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Review Article

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The Potential Antioxidant Properties of Date Products: A Concise Update

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ABSTRACT

Background: Free radicals are highly unsteady reactive molecules containing one or more free electrons. These molecules can cause organ damage, disease and even death. *Phoenix dactylifera L*, commonly known as 'date palm' is one of the oldest cultivated plants. Date fruit is considered a source of antioxidants. **Objective:** This study aims to review the role of antioxidants in scavenging free radicals together with the functional properties of date fruit and their by-products. **Results:** The review shows that date fruits and their by-products, date syrup and date pits, are good sources of antioxidants. Phenolics, which are considered to be a good source of antioxidants, were found in dates and their by-products along with other antioxidant compounds such as carotenoids and flavonoids. **Conclusion:** Dates and their by-products have the potential to be used in the production of different types of functional foods due to their antioxidant properties.

Keywords: *Free Radicals, Antioxidants, Date Fruit, Date Syrup, Date Seed*

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INTRODUCTION

Date palm (*Phoenix dactylifera L*) is one of the most important fruit crops produced in hot desert regions, predominantly in South West Asia and North Africa. There are four main stages in the production of date fruit which are known by their Arabic names: Kimri, Khalal, Rutab, and Tamer. Dates are usually eaten at Rutab or Tamer stage (1-5). Dates are important because they are believed to be rich in nutrients and they are economical to produce in arid conditions. The fruit is also an important part of culture and tradition in the Middle East, where it is considered a staple food. (4). The date fruit is composed of two parts, the flesh and the seed (pits). The date pit represents 11-15 % of the total weight of the date fruit (6). Date pits are usually the waste of different value-added products of date fruit such as date juice and date syrups, where the seed or pit is removed from the flesh of the date and disposed of or converted into animal feed (2). However, date fruit, including the flesh and the seed, has many beneficial nutrients, particularly polyphenols which have been shown to have antioxidant properties (2, 4, 7). Antioxidants play an important role in scavenging free radicals that are produced in the body as a result of biochemical processes. Several studies have shown that free radicals are linked to many chronic diseases including heart disease, cancer and others (8). Antioxidant substances in food have been shown to reduce the effects of free radicals on the brain (9-16), the heart (17-21), diabetes (22), aging (23, 24), genetics (25), inflammation (26-28), cancer (29-32) gastrointestinal (33), and reproduction (34-37). On the other hand, date fruit and its functional properties have garnered the attention of different research groups (2-5, 38-41). Studies include date fruit composition, polyphenols extraction (2-5, 38-41), antioxidant properties against anti-inflammatory, anti-angiogenic and the antibacterial properties of date fruit including its impact on several other health conditions (42). The aim of this review is to highlight the antioxidant properties of date fruit and its by-products.

Free Radicals: Free radicals are unsteady, highly reactive molecules containing one or more free electrons. They are mainly produced in the mitochondria as part of metabolism through xanthine oxidase, peroxisomes, inflammation processes, phagocytosis, arachidonate pathways, ischemia, and physical exercise. The internal mechanism is not

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the only way to produce free radicals; external factors such as smoking, environmental pollutants, radiation, drugs, pesticides, industrial solvents and ozone also contribute to the formation of free radicals (8). Free radicals can be derived from oxygen (Reactive Oxygen Species ROS) or biosynthesized from nitrogen (Reactive Nitrogen Species, RNS) or from sulfur (Reactive Sulfur Species, RSS). ROS and RNS can be both radical reactive species and non-radical reactive species. The reactive species includes superoxide, hydroxyl, peroxyl, nitric oxide, and nitrogen dioxide. The non-radical reactive species includes hydrogen peroxide, hypochlorous acid, hypobromous acid, and peroxynitrite. RSS are formed from the reaction of ROS and thiols (17, 43-46). Free radicals have several roles in human and animal cells such as the generation of energy (in the form of adenosine triphosphate (ATP) from adenosine diphosphate (ADP)) through oxidative phosphorylation in the mitochondria; the detoxification of xenobiotic by oxidizing enzymes such as cytochrome P450; the apoptosis of effete or defective cells; killing micro-organisms and cancer cells by macrophages and cytotoxic lymphocytes and in oxygenases for the generation of prostaglandins and leukotrienes, which have many regulatory functions (8).

Even though free radicals play an important role in the body, ROS (and other reactive species) induced oxidation can be the main cause of cellular damage and death and may also lead to many degenerative diseases such as atherosclerosis, cancers, stroke, trauma, asthma, heart attack and others. This occurs because of an imbalance between the systemic manifestation of reactive oxygen species and the biological system's ability to readily detoxify the reactive intermediates or to repair the resulting damage. This phenomenon is called oxidative stress (17, 43-47).

Antioxidants: An antioxidant is any substance that when present at concentrations below those of their oxidizable substrate significantly delays or prevents the oxidation of that substrate. During human growth, the endogenous defense system will gradually evolve to maintain a balance between oxidative stress and the defense system. Antioxidant activity can act in various ways, for example inhibiting free radical oxidation reactions by preventing the formation of free lipid radicals; acting as singlet oxygen quenchers; reducing agents which produce stable compounds from hyperperoxide; acting as metal

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chelators and acting as inhibitors of pro-oxidative enzymes (17, 45, 47). Antioxidants can be classified into two categories, endogenous antioxidants and non-endogenous antioxidants. The endogenous antioxidants are classified into enzymatic antioxidants and non-enzymatic antioxidants. Examples of enzymes include catalase, glutathione peroxidase, superoxide dismutase, glutathione reductase and glucose-6-phosphate. Non-enzymatic endogenous antioxidants include some vitamins, enzyme cofactors (Q10), nitrogen compounds (e.g., uric acid), and peptides (e.g., glutathione) (17, 44). The endogenous antioxidants are not sufficient to scavenge all the free radicals produced in the body. Diet can provide humans with additional antioxidants such as vitamin C (ascorbic acid), vitamin E (tocopherols), vitamin K, carotenoids, flavonoids, phenolic acids, selenium and zinc (43, 44).

Date Fruit: *Phoenix dactylifera* L, commonly known as 'date palm' is one of the oldest cultivated plants. The most important part of the tree is the date fruit. It is a valuable fruit in all Asian, Middle Eastern, and North African countries. The chemical composition of fresh and dried dates is shown in Table 1. The main components of date fruit are carbohydrates (mainly glucose and fructose); protein and fats are generally found in low concentration. Dates provide an average of 213 Kcal per 100g and this increases with dried dates. Dates are rich in minerals and vitamins. A 100g of dates can provide over 15% of the recommended daily allowance for certain minerals. B-complex vitamins and vitamin C are considered the major vitamins in fresh dates. Moreover, the fruit is high in fiber as it contains about 8% of dietary fiber. In addition, dates are a good source of antioxidants, mainly phenolic, flavonoids and carotenoids (2-5, 38-40).

Antioxidants in Date Fruit: The main antioxidants found in date fruit are polyphenols and carotenoids. According to Abu-Reidah et al., (55), around 52 phenolic compounds have been identified in date fruit, mainly flavonoid glycosides of quercetin, luteolin, apigenin, chrysoeriol, kaempferol, isorhamnetin, 3-methyl-isorhamnetin, sulfates, and malonyl derivatives. Among them, 30 phenolic derivatives were discovered for the first time in dates, for example kaempferol glycosides and malonyl.

The effect of date extracts on different diseases has been studied by many researchers and scientists around the globe. These diseases include cancer (41, 56, 57) oxidative stress

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(58, 59) inflammation (42, 57, 60), liver and kidney diseases (61-63). Kehili et al., (64) have studied the anti-inflammatory effect of Algerian date fruits in mice. A significant decrease was observed in the edema size, the level of homocysteine in the blood and in CRP values compared to the control group. Vayalil (65) has studied the antioxidant and anti-mutagenic properties of the aqueous extract of date fruit and found that it can inhibit superoxide and hydroxyl radicals, lipid peroxidation, and protein oxidation via free radical scavenging.

Phenolic Acids Content: The phenolic compounds that are found in date fruit are free phenolic acids, namely protocatecoic acid, vanilic acid, syringic acid, and ferulic acid; and bonded phenolic acids mainly gallic acid, protocatecoic acid, p-hydroxy benzoic acid, vanillic acid, caffeic acid, syringic acid, p-coumaric acid, ferulic acid, and o-coumaric acid, sinapic acid, rutin and trans-cinnamic. The major phenolic acids in date fruits are ferulic, vanillic, and syringic compounds (2, 3, 7, 50, 66-68). In dried dates, the phenolic compounds increase during the drying process due to the degradation of tannins by heat and enzymes, which leads to the release of phenolics (2, 3).

Flavonoids Content: Different kinds of flavonoids are found in date fruit. These flavonoids are flavanes, flavones, flavanones, and flavonol glycosides (luteolin, methyl luteolin, quercetin, and methyl quercetin), anthocyanins (cyanidin 3-glucoside (68-71). However, flavanes decrease and anthocyanins are lost during ripening and storage because they are susceptible to enzymatic browning (3, 50, 72). Flavonoids and phenolics are considered the most effective antioxidants. Phenolics are considered effective inhibitors of lipid peroxidation due to their metal-chelating and radical-scavenging properties (65, 73).

Carotenoids: Date fruit also contains carotenoids such as lutein, β-carotene, and neoxanthin. Carotenoid values vary due to differences of variety, maturation, drying, and analytical methods. The highest content of carotenoids is in the ‘khalal’ stage because of its yellow color. However, the carotenoid content decreases in the ‘tamer’ stage due to the drying process and enzyme activity (3, 50).

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Extraction Methods: Different solvents have been used to extract different kinds of antioxidant compounds. These solvents can release antioxidant compounds from the date fruit matrix. The solvents used include ethanol (74), methanol (75), HCL (76), water (77) and others. It was found that more phenolic compounds were obtained using water as a solvent than alcohol (78). However, there are other factors that affect the extraction efficacy other than the type of solvent. These factors include the concentration of the solvent, the time of extraction, the temperature and the method used for extraction. Al udhaib (79) studied the effect of different solvent types, ratios, concentrations, reaction temperatures and reaction times on the yield of antioxidant compounds specifically phenolic and flavonoids in the Ajwa date. Their findings show that acetone produces a higher extraction of antioxidant compounds than ethanol, with a three-hour reaction time at 65°C, a sample-solvent ratio of 1:20 and 75% acetone. However, Kchaou, Abbes (7) found that 50% ethanol extracted the highest number of phenolic compounds in date fruit. In addition, the extraction methods used to quantify the phenolic compounds are important. According to Kchaou et al., (82), the phenolic content estimated by the High-Performance Liquid Chromatography (HPLC) method was much lower than that determined by the Folin–Ciocalteu method (82). This could be due to the presence of chemical groups of amino acids and proteins that may react with the Folin–Ciocalteu reagent, and to limitations pertaining to the standard phenolic compounds. Overall, the method of extraction and quantification has a significant effect on the final yield resulting from a specific method.

Table 2 shows the antioxidant compounds and antioxidant activity of different varieties of dates. The differences in antioxidant compounds may result from the extraction methods and solvents used. Furthermore, these differences may be due to the variety of the date, the ripening stage, the location of collection, the storage time and the drying method (2-4, 50, 69, 80, 85-88).

Date Syrup: Date syrup is one of the major date fruit products. Due to the excess production of date fruit and its limited marketing and industrial uses, it is more feasible to produce date syrup as it can be stored for longer periods and used as an ingredient for different products. Date syrup is used in products such as breads, dairy products and

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others. The composition of date syrup (dry basis) is similar to that of date fruit. The only difference is the moisture content which is lower (approximately 16%) because of the evaporation of moisture needed to produce syrup with high a soluble solid (89). Date syrup can be made either by traditional or industrial processes. The traditional process relies on stacking bags of dates on top of each other. Over a period, most of the date syrup naturally oozes out. The industrial process involves adding water to the dates followed by blending, filtration and finally the evaporation of excess water using heat. The process has some advantages, for example a reduced extraction time and the ability to produce syrup with a consistent concentration of total solids. However, heating may cause changes in the quality of the syrup such as a darker color (61, 90). There are ways to counteract this by using enzymes such as pectinases and cellulose with a specific ratio of date to water (91, 92).

In date syrup there are less phenolic compounds and flavonoids than in the flesh of the fruit (Table 3). This might be due to the extraction method particularly when using thermal extraction, which can lead to the loss of these compounds (93). Moreover, the antioxidants in date syrup are affected by processing conditions (Table 3). According to Abbes, et *al.*, (61) the antioxidant activities and total phenolic contents in date syrup are greater when processed at lower temperatures, for example (60˚C).

Furthermore, Ganbi and Hassan (93) have compared extraction methods and found that date syrup prepared after extraction with pectinase and cellulase enzymes mixture has the highest flavonoid contents while ultrasonic extraction produces the highest phenolic and antioxidant activity. These enzymes hydrolyze cellulose and pectin components which help to release the antioxidant compounds, leading to an increase in the phenolic compounds (92-94). The high efficiency of the ultrasonic extraction is due to the effect of ultrasound waves which cause the cell wall to collapse and release antioxidant compounds (93, 95). Date syrup can thus be considered a good source of antioxidants, as confirmed in the study by Taleb and others (76). The study showed that polyphenols in date syrup reduce angiogenic responses such as cell migration, tube formation, and matrix metalloproteinase activity. The study used an inflammatory model, showing anti-inflammatory activity mediated by vascular endothelial growth factor (VEGF) and the

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prostaglandin enzyme cyclooxygenase-2 (COX-2) in endothelial cells when a certain amount of date syrup polyphenols was injected into to them. The results showed that date syrup polyphenols at 60 and 600μg/mL reduced inflammation and suppressed several stages of angiogenesis, including endothelial cell migration, invasion, matrix metalloproteinase activity, and tube formation, without evidence of cytotoxicity. It also significantly reduced VEGF and COX-2 expression induced by tumor necrosis factor–alpha at both gene expression and protein level, compared to the control **(76)**. Al-Khusaibi et al (97), compared the antioxidant properties of fresh and old date syrup. 1, 1-diphenyl-2-picrylhydrazyl (DPPH) and Folin-Ciocalteu's tests were used to measure antioxidant activity and total polyphenolic contents. The results of the study showed that both date fruit and old syrup had significantly higher polyphenolic contents in the Folin-Ciocalteu's assay and in reductive activities in DPPH radicals, confirming the natural antioxidant properties of date fruit and syrup. The study recommended that underutilized old dates be used as syrup-rich, natural antioxidants in the food industry during food processing.

Date Pit: Pits are the waste of different value-added products of date fruit. Pits are commonly disposed of as waste products or converted into animal feed. (2). However, studies show that date pits have many beneficial nutrients. They are a very rich source of dietary fiber, phenolic and antioxidants. Date pits should therefore be considered an inexpensive source of dietary fiber and natural antioxidants (98, 99) Date pits are mainly composed of carbohydrates while moisture, protein, sulfate and ash content is low. However, the antioxidant compounds in date seed were higher compared to the date flesh and date syrup as shown in Table 4.

Pit extracts can be effective in scavenging free radicals and in relation to certain diseases (100-106). Hasan and Mohieldein (101) have investigated the effect of date pit extracts on diabetes by using rats induced with diabetes; the rats were given a certain amount of date pit extract every day and subjected to certain clinical analyses such as weight, blood glucose levels on a weekly base for eight weeks (101). The results show that the aqueous seed extract leads to a significant reduction of blood glucose levels in diabetic-compared control rats.

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CONCLUSION

Free radicals are reactive molecules with one or more free electrons. These free radicals can cause damage to organs resulting in chronic diseases. Antioxidants are substances that delay or prevent the oxidation of a substrate. The review showed that date fruits and date by-products, such as date syrup and date pits, are good sources of antioxidants specifically phenolic and flavonoids found in fruit and date syrup and phenolic compounds found in date pits. These antioxidants are extracted by using different solvents to release the antioxidant compounds from the date fruit. The efficacy of these solvents depends on concentration, time, and reaction temperature. Antioxidants showed effectiveness in different studies, which indicates that dates and their by-products have the potential to produce different types of foods and functional foods.

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Table 1 Chemical composition of fresh and dried date (2, 48-54)

Parameter	Fresh date fruit	Dried date fruit
Moisture g/100 g	37.6-50.4	1.9-34.2
Carbohydrate g/100 g	47.8-58.8	54.0-83.1
Fructose g/100 g	13.6-24.1	16.5-48.5
Glucose g/100 g	17.6-26.1	18.3-52.3
Dietary fiber g/100 g	6.9-8.6	1.9-8.4
Protein g/100 g	1.1-2.0	1.5-4.7
Fat g/100 g	0.1-0.2	0.1-0.7
Ash g/100 g	1.0-1.4	1.5-3.9

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Table 2 Antioxidant compounds and antioxidant activity of different varieties of dates

Varieties	Flavonoids mg/100 g	Phenolics mg/100 g	Total Carotenoids μg/100 g	ORAC μmol trolox/ 100g	Inhibition of DPPH %	References
Fresh Fardh	-	34.6±0.2	-	-	40.1-58.5[a]	(80)
		280	1390	1738	-	(50)
Fresh Khasab	-	35.8±0.1	-	-	32.9-62.6[a]	(80)
		167	1310	1169	-	(50)
Fresh Khalas	-	32.2± 0.2	-	-	26.7-70.6[a]	(80)
		134	3030	2060	-	(50)
Bunarinja	-	34.9±0.2	-	-	43.0-64.7[a]	(80)
Mabseeli	-	246±8.3	-	150±3.4	-	
Um-sellah	-	186±13.3	-	146±5.6	-	(7)
Shahal	-	172±6.6	-	162±5.9	-	
Fardh	-	343	1200	999	-	
Khasab	-	217	900	821	-	(50)
Khalas	-	339	2900	1254	-	
Mech Degla	45.1±2.5	277.3±8.5	-	-	60.2±0.1	(81)
Deglet Ziane	33.0±1.6	288.7±8.1	-	-	60.4±1.4	(81)
Deglet Nour	58.9±2.1	240.4±1.1	4.02±0.45[b]	-		(82)
Deglet Nour	15.2±0.5	225.6±9.7[a]	-	-	60.0±1.4	(81)
Deglet Nour	-	230.9±0.2	-	866.8±28.8	-	(83)
Deglet Nour	-	6.7±0.3	-	-	-	(69)
Thouri	21.9±0.7	255.8±8.6	-	-	32.4±1.3	
Sebt Mira	231.7±7.3	858.7±25.1	-	-	82.4±0.8	
Ghazi	299.7±5.9	954.6±6.9	-	-	86.0±1.4	
Degla Beida	72.8±3.8	331.3±10.1	-	-	67.8±3.0	(81)
Arechti	153.9±6.8	947.6±25.3	-	-	76.6±0.8	
Halwa	133.7±4.1	562.1±12.3	-	-	79.1±2.0	
Itima	19.6±0.9[a]	229.9±6.4	-	-	52.2±1.8	

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Con…Table 2 Antioxidant compounds and antioxidant activity of different varieties of dates

Varieties	Flavonoids mg/100 g	Phenolics mg/100 g	Total Carotenoids μg/100 g	ORAC μmol trolox/ 100g	Inhibition of DPPH %	References
Allig	213.8±1.5	505.5±3.4	8.1±0.2[b]	-	-	(82)
Allig	-	447.7± 14.0	-	891.3±75.8	-	(83)
Bejo	150.1±0.7	391.9±5.2	12.4±0.6[b]		-	(82)
Tazizaout	-	2.5±0.1	-	-	-	
Ougherouss	-	2.8±0.4	-	-	-	
Akerbouche	-	3.55±0.33	-	-	-	(69)
Tazerzait	-	3.9±0.4	-	-	-	
Tafiziouine	-	4.6±0.4	-	-	-	
Tantbouchte	-	8.4±0.6	-	-	-	
Ajwa	-	455.9±6.9	-	-	2.6-3.8[a]	
Sukari	-	377.7±6.4	-	-	4.1-4.3 [a]	(78)
Khalas	-	238.5±10	-	-	6.6-9.1 [a]	
Fardh -Rutab	66±0.2	178±0.2	-	-	65	
Khasab-Rutab	46±0.4	116±0.7	-	-	62.5	
Khalas- Rutab	19±0.3	81±0.6	-	-	63.4	(84)
Fardh-Tamr	34±0.6	235±0.3	-		72.7	
Khasab-Tamr	27±0.7	194±0.4	-		69.5	
Khalas- Tamr	25±0.1	231±0.4	-		72.1	
Boufgous	84.4±2.9	506.8±23.9	-		3.4±0.1[b]	
Bouskri	68.9 ±2.1	331.7±13.2	-		6.3± 0.1[b]	
Bousrdon	188.6±4.5	537.1±19.3[a]	-		3.1±0.2 [b]	
Bousthammi	85.1±10.0	441.9±29.8	-		4.8±0.1 [b]	(53)
Bouzgagh	136.9±2.3	493.0±21.3[b]	-		3.8±0.1[b]	
Jihl	208.53±4.51	495.3±20.5	-		2.1±0.1[b]	
Majhoul	77.73±3.65	398.2±21.6	-		5.3±0.2[b]	
Najda	142.89±2.34	525.957±17	-		2.9±0.3[b]	

Means ±Standard deviation
[a] DPPH in mg/ml
[b] DPPH g of date/l

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Table 3 Antioxidant compounds and antioxidant activity of different date syrups

Varieties	Total flavonoids mg/100g	Phenolics mg/100 g	Total Carotenoids μg/100 g	ORAC μmol trolox/ 100g	Inhibition of DPPH %	References
Date syrup	-	-	-	-	-	
Mabseeli	-	162.0±10.4	-	84±0.9	-	(7)
Um-sellah	-	14.0±9.3	-	174±6.6	-	
Shahal-	-	96.0±2.3	-	106±0.2	-	
Deglet Nour	-	461.2±7.9	-	-	-	(92)
Allig	-	356.4±10.2	-	-	-	
Kentichi	-	400.5±4.6	-	-	-	
Rotab	554.0±8.7	769.6±7.2	-	-	88.6-94.0	(96)
Iragi	310.5±2.8	434.3±1.8	-	-	67.9-61.5	
Saudi	372.7±1.7[b]	600.3±4.0	-	-	75.8-94.3	
Processing method	-		-	-	-	
Water bath	13.9±0.5	66.0±5.2	-	61.49±.90	-	(93)
Magnetic stirring	15.3±0.6	69.9±4.8	-	67.9±3.7	-	
Enzymatic extraction	21.7±0.9	80.5±5.1	-	88.2±5.6	-	
Microwave extraction	17.7±0.7	83.6±4.9	-	79.4±4.8	-	
Ultrasonic extraction	20.9±1.0	89.1±6.1	-	91.1±6.3	-	
Deglet Nour conc at 100°C	41.4±0.7	293.0±1.6	0.110± 0.002	-	58.0±0.5	(90)
Deglet Nour conc at 60°C	43.9±0.2	217.9±3.5	0.117±0.001	-	70.2±0.5	
Kentichi conc at 100°C	106.1±0.5	376.8±7.0	0.128±0.007	-	30.5±0.23	
conc at 60°C	126.5±0.9	284.8±8.8	0.138±0.005	-	33.8±0.2	
Allig conc at 100°C	74.5±0.6	369.1±10.4	0.147±0.003	-	35.4±0.9	
Allig conc at 60°C	79.9±1.1	270.6±1.2	0.156±0.002	-	44.7±0.6	

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Table 4 Antioxidant compounds and antioxidant activity of different date pits

Varieties	Phenolics mg/100 g	ABTS (µmole TEAC/100 g DW)	ORAC µmol trolox/ 100g	Inhibition of DPPH %	References
Mabseeli	4430 ± 297	-	580±29	-	(7)
Um-sellah	4293 ± 1.80	-	903±46	-	
Shahal-	3102 ± 58	-	929±24	-	
Sukari	6150	15755	-	-	(104)
Khalasa	4712	14155	-	-	
Soughi	4.65	-	-	78.43[a]	(105)
Monaif	3.66	-	-	78.03 [a]	
Soulag	4.50	-	-	78.21 [a]	
Soukari	3.71	-	-	78.33 [a]	
Barhi	1.98	-	-	79.94 [a]	
Khalas	4.05	-	-	78.88 [a]	
Rozaiz	3.21	-	-	78.11 [a]	
Boufgous	2.69±0.04[b]	4.8± 0.06[c]	-	0.17±0.01[d]	(106)
Bousthammi	5.34±0.07[b]	8.01±0.08[c]	-	0.11±0.01[d]	
Majhoul	3.08±0.04[b]	5.29±0.13[c]	-	0.133±0.01[d]	

[a] mg/ml
[b] g GAE/100 g DW
[c] mmol TE/100 g D
[d] g/L

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