block, Littlejohn, Putman, & Bussard, 1994). Onion flavour is traditionally measured through the use of a combination of conventional analytical instrumentation and human organoleptic profiling panels. These methods are expensive not only in terms of time, but are also inaccurate because of a lack of either sensitivity or quantitative information. In this paper an investigation was carried out to determine the flavour of different onion samples using an electronic nose (e-nose) and thus to explore the possibility of replacing existing analytical methods.

The e-nose is a relatively novel device used for volatile sensing. The first pioneering studies about the concept of an artificial nose system able to measure odours was reported in 1982 by Persaud and Dodd of the University of Warwick, Coventry, UK (Cho et al., 2010). The e-nose has been designed for automated detection and recognition of odours, vapours and gases (Cho et al., 2010). It does not separate the volatile fraction of the matrix into its constituents but supplies a global evaluation of aroma, mimicking the human olfactory system with instrumental objectivity.

Electronic nose technology has been successfully used to discriminate quality and flavour of various products, including tomatoes, citrus, spices and onions (Abbey & Joyce, 2007; Russo, Serra, Suraci, & Postorino, 2012). The technology may also be used to assess quality of stored grain, fish, drugs, drinks and food spoilage (Abbey, Aked, & Joyce, 2001).

The e-nose used in this work comprises an array of semiconductor gas sensors (MOS), each of which has an electrical resistance that has partial sensitivity to the headspace of onion. The signals from the sensor array are then conditioned by suitable interface circuitry, resulting in an onion data-set. The data were processed using a canonical discriminant function analysis (DFA) pattern recognition tool. DFA has been used extensively to perform pattern recognition and it has been reported to produce good performance for the classification of foodstuffs (Russo et al., 2012). DFA was used to check the capability of the e-nose system in assigning onion samples to a specific group.

Finally, the aim of this study was to discriminate flavour and aroma characteristics of the early, middle and late crops of Tropea Red Onion and also distinguish between them and the common red onion by the use of an electronic nose. Studies on different ecotypes, to the best of our knowledge, have not been carried out before. The analysis of pyruvic acid by HPLC with UV detection was also carried out.

2. Materials and methods

2.1. Plant materials

In 2011 the three local ecotypes of Tropea red onion and one red onion cultivar usually sold as Tropea, were analysed and compared (Table 1). All onion types were grown in a field in IGP district and on the same farm, so that the evaluation was not influenced by environmental factors and/or cultural practices. Three different samples were collected for each type, consisting of five onions. Each analysis was performed in triplicate for each sampling.

2.2. Electronic nose

An electronic nose (ISENose 2000, Labservice Analytica, Bologna, Italy) was used to discriminate aroma fingerprints of onion ecotypes according to the method of Abbey et al. (2001). The edible parts of the onions were homogenised in an Ultra-Turrax system (T50 basic, IKA Werke, Staufen, Germany) at room temperature. The slurry was filtered after 20 min and 20 ml of the filtrate were transferred into a 250-ml flask.

Twenty millitres of 5% trichloroacetic acid (TCA; Sigma Chemical Co., Milano, Italy) were added to terminate alliinase activity. The mixture was agitated vigorously and allowed to stand for 30 min. Deionised water (10 ml) was added to 10 ml of filtrate/TCA solution and mixed. One millilitre of this diluted solution was put into a 25-ml vial, and equilibrated for 10 min at 25 °C to allow the development of headspace before e-nose analysis. The instrument, equipped with 12 metal oxide semiconductor (MOS) sensors, was used to generate a pattern for the compounds present in the headspace of the extracted red onion samples. The operating conditions in the acquisition phase were: baseline correction 10 s; injection time 10 s; sampling 180 s; delay 300 s; purge 60 s; carrier chromatographic air (80% N_2, 20% O_2) flow 300 ml/min; vial volume 25 ml.

2.3. Pyruvic acid extraction procedure and HPLC analysis

The quantification of the pyruvic acid content in the onion was conducted using a modified method of Yoo and Pike (2001). The neck, base and central leaf tissues (about 5 cm long) were removed and the remaining fresh scales were cut into 1–2 cm squares using

Table 1
Red Onion ecotypes.

ID	Sample
TrT	Tropea Ecotype "Tonda"
TrMC	Tropea Ecotype "Mezza Campana"
TrA	Tropea Ecotype "Allungata"
RO	Red Onion