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Effect of heat treatments on the essential oils of kumquat (*Fortunella margarita* Swingle)

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ABSTRACT

Kumquats (*Fortunella margarita* Swingle) cultivated in Taiwan are eaten raw or made into candied fruit or fruit tea. For the experiments described in this paper, essential oils were obtained from kumquat peels or whole fruit by cold pressing, steam distillation or heating in water at 90 °C for 15 min followed by steam distillation. The volatile components contained in the essential oils were identified by direct injection (DI) or headspace-solid phase microextraction (HS-SPME) coupled with gas chromatography (GC). A total of 43 compounds were identified, of which 37 were verified by DI/GC and 31 by HS-SPME/GC. Hot water heating increased the yields of essential oils from both peels and whole fruit. The principal constituents of the oils were similar except for the minor compounds, including linalool, terpinen-4-ol and α-terpineol, the levels of which increased after steam distillation. The whole fruit also contained higher levels of terpene alcohols.

1. Introduction

Kumquat (*Fortunella margarita* Swingle) is the smallest of the true citrus fruits belonging to the family Rutaceae, which is native to Central China. The round-oval fruit is orange-yellow and approximately 2 cm in diameter. The flesh is sour, and the fruit is eaten together with the peel. Kumquats were first cultivated in China and then introduced to Taiwan from Japan in the 19th century (Hsueh, 2001). Today, they are commonly grown in I-Lan, Taiwan. *F. margarita* Swingle is the major species. Kumquats are suitable for various products such as candied fruit, wine and marmalade, and they can be eaten raw, as whole fruit or added to beverages. Kumquat fruit tea is a special use for the fruit in Taiwan. Fruit tea is prepared by adding boiling water into a glass cup containing kumquat fruits and is a hot beverage admired by many Taiwanese especially in winter, because of its aroma and taste. There are only a few studies of rare citrus fruits, such as kumquats. Bernhard and Scrubis (1961) conducted one of the first studies of the volatile constituents of kumquats, They extracted kumquat oil by steam distillation and determined that it consisted of α-pinene, myrcene, terpene esters, aldehydes, ketones, free alcohols and limonene, which was the most abundant compound. Koyasako and Bernhard (1983) identified 71 volatile compounds in kumquat oil extracted by simultaneous distillation and extraction. They also reported that the most abundant compound was limonene, which comprised 93% of the oil. Umano, Hagi, Tamura, Shoji, and Shibamoto (1994) identified 84 compounds in steam-distilled extracts and 35 compounds were identified following simultaneous purging/extraction. The most abundant compound was again limonene (87%), and other compounds included linalool, myrcene, and geranyl acetate. An additional 35 compounds were identified from the oil extracted by SPE, including limonene (97%), myrcene, α-pinene, and β-phellandrene. Choi (2005) identified 82 compounds in oil extracted by cold pressing. The major compounds were limonene (93.73%), myrcene (1.84%), and ethyl acetate (1.13%). The flavour dilution (FD) factors and relative flavour activities (RFAs) of volatile constituents were evaluated by aroma extract dilution analysis with gas chromatography–olfactometry (GC–O). Results indicated that limonene made only a small contribution to the aroma. This was confirmed by GC–sniffing analysis, which indicated that citronellyl acetate was the odour component most similar to kumquat

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by evaluation with GC–O. Schirra et al. (2008) investigated the influence of a hot water dip for 2 min at 50 °C on the volatile compounds in the fruit. The results indicated that the small amount of *p*-menta-1,5-dien-1-ol increased without significantly affecting the levels of other compounds.

The aim of this work was to investigate the volatile constituents produced by different extraction methods of essential oils and the effects of heating on the constituents in the essential oil of Kumquat peels or whole fruits. Two extraction methods involving heating were used: steam distillation and immersion in hot water. The differences in aromatic notes caused by heating will be discussed.

2. Materials and methods

2.1. Plant material

Kumquats were purchased from the Taipei Agricultural Products Marketing Co., Taiwan. They were washed under running water, dried and separated into two piles, one to be hand-peeled for peels analysis and the other for whole fruit analysis.

2.2. Methods

2.2.1. Extraction of essential oil

(1) *Cold pressing:* The kumquats were peeled by hand and a sugarcane squeezer was then used to squeeze 2 kg of peels. The vacuoles containing oil in the peel were broken, releasing the oil. The mixture of squeezed oil and pomace was stored in a beaker at 4 °C for one day to achieve perquisite lamination. The oil layer was separated by a high-speed centrifuge (9000*g*) at 4 °C, for 40 min. After collection of the essential oil, centrifugation was repeated (3000*g*) for 10 min to isolate the fine oil layer in the essential oil sample. This sample was then stored in the dark at 0 °C. This experiment and all other experiments in this study were carried out in triplicate.

(2) *Extraction of essential oils from peels:* Kumquat peels (150 g) were homogenised for 2 min with 600 mL of deionised water and placed into a 5 L round-bottom flask. The homogenate was steam-distilled for 2 h to obtain the essential oils. Samples were then stored in the dark at 0 °C.

(3) *Extraction of essential oils from whole fruit:* Whole fruits (1000 g) were homogenised for 2 min with 1000 mL of deionised water and placed into a 5 L round-bottom flask. The homogenate was steam-distilled for 2 h to obtain the essential oils. Samples were then stored in the dark at 0 °C.

(4) *Extraction of essential oils from peels using hot water:* Peels (150 g) were heated in water at 90 °C ± 3 °C for 15 min, homogenised for 2 min with 600 mL of deionised water and placed into a 5 L round-bottom flask. The homogenate was steam-distilled for 2 h to obtain the essential oils. Samples were then stored in the dark at 0 °C.

(5) *Extraction of essential oils from whole fruit using hot water:* Whole fruits (1 kg) were heated in hot water at 90 °C ± 3 °C for 15 min. They were homogenised for 2 min with 1 L of distilled water and placed into a 5 L round-bottom flask. The homogenate was steam-distilled for 2 h to obtain the essential oils. Samples were then stored in the dark at 0 °C.

2.2.2. Analysis of volatile compounds

(1) *Direct injection analytic method (DI):* One microliter of each sample was injected and the volatile compounds were injected into a gas chromatograph injection unit.

(2) *HS-SPME analysis:* A 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (PDMS) fiber (Supelco Inc., Bellefonte, PA) was used for aroma extraction. Each sample (1 mL) was placed in a 5 mL vial. The SPME fiber was exposed to each sample for 20 min at 25 °C; then each sample was injected into a gas chromatograph injection unit.

(3) *Analysis of the components of the essential oils by GC/FID and GC/MS:* Qualitative and quantitative analyses of the volatile compounds were conducted using an Agilent 6890 GC equipped with a 60 m × 0.25 mm i.d. DB-1 fused-silica capillary column with a film thickness of 0.25 μm and a flame ionisation detector. Injector and detector temperatures were maintained at 250 °C and 300 °C, respectively. The oven temperature was held at 40 °C for 1 min and then raised to 200 °C at 2 °C/min and held for 9 min. The carrier gas (nitrogen) flow rate was 1 mL/min. Kovats indices were calculated for the separated components relative to a C_5–C_{25} *n*-alkanes mixture (Schomburg & Dielmann, 1973).

(4) *Analysis of the components of the essential oils by GC–MS:* Identification of the volatile compounds was conducted using an Agilent 6890 GC equipped with a 60 m × 0.25 mm i.d. DB-1 fused-silica capillary column with a film thickness of 0.25 μm and an Agilent model 5973 N MSD mass spectrometer (MS). The injector temperature was maintained at 250 °C. The GC conditions in the GC–MS analysis were the same as for the GC analysis. The carrier gas (helium) flow rate was 1 mL/min. The electron energy was 70 eV at 230 °C. The constituents were identified by matching their spectra with those recorded in the MS library (Wiley 7n).

2.2.3. Statistical analysis

Each sample was extracted in triplicate and the concentration of volatile compounds was determined as the mean value of three repetitions. The data were subjected to a mono-factorial variance analysis, with Duncan's multiple range method used to identify significant differences of $p < 0.05$ (SPSS Base 12.0).

3. Results and discussion

3.1. Constituents of kumquat essential oils

3.1.1. Yields of essential oils

Using steam distillation, we obtained colourless essential oils from kumquat peels and light-yellow essential oils from whole fruit. Cold pressing kumquat peels resulted in essential oils that were a golden-orange colour. The yields were: 0.125 ± 0.010% (cold-pressing peels, indicated by CP/P); 0.266 ± 0.006% (steam distilled peels, indicated by SD/P); 0.343 ± 0.005% (peels heated in hot water followed by steam distillation, indicated by HWH/SD/P); 0.052 ± 0.004% (steam distilled whole fruit, indicated by SD/F); and 0.056 ± 0.010% (whole fruit heated in hot water followed by steam distillation, indicated by HWH/SD/F). These results indicate that hot-water heating (HWH) increased the yields of essential oils for both peels and whole fruits (HWH/SD/P) and (HWH/SD/F) when compared to steam distillation alone (SD/P and SD/F) (Table 1). It is likely that hot-water heating causes tissues in the peel or in the flesh be damaged, thus releasing the essential oils. When Schirra et al. (2008) dipped kumquats (*Fortunella japonica* Lour. Swingle Cv. Ovale) cultivated in Italy in hot water (50 °C, 2 min) and then stem-distillated them, the yield of essential oils was 0.18 ± 0.02%. Choi (2005) extracted essential oils by hand-pressing the flavedo (*F. japonica* Swingle), and the yield was 0.25%. Umano et al. (1994) used steam distillation and simultaneous purging/extrac-