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Article

Polyphenolic Profile and Antioxidant Potential of Medjool Date Tissues from the Jordan Valley

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Abstract: This study investigated the polyphenolic composition and antioxidant potential of Medjool date tissues (flesh and seeds) from two plantations in the Jordan Valley, using chromatographic (HPLC/DAD) and spectrophotometric methods (Folin-Ciocalteu and DPPH assays). Significant levels of phenolic compounds, including gallic acid, ferulic acid, tannins, and flavonoids, were identified. The analysis revealed that polyphenol concentrations in date pulp varied depending on plantation practices and environmental conditions. Additionally, date seed extracts exhibited substantially higher antiradical efficiency compared to flesh extracts. These findings highlight the excellent nutritional and health-promoting properties of Medjool dates. Furthermore, the research emphasizes the potential of date seeds and downgraded fruits for applications in nutraceuticals and functional foods, supporting sustainability and circular economy principles. The study underscores the significance of Medjool dates as a premium cultivar for health-oriented products and suggests strategies to enhance Palestinian date exports despite ongoing logistical and geopolitical challenges.

Keywords: medjool date; HPLC/DAD; flesh and seeds; antiradical efficiency; circular economy

1. Introduction

The date palm (*Phoenix dactylifera* L., *Arecaceae*) is among the oldest cultivated plants in human history, and is widely distributed across various regions, including Asia, Africa, Arabian countries, and the Middle East. Currently, more than 2,000 cultivars of date palms are known worldwide, with both production and consumption of date fruits steadily increasing. As of 2022, global date production has reached approximately 9.8 million tons (9,747,570 t) [1]. Date palm cultivation in the Palestinian territories is concentrated in the regions of Jericho and the Jordan Valley in the West Bank, as well as in the Gaza Strip. Over the past few decades, there has been a substantial expansion in the total harvested area dedicated to date production in Palestine, reaching approximately 725 hectares by 2012 [2]. The Mediterranean climate prevailing in these areas offers optimal conditions for the growth and development of date palms.

Traditionally, Palestinian dates were primarily traded and consumed locally within producing countries. However, this pattern has evolved in recent years, with efforts to strengthen and sustain an export market. The export trade predominantly focuses on dry and semi-soft dates, which are easier to preserve compared to fresh dates that have a higher water content. Nevertheless, fresh dates are increasingly favored by modern consumers for their superior nutritional value. Addressing these issues through improved infrastructure and trade facilitation could enhance competitiveness and sustain export growth. In 2022, Palestine produced 25,494 tons of dates [1], with a significant portion

(13,000 tons) destined to the export (i.e. under HS code 080410) [3]. Thus, Palestinian dates have shown significant export growth, particularly to the United Arab Emirates (UAE), Turkey, and Europe, including Italy. The UAE emerged as a primary market, importing 3,236 tons in 2022, reflecting not only cultural and regional preferences but also the UAE's role as a strategic trade hub for re-exportation. Similarly, Italy imported 451 tons in 2022, highlighting the increasing European demand for premium-quality dates [3]. Despite this growth, date cultivation and development face several challenges, including high investment costs, limited marketing strategies, competition with Israeli products, water scarcity (i.e., restricted access to water), as well as pests and diseases. Furthermore, export logistics, dependence on Israeli ports, and customs restrictions continue to pose barriers to further market expansion.

There are hundreds of named varieties of *P. dactylifera* date palms, among which the large, soft Medjool date is one of the most renowned. Medjool dates are often referred to as the “King of Dates” due to their widespread global availability and their classification as a soft variety, in contrast to semi-dry and dry types. The Medjool cultivar is considered one of the finest dates produced in Palestine and is highly regarded both regionally and globally. The Jericho area offers a distinct comparative advantage for cultivating Medjool dates, as its location below sea level results in higher oxygen availability, enhancing palm respiration and contributing to the fruit's rich flavor and characteristic color. Additionally, the region's climate, with temperatures ranging from 12 °C in March to as high as 50 °C between July and October, provides optimal conditions for Medjool date production, which thrives in hot and dry environments.

Dates are known to contain a variety of polyphenolic compounds, including phenolic acids (e.g., gallic acid), hydroxycinnamates (e.g., caffeic and ferulic acids), flavonoids, and proanthocyanidin oligomers. The total polyphenol content is influenced by the cultivar and ripeness stage, showing a marked decline as the fruit matures [4]. Recent investigations into the antioxidant profile of Palestinian Medjool dates employed HPLC-DAD-ESI/MS analysis for tentative identification, revealing over fifty compounds, predominantly phenolics such as flavonoids and phenolic acids. These compounds were detected across different date parts, including fruit pulp and skin, fronds, clusters, and pollen. Notably, a qualitative similarity in phenolic composition was observed among the various parts of the date [2].

In the Middle East and Arabian countries, date fruits represent a staple crop with multiple biological functions, largely attributed to their phenolic compounds. These include hepatoprotective and nephroprotective activities, as well as a high capacity for scavenging free radicals, thereby stimulating the immune system, as highlighted in a comprehensive review on the biological and pharmacological properties of dates [5]. Date palm fruits are highly valued for their nutritional and therapeutic properties, exhibiting significant antioxidant, antibacterial, antifungal, and anti-proliferative activities [6]. Moreover, β -glucan extracted from date fruits demonstrates promising potential in combating tumors, modulating immune responses, managing diabetes, reducing inflammation, and lowering cholesterol levels, while also promoting the growth of beneficial gut microbiota [7]. Flavonoids, such as catechin and rutin, have been identified as key contributors to the antioxidant activity of dates [8,9]. Indeed, a recent study on Medjool dates from the Jordan Valley [10] proposed that supplementation with ethanolic date extracts may reduce anxiety-like behaviors in mice. This effect was attributed to flavonoids, phenols, and sterols, which appear to influence brain function and exhibit anxiolytic properties. It is also noteworthy that date seeds represent a promising source of antioxidants in the diet. In Middle Eastern countries, roasted and unroasted seed powders are commercially marketed as caffeine-free beverages [11]. Traditionally regarded as a by-product used for animal feed, date seeds are rich in carbohydrates, oils, dietary fiber, and proteins, in addition to bioactive phenolic compounds with potential health benefits. A recent review has emphasized the diverse chemical composition of date seeds, which are increasingly regarded as valuable ingredients for applications in food formulations, cosmetics, and medicinal supplements [12].

1.1. Outline of the Aims

The aim of the present study is to explore the potential antioxidant activity, using the DPPH test, estimate the phenolic content using the Folin–Ciocalteu method and record the phenolic profile by the HPLC/DAD technique, for the evaluation of date phenolic fraction in samples of Medjool dates (fruit flesh and seeds) collected in two plantations of two farmers in the Jericho Governorate, Jordan Valley, Palestine. Farmers have been selected among the members of Palm Farmers Cooperative Association (PFCA). The association was the main target beneficiary of the project “Sostegno alla riorganizzazione produttiva, manageriale e commerciale delle cooperative di datteri palestinesi ed egiziani” (AID 10601), implemented by Jean Paul II Foundation and funded by the Italian Agency for Development Cooperation, and aimed to enhance the quality and the sustainability of the management and strategic organization of the rural enterprises involved in the productions of dates in West Bank [13,14].

2. Results and Discussion

Medjool dates analyzed in the present study were collected during the harvesting and sorting operations carried out by two members of PFCA. At the farming level, post-harvest procedures consist in a preliminary sorting of date fruits, taking into consideration the indicator of the skin separation, which means the residual air inside the skin. This skin separation is related to the quality of the products, since it diminishes their market value. In the Jordan Valley, with a Mediterranean climate, the percentage of skin separation is high, it may exceed 10% of the skin area and only about 10-20% of the harvest is qualified for export [15]. PFCA farmers carry out a visual assessment, by adopting the following procedure: if separated skin is less than 10%, date is graded A; if it is 10-25% the date obtains grade B, and finally, in dates with more than 25% of separated skin the grade C (see Figure 1). Date adhesiveness and cohesiveness are functions of date flesh moisture content, a mechanical parameter that could be less empirically evaluated by an instrumental texture analysis [16]. Concerning the different level of quality of dates, it is important to make the following considerations: dates of grade A are easily placed on the market, also if they are smaller than usual Medjool date; dates of B grade are preferably placed on the local market; for C grade dates there are the major commercial difficulties and they could be proposed for processing, even because their shelf-life is six months without refrigeration, instead of two years, according to the experience of PFCA farmers.

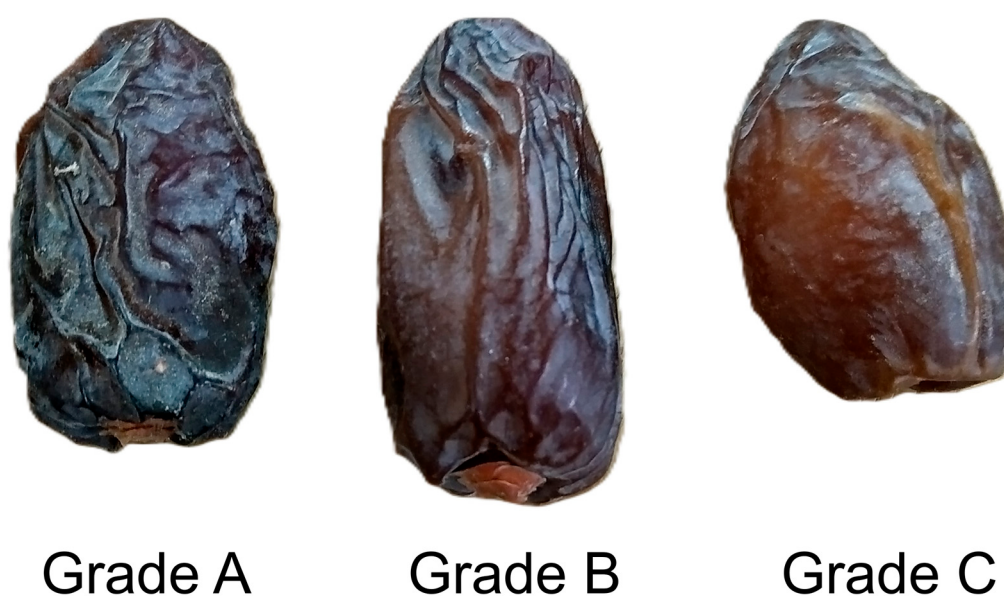


Figure 1. Dates with different grade of quality.

The hydroalcoholic mixture used for obtaining the raw extracts of date fruits was chosen according to previous papers [17,18] respectively for Oman dates, and a Spanish date variety, similar to the Medjool cultivar (cv. Confitera).

The characterization and the quali-quantitative evaluation of polyphenol compounds present in two samples of dates collected during the in-field mission was carried out through HPLC/DAD analyses.

The chromatographic profile of date flesh extracts is reported in Figure 2, where (a) shows the hydroalcoholic extract registered at 280 and 330 nm, and (b) reports the ethylacetate fraction from Extrelut® cartridge, registered at 350 nm. The fractionation was carried out in the date's fruit pulps with the purpose of a better detection of the flavonoid glycosides. Tannin compounds, flavonoids and single hydroxycinnamic acids and derivatives were tentatively identified and quantified in the investigated extracts by comparison with the retention times and UV spectra of standards, that were analyzed under identical conditions.

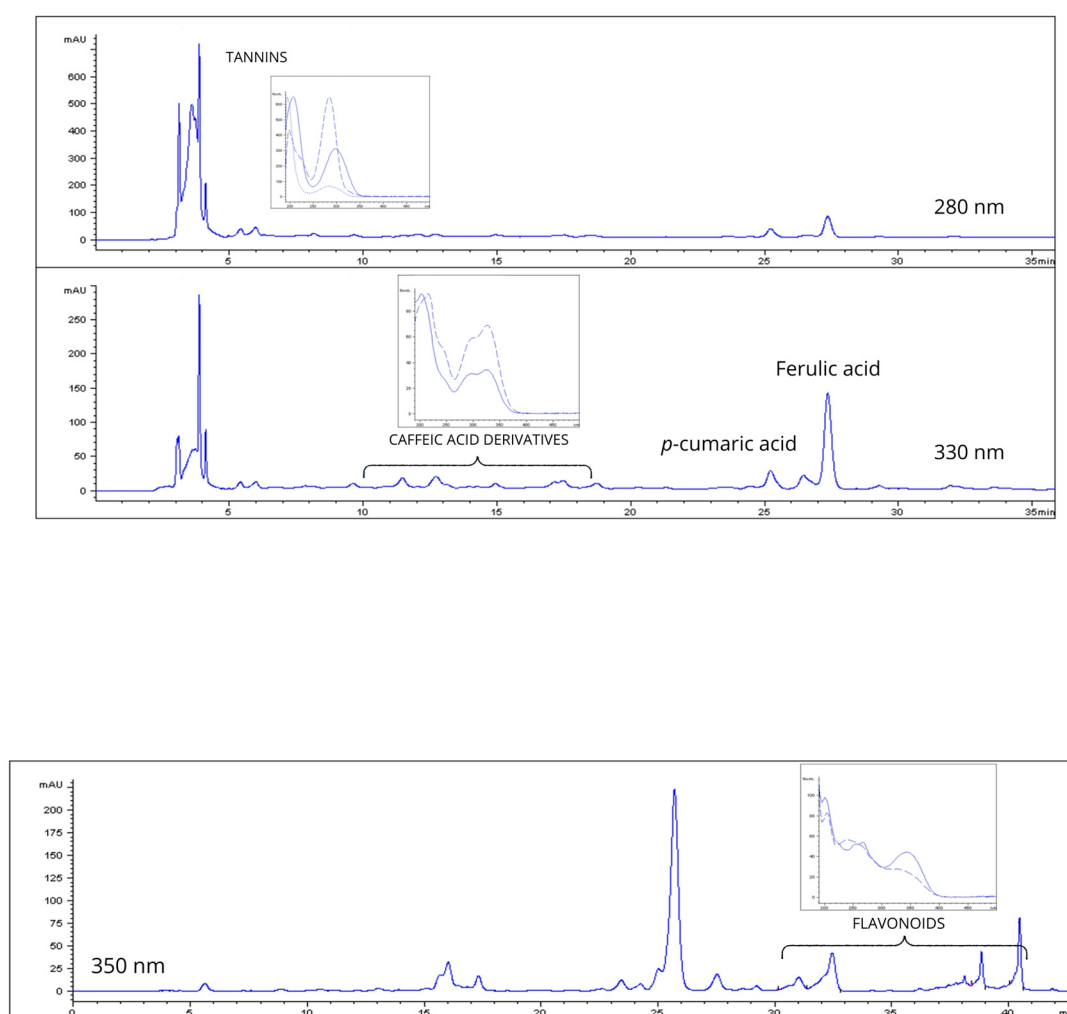


Figure 2. HPLC/DAD chromatographic profiles of Medjool date pulp extracts (a) raw hydroalcoholic extract at 280 and 330 nm, (b) ethylacetate extract from Extrelut cartridge at 350 nm.

The composition and concentration of major phenolic substances that were determined by HPLC analysis in ethylacetate fractions are presented in Table 2, in samples collected from plantations

(Sample 1 and 2, or S1 and S2) and in a sample of Palestine Medjool dates taken from the Italian market (Sample 3 or S3).

In ethylacetate fractions, the tannin molecules were identified and calibrated by using catechin and gallic acid, respectively, depending on the maximum of the UV absorbance. Reporting the total tannin concentrations, these are 37.4% (in S1), 34.9% (in S2), and 16.9 % (in S3), with respect to the total polyphenol content. Hydroxycinnamic acids are 47.9% (in S1), 60.0% (in S2), and 76.1% (in S3), of the total polyphenols. Flavonoids (two quercetin and two luteolin glycosides) are 14.7% (in S1), 5.1% (in S2), and 7.0% (in S3). Flavonoids were undetectable in raw extracts, according to the type of samples (S1, S2 and S3), considering the low levels of these molecules and in particular because the flavonoid content in dates decreases with ripening [19]. These antioxidants were then concentrated by using the Extrelut® fractionation method, and the ethylacetate fractions were evaluated by HPLC/DAD. The Extrelut® methanolic fractions were too rich of sugary compounds and, then, unsuitable for the HPLC analysis (the Brix degree of methanol fractions was in the range 43-45%). The concentration of flavonoids shown in Table 2 is consistent, in terms of order of magnitude, with that reported in the work [19], with the Medjool cultivar appearing richer of these molecules. In our samples, a higher concentration is registered for other antioxidants, for example the ferulic acid, confirming that this cultivar from the Palestinian area is particularly interesting from the point of view of the content of bioactive molecules and for its potential in the production of antioxidant extracts.

The concentration of total polyphenols on raw hydroalcoholic extracts was determined by Folin-Ciocalteu method. The different fruit samples presented a phenolic content in the range 157.08-197.56 mg/100 g of date weight (Table 3).

Table 1. Data about sample harvesting, plantation dimensions, date quality and yields.

	Famer 1	Farmer 2
Plantation size (hectare, ha)	8	15
Land in Area A (ha)	2	0
Land in Area B (ha)	0	7
Land in Area C (ha)	6	8
Palm/ha	117.5	133.3
Total number of palms	940	2000
Palm age (Average years)	9.9	11.8
Harvest in 2016 (t)	63	88
Yield in 2016 (t/ha)	7.87	5.86
Harvest in 2017 (t)	74	99
Yield in 2017 (t/ha)	9.25	6.6

Table 2. HPLC/DAD quali-quantitative analysis of single compounds and polyphenolic classes in ethylacetate fractions of *Medjool* date fruit pulps. Analyses were carried out in triplicate and data are average values $\pm$ SD expressed as mg/Kg.

Compounds	Sample 1	Sample 2	Sample 3
Gallic acid	17.53 $\pm$ 0.60	10.23 $\pm$ 5.19	5.81 $\pm$ 2.25
Siringic acid	1.46 $\pm$ 1.19	2.11 $\pm$ 0.66	0.95 $\pm$ 0.09
Tannins	12.33 $\pm$ 1.56	7.45 $\pm$ 2.26	5.83 $\pm$ 1.59
Ferulic acid	20.58 $\pm$ 0.14	20.02 $\pm$ 2.66	26.57 $\pm$ 3.09
Caffeic derivative	7.97 $\pm$ 3.30	5.75 $\pm$ 3.12	24.62 $\pm$ 0.05

<i>p</i> -Coumaric derivative	7.57 ± 0.36	8.31 ± 0.67	5.50 ± 0.61
Quercetin derivatives	7.12 ± 1.53	2.89 ± 0.92	5.23 ± 1.09
Luteolin derivatives	3.99 ± 1.24	ND	ND
Total polyphenols	75.48±6.12	56.77±12.92	74.48±13.65

Table 3. Total phenolic contents, efficient concentration (EC₅₀), and antiradical efficiencies (AE) of different Medjool date samples. Results are means ±SD (n=6).

	Total phenolic content ^A	EC ₅₀ ^B	AE ^C
<i>Date Flesh</i>			
Sample 1	175.71±15.04	167	0.59
Sample 2	157.08±16.84	285	0.35
Sample 3	160.34±13.41	267	0.37
<i>Date Seeds</i>			
Sample 1	1345.5±232.2	0.075	1333.3
Sample 2	1188.4±198.7	0.130	769.2
Sample 3	1057.2±187.5	0.122	819.6

^Amg gallic acid equivalents (GAE)/100 g date fruit (flesh or seed); ^BEfficient concentration (mg sample/mg DPPH): amount of date tissues to decrease the initial DPPH concentration by 50%; ^CAntiradical efficiency: (100/EC₅₀).

It is worth of noting that the date fruits drying methods have a great importance to maintain a high quality of these fruits. The optimal dates moisture content is 23-25%, and the most common drying treatments generally reach lower moisture amounts [20], affecting fruit color, firmness and nutrient concentration. In this study, the date fruits were analyzed immediately after sampling collection, hence, the dates have been drying while on tree. It is important to underline the importance of a natural drying process, which can be achieved with good agricultural practices and correct irrigation management, despite the natural drying that occurs during date ripening can cause a loss of antioxidants, as it can lead to oxidative degradation. Although determination on a dry weight basis may overcome the issue of moisture difference, fresh weight calculation was deemed to be more appropriate from a consumption viewpoint, and this clearly represents the nutritional benefits of these fruits. Moreover, the investigated samples correspond to marketable samples of dates, since Medjool dates were ready to be introduced in the market, without the necessity of additional drying processes.

The data obtained from DPPH test were considered from the point of view of the antioxidant efficiency of the sample, through the EC₅₀ parameter, which is independent of the sample concentration.

As reported in Table 3, the total phenolic content is very similar in the three samples, varying from 157 to 175 mg GAE/100 g of date fruits, nevertheless the AE (antiradical efficiency) of Sample A is 1.6-1.7 higher than that of samples B and C. A similar consideration can be made for the EC₅₀, which shows the lowest value in sample A. The higher antioxidant activity, the lower EC₅₀ value, then, the order of the activity is: Sample 3 < Sample 2 < Sample 1.

Since date sugar is a completely natural product, unrefined and free from additives or preservatives, we decided to compare the antioxidant power of date flesh hydroalcoholic extracts

with that of hydroalcoholic extracts of honey, the most well-known and widely used natural sugar substitute, previously analyzed by ours in the same analytical conditions [21]. The antiradical efficiency of date pulp extracts is 3 to 4 times greater than that of the honey samples. Only strawberry tree honey, renowned for its high tannin content, exhibits an EC50 value slightly exceeding that of Sample 1 in this study.

Concerning the antioxidant properties of date fruits reported in the literature, a previous investigation about seven varieties of Algerian dates shows that phenolic contents and antiradical efficiencies are highly correlated. All the Algerian varieties were found to contain mainly hydroxycinnamic and phenolic acids, and flavonoids, as flavones, flavanones and flavonol glycosides [22]. Another study, also on Algerian dates, reports the quantitative analysis of phenolic acids (gallic, ferulic, cumaric and caffeic acids) and flavonoids (isoquercetrin, quercetrin, rutin, quercetin and luteolin) and the correlation between the composition of the phenol classes with the antioxidant capacities [23].

Our results regarding phenol molecules are consistent with the findings of a study about Medjool dates from Egypt, which suggests that the concentration of tannins is strongly dependent on different climatic conditions [24]. It is interesting to point out that sample containing more flavonoids (Sample 1) shows the more relevant activity and antiradical efficiency. Several studies have confirmed that the antioxidant potential of date fruits is strongly correlated with their total phenolic and, particularly, the flavonoid content [25].

In our study, Plantation 1 is predominantly located between Areas A and C, while Plantation 2 is situated between Areas B and C. It should be noted that, in Palestine, Areas A, B, and C were established under the Oslo Accords to define different levels of administrative control: Area A is under full Palestinian Authority control, both for civil administration and security; Area B involves a division of responsibilities, where the Palestinian Authority manages civil affairs while Israel retains control over security; Area C, on the other hand, is fully controlled by Israel.

In Plantation 2, the palm trees are planted closer together, limiting adequate sunlight exposure to branches and leaves. In contrast, Plantation 1 features a more spaced arrangement of palm trees (Figure 3). The annual yield (t/ha) in Plantation 1 is higher than that in Plantation 2 (Table 1). This difference suggests that tree spacing may influence both yield and antioxidant properties. Concerning tree density, we can infer that the wider spacing of palm trees in Plantation 1 allows for better sunlight exposure—an important factor that likely stimulates a higher flavonoid content in the fruits. In fact, it is well known that light is one of the most important environmental factors affecting the plant biosynthesis of such UV-screening pigments [26]. The importance of flavonoid biosynthesis is particularly important in fruits, where a largest flavonol content, make the fruit less susceptible to pathogen attack, then improving the storage durability [27,28].



Figure 3. Plantation 1, where Sample 1 was collected, and Plantation 2, where Sample 2 was collected.

In this research, different date tissues (pulp and seeds) were studied. In general terms, date seeds are a valuable and abundant by-product (10-15% of date fruit weight), with interesting potential food applications, and possibly used as low-cost functional food ingredient [29]. At present, date seeds are mainly used for animal feeds in the cattle and poultry industries, but this vegetal matrix should be valued, because it contains molecules with important biological activities, such as procyanidin [11]. The occurrence of bioactive compounds, especially in non-edible fraction of fruits that are usually discarded, is the main reason for a revalorization of downgraded or wasted fruits as source of functional compounds for the proposal of innovative value-added products, in industrial application, such as food, food supplements and cosmetics [30,31].

In our study, date seed extracts of sample 1 were analyzed by HPLC and spectrophotometric methods. The HPLC qualitative analysis of date seed extracts shows the presence of phenolic molecules, mainly catechins and caffeic acid derivatives. Analogously to date flesh extracts, the quantitative evaluation of phenolics in date seed extracts was performed by Folin-Ciocalteu method. As reported in Table 3, the total phenolic content varies from 1057.2 to 1345.54 mg GAE/100 g of date seeds. These concentrations are in accordance with a previous paper that reports date seeds as one of the highest sources of total polyphenols, surpassing important antioxidant food items, such as tea,

grapes and nut seeds [32]. Our findings are also in agreement with those of a recent paper about date seed extracts obtained with environmentally friendly solvents [33]. Moreover, the reported polyphenol concentrations herein are an order of magnitude higher than those reported in a previous study on the Medjool date cultivar grown in Mexico [30], underlining the high influence of the territory of origin and the climate, on the characteristics of the product, and its functional properties. Finally, in Table 3 is worthy of interest the antiradical potential of date seed, being the antiradical efficiency of seed extracts about two thousand times higher of that of the corresponding date flesh extracts.

A recent work put in evidence the importance of by-products from the date industry, such as pastes and blanching water, which are rich in antioxidants like phenols and flavonoids, including in the Medjool cultivar. Their incorporation into food and nutraceutical products enhances antioxidant activity while promoting sustainability by reducing waste and adding value to the date supply chain [34]. Another study evidences that the underutilization of date seed extracts in human diets constitutes a substantial loss, due to their nutritional benefits, especially the bioactive compounds like flavan-3-ols and bound polyphenols [35]. Dates classified as B and C grade (i.e. destined to less value-added chains or for the domestic market) could be exploited as an excellent alternative to refined sugars obtained by grain products, as demonstrated by a previous study, reporting date sugar as a promising sugar substitute with antioxidant properties [36].

Sustainable processing and use of date processing by-products are in line with the circular economy approach as in a recent study [37], where the addition of a polyphenolic extract and fractions from date seed powder to enriched biscuits, improved their antioxidant properties and nutritional value, also maintaining consumer acceptance. In the future, by analyzing dates of other quality categories, such as dates of B and C grades, it should be possible to put in evidence, if any, their antiradical properties. Indeed, new solutions are requested or could be exploited using these fruits in food supplements or using dates and by-products as raw materials for new transformed or processed products.

3. Materials and Methods

3.1. Plant Material

Medjool dates (Samples 1 and 2) were supplied by two farmers of the Palm Farmers Cooperative Association. Farmer 1, with a plantation size of 80 dunam (i.e. 20 dunam placed in area A, 60 in area C, Palestinian West Bank administrative division) provided sample 1. Farmer 2, with a plantation size of 150 dunam (70 in area B, 80 in area C) provided sample 2. The samples have been collected at the final stage of fruit ripeness during the sorting procedures in September 2017. Additional information regarding the farmers (i.e. total number of palms and palms per hectare and 2017 yield) are reported in Table 1. The fruits were rapidly cooled after harvest and transported to Italy at 4°C.

Sample 3 was a packed commercial Medjool dates coming from the same area, taken from an Italian large scale retail trade. Samples of date seeds were also analyzed, following the same procedure applied for date flesh extracts.

The dates analyzed in this study were of premium quality (grade A). In the future, the results of this study could be further improved by analyzing dates of other quality categories, such as dates of B and C grades.

3.2. Extraction and Fractionation of Medjool Dates

The fruit pulps were manually separated from the seeds and immersed in liquid nitrogen for about 20 minutes, and then, ground into a fine powder in a mill (Model M20, IKA® - WERKE). The samples were analyzed in triplicate.

The seeds were first soaked in water, washed to remove any adhering date flesh, air-dried, and ground into coarse powder, using a hammer mill, analogously to fruit pulps.

For each sample, an amount of 16-20 grams of the powder was extracted with a volume of 100 mL of a hydro-alcoholic solution consisting of EtOH (ethanol) 70% and acidic water at pH 3.2 for

formic acid (30%). The extraction was carried out for a whole day, including the night. Subsequently, the extract was centrifuged at 5000 rpm for 5 minutes in a centrifuge with temperature control (18°C) to separate the hydroalcoholic supernatant from the solid residue.

A volume of 5 mL of hydroalcoholic extract was concentrated to a final volume of 1 mL with a rotary evaporator (Rotavapor 144 R, Büchi, Switzerland), and used for HPLC analysis. The remaining volume (95 mL) of each fruit pulp extract was concentrated to completely eliminate ethanol and subsequently deposited on Extrelut® cartridge (Merck, Darmstadt, Germany) by 20 cc, filled with an inert phase (diatomaceous earth). After 20 minutes of waiting, the following solvents were eluted, i) Hexane (about 40-50 mL), ii) Ethyl acetate (about 40-50 mL). iii) Methanol/Formic acid (45: 5) until the cartridge is completely discolored. The first fraction was eliminated, the second fraction was concentrated to dryness, and dissolved in 1.5 mL of the solvent CH₃CN / H₂O (pH 2 by formic acid) 1:1 (v/v), for HPLC/DAD analysis. The methanol fraction from Extrelut® was used for the evaluation of the sugar content (Brix degree) with a hand refractometer.

3.3. HPLC/DAD Analysis

The HPLC/DAD analyses were performed with an HP 1100L instrument equipped with an HP DAD (Agilent Technologies, Palo Alto, CA). In particular, the analytical column used was Luna C18 250×4.60 mm, 5µm (Phenomenex). The eluents were H₂O at pH 3.2 for HCOOH (solvent A) and acetonitrile (CH₃CN, solvent B). The following multi-step linear gradient was applied: from 100% to 75% of A in 15 min, which was maintained for 5 min; 5 min to reach 60% of A, which was maintained for 5 min; 5 min to arrive at 0% of A, which was maintained for 5 min, and then, 3 min to arrive at 100% of A. Total time of analysis was 43-min, flow rate 0.8 mL/min and oven temperature 27±0.5°C. A sample volume of 25 µL was injected into HPLC. The UV-Vis spectra were recorded in a range of 190-600 nm and the chromatograms acquired at 280, 315, 330 and 350 nm.

In order to calibrate the individual polyphenolic compounds, specific calibration curves ($R^2 \geq 0.998$) of 5-level of concentration were built using standard substances (98-99% of purity). In case of lack of the specific molecule, the calibration was carried out with compounds having similar chromophore, measuring the absorbance at the maximum UV absorption. In details, the amount of ferulic acid was calculated at 330 nm, using pure ferulic acid as a reference; caffeic acid derivatives were evaluated at 330 nm, using chlorogenic acid (5-O-caffeoylquinic acid) as standard; gallic acid and the other compounds (tannins) with similar chromophore were evaluated at 280 nm, using a standard solution of gallic acid; finally, the flavonoids were calibrated at 350 nm using pure standards (luteolin-7-O-glucoside and rutin).

3.3.1. Standards and Solvents

The pure standards used in the HPLC/DAD analysis were provided by Extrasynthese (Lyon, France) or by Sigma Aldrich Laborchemikalien (GmbH, Germany).

The solvents used for the chromatographic analysis are of a high degree of purity: acetonitrile, methanol (BDH Laboratory Supplies, United Kingdom), formic acid (ACS reagent).

The water used for the HPLC analysis comes from a Milli-Q Millipore system, (Bedford, MA, USA).

3.4. Estimation of the Phenolic Content by Folin-Ciocalteu Test

Total polyphenols were determined as follows: the hydroalcoholic date extract (125 µL) was mixed with 500 µL of water and 125 µL of Folin-Ciocalteu reagent and allowed to stand for 6 min; 1250 µL of a solution of sodium carbonate (7%) was added to the mixture. After 85 min, the absorbance of centrifuged samples was measured at 725 nm against water as a blank, by using a DAD 8453 spectrophotometer (Agilent Technologies). The amount of total phenolics is expressed as Gallic Acid Equivalents (GAE, mg gallic acid / 100 g of sample, on Weight basis), through the calibration curve of gallic acid. The calibration curve range was 20 - 500 µg/mL (R^2 0.9976).

3.5. Evaluation of Antiradical Activity by DPPH Test

The antiradical capacity of the hydroalcoholic extracts was estimated according to a previously reported procedure [38], with slight modifications. More specifically, the extracts were opportunely diluted and an amount equal to 1:1 added to an ethanol solution of DPPH (0.025 mg/mL). Measurements were carried out at 517 nm with a DAD 8453 spectrophotometer (Agilent Technologies) at time 0, after 15 sec, 30 sec, 45 sec, 1 min, 2 min and then every 2 min for the following 20 min. The antiradical activity (AR%) was calculated through the following relationship:

$$[AR\% = 100 (A_0 - A_{20})/A_0]$$

where A_0 and A_{20} were the absorbance of DPPH, at time 0 and 20 min., respectively, after adding the diluted extract. The EC_{50} of the extracts was determined through the use of five-point linearized curves [AR%-ln (concentration in polyphenols)], built determining AR% for five different dilutions of each extract and, then, by calculating the molar concentration in polyphenols of the solution that inhibits the DPPH activity to 50%.

The antiradical efficiency (AE) was calculated according to a previous paper [22] slightly modified, as follows: $AE = 100/EC_{50}$.

4. Conclusions

Despite challenges related to customs and logistics in date exports, the European market shows strong potential interest in importing dates produced in Palestine. Moreover, on an international scale, Medjool dates are regarded as a premium cultivar, renowned for their nutritional value and health benefits, which have also been validated by this study. A key objective for commercial date palm growers today should be to produce high-quality fruit with minimal pesticide residues and reduced water usage. This research aimed to enhance the local product, the Medjool date, as Palestinian farmers in the Jordan Valley seek to expand their plantations and to adopt good agricultural practices in order to enhance the yield and improve quality of their production.

The primary goal for Palestinian farmers is to access value-added markets, such as the European market, with high-quality dates, despite facing numerous challenges and threats stemming from the region's complex geopolitical situation and related issues. This study focused specifically on Grade A dates, which are intended to be sold as whole fruits, including to international markets such as Europe and Italy, thereby generating added value. However, as highlighted in this research, not only the fruits but also the seeds possess significant commercial potential. In particular, seed extracts, rich in bioactive compounds, can find applications in industries such as cosmetics, pharmaceuticals, and food supplements. These applications not only enhance the nutritional and antioxidant properties of products but also support sustainable practices by minimizing waste and increasing the value of the date supply chain, aligning with circular economy principles. A viable proposal for Palestinian farmers could involve the activation of two complementary supply chains. The first would focus on the production of high-quality Grade A dates for the European market, emphasizing premium quality and added value. The second would target the utilization of seeds, leveraging their antioxidant properties to develop extracts for various industries.

A similar strategy could also be extended to the Grade B and C dates. While these downgraded fruits (i.e. characterized by damage, smaller size, or less attractive appearance) may not meet the standards for direct consumption, they can be repurposed. Their tissues, seeds, or extracts can be processed into functional ingredients rich in bioactive compounds, further supporting sustainability and waste reduction. This dual approach not only diversifies income streams for farmers but also reinforces the resilience and competitiveness of Palestinian agriculture in international markets. By maximizing the value derived from both high-quality dates and their by-products, Palestinian farmers can create a more robust and sustainable supply chain that caters to multiple industries.

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