H. Yıldırım et al. / Hacettepe J. Biol. & Chem., 2026, 54 (1), 1-7

Research Article

Hacettepe Journal of Biology and Chemistry

journal homepage: https://hjbc.hacettepe.edu.tr/
Dergipark Akademik: https://dergipark.org.tr/en/pub/hjbc

Investigation of Molecular Compounds in Kumquat (*Fortunella* Spp.) Peel via Raman Spectroscopy

Kamkat (*Fortunella* Spp.) Kabuğundaki Moleküler Bileşiklerin Raman Spektroskopisi ile İncelenmesi

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ABSTRACT

In this study, Raman spectroscopy is employed to investigate the chemical compounds of kumquat peels and compared that of orange. Kumquat is a citrus fruit belonging to the genus Fortunella in family Rutaceae. It is observed that kumquat peel has 3 main Raman active characteristic vibration modes specified to carotenoids, which is dominated by β-carotene at 1007, 1158 and 1526 cm^{-1}, as it is well known for orange. The carotenoid distribution within the cross-section of kumquat is also investigated. The carotenoid-related Raman vibration modes are relatively stronger on the peel of kumquat, which is an important finding especially for the fruits that can be eaten with its peel. Our results pave the way to take an attention for the importance of kumquat as being a fruit that can be grown up in different climates compared to orange, which grow in warm climates.

Key Words
Kumquat, citrus peels, functional components, raman spectroscopy, spectral mapping, carotenoid.

ÖZ

Bu çalışmada, Raman spektroskopisi kullanılarak kamkat kabuklarının kimyasal bileşenleri araştırılmış ve portakal kabukları ile karşılaştırılmıştır. Kamkat, Rutaceae familyasından Fortunella cinsine ait bir turunçgil meyvesidir. Kamkat kabuğunun, portakal için iyi bilindiği gibi 1007, 1158 ve 1526 cm^{-1}'de β-karoten tarafından domine edilen karotenoidlere özgü 3 ana Raman aktif karakteristik titreşim moduna sahip olduğu gözlemlenmiştir. Kamkatın enine kesiti içindeki karotenoid dağılımı da araştırılmıştır. Karotenoidle ilişkili Raman titreşim modları kamkatın kabuğunda nispeten daha güçlüdür, bu da özellikle kabuğuyla yenebilen meyveler için önemli bir bulgudur. Sonuçlarımız, sıcak iklimlerde yetişen portakala kıyasla kamkatın farklı iklimlerde yetişebilen bir meyve olmasının önemine dikkat çekmektedir.

Anahtar Kelimeler
Kamkat, turunçgil kabukları, fonksiyonel bileşenler, raman spektroskopisi, spektral haritalama, karotenoid.

Article History: Received: Jun 30, 2025; Accepted: Aug 14, 2025; Available Online: Dec 30, 2025.
DOI: https://doi.org/10.15671/hjbc.1729832
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INTRODUCTION

Kumquat is a citrus fruit belonging to the genus Fortunella of the Rutaceae family. It is also known as golden orange in Türkiye. Up to date, Kumquat is classified into four main types: Fortunella japonica, Fortunella margarita, Fortunella crassifolia and Fortunella hindsii [1]. Kumquat fruits exhibit an orange-yellow hue, an elliptical shape and measuring approximately 2 cm in diameter, and it is regarded as one of the smallest citrus fruits [2]. Kumquats have numerous advantages, such as cold resistance, an eatable peel, small size, and adaptability to various soil types [3-4]. These advantageous make them easy to care for and ideal for smaller spaces, offering a versatile citrus option suitable for diverse environments, ranging from greenhouses to terraces, and as a cold-tolerant citrus fruit [4].

Compared to other citrus fruits, kumquat can be consumed whole with its peel, which provides an advantage in the intake of bioactive substances. While the pulp part of the fruit is sour, the peel part has a characteristic aroma due to flavonoids and terpenoids, which are important in the essential oil composition [5-6]. Because of its acidic taste and soft peel, kumquat is used in products such as jams, pickles and sauces, in addition to its natural consumption [7-8]. Besides, considering its use in the food industry, kumquat contains a variety of phytochemicals, including carotenoids, essential oils, ascorbic acid and flavonoids. These components are small molecules that are not essential for the survival of plants but represent pharmacological activity [9]. Kumquat is becoming increasingly important in traditional medicine because it contains many beneficial phytochemicals with diverse biological effects [5-10]. Phytochemicals are known to have beneficial biological effects. These include antibacterial, anti-oxidative, anti-inflammatory, anti-cancer, as well as cardiovascular protective effects [12-13]. For example, carotenoids, an important component in citrus peel, have the ability to detoxify

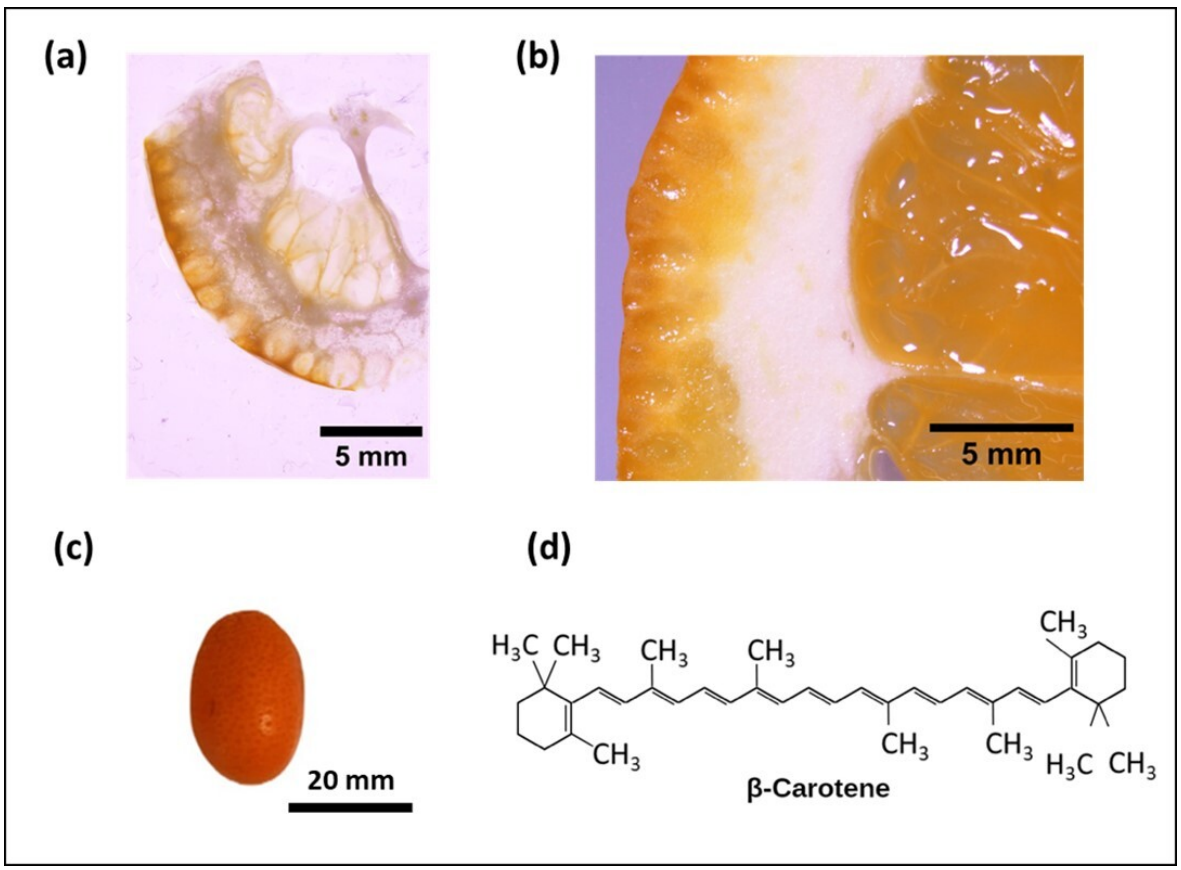

Figure 1. Optical microscope image of a) kumquat and (b) orange. c) Image of kumquat and d) Chemical structures of β -carotene (Mortensen & Skibsted, 1997).

free radicals in cells. An important feature of carotenoids is that they are precursors of vitamin A. The body can convert certain carotenoids into active vitamin A [14]. Carotenoids are used as nutraceuticals in various diseases such as eye diseases, cardiovascular diseases, neurodegenerative diseases and cancer [15]. It is crucial to find and analyse bioactive compounds in citrus peels. Many methods such as Gas Chromatography-Mass Spectrometry, High-Performance Liquid Chromatography, Fourier Transform Infrared Spectroscopy are used for biocomponent analysis of citrus peel [16-17-18]. These methods for component analysis have the advantages of high sensitivity and accuracy, but also disadvantages such as complexity and time-consuming for sample preparation [19]. In this study Raman spectroscopy, which is a non-destructive method, is employed to determined and analysis the compounds of kumquat peel. Raman spectroscopy is an analytical technique where inelastic scattered photons is used to measure the vibrational energy modes of a molecules. When photons interact with a substance, the frequency of most of the scattered light does not change, which is called Rayleigh scattering. However, inelastic light scattering processes can also occur due to molecular vibrations, so-called Raman scattering [20-21-22]. The spectrum of scattered photons in Raman spectroscopy is fingerprint of the investigated material therefore allows easy identification of the molecule of interest. Raman spectroscopy has many advantages such as ease of sample preparation, non-destructive and the ability to work with aqueous samples. Because of these advantages, Raman spectroscopy has become a powerful alternative tool to other commonly used techniques. Accordingly, Raman spectroscopy has been used as a promising analytical tool in recent years as it provides a chemical fingerprint for molecular identification [22-23].Raman spectroscopy is becoming increasingly popular in research on food, environment, medicine and many other fields. In various application areas such as pesticide detection [24], pathogen detection in food [25], water pollution [26] and neurodegenerative disease diagnosis [27].

In 2017, Yang et al. used Raman spectroscopy for chemical mapping of functional compounds in citrus peels. The relative amount and distribution of essential oils, carotenoids and flavonoids in citrus peels at different locations (flavedo, albedo and longitudinal section) were studied [19]. To the best our knowledge, there is no study that uses Raman spectroscopy for the determination of functional components on kumquat fruit. In this study, carotenoids were determined in different locations (flavedo, albedo and crosssection) of kumquat fruit peel without any extraction process and a comparison was made between two kinds of citrus fruits (orange and kumquat). The fact that kumquat fruit can be consumed with its peel unlike other citrus fruits thanks to the terpenoids and flavonoids in the peel composition makes our research valuable. Kumquat is becoming increasingly important in food and pharmacology due to its nutritional and phytochemical content [11]. Therefore, a rapid and non-destructive determination of shell composition is very critical. The results obtained in our research are valuable in terms of advances in the use of Raman spectroscopy for the detection of biocomponents in citrus peels.

MATERIALS and METHODS

Sample Preparation

Kumquats and oranges from Verita (Verita, Istanbul, Türkiye) were soaked in saline for 10 min. The fruits were then washed three times with distilled water to remove the chemicals in the peel. Citrus peels were peeled. Pieces were cut for the Flavedo and Albedo parts. Cross-sectional pieces were also taken to understand the component distribution. Samples were adhered to the slide with double-sided tape and measured.

Raman Spectroscopy

Raman spectroscopy measurements was carried out using a free space custom modular micro-spectroscopy set-up equipped a thermoelectric cooled CCD (Newton BEX2-DD, Andor) with a 1800 grooves/mm of grating in a spectrometer (Shamrock 500i, Andor). To excite the samples, a 532 nm CW laser (Gem532, Novanta Photonics) was used, and the excitation laser beam is focused to a spot of 1.2 m in diameter and on the devices placed on a XYZ sample stage. Raman spectra from the samples were collected *via* a 50x objective (NA = 0.42) [29, 30].

RESULTS and DISCUSSION

The flavedo and albedo structures of kumquat and orange fruits were observed by optical microscope (Figure 2). It was noted that the flavedo layer of the kumquat (N~1,5 mm) was 2.5 times thinner than that of the orange (N~4 mm).

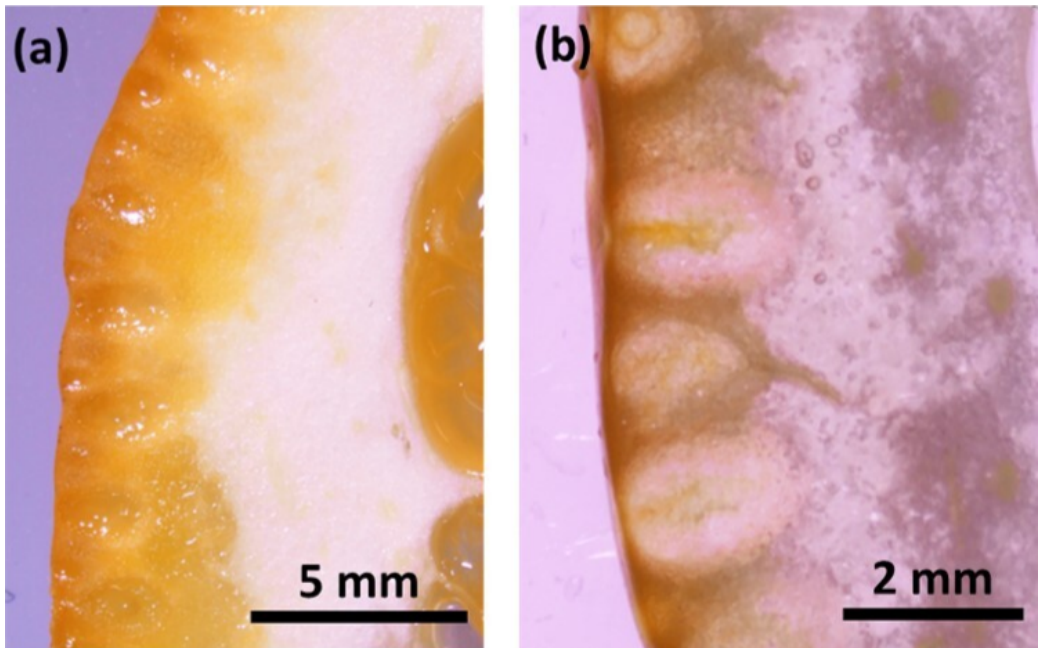

Figure 2. Cross-sectional optical microscope images of a) orange and b) kumquat.

The thinner flavedo part makes the kumquat fruit eatable with its peel. In addition to that the thinner flavedo layer of kumquat compared to orange is important for obtaining a higher concentration of beneficial components from a smaller part of the fruit.

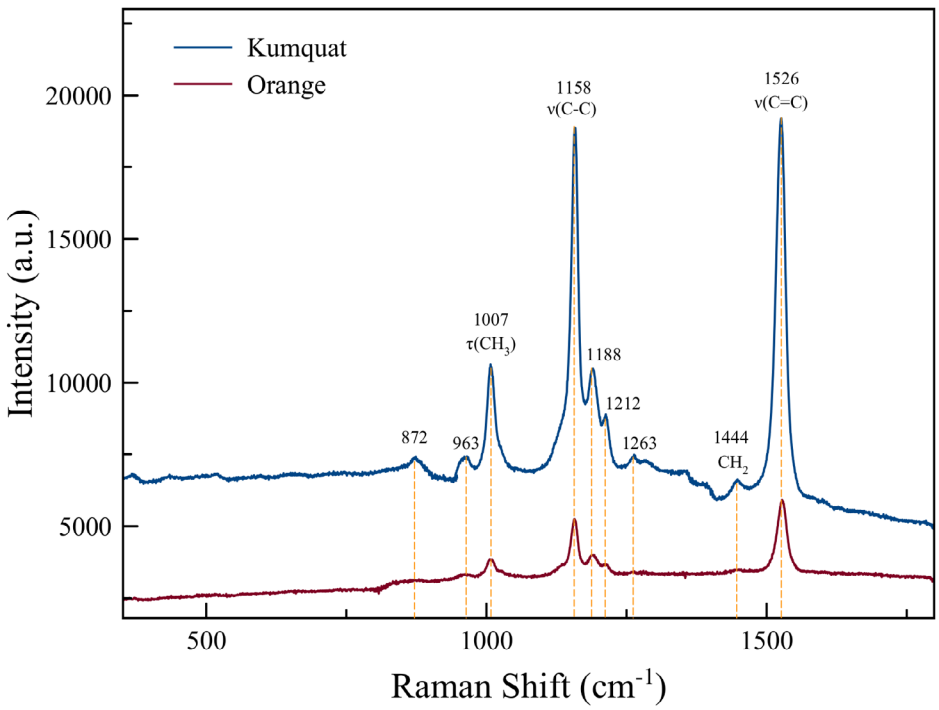

Figure 3. Raman Spectra of Orange and Kumquat.

Table 1. Wavenumbers of v1, v2 and v3 modes (cm−1) of the predominant carotenoids obtained from several products by Raman spectroscopy.

Sample	v_1 (C=C)	v_2 (C–C)	v_3(C–CH_3)	
Citrus	1528	1156	1010	Yang et al. 2017
Tomato	1510	1156	1005	Baranska et al. 2006
Carrot	1520	1156	1007	Schulz et al. 2005
Pumpkin	1527	1157	1008	Oliveira et al. 2009
Kumquat	1526	1158	1007	This work

Figure 3 shows the Raman spectra of kumquat and orange peel. The strong Raman peaks were observed at 1007, 1158 and 1526 cm^{-1} as well as the relatively weak peaks were observed at 872, 963, 1188, 1212 and 1263 cm^{-1} (Figure 3). Peaks at 1007, 1158 and 1526 cm^{-1} are assigned to carotenoids, a vitamin A precursor according to previous literature data [19] *β-carotene* containing 9 conjugated double bonds (Figure 1d) has been detected by Raman spectroscopy in foods such as tomatoes, carrots and pumpkin in previous studies. The bands attributed to carotenoids in the studies are shown in the Table 1.

Raman spectrum of carrot showed strong bands at 1520, 1156 and 1007 cm^{-1} assigned to ν(C=C), ν(C-C) and τ(CH_3) of *β -carotene* , respectively; in the Raman spectrum of tomato puree, *β -carotene* was observed with three intense bands at 1510 (v_1), 1156 (v_2) and 1005 cm^{-1} (v_3) [31-32]. According to the reported values in the literature, the results obtained confirmed the characteristic Raman bands at 1526 cm^{-1} and 1158 cm^{-1} assigned to the in-phase C=C and C-C stretching vibrations of the polyene chain and 1007 cm^{-1} assigned to the in-plane rocking modes of CH_3 groups attached to the polyene chain joined by C-C bonds [33-34]. In addition, the peak at 1444 cm^{-1} is assigned to the CH_3-CH_2 bending modes indicates essential oil [35, 36].

In the cross-sectional piece taken from kumquat fruit, the carotenoid content was investigated from the albedo layer to the flavedo layer. Looking at the distribution of carotenoids, it was found that the carotenoid density decreased when going from the albedo layer to the flavedo layer (Figure 4).

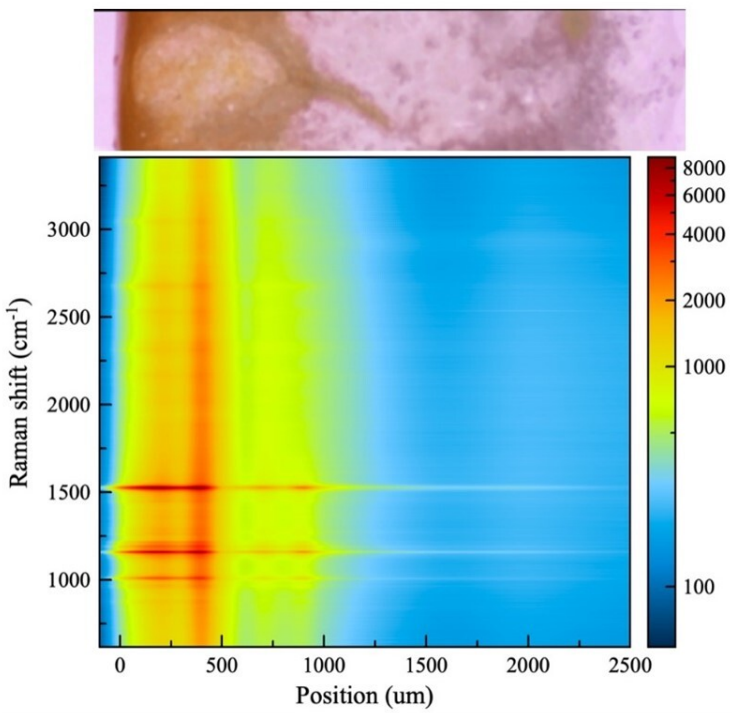

Figure 4. Raman spectrum mapping of transverse section of kumquat peel.

The thinner flavedo layer of kumquat compared to orange has significant effects on both the edibility of the fruit with the skin and the concentration of beneficial components inside. It is observed that the Raman peak intensities of both carotenoid and essential oils are 6 times stronger on the kumquat peel compared to that of orange. This makes kumquat a strong alternative for vitamin A intake beyond its advantageous properties such as cold resistance, compatibility with various soil types and edibility with its peel compared to other citrus fruits. In addition, the distribution of carotenoids in kumquat fruit reveals potential differences in the nutrient content of different parts of the fruit.

In conclusion, we have used Raman spectroscopy for a rapid and non-destructive detection of carotenoids in kumquat and compared that of orange peels. Raman spectrum analysis of kumquat peel have revealed distinct characteristic bands at 1007, 1158 and 1526 cm^{-1} associated with carotenoids, particularly dominated by β-carotene. This result indicates the potential of kumquat to be a valuable alternative among citrus fruits for obtaining vitamin A. It has been observed that the concentration of carotenoids is more pronounced in the flavedo part compared to the albedo part. The findings of this study address the differences in the biochemical profiles of citrus fruit peels and highlight the potential health benefits associated with kumquat peel consumption. The information obtained from our study will contribute to the quantitative analysis of the materials in the fruits. Furthermore, the successful application of Raman spectroscopy as a robust analytical tool for non-destructive compositional analysis in the field of food science and nutrition research.

Acknowledgments

This work was supported in part by the Scientific Research Projects Coordination Unit of Istanbul University (FBG-2022-38573, FBG-2021-37896).

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