

Integral Extraction of *Opuntia ficus-indica* Peel Bioproducts via Microwave-Assisted Hydrodiffusion and Hydrodistillation

Rosaria Ciriminna,[†] Alexandra Fidalgo,[‡] Giuseppe Avellone,[§] Carmelo Danzi,^{||} Giuseppe Timpanaro,^{||} Mattia Locatelli,[⊥] Diego Carnaroglio,[⊥] Francesco Meneguzzo,[#] Laura M. Ilharco,^{*,‡,Ⓛ} and Mario Pagliaro^{*,†,Ⓛ}

[†]Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy

[‡]Centro de Química-Física Molecular and IN-Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, University of Lisboa, Complexo I, Avenida Rovisco Pais 1, 1049-001 Lisboa, Portugal

[§]Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche, Università degli Studi di Palermo, 90133 Palermo, Italy

^{||}Dipartimento di Agricoltura, Alimentazione e Ambiente, Università degli Studi di Catania, via Santa Sofia 100, 95123 Catania, Italy

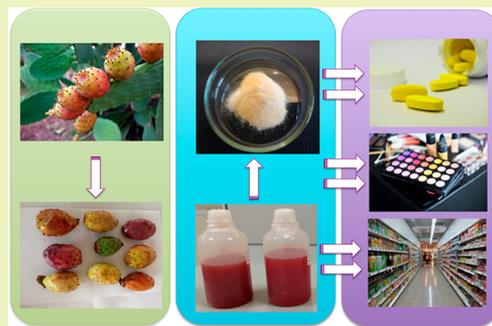
[⊥]Milestone, via Fatebenefratelli 1/5, 24010 Sorisole BG, Italy

[#]Istituto di Biometeorologia, CNR, via Madonna del Piano 10, 50019 Sesto Fiorentino FI, Italy

Supporting Information

ABSTRACT: The microwave-assisted hydrodiffusion extraction process affords high quality pectin and betanin from the peel of red and green *Opuntia ficus-indica* fruits under mild conditions. An aqueous mixture of valued bioproducts is readily obtained from the fruit peel cell water itself, without any water addition. The integral extract can be used as such to formulate nutraceutical beverages and products or, upon straightforward separation, to isolate pectin and betanin devoid of chemical contaminants suitable as ingredients for products ranging from food and beverage to cosmetic and pharmaceutical sectors. Betanin shows exceptional stability thanks to the high amounts of antioxidant polyphenols in the extract. Here, we describe the simple extraction process and present spectroscopic characterization of the extracts from red and green *Opuntia ficus-indica* peel.

KEYWORDS: *Opuntia*, Prickly pear, Biophenol, Betanin, Pectin, Antioxidant, Anti-inflammatory



INTRODUCTION

Once economically viable and environmentally friendly industrial processes for the extraction of valued bioproducts from agriculture and food processing byproducts will be developed, they will become a common practice in all the countries hosting significant agricultural activities.¹ So far mostly disposed of as waste, such byproducts are numerous and generally available in large amount at low or virtually no cost, whereas the economic value of the related byproducts is high and generally growing. Examples include waste orange peel as source of essential oil, polyphenols, and pectin;² coffee processing byproducts as a source of colorants, biophenols, and pectin;³ and waste tomato peel as a source of amino and fatty acids, biophenols, and carotenoids.⁴

Ubiquitous in Mexico, Arizona, and other sunny U.S. States; in many parts of Central American, North African, and Middle East countries; and widely cultivated in Brazil, South Africa, and Argentina, cactus pear *Opuntia ficus-indica* (OFI) is a perennial plant species belonging to the *Cactaceae* family, whose fruits and stems (cladodes) afford a number of phytochemicals of significant nutraceutical importance.⁵

Accommodating up to 90 wt % water in the cladodes,⁶ the cactus pear is a water livestock feed reserve that plays an increasingly important role to combat desertification in several arid and semiarid countries.⁷

The OFI fruits are a source of nutritionally relevant compounds such as amino acids and essential minerals (especially of calcium, potassium, and magnesium). They are also rich in antioxidant vitamin C (20–40 mg/100 g)⁸ and sterols,⁹ as well as anti-inflammatory betalain pigments¹⁰ (particularly indicaxanthines)¹¹ and biophenols, imparting them with neuroprotective, antiulcerogenic, and hepatoprotective properties.¹² Even the OFI seed oil is a valued bioproduct rich in unsaturated fatty acids, exerting unique skin and hair hydrating action, whose antioxidant and anti-inflammatory properties offer further significant potential as a functional ingredient of nutraceutical and food supplement products.¹³

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The production of waste *Opuntia* peel is significant, lasting for several months, with most peel ending either landfilled or used as animal feed, and a smaller fraction feeding anaerobic biodigestors.¹⁴ Being not edible, indeed, the peel is removed from the fruit by all companies selling packaged fresh fruits, jams, and fruit juice.

Sourcing betalains, and betanin in particular, from *Opuntia* fruits in alternative to the current industrial practice to extract this natural dye from red beetroot (*Beta vulgaris* L.)¹⁵ has been widely investigated, in light of significant potential advantages. For instance, betalains were extracted from *Opuntia dillenii* under various technological conditions,¹⁶ from *Opuntia joconostle* pulp by water/ethanol or water/methanol mixtures,¹⁷ or from hydroponic cultivated red-tube spinach (*Spinacia orelacea* L.).¹⁸ Contrary to red beetroot, which slowly affords its rizoma betanin content after two years of cultivation, the *Opuntia* plant gives fruits several times a year. Betanin is a valued violet–red betacyanin, stable at pH between 3.8 and 6.8. It is approved as a food additive by the European Union, labeled E162, and is particularly well-suited for use as a natural colorant in beverage, confectionary, bakery, dairy, and frozen products. Only the potential application in pharmaceuticals and cosmetics has been questioned because of the poor stability of betanin; thus, a variety of stabilization techniques have been proposed and thoroughly reviewed.¹⁹

The same search for new sources can be said of pectin, currently mostly obtained from dried lemon peel and, to a lesser extent, from apple pomace.²⁰ The first study suggesting OFI peel as a source of pectin to be used as thickening material goes back to 1994, when a team in Italy found out that hot-acid-extracted OFI pectin had a galacturonic acid content of 64%, and a low degree of methoxylation (10%).²¹ Scholars in Morocco and in France reported the first structural analysis of the pectic material contained in the OFI peel 10 years later.²² Another 10 years later, Rodríguez-Hernández and co-workers in Mexico,²³ relying on conventional hydrolytic extraction in hot acidic water (treatment of the milled peel with 1 wt % ethylenediaminetetraacetic acid for 2 h at 70 °C and pH 4.0), reported that pectin extracted from the peel of *Opuntia albicarpa* Scheinvar “Reyna” fruits has a low methoxyl content (30.7%), and high molecular weight ($M_w = 10.16 \times 10^5$ g mol⁻¹ versus $M_w = 76 \times 10^3$ g mol⁻¹ of lemon pectin), which imparts the OFI pectin the ability to form soft and elastic gels.

We now report the first outcomes of four separate tests aimed to extract pectin and red dye from the peel of two different types of OFI fruits harvested in Sicily, Italy, via microwave-assisted hydrodistillation and solvent-free microwave-assisted hydrodiffusion. The latter process, combining microwave (MW) heating and Earth gravity at atmospheric pressure, has rapidly emerged as the most attractive technique to extract and to separate value-added bioproducts from solid samples with various advantages, which include high reproducibility, less energy consumption, shorter procedures, higher purity of the final product, elimination of organic solvent, and consequent elimination of waste effluents.²⁴

■ EXPERIMENTAL SECTION

Sicily's OFI fruits were used in all the tests. The initial samples of green and red OFI fruit weighed 8 kg each (Figure 1). Two extractions were performed for each sample, using only the peel of the OFI fruits, and thus releasing the valued edible pulp. Furthermore, the peel has been milled to enhance the contact surface area during the MW-assisted extraction.

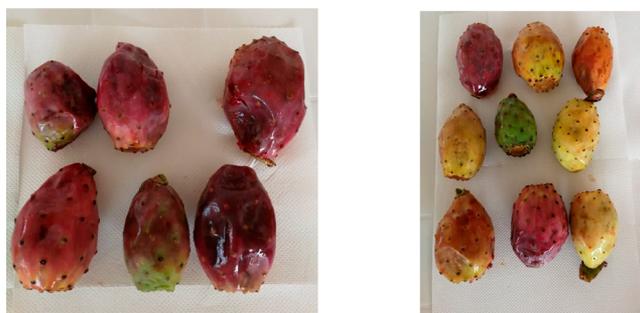


Figure 1. OFI red fruits (left) and mixed red and green fruits (right). All fruits from Sicily, treated fresh as received.

The tests were carried out on a 1–2 kg scale using an Ethos X (Milestone) commercial extractor, as this instrument simulates exactly the process occurring in the MAC-75 (Milestone), namely, a semi-industrial multimode microwave extractor able to process 30 kg of biological matrix per hour, containing a removable, rotating drum that allows the loading and processing of up to 75 L of biological material.²⁵ The rotation ensures a homogeneous microwave distribution to the material inside the drum.

In each test, a weight (w) of OFI peel was milled and water added (only in the hydrodistillation process). The extraction program used microwave generated by a magnetron at an appropriate power for a time period. The extraction temperature rapidly reached 70 °C, and did not further change. A summary of the conditions used and the liquid amounts recovered is given in Table 1.

At the end of the procedure, all the solution contained in the extraction vessel was recovered (Figure 2) and made available for pectin, dye, and sugar separation and analysis.

Photographs of the aqueous extracts are provided in Figure 3.

The aqueous extracts as such were characterized by infrared spectroscopy in diffuse reflectance (DRIFT) mode. Pectin was removed by precipitation with ethanol at –18 °C (ethanol:water molar ratio of 25:1), followed by centrifugation at 4000 rpm for 40 min. The pectic polymer was readily separated via dialysis and lyophilized, and the powder was characterized by DRIFT. The pectin-free extracts were analyzed by UV–vis spectroscopy immediately after pectin removal and again after aging for 4 months in the initial vessels, without any additives. The aged extracts were also analyzed by infrared spectroscopy in attenuated total reflection (ATR) mode.

The DRIFT spectra of the extracts were recorded on a Mattson Research Series 1 FTIR spectrometer using a Specac selector, with 4 cm⁻¹ resolution and a wide band MCT detector (400–4000 cm⁻¹). They were the result of 500 single-beam scans for the sample (ground with KBr) made as a ratio of 500 single-beam scans for ground KBr, taken as the background. Those of the pectin powder were recorded on a Bruker V70 FTIR spectrometer with 2 cm⁻¹ resolution.

The ATR spectra were also recorded on a Mattson RS1 FTIR spectrophotometer, using a horizontal accessory from Pike Technologies, with a 10 reflections ZnSe crystal. The spectra were scanned with 2 cm⁻¹ resolution and were the result of making a ratio of the single-beam spectrum of the aqueous sample to that of a thin film of distilled water (100 scans each), used as background. The UV–vis spectra were taken on a double-beam JASCO V-650 spectrometer in the 350–700 nm region, using 10 mm quartz cells. The baseline was scanned with distilled water, which was further used as reference.

The analyzed solutions are identified in Table 2, according to their source and extraction procedure.

For future commercialization, the water-soluble betalain dye mixture may be processed as such or converted into a stable powder via lyophilization.

■ RESULTS AND DISCUSSION

The fingerprint region (1800–900 cm⁻¹) of the DRIFT spectra of the initial aqueous extracts (Figure 4) are better

Table 1. Conditions Used in the Different Tests and Amounts Recovered

test	source	w (kg)	procedure	water (mL)	power (W)	period (min)	V _{extract} (mL)
1	green <i>Opuntia</i>	2.4	hydrodistillation	150	1500	60	310
2	green <i>Opuntia</i>	1.15	hydrodiffusion		1200	40	365
3	red <i>Opuntia</i>	2.1	hydrodistillation	150	1500	60	265
4	red <i>Opuntia</i>	1.34	hydrodiffusion		1200	40	490



Figure 2. Ethos X extractor (left) whose vessel was filled with milled OFI peel (middle) affording the aqueous extract (right).

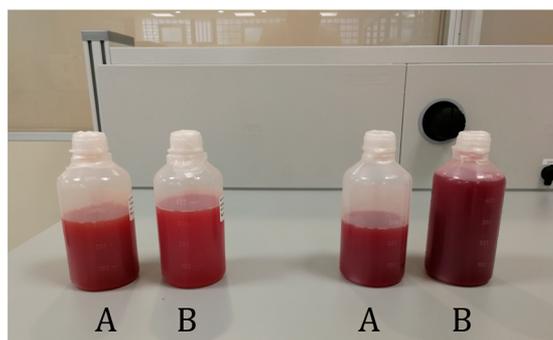
Figure 3. Aqueous extracts from green *Opuntia ficus-indica* peel (left) and from red *Opuntia ficus-indica* peel (right). (A) Samples obtained via microwave-assisted hydrodistillation. (B) Samples obtained via microwave-assisted hydrodiffusion.

Table 2. Identification of the Extracted Products According to Their Source and Extraction Procedure

sample	source	procedure	
		hydrodistillation	hydrodiffusion
initial aqueous extract	green <i>Opuntia</i>	HDstG ₀	HDfG ₀
	red <i>Opuntia</i>	HDstR ₀	HDfR ₀
pectin-free solution	green <i>Opuntia</i>	HDstG	HDfG
	red <i>Opuntia</i>	HDstR	HDfR

resolved when the process is hydrodiffusion-assisted, and especially when the source is red *Opuntia* peel. Under the solvent-free extraction conditions the known efficacy of microwave-assisted hydrodiffusion extraction process affords, for both white and red *Opuntia* peels, a red aqueous solution weighing approximately between 32% and 35% of the original peel weight (Table 1).

There are strong contributions from the pectin bands,²⁶ as shown in the assignments summarized in Table 3. The strong and broad band in the 1800–1500 cm⁻¹ region is assigned to the stretching mode of carboxylate groups ($\nu_{\text{as}}\text{COO}^-$), overlapped with bands from carbonyl groups (mostly from esterified galacturonic acid, $\nu(\text{C}=\text{O})_{\text{ester}}$, and nonesterified acidic carbonyl groups, $\nu(\text{C}=\text{O})_{\text{acid}}$), and also with the water

deformation band. A component of the $\nu(\text{C}\cdots\text{C})$ aromatic modes of betanin may also contribute to this band.

The band at ~ 1456 cm⁻¹, visible in all the spectra, is assigned to the antisymmetric methyl deformation mode, $\delta_{\text{as}}(\text{CH}_3)$, of ester methyl groups in the galacturonic rings, and of rhamnose rings of the pectin backbone, overlapped with another $\nu(\text{C}\cdots\text{C})$ mode of betanin. The carboxylate $\nu_{\text{s}}\text{COO}^-$, ester $\nu(\text{C}-\text{O}-\text{C})$, and different $\nu\text{C}-\text{O}$ modes appear at 1410–1417, 1270–1280, and 1234–1240 cm⁻¹, respectively. In the extracts by hydrodistillation the last two bands are much overlapped. In the spectra of red *Opuntia* extracts, a small band at ~ 1313 cm⁻¹ is observed that may be assigned to the $\delta(\text{C}-\text{O}-\text{H})$ mode of pyranose rings or of phenolic rings of polyphenols.

The group of three intense and partially overlapped bands observed at ~ 1120 , ~ 1080 , and ~ 1040 cm⁻¹ are typical of pectin, assigned to the C–O–C stretching modes of the pyranose ring and of the glycosidic bond, and to a combination of the C–OH and C–C stretching modes of pyranose rings. The 950–700 cm⁻¹ region contains the bands related to the external deformation vibrations of methyl, methylene, and methyne groups. The band at ~ 920 cm⁻¹ observed for the extracts by hydrodistillation is assigned to the rocking mode of the ester methyl group, $\rho(\text{CH}_3)$.

The UV–vis spectra of the fresh pectin-free extracts (not shown) were comparable to those published for aqueous solutions of ultrasound-assisted beetroot extracts.²⁷ This fact reveals the quality of the present extraction processes, since no chemical additive was added at any step. Such quality was already self-evident from the colors of the samples (Figure 3). The UV–vis spectra of the pectin-free solutions, aged for 4 months in the absence of additives, are shown in Figure 5.

The spectra show that the hydrodiffusion extracts are much more stable than those obtained by hydrodistillation: the samples extracted by hydrodiffusion, mainly from red OFI, show two partially overlapped bands at 536 and ~ 490 nm, assigned to betanin and betaxanthin, respectively.²⁸ As proven by density functional and time-dependent density functional theory (DFT and TDDFT) calculations,²⁹ the HOMO of betanin is mostly localized on the benzene ring. The main LUMO \leftarrow HOMO transition observed at ~ 540 nm is, thus, essentially a $\pi-\pi^*$ charge transfer in which electron density from the benzene ring is transferred to the dihydropyridinic ring.

A very strong phenolic absorption (not shown) was also observed at 280 nm in the spectra of these extracts. The presence of polyphenolic compounds may have a stabilizing effect, protecting the betalain extract under the simple storage conditions employed: the aqueous extracts were kept at room temperature for over 4 months, with visible light easily penetrating the semitransparent polyethylene bottles. In fact, no change in color or in its intensity has been observed, addressing the betalain chemical instability issue which so far has limited its widespread commercial utilization.³⁰ In contrast, the hydrodistillation extracts changed color to brown over the

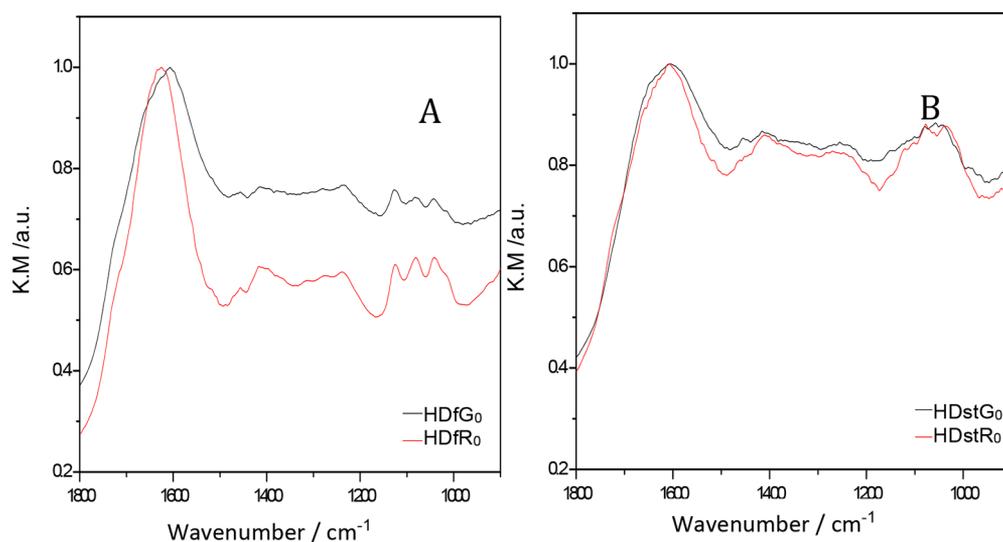


Figure 4. DRIFT spectra of the initial aqueous extracts by (A) hydrodiffusion and (B) hydrodistillation, normalized to the most intense band.

Table 3. Band Assignments of the DRIFT Spectra (Observed Maxima) of the Initial Extracts

assignment	wavenumber (cm ⁻¹)			
	extraction by hydrodiffusion		extraction by hydrodistillation	
	red <i>Opuntia</i> HDfR ₀	green <i>Opuntia</i> HDfG ₀	red <i>Opuntia</i> HDstR ₀	green <i>Opuntia</i> HDstG ₀
$\nu(\text{C}=\text{O})_{\text{ester}}$	1721 _{sh}	1728 _{sh}	1724 _{sh}	
$\nu(\text{C}=\text{O})_{\text{acid}}$	1665 _{sh}	1653 _{sh}	1656 _{sh}	
$\nu_{\text{as}}\text{COO}^-/\delta\text{HOH}/\nu(\text{C}\cdots\text{C})_{\text{aromatic}}$	1626 _s	1606	1608	1604 _{broad}
$\nu_{\text{as}}\text{COO}^-$	1518 _{sh}		1516	
$\delta_{\text{as}}\text{CH}_3/\nu(\text{C}\cdots\text{C})_{\text{aromatic}}$	1456 _w	1456	1462	1456
$\nu_{\text{s}}\text{COO}^-$	1417 _m	1414	1410	1416
$\delta(\text{C}-\text{O}-\text{H})_{\text{pyranose}}/\delta(\text{C}-\text{O}-\text{H})_{\text{phenol}}$	1313 _{sh}		1311	
$\nu(\text{C}-\text{O}-\text{C})_{\text{ester}}$	1273 _{sh}	1281	1282	1255 _{broad}
$\nu(\text{C}-\text{O})$	1240 _m	1234	1230 _{sh}	1255 _{broad}
			1149 _{sh}	1153
$\nu(\text{C}-\text{O}-\text{C})_{\text{pyranose}}/\nu(\text{C}-\text{O}-\text{C})_{\text{glycoside}}$	1124 _m	1126	1120	
		1103 _{sh}	1103	1103
$\nu(\text{C}-\text{OH})_{\text{pyranose}} + \nu(\text{C}-\text{C})_{\text{pyranose}}$	1080 _m	1082	1078	1078
			1059	1057
	1041 _m	1043	1039	1045
	1012 _{sh}	1014 _{sh}		1016 _{sh}
$\rho(\text{CH}_3)_{\text{ester}}$			920	918

storage period, and betanin was no longer detected by UV-vis spectroscopy after 4 months; this may be explained by a sequence of reactions that occur in aqueous solution, consisting of the hydrolysis of betanin to betanidin (by loss of the glucose moiety), which undergoes further oxidation.^{31–33}

We are reminded here that microwave distillation, with its 90–95% shorter extraction times when compared, for example, to conventional hydrodistillation, affords essential oils of better quality in terms of yield and quantity of pharmacologically active products, especially because of the involvement of long extraction periods which favor the release of oxidative enzymes that promote degradation.³⁴ The solvent-free MW-assisted hydrodiffusion further improves microwave-assisted extraction by reducing the amount of water, thereby dramatically increasing the concentration of biophenol antioxidants which prevent degradation of the coextracted natural products.

Since solvent-free hydrodiffusion was the most effective extraction process also in the case of *Opuntia ficus-indica* peels,

the ATR spectra of the solutions extracted by hydrodiffusion after separation of pectin are compared in Figure 6 for the fingerprint region (below 1800 cm⁻¹).

The spectral pattern is very different from the pectin-containing extracts, being dominated by the bands at 1550/1544, 1417, and 1044 cm⁻¹, assigned to the $\nu\text{C}=\text{N}/\nu_{\text{as}}(\text{C}-\text{O}-\text{O}^-)$, $\nu_{\text{s}}(\text{C}-\text{O}-\text{O}^-)$, and $\nu(\text{C}-\text{O})$ modes, respectively. Although the betanin molecule also contains a pyranose ring, the relative intensities in the 1200–1000 cm⁻¹ region are no longer characteristic of pectin. In addition, considerable shifts are observed in the carbonyl and carboxylate bands. Apparently these extracts are poor in pectin or even pectin-free.

The weak bands at 1644, 1506, and 1457 cm⁻¹ are assigned to the C \cdots C stretching modes of the aromatic ring of betanin, whose infrared spectrum is well-documented in the literature.³⁵ The band assignments are summarized in Table 4.

The pectin powder obtained by lyophilization (from mixed green and red OFI peel) and its infrared spectrum in diffuse reflectance mode are shown in Figure 7.

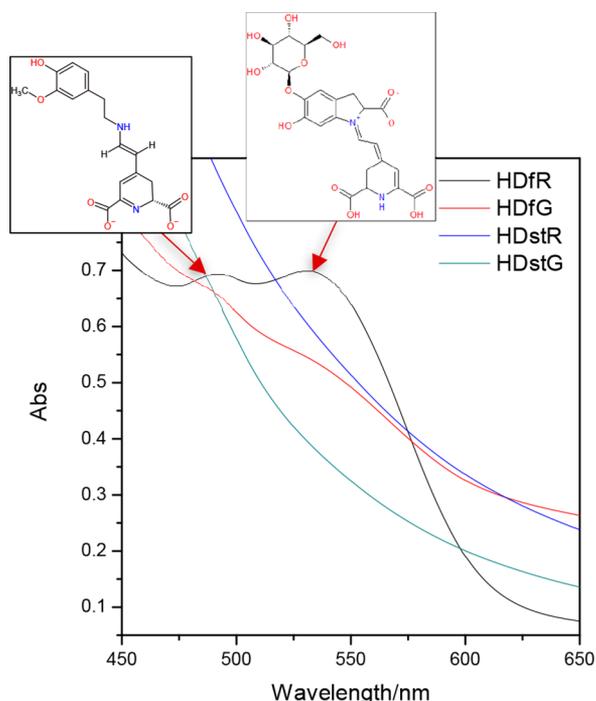


Figure 5. UV-vis spectra of the pectin-free solutions after a 4 month storage period for both green and red fruit peels extracted via microwave-assisted hydrodistillation and hydrodiffusion.

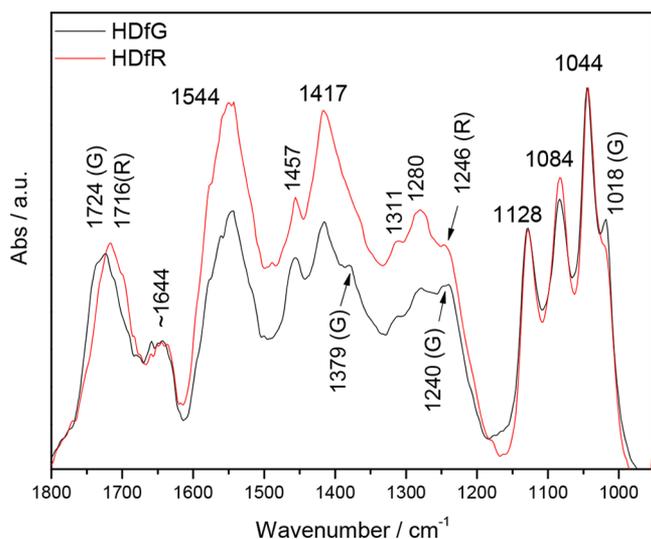


Figure 6. ATR spectra of the extracts obtained by hydrodiffusion after separation of pectin, normalized to the band at 1044 cm^{-1} .

The pectin spectrum shows that it is very pure, and the well-resolved bands in the fingerprint region suggest a high degree of crystallinity. The spectrum was quantitatively analyzed in the region between 900 and 1850 cm^{-1} , to estimate the methoxyl content and the relative content in galacturonic acid regions. A deconvolution into Gaussian and Lorentzian components was performed, using the procedure already published.^{25,36}

The degree of esterification (DE) was determined by the ratio of band intensities of the esterified carboxyl stretching components to the total band intensities of the esterified plus nonesterified carboxylate bands. The fraction of galacturonic-acid-rich (HG) regions is proportional to the added areas of

Table 4. Assignment of the ATR Bands of the Pectin-Free Extracts by Hydrodiffusion

assignment	wavenumber (cm^{-1})	
	extract from red <i>Opuntia</i>	extract from green <i>Opuntia</i>
$\nu(\text{C}=\text{O})_{\text{carb.acid}}$	1716 _m	1724 _m
$\nu(\text{C}\cdots\text{C})$	1658 _{sh}	
	$\sim 1644_{\text{w}}$	$\sim 1644_{\text{w}}$
$\nu\text{C}=\text{N}$	1577 _{sh}	
$\nu\text{C}=\text{N}$	1550 _s	
$\nu_{\text{as}}(\text{C}-\text{O}-\text{O}^-)$	1544 _s	1544 _s
$\nu(\text{C}\cdots\text{C})$	1506 _w	
$\nu(\text{C}\cdots\text{C})$	1457 _m	1457 _m
$\nu_{\text{s}}(\text{C}-\text{O}-\text{O}^-)$	1417 _s	1417 _s
		1379 _m
$\delta(\text{C}-\text{O}-\text{H})_{\text{phenol}}$	1311 _m	1311 _m
$\nu(\text{C}-\text{O}-\text{C})_{\text{ester}}$	1280 _m	1280 _m
$\nu\text{C}-\text{N}/\nu\text{C}-\text{O}(\text{H})_{\text{phenol}}$	1246 _m	1240 _m
$\nu(\text{C}-\text{O}-\text{C})_{\text{pyranose}}/\nu(\text{C}-\text{OH})/\nu(\text{C}-\text{C})$	1128 _m	1128 _m
	1084 _s	1084 _s
$\nu(\text{C}-\text{O})$	1044 _s	1044 _s
		1018 _m

the carbonyl plus carboxylate bands made as a ratio against the total areas of carbonyl plus carboxylate plus pyranose bands. This ratio yields just a trend when comparing the different samples characterized by the same method, not a true fraction of HG regions. The details of the spectral deconvolution and the intermediate results are shown in Table S1 in the Supporting Information. The final results were compared with those of pectin obtained by different extraction methods and from other sources (Table 5).

The degree of esterification obtained in this work (53%) is higher than the values published by other authors for OFI peel pectin extracted using hot acid,²¹ and lies between those for commercial and hand-cut citrus and grapefruit pectin.²⁶

On the other hand, the relative content in galacturonic acid (HG) regions estimated for pectin from OFI peel is quite low in comparison to those of citrus or grapefruit pectin and for most commercial ones, using the same evaluation method.²⁶ This confirms that the percentage of HG regions is very much dependent on the source and also on the extraction procedure. Apparently, milling OFI peel, followed by microwave hydrodiffusion, dialysis, and lyophilization results in pectin with larger percentages of hairy RG regions that promote the formation of more entangled structures, playing a gel-stabilizing role.

CONCLUSIONS

Extending our recent studies on microwave-assisted extraction of pectin and essential oils from citrus (lemon, orange, and grapefruit) fresh peel,³⁶ we have used microwave-assisted hydrodistillation and microwave-assisted hydrodiffusion to obtain highly promising aqueous extracts from the peel of red and green fresh *Opuntia ficus-indica* fruits harvested in Sicily. Under mild conditions (1 h extraction at 70 °C) both fruit wastes afford red natural extracts of pronounced stability under ambient conditions.

Hydrodiffusion, regardless of the absence of added water, yields higher amounts of aqueous integral extract. Furthermore, after 4 months of storage at room temperature, the hydrodiffusion extract fully retained its original red color,

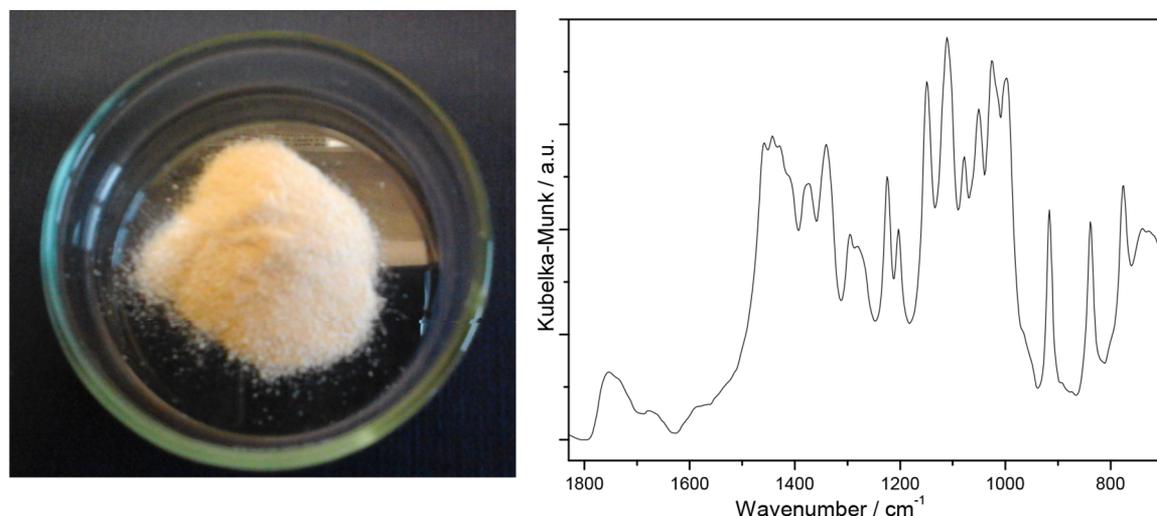


Figure 7. Pectin powder from the peel of red/green fruit and DRIFT spectrum in the fingerprint region.

Table 5. Degree of Esterification (DE) and Relative HG Content for Pectin Samples Obtained from OFI Peel (This Work and Others), from Citrus Matrices and for Commercial Pectin Samples

pectin source	procedure	DE (%)	HG α to (%)	ref
OFI peel	microwave-assisted hydrodiffusion	53	23	this work
OFI peel	hot acid	10	64 ^a	21
<i>Opuntia albicarpa</i> peel	hot acidic water	30.7		23
red orange outer skin	microwave-assisted hydrodiffusion	39	43	26
red orange peel	microwave-assisted hydrodiffusion	30	58	26
red orange waste	microwave-assisted hydrodiffusion	25	48	26
lemon outer skin	microwave-assisted hydrodiffusion	24	37	26
lemon peel	microwave-assisted hydrodiffusion	34	42	26
lemon waste	microwave-assisted hydrodiffusion	40	58	26
grapefruit peel	microwave-assisted hydrodiffusion	34	55	26
commercial citrus pectin A		68	17	26
commercial citrus pectin B		62	44	26
commercial citrus pectin C		67	35	26
commercial citrus pectin D		86	37	26

^aAbsolute value.

whereas the hydrodistillation extract turned brown, pointing to the well-documented betanin hydrolysis (i.e., molecular degradation). The aqueous extract itself, mostly containing betalains, pectin, polyphenols, sugars, and enzymes, can be used as such as a value-added nutraceutical product. The pectic polymer readily separated via dialysis and lyophilized has a high degree of crystallinity and high methoxyl content (53% degree of esterification).

Ferreira and co-workers have recently emphasized how it will be very important to establish optimum processing conditions to maximize the stability of betalain natural

pigments and their extraction yields, because of their application as functional ingredients and health promoters in nutraceutical, pharmaceutical, and cosmetic products.³⁰ This is exactly what the microwave-assisted hydrodiffusion extraction process described in this study achieves under mild conditions, affording high-quality pectin and betanin of endless stability, thanks to the high amounts of antioxidant polyphenols, saving on water to directly obtain an aqueous mixture of valued bioproducts in the fruit peel cell water itself. Alternative to conventional extraction processes in organic solvents or in water, the extraction of natural products based on microwave irradiation of plant material and volumetric heating is now an industrial reality, though in its early days, offering important economic and environmental benefits.³⁷

Chemat and co-workers have already shown that industrialization of microwave-based hydrodiffusion processes is possible, for example, by using an existing large-scale continuous microwave suitable for the extraction of 10, 20, 100, or 1000 kg of plant material per hour in a batch.³⁸

Driven by the consumer demand for healthy and natural products, the global market of natural food colors (derived from fruits, vegetables, seeds, algae, insects, and minerals) is growing at a much faster rate than forecasted. For example, in 2016 the market was reported generating \$1.31 billion in revenue in 2015 and was expected to grow at over a 5% annual rate between 2016 and 2021.³⁹ However, the same market analyst three years later was reporting that the global market was valued at \$3.51 billion in 2017.⁴⁰ Betalains are a small niche of this market, but their growth potential is very significant.³⁰ Though more expensive than synthetic red color molecules, such as “red aza” or “red paba”, used to increase the appearance of food and make it attractive, betalains have the potential to transform a public health issue into an opportunity for enhancing public health, exactly as it would happen when replacing synthetic food antioxidants with olive biophenols.⁴¹ As nations across the world increasingly uptake bioeconomy as a key asset of their economies,⁴² these findings are of significant relevance to all countries and regions of the world where *Opuntia ficus-indica* is harvested. The route is open to food, pharmaceutical, nutraceutical, beverage, and cosmetic companies willing to replace synthetic red colorants and citrus-derived pectin with *Opuntia*-derived betanin and *Opuntia*-derived pectin.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b00502.

Table summarizing results obtained by deconvolution of the DRIFT spectra of lyophilized pectin in two wavenumber regions (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: lilharco@tecnico.ulisboa.pt.

*E-mail: mario.pagliaro@cnr.it.

ORCID

Laura M. Ilharco: 0000-0001-6994-1464

Mario Pagliaro: 0000-0002-5096-329X

Notes

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■ DEDICATION

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