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Volatile compound composition and antioxidant activity of cooked ham slices packed in propolis-based active packaging

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ABSTRACT

Aiming at studying the possibility of application of propolis as food preservative, active paper sheets obtained by either surface spreading (APP) or by incorporating propolis in paper mass at 0.4% (API) were used to pack slices of cooked ham. A 4 days consumer storage simulating trial, at 4 °C, was performed and cooked ham packed with APP, API and no-propolis (control) papers was analysed for volatile composition by HS-SPME GC–MS, antioxidant properties and samples were submitted to sensory analysis (triangle test). Slices packed in API paper showed antioxidant properties similar to control slices and the gradual migration of terpenoids from packaging into ham slices did not influence the sensory properties. In contrast, in slices packed in APP paper, both DPPH radical scavenging activity and reducing compounds increased with storage, and the changes in aldehydes, ketones, carboxylic acids and alcohols amounts and composition indicated lipid and non-lipid oxidations, which impacted on the sensory characteristics of cooked ham.

1. Introduction

Packaging is no longer considered a passive component, but it has an active role, interacting with the external environment and with the food inside by the release of active molecules that will extend shelf life providing protection against microbial spoilage and oxidation. The use of active packaging materials is not meant to be a substitute for good sanitation practices, but it should enhance the safety of food as an additional hurdle for the growth of pathogenic and/or spoilage microorganisms (Cooksey, 2005).

Propolis is a resinous substance collected by *Apis mellifera* that is used in the hive as building material and defensive agent. Due to its complex composition it has many biological properties, having antibacterial, antifungal, antioxidant and antiviral activities (Koo et al., 2000), and it is used as a component of food additives, cosmetics and over-the-counter preparations (Bankova, Popova, & Trusheva, 2014). The antioxidant and antimicrobial activity of propolis makes it a suitable component in the formulation of

Abbreviations: API, active packaging with incorporated propolis extract; APP, active polyehtylene paper with propolis extract surface spreading; DPPH, 1,1-diphenyl-2-picrylhydrazyl radical; TRC, total reducing compound content; HS-SPME, headspace-solid phase microextraction; GC–MS, gas chromatography–mass spectrometry; ANOVA, analysis of variance; LSD, least significant difference.

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bioactive food packaging (Tosi, Re', Ortega, & Cazzoli, 2007). It has been proposed as a chemical preservative in meat products (Han and Park, 1995) and as germicide and insecticide for food packaging (Mizuno, 1989a, 1989b).

Since 2010, a demonstration project was funded by the Italian Ministry of the Economic Development with the aim of developing controlled release packaging systems that act as a "case" and as a "time controlled dispenser" (Mascheroni, Guillard, Nalin, Mora, & Piergiovanni, 2010) for active compounds from propolis, not directly embedded to the food and released after the contact with the moisture content of food (Cattaneo, Cremonesi, & Barzaghi, 2014).

The chemical composition of propolis is very complex and high variable according to its botanical and phytogeographical origin (Bankova, 2009). As a consequence the different propolis types are characterized by distinct chemical profiles, according to their plant origin,which have been associated with the presence of specific compound types, such as polyphenols, terpenoids, prenylated acetophenones and isoflavonoids (Kumazawa, Hamasaka, & Nakayama, 2004; Melliou, Stratis, & Chinou, 2007; Popova et al., 2011; Velikova et al., 2000). Bankova, Christov, Popov, Pureb, and Bocari (1994) reported that the volatile compound composition of propolis differed significantly according to the sample, even if phenolic composition was similar in the various propolis samples. The main volatile compounds in propolis are terpenoids (Melliou et al., 2007; Popova et al., 2011), in which sesquiterpenoid alcohols and hydrocarbons predominate, accompanied by some monoterpenes, mainly alcohols (Bankova et al., 1994). Most of these compounds has a low odor detection threshold (Leffingwell and Leffingwell, 2000), which may influence the odor of the propolis samples and, therefore, they might interfere with food flavor. Bianchi, Rizzolo, Migliori, and Cattaneo (2014) studied the sensory properties by gas chromatography-olfactometry of different types of active packaging, made through the incorporation or the surface spreading of a propolis extract, and found that the propolis addition method to the packaging material exerted a major influence on the olfactometric profile of packaging. In fact the packaging made with the surface spreading method had similar olfactometric profiles, different from those of paper packaging prepared by propolis incorporation. However, the olfactometric profiles of the active packaging showed the prevalence of odor notes such as "balsamic" and "floral", which are characteristics of terpenes (Acree and Arn, 2004), whereas other descriptors such as "chemical", "burnt" and "paper", which could be referred to the packaging material, were the main descriptors of control packaging (without propolis).

The objective of the present work was to study the effect of propolis-based active paper sheets obtained by either surface spreading or by incorporating propolis in paper mass on volatile compound composition and antioxidant activity of cooked ham slices in a consumer storage simulating trial, in conjunction with the evaluation of the impact on cooked ham sensory characteristics by means of triangle test.

2. Material and methods

2.1. Raw materials and sample preparation

A 2 kg of cooked ham, a typical Italian cooked pork product, was purchased from a local market and sliced by machine (ABM, Milano, Italy). Then, freshly prepared slices (thickness 0.5 mm) were manually packed (4 slices/pack) with paper sheets (30 × 16 cm) either incorporated by 0.4% propolis extract (API) or sprayed with propolis extract (2.4 g/m^2) on the polythene surface (APP). In API paper the percentage of propolis extract was determined by the flow rate (as it is) of the dosing pump in ratio with the flow of the fibrous materials (chemical pulps) bone dry and the propolis was incorporated through dosing on mixed fibrous raw materials inside the stock approach system of the paper machine. As for APP paper, the thickness of paper plus polythene (totally 75 g m^{-2}) was 94 μm and the propolis was applied through a printing cliché and, by difference of the initial and final grammage, evaluated as a layer of 1 g m^{-2}. A value in μm was not possible to be measured due to the small variations of thickness along the reel profile of paper plus polythene. A commercial food-grade polyethylene paper was used as control packaging. Eight replicates/active packaging, and 12 replicates for control packaging containing 4 slices/pack have been prepared.

2.2. Consumer storage simulating trial

All the packs (control, API, APP) have been stored at 4 °C up to 4 days and samplings were carried out after 0, 2 and 4 days. This storage time was established basing on the average home storage duration. At each sampling time two packs/packaging were analysed for 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity and total reducing compounds content (TRC) and other two for volatile composition by HS-SPME GC/MS analysis. After 2 and 4 days samples were submitted to sensory analysis. Hereafter control and API samples at the beginning of storage are referred to with the same caption (day0), while the APP sample at day 0 is referred to as APP_d0; the control, API and APP samples after 2 days of storage are referred to as C_d2, API_d2 and APP_d2, and those after 4 days as C_d4, API_d4 and APP_d4, respectively.

2.3. DPPH radical scavenging activity and total reducing compounds content

2.3.1. Samples extraction

A methanolic extraction was performed according to Rashidinejad, John Birch, Sun-Waterhouse, and Everett (2013). Cooked ham samples (10 g) were homogenized with an Ultraturrax and extracted for 30 min with 50 ml of a methanolic solution (95: 5 methanol: HCl 6 N in H_2O) at 50 °C on an orbital shaker at 100 rpm. After cooling, the mixture was filtered on glass wool.

2.3.2. DPPH radical scavenging activity

The radical scavenging activity analysis was performed following the method proposed by Brand-Williams, Cuvelier, and Berset (1995) with modifications. 500 μl of a 0.5 mM DPPH solution were diluted in 2 ml methanol and 50 μl of extract were added; the final absorbance was read with a Jasco 7800 UV/VIS spectrophotometer (Jasco Europe S.r.l., Cremella, LC, Italy) at 517 nm after 10 min of incubation. The DPPH scavenging activity was quantified by a calibration curve using caffeic acid as standard and expressed as mM caffeic acid equivalent (mM CAE)/kg product. The caffeic acid was chosen as standard due to its predominance in the phenolic acid composition of the Italian propolis used in the preparation of the active packaging (Scaglianti, personal communication).

2.3.3. Total reducing compounds content

The total reducing compounds content (TRC) was determined by the Folin-Ciocalteu method (Singleton, Orthofer, & Lamuela-Raventos, 1999) with some modifications. 150 μl of extract were mixed with 1 ml of Folin-Ciocalteu reagent and 5 ml H_2O, and then 2 ml of 20% Na_2CO_3 solution were added. After vortexing, the reaction mixture was kept 120 min in the dark and the resulting absorbance was read with a Jasco 7800 UV/VIS spectrophotometer (Jasco Europe S.r.l., Cremella, LC, Italy) at 730 nm against a blank made with extraction solvent. The TRC was quantified by a calibration curve using caffeic acid as standard and expressed as mg caffeic acid equivalent (mg CAE)/kg product.