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Sulfur aroma compounds in gum Arabic/maltodextrin microparticles

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ABSTRACT

The sulfur compounds 2-furfurylthiol (2FFT), dimethyl disulfide (DMDS) and thiophene (THIO) are important sulfur contributors to roasted coffee aromas. Their loss by evaporation and/or degradation directly impacts the freshness and aroma intensity of coffee brews. To improve their stability, 2FFT, DMDS and THIO were microencapsulated by spray drying in Gum arabic (GA) and maltodextrin (MD). A CG-qMS method was developed and validated to accurately quantify the sulfur compounds as well as their microencapsulation process and storage stability. Selectivity was obtained by CG-SIM-qMS despite an observed matrix effect. The calibration curves were linear over the tested range. The LOQ for 2FFT, THIO and DMDS were 10, 15 and 23 μg mL^{-1}, respectively, and the corresponding LOD were 3, 5 and 7 μg mL^{-1}. Repeatability, reproducibility and recoveries were obtained within acceptable levels. Microparticles production was tested at different inlet temperatures, and the best encapsulation efficiency was found to be 67% for 2FFT, at 140 °C. The microcapsules were characterized in terms of moisture content, hygroscopicity, solubility, surface morphology, particle size distribution and X-ray diffraction characteristic. A fifteen-week storage stability study at −18 °C indicated that GA and MD offered good protection for the sulfur aromas, especially for THIO and DMDS.

1. Introduction

Volatile sulfur compounds contribute to the aromas of food and beverages, most with extremely low odor thresholds that affect the overall aroma. These compounds are powerful odorants in wine and coffee. For example, 2-furfurylthiol (2FFT) is a character-impact compound with a sulfury-roasty aroma present in roasted Arabica coffee (Buffo & Cardelli-Freire, 2004; Tressl & Silwar, 1981) and has been used to compose artificial aromas for coffee preparations (Kawasaki, 2006; Kerler, Liardon, & Poisson, 2013).

Sulfur compounds are prone to oxidation and/or degradation in air, water and light. Perez-Martinez, Sopelana, Paz de Peña & Cid (2008) have studied the aroma change in brewed coffees and showed that the contents of methanethiol and dimethyl disulfide (DMDS) gradually decrease when the brew is stored at 25 or 4 °C. Thiophene (THIO), present in heat-treated foods such as coffee, also decreases under these conditions. Hofmann and Schieberle (2003) observed a similar behavior for 3-methyl-2-butene-1-thiol and 2-methyl-2-furfurylthiol upon coffee processing or storage.

The loss of sulfur volatile compounds contributes negatively to the consumer acceptance of coffee products. Thus, food aroma complementation may be a way to maintain product quality. Spray drying, a microencapsulation techniques is a fast and relatively low-cost process of improving the chemical stability of liquid and solid food flavorings, allowing their incorporation into dry food systems and improving the 'sensory profile' of food products (Osorio, Forero, & Carriazo, 2011; Ré, 1998; Teixeira, Andrade, Farina, & Rocha-Leao, 2004). Gum arabic (GA) is a natural product with high solubility, good emulsifying properties and low viscosity (Fernandes et al., 2008). The combination of GA with maltodextrin (MD) is an interesting alternative for aroma encapsulation, as described by Turasan, Sahin, and Sumnu (2015) for rosemary essential oil. MD is a relatively low-cost hydrolyzed starch with neutral aroma and taste and excellent oxygen-blocking properties, despite having low emulsification capacity. This combination has also been used in confectionary applications and frozen desserts, which constitute a large market worldwide. Therefore, to develop

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new techniques for increasing the stability of sulfur compounds for coffee flavor, we have investigated the spray drying of 2FFT, THIO and DMDS using GA/MD, these MD and GA are approved as food additives and that no genotoxic or mutagenic effects are described for the sulfur compounds used herein (EFSA, 2013). The proper quantification of these compounds, which is necessary to evaluate the microencapsulation efficiency, is quite challenging due to their high volatility. Therefore, a method to quantify the microencapsulated sulfur volatiles and monitor the storage stability was developed and validated.

2. Materials and methods

2.1. Materials

Gum arabic (GA, from the acacia tree) was obtained from Isofar® (Isofar Indústria e Com de Produtos Químicos, Duque de Caxias, Brazil). Maltodextrin (MD) MOR REX 910®, 10 DE was obtained from Ingredion™ (Brasil Ingred. Ind. Ltda, Mogi-Guaçu, Brazil).

The sulfur core materials 2-furfurylthiol (2FFT), dimethyl disulfide (DMDS) and thiophene (THIO) (all with purity >98%) were purchased from Sigma–Aldrich (São Paulo, Brazil). Ethanol and dichloromethane (analytical grade) were purchased from Tedia (Rio de Janeiro, Brazil).

2.2. Encapsulation of sulfur compounds

The GA (7 g 100 g^{-1}) and MD (5 g 100 g^{-1}) wall materials were prepared in distilled water. The solutions were mixed by a Quimis Q250 magnetic stirrer (Quimis Aparelhos Científicos, Diadema, Brazil) at 25 °C until complete dissolution. The 2FFT, THIO and DMDS were diluted separately in ethanol to obtain a concentration of 40, 70 and 55 mg mL^{-1}, respectively to produce the core solutions. Next, each sulfur compound solution was slowly added to the coating material solution dropwise under continuous stirring in the Ultra Turrax high-speed homogenizer (Ika, Staufen, Germany) over 30 s at 9500 rpm, to obtain an emulsion. The total solid soluble content of the final mixture was maintained at 16 g 100 g^{-1}, and the ratio of core materials to coating was 1:3 (data not shown).

2.3. Spray drying

The fully homogenized emulsion was dried in a Mini Spray Dryer B290 (Büchi Laboratory Equipment, Flawil, Switzerland) with a 0.3 mm nozzle at a 6 mL min^{-1} flow rate. The dried samples (microparticles) were collected, hermetically sealed in amber packaging and stored in the freezer during all experiments (−18 °C, relative humidity 56%).

The effect of inlet drying temperature on the feed solution was evaluated based on the microencapsulation yield (Y%), encapsulation efficiency (EE%) and microparticle morphology (photomicrographs). The inlet drying air temperatures studied were 120, 140, 160 and 180 °C and the outlet temperatures were 56 °C, 62 °C, 75 °C and 80 °C, respectively.

2.4. Extraction of sulfur compounds from microparticles

One gram of each of the microparticles was weighed in 50 mL falcon tubes and then diluted with 4 mL of distilled water and dichloromethane. The mixture was stirred using a K45- 2810 vortex mixer (Kasvi, Curitiba, Brazil) for 5 min, sonicated for 1 min in an ultrasonic water bath, and centrifuged at 3881× g at 25 °C for 10 min (Thermo Scientific ST 168, Waltham, MA, USA) to separate the organic phase.

2.5. GC-qMS method validation

A gas chromatograph-mass spectrometer (GC-qMS) operating in selective ion monitoring (SIM) mode (GC 6850 series and MS 7975C, Agilent Technologies, Inc., CA, USA) was used to analyze the sulfur compounds equipped (30 m × 0.25 mm d_i × 0.25 μm d_f). The oven temperature was programmed from 35 (5 min) to 40 °C at 2 °C min^{-1}, 100 °C at 5 °C min^{-1} and 290 °C at 25 °C min^{-1} (3 min). The injector was kept at 240 °C. The transfer line, ion source and quadrupole were maintained at 290, 230 and 150 °C, respectively. Helium was used as the carrier gas at a constant flow of 0.6 mL min^{-1} and a split ratio of 1:20.

The method was validated to support the storage study according to the usual parameters, namely, working range, selectivity, linearity, limit of quantification (LOQ), limit of detection (LOD), trueness (recovery) and precision (repeatability and reproducibility) (Brasil, 2010; Ribani, Bottoli, Collins, Jardim, & Melo, 2004). The working range was defined in terms of the amount of the sulfur aroma compounds added to the wall material mixture to obtain the microparticles. Selectivity was evaluated using SIM mode for GC-qMS and by comparison with the calibration curves constructed for the wall materials spiked with different concentrations of the sulfur aroma compounds prepared in dichloromethane via *F* and *t* tests conducted using the same analytical conditions (to investigate matrix effects). Linearity was evaluated by triplicate injections of spiked wall materials corresponding to each of the five points in the calibration curve plotted as peak area *vs*. sulfur compounds concentration. A regression equation was generated based on the calibration curves using linear least-squares regression. The distribution was verified by Cochran's test, and deviations from randomness of residues were assessed.

The LOD and LOQ were determined as 3 and 10 times the signal-to-noise ratio, respectively of injection performed of standards in triplicate and blank matrix. Trueness was assessed through recovery trials by spiking the wall material with three concentrations of the sulfur compounds. Triplicate analyses were performed at each level, and the recovery percentage as calculated using Equation (1):

$$Recovery(\%) = \frac{Measuredconcentration}{Spikedconcentration} \times 100 \quad (1)$$

Acceptable recovery was defined between 80 and 110%. Precision was assessed by analyzing the same samples as for the recovery studies either on the same day (repeatability) or on two consecutive days (reproducibility). Acceptable precision was defined using the coefficient of variation: CV <20% (Ribani et al., 2004).

2.6. Microparticle characterization

2.6.1. Moisture content, hygroscopicity and solubility

The water content of the microparticles was quantified by a thermogravimetric method. First, a sample of 1.0 g was heated in a Model MA35 Moisture Analyzer from Sartorius (Sartorius, Göttingen, Germany) for 90 min, and moisture loss was determined by weight loss in triplicate.

For hygroscopicity measurements, the method adapted by Frascareli, Silva, Tonon, and Hubinger (2012) was applied. Microparticle samples (approximately 1.0 g, in triplicate) were placed in a 3 mL vial and stored at ambient temperature in a desiccator filled with a NaCl saturated solution (61% relative humidity) for one week. The hygroscopicity was then determined and expressed as g of water absorbed per 100 g of dry solids (g 100 g^{-1}).

For solubility determination, the method adapted from Fernandes, Borges, and Botrel (2014) was used. Microparticle