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Chemical changes in the volatile fractions of Brazilian honeys during storage under tropical conditions

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ABSTRACT

The chemical transformations of the volatile fractions of two different Brazilian honeys (cashew and marmeleiro) were monitored during storage under tropical conditions. Five systems, namely: 1 – fresh samples; 2 and 3 – samples heated for 3 and 6 months at 35 – 40 °C; 4 and 5 – samples kept under similar conditions to systems 2 and 3, but containing sodium metabisulphite, were tested. The transformations noted in the volatile fractions of these honeys could be mainly associated to acid or enzymatic hydrolysis of glycosides, volatilization, oxidation or esterification processes. The formation of furan derivatives, linalool derivatives and esters appears to be quite affected by the sodium metabisulphite. The concentrations of most powerful odorants increased during the storage (e.g.: benzenemethanol and isovaleric acid) or remained unchangeable (e.g.: vanillin, furfuryl mercaptan, 2-methoxyphenol).

1. Introduction

Honey is a natural sweet, high energy food with medicinal properties. Due to these features, there is a global trend favouring the consumption of honey (Aparna & Rajalakshmi, 1999; De Maria & Moreira, 2003; Mendes, Brojo Proença, Ferreira, & Ferreira, 1998). In this context, Brazil has a considerable potential to play a major role in the global market, since the climate variety and its rich flora facilitate the attainment of honey with unique properties (Moreira, Trugo, Pietroluongo, & De Maria, 2002). Honey is a product in which many variations in its sensory properties and composition are expected during storage. Some of these variations could be associated with reactions (e.g.: caramelization and Maillard reaction) catalyzed by heating, so they deserve more attention in tropical countries, like Brazil, where the mean annual temperature is higher than 20 °C. Moreover, due to commercial aspects, sometimes honeys must be stored in these underdeveloped countries for almost 1 year before consumption (Kaushik, Joshi, & Gupta, 1993). A better knowledge of the changes that occur in honey samples during storage could be useful to the development of mechanisms to guarantee the original freshness of this kind of food. There are several studies on this topic in the specialized literature, but most are concerned with changes that develop in the non-volatile fraction of honey (Bath & Singh, 2000; Gonzales, Burin, & del Pilar Buera, 1999; Jiménez, Mateo, Huerta, & Mateo, 1994; Kaushik et al., 1993; Mendes et al., 1998; Papoff, Campus, Floris, Prota, & Farris, 1995; Sancho, Muniategui, Huidobro, & Lozano, 1992). To the best of our knowledge, just a few investigations have focused on establishing the impact of storage on the volatile profile of honeys (Visser, Allen, & Shaw, 1988; Wooton, Edwards, & Faraji-Haremi, 1978). The study of this specific fraction is very important, since consumers consider the aroma as one of the most important attributes to select a specific kind of honey. Then, the aim of this study was to monitor the chemical transformations that the volatile fractions of Brazilian honeys undergo during their storage under tropical conditions. Sodium metabisulphite was added to part of these honey samples in order to examine the influence of some processes (e.g.: Maillard reaction, enzymatic browning, microorganism development) on these chemical transformations, since this salt efficiently controls food degradation, inhibiting the above mentioned processes (Araújo, 1995; Kaushik et al., 1993).

2. Materials and methods

2.1. Samples

Two samples of Brazilian cashew (caju) honey (Anacardiaceae) and two of marmeleiro honey (Rosaceae) were obtained directly from reliable beekeepers from Ceará and Piauí States, respectively. These samples were harvested between 1997 and 1998 and immediately stored under nitrogen at −18 °C in small closed glass bottles (with metallic thread covers) normally used by Brazilian

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beekeepers and traders to store this kind of product. All the data showed in this manuscript were obtained before the year of 2002.

2.2. Materials

Acetone (purity grade = 99.5%) and the volatile standards of 1-hydroxy-2-propanone (90%), tetradecane (>99%), 2-cyclohexen-1-one (>95%), 2-furfural (99%), pentadecane (>99%), 2-methylpropanoic acid (99%), hexadecane (99%), heptadecane (99%), 2-(2-butoxyethoxy)-ethanol (>99%), octadecane (99%), 2-butyloctanol (95%), benzenemethanol (99%), nonadecane (99%), benzeneethanol (99%), eicosane (99%), heneicosane (98%), docosane (99%), tricosane (99%), tetracosane (99%), pentacosane (99%), 5-(hydroxymethyl)furfural (5-HMF; 99%), vanillin (99%), 1-octadecanol (99%), hexacosane (99%), 1-eicosanol (98%), hexadecanoic acid (98%), oleic acid (>99%), isovaleric acid (99%), 2,3-butanedione (97%), butyl butanoate (98%), menthol (99%), furfuryl mercaptan (98%), linalool (97%), 2-methoxyphenol (98%) and eugenol (99%) were purchased from Aldrich (Milwaukee, WI). δ-Octalactone (>95%) and γ-decalactone (>95%) were gently supplied by IFF Essências e Fragrâncias Ltda (Rio de Janeiro, Brazil). Benzoic acid (99.5%) was obtained from Carlo Erba (Milan, Italy). Porapak Q (50–80 mesh) was from Millipore Corp. (Bellefonte, PA, USA). All other reagents were of analytical grade.

2.3. Storage experiments simulating tropical conditions

Forty grams of each honey sample were kept in small glass bottles. The bottles were kept closed with appropriate metallic covers to guarantee a complete isolation of the samples from the external environment. These bottles were maintained in an oven at temperatures ranging from 35 to 40 °C (simulating tropical conditions) over 3 and 6 months. Sodium metabisulphite was added as a powder in some of the samples in an initial amount of 120 ppm and, then, it was thoroughly mixed over ten minutes using a glass stirring rod. The work was carried out by employing five different systems: system 1, fresh samples (cashew honey, C_1 and marmeleiro honey, M_1); systems 2 and 3, samples heated for 3 (C_2 and M_2) and 6 months (C_3 and M_3); systems 4 and 5, sodium metabisulphite added samples heated for 3 (C_4 and M_4) and 6 months (C_5 and M_5).

2.4. Isolation of volatile flavour compounds

2.4.1. Column extraction method

The isolation of the volatile components of both honeys was carried out using a column extraction technique modified from a previously proposed method (Moreira et al., 2002; Shimoda, Wu, & Osajima, 1996). First of all, a small glass column (14.0 cm × 1.0 cm i.d.) packed with 750 mg of Porapak Q porous polymer beads (50/80 mesh) (Supelco, Bellefonte, PA) was activated by heating at 225 °C during 3 h under a N_2 flow of 0.9–1.0 L min^{-1}. Then, 100 mL of an aqueous honey solution (0.20 g/mL) was passed through the column. After that, the column was inverted and washed with 20 mL of deionised water. Adsorbed volatiles were then eluted with 100 mL of acetone; the eluate was rotaevaporated (20 °C) until dryness and then taken up in 200 μL of acetone. Two different replicates were prepared from each sample.

2.5. Capillary gas chromatography (GC)

Capillary GC analysis was carried out on a Carlo Erba gas chromatograph model FTV 4300 (Milan, Italy) equipped with a flame ionization detector (FID). The chromatograms were obtained using a Shimadzu Chromatopak C-R6A integrator (Kyoto, Japan). Separation was achieved on a 30 m × 0.25 mm i.d. fused silica capillary column, coated with cross-linked poly(ethylene glycol) 20 M, with a film thickness of 0.25 μm (Supelcowax™-10, Supelco, Bellefonte, PA, USA). The oven temperature was programmed to rise from 50 to 230 °C at 3 °C/min and kept there for 30 min. The injector temperature was 230 °C and the detector was held at 240 °C. Helium was employed as the carrier gas at an optimum linear speed of 28 cm/s (50 °C). An injection splitter was used at a split ratio of 20:1. Retention indices were estimated by a modified Kovatz method (Van den Dool & Kratz, 1963). The concentrations of the impact volatile compounds were evaluated by external standardization. In order to quantify the relative amount of the remaining volatile compounds in the analyzed honey systems, chromatographic responses in terms of peak areas, were considered.

2.6. Capillary GC/MS

Electron-impact mass spectrometric analyses were developed on a gas chromatograph–mass spectrometer system GC-17A/QP5050 from Shimadzu (Kyoto, Japan). The column and chromatographic conditions were the same as those described for GC analyses. The mass spectrometer was operated at an ionization voltage of 70 eV and an ion source temperature of 240 °C. The MS identification was on the basis of comparison with the NIST12.lib and NIST62.lib mass spectral libraries. Besides the mass spectral libraries, the identification was also carried out using reference substances and the odour qualities of the compounds eluted from the column of the GC/FID system. Only the compounds identified using reference materials and mass spectral data were considered to be definitely identified (see Tables 1–3).

2.7. Gas chromatography-olfactometry (GC-O) and aroma extraction dilution analysis (AEDA)

The odour profile of each honey was assessed by direct sniffing the GC eluate as it flew from the chromatograph. The chromatographic conditions were the same reported previously, excluding the use of a flow splitter to divide the GC effluent between the chemical detector and the sniffing-port (1:10 – FID: sniffing-port). Five trained panellists (two men and three women; 20–40 years old) performed the sensorial analysis both on standard solutions and on the samples. Volatile compounds with a detectable odour were characterized by description of their odours and their retention times were recorded. In order to identify the impact odour compounds that govern the overall aroma of the samples, the AEDA was carried out. The aroma extracts of the samples were diluted by a factor of 2 several times to form a series in which each member was two times as concentrated as the next most diluted sample (Acree, 1993).

2.8. Statistical analysis of data

The variance analysis (ANOVA) was carried out to check statistical differences between the systems ($p < 0.05$). Duplicate analyses of each one of the samples (two samples of cashew honey and two samples of marmeleiro honey) were always carried out.

3. Results and discussion

Nineteen hydrocarbons were found in the cashew honey, but only one (pentacosane) in the marmeleiro honey. During the storage, the majority of the hydrocarbons underwent a considerable concentration reduction. Since these compounds are little reactive, probably this reduction was associated to volatilization processes. In general, these losses had diminished with the increase of the molar masses of these hydrocarbons. In this context, the behaviour