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Study of free and glycosidically bound volatile compounds in air-dried raisins from three seedless grape varieties using HS–SPME with GC–MS

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ABSTRACT

Volatile compounds in air-dried raisins from Turpan, China were analysed, with 77 volatiles identified in Flame Seedless, Thompson Seedless, and Crimson Seedless raisins, 37 of which had never been reported as raisin volatiles. Odour activity values (OAVs) of these volatiles were calculated; 20 compounds had OAVs above 1. The aroma characters of the three varieties were quite similar except for some differences in the intensity of each aroma character. The main free-form volatiles were ethyl acetate, hexanoic acid, (*E,E*)-2,4-heptadienal and geraniol, with β-damascenone, 3-ethyl-2,5-dimethylpyrazine, 1-octen-3-ol and hexanal making the highest contribution to the aroma. Fruity and floral were the main characteristics of the free-form aromas in raisins. The main bound-form volatiles were benzyl alcohol and acetoin, with β-damascenone contributing most to the bound-form aromas, enhancing the floral, fruity and fatty aroma.

1. Introduction

Raisins are rich in nutritional content, and they are not only consumed as a snack, but also can be added to other foods for improving the flavour and nutrition of related products. According to the statistics from the United States Department of Agriculture for the year 2013, the world raisin production is approximately 1.2 million tons. China accounted for nearly 14% with a production of 165,000 tons, and ranked fourth after the United States, Turkey, and Iran. The raisins in Turpan, Xinjiang account for approximately 75% of the total output of the country. There were more than 20 varieties of grapes planted in Turpan, such as Horse Milk, Ruby Seedless, Flame Seedless, Muscat Hamburg, Crimson Seedless, Centennial Seedless and Beauty Seedless, of which Thomson Seedless raisin (green variety), Flame Seedless raisin (red variety) and Crimson Seedless raisin (red variety) are the main varieties for raisin making. This study focused on these three varieties.

Raisins are traditionally produced by drying fully ripe grapes in the sun or in the air, or even using modern technologies such as microwave heating, freeze-drying, and oven-drying (Christensen, 2000). Different from raisins produced in other areas, most raisins in Turpan are dried in air instead of in the sun. This unique air-drying method may have an effect on the aroma of raisins compared with the more common sun drying method. The volatile compounds of air-dried raisins had not been studied before.

Aroma is a very important attribute in the sensory quality of raisins for determining consumers' acceptance. Raisin aroma may depend on such factors as the grape variety, geographical origin, vintage, drying method, and storage conditions. The majority of raisin volatiles are derived from three sources: fresh grapes, the oxidative degradation of unsaturated fatty acids, and the Maillard reaction (Guiné et al., 2010, Chap. 31). Raisin volatiles consist of free and glycosidically bound volatile compounds. The glycosidically bound compounds can barely be tasted in raisins, but they constitute important potential aroma components (Spagna, Romagnoli, Angela, Bianchi, & Pifferi, 1998). When raisins are added to bread, jam and beverages the non-volatile glycosidically bound compounds can be released, thus increasing and changing the flavour. The bound-form volatiles in grapes have been widely researched (Fenoll, Manso, Hellin, Ruiz, & Flores, 2009) but, so far, few reports are available on the glycosidically bound aroma compounds of raisins.

Moreover, almost all research on raisin aroma was carried out 25 years ago and focused mostly on sun-dried raisins. Although 67 volatile compounds have been identified qualitatively (Buttery, Seifert, Ling, Soderstrom, & Yerington, 1981; Guiné

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et al., 2010; Joulain & Fourniol, 1990; Ramshaw & Hardy, 1969), many important volatile components have been missed because of the lack of sophisticated extraction and isolation equipment (Guiné et al., 2010). The volatile components of air-dried raisins are quite different from those of sun-dried raisins in variety and concentration. There is still much work left to study regarding raisin aroma compounds. The purpose of our research is to identify the free and glycosidically bound volatile compounds of air-dried raisins, using solid-phase micro extraction (SPME), figure out the aroma profiles of both free and bound volatiles, and evaluate the contribution of glycosidically bound volatiles to the aroma of foods containing raisins.

2. Materials and methods

2.1. Materials

Thompson Seedless, Flame Seedless and Crimson Seedless grapes (Fig. 1) were harvested in the same parcel of land in Turpan (Xinjiang, China) in 2011. Fully ripe grapes with total soluble solids (TSS) of 20.0–22.0 °Brix were used for making raisins. All of the grape varieties were dried by air in the same drying house [Supplementary Fig. 1(A)], and 100 kg of each grape variety hung on a piece of "curtain" [Supplementary Fig. 1(B)]. The grapes are dried by the hot and dry desert winds in ventilated and lucifugal adobe houses, which are made of claw bricks measuring approximately $3 \times 4 \times 6–8\ m^3$, with many brick-sized and cross-shaped openings in the walls (Fang et al., 2010). The drying process finished when the weight of raisins was constant for three days; the water loss of Thompson Seedless, Flame Seedless and Crimson Seedless grapes reached 77.72%, 71.89% and 73.28% of their fresh weight after 45, 30 and 40 days, respectively. Then three 1-kg samples of each raisin variety were collected randomly and covered with ice during transportation from Xinjiang to Beijing by air. All of the samples were frozen at −40 °C until analysis and every sample was analysed in triplicate. The detailed physicochemical parameters information is listed in Supplementary Table 1.

2.2. Chemicals

Sodium chloride (NaCl), tartaric acid, glucose, sodium hydroxide (NaOH), citric acid, and sodium dihydrogen phosphate were obtained from Beijing Chemical Works. Pure water was obtained from the Milli-Q purification system (Millipore, Bedford, MA). Ethanol, dichloromethane, and methanol were purchased from Honeywell (Morris Township, NJ).

The following chemical standards purchased from Sigma–Aldrich (St. Louis, MO) were used for identification and quantification: 3-methyl-1-butanol (99.0%), 1-octanol (99.0%), 1-octen-3-ol (98.0%), 2-ethyl-1-hexanol (99.0%), 1-nonanol (99.0%), benzyl alcohol (98.0%), octanoic acid (99.0%), 2-methylpropanoic acid (99.5%), hexanoic acid (99.5%), heptanoic acid (99.0%), hexanal (98.0%), (*E*)-2-hexenal (98.0%), octanal (99.0%), nonanal (95.0%), benzaldehyde (99.0%), benzeneacetaldehyde (90.0%), ethyl acetate (99.8%), diethyl succinate (99.0%), ethyl phenylacetate (99.0%), methyl salicylate (99.0%), ethyl nonanoate (98.0%), 6-methyl-5-hepten-2-one (99.0%), acetoin (96.0%), limonene (97.0%), *p*-cymene (98.0%), terpinolene (97.0%), α-terpineol (90.0%), linalool (97.0%), hotrienol (97.0%), neral (95.0%), β-damascenone (>90.0%), β-citronellol (95.0%), geraniol (99.5%), geranylacetone (containing 35% nerylacetone), geranic acid (85.0%), 2-ethyl-6-methylpyrazine (99.5%), 2,3-diethylpyrazine (98.0%), 3-ethyl-2,5-dimethyl pyrazine (98.0%), phenol (99.9%), naphthalene (99.0%), furfural (99.5%), 5-methyl-2-furfural (99.0%) and 4-methyl-2-pentanol (98.0%, internal standard).

Glycosidase AR2000 (Rapidase) was obtained from DSM Food Specialties (France). Cleanert PEP-SPE (200 mg/6 mL) was purchased from Bonna-Agela Technologies (Tianjin, China).

2.3. Sample pretreatment

One hundred raisins were soaked overnight in an equal weight of distilled water at 4 °C. Each variety was prepared in triplicate. The next day, the samples were homogenised in a Waring blender and macerated for 240 min. Then, the pulp was centrifuged three times at 8000 rpm, 4 °C for 10 min until the entire supernatant was obtained (Luning, Ebbenhorst-Seller, de Rijk, & Roozen, 1995; Möller & Nyberg, 2003).

2.4. Preparation of free- and bound-form volatiles

The free-form volatiles were detected using the supernatant directly, while the extraction of the bound-form volatiles was carried out as per our previous report (Wen et al., 2014) with some modifications. All samples were tested in triplicate.

The Cleanert PED-SEP column was activated by 10 mL methanol and 10 mL water separately before 1 mL supernatant was added. Then, sugar and acid were removed by 5 mL water, and most of the free-form volatiles were washed out by 5 mL dichloromethane. Finally, 20 mL methanol was used to elute the glycosidically bound volatiles, which were collected in a 50 mL round-bottom flask. Then, the solvent was removed by reduced pressure distillation in 30 °C water bath to finally obtain the bound-form volatile compounds. Then 5 mL citrate/phosphate (2 M) buffer solution at pH 5 was added into the flask, the bound-form volatile compounds were enzymatically hydrolysed with the action of 100 μL AR2000 (100 mg/L in 2 M citrate/phosphate buffer at pH 5.0) for 16 h at 40 °C in an incubator (Ubeda et al., 2012; Wen et al., 2014).

2.5. SPME conditions

The extraction of the free and bound-forms raisin volatiles was carried out with the following conditions: 5 mL sample and 10 μL 4-methyl-2-pentanol (1.0018 mg/L) were blended in a 15 mL glass vial containing a magnetic stirrer. Then 1.3 g NaCl were added, and the sample vial was closely capped with a PTFE-silicon stopper.

Fig. 1. Photographs of the three raisin varieties. (A) Thompson Seedless raisins; (B) Flame Seedless raisins; (C) Crimson Seedless raisins.