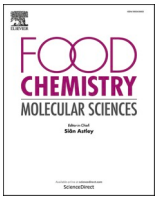
Food Chemistry: Molecular Sciences 8 (2024) 100204

Contents lists available at ScienceDirect

Food Chemistry: Molecular Sciences

journal homepage: www.sciencedirect.com/journal/food-chemistry-molecular-sciences



Ripening process in exocarps of scarlet eggplant (*Solanum aethiopicum*) and banana (*Musa* spp.) investigated by Raman spectroscopy

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ARTICLE INFO

Keywords:
Raman spectroscopy
Ripening
Bananas
Scarlet eggplant
Carotenoids
Flavonoids

ABSTRACT

In this work, we used Raman spectroscopy to identify compounds present at different maturation stages of the exocarp of scarlet eggplant and two banana cultivars, 'prata' and 'nanica'. Raman spectral analyses of both fruits showed bands attributed to phenolic acids, flavonoids, carotenoids, and fatty acids. During the scarlet eggplant's maturation process, Raman spectral profile changes are mainly observed in the carotenoid content rather than flavonoids. Furthermore, it is suggested that naringenin chalcone together with β-carotene determines the orange-red color of the ripe stage. Variations in chemical composition among the maturation stages of bananas were observed predominantly in 'prata' when compared to 'nanica'. In contrast to scarlet eggplant changes in the spectral profile were more evident in the content of the flavonoid/phenolic acids. The *in situ* analysis was demonstrated to be useful as a guide in selecting bioactive compounds on demand from low-cost horticultural waste.

1. Introduction

A great number of colorful fruits and vegetables biosynthesize bioactive pigments, and a vast array of other compounds such as phenolics, polyphenols, alkaloids, saccharides, dietary fiber, vitamins, and enzymes in both edible pulp (endocarp) and non-edible peel (exocarp) (Hussain et al., 2022; Kumar et al., 2023). Besides nutritional value, the coloration of exocarp or peel along the different stages of maturation is an important sensory attribute that increases consumer acceptability and is associated with quality. The color change of the exocarp progressively occurs between the mature green stage, and the fully ripe stage (Gonzali & Perata, 2021), due to an increase or decrease in the synthesis of pigments, such as chlorophyll, carotenoids, and flavonoids (Martin & Li, 2017). Carotenoids are the most widespread natural pigments in plant sources and are usually responsible for the yellow, orange, and red colors (Rodriguez, 2001). Flavonoids, on the other hand, are responsible for most of the orange to purple and blue coloration of plant tissues, flowers, and seeds (Paauw et al., 2019). The role of these molecules in nature is essential, as they have important ecological and physiological functions, such as protection against photo-oxidation, sexual signaling, and chemical defense, in addition to being phytohormone precursors (Cazzonelli & Pogson, 2010; Falcone Ferreyra et al., 2012). In the human diet, carotenoids and flavonoids are known to promote health benefits, since there is evidence that the consumption of plant-based foods, especially fresh fruits, and vegetables, is inversely related to the risk of chronic diseases, such as obesity, cardiovascular disease, diabetes type 2, and some types of cancer (Martin & Li, 2017). However, a significant portion of these compounds is lost when peels, seeds, and skins from fruit and vegetables are discarded during preparation and processing resulting in waste, i.e. by-products (Hussain et al., 2022).

The agriculture-based food wastes from exocarps are a source of phytonutrients with potential application in cosmetic, pharmaceutical, food, and beverage industries, including in the development of edible films, probiotics, nanoparticles, carbon dots, microbial media, biochar, and biosorbents (Ben-Othman et al., 2020; Kumar et al., 2020). Conversely, losses and wastes from household kitchens, and processing in industries, are becoming serious nutritional, economic, and

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https://doi.org/10.1016/j.fochms.2024.100204
Received 15 November 2023; Received in revised form 26 January 2024; Accepted 13 April 2024
Available online 16 April 2024

environmental problems (Sagar et al., 2018). In the present scenario, a sustainable solution for managing fruit and vegetable waste has become an important task in developed and developing countries. For instance, bananas are the fourth most important staple crop worldwide (Voora et al., 2020), consequently, plantation generates huge amounts of residues after each harvest season and during processing to obtain banana pulps. The potential use of banana peels has been suggested in the literature (Mohd Zaini et al., 2022), but peels of less profitable crops such as scarlet eggplants have been neglected (Plazas et al., 2014; Sánchez-Mata et al., 2010). The scarlet eggplant crop is widely cultivated in Africa, Brazil, and southern Italy (Sunseri et al., 2010). The growing interest in this species is related to crop diversification, agricultural sustainability, genetic improvement, and nutritional and medicinal benefits (Aguessy et al., 2021; Han et al., 2021).

Scarlet eggplants and bananas present distinct types of consumption associated with the ripening stages and their taste. In this work, we used Raman spectroscopy, a fast and reliable technique that detects compounds *in situ* and a single step to investigate the chemical composition of exocarps along the ripening from the scarlet eggplant (*Solanum aethiopicum*) and two banana cultivars (*Musa* spp). The scarlet eggplant (*Solanum aethiopicum*) also known as African eggplant, garden eggs, and bitter tomato (Han et al., 2021), is a fruit harvested with an intense green color and generally loses its commercial value as it ripens, turning orange-red colored (Mendes, 2013). On the other hand, banana (*Musa* spp.) is harvested with a green color, but it gains commercial value when it matures reaching a yellow coloration (Maduwanthi & Marapana, 2021). Although the eggplants (eudicotyledons) diverged morphologically from their relative bananas (monocotyledonous) quite early in angiosperm evolution, they share a similar biosynthetic pool in the production of carotenoids and flavonoids (Zhang et al., 2021). They are known to be a source of antioxidant molecules such as phenolic acids, flavonoids, and carotenoids (Aquino et al., 2018; Faraone et al., 2022; Ferreira-Santos et al., 2021).

Raman spectroscopy has already been used in several samples of fruits and vegetables for the *in situ* analysis of different carotenoids and flavonoids, in which the analysis can be done quickly, and non-destructively, an essential advantage for biological materials (Baranski et al., 2005; Campos et al., 2022; Pećinar et al., 2021). Given these advantages, many studies have used Raman spectroscopy to monitor different stages of fruit maturation, such as tomatoes, mangoes, and peppers (Campos et al., 2022; Kolašinac et al., 2021; Qin et al., 2011; Ullah et al., 2019). Hence, studies monitoring compounds along the fruit ripening may reveal which stage is more suitable to extract a selected metabolite. In this sense, carotenoids and polyphenols (flavonoids and non-flavonoids) (Fig. 1) are target compounds, due to their remarkable antioxidant activity which are present in different concentrations in peels along the maturation process.

From the structural point of view, carotenoids and flavonoids have a carbon chain containing conjugated unsaturated bonds, with highly polarizable π electrons. Due to this characteristic, Raman spectroscopy has been revealed to be the technique of choice to study these molecular systems, it is based on inelastic scattering of light which provides information about the molecular vibrations. The vibrational spectrum of carotenoids is characteristic and can be used to distinguish conjugated polyenes according to the length of their conjugated unsaturated chains; its main vibrational bands occur between 1570–1500 cm^{-1} due to the ν(C=C) vibrational mode and between 1170–1150 cm^{-1} to the ν(C-C) mode (Baranski et al., 2005; Maia et al., 2021). Distinct from carotenoids, the bands related to phenolic compounds such as flavonoids are those assigned to the phenyl ring in the range of 1630–1550 cm^{-1} and to the δ(C-OH) modes of the phenol group around 1360–1300 cm^{-1} (Aguilar-Hernández et al., 2017; Wang et al., 2020).

Regardless of the maturation stage, pulp is particularly valuable for consumption and industrial application; however, peels are discarded as waste (H. Kumar et al., 2020). A classic example is the banana peel, the non-edible portion of the fruit accounting for ~35% of the whole fruit weight, which has been traditionally used as a remedy for treating common ailments like cough, burns, and inflammation, as well as for managing anemia and diabetes (Ben-Othman et al., 2020). Concerning the scarlet eggplant, the waste content has been underexplored (Ben-Othman et al., 2020), despite the anti-inflammatory activity (Anosike et al., 2012), and the inhibition properties of nitric oxide (NO) (Plazas et al., 2014). Recently, the exploitation of these low-cost waste horticultural has gained attention, since many of the bioactive compounds found in the peel can be used by food, textile, cosmetics, and pharmaceutical industries (Dorta & Lobo, 2022; Khawas & Deka, 2016; Kumar et al., 2020; Vu et al., 2018).

In this context, Raman spectroscopy is being utilized to identify the main pigments, present in the exocarps, at different stages of maturation of scarlet eggplant, and two cultivars of banana, 'prata' and 'nanica'. The analyses were performed *in situ* and with crude extracts which monitored phenolic acids/flavonoids and carotenoids along the maturation process of each fruit. Moreover, the *in situ* analysis was demonstrated to be useful as a guide in selecting bioactive compounds on demand. *In situ* characterization of bioactive molecules present in non-edible parts of fruits such as peels from scarlet eggplant and banana is an emerging research subject. The valorization of food wastes and by-products may be a solution to improve economic and environmental

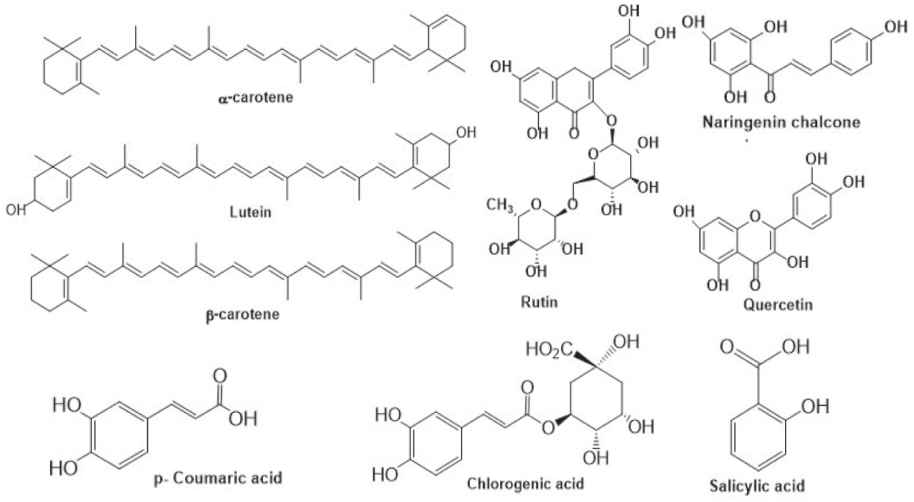

Fig. 1. Some of the carotenoids, phenolic acids, and flavonoids structures biosynthesized in scarlet eggplant and banana.

sustainability. In addition, understanding the mechanism of fruit maturation is crucial to ameliorating shelf life and storage duration (Wee et al., 2023).

2. Materials and methods

2.1. Sample preparation and experimental design

All samples used in this work were acquired in the local market, in the city of Juiz de Fora, Minas Gerais (MG), Brazil. The scarlet eggplant (*Solanum aethiopicum*), acquired in July of 2021 and 2022, samples were selected at different stages of maturation, by visual inspection of the degree of maturation, with S1 being the greenest and S4 the most mature, to analyze the compounds produced at each stage of maturation. The exocarps of four individual scarlet eggplants were analyzed in two different excitation lines with three samples in 1064 nm (Fig. 2A, Fig. 3A, and Fig. S1) and one sample in 532 nm (Fig. 2B and Fig. 3B). The two banana cultivars (*Musa* spp.) 'prata' and 'nanica', were purchased in June of 2023, and the exocarps were analyzed at two different maturation stages, unripe and ripe. The exocarps of four individual banana 'prata' and four individual banana 'nanica', in their respective maturation stages, were also analyzed in two different excitation lines with three samples of each cultivar in 1064 nm (Fig. 2C, Fig. 2D, Fig. 6 and Fig. S2), and one sample of each cultivar in 532 nm (Fig. 2E, Fig. 2F and Fig. 7).

2.2. Extraction

Scarlet eggplants and bananas were subjected to extraction with ethanol to obtain carotenoids and flavonoids. For eggplant, three different extracts were performed according to the maturation stages (S1-Et, S2-Et, S3/S4-Et), and for bananas, two extracts for each variety ('prata' and 'nanica') according to the maturation stage: unripe (green) and ripe (yellow). The samples were sanitized and the exocarps were removed. Then, the exocarps (approximately 100 g) were moistened with 100 ml of ethanol at 25 °C and crushed with the aid of a mixer for about 10 min. This process was repeated two more times (de Miamoto et al., 2020). The solution was filtered, and the solvent was removed under reduced pressure. Ethanol extracts were analyzed with a laser line at 1064 nm.

2.3. Spectroscopic analyses

2.3.1. Raman spectroscopy

Analyses performed directly on scarlet eggplants exocarp, banana peel (*in situ*), and the respective crude extracts, were recorded in an FT-Raman Bruker RFS 100 instrument, with a Nd: YAG laser operating at 1064 nm, with the spectral resolution of 4 cm^{-1} in the wavenumber ranging from 4000 to 50 cm^{-1}. For the banana samples were used laser power of 300 mW, and 1024 scans while for the scarlet eggplants were used 250 mW and 512 scans, and for the crude extracts 80 mW and 512 scans. *In situ,* Raman analysis of the scarlet eggplant samples using excitation wavelength at 532 nm was recorded on a Renishaw in Via Reflex fitted with a Peltier-cooled CCD camera and coupled to a Leica Microscope (DM2500 M), with a work 20x objective. A good signal-to-noise ratio was obtained with the acquisition time of 10 s and 2 additions, and all spectra were obtained at least twice to confirm sample integrity based on the position and intensity of the observed bands. *In situ,* Raman analysis of the bananas using excitation wavelength at 532 nm was recorded on a Bruker SENTERRA dispersive Raman microscope instrument equipped with a CCD detector, with the incident laser beam focused on the sample using a microscope with a long-distance work 50x objective. A good signal-to-noise ratio was obtained using a laser power of 10 mW, with the acquisition time of 2 s and 5 coadditions, and all spectra were obtained at least twice to confirm sample integrity based on the position and intensity of the observed bands.

The Raman spectra were processed by the Bruker Opus software package version 6.0, and Raman baseline correction and curve fitting were performed using Origin 2018 software. Deconvolution of broad bands was performed using PeakFIT and Origin 2018 software to separate overlapping signals, using a Gaussian response function with a Fourier deconvolution/filtering algorithm.

2.3.2. UV/Visible spectroscopy (UV/Vis)

The extracts obtained were analyzed in an Ocean Optics spectrometer, between 200 and 1100 nm. The samples were diluted in ethanol and added to a quartz cuvette with a 10 mm optical path to obtain the electronic spectra.

Fig. 2. Scarlet eggplant in each of the four stages of maturation, analyzed in (A) 1064 nm and (B) 532 nm, and bananas analyzed in 1064 nm (C) 'prata', (D) 'nanica', and 532 nm (E) 'prata' and (F) 'nanica'.

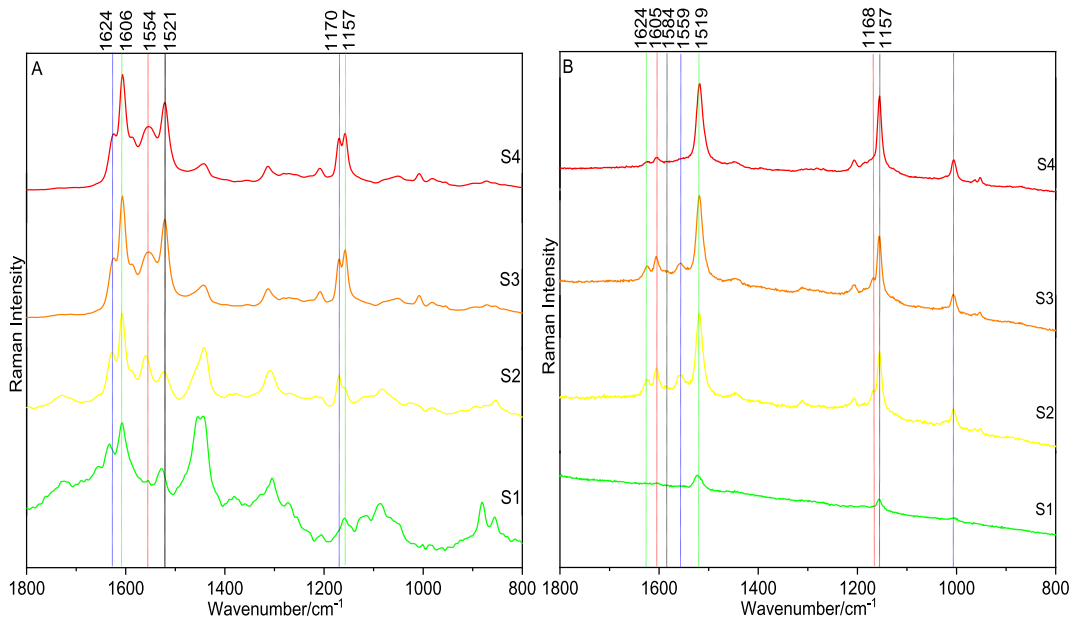

Fig. 3. Mean Raman spectra of each of the four maturation stages (S1 a S4) from scarlet eggplant obtained with a laser line at (A) 1064 nm and (B) 532 nm.

3. Results and discussion

3.1. *In situ* Raman measurements of the scarlet eggplant exocarp at different stages of ripening with the excitation line in 1064 nm

Analyzing the *in situ* Raman spectra obtained in four stages of scarlet eggplant maturation (Fig. 2A) performed with an excitation line at 1064 nm, it can be observed main bands characteristic of polyphenols and carotenoids (Fig. 3A, and Fig. S1). Bands of polyphenols observed around 1630–1554 cm^{-1} were assigned to ν(C=C), 1370–1340 cm^{-1} to ν(C-O), 1360–1300 cm^{-1} to δ(COH) and 1270–1250 cm^{-1} to δ(OH)/ν(C-O) (Table 1) (Aguilar-Hernández et al., 2017; González Moreno et al., 2021; Machado et al., 2013; Teslova et al., 2007; Wang et al., 2020). The bands attributed to carotenoids were in the range of 1527–1521 cm^{-1}, assigned to ν(C=C), 1159–1155 cm^{-1} to ν(C-C) and 1008 cm^{-1} assigned to ρ(C-CH_3) (Table 1) (de Oliveira et al., 2009; Koyama et al., 1988; Maia et al., 2021; Saito & Tasumi, 1983). Bands from fatty acids are also observed, mainly in the S1 and S2 stages, such as those at 1656 ν(C=C), 1444 δ(CH_2), 1305 δ(CH_2), 1274 δ(=CH), and 1065 cm^{-1} ν(C-C) (Beattie et al., 2004; Popović-Djordjević et al., 2023; Windarsih et al., 2023).

The four different stages of scarlet eggplant maturation presented some differences in spectral profile for the bands attributed to the phenolic compounds and carotenoids. Raman spectrum obtained in 1064 nm of the sample in stage S1 suggested the presence of flavonoids/phenolics due to bands at 1633, 1608, 1580, 1556, and 1170 cm^{-1}, and carotenoids due to bands at 1527, 1158, and 1000 cm^{-1}. From the ripening stage S2 (yellow) to S4 (orange), it was observed a Raman shifting to shorter wavenumbers of ν(C=C) bands in both classes of compounds (Fig. 3A, Fig. S1, and Table 1). Bands at 1627, 1608, 1560 ν(C=C) and 1170 cm^{-1} ν(C-C) were attributed to the flavonoid naringenin chalcone, previously identified in tomato (Campos et al., 2022); and the broad band in the range of 1523–1521 ν(C=C), 1158 ν(C-C) and 1008 cm^{-1} ρ(C-CH_3) to regular carotenoids with 9 conjugated unsaturation (Campos et al., 2022; de Oliveira et al., 2009). Bands addressed to phenolics showed differences in the intensity and position only from stages S1 to S2 (Fig. 3A; Table 1). On the other hand, carotenoids presented Raman shifting of ν(C=C) (1527 to 1521 cm^{-1}) along all stages (S1 to S4) suggesting structural diversification. In stage S2 when the fruit is yellow the bands attributed to naringenin chalcone are more intense than bands from carotenoids, indicating that this flavonoid contributes to the pigmentation (Fig. 3A and Fig. S1). Comparison

Table 1
Tentative assignment of the Raman bands observed in the four stages of eggplant maturation, obtained with a laser line at 1064 nm and 532 nm.

Bands (cm^{-1})								**Tentative Assignments**
1064 nm				532 nm				
S1	S2	S3	S4	S1	S2	S3	S4	
1724w	1726w							$\nu(C{=}O)^{a}$
1633w	1627w	1624w	1624w		1625w	1620w	1625vw	$\nu(C{=}C)^{b}_{flav}$
1608s	1608s	1607s	1606s		1606w	1606w	1603vw	$\nu(C{=}C)^{b}_{flav}$
	1589vw	1587vw	1587vw		1588w	1583w		$\nu(C{=}C)^{b}_{flav}$
1554vw	1560m	1554w	1554w		1556w	1556w		$\nu(C{=}C)^{b}_{flav}$
1527w	1523w	1521m	1521m	1523w	1519s	1519s	1518s	$\nu(C{=}C)^{c}_{car}$
1440br	1442br	1442w	1442w		1445vw	1445vw	1449vw	$\rho(C\text{-}H)^{b,c}_{flav/car}$
1305w	1309w	1313w	1313w		1311w	1311w		$\rho(C\text{-}H)^{a}$
	1170m	1169w	1169w		1168w	1168w		$\nu(C\text{-}C)^{b}_{flav}$
1159w	1159w	1157m	1157m	1156w	1155s	1155s	1155s	$\nu(C\text{-}C)^{c}_{car}$
		1008vw	1008vw		1007w	1007w	1005w	$\rho(C\text{-}CH_3)^{c}_{car}$

Raman intensities: s-strong; m-medium; w-weak; vw-very weak; br-broad band.
flav: Flavonoids; car: Carotenoids. References citation: a: (Beattie et al., 2004; Popović-Djordjević et al., 2023); b: (Aguilar-Hernández et al., 2017; González Moreno et al., 2021; Machado et al., 2013; Teslova et al., 2007; C.-H. Wang et al., 2020); c: (Koyama et al., 1988; Saito & Tasumi, 1983).

among intensity ratios of ν(C=C) carotenoids/flavonoids ($I\nu_{c:1527-1521}/I\nu_{f:1608-1606}$) in the stages S1 ($I\nu_c/I\nu_f = 0.35$), S2 ($I\nu_c/I\nu_f = 0.33$), S3 ($I\nu_c/I\nu_f = 0.79$), and S4 ($I\nu_{1c}/I\nu_{1f} = 0.74$) showed that phenolics predominates over carotenoids, however, the ν(C=C) band enhancement centered at 1518 cm^{-1} indicated an increasing of carotenoids in the peel along the fruit ripening.

3.2. *In situ Raman measurements of the scarlet eggplant exocarp at different stages of ripening with the excitation line in 532 nm*

In attempt to evaluate the influence of the laser in line in the characterization of the fruit, Fig. 3B shows Raman spectra obtained in a 532 nm laser line from another set of scarlet eggplant samples in four stages of maturation (Fig. 2B). In the S1 stage, only bands attributed to carotenoids are observed at 1523 ν(C=C), and 1156 ν(C-C) cm^{-1} (Fig. 3B; Table 1). In subsequent stages (S2, S3, and S4), bands of flavonoids are also observed, however, the intensity of carotenoid bands predominates over flavonoids, due to resonance with the electronic transitions of carotenes (between 270 and 550 nm) (Fig. 3B; Table 1) (Campos et al., 2022; Rodriguez, 2001). As previously reported by Campos et al. (2022), the analyses performed with a laser line in 1064 nm are more suitable for characterizing both pigments carotenoids, and flavonoids produced in the different stages of fruit maturation.

3.3. *Vibrational and electronic spectral data from ethanolic extracts of scarlet eggplants*

The extraction of peels was performed to trace the compounds of interest such as carotenoids and flavonoids. The crude extract of scarlet eggplant peels (Fig. 2B) in the S1 stage (S1-Et) presented a similar Raman spectral profile to the obtained in the *in situ* analysis (Fig. 3A and Fig. 4; Table S1). Vibrational bands attributed to phenolics/flavonoids can be seen around 1630, 1607, 1574, 1167 cm^{-1}; carotenoids were identified due to a broad band in the range of 1540–1516 ν(C=C), band at 1157 cm^{-1} ν(C-C) (Fig. 4). Additional bands at 1659, 1446, 1306, 1268, 1065 cm^{-1} could be attributed to fatty acids (Fig. 4, Table S1). The S2-Et crude extract presented a similar Raman spectrum to the stages S3/S4, where flavonoid bands were at 1624, 1607, 1597, 1557, and 1170 cm^{-1}, and carotenoids broad band centered at 1518, 1170 and 1018 cm^{-1}. In agreement with the *in situ* analysis differences in chemical composition among the maturation process were observed due to Raman shifting of the ν(C=C) band from 1630 cm^{-1} (S1-Et) to 1624 cm^{-1} (S2-Et, S3-Et/S4-Et) together with the increasing in intensity of bands around 1554 and 1170 cm^{-1}, which are some of the marker bands of naringenin chalcone.

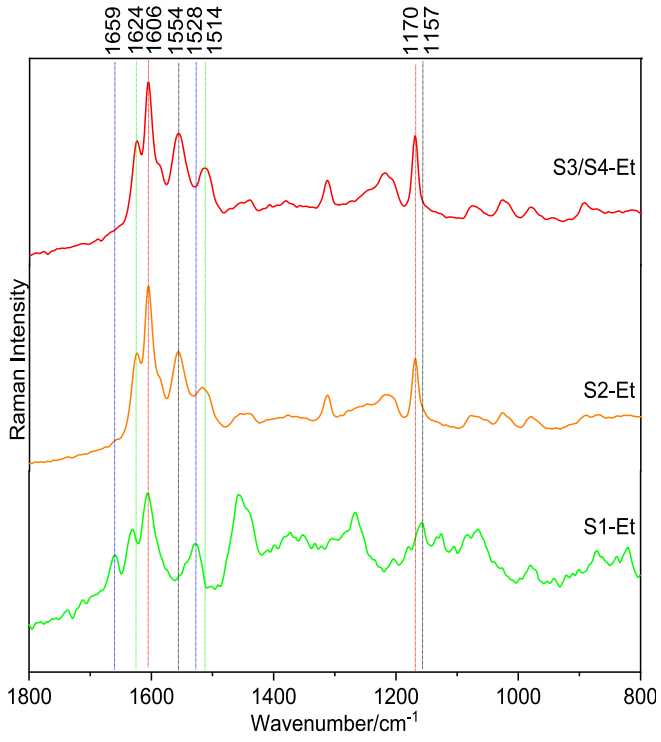

Fig. 4. Mean Raman spectra of ethanolic extracts from maturation stages (S1 a S4) of scarlet eggplant obtained with a laser line at obtained with a laser operating at 1064 nm.

The UV–vis analysis was used as a complementary technique to monitor the main pigments present in the different stages of maturation based on the absorption range of crude extracts compared with standard samples from the literature. The electronic spectra performed with the different crude extracts confirmed the changes in the chemical composition observed in the Raman analyses; stage S1-Et showed a broad band with maximum absorption at 330 nm and a shoulder at 300 nm (Fig. 5, Fig. S3), which are characteristic of phenolic acids (Kowalski & Kowalska, 2005; Martin et al., 2017), but are also typical of some flavonoids (K. Jash, 2023; Tsimogiannis et al., 2007). Very weak bands at λmax 420 and 667 nm may be attributed to chlorophylls (Matti Linnanto, 2022). Nevertheless, stage S2-Et showed a broad band with maximum absorption at 330 nm, a shoulder at 300 nm, and at 369 nm; the latter has been assigned to the flavonoid naringenin chalcone (González Moreno et al., 2021) (Fig. 5, Fig. S3). Conversely, the stages S3/S4 showed a shoulder around 315 nm and a broad band centered at 371 nm (Fig. 5, Fig. S3). The increasing band addressed to the yellow naringenin chalcone in both electronic and Raman spectra suggests the contribution of flavonoids in the coloration of the peel. Although Raman spectra have shown bands of carotenoids in all stages (Fig. 4; Fig. 5), the electronic spectra (UV–vis) showed a very weak band around 422 nm revealed by the deconvolution of the absorption bands in the UV–vis spectra (Fig. 5, Fig. S3), which may be addressed to carotenoids (Rodriguez, 2001).

Scarlet eggplant is a fruit belonging to the Solanaceae family, the same as the tomato, potato, pepper, and others. The scarlet eggplant is a close relative of the species *Solanum melongena* and *S. macrocarpon* (Han et al., 2021). The commercial value of scarlet eggplant is given by its green color and bitter taste; therefore, the fruits are harvested with an intense green color (Mendes, 2013). The Raman spectral data obtained in 1064 and 532 nm showed that the carotenoid content increases as fruit matures, but phenolics/flavonoids do not seem to change much (Fig. 3A, Fig. 3B and Fig. 4). Both classes of compounds act as antioxidants, however, flavonoids are also of high relevance for the plant defense mechanism (Mierziak et al., 2014) and can impart unpleasant bitterness (Danton et al., 2018; Roland et al., 2013) as reported for naringenin chalcone derived compounds (Danton et al., 2018; Mierziak et al., 2014; Peterson et al., 2006; Roland et al., 2013). Among the fruit tissues tested in Faraone et al. (2022), peel extract from *S. aethiopicum* demonstrated the best antioxidant activity. Scarlet eggplant contains substantial amounts of flavonoids (Chinedu et al., 2011; Eletta et al., 2017), nine phenolic compounds (3 hydroxycinnamic acids, 4 flavanones, and 3 flavanols) were identified from the ethanol extract of scarlet eggplant peel using HPLC-DAD analysis (Faraone et al., 2022). A significantly higher content of total phenolics was observed in the peel compared to the endocarp (Faraone et al., 2022). In addition, other flavonoids and phenolic acids have already been identified in scarlet eggplant samples, such as rutin, catechin, kaempferol, chlorogenic, syringic, synapic, ferulic, p-coumaric, ellagic, and salicylic acids (Faraone et al., 2022; Seal et al., 2016). Naringenin chalcone as the yellow pigment of fruits plays an important role in determining the purple eggplant (*Solanum melongena*) color changes at maturity stages (Wang et al., 2022), it was also identified in the maturation stages of tomato (*Lycopersicon esculentum*) (Ballester et al., 2009; Campos et al., 2022) and pepper (*Capsicum baccatum* L.) (Zhang et al., 2022). *S. aethiopicum* has been reported to express low susceptibility to pests and diseases

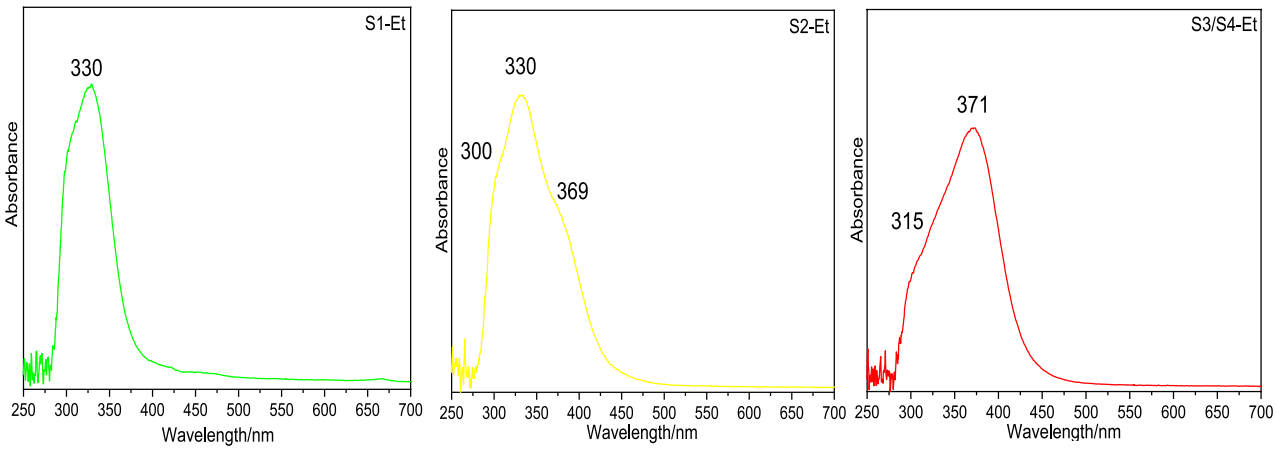

Fig. 5. Electronic spectra of ethanolic extracts from maturation stages (S1 a S4) of scarlet eggplant.

(Han et al., 2021).

The carotenoid content of the scarlet eggplant extracts (peel, pulp, and the whole fruit) reported by Faraone et al., 2022 showed that they are concentrated in the peel and the most abundant is β-carotene, followed by α-carotene, lutein, and lycopene, however, other studies showed that carotenoid composition might vary among varieties of *S. aethiopicum* as well as ripening stages (Msogoya et al., 2014). In most fruits and vegetables, the composition and concentration of carotenoids determine the intensity and the type of color, respectively. Factors such as genotype, maturation phase, cultivation, and climatic conditions, as well as postharvest and processing practices, influence the content and types of carotenoids in fruits and vegetables. The composition of carotenoids in carotenoid-rich sources is a species-determined characteristic (Kolašinac et al., 2021; Msogoya et al., 2014). β-Carotene in addition to α-carotene and xanthophylls, is responsible for yellow-orange color, whereas the color of orange fruits may be attributed to cryptoxanthin and zeaxanthin (Kolašinac et al., 2021; Saini et al., 2015), however, it does not seem to be the case of scarlet eggplant. Our results together with literature data (Ballester et al., 2009; Mutalib et al., 2016) suggest that the main flavonoid found in scarlet eggplants is naringenin chalcone, which may be responsible for the yellow color of the fruit and, together with β-carotene, the main carotene of scarlet eggplant, determines the dark orange color of the fruit (Faraone et al., 2022; Seal et al., 2016).

3.4. *In situ Raman measurements of the banana's exocarp at different stages of ripening*

The Raman spectra obtained with an excitation line at 1064 nm from the peels of two different maturation stages of banana 'prata' (Fig. 2C) and 'nanica' (Fig. 2D) are shown in Fig. 6A, B and S2, respectively. At unripe and ripe stages, it can be observed bands around 1740 ν(C=O), 1672–1662 cm^{-1} ν(C=C), 1462 cm^{-1} $\delta(CH_2)$, 1300 $\delta(CH_2)$ 1270 δ(=CH) and 1060 cm^{-1} ν(C-C), which can be attributed to the vibrational modes of fatty acids (Beattie et al., 2004). Bands at 1630, 1600 ν(C=C), 1350 ν(C-O), 1325 δ(COH), and 1270–1250 cm^{-1} δ(OH)/ν(C-O) were assigned to vibrational modes from phenolic compounds (Machado et al., 2013; Teslova et al., 2007; C.-H. Wang et al., 2020). Bands referring to carotenoids in the range of 1527–1521 ν(C=C), 1159 ν(C-C), and 1006 cm^{-1} $\rho(C\text{-}CH_3)$, are typical of vibrational modes from conjugated polyenes such as C9 carotenes (de Oliveira et al., 2009; Koyama et al., 1988; Maia et al., 2021; Saito & Tasumi, 1983). Tentative

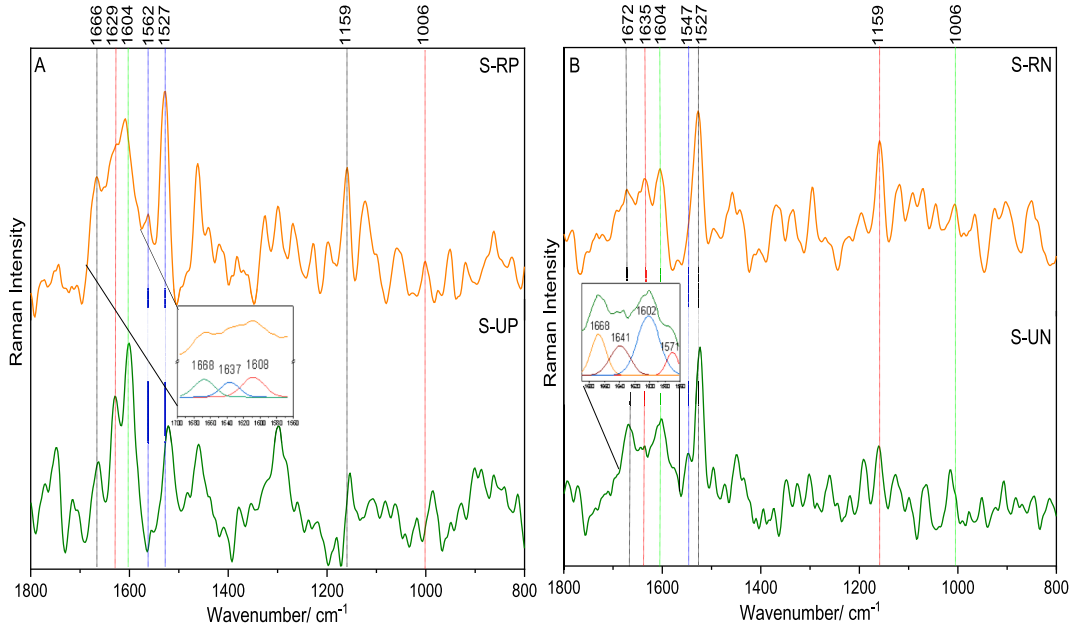

Fig. 6. Mean Raman spectra of the two maturation stages from banana: (A) 'prata'- unripe (S-UP) and ripe (S-RP), and (B) 'nanica'- unripe (S-UN) and ripe (S-RN), obtained with a laser line at 1064 nm.

assignment for the main Raman bands observed in the spectra of 'prata' and 'nanica' bananas, respectively, can be seen in Table 2.

The spectra of the two maturation stages of bananas 'prata' (S-UP, S-RP) and 'nanica' (S-UN, S-RN) showed similar spectral profiles. During the maturation process, it was observed a slight increase in the intensities of the carotenoid bands about phenolic acids only in the 'prata' variety. In the unripe maturation stage, where the bananas were green colored the main bands for 'prata' were observed at 1747, 1714, 1706, 1662, 1630, 1600, 1556, 1521, 1460, 1379, 1298, and 1154 cm^{-1} and for 'nanica' at 1710, 1668, 1635, 1602, 1571, 1547, 1523, 1448, 1347, 1302, 1160, 1064 and 1014 cm^{-1} (Fig. 6A, Fig. 6B and S2, Table 2). In the ripe stage, with the bananas almost completely yellow, the bands occur at 1743, 1705; 1668, 1637, 1608, 1562, 1527, 1462, 1383, 1300, 1159 and 1006 cm^{-1} for 'prata' and 1751, 1693, 1672, 1635, 1604, 1570, 1527, 1458, 1369, 1296, 1159 and 1006 cm^{-1} for 'nanica' (Fig. 6A, Fig. 6B and S2, Table 2). Comparing the unripe with the ripe maturation stage of 'prata', it can be observed an increase in the intensity of the characteristic bands from carotenoids around 1527 and 1159 cm^{-1}, while the bands from phenolic acids did not show a visible increment. From the unripe to the ripe maturation stage of 'nanica', no significant differences were observed in the intensity of both phenolic acids and carotenoid bands.

Raman spectra of another set of S-UP, S-RP (Fig. 2E) and S-UN, S-RN (Fig. 2F) in the 532 nm excitation line have also been provided (Fig. 7A and B, Table 2). Raman analysis of 'prata' showed an increase in the intensity of bands addressed to both phenolics and carotenoids as it goes from unripe to ripe stages (Fig. 7A). At the same time, for 'nanica', it was observed an intensification of bands attributed only to carotenoids (1525, 1158, and 1006 cm^{-1}) (Fig. 7B, Table 2).

3.5. Vibrational and electronic spectral data from ethanolic extracts of bananas

The Raman spectra of ethanolic extracts of unripe and ripe peels from 'prata' (Et-UP, Et-RP, Fig. 2E) and 'nanica' (Et-UN, Et-RN Fig. 2F) also showed main vibrational bands attributed to phenolics and carotenoids. For Et-UP it was observed bands at 1618, 1529, 1456, 1155 and 1008 cm^{-1} and for Et-RP bands at 1645, 1608, 1529, 1456, 1155 and 1014 cm^{-1} (Fig. 8A, Table S2). During the ripening process, it can be observed differences in the Raman and the electronic spectra mainly concern phenolic acid content, suggesting changes in the chemical composition of these compounds (Fig. 8A and Fig. 9A). A Raman broad band centered at 1618 cm^{-1} in Et-UP appears as a shoulder in the Et-RP together with medium bands at 1608 cm^{-1} and 1645 cm^{-1}. From the unripe to ripe stage, it can be seen a decrease in the intensity of Raman bands assigned to phenolic acids when compared to carotenoids, but no Raman shifting was observed in the band centered at 1529 cm^{-1} in both unripe and ripe stages (Fig. 8A).

The electronic spectrum of Et-UP showed a band with λmax at 233, 265 nm and shoulder at 301 and 357 nm which could be addressed to phenolic acids, and flavonoids (Fig. 9A and Fig. S4) (Kowalski & Kowalska, 2005; Martin et al., 2017; Tsimogiannis et al., 2007). Weak bands at 427, 470, and 660 nm could be attributed to carotenoids (427 and 470 nm) (Rodriguez, 2001) and chlorophylls (427 and 660 nm) (Matti Linnanto, 2022). However, changes in the UV spectral profile from unripe to ripe stage indicated differences in the flavonoid/phenolic acids chemical composition and an increase in the carotenoid content due to bands at 421, 442, and 470 nm (Fig. 9A).

On the other hand, a comparison between Et-UN and Et-RN showed major spectral differences in the electronic spectra, since Raman spectra did not show any shifting in the position of the bands. In the unripe fruit, main bands occur at 1658, 1604, 1558, 1527, 1444, 1303, 1270, 1159, 1005 cm^{-1}, and in ripe one at 1654, 1604, 1527, 1444, 1302, 1273,1159 and 1006 cm^{-1} (Fig. 8B, Table S2).

The electronic spectra of Et-UN showed a complex mixture which may be attributed to phenolic acids and flavonoids due to bands with λmax at 282, 312, 332 nm, and shoulder around 380 nm. Bands at 433 and 467 nm could be assigned to carotenoids (Fig. 9B) (Rodriguez, 2001), and bands at 665 nm to chlorophylls (Matti Linnanto, 2022). As the fruit matures changes in most bands are observed, especially absorption bands at 422, 442, and 470 nm which is typical of lutein. (Fig. 9B).

Banana peel is an abundant source of dietary fiber, proteins, lipids, pectin, essential amino acids, polyunsaturated fatty acids, and micronutrients, in addition to other bioactive compounds (Ibiyinka et al., 2021; Khawas & Deka, 2016; Naksing et al., 2021). Regardless of the fruit type (climacteric or non-climacteric), fruit ripening ultimately leads to transformations like cell wall softening, accumulation of sugars and phenolic compounds, color changes (anthocyanin and carotenoid accumulation), and the formation of aroma and volatile compounds. During the post-harvesting ripening of banana, degradation of chlorophyll and accumulation of carotenoids occur in the fruit peel. The ripe peel of bananas is richer in total carotenoids in comparison to other banana parts regardless of the maturation stage (Aquino et al., 2018). Carotenoids contribute to the color of the banana to a higher degree compared to flavonoids, which is attributed to their properties and distribution within the peel cells (Fu et al., 2018).

The phenolic composition in bananas is dependent on several factors,

Table 2
Tentative assignment for the Raman bands observed in the spectra of 'prata' and 'nanica' banana peels.

Bands (cm^{-1})								Tentative Assignments
1064 nm				532 nm				
'Prata'		'Nanica'		'Prata'		'Nanica'		
Unripe	Ripe	Unripe	Ripe	Unripe	Ripe	Unripe	Ripe	
1662w	1668m	1668m	1672w					$\nu(C{=}C)^{a}$
1630m	1637sh	1641w	1635w		1632m			$\nu(C{=}C)^{b}_{flav}$
1600s	1608m	1602m	1604m	1612w	1604m			$\nu(C{=}C)^{b}_{flav}$
	1562vw	1571sh	1570vw	1570w				$\nu(C{=}C)^{b}_{flav}$
1556vw		1547w						$\nu(C{=}C)^{c}_{car}$
1521m	1527s	1523s	1527s	1525s	1525s	1525s	1525s	$\nu(C{=}C)^{c}_{car}$
1460m	1462m		1458w		1462m			$\delta(C\text{-}H_2)^{a}$
		1448w		1440vw	1440m	1442vw	1442vw	$\rho(C\text{-}H)^{b,c}_{flav/car}$
1298m	1300w	1302w	1296w		1296s			$\rho(C\text{-}H)^{a}$
1180w	1194w	1192m	1196w					$\nu(C\text{-}C)^{a}$
1154m	1159m	1160m	1159s	1158s	1158s	1158s	1158s	$\nu(C\text{-}C)^{c}_{car}$
	1006w	1014w	1006w	1006w	1006w	1006w	1006w	$\rho(C\text{-}CH_3)^{c}_{car}$

Raman intensities: s-strong; m-medium; w-weak; vw-very weak; sh-shoulder; br-broad band.
flav: Flavonoids; car: Carotenoids. References citation: a: (Beattie et al., 2004; Popović-Djordjević et al., 2023); b: (Aguilar-Hernández et al., 2017; González Moreno et al., 2021; Machado et al., 2013; Teslova et al., 2007; C.-H. Wang et al., 2020); c: (Koyama et al., 1988; Saito & Tasumi, 1983).

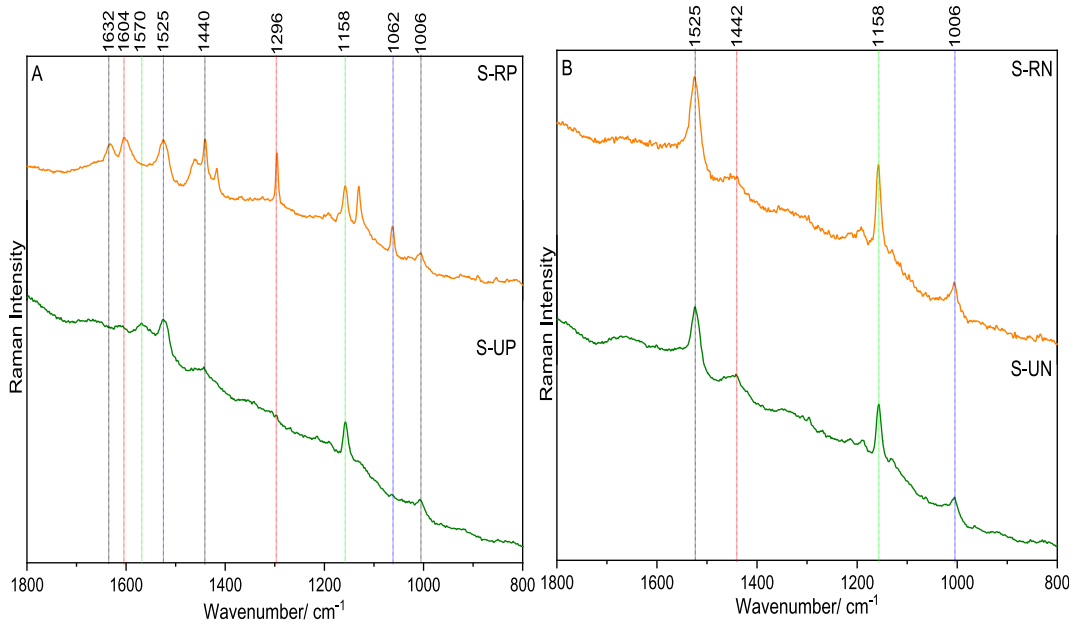

Fig. 7. Mean Raman spectra of the two maturation stages from banana: (A) 'prata'- unripe (S-UP) and ripe (S-RP), and (B) 'nanica'- unripe (S-UN) and ripe (S-RN), obtained with a laser line at 532 nm.

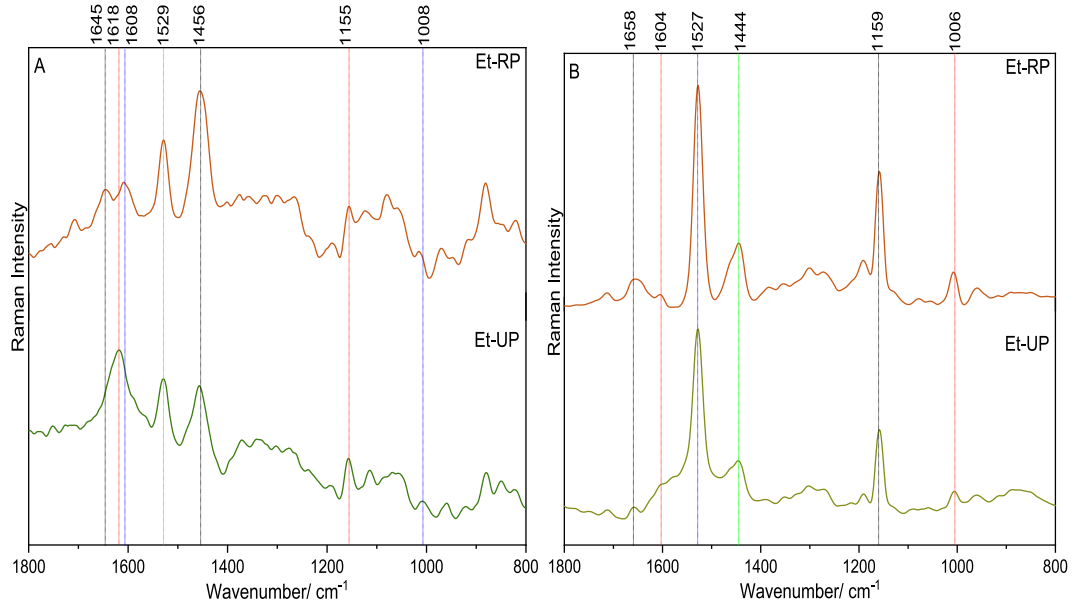

Fig. 8. Mean Raman spectra of ethanolic extracts in the two maturation stages from banana: (A) 'prata'- unripe (S-UP) and ripe (S-RP), and (B) 'nanica'- unripe (S-UN) and ripe (S-RN), obtained with a laser line at 1064 nm.

such as region of production, cultivation method (organic and non-organic), and variety (Sidhu & Zafar, 2018; Vu et al., 2019), but among the main flavonoids found in bananas are quercetin, myricetin, kaempferol, and cyanidin (Kevers et al., 2007). In a study that investigated the phenolic profiles of nine banana cultivars in the pulps and peels, it was found that hydroxycinnamic acids are dominant in the pulps and, a predominance of flavonol glycosides in the peels, with rutin being the most abundant (Passo Tsamo et al., 2015). In another study on the antioxidant compounds of banana (*Musa cavendish*), the peel was found to be more abundant in antioxidant compounds than the pulp, in addition, it was observed that the ripe banana peel has around 45% less total phenolic content, and approximately 15% less total flavonoids than the green peel (Fatemeh et al., 2012). Vu et al., 2019 reported that the content of phenolic compounds and antioxidant activity increased during the maturation of banana fruits, which is in line with the results of the present study about the occurrence of both phenolic and carotenoid content.

The main carotenoids reported in the peel of 'prata' and 'nanica' are α-carotene, β-carotene, and lutein as the most abundant one (Aquino et al., 2018), which is in agreement with other fruits that have a yellow peel when ripe, such as passion fruit and melon (dos Reis et al., 2018; Tuan et al., 2019). It was reported that lutein constitutes 58.6–74.2% of carotenoid content in the peel tissue of different banana varieties (Fu et al., 2018). However, it is known that the concentration of these metabolites varies according to the crop and the stage of maturation (Aquino et al., 2018; Fu et al., 2018; Sidhu & Zafar, 2018; Vu et al., 2019). Vu et al., 2019 reported a decrease in chlorophyll content at about 90%, and an increase in carotenoid and flavonoid content up to

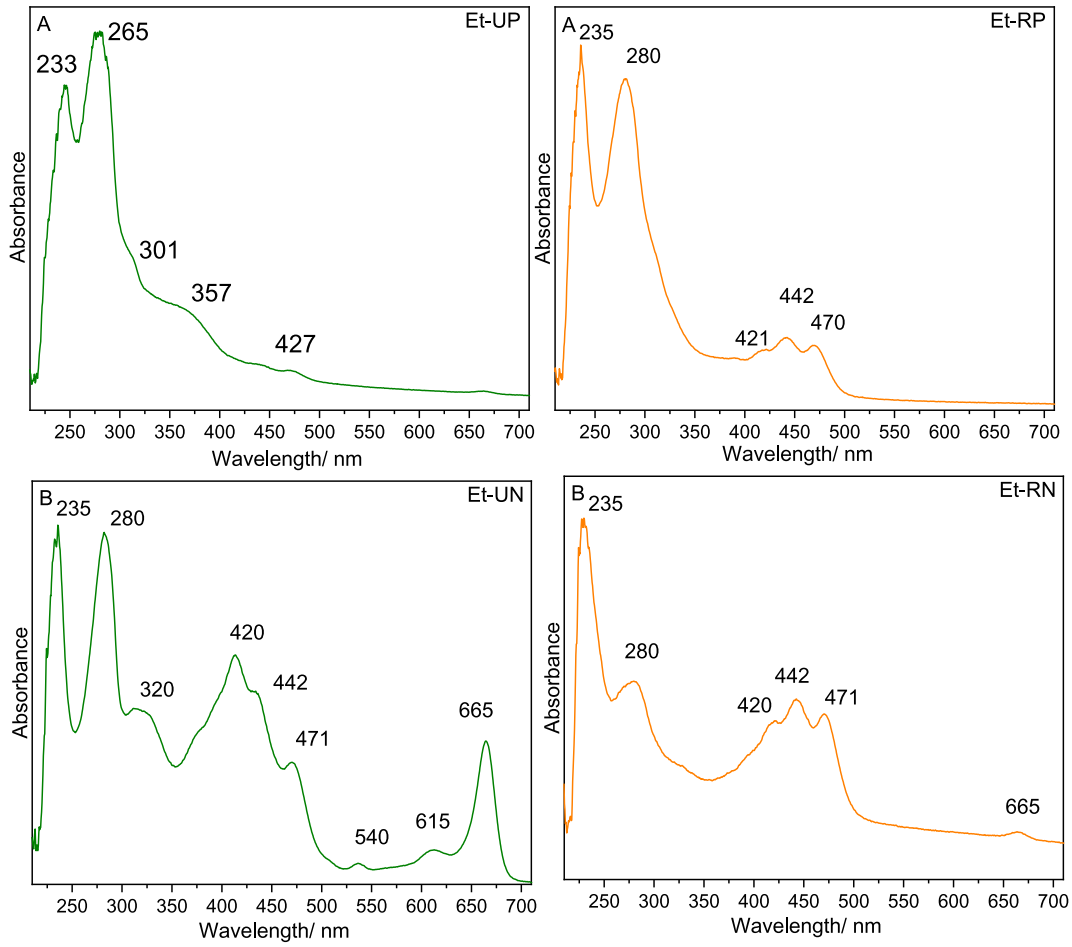

Fig. 9. Electronic spectra of ethanolic extracts of two stages of banana maturation: (A) 'prata'- unripe (S-UP) and ripe (S-RP), and (B) 'nanica'- unripe (S-UN) and ripe (S-R).

50% and 27%, respectively, during the maturation of banana fruit. Lutein was the dominant carotenoid in the unripe and ripe peel of 15 Brazilian cultivars (including 'prata' and 'nanica'), and its content did not differ much between both stages in most of the cultivars. Moreover, a slight decrease of the α- and β-carotene in the peel was observed during the fruit maturation. The content of α-carotene varied notably between cultivars and maturation stages, whereas in 'prata' and 'nanica' higher content of β-carotene compared to α-carotene was observed (Aquino et al., 2018).

It is important to point out that despite Raman spectroscopy obeying the Lambert-Beer law predicts that concentration and intensity are linear of the spectroscopic signal, the absolute intensity for each one of the constituents in a very complex matrix like a fruit is not so simple. In this sense, even if the concentration of carotenes in some samples is low, such as scarlet eggplant and banana, the intensity of the Raman signal is very high, as it is well established in the literature of Raman investigations of carotenes (de Oliveira et al., 2009). In addition, it also should take into consideration the laser line since the intensity of Raman bands due to resonance with the electronic transitions may vary in each one of the constituents such as flavonoids (between 240 and 400 nm) and carotenoids (between 270 and 550 nm).

4. Conclusion

In this work, Raman spectroscopy has been used for the first time to characterize the ripening processes of a scarlet eggplant and two varieties of bananas such as 'prata' and 'nanica'. The Raman data showed that the yellow coloration in each type of fruit has a distinct origin, despite both species being rich sources of the same classes of compounds namely phenolic acids, flavonoids, and carotenoids. Differences in carotenoids and phenolic acids/flavonoid composition among the two species were shown by Raman and electronic spectral analyses. A combination of flavonoids and carotenoids may be responsible for the coloration of the scarlet eggplant and bananas. Based on Raman and UV data the orange pigment of the ripe scarlet eggplant is naringenin chalcone associated with β-carotene, which was previously reported as the major carotenoid in the peel. The yellow color of ripe bananas is known to be due to the carotenoid lutein and here, the UV spectra of crude extracts of both varieties corroborated the literature.

Our results have shown that the *in situ* Raman spectroscopy can identify and track the main pigments present during the ripening process of both species. Comparison among unripe and ripe stages of both species showed that scarlet eggplant is richer in phenolic acids/flavonoids than bananas. Although Raman spectroscopy has demonstrated intense bands of carotenoids in the peel of both species, it cannot be correlated with the concentration. However, the advantage of the technique is the detection of small amounts of the bioactive carotenoids and flavonoids in complex matrices, under different laser lines, according to different maturation stages. Analyses of the electronic spectra as well the Raman data of crude extracts along the maturation process of both species have shown how complex the metabolite profiles biosynthesized from diverse enzymatic pools to produce different pigments which jointly are responsible for the fruit colors.

At last, peels are agri-food by-products that have been recognized as a good and inexpensive source of phenolic and carotenoid compounds. The identification and characterization of bioactive molecules present in

the peel foment ongoing research worldwide in developing value-added products. Moreover, the valorization of wastes/by-products can positively impact economic, social, and environmental sectors.

CRediT authorship contribution statement

Mariana T.C. Campos: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Lenize F. Maia:** Formal analysis, Investigation, Methodology, Software, Validation, Writing – original draft. **Jelena Popović-Djordjević:** Formal analysis, Investigation, Writing – original draft. **Howell G.M. Edwards:** Formal analysis, Writing – original draft. **Luiz F.C. de Oliveira:** Conceptualization, Funding acquisition, Resources, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgments

Authors are grateful for the financial help by CNPq, CAPES and FAPEMIG. JPDj acknowledges the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for support (Grant No. 451-03-47/2023-01/200116). This research was also funded by FAPEMIG, grant number APQ-03079-23, and CNPq grant numbers 406853/2021-5 and 303569/2022-0.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochms.2024.100204.

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