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Changes in volatile compounds of palm sap (*Arenga pinnata*) during the heating process for production of palm sugar

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Abstract

This study was carried out to determine the changes of volatile compounds composition during palm sugar production. The samples were collected at every 30 min interval for 4 h of heating process at 150 °C from a local traditional manufacturer in Kuala Pilah, Malaysia. The analyses were performed by gas chromatography–mass spectrometry after headspace solid phase micro extraction. The results showed that *N*-heterocyclic chemical class possessed the highest relative percentage area (RPA) 83.69%, followed by *O*-heterocyclic group with RPA of 14.5%. Main volatile compounds the determined were 5-methyl-6,7-dihydro-5H-cyclopenta pyrazine and 4-hydroxy-2,5-dimethyl-3(2H) furanone which were responsible for roasty and sweet caramel-like aroma notes, respectively. The pyrazine compounds increase exponentially with heating time but furan derivatives compounds were formed at a later stage, i.e. at 180 min of heating time and above 105 °C.

Keywords: Palm sugar (*Arenga pinnata*); Volatile compounds; Solid phase micro extraction; Gas chromatography–mass spectrometry

1. Introduction

Palm sugar which is one of the local delicacy widely consumed by Asians is used for making cakes, desserts, food coating or mixed with drinks and is produced by heating the sap derived from the tropical coconut tree (*Cocos nucifera*) or a kind of palm tree called *Arenga pinnata* (Panyakul, 2001). For the traditional production of palm sugar, a large volume of filtered palm sap is transferred into a big wok, where the filtered palm saps are heated on the wood fired stove for a few hours at >100 °C until it becomes concentrated to obtain a typical aroma. Mainly, two major reactions occur during the heating process of palm sap: Maillard reaction and caramelisation. After the heating process, the palm sap liquid is poured into bamboo moulds to form pure solid palm sugar which is ready for consumption.

Palm sap contains abundant sucrose and polar side chain amino acids especially asparagine and glutamine. Sohn and Ho (1995) reported that these polar side chain amino acids were essential precursors to the volatile compound formation by releasing more free amino groups during the Maillard reaction than other amino acids. The released amino group substrate will catalyzes sucrose conversion into their reactive component of monosaccharides or can directly undergo retro-aldol reactions producing more reactive C2, C3, C4 and C5 dicarbonyl compounds, depending on the environment conditions (Carline & van Boekel, 2003). All these compounds are highly reactive and take part in further reactions. In essence, dicarbonyl compounds can react with amino acids to form aldehydes and α-aminoketones. This reaction is known as the Strecker degradation. Subsequently, in the advanced stage, a range of reactions takes place, including cyclisation, dehydrations, retro-aldolisations, rearrangements, isomerisations and further condensations, which ultimately, in the final stage, lead to the formation of volatile compounds

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and melanoidins. The relative proportions of these compounds influenced by the cooking temperature, heating time and whether the conditions are acidic or basic are important to the Maillard reaction (Martins, Jongen, & van Boekel, 2001).

Till date, volatile compounds produced by the heating of palm sap have not been investigated. The origin of the volatile compounds responsible for the flavour of palm sugar is still relatively difficult to determine, due to their multiple origin. Therefore, this study was carried out to determine the volatile compounds produced during traditional palm sugar process.

2. Materials and methods

2.1. Materials

A sample of the sweet liquid generated during the heating of palm sap for production of palm sugar was collected from the traditional palm sugar producer in Kuala Pilah, Negeri Sembilan, Malaysia. The samples were collected at every 30 min interval for 4 h. Each time approximately 1 ml of the sample was collected. An internal standard, tridecane (1 ppm) was spiked into the sample. The mixture was then placed into a 12 ml headspace vials and sealed tightly with a crimp cap and a PTFE/silicone septum. The initial temperature of each sample was measured using an infra-red thermometer (Quicktemp 826 T4. Testo, Vienna, Austria). The samples were then immediately chilled in an ice bath and were kept frozen at −18 °C.

The standard solutions 2-methyl pyrazine, 2,5-dimethyl pyrazine, 2,3-dimethyl pyrazine, 2-ethyl pyrazine, 2-ethyl-5-methyl pyrazine, 2-ethyl-3,5-dimethyl pyrazine, 2,3-diethyl-5-methyl pyrazine, 5H-5-methyl-6, 7-dihydrocyclopentapyrazine, 2-furfural, 2,5-dimethyl-4-hydroxy-3(2H)-furanone and 5-methyl furfural, as well as tridecane (internal standard) were purchased from Sigma–Aldrich, USA. The purity of the standard solutions was 97–99.9%.

2.2. Extraction of volatile compounds

The volatile compounds of each sample were extracted using solid phase micro extraction (SPME). A 50/30 μm Divinylbenzene/Carboxen/Polydimethylsiloxane SPME fibre was used (Supelco, Bellefonte, PA, USA). This fiber was chosen because it was reported by Ho, Wan Aida, Maskat, and Osman (2006) to be the most efficient for trapping *N*- and *O*-heterocyclic group volatile compounds of palm sugar. The vial was equilibrated at 50 °C for 10 min in a water bath. A manual SPME holder containing fibre was inserted into the vial and was exposed to the sample headspace for 10 min at 50 °C. The fiber was then transferred directly into the injector port of the GC–MS system. Thermal desorption of the analytes from the fiber in the GC injector port was carried out with an SPME inlet liner (0.75 mm i.d., Supelco) in the splitless mode at a desorption temperature of 250 °C. The SPME fibre was conditioned at 250 °C for 30 min before the first measurement and left in the injection port for re-conditioning during the whole GC run before it was exposed to the headspace of the next sample.

2.3. Gas chromatography–mass spectrometry analysis

All samples were analyzed using gas chromatography–mass spectrometry (Hewlett–Packard). The separation was achieved on a nonpolar HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) purchased from J & W Scientific, Agilent Technologies. The injector and detector temperatures were 240 °C and 280 °C, respectively. Carrier gas helium was used at a flow rate of 2 ml/min and was held at a constant pressure of 117.5 kPa. The column temperature was programmed from 50 °C (held for 2 min), at 20 °C/min to 80 °C (held for 1 min), at 20 °C/min to 100 °C (held for 1 min), then at 30 °C/min to 230 °C (held for 2 min). Other conditions were as follows: scanning mass range (m/z) 50–550 a.m.u at a rate of 1.5 scan/s; electron ionization energy, 70 eV.

2.4. Identification and quantification

The measured mass spectra were compared with those obtained from reference compound if available, as well as with data found in the literature (the respective references are given in Table 2) and also from a commercially available mass spectra database (Wiley 275.1). Additionally, the volatile compounds were identified by matching the retention indices (RI), calculated according to the equation of Van den Dool and Kratz (1963) and based on a series of alkanes (C6–C22) (i.e., RI of hexane is 600). The retention indices for the compounds of interest are given in Table 2.

$$\text{Retention Indices (RI)} = 100Z + 100\left[\frac{\ln\ t_{R,A} - \ln\ t_{R,Z}}{\ln\ t_{R,Z+1} - \ln\ t_{R,Z}}\right]$$

where retention time (t_R) of $t_{R,Z} < t_{R,A} < t_{R,Z+1}$; Z = number of atom carbon.

Tridecane (TDC) was used as an internal standard, as this compound was not found in the palm sugar. It is well known that discrimination of compounds with high or low volatility occurs in SPME. Consequently, quantification cannot be carried out seriously by the use of one single internal standard. We used the internal standard, not for quantification, but for correction of variations of the capacity of the SPME fibre, as well as the variations of the sensitivity of the GC–MS system. In addition, it was not the aim of this study to quantify volatile compounds, but to determine the relative concentration changes of volatile compounds during the traditional production of palm sugar. Therefore, given concentration values are not noted as absolute concentration values but as equivalents to the internal standard. The relative concentrations of the investigated compounds were calculated by relating the areas of