Investigation of Optical and Flow Properties of Avocados by Spectroscopy and Rheology Methods

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Structural, optical and rheological properties of pulp and seed extracts of three different avocado cultivars were analyzed using spectroscopy and rheology techniques at room temperature. Ultraviolet spectra and Fourier transform infrared spectroscopy signals for the pulp and avocado seed extracts were recorded in the wavelength range 190–600 nm and the wave number range 4200–400 cm^{-1}, respectively. The flow behaviours for all avocado pulp and seed samples were also analysed in the shear rate range of 10^{-2}–10^{2} s^{-1} and in the frequency range of 10^{-1}–10^{3} rad/s, respectively. The ultraviolet spectra of all the samples were observed as two peaks around 210 and 290 nm. The optical energy band gaps for all samples were found to be consistent with Planck's radiation approach.

topics: spectroscopy, avocado, rheology, viscosity

1. Introduction

Avocado (*Persea americana* Mill.) is a tropical and subtropical fruit that is native to Mexico and Central America. There is evidence that it has been cultivated in Mexico for about 10000 years [1]. At the present time, avocado is produced in 65 countries [2]. The countries producing the most avocados in the world are Mexico (31.5%), Dominican Republic (9%), Peru (7.3%), Colombia (7.3%) and Indonesia (6.3%) [2]. The avocado tree belongs to the *Lauraceae* family and the genus *Persea* and has more than 150 varieties [3]. Fuerte, Hass, Ettinger, Zutano and Bacon are the most produced avocado cultivars in Turkey [4]. In the Mediterranean region of Turkey, around 4200 tonnes of avocados are produced annually on 949 hectares of harvested areas [2].

An average avocado fruit weighs approximately 150 to 400 g. An avocado fruit contains pulp, seed, and peel weighing about 73%, 16%, and 11%, respectively, and these proportions differ according to the cultivars [5]. Avocado pulp is a source of dietary fiber (1.4–3%), protein (1–3%), carbohydrates (0.8–4.8%), vitamins (C, E, K, B1, B2, B6, choline, nicotinic acid and pantothenic acid) and minerals (0.8–1.5%) [6]. In addition to all these ingredients, the most distinctive characteristic feature that distinguishes avocado from other fruits is the high lipid ratio (12–24%) and most of them is an unsaturated fatty acid (70 to 90%), which is very beneficial for health [6]. However, avocado seed is also a rich source of carbohydrates (42–81%), lipids (3–15%), proteins (0.14–9%), fibers (2–4.2%), minerals (1.3–4.3%) and other bioactive compounds [3].

Spectroscopy technique is one of the most important methods used in the analysis of physical and chemical properties of materials [7–9]. In our previous study, the qualitative analysis of organic vinegar was made using ultraviolet (UV) spectroscopy and rheology technique [10]. The present study occupies an important position in food physics as now it is avocado fruits and their seeds using UV spectroscopy and rheology techniques are investigated. Some studies have been carried out on avocado pulp and seed using UV spectroscopy [11, 12], Fourier transform infrared spectroscopy (FTIR) [11, 13] and rheological analysis [14–16]. In this work, to the best of our knowledge, for the first time a food quality control and identity control for pulp and seed extracts of three avocado cultivars (Hass, Fuerte, Ettinger) were conducted and analyzed using spectroscopy (UV and FTIR) and rheological techniques. Quality analyses of phenolic compounds-rich cultivars of avocado have not been studied before by comparing the quality in any study. In the scope of this work, we focused on examining the optical, spectral fingerprints and flow properties together for the first time in order to classify these avocados in terms of quality. In this context, the quality of the avocados was carried out in special measuring ranges by using UV spectroscopy, FTIR and rheology techniques.

2. Materials and methods

2.1. Sample preparation

The avocado fruits of Hass, Fuerte and Ettinger cultivars were harvested from one farm located in the district of Gazipaşa (Antalya-Turkey) (latitude 36° 10' N, longitude 32° 24' E) in December 2020. After harvesting, avocados were stored in the dark at room temperature for maturation. After the natural maturing process, the avocado fruits were peeled and cut into small pieces. Then, the pulp and seeds of avocado fruits were separated. Finally, avocado pulp and seed extract were taken from the fresh fruits. The avocado pulp was crushed in a masher to obtain a puree. By adding 3 g of puree to 300 mL of distilled water, a weight-to-volume (w/v) mixing ratio of $d = 0.01$ g/L was obtained. Avocado seeds were mixed in a food mixer in order to get seed extract. Then, by adding 2 g of the seed extract to 200 mL of distilled water, $d = 0.01$ g/L mixing ratio was obtained. After these processes, pulp and seed samples of the avocado fruits were prepared for the UV spectroscopy and rheology measurements.

2.2. UV spectroscopy, FTIR spectroscopy and rheology

UV spectra of the pulp and seeds for Hass, Fuerte and Ettinger avocados with 0.15% w/v containing an aqueous solution were measured in the wavelength range 190–600 nm using an A 360 Spectrophotometer (AOE Instruments) at room temperature. The distilled water put into the quartz tube of the UV spectrophotometer was used as the baseline for the absorbance spectra in the selected wavelength range. Rectangular quartz cuvettes with a path length of 1 cm were filled with 3% w/v deionize water solutions with pulp and seed extracts. The absorbance coefficient and energy band gaps for the pulp and seed samples of the avocados were calculated from the absorbance values obtained from the absorbance spectra.

Rheological behaviour of the pulp and seed of avocado fruits were investigated using a rheometer (Malvern Kinexus Pro.) compatible with liquid samples. For the rheological measurements of pulp and avocados seed extracts, the shear stress values for all samples were measured from the steady state shear rates, starting from one point and changing step by step. In additional, the viscosity of the pulp and seed extracts of avocados was calculated as the ratio of the steady state shear stress to shear rate.

Chemical functional groups and functional group orientations for the pulp and seed extracts of avocados were made with a Bruker Vertex 70 Fourier-Transform Infrared Spectrometer (FTIR) device. FTIR spectroscopy of the samples were performed in the wave number range from 4200 to 400 cm^{-1} with a 1 cm/s scanning speed and a resolution of 4 cm^{-1} for each spectrum at room temperature.

3. Results and discussion

Optical microscope images for the pulps of Hass, Fuerte and Ettinger avocados are shown in Fig. 1. The bubble-like shapes seen in the images are oil of pulps of Hass, Fuerte and Ettinger avocados. We did not investigate texture and oil separately in this study, as that will be the focus of our future research. The fact that the oil of avocado pulp is grainy indicates that the viscosity characteristic of avocado oil can be different from that of other oils.

The development of the UV spectra for 7.5% w/v of Hass, Fuerte and Ettinger avocado samples in the wavelength range 190–600 nm is presented in Fig. 2. The absorbance spectra of the avocado pulps and seeds of Hass, Fuerte, Ettinger are shown in Fig. 2a and b, respectively.

Beer–Bouguer–Lambert law states that the UV spectra of an electromagnetic beam are proportional to the light path length and the concentration of absorbing materials in the tube [17]. This law is expressed as

$$A = -\log_{10}(T) = \log_{10}(I_0/I) = \varepsilon\, l\, c. \tag{1}$$

Here, A, T, I, I_0, ε, l and c correspond to the absorbance, transmittance, transmitted intensity, incident intensity, extinction coefficient, path length and concentration of the type of absorbent material. In addition, the optical band spacing in the avocado is calculated with

$$\alpha h\nu = B\,(h\nu - E_{\mathrm{g}})^n, \tag{2}$$

where α, h, ν, B, E_{g} and n refers to the absorption coefficient, Planck's constant, frequency of incident photon, constant dependent on electron mobility, optical band gap and an index, respectively.

The wavelength variations of the absorbance of 7.5% w/v of Fuerte and Ettinger avocado pulps in the range 245–600 nm are very similar, while the spectrum of Hass avocato pulps differs from the others. As for the UV spectrum of Ettinger, it differs from the others in the wavelength range 190–220 nm. It was observed that the UV

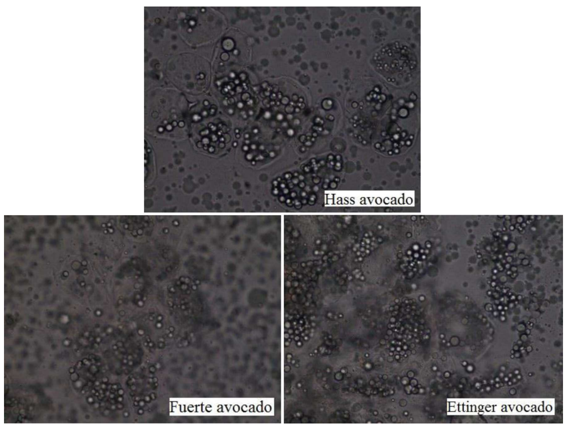

Fig. 1. Optical microscope images of the pulps of Hass, Fuerte and Ettinger avocados.

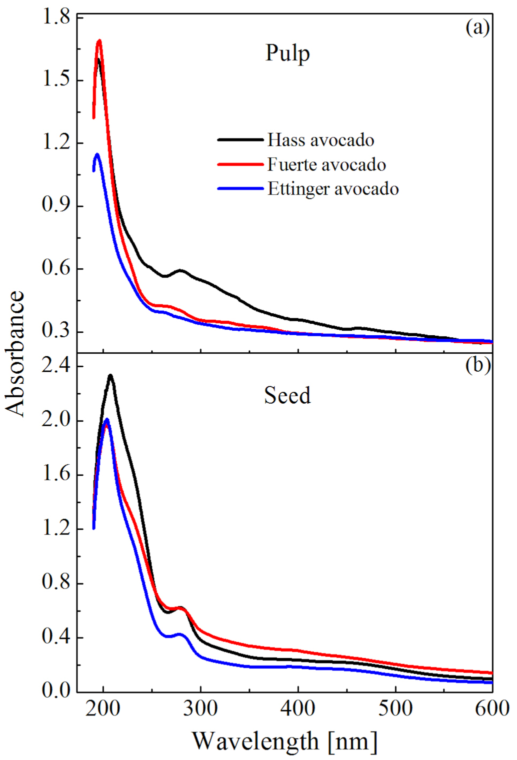

Fig. 2. UV spectra for avocado pulp and seed samples.

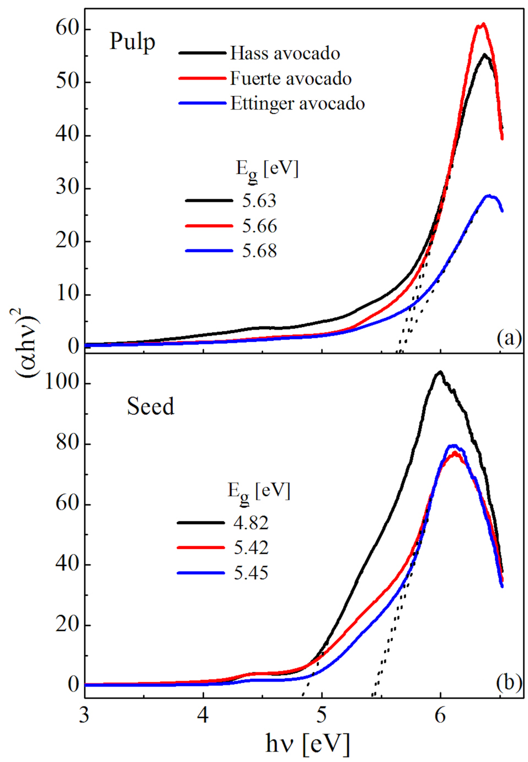

Fig. 3. Energy evolution of $(\alpha h\nu)^2$ for avocado pulp and seed samples.

spectra of Hass, Fuerte and Ettinger avocado pulps have two peak in the range of 190–350 nm. Spectra peaks of avocado pulps at a wavelength between 190 and 250 nm were caused by hydroxycinnamic acids such as p-coumaric acid, sinapic acid, gallic acid, chlorogenic acid, gentisic acid, and so on [18–20]. Moreover, it was attribute that the peak values of the samples in the range of 250–350 nm originated from the concentration of polyphenolic compounds in avocado pulps, such as flavonoids, hydroxybenzoic acids, catechins and hydroxycinnamic acids [11, 21, 22]. Based on the results of the UV spectra of avocado pulps, it was concluded that the peak value of the Hass avocado pulp between 250 and 350 nm wavelength, resulting from the phenolic compound concentration, is higher than the others, so the antioxidant capacities and phytochemical composition are the highest [11, 23]. There is a shift in the peak values of the UV spectra of Hass, Fuerte and Ettinger avocados due to different pigment concentration in the avocado pulps such as carotenoid and chlorophyll [24]. On the other hand, the UV spectra of Hass, Fuerte and Ettinger avocado seeds behave very similar. It was observed that the UV spectra of avocado seeds had two peaks in the wavelength range 190–250 nm and 250–300 nm, originating from ethyl acetate, acetone extract and flavonoids (catechins), respectively [12].

Energy evolution of $(\alpha h\nu)^2$ for 7.5% w/v of Hass, Fuerte and Ettinger avocados in the energy range of 2–7 eV is shown in Fig. 3. The results of $(\alpha h\nu)^2$ versus $h\nu$ for Hass, Fuerte and Ettinger avocado pulps are depicted in Fig. 3a. Furthermore, the results of $(\alpha h\nu)^2$ versus $h\nu$ for seeds of these samples are depicted in Fig. 3b.

It was observed that the Hass avocado pulp dependence shows different behaviour in the 4–5 eV energy range, which is consistent with the absorbance dependence. This different behaviour is thought to be the result of phenolic compounds found in the avocado pulps being more effective in Hass avocado pulp. Optical energy gaps of different types of avocado pulp and seeds depend on the absorbance and surface structure of the samples are calculated using the absorption coefficient values. In this case, the electron transitions of Hass, Fuerte and Ettinger avocado pulp and seeds were determined by the optical energy gap (E_g) values [12, 18–20, 25, 26]. It was observed that the $h\nu$ evolution as a function $(\alpha h\nu)^2$ for all pulp and avocado seed samples behaves the same in the low energy region regardless of energy change while reaching the peak values in the high-energy region [27]. At the point where $(\alpha h\nu)^2$ reach the peak value, the values of E_g are calculated from the gradient of the relation $(\alpha h\nu)^2$ versus $h\nu$ for all samples. It was concluded that the exposure of phenolic compounds and flavonoids in the structure of pulp and seeds to the quantum confinement effect was effective in the case of the E_g values of the pulp and avocado seeds, which display energy behaviour according to Rayleigh–Jeans law [28, 29].

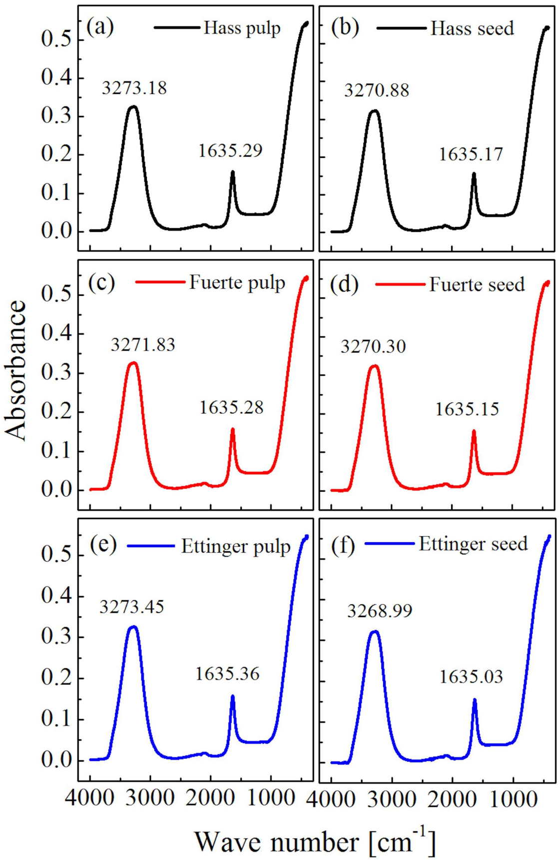

Fig. 4. FTIR spectra for Hass, Fuerte and Ettinger avocado pulp and seed samples.

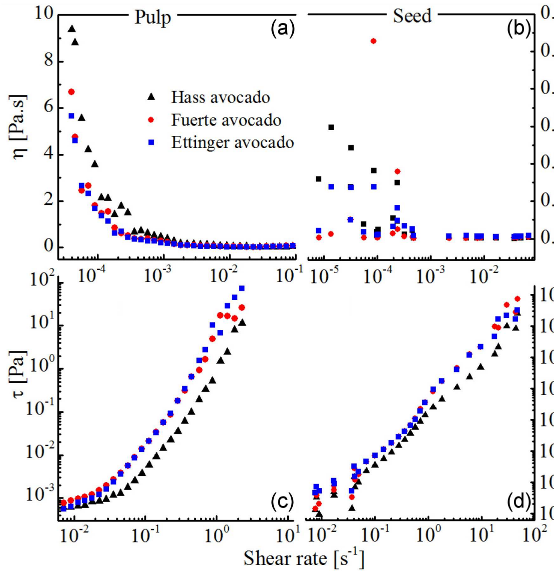

Fig. 5. Shear rate evolution of viscosity and flow curve for avocado pulp and seed samples.

The wave number evolutions of the Fourier transform infrared spectroscopy (FTIR spectra) for Hass, Fuerte, Ettinger avocado pulps and seeds in the wave number range of 4200 to 400 cm^{-1} are depicted in Fig. 4a–d and Fig. 4e–f, respectively.

It was observed that the spectral fingerprints of FTIR spectra for Hass, Fuerte, Ettinger avocado pulps and seeds behave very similarly in the mid-infrared frequency region. Although the FTIR spectra of the pulps and avocado seeds are very similar to each other, there are small differences in the absorbance peak frequency. The small differences in these two important peaks of the absorbance spectra of avocado pulp and seeds are thought to be caused by the different concentrations of organic acids and phenolic compounds in the structure that determine the quality of avocados. Therefore these small differences are of great importance in determining the quality of the avocado types [30, 31]. FTIR spectra for all avocado pulps and seeds were found to have two peaks at the wave numbers around 3200 cm^{-1} and 1635 cm^{-1}, respectively. The peaks of spectral fingerprints of all samples at 3200 cm^{-1} are originated from OH–groups of phenols and alcohols. It was also believed that C–H aliphatic vibrations were effective for peaks in this wave number region. Vibrations of OH–group and C–O interactions caused by phenolic compounds and carboxylic acids have been identified as the main reason why the avocado pulp and seed samples have absorbance peaks at around 1635 cm^{-1}. Moreover, it was predicted that C–C aromatic groups could be effective at spectral fingerprint peaks in this region [32, 33].

Evolution of the shear rate of viscosity (η) and shear stress (τ) for Hass, Fuerte and Ettinger avocado pulp (Fig. 5a and c) and seeds (Fig. 5b and d) in the shear rate range of 10^{-2}–10^{2} s^{-1} is presented in Fig. 5.

The flow behaviour (viscosity) and flow curves of Hass, Fuerte and Ettinger avocado pulp and seeds are given together in Fig. 5. It was observed that the viscosity of all avocado types is high in the low shear rate region where resistance to the flowing tendency of the avocado pulps is the highest. Avocado pulp viscosity values in this region were found to be different from each other, with Hass avocado pulp having the highest value. These differences in the flow behaviour were predicted to be due to the different microstructural states that avocados acquire during the maturation process [15]. It has been determined that the flow behaviour of avocado seeds is compressed in the region below the 10^{-3} s^{-1} shear rate due to their heterogeneous structure and thus display instability flow. It was believed that the reason for the lower viscosity values of avocado seeds compared to avocado pulps is this instability flow behaviour. In the high shear rate region, it was observed that the flow behaviours of both avocado pulps and seeds is maintained regardless of the shear rate. Flow curves of Hass, Fuerte and Ettinger avocado pulps were observed to behave compatible with non-Newtonian dilatant flow (thickening liquids) [34, 35]. It has been determined that the experimental results of the flow curves of avocado

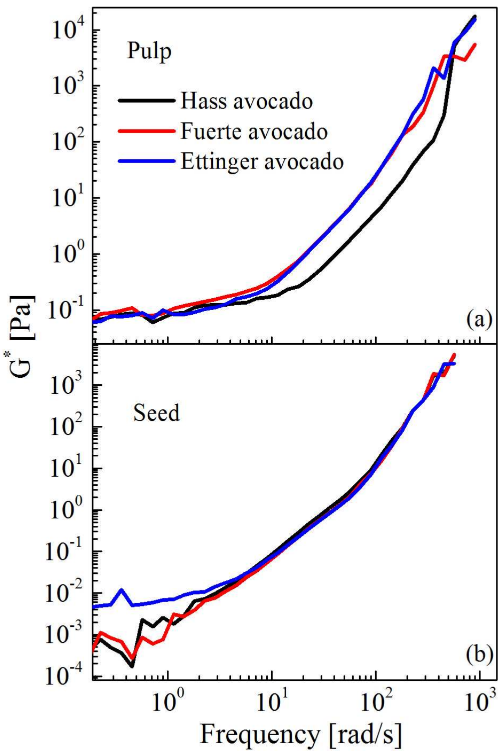

Fig. 6. Frequency evolution of the complex modulus of the avocado pulp and seed samples.

pulps are compatible with the non-Newtonian dilatant flow properties by Ostwald-de Waele or the power law model [36, 37]. On the other hand, it was seen that the flow curves of the avocado seeds exhibited two different flow behaviour patterns. Avocado seeds, which displayed unstable behaviour in the lowest shear rate region, was found to exhibit non-Newtonian dilatant flow and subsequently pseudo plastic (thinning liquids) flow with increasing shear rate [34–37]. Moreover, it can be said that the flow curves of avocado seeds, which have different flow characteristics, are generally compatible with Herschel–Bulkley model [15].

Frequency evolution of complex modulus for Hass, Fuerte and Ettinger avocado pulp and seeds in the frequency range of 10^{-1}–10^3 rad/s is presented in Fig. 6a and b, respectively.

The complex modulus $G^* = \sqrt{G'^2 + G''^2}$ of avocado pulp and seed samples increase almost exponentially with increasing angular frequency. The exponential increase of the complex modulus defined by the elastic modulus G' and the viscous modulus G'', i.e., its conformity to the power law model, is consistent with the fluid flow behaviour [38]. The main reason why the G^* values of avocado pulp and seed with non-liner viscoelastic behaviour are low in the low frequency region, is that the effect of viscous behaviour is dominant in this region. The values of G^* show unstable behaviour because the viscous behaviour on avocado seed is more dominant in this region. The fibrous structure in the pulp and seed of avocado fruit makes the elastic behaviour more dominant in the increasing frequency region. The prevalence of elastic behaviour over the G^* values causes it to take higher values with increasing frequency [15]. The viscoelastic behaviour of avocado pulp and seed is determined by the presence of strong intermolecular forces and therefore they show weak, gel-like flow behaviour [39].

4. Conclusion

In the scope of this work, we focused on a detailed investigation of the quantitative, qualitative and quality characteristics of the pulps and seeds for Hass, Fuerte and Ettinger avocados using UV spectroscopy and rheology techniques at room temperature. It was determined that the optical and rheological properties of the pulps and seeds of avocados show different characteristics with different wavelengths, wave numbers and frequencies. It was observed that while Hass and Fuerte absorbance have at the same high value for the pulps of avocados in the low wavelength region, Fuerte and Ettinger seeds have similar absorption values at the same low wavelength values. It was evident that the peaks of absorption coefficient for all pulp and seed samples of avocados are due to the quantum yield and optical transmission of organic molecules [17–25]. In addition, the energy gaps for the pulp and seed samples of avocados were evaluated using with Planck's radiation approach known as Rayleigh-Jeans law [26–29]. All avocado pulp samples were observed to have high viscosity in the low shear rate region where the resistance to the flow tendency of avocado pulp is greatest, along with the different microstructural conditions resulting from the avocado ripening process. However, it was understood that the seeds of avocados have an unstable flow behaviour. The compatibility of the flow curves of Hass, Fuerte and Ettinger avocados pulp samples with the Ostwald-de Waele model or the power law theoretical models of non-Newtonian dilatant flows was determined. In addition, it was found that the flow curves of avocado seeds with different flow characteristics are generally compatible with the Herschel–Bulkley model [15, 34–37].

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