



A novel analytical approach in the assessment of unprocessed Kaffir lime peel and pulp as potential raw materials for cosmetic applications



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ABSTRACT

Volatile fraction of fruits is a rich source of bioactive and aroma compounds, which can be used in the cosmetics industry after meeting relevant criteria. This is particularly evident in citrus fruits, especially in *Citrus hystrix*, in which the headspace consists mainly of terpenes. Due to the insufficient sensitivity of analytical methods, essential oils are used in investigations in contrast to fresh fruits. Therefore, a novel approach in the assessment of unprocessed *Citrus hystrix* was proposed for the first time. It was proven that the application of two-dimensional gas chromatography coupled with time-of-flight mass spectrometry combined with solid phase microextraction gives reliable results in this context. Quantitation of key aroma compounds (α -pinene, limonene, citronellal, linalool, terpinen-4-ol, myrcene, α -terpineol, and citral), in the peel and pulp of fruit after prior assessment of bioactive properties measured as total phenolic content, ferric-reducing/antioxidant power and binding to human serum albumin, gives opportunity to use *Citrus hystrix* as a raw material in the cosmetic industry. Terpinen-4-ol and citronellal appeared to be the most important constituents of *Citrus hystrix* with the highest concentrations in the peel ($34.58 \pm 0.75 \mu\text{g/g}$) and pulp ($66.02 \pm 0.85 \mu\text{g/g}$), respectively. Polyphenols and antioxidant activities and binding properties revealed approximately twice higher bioactivity of Kaffir lime peel than pulp. Fluorescence studies of interaction of polyphenol extracts and some volatile standards with human serum albumin (HSA) showed relatively high binding properties and the correlation between biological activity and the volatile composition. Terpenes are primarily used as components of the fragrances of new perfumes and also as additives to creams, lotions or shampoos. The natural origin of terpenes is recommended in cosmetics industry.

1. Introduction

Kaffir lime (*Citrus hystrix*, *Citrus hystrix*) belongs to the plants of Ruta family (*Rutaceae*). The fruit is also known as Kaffir lime, Thai lime, Makrut or Angel Wings, due to the shape of the leaves (Wongpornchai, 2012). Most often it occurs in Indonesia, Malaysia, the Philippines, Laos, Thailand and Vietnam (Tunjung et al., 2015). In this region of the world Kaffir lime leaves are, besides ginger and lemon grass, the most important spice added to almost every dish. Kaffir lime juice and pulp is not directly consumed because of their pungent taste. However, it is an excellent source of antimicrobial, antiviral, and antioxidant substances that can be used in the cosmetic industries (Fortin et al., 2002; Rafiq et al., 2016; Tunjung et al., 2015). Kaffir lime peel except for small culinary applications is also industrial waste (Shaha et al., 2013).

Citrus fruits are one of the more readily consumed fruits in the

world, not only due to their flavorful, but also pro-health properties. The main part of citrus fruit, which is used on an industrial scale, is the pulp from which juices are squeezed. It is estimated that more than half of the fruit after the production process is an industrial waste. This problem is greater in the case of Kaffir lime, which juice is not consumed directly, so a significant part of the fruit is a post-production waste. For this reason, new methods of waste management are sought. However, still much of the waste remains unused. Other way to utilize fruit peel is the production of bioethanol and biogas (Negro et al., 2016; Taghizadeh-Alisarai et al., 2017). However, this process can be disturbed by the presence of terpenes, especially limonene, in the fruit peel (Ruiz and Flotats, 2014). There are some reports on the disposal of terpenes, including mainly limonene, from citrus waste. Pourbafrani et al. (2010) proposed a method of removing limonene during the production of biogas from citrus waste. It is important to know exact

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concentrations of terpenes in the sample in order to receive fragrances, essential oils and bioactive ingredients from citrus peel or pulp. It will allow to designate which part of the fruit is more aromatic and its differences. There are no reports on the methodology of fresh Kaffir lime analysis. In general, the essential oils are analyzed. The composition of Kaffir lime peel essential oil (EO) was assessed using gas chromatography and mass spectrometry (GC–MS) (Haiyee and Winitkitcharoen, 2012; Kasuan et al., 2013). The reason of use EOs for the analysis could be too low sensitivity of the analytical devices. Analysis of fresh citrus could prevent the formation of artifacts and loss of analytes, which takes place in the extraction and distillation processes carried out to obtain EOs (Ziino and Romeo, 2004). The solution that enables the analysis of fresh fruit is the application of novel analytical techniques which are characterized by high resolution, as two-dimensional gas chromatography (GC×GC). According to the best of our knowledge, there is a lack of reports about the analysis of volatile fraction peel and pulp of *C. hystera* using two-dimensional gas chromatography. Lubinska-Szczygeł et al. (2018) analyzed the volatile fraction of lime juice. This technique, in combination with solid phase microextraction and time of flight mass spectrometer, has been used repeatedly for fruit analysis (Dymerski et al., 2015).

The aim of the research was to develop an analytical methodology to identify, determine and compare the contents of volatile compounds present in the samples of Kaffir lime pulp and peel using the two-dimensional gas chromatography technique coupled with time-of-flight mass spectrometry (GC×GC-TOFMS). It will explain the potential causes of different taste of peel and pulp, restrictions on use of this fruit in gastronomy and provide an information, which could be a basis for further elaboration of isolation method for cosmetology applications. For this reason, two-dimensional gas chromatography couples with time-of-flight mass spectrometry was selected as a proper tool for the analysis of complex matrix of Kaffir lime fruit (Dymerski et al., 2013). In order to find correlation between the biological activity and volatile composition total polyphenols, antioxidant activities and binding properties of main volatiles to human serum albumin were carried out. Fluorescence measurements and antioxidant assays were performed.

2. Materials and methods

2.1. Samples and standards solutions

The subject matter was the peel and pulp of Kaffir lime (*Citrus hystera*, *Citrus hystrix*). Kaffir lime fruits were bought in Bangkok (Thailand). Fruit samples were imported to Poland in sealed plastic bags in portable fridge maintained at between 10 and 15 °C. The procedure of sample preparation is shown in Fig. 1A. Standard solutions of terpenes: α -pinene, limonene, citronellal, linalool, terpinen-4-ol, myrcene, α -terpineol, and citral (Sigma-Aldrich, St. Louis, MO, USA) were prepared using methanol (Avantor Performance Materials Poland S.A.) as a solvent. Trolox (6-hydroxy-2,5,7,8-tetramethyl-chroman-2-carboxylic acid); Folin–Ciocalteu reagent (FCR); Tris, tris (hydroxymethyl)aminomethane; $\text{FeCl}_3 \times 6\text{H}_2\text{O}$; were obtained from Sigma Chemical Co., St. Louis, MO, USA. 2, 4, 6-tripyridyl-s-triazine (TPTZ) was purchased from Fluka Chemie, Buchs, Switzerland. All reagents were of analytical grade. Deionised and distilled water were used throughout.

2.2. Apparatus

Agilent 7980A (Agilent Technologies, Palo Alto, CA, USA) two-dimensional gas chromatograph equipped with a liquid nitrogen cooled two-stage cryogenic modulator (Zoex Co., Houston, USA) and MPS (Gerstel Co., Mülheim, Germany) configured as headspace autosampler was used. Liquid nitrogen was used as the cooling medium. The column set consisted of a 30 m \times 0.25 mm i.d. \times 0.25 μm – Equality 1 (Supelco Bellefonte, PA, USA) primary column and 2 m 0.1 mm i.d. \times 0.1 μm –

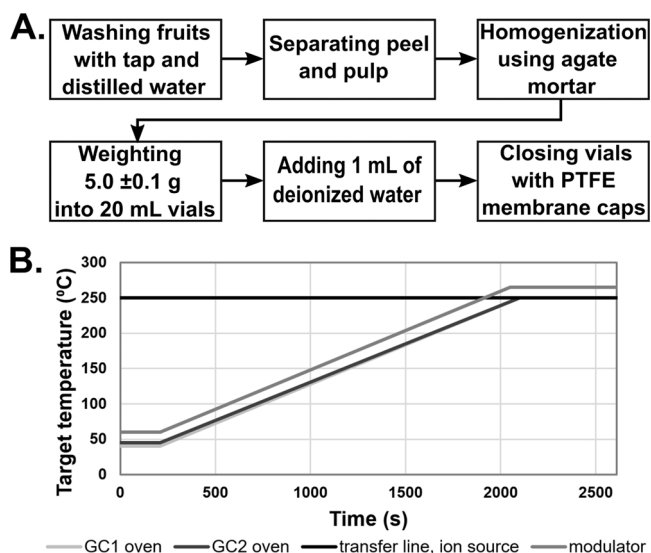


Fig. 1. A Scheme of sample preparation; B. Chromatographic temperature program applied in HS-SPME/GC×GC-TOFMS analytical procedure.

SGWAX (SGE Analytical Science Austin, TX, USA) secondary column. Applied temperature program is shown in Fig. 1B. Modulation period was 4 s (hot pulse of 0.80 s). Helium N6.0 was used as carrier gas and its volumetric flow rate was set up to 1 mL/min. The injector worked in splitless mode at a temperature of 250 °C. A Pegasus[®] IV time-of-flight mass spectrometer (LECO Corp.) was used as detector. The transfer line and the ion source were maintained at 250. The detector voltage was set to –1600 V and the MS was operated in electron impact ionization mode (70 eV). Cool time between stages was 1.20 s. In the step of isolation and enrichment of analytes a solid phase microextraction (SPME) was used. SPME 50/30 μm of thickness and 2 cm of length Carobxen/Polydimethylsiloxane/Divinylbenzene (CAR/PDMS/DVB) fiber was used (Sigma-Aldrich, St. Louis, MO, USA). The temperature of extraction was set up to 35 °C, and the time of a single extraction was 35 min. Before the extraction the samples were kept at 40 °C for 2 min and agitated with a magnetic stirrer (700 rpm). Thermal desorption was set up to 250 °C for 5 min to release the analytes from the surface of fiber. Between each analysis, the fiber was cleaned for 2 min at 250 °C.

2.3. Data acquisition and qualitative analysis

ChromaTOF (LECO Corp., version 4.44.0.0) software was used to collect data. Tentative identification was done by correlation of retention times of analytes with retention times of authentic standards. The time of flight mass spectrometer (Pegasus 4D), which identified the chemicals time of flight, was produced by LECO Corp. (St. Joseph, MI, USA). Automated peak find and spectral deconvolution have been employed during data treatment. The mass range (m/z) from 40 u up to 500 u and the acquisition rate of 125 spectra/s were used to collect data. Major chemicals were identified by comparison of mass spectra with data included in NIST 11 and Wiley library.

2.4. Quantitative analysis

Quantitative analysis was performed using analytical procedure described above. Chemical compounds with the highest peak area in both samples were selected for quantitative determination. The standard addition method was used as a method of quantitative determination. Using this method, it was possible to compensate effects of matrix. Sample was spiked with the terpenes standards mixture to generate nine amendment levels of 0.1, 0.2, 0.5, 1.0, 5.0, 10.0, 20.0, 50.0, 100.0 $\mu\text{L/L}$ (v/v). The analysis was performed in three replicates

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