Future Foods 6 (2022) 100182

Contents lists available at ScienceDirect

Future Foods

journal homepage: www.elsevier.com/locate/fufo

Candying process for enhancing pre-waste watermelon rinds to increase food sustainability

Laura Maletti[a,*], Veronica D'Eusanio[a], Lisa Lancellotti[a], Andrea Marchetti[a,b,c], Luca Pincelli[a], Lorenzo Strani[a], Lorenzo Tassi[a,b,c]

[a] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy
[b] INSTM, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Firenze, Italy
[c] BIOGEST-SITEIA, Centro di Ricerca Interdipartimentale per Il Miglioramento e la Valorizzazione Delle Risorse Biologiche Agro-Alimentari, University of Modena and Reggio Emilia, Reggio Emilia, Italy

ARTICLE INFO

Keywords:
Pre-waste materials
Valorization
Sustainable foods
Watermelon rinds
Candying processes

ABSTRACT

This work describes two alternative laboratory methods 'candying fruit' methods of fresh mesocarp of Crimson sweet watermelon, a typical waste and unappetizing material. Our experimental candying process was conducted by slow osmosis, lasting 24 weeks at room temperature. It was activated with granular sucrose according to our two alternative laboratory methods, WET and DRY. Fresh watermelon rinds were transformed into candied fruit with excellent flavor and aromas. The aromatic profile of all the materials was characterized with HS-SPME-GC–MS technique. The results highlighted some significant differences in the Volatile Organic Compounds fraction, probably attributable both to the cultivar and to the two candying methods, as verified also by a panel test. The class of alcohols remains almost constant in all the samples. Terpenoids are highly present in FRESH samples, while they disappear in DRY candied ones. Acetate esters are absent in FRESH rinds, they reach the maximum level in WET, and stop at the middle in DRY samples. The trend of the values relating to the class of acids is opposite: absent in the FRESH aromatic profile, maximum and average for DRY and WET samples, respectively.

1. Introduction

In this paper, we can address some attention to a case study represented by watermelon cultivation and processing pre-waste byproducts. The rinds of the watermelon constitute a rather substantial fraction of the fruit, varying from about 15–30%, up to 40% (Tarazona-Díaz et al., 2011; FAO, 2020) of the total mass for the various commercial cultivars (Zia et al., 2021). The peels therefore remain the form of massive by-product most important among the agri-food waste generated by many players operating along the value-chain (www.imarcgroup.com). Above all, by producers in the farmers and by food industries that produce vegetable juices (Souad et al., 2012). This view is strongly shared in literature, and many other authors agree with us (Lowe and Buckmaster, 1995; Zamus et al., 2021; Rico et al., 2020).

In previous literature studies, it has been shown that watermelon rinds have some potential for the possible recovery of derived materials (Khanam and Haq Bhat, 2017). For example, after processing - drying and grinding the mesocarp, the white and thick intermediate layer, a neutral dietary fiber can be obtained for use in the pharmaceutical industry (Dammak et al., 2019), for the preparation of nutraceutical-enriched flours for the bakery production (Fabani et al., 2021), pasta, pastry and ice cream products, stabilizing agent of water content (Souad et al., 2012) and as a natural food additive (Hoque and Iqbal, 2015; Ho and Dahri, 2016), a useful product for new forms of packaging materials (Han and Song, 2021), among others. In addition to all the opportunities described above (Velmourougane and De Souza, 2017), in this paper we report the results from a series of candying tests that we carried out on some samples of mesocarp obtained from thick peels of Crimson sweet watermelon. This way, it is possible to improve the recovery of some byproducts through processing into other foods (Baldwin and Wilberforce, 2009), helping to achieve at least 3 goals : (i) increasing availability to cover basic needs (Shivapour et al., 2020); (ii) minimizing waste and environmental impact (Aronson et al., 1999; Fish et al., 2009); (iii) maximizing agricultural profit (Kausar et al., 2020).

The rinds have a very high moisture content, about 95% on a wet basis. The candying process involves the reduction of the moisture content to safe levels, slowing down and inhibiting the microbial growth and enzymatic activity associated with the fermentation processes (Athmaselvi et al., 2012), thus extending the shelf life of the obtainable products (Deiana et al., 2019). Obviously, these last are very sweet products with great added value, mainly intended for the con-

* Corresponding author.
E-mail address: laura.maletti@unimore.it (L. Maletti).

https://doi.org/10.1016/j.fufo.2022.100182
Received 21 December 2021; Received in revised form 15 May 2022; Accepted 5 September 2022
2666-8335/© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/)

fectionery sector, ice cream production, yoghurt and dairy products, as well as candied fruits in general, among others.

In particular, we have monitored the composition of the volatile aromas associated to different candying processes, in relation to the characteristics of the fresh rinds. In fact, the fresh product is absolutely unappetizing, it is almost devoid of aromas that could make it interesting and recognizable for a particular scent, as in the case of other fruits. Conversely, the candying process associated with some partial fermentation processes, leads to the development of volatile analytes that express a very pleasant aromatic profile, making the finished product unique and perfectly recognizable. Unfortunately, extensive literature and market research shows that in the panorama of both candied fruits and vegetables, there is no other species that can resemble our finished products. This fact makes very difficult any possible comparison with any matrix, alternative or substitute, of commodity interest (www.indexbox.io).

2. Materials and methods

2.1. Samples preparation

We procured 3 large watermelons of about 10 kg each, ripe at the right point for consumption. They were bought one in a city supermarket, the other 2 purchased directly from 2 different producers in the Modena territories. The fresh rinds taken from 3 Crimson sweet watermelons, about 2 cm thick, have been rinsed and cleaned, carefully eliminating both the pulp with the red fiber, and the green external cuticle having a nearly woody-like consistency, whose thickness was about 3–4 mm. For this study, we took a fraction of peel from each watermelon, cutting the slices obliquely from the stalk to the bottom, to obtain greater representativeness especially in the rinds thickness. Subsequently, the peeled rinds were cut into pieces approximately $5 \times 5 \times 1.5$ cm in size for the candying process.

For the candying of the white mesocarp, we have identified 2 alternative very slow osmotic procedures (lasting 24 weeks) at room temperature, which we indicate WET and DRY, and which are very different from industrial-type processes. In this regard, we remind that industrial processes are generally carried out either at hot or at low temperature, by boiling or dipping the fruits in syrupy solutions at fixed glucides concentrations (Deiana et al., 2019). Our methods do not use sugar solutions, as we have not added the solvent. Conversely, the solutions in our samples were slowly formed by the extraction of water from the skins, due to the osmotic effect. Finally, industrial products undergo a drying / dehydration process under vacuum to remove excess water.

The pieces of rinds (about 1 kg) were immersed and layered in a bed of solid sucrose in a rectangular glass container [dimensions 32 (length) x 16 (width) x 8 (depth) cm] until completely filled (mass ratio rinds : sucrose = 1 : 1). The containers were covered with a steel plate onto which weights equivalent to 2 kg were loaded to exert a constant pressure. The system was then covered with a plexiglass cloche to avoid equilibrium exchange with external atmospheric oxygen. The dataset provided in this study is related to fruits collected in the Modena territory and processed in the year 2020.

WET process: the glass container was placed in a horizontal position and maintained in this initial condition for the entire duration of the candying process (Fig. 1). This way, the rinds always remained in contact with the concentrated sucrose solution that was slowly formed as the osmosis process contributes to remove the water from the peels themselves.

DRY process: the container was inclined to a suitable extent to allow the major part of the saccharide solution to constantly drain into another external collection pan (Fig. 1). The rinds have undergone a particularly stressful and effective dehydration process, in the absence of continuous contact with the exceeding preserving liquid, the physiological solution generated autonomously. In this way, the rinds remain in contact only with a very small fraction of the concentrated and saturated solution. Therefore, they remain strongly impregnated with thick and viscous saccharide solution, with the result that the final product is particularly dehydrated and scarcely dripping.

Once the candying cycle was completed, the rinds were collected and placed in jars with their residual contact solution, highly sugary, dense, with a honey-like consistency, for the tests necessary to evaluate the qualitative and aromatic characteristics of the final product.

2.2. Materials

The dichloromethane used is an analytical grade Sigma-Aldrich product for HPLC and GC chromatography, distributed by Merck KGaA, Darmstadt, Germany. Others chemicals such as: 2-methyl-1-propanol; 3-methyl-1-butanol; 2-ethyl-1-hexanol; phenylethyl alcohol; 3-methy-l-butanal; ethyl butanoate; ethyl hexanoate; 3-hydroxy-2-butanone (acetoin); β-pinene; β-Caryophyllene and limonene were obtained from Sigma – Aldrich product, distributed by Merck KGaA, Darmstadt, Germany. Decanal; methyl acetate; 2-methylfuran and 2-ethylfuran were obtained from Carlo Erba Reagents, Milano (Italy). n-hexane, nonane, dodecane, tetradecane and hexadecane, obtained from Carlo Erba Reagents, Milano (Italy), have been injected both for the for the identification of analytes through the mass spectra and for the calculation of the Linear Retention Index (LRI).

A Solid Phase Micro-Extraction (SPME) holder (Supelco Inc., Bellefonte, PA, USA) was used to manually perform the SPME headspace (HS) analysis. The SPME device consists of a fused silica fiber coated with Carbowax/Divinylbenzene/ Polydimethylsiloxane (CW/DVB/PDMSO). The triple fiber covering material CW/DVB/PDMSO is a mixed coating that contains a liquid polymer, a semi-solid polymer and solid particles. This type of coating is highly performing as it combines both the absorption and adsorption properties of the different coating particles with a synergistic effect. This multiple effect facilitates the balance of analyte distribution between the stationary phase and the gas phase in the headspace, promoting the retention capacity and improving the sensitivity of the multiple-coated fiber compared to other types of similar devices. Furthermore, given the characteristics of different polarity of the 3 constituents of the coating, the fiber seems suitable for the capture of analytes with significantly different molecular properties and dimensions, resulting adequate for the characterization of complex matrices as in this case (Roberts et al., 2000; Song et al., 1998).

The candying experiment was conducted in single, preparing only one candying batch for the two methods. The reproducibility of the experimental data is established on the basis of the replicas obtained from different vials, containing samples collected in different points of the candying tank.

2.3. HS-SPME analysis

Initially, a set of specimens was prepared consisting of a freshly shredded mesocarp sample, representative of the material subjected to candying process. The rinds were quickly ground with a mixer, obtaining a rather coarse and relatively dry pomace, therefore without significant losses of endogenous liquids.

Each sample consists of 10 ± 1 g of pomace, introduced in 20 mL vials which corresponds to a solid phase to headspace volume ratio of ~ 0.5, and sealed tightly with Teflon / silicone septa. The vials thus prepared were processed as follows in order to verify the compositional characteristics of the matrix with reference to the volatile aromatic fraction.

Some vials have been loaded with 7 mL of CH_2Cl_2 to facilitate the extraction of any soluble and easily volatilizable compounds from this phase. Other vials were added with 7 mL of supersaturated NaCl solution to favor the effect of displacement from the pomace and relative salting out of the volatile compounds. Reproducibility of experimental procedures have been established working with at least three replicates samples of the same matrix and making many different measures for each vial.

All the samples, regardless of the manipulations undergone, were sonicated for 30 min in a thermostated bath at 40.0 ± 0.1 ˚C to favor the transfer of volatile compounds from the matrix to the headspace. After this step, the SPME fiber was manually inserted into the headspace of the sample vial thermostated at 40.0 ± 0.1 ˚C, with exposure to volatile compounds for 15 min.

Some blank tests, corresponding to the analysis of an external standard solution containing 1-decanol (conc. 150 μg/g ethanolic solution) were performed periodically after a certain number of chromatographic runs (5) relating to real samples. All measurements were performed in at least 3 replicates for each sample/vial.

The candied rinds obtained according to the 2 methods previously described (WET and DRY) were drained of their syrup until the dripping disappeared. The samples then obtained were prepared and analyzed following the same procedures described above for the fresh peels. However, a more homogeneous pomace after grinding was obtained from candied rinds due to its softer consistency compared to fresh rinds which were relatively hard.

2.4. GC-MS analysis

The liquid dichloromethane extracts and the volatile compounds desorbed from the SPME fiber were analyzed in GC – MS, Agilent Technologies 6890 N Network gas chromatograph. The GC was equipped with a 60 m x 0.25 mm i.d., 1.00 μm film thickness, DB-5MS UI capillary column (J&W Scientific, Folsom, CA, USA) connected to an Agilent 5973 mass spectrometer. The SPME injections were performed in splitless mode and the temperature of the injector was setted at 250 ˚C.

Some specific chromatographic conditions were used:

(i) for CH_2Cl_2 liquid extracts (0.5 μl) were injected in the injection port lined with a splitless glass liner. The detector started to operate after 8 min of injection (solvent delay);
(ii) for SPME samples, the injection port was lined with a splitless glass liner.

The fiber was introduced into the injector for 15 min. The detector started operate immediate after injection. The oven temperature was programmed from 40 to 250 ˚C with a scan rate of 10 ˚C / min up to 160 ˚C, and 8 ˚C/min up to 250 ˚C, while the transfer line was heated to 270 ˚C. The carrier gas (He) was fluxed at 1 mL/min, with a column head pressure of 15 psi.

The mass spectrometer was used in electron impact mode at 70 eV, scanning the range m/z 25–300 and in full scan acquisition mode. The identification of volatile compounds was obtained from comparison of the retention times of the GC, by comparing the mass spectra with literature, with those of the libraries supplied with the operating system of the GC-MS (NIST14/NIST05/WILEY275/NBS75K), National Institute for Standards and Technology (NIST database https://webbook.nist.gov), Mass Bank of North America (https://mona.fiehnlab.ucdavis.edu), and spectra of pure standard compounds (when available).

The estimation of concentrations for all compounds identified in the SPME analysis was carried out by comparing the GC peak area, expressed as total peak ion current. All the data shown in the tables relate to values obtained from analysis performed at least in triplicate. The reproducibility of the results was expressed as standard deviation in the tables.

2.5. Metals content

The ashes obtained by incineration of the samples, about 100–150 mg, were directly solubilized in a volumetric flask with 5 mL of HNO_3 65% (Suprapure, Merck; Darmstadt, Germany) and 5 mL of deionized water (from a Milli-Q Plus, Millipore system; Burligton, MA, USA); a clear solution was immediately obtained. Afterwards, final volume was adjusted up to 50 mL with deionized water. The final solutions are perfectly clear and apparently colorless, stable over time, and we have never observed the formation of turbidity or precipitates.

Along with a batch of 9 samples (3 original ones, each of which replicated 3 times), a blank was also prepared in the same way. Quantification of selected metals was done using the ICP-OES spectrophotometer Perkin Elmer - Optima 4200 DV (Baraldi et al., 2020). The spectrophotometer is equipped with an ultrasonic nebulizer (Cetac Technologies Inc.; Omaha, NE, USA) and Charge-Coupled Device (CCD) area detector complete the instrumental setup. Working Merck ICP standards for tested metals were prepared from stock solutions (1000 mg/L). Optimum analytical conditions maintained on ICP spectrophotometer have been reported in our recent paper (Durante et al., 2021).

2.6. Other determinations

The UV-vis spectrophotometric determination (Jasco V-570 UV/VIS/NIR spectrophotometer, JASCO Corporation, Tokyo, Japan) of phosphate is based on the molybdenum-blue chemistry, recording the absorbance at 880 nm. Ascorbic acid is the common reductant in the manual analysis of phosphate (Ben Mussa et al., 2009; Hassan et al., 2022).

Estimation of total sugar content in our samples was carried out using Fehling's solution reagents as described in the literature (Ranganna, 1986). For easiness of interpretation and comparison between different samples, we expressed all the results as sucrose equivalents.

The water content was measured in two steps. At first, the samples were dried at 101 ˚C, eliminating all the free water and mechanical assorbed/adsorbed water on the matrix. This fraction represents the largest amount. Subsequently, the samples were heated to 105 ˚C to also eliminate the contribution due to water strongly bound to the fraction of inorganic compounds (water of crystallization = residual moisture at 101 ˚C).

Water activity hygrometer LabSwift-aw (Novasina, Switzerland) was used to determine the a_w of the fresh and candied watermelon rinds at room temperature.

2.7. Statistical analysis

Experimental data were compared by applying analysis of variance (one-way ANOVA), by running in the Matlab® 2019b environment (The Mathworks Inc., Natick, MA, USA). The level of significance was determined at $p < 0.05$ to see whether there are statistical differences between the mean values.

2.8. Sensory evaluation

Sensory evaluation of the different samples was performed using 8 parameters (appearance, mouth feel, after taste, aroma, pungency, sweetness, sourness, overall sensory score) and 7 levels hedonic scale to compare the degree of acceptability of FRESH watermelon rinds and the candied ones obtained by applying the two alternative WET and DRY methodologies. The 7 levels were denoted as: 1 = extremely dislike; 2 = slightly dislike; 3 = moderately dislike; 4 = neither like or dislike; 5 = moderately like; 6 = slightly like; 7 = extremely like. A total of 30 panelists consisting of untrained or semi-trained people, such as students, technicians, maintainers and teachers of our Department, participated in sensory evaluation.

The people engaged in this activity for an acceptability test, are equally distributed between males and females, are aged between 21 and 65 years, constitute a small group that, even if limited, represents an average population of various cultural backgrounds, able to perceive different aromatic and gustatory sensations, and able to express a critical judgment according to the suggested indexes and 7-point hedonic scale. A group of 30 panelists is probably adequate for the minimal aims of

Table 1
Some selected analytical parameters* of some samples obtained from the starting material (FRESH rinds of Crimson sweet watermelon) and candied products from different procedures (WET and DRY).

	FRESH rinds	WET candied	DRY candied
water content%	94.5 ± 0.4	53.1 ± 0.5	28.2 ± 0.4
water activity - a_W	0.985 ± 0.003	0.875 ± 0.002	0.641 ± 0.002
moisture% at 101 °C	0.42 ± 0.04	1.28 ± 0.03	1.27 ± 0.04
residue% at 105 °C (db)	5.4 ± 0.5	46.7 ± 0.4	71.5 ± 0.5
ashes% (db)	1.20 ± 0.03	1.01 ± 0.03	0.97 ± 0.03
# total soluble glucides% (db)	0.2 ± 0.1	32.6 ± 1.2	49.8 ± 1.4
Metal content, expressed as mg/100 g sample db (dry basis)			
K	2766 ± 75 *2998 – 3065*	2675 ± 59	2721 ± 62
Ca	264 ± 29 *353 – 372*	216 ± 15	236 ± 34
PO_4^{3-}	815 ± 32 *972 - 1006*	802 ± 20	807 ± 13
Mg	195 ± 18 *181.6 – 234.9*	185 ± 16	192 ± 25
Na	17 ± 5 *21.3 – 26.2*	12 ± 6	10 ± 7
Cu	0.25 ± 0.08 *0.43 – 0.28*	0.27 ± 0.09	0.20 ± 0.07
Fe	2.07 ± 0.04 *2.66 – 3.07*	2.04 ± 0.05	2.40 ± 0.05
Mn	1.33 ± 0.05 *1.02 – 1.42*	1.38 ± 0.06	1.35 ± 0.08
Zn	2.26 ± 0.06 *1.97 – 1.34*	2.15 ± 0.06	2.69 ± 0.08

* mean of three replicates and uncertainties expressed as standard deviation, $s_{(3)}$.
# total content of soluble glucides % was expressed as saccharose %.Values in italic characters were taken from Tufeanu et al. (2017).

this work, as the main goal is unrelated to a market survey but rather to evaluate the acceptability characteristics of the new candied products.

Each panelist, completely unaware about the nature of the samples to be tasted, received three anonymized specimens: i) FRESH rind, easily identifiable because very different from the candied ones, but unrecognizable the origin and the cultivar; ii) two samples, WET and DRY candied rinds, coded by a letter and two-digit random number to avoid bias. In addition, bread and water to rinse the palate before or in the middle of the evaluation procedure have been provided. All variables, factors and parameters needed to perform these assessments were considered unweighted and all equally balanced (seven-level hedonistic representation, as defined above).

3. Results and discussion

The industrial candying processes carried out by osmotic dehydration, require that the water content of the fruits is reduced while the sugar content is gradually brought to about 70–75 °Brix. In these cases, the fresh fruits cut into pieces are firstly soaked in sugar syrup, working in batch systems, at temperatures in the range of 30–80 °C. At the end of the candying cycle, the product is then semi-dried, up to the residual water content comprised, on average, in the range of 15–20% (w/w). In addition, industrial processes are much faster than our conditioning time (24 weeks) set to obtain the final product, as they reach the candying goal in the short period of 1–2 week (Bonazzi and Dumoulin, 2011). Since the chopped material was immersed in granular solid sugar, the candying solution was slowly formed as the dehydration process proceeds. We also have chosen to work at room temperature for the entire duration of the process, avoiding thermal stress on the rinds.

Fig. 2 shows the initial state of the fresh mesocarp and the final result of the candying process carried out according to the previously illustrated WET and DRY methods.

Table 1 shows some analytical data relating to the fresh material and the finished products obtained from the two different candying procedures.

The water content (AOAC, 1990) measured on fresh rinds is perfectly aligned with the general trend of literature (Chakrabarty et al., 2020; Romelle et al., 2016). Conversely, our candied products have a water content (~ 53% WET, and ~ 28% DRY) that is far from the average values of industrially produced candied fruit, which are estimated on average around 15–20% (USDA, 2011). Furthermore, the WET candied contains ~ 90% more water than the DRY type.

To this respect, industrial candied seem really dry to the touch, apparently stiff and rigid, while those obtained from this work are very moist, relatively soft and elastic. The consistency of our samples could be on the borderline between that of industrially dry candied products and cooked fruit in syrup drowned in its own liquid. However, let's remember that even with a water content of about 53% for wet candied, the stability of our product is ensured by a high content of soluble compounds that increase osmotic pressure, preventing bacterial and mold growth.

The residual moisture at 101 °C is eliminated by heating the previously dried sample up to 105 °C. The obtained values seem stabilized at around 1.27–1.28% for our candied products. This type of moisture represents the amount of strictly bounded water, mainly coordinated to the cationic metals and inorganic compounds present in the matrix. In fact, if the data are associated with the ash content (1.01% and 0.97% for WET and DRY, respectively), it is evident that there is a relation between them. Only the double measurement at 101 and 105 °C allows to quantify the water fraction strongly bound to the matrix.

As regards the values of a_W, we observe that the DRY sample (a_W = 0.641) is perfectly aligned with the literature data that establish adequate levels of food safety ($a_W \leq 0.78$) and product stability against the onset of bacterial growth. The WET sample (a_W = 0.875) is placed at the limit of the variability domain of a_W to have shelf life stability of products intended for long storage periods ($a_W \leq 0.88$). However, also in this case the saturation with crystalline sucrose leads to osmotic pressure effects incompatible with the proliferation of undesired species, guaranteeing stability and food safety for the product

The dry residue at 105 °C consists of all the non-volatile components present in the sample. The DRY candied product, with a lower water content, has a dry residue value that exceeds the equivalent WET candied fruit by 53%.

As regards the content of total soluble saccharides, expressed as sucrose, we pass from a not very significant content in the FRESH material (~ 0.2% wet basis), to increasing values for the candied products WET (~ 32%) and DRY (~ 50%). Noteworthy is the fact that industrial candied fruits have a total sugars content between 70 and 90%, while the reference value of about 81% is reported by the Agricultural Research Service (USDA, 2011). The high% sugar values in industrial candied fruits are reached as the last stage of the production method consists of a vacuum drying step of the residual syrup. The glucidic content of candied fruit is a stabilizing factor, which allows it to be stored for a long time, but which makes it unsuitable for diabetics and obese people. We are fully aware that the strategy of using sweets as a form of enjoyment is not the best one, as sugar consumption is increasingly discouraged, especially in Western countries where obesity is a fairly widespread and impactful pathology. However, for the products we obtained with this home-made experiment, the reduced sugar content certainly helps to limit risk factors and health damage.

Table 1 also shows data relating to some metal content of macro- and micro-constituents, in addition to the quantity of phosphorus determined as PO_4^{3-}, i.e. the most significant components of the inorganic fraction, the ashes. Potassium is the most abundant analyte for all the samples. For FRESH rinds, our results (2766 mg/100 g db) differ to some extent from those reported by Tufeanu et al. (2017). These researchers have obtained very interesting results comparing two techniques of sample drying, vacuum freeze-drying and oven heating. For the sake of completeness, their results are reported, in italic characters, as an interval also in Table 1, taking into account that the first value relates to cryo-technique while the second to hot drying. Obviously, the cold technique is respectful of the composition of the rinds as it maintains the bioactive ingredients such as vitamins and other compounds which, in turn, being thermolabile are lost by applying the hot technique.

In addition to the above considerations, we observe that the K content does not vary significantly for both candied samples. The same trend is valid for the other main components Ca, PO_4^{3-}, Mg and Na. Similarly, a good agreement is also observed for the microelements Cu, Fe, Mn and Zn. The presence and quantification of metals could represent a discriminating element, or a traceability marker, to identify the origin and provenance of the raw material, as well as the manufacturing processes. Since the two WET and DRY methods proposed in this work are quite different, it was expected that the candying process caused differences in the metal content of the samples. In fact, the DRY sample continuously loses the saturated solution that forms in the candying tank, probably thus eliminating even in part the soluble inorganic compounds. However, the experimental values of Table 1 seem quite stable regardless of the candying process undergone by the sample, and are also aligned with the trend of the values related to the FRESH rinds.

It is common opinion that watermelon rinds, as well as many other *Cucurbitaceae* fruits, are a rather 'hard and poor' natural matrix, since at first glance they are considered inedible, scarce in bioactive principles and of little or no nutritional value. In fact, the compact appearance and natural hardness of this material seems more suitable to protect the edible internal fraction than to suggest alternative use.

Also the organoleptic aspects do not make it particularly palatable, as it is weakly perfumed and therefore very poor in volatile and gustatory aromas. The combination of all these not particularly pleasant characteristics contribute to make it a real waste material. However, even if poor in volatile compounds, for completeness of information, the fresh mesocarp was also analyzed in this work. Most of the studies reported in the literature are related to the aroma of the edible fraction, which expresses the best qualities of the fruit. Contrary to the case of watermelon cultivars in which exocarp (rinds) and mesocarp do not communicate any olfactory information to the consumer, the other large family of *Cucurbitaceae* represented by melons, excluding the Inodorous group, releases aromas and fragrances that are extremely important for the attractiveness of the product (Portnoy et al., 2008; Esteras et al., 2020).

Before describing the results obtained with the HS-SPME analysis, it is necessary to remember that the samples extracted with CH_2Cl_2 as a solvent, introduced into the GC-MS system did not produce any signal other than the solvent itself. This fact denotes the total lack of analytes soluble in CH_2Cl_2 for all the samples, although several attempts have been made with ultrasound and microwave techniques, to displace in solution at least some particularly resistant compound.

On the other hand, this evidence is not quite unexpected, being CH_2Cl_2 a moderately dipolar solvent with little affinity for polar and hydroxylated compounds, especially due to its low solvating power and modest ability to form hydrogen bonding networks.

Fig. 3 shows the HS-SPME chromatogram obtained from a mesocarp sample freshly grinded, manipulated as illustrated in Section 2.3, and immediately processed with the GC-MS instrumentation.

Table 2 collects the descriptive elements of the chromatogram of Fig. 3. As can be seen, 32 analytes have been identified, which are based on as many peaks, among which the class of alcohols predominates (11 ALC) with a relative amount of 51.8% of the total area evaluated as the total ionic current (TIC) of the selected peaks in the chromatogram. This class is followed by the group of terpene compounds (12 TER) with the 15.6%, acetic acid-methyl ester as the only non-acetate ester (1 NAE; 12.9%), ketones (2 KET) with a total amount of 9.4%, alkanes (1 AHA; 2.2%) and, finally, aldehydes (3 ALD) and other compounds (2 OTH) that are present in a quantity equivalent to 2.0% and 6.1%, respectively.

Tables 2–4 show the peak area expressed as Total Ion Current (TIC) instead of the relative area%. This choice is justified considering that the HS compositions of these samples are quite diverse owing to the different matrices compared.

The specific literature seems rather poor in information regarding the volatile aromatic fraction (VOCs) of this fresh material. However, in a very recent study, Ramirez et al. (2020, 2021) agreed with us about the presence of a relevant number of volatile components as reported in Table 2. Among the analytes listed in the table, the class of terpene compounds arouses great interest. These molecules, some of which are displayed in Scheme 1, are generally identified in most plant species as they play different roles in nature and, in particular, they seem to be mainly engaged in developing communication signaling and defense capabilities against herbivores, insects, aphids and other parasites (Maruyama et al., 2001).

Apart from the aroma expressed on the outside of the fruit for cultivars having this characteristic, the physiological role and phylogenetic function of the sesquiterpenes present in the peel/rind of *Cucurbitaceae* have not yet been completely understood. Nevertheless, the results obtained by other researchers (Portnoy et al., 2008) are very interesting. Working with some cultivars of melons, they have shown that the group of sesquiterpenes is present only in the outer layers of the fruit. In fact, the enzymatic activity of the sesquiterpene-synthases is detectable only in cell extracts derived from the peel and not from the endocarp. In addition, this enzymatic activity in melons is completely lacking in young and unripe fruits, while it develops starting from the ripening stage and in fruits ready for harvest.

Fig. 4 shows the HS-SPME-GC-MS chromatogram of a sample of candied mesocarp (WET procedure) and Table 3 reports the descriptive elements.

In particular, 28 analytes have been identified, which are based on as many peaks, among which the class of alcohols predominates (8 ALC) with a relative amount of 41.3% of the total area computed as the total ionic current of the selected peaks in the chromatogram. The ALC group is followed by the class of acetate esters (3 ACE) that are present in a quantity equal to 38.3%, organic acids (1 ACD), the only one of which is acetic acid with 8.3%, 3-hydroxy-2-butanone as the only ketone (1 KET, 3.8%), limonene (1 TER; 3.0%), non-acetate esters (8 NAE; 2.9%) and, finally, aldehydes (5 ALD) and other compounds (1 OTH) present at 1.7% and 0.6%, respectively.

Table 2
Composition of the volatile fraction of FRESH watermelon rinds, identified by HS-SPME-GC-MS analysis; substances grouped by chemical classes.

Peak n°	LRI	Analyte	Identification[#]	Aroma	Area x 10^{-6}	REF
		Alcanes				
13	988	nonane	A, B, C	waxy	3.19±0.58	
Alcohols						
3	646	2-methyl-1-propanol	A, B, C	ethereal	3.57±0.34	
7	794	3-methyl-1-butanol	A, B, C	winey, fruity	15.2 ± 1.3	
8	799	2-methyl-1-butanol	A, B	winey, fruity	7.12±0.62	Ramirez et al. (2020, 2021)
9	834	1-pentanol	A, B	fruity, buttery	3.72±0.32	Ramirez et al. ,2020, 2021)
10	850	2,3-butanediol	A, B	green, leafy	13.1 ± 1.1	
11	941	3-hexen-1-ol	A, B	green, flowery	15.5 ± 1.3	(Ramirez et al., 2020, 2021)
12	952	1-hexanol	A, B	fruity, alcoholic	9.92±0.83	Ramirez et al. (2020, 2021)
14	1065	phenol	A, B	pungent	4.19±0.35	
18	1116	2-ethyl-hexanol	A, B, C	citrus, fresh	0.896±0.070	Ramirez et al. (2020, 2021)
19	1137	benzyl alcohol	A, B	floral, fruity	0.678±0.060	
21	1216	phenylethyl alcohol	A, B, C	floral, sweet	1.09±0.09	
Aldehydes						
4	692	3-methyl-butanal	A, B, C	fruity, cocoa	1.21±0.30	Esteras et al. (2020), Ramirez et al. (2020, 2021)
20	1160	3,7-Dimethyl-2,6-octadienal	A, B	fresh, lemon	0.432±0.110	
22	1283	decanal	A, B, C	citrus, melon	1.25±0.31	Ramirez et al. (2020, 2021)
Esters						
1	506	methyl acetate	A, B, C	ethereal, winey	18.6 ± 3.0	
Ketones						
6	761	3-hydroxy-2-butanone (acetoin)	A, B, C	acid, yogurt	11.7 ± 2.9	
15	1074	6-methyl-5-hepten-2-one	A, B	citrus, fruity	1.97±0.51	Esteras et al. (2020), Ramirez et al. (2020, 2021)
Terpenoids						
16	1081	*β*-myrcene	A, B	spicy, peppery	1.03±0.18	Ramirez et al. (2020, 2021), Vella et al. (2020)
17	1093	*β*-pinene	A, B, C	fresh, pine,	0.396±0.070	Vella et al. (2020)
23	1428	*α*-cubebene	A, B	herbal,	0.458±0.0.80	Vella et al. (2020)
24	1460	*α*-copaene	A, B	spicy, honey	0.792±0.138	Portnoy et al. (2008), Esteras et al. (2020), Vella et al. (2020)
25	1463	*α*-elemene	A, B	herbal, fresh	8.02±1.44	Portnoy et al. (2008), Vella et al. (2020)
26	1472	*α*-Gurjunene	A, B	woody, balsamic	2.26±0.41	Portnoy et al.(2008)
27	1492	*β*-cadinene	A, B	green, woody	1.77±0.32	
28	1506	*β*-Caryophyllene	A, B, C	sweet, spicy	2.56±0.46	Portnoy et al. (2008), Esteras et al. (2020), Vella et al. (2020)
29	1539	Aromadendrene	A, B	woody	1.63±0.29	Portnoy et al. (2008), Vella et al. (2020)
30	1554	*α*-muurolene	A, B	woody	0.871±0.160	
31	1569	*δ*-cadinene	A, B	herbal, woody	2.19±0.39	Portnoy et al. (2008)
32	1577	calamenene	A, B	herbal, spicy	0.529±0.090	
Others						
2	627	2-methyl-furan	A, B, C	ethereal	4.49±2.12	
5	752	2-ethyl-furan	A, B, C	sweet, malty	4.35±2.07	Ramirez et al. (2020, 2021)

[#] The identification is indicated by: (A) mass spectral data of the libraries supplied with the operating system of the GC-Ms and from mass spectra databases; (B) mass spectra found in the literature; (C) mass spectra and retention time of an injected standard.

The most significant compound of this chromatogram is represented by ethanol (37.0%) and ethyl acetate (36.4%) in quantities greater than any other analyte. The sum of these two components is approximately 73% of the volatile fraction. Evidently, the extraction of the vegetation water from the rind favors the alcoholic fermentation of the physiological solution which is gradually formed, while the osmotic equilibrium between the saccharide solution penetrating the skin tissues and the liquid phase itself is stabilized. Acetic acid is the third component of the VOCs fraction with 8.4% which probably derives from the subsequent oxidation stage of ethanol. Conversely, terpene compounds are almost no longer detected in candied fruit. Probably their thermodynamic stability could be compromised by the candying procedure since the presence of atmospheric oxygen under the plexiglass cloche still guarantees oxidizing conditions for the entire duration of the process.

Fig. 5 shows the HS-SPME-GC-MS chromatogram of a sample of candied mesocarp from Crimson sweet (DRY procedure) and in Table 4 the descriptive elements of the same profile are collected.

In this case, 29 analytes have been individuated, based on as many peaks, among which the class of alcohols predominates (13 ALC) with a relative amount of 55.3% of the total area evaluated as the total ionic current of the selected peaks in the chromatogram. Acetic acid is the only one belonging to the class of organic acids (ACD; 17.6%), followed by acetate esters (2 ACE) with a total amount of 16.7%, non-acetate esters (2 NAE) present at 4.4%, ketones (3 KET) at 3.1% and, finally, aldehydes (5 ALD), alkanes (1 AHA) and other compounds (2 OTH) in a quantity equivalent to 0.9%, < 0.1% and 1.9%, respectively.

The DRY candying method leads to the formation of ethanol at about 42.8% (+ 16% compared to the WET condition, ≈ 37%), while ethyl acetate reaches 16.6% (about - 54% compared to the WET procedure, equal to 36.4%). These strongly aromatic compounds describe about 59% of the VOCs fraction, while acetic acid represents ≈ 17.6% (+ 110% compared to WET sample, ≈ 8.4%). From the comparison with the similar results obtained by the WET procedure, it can be concluded that ethanolic fermentation is guaranteed in both experimental candying conditions. However, the constant elimination of the syrupy solution

Table 3
Composition of volatile fraction of WET candied watermelon rinds; substances identified by HS-SPME-GC-MS analysis, grouped by chemical classes.

Peak n°	LRI	Analyte	Identification[#]	Aroma	Area x 10^{-7}	REF
Acids						
2	611	acetic acid	A, B	sour, pungent	59.1 ± 6.4	
Alcohols						
1	425	ethanol	A, B	alcoholic	261 ± 23	Ramirez et al. (2020, 2021)
6	793	3-methyl-1-butanol	A, B, C	winey, fruity	12.3 ± 1.1	
7	798	2-methyl-1-butanol	A, B	winey, fruity	8.07 ± 0.69	Ramirez et al. (2020, 2021)
13	940	3-hexen-1-ol	A, B	green, leafy	1.16 ± 0.11	Ramirez et al. (2020, 2021)
14	950	1-hexanol	A, B	green, flowery	2.12 ± 0.18	Ramirez et al. (2020, 2021)
19	1067	1-octen-3-ol	A, B	mushroom	0.515±0.045	
23	1142	5-nonanol	A, B		1.62 ± 0.14	
24	1213	phenyl-ethyl alcohol	A, B, C	floral, sweet	4.41 ± 0.38	
Aldehydes						
10	878	hexanal	A, B	grass, green	3.08 ± 0.72	Esteras et al. (2020), Ramirez et al. (2020, 2021)
12	919	furan-2-carbaldehyde (furfural)	A, B	woody, almond	7.42 ± 1.74	
17	990	heptanal	A, B	fresh, herbal	0.292 ± 0.069	Esteras et al. (2020), Ramirez et al. (2020, 2021)
18	1050	2-heptenal	A, B	green, fatty	0.586 ± 0.131	Esteras et al. (2020), Ramirez et al. (2020, 2021)
21	1092	octanal	A, B	waxy, citrus,	0.678 ± 0.157	Esteras et al. (2020), Ramirez et al. (2020, 2021)
Esters						
3	624	ethyl acetate	A, B	fruity, sweet	257 ± 22	Esteras et al. (2020), Ramirez et al. (2020, 2021)
8	840	2-methylpropyl acetate	A, B	sweet, fruity	3.84 ± 0.33	
9	872	ethyl butanoate	A, B, C	fruity	5.32 ± 0.92	
11	888	ethyl-2-hydroxy-propanoate	A, B	Fruit, acidic	10.2 ± 1.8	
15	957	3-methyl-1-butanol acetate	A, B	sweet, fruity	9.46 ± 0.81	
16	982	ethyl pentanoate	A, B	apple, green	0.425 ± 0.073	
20	1080	ethyl hexanoate	A, B, C	fruity green	2.93 ± 0.50	Esteras et al. (2020)
25	1242	diethyl succinate	A, B	fruity, sweet	0.393 ± 0.068	
26	1263	ethyl octanoate	A, B	fruity, waxy	0.788 ± 0.136	Esteras et al. (2020)
27	1349	ethyl nonanoate	A, B	waxy, winey	0.210 ± 0.036	
28	1432	ethyl decanoate	A, B	fruity, apple	0.118 ± 0.020	
Ketones						
4	760	3-hydroxy-2-butanone (acetoin)	A, B, C	acid, yogurt,	27.1 ± 7.2	
Terpenoids						
22	1133	limonene	A, B, C	citrus, fresh	20.9 ± 4.2	
Others						
5	784	2,4,5-trimethyl-1,3-dioxolane	A, B, C	green, earthy	4.45 ± 2.96	

[#] The identification is indicated by: (A) mass spectral data of the libraries supplied with the operating system of the GC-Ms and from mass spectra databases; (B) mass spectra found in the literature; (C) mass spectra and retention time of an injected standard.

during DRY process reduces the reactivity of acetic acid and ethanol, which are converted more slowly to ethyl acetate.

Again, the presence of terpenoid compounds is considerably reduced in the WET sample (3.0% of VOCs) if compared to the fresh material (15.6%), until total disappearance in the DRY specimen. Table 5 summarizes the results obtained from the HS-SPME-GC-MS analysis for the different samples of Crimson sweet watermelon rinds (fresh, WET and DRY candied), represented in comparative form for the classes of compounds identified.

The final product obtained with two alternative methodologies, WET and DRY, contains volatile compounds that derive from very different origins, basically represented by three large groups of substances that we comment as follows.

(i) VOCs typical of the fruit and probably of the selected cultivar (acids, terpenoids and esters). For example, free organic acids are totally absent in the fresh mesocarp of the Crimson Sweet watermelon, while they increase to about 8% in the WET product and to ≈ 17% in the DRY one. Acetate esters are also absent in the fresh rinds, while the contrary is true for the candied material. In fact, they reach 38% in the WET product, while their concentration is halved to about 17% in the case of the DRY one. Furthermore, terpenoid compounds are present in high concentration in the selected initial matrix (≈ 15%), are reduced to 3% in the WET product while they tend to zero in the DRY one.

(ii) Volatiles lost during the long osmotic treatment (furans and terpenoid compounds). Furans are preferably formed when the production processes of candied fruit are thermally activated, as industrially it happens. To carry out this study, we did not use heat sources. Therefore, the absence of furan compounds in both WET and DRY final products could be due to the choice of always working at room temperature throughout the candying process. Regarding terpenoid molecules, the loss of analytes due to completely natural causes is observed. Among these causes, we can hypothesize their volatilization or their metabolic degradation induced by particular chemical reactions.

(iii) The third group is represented by flavoring compounds deriving from fermentation processes (ethanol and other alcohols, esters and acetic acid). The fraction of alcohols is definitely the largest group (52% in fresh, 41% and 55% in WET and DRY, respectively). Given this classification, it should be noted that some compounds may have different origins.

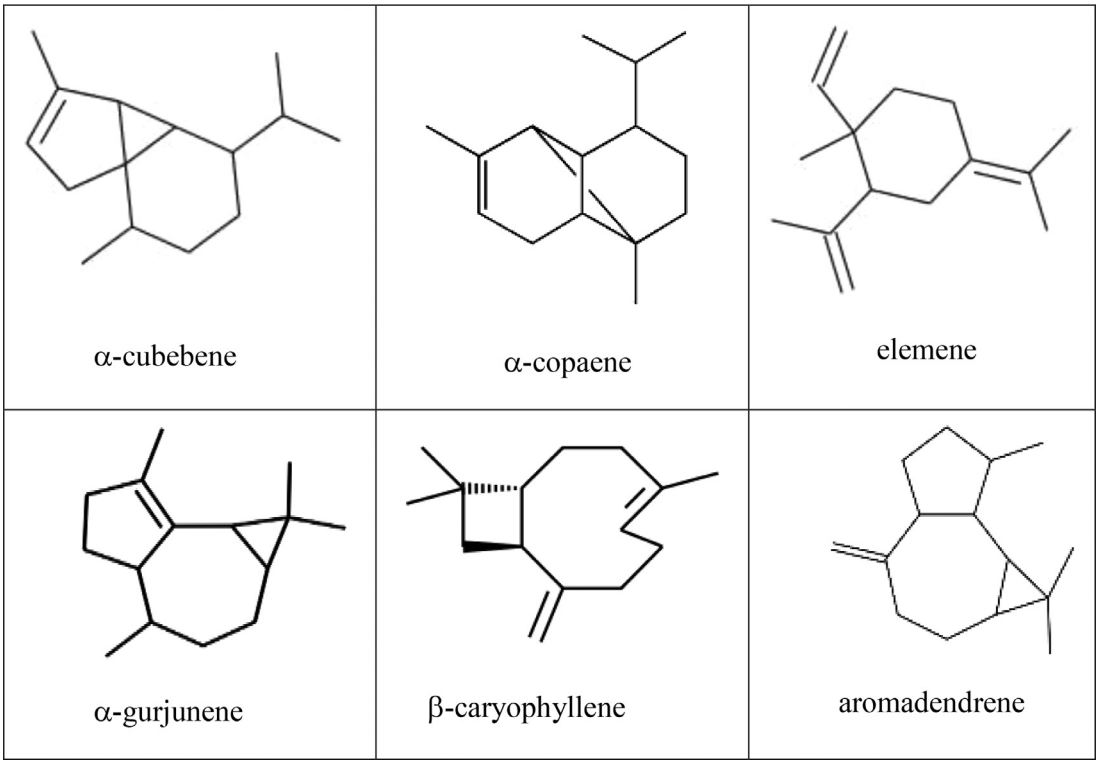
Evidently their different origin is due to enzymatic and fermentation processes that work differently for the 2 candied samples. To this we can add that we did not start from sterile material, as the rinds were only carefully washed and dried on a cloth and exposed to the air.

Since the ingredients used are only rinds and solid sugar, the activity of free water extracted from the substrate, probably plays a significant role in the compositional evolution of the 2 samples during the candying process. Therefore, the hypothesis that different fermentation path-

Table 4
Composition of volatile fraction of DRY candied watermelon rinds; substances are identified by HS-SPME-GC-MS analysis, grouped by chemical classes.

Peak n°	LRI	Analyte	Identification[#]	Aroma	Area x 10^{-7}	REF
Alcanes						
27	1441	tetradecane	A, B, C	waxy	0.183±0.179	
Acids						
2	615	acetic acid	A, B	sour, pungent	75.7 ± 5.6	
Alcohols						
1	423	ethanol	A, B	alcoholic	184 ± 16	Ramirez et al. (2020, 2021)
6	793	3-methyl- 1-butanol	A, B, C	winey, fruity	12.8 ± 1.1	
7	798	2-methyl-1-butanol	A, B	winey, fruity,	7.70 ± 0.68	Ramirez et al. (2020, 2021)
8	849	2,3-butanediol	A, B	fruity, buttery	11.8 ± 1.0	
9	860	2,3-butanediol		fruity, buttery	6.26 ± 0.55	
11	917	3-ethoxy-1-propanol	A, B	fruity	3.74 ± 0.33	
13	940	3-hexen-1-ol	A, B	green, leafy	0.584±0.052	Ramirez et al. (2020, 2021)
14	950	1-hexanol	A, B	green, flowery	0.344±0.032	Ramirez et al. (2020, 2021)
18	1114	2-ethyl-1-hexanol	A, B, C	citrus, sweet	0.108±0.010	Ramirez et al. (2020, 2021)
19	1135	benzyl alcohol	A, B	floral, fruity	0.367±0.033	
20	1143	1-octen-4-ol	A, B	fresh, yeasty	0.485±0.043	
23	1213	phenylethyl alcohol	A, B, C	floral, sweet	7.88±0.70	
29	1502	1-dodecanol	A, B	earthy, waxy	1.90±0.17	
Aldehydes						
12	918	furan-2-carbaldehyde (furfural)	A, B	woody, almond	3.05±0.68	
17	1093	octanal	A, B	waxy, citrus	0.123±0.027	Esteras et al. (2020), (Ramirez et al. (2020, 2021)
21	1148	benzeneacetaldehyde	A, B	floral, honey	0.175±0.039	
22	1189	nonanal	A, B	waxy, green	0.308±0.068	Ramirez et al. (2020, 2021)
25	1281	decanal	A, B, C	citrus, melon	0.230±0.051	Ramirez et al. (2020, 2021)
Esters						
3	622	ethyl acetate	A, B	fruity, sweet	71.2 ± 7.7	Esteras et al. (2020), Ramirez et al. (2020, 2021)
10	888	ethyl 2-hydroxy-propanoate	A, B	sweet, fruity	18.6 ± 2.5	
15	957	3-methyl-1-butanol acetate	A, B	sweet, fruity	0.586±0.063	
24	1242	diethyl succinate	A, B	fruity	0.349±0.048	
		Ketones				
4	759	3-hydroxy-2-butanone (acetoin)	A, B, C	acid, yogurt	12.4 ± 4.3	
16	1072	6-methyl-5-hepten-2-one	A, B	citrus, fruity	0.914±0.324	Esteras et al. (2020), (Ramirez et al. (2020, 2021)
28	1486	6,10-dimethyl-5,9-undecadien-2-one	A, B	floral, fresh	0.193±0.068	
Others						
5	784	2,4,5-trimethyl-1,3-dioxolane	A, B	herbal, woody	5.34 ± 3.65	
26	1377	2-ethylhexyl glycidyl ether	A, B	floral, sweet	2.64 ± 1.80	

[#] The identification is indicated by: (A) mass spectral data of the libraries supplied with the operating system of the GC-Ms and from mass spectra databases; (B) mass spectra found in the literature; (C) mass spectra and retention time of an injected standard.



Scheme 1. Molecular structures of some volatile terpenoids identified in fresh rinds and/or candied ones from Crimson sweet watermelons.

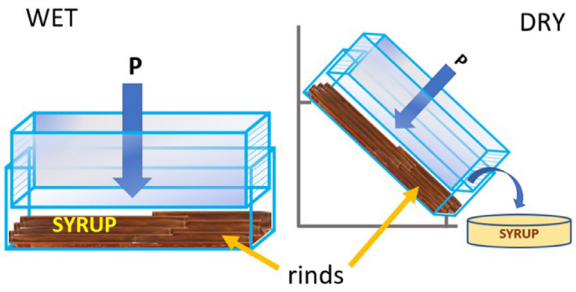


Fig. 1. Experimental set-up realized for WET and DRY candying methods.

Table 5
Compound classes identified in the HS-SPME-GC-MS analysis of the Crimson sweet watermelon rind: FRESH, WET and DRY candied. Data* are expressed as mean % of each class with respect to the total normalized peak areas on the basis of the sum of the total peak ion current.

Compound class	FRESH $\bar{x} \pm s_{(3)}$	WET $\bar{x} \pm s_{(3)}$	DRY $\bar{x} \pm s_{(3)}$
ALC	$51.8^{ab} \pm 4.3$	$41.3^{a} \pm 3.6$	$55.3^{b} \pm 4.9$
TER	$15.6^{a} \pm 2.8$	$3.0^{b} \pm 0.6$	—
NAE	$12.9^{a} \pm 2.1$	$2.9^{b} \pm 0.5$	$4.4^{b} \pm 0.6$
KET	$9.4^{a} \pm 2.4$	$3.8^{b} \pm 1.0$	$3.1^{b} \pm 1.1$
OTH	$6.1^{a} \pm 2.9$	$0.6^{b} \pm 0.4$	$1.9^{ab} \pm 1.3$
AHA	$2.2^{a} \pm 0.4$	—	$0.1^{b} \pm 0.1$
ALD	$2.0^{a} \pm 0.5$	$1.7^{ab} \pm 0.4$	$0.9^{b} \pm 0.2$
ACE	—	$38.3^{a} \pm 3.3$	$16.7^{b} \pm 1.8$
ACD	—	$8.3^{a} \pm 0.9$	$17.6^{b} \pm 1.3$

* mean of three replicates of the chromatograms (± standard deviation, $s_{(3)}$)Compound classes: ACD, acids; ACE, acetate esters; AHA, alkanes; ALC, alcohols; ALD, aldehydes; KET, ketones; NAE, non-acetate esters; OTH, others; TER, terpenes#In a row, results with a different superscript letter indicate a statistically significant difference between each other ($p < 0.05$).

Table 6
Some most representative analytes obtained from HS-SPME-GC-MS for the three samples of Crimson sweet rinds: FRESH, WET and DRY.

	FRESH $\bar{x} \pm s_{(3)}$	WET $\bar{x} \pm s_{(3)}$	DRY $\bar{x} \pm s_{(3)}$
3-hydroxy-2-butanone	$1.17^{a} \pm 0.29$	$27.1^{b} \pm 7.2$	$12.4^{c} \pm 4.4$
3-methyl-1-butanol	$1.52^{a} \pm 0.13$	$12.3^{b} \pm 1.1$	$12.8^{b} \pm 1.2$
2-methyl-1-butanol	$0.712^{a} \pm 0.062$	$8.07^{b} \pm 0.70$	$7.70^{b} \pm 0.69$
3-hexen-1-ol	$1.55^{a} \pm 0.13$	$1.16^{b} \pm 0.11$	$0.584^{c} \pm 0.052$
1-hexanol	$0.992^{a} \pm 0.083$	$2.12^{b} \pm 0.18$	$0.345^{c} \pm 0.032$
phenylethyl alcohol	$0.109^{a} \pm 0.009$	$4.41^{b} \pm 0.38$	$7.88^{c} \pm 0.70$

*Data are expressed as TIC Area $\times 10^{-7} \pm$ standard deviation, $s_{(3)}$. In a row, results with a different superscript letter indicate a statistically significant difference between each other ($p < 0.05$).

ways accompanied the candying process of the 2 WET and DRY samples, seems quite plausible.

In Table 6 and Fig. 6 we have collected some experimental evidence obtained from this study, which we believe to be particularly significant. For example, the two methyl-derivative isomers of 1-butanol, both strongly flavoring compounds of pleasant perception (Ramirez et al., 2020, 2021), are present in low concentration in the initial matrix (expressed as total ion current of peak area), while they seem to develop in equivalent quantities in the candied samples through the two different procedures. However, the 3-methyl-1-butanol isomer seems to be favored over the 2-methyl-1-butanol one, as its concentration increases of about 50% in candied products.

Instead, the case of 3-hydroxy-2-butanone (acetoin) is different: it is scarcely present in the fresh mesocarp ($1.17 \times 10^{+7}$), it rises to $12.4 \times 10^{+7}$ in the DRY candied sample, to $27.1 \times 10^{+7}$ in the WET one, with an increase of about 120% with respect to the DRY form. This molecule derives from metabolic fermentation processes of various kinds, and provides a mix of pleasant aromas ranging from mildly acidic, recalling the creamy notes of yogurt, to the pleasantness of the fruity odor.

The presence of acetoin seems closely related to that of 2,3-butanediol. Both of these compounds are currently undergoing an in-depth study, as their performance as bio-based platform chemicals is being evaluated (Maina et al., 2021). They are considered platform compounds because they are applied in a wide variety of contexts, from the heavy chemical industry - fine and secondary, cosmetics, food, agriculture, and pharmaceutical productions.

The specimen 3-hexen-1-ol undergoes increasing depletion starting from the fresh peel sample ($1.55 \times 10^{+7}$), passing to the candied WET form ($1.16 \times 10^{+7}$), and being reduced to a minimum in the DRY one ($0.584 \times 10^{+7}$). This compound has a typical freshly cut green grass aroma (Ramirez et al., 2020, 2021).

An analyte having a singular behavior is certainly 1-hexanol. In the volatile aromatic fraction of the fresh peel it is present with a peak area equivalent to $0.990 \times 10^{+7}$, it doubles the concentration in the WET product ($2.12 \times 10^{+7}$), while it halves in the DRY candied one ($0.345 \times 10^{+7}$). This compound contributes to the aroma with a freshly cut grass scent, as well as a pleasant floral fragrance (Ramirez et al., 2020, 2021).

In this examination of the experimental results, also the phenyl-ethyl alcohol concentrations trend is represented in Fig. 6. As can be seen, its presence in the volatile fraction of fresh skins is minimal and limited to $0.109 \times 10^{+7}$, increases up to $4.41 \times 10^{+7}$ in the WET sample and reaches the maximum value ($7.88 \times 10^{+7}$) for the DRY one, gaining ≈ +180% with respect to WET. It should be noted that it is a particularly valuable compound in the context in which it is found. In fact, it plays a role as flavoring and natural antimicrobial, antiseptic, disinfectant and preservative agent in the food industry, pharmaceutical, cosmeceutical and perfumery (Boukaew et al., 2018).

Furthermore, phenyl-ethyl alcohol is a typical plant metabolite that plays a growth retarding action, it is present in the metabolic cycles of *Aspergillus* as well as in the fermentative processes induced by *Saccharomyces cerevisiae* and other biocenosis (Larroque et al., 2021). Its presence ennobles the candied final product and confers a sweet aroma, recalling that of peach.

3.1. Sensory analysis

For the 3 samples submitted to the panel, the elements of perceived quality were evaluated according to the attributes: appearance (including color, chromatic brilliance, compact or spongy consistency); gustatory sensation (softness on the palate, crunchiness, pleasant taste); persistence after tasting (aftertaste, duration of the perceived sensation); aroma (recognizability of the product, distinguishability from substitutes because of fragrance uniqueness, or evocative perfumes of other origin); pungency (prevalence or hint of pungent aromas); sweetness (sugarness level to taste); sourness (acidity, flavor); and overall sensory score (pleasantness, and overall acceptability of the product).

One-way analysis of variance (ANOVA) was performed to assess whether there is a statistically significant difference between the sensory scores of the FRESH, WET, and DRY products. The numerical results of the sensory evaluation of the panel test are shown in Table 7.

ANOVA results show how the sensory scores of the three different products present, in almost all cases, a statistically significant difference ($p < 0.05$) between them. The only exceptions are represented by aroma and overall sensory score of WET and DRY products, which achieved comparable responses.

The aroma is generally developed from the type of vegetable raw material used in the candying process. Obviously, fruits and vegetables bring their own typical and distinctive contributions, but the same osmotic method, if carried out at room temperature, may favor the appearance of specific analytes due to particular fermentation processes, or to singular chemical reactions between reactive species. A typical case is

Table 7
Sensory profile attributes* for the 3 samples tested.

sample attribute	FRESH rinds	WET candied	DRY candied
appearance	1.83 ± 0.95 [a]	3.97 ± 0.67 [b]	5.83 ± 0.65 [c]
mouth feel	2.80 ± 0.92 [a]	5.30 ± 0.65 [b]	5.87 ± 0.82 [c]
after taste	3.33 ± 0.71 [a]	5.57 ± 0.58 [b]	6.13 ± 0.57 [c]
aroma	3.63 ± 0.49 [a]	6.10 ± 0.55 [b]	6 0.13 ± 0.57 [b]
pungency	3.93 ± 0.25 [a]	4.57 ± 0.57 [b]	5.50 ± 0.63 [c]
sweetness	3.83 ± 0.38 [a]	5.87 ± 0.35 [b]	6.50 ± 0.51 [c]
sourness	1.43 ± 0.57 [a]	3.60 ± 0.56 [b]	4.57 ± 0.68 [c]
overall sensory score	3.37 ± 0.76 [a]	6.07 ± 0.37 [b]	6.23 ± 0.63 [b]

* The values represent the mean of the scores obtained ± standard deviation $s_{(30)}$.In a row, results with a different superscript letter indicate a statistically significant difference between each other ($p < 0.05$).

Fig. 2. Images of fresh rinds, WET and DRIED candied ones. The colored scales are represented at 1 cm.

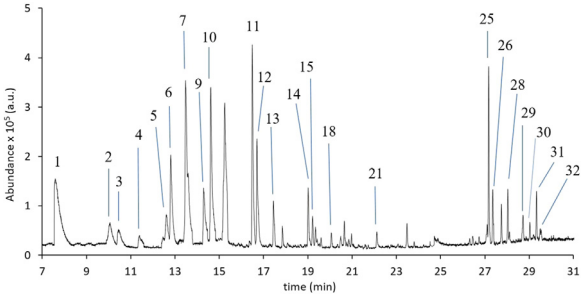


Fig. 3. Total ion chromatogram of the volatile compounds from FRESH mesocarp sample of Crimson sweet watermelon, obtained by HS-SPME-GC-MS. (a.u. – arbitrary units).

the spontaneous condensation between alcohols and acids to generate esters, since both the reactive species and the ACE and NAE products in the candied rinds are widely detected.

Fig. 7 offers a much more effective impact of the panel test results, as it simultaneously reports the three different profiles of the samples checked, and the judgments collected well detailed through the specific descriptors.

As can be seen, the FRESH sample systematically received judgments below the dashed line of level 4, which corresponds to the total indifference of the panelists towards the product. In other words, the level 4 curve of our radar plot can be considered representative of the minimum threshold of edible acceptability of the material. This result is perfectly compatible with what has been indicated so far, i.e. the mesocarp is not considered palatable, even if there are no contraindications for human consumption. On the contrary, higher acceptability scores were obtained by candied rinds over fresh rinds, showing however a fair competitive advantage for the DRY sample over the WET one.

The greater distance of the sensory analysis for the WET and DRY samples is found for the contribution of 'appearance'. The fine brownness is very similar for both products, but the chromatic brilliance and compactness of DRY candied rinds, Fig. 2, make it much more similar to other different candied fruits of industrial origin. This aspect probably predisposes the panelists positively, as the visual stimulus could induce a sense of gratification for what is seen and perceived. Therefore, the

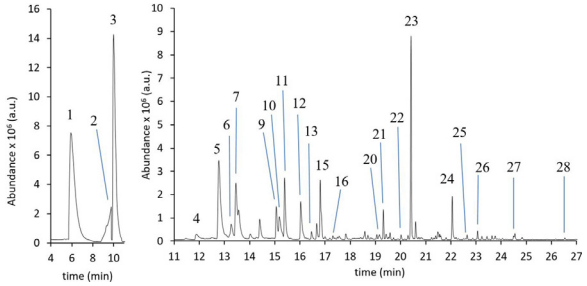


Fig. 4. Total ion chromatogram of the volatile compounds from WET candied rind sample of Crimson sweet watermelon, obtained by HS-SPME-GC-MS.

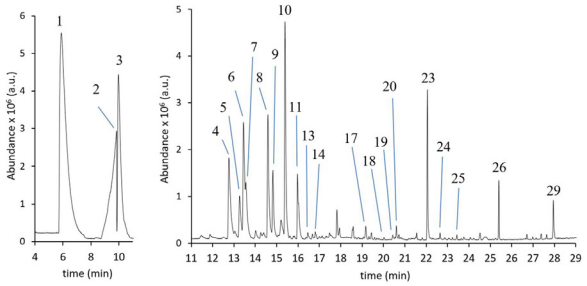


Fig. 5. Total ion chromatogram of the volatile compounds from DRY candied rind sample of Crimson sweet watermelon, obtained by HS-SPME-GC-MS.

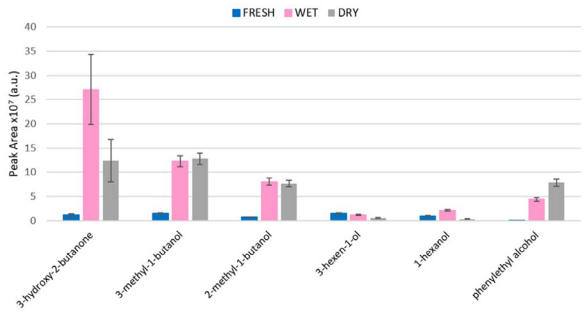


Fig. 6. Some most representative analytes obtained from HS-SPME-GC-MS for the samples of Crimson sweet rinds: fresh, and candied with different procedures (WET and DRY).

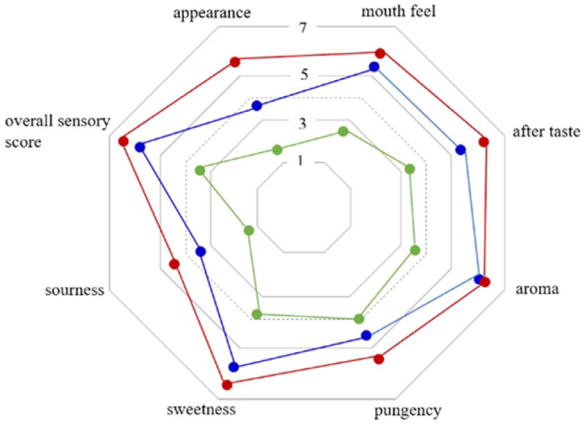


Fig. 7. Spider plot of acceptability specific attributes for each sample of watermelon rinds subjected to the panel test: FRESH (), WET () and DRY () candied ones.

higher brilliance of the DRY product could induce a more consensus attitude than the WET sample, the latter being much more opaque.

4. Conclusions

This study allowed to establish the composition of the aroma of the fresh and candied mesocarp, obtained from Crimson Sweet watermelon. The aroma compounds identified belong to 9 major chemical groups, such as acids, esters, furans, aldehydes, alcohols, phenols, ketones, terpenoids and alkanes. In addition, we have mentioned another class (OTH) collecting some minor analytes not pertaining to any of the previously mentioned groups. The initial matrix has a tough consistency, whose structure is generally composed by water (~95%) and a combination of not digestible polysaccharides (~5%) such as celluloses, hemicelluloses, lignins and pectins, entrapping a variety of functional compounds even if in traces and a very small quantities. Therefore it is considered energetically very poor food, inedible and intended for disposal as waste. On the contrary, the candying process makes the mesocarp particularly pleasant, soft and with a consistency similar to that of all other candied fruits.

The composition of the aroma of the candied mesocarp reflects the complexity of the enzymatic processes and other reactions that occur during the period of treatment of the fruit in the presence of a high concentration of sucrose.

What we propose can represent a real industrial challenge and opportunity for the recovery of large quantities of watermelon rinds, regardless of the production methodology of the candying process. This process is certainly expensive but, considering that it ennobles a fresh and zero-value matrix, mainly made of hard cellulose and with very poor nutritional properties, it allows to extend the mass of edible foods for human consumption.

The WET and DRY candying processes we have carried out, are free from any treatment that may leave residues or other exogenous chemical food compounds. In fact, they are respectful of the naturalness of the raw material and of the finished products, since it is not necessary to introduce any other preservative and anti-fermentative ingredient, as it happens with the industrial sulphitation for the production of candied fruit. Finally, the panel of tasters expressed positive opinions, approving the candied fruit obtained from a very poor matrix.

Funding

This research program has been funded by MIUR, the Italian Ministry of Education, University and Research. L.M. gratefully acknowledges financial support from POR FSE 2014–20 of Emilia-Romagna region (Italy) for doctoral fellowship.

Ethical statement

Informed consent was obtained from subjects involved in the sensory evaluation phase. Their privacy rights have always been observed.

Declaration of Competing Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

CRediT authorship contribution statement

Laura Maletti: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Veronica D'Eusanio:** Software, Investigation, Writing – original draft, Visualization. **Lisa Lancellotti:** Validation, Formal analysis, Data curation, Writing – review & editing. **Andrea Marchetti:** Methodology, Investigation, Writing – original draft, Supervision. **Luca Pincelli:** Methodology, Investigation, Data curation, Visualization. **Lorenzo Strani:** Formal analysis, Data curation, Writing – review & editing. **Lorenzo Tassi:** Conceptualization, Resources, Writing – review & editing, Project administration, Funding acquisition.

Acknowledgments

The authors gratefully thank Dr. Alessandro D'Alessandro (Barilla s.p.a.) who kindly provided us the experimental measurements of water activity.

References

AOAC, 1990. Official Methods of Analysis, 14th ed. Association of Official Analytical Chemists, Washington, D.C., USA.

Aronson, D., Citra, M., Shuler, K., Printup, H., Howard, P.H., 1999. Aerobic Biodegradation of Organic Chemicals in Environmental Media: A Summary of Field and Laboratory Studies. U.S. Environmental Protection Agency, Athens, GA.

Athmaselvi, K.A., Alagusundaram, K., Kavitha, C.V., Arumuganathan, T., 2012. Impact of pre-treatment on colour and texture of watermelon rind. Int. Agrophys. 26 (3), 235–242.

ed. Baldwin, C., Wilberforce, N.T., Baldwin, C.J., 2009. Sustainability principles and sustainable innovation for food products. Sustainability in the Food Industry Wiley-Blackwell, NY. ed.Chpt 11.

ed. Baraldi, C., Foca, G., Maletti, L., Marchetti, A., Roncaglia, F., Sighinolfi, S., Tassi, L., Preedy, V.R., Watson, R.R., 2020. Red horse-chestnut seeds of *Aesculus x Carnea*: a new way for health and food design? Nuts and Seeds in Health and Disease Prevention, 2nd ed. Academic Press, London. ed.Chpt 3.

Ben Mussa, S.A., Elferjani, H.S., Haroun, F.A., Abdelnabi, F.F., 2009. Determination of available nitrate, phosphate and sulfate in soil samples. Int. J. Pharm Tech Res. 1 (3), 598–604.

ed. Bonazzi, C., Dumoulin, E., Tsotsas, E., Mujumdar, A.S., 2011. Quality changes in food materials as influenced by drying processes. In: Modern drying technology, Volume 3: *Product Quality and Formulation*. Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, pp. 1–20 ed..

Boukaew, S., Petlamul, W., Bunkrongcheap, R., Chookaew, T., Kabbua, T., Thippated, A., Prasertsan, P., 2018. Fumigant activity of volatile compounds of Streptomyces philanthi RM-1-138 and pure chemicals (acetophenone and phenylethyl alcohol) against anthracnose pathogen in postharvest chili fruit. Crop Prot. 103, 1–8.

Chakrabarty, N., Mourin, M.M., Islam, N., Haque, A.R., Akter, S., Siddique, A.A., Sarker, M., 2020. Assessment of the potential of watermelon rind powder for the value addition of noodles. J. Biosyst. Eng. 1–9. doi:10.1007/s42853-020-00061-y.

Dammak, M.I., Salema, Y.S., Belaid, A., Mansour, H.B., Hammami, S., Le Cerf, D., Majdoub, H., 2019. Partial characterization and antitumor activity of a polysaccharide isolated from watermelon rinds. Int. J. Biol. Macromol. 136, 632–641.

Deiana, M., Montoro, P., Jerković, I., Atzeri, A., Marijanović, Z., Serreli, G., Piacente, S., Tuberoso, C.I.G., 2019. First characterization of *Pompia intrea* candied fruit: the headspace chemical profile, polar extract composition and its biological activities. Food Res. Int. 120, 620–630.

Durante, C., Cocchi, M., Lancellotti, L., Maletti, L., Marchetti, A., Roncaglia, F., Sighinolfi, S., Tassi, L., 2021. Analytical concentrations of some elements in seeds and crude extracts from Aesculus hippocastanum, by ICP-OES technique. Agronomy 11, 47. doi:10.3390/agronomy11010047, 11010047.

Esteras, C., Rambla, J.L., Sánchez, G., Granell, A., Picó, M.B., 2020. Melon genetic resources characterization for rind volatile profile. Agronomy 10, 1512. doi:10.3390/agronomy10101512.

Fabani, M.P., Capossio, J.P., Roman, M.C., Zhu, W., Rodriguez, R., Mazza, G., 2021. Producing non-traditional flour from watermelon rind pomace: artificial neural network (ANN) modeling of the drying process. J. Environ. Manag. 281, 111915. doi:10.1016/j.jenvman.2020.111915.

FAO, 2020. Fruit and vegetables – your dietary essentials. The International Year of Fruits and Vegetables, 2021. FAO, Rome background paper doi:10.4060/cb2395en.

Fish, W.W., Bruton, B.D., Russo, V.M., 2009. Watermelon juice: a promising feedstock supplement, diluent, and nitrogen supplement for ethanol biofuel production. Biotechnol. Biofuels 2, 18. doi:10.1186/1754-6834-2-18.

Han, H.S., Song, K.B., 2021. Antioxidant properties of watermelon (*Citrullus lanatus*) rind pectin films containing kiwifruit (*Actinidia chinensis*) peel extract and their application as chicken thigh packaging. Food Packag. Shelf Life 28, 100636. doi:10.1016/j.fpsl.2021.100636.

Hassan, H.M., Alsohaimi, I.H., Khan, M.R., Alfalah, A.Y.A., Alruwaili, M.A.H., Alam, P., Ahmad, N., Ouladsmane, M., 2022. Quantitative assessment of phosphate food additive in frozen and chilled chicken using spectrophotometric approach combined with graphitic digestion. Food Chem. 389, 133050.

Ho, L.H., Dahri, N.C., 2016. Effect of watermelon rind powder on physicochemical, textural, and sensory properties of wet yellow noodles. CyTA J. Food 14 (3), 465–472.

Hoque, M.M., Iqbal, A., 2015. Drying of watermelon rind and development of cakes from rind powder. J. Novel Res. Life Sci. 2 (1), 14–21.

Kausar, T., Hassan, M.T., ud Din, G.M., 2020. Utilization of watermelon seed flour as protein supplement in cookies. Pure Appl. Biol. PAB 9, 202–206.

ed. Khanam, Z., Haq Bhat, I.U., Bhat, R., 2017. Agrofoods for sustainable health benefits and their economic viability. In: Sustainability Challenges in the Agrofood Sector. Wiley-Blackwell, NY, pp. 435–450 ed.Chpt 18.

Larroque, M.N., Carrau, F., Fariña, L., Boido, E., Dellacassa, E., Medina, K., 2021. Effect of Saccharomyces and non-Saccharomyces native yeasts on beer aroma compounds. Int. J. Food Microbiol. 337, 108953. doi:10.1016/j.ijfoodmicro.2020.108953.

Lowe, E.D., Buckmaster, D.R., 1995. Dewatering makes big difference in compost strategies. Biocycle 35 (1), 78–82.

Maina, S., Prabhu, A.A., Vivek, N., Vlysidis, A., Koutinas, A., Kumar, V., 2021. Prospects on bio-based 2,3-butanediol and acetoin production: recent progress and advances. Biotechnol. Adv. 52, 107783. doi:10.1016/j.biotechadv.2021.107783.

Maruyama, T., Ito, M., Honda, G., 2001. Molecular cloning, functional expression and characterization of (E)-beta-farnesene synthase from citrus junos. Biol. Pharm. Bull. 24, 1171–1175.

Portnoy, V., Benyamini, Y., Bar, E., Harel-Beja, R., Gepstein, S., Giovannoni, J.J., Schaffer, A.A., Burger, J., Tadmor, Y., Lewinsohn, E., Katzir, N., 2008. The molecular and biochemical basis for varietal variation in sesquiterpene content in melon (Cucumis melo L.) rinds. Plant Mol. Biol. 66, 647–661.

Ramirez, J.L., Du, X., Wallace, R.W., 2020. Investigating sensory properties of seven watermelon varieties and factors impacting refreshing perception using quantitative descriptive analysis. Food Res. Int. 138, 109681. doi:10.1016/j.foodres.2020.109681.

Ramirez, J.L., Juma, S., Du, X., 2021. Consumer acceptance of watermelon flesh-rind blends and the effect of rind on refreshing perception. J. Food Sci. 86 (4). doi:10.1111/1750-3841.15648.

Ranganna, S., 1986. Handbook of Analysis and Quality Control for Fruit and Vegetable Products. Tata McGraw-Hill, New Delhi, India ed..

Rico, X., Gullón, B., Alonso, J.L., Yáñez, R., 2020. Recovery of high value-added compounds from pineapple, melon, watermelon and pumpkin processing by-products: an overview. Food Res. Int. 132, 1090862. doi:10.1016/j.foodres.2020.109086, (2020).

Roberts, D.D., Pollien, P., Milo, C., 2000. Solid-phase microextraction method development for headspace analysis of volatile flavor compounds. J. Agric. Food Chem. 48 (6), 2430–2437.

Romelle, F.D., Rani, A., Manohar, R.S., 2016. Chemical composition of some selected fruit peels. Eur. J. Food Sci. Technol. 4, 12–21.

Shivapour, M., Yousefi, S., Ardabili, S.M.S., Weisany, W., 2020. Optimization and quality attributes of novel toast breads developed based on the antistaling watermelon rind powder. J. Agric. Food Res. 2, 100073. doi:10.1016/j.jafr.2020.100073.

Song, J., Fan, L.H., Beaudry, R.M., 1998. Application of solid phase microextraction and gas chromatography time-of-flight mass spectrometry for rapid analysis of flavor volatiles in tomato and strawberry fruits. J. Agric. Food Chem. 46 (9), 3721–3726.

Souad, A.M., Jamal, P., Olorunnisola, K.S., 2012. Effective jam preparations from watermelon waste. Int. Food Res. J. 19 (4), 1545–1549.

Tarazona-Díaz, P.M., Viegas, J., Moldao-Martins, M., Aguayo, E., 2011. Bioactive compounds from flesh and by-product of fresh-cut watermelon cultivars. J. Sci. Food Agric. 91 (5), 805–812. doi:10.1002/jsfa.4250.

Tufeanu, R.E., Georgescu, C., Frum, A., Tita, M.A., Tita, O., 2017. Minerals and Total Polyphenolic Content of Some Vegetal Powders. Bulletin UASVM Animal Science and Biotechnologies. 74 (2) 185. doi:10.15835/buasvmcn-asb:0002. https://www.researchgate.net/publication/321632512_Minerals_and_Total_Polyphenolic_Content_of_Some_Vegetal_Powders.

USDA (2011). U.S. Department of Agriculture, Agricultural research service. USDA national nutrient database for standard reference, release 24 (http://ndb.nal.usda.gov/). Accessed 07.09.2021.

Vella, F.M., Calandrelli, R., Cautela, D., Fiume, I., Pocsfalvi, G., Laratta, B., 2020. Chemometric screening of fourteen essential oils for their composition and biological properties. Molecules 25, 5126. doi:10.3390/molecules25215126.

ed. Velmourougane, K., De Souza, B, Bhat, R., 2017. Soil health, crop productivity and sustainability challenges. In: Sustainability Challenges in the Agrofood Sector. Wiley-Blackwell, NY, pp. 509–531 ed.Chpt 21.

Zamus, S., Munekata, P.E.S., Gullon, B., Rocchetti, G., Montesano, D., Lorenzo, J.M., 2021. *Citrullus lanatus* as source of bioactive components: an up-to-date review. Trends Food Sci. Technol. 111, 208–222.

Zia, S., Khan, M.R., Shabbir, M.A., Aadil, R.M., 2021. An update on functional, nutraceutical and industrial applications of watermelon by-products: a comprehensive review. Trends Food Sci. Technol. 114, 275–291.