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COMPARATIVE STUDY OF THE PHYSICOCHEMICAL CHARACTERISTICS AND ANTIOXIDANT ACTIVITY OF THREE DATES VARIETIES (*PHOENIX DACTYLIFERA* L.) GROWN IN ALGERIA

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Abstract

This work aimed to study the morphological and physicochemical characteristics and antioxidant capacity of three cultivars of dates: Mech-Degla, Degla-Beida and Deglet-Nour. Duncan's test ($p<0.05$), brought out significant differences between the whole weight, the length and the ratio pulp/seed of the three varieties. The physicochemical composition showed the richness of the fruit in total sugars (63.06-69.29% fresh weight), with relatively low moisture content (9.58-11.98 % fresh weight), protein contents ranged between 1.95 and 3.95% and ash varied from 2.14 to 2.50 % of dry matter. The mineral profile of dates showed that potassium is the major component (714.27-897.31 mg/100g dry weight). Significant differences ($p<0.05$) were observed on dry matter content, pH, reducing sugars, proteins, calcium and copper between the varieties of dates studied. Moreover, dates contain polyphenols varying from 116.74 to 189.60mg of gallic acid equivalents (GAE)/100g fresh weight. Their antioxidant capacity was examined by the radical DPPH (2,2-Diphenyl-1-picrylhydrazyl). It varied between 89.73 and 93.41%. Therefore, dates are considered a good source of natural antioxidants which have benefits to human health. Statically, Pearson correlation ($p<0.05$) showed there were positive correlation ($r=0.51$) between total phenolic compounds and antioxidant activity. These results revealed that date fruits have a high nutritional value.

Keywords: Date fruits, characterization, polyphenols, antioxidant property, functional food, biodiversity.

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1. INTRODUCTION

The date palm (*Phoenix dactylifera* L.) is an important cultivar in the desert regions of North Africa and Middle East. It plays an important ecological and socio-economic role. Algeria is the 4th largest dates producer (FAO, 2012) with a rich gene heretage of up to 940 cultivars (Hannachi et al., 1998) and an annual production of about 789357 tons in 2012 (FAO, 2012). Date is indeed an excellent food with a high nutritional value and calories. It contains an average of 40 to 88% sugars, depending on the variety type, proteins (2.3-5.6%), fat (0.2-0.5%), ash (1-1.9%), fibers (6.4-11.5 %), vitamins (C, B_1, B_2, B_3 and A), organic acids and polyphenols (Booij et al., 1992; Barreveled, 1993; Al- Shahib and Marshall, 2003; Al-Farsi et al., 2005a, Mansouri et al., 2005; Baliga et al., 2010).

Besides, the nutritional value and biochemical aspects, date fruits possess biological and pharmacological properties such as antimutagenic, antioxidant, anticancer, anti-inflammatory, antimicrobial and gastroprotective activities. The compounds thought to be responsible of these properties include minerals, vitamins and other phytochemicals such as polyphenols and fibers (Baliga et al., 2010).

The phenolic compounds possess free radical scavenging, antioxidant and antimutagenic activities. They have an effect on the prevention of various chronic diseases such as cancer, Parkinson's diseases and atherosclerosis (Ndhlala et al., 2007; Ben Thabet et al., 2009).

Dates are a substantial business activity, in particular the famous 'Deglet-Nour' variety. The latter is solely marketeds in the national and international market. The other varieties,

called common dates are downgraded. This situation has created new agricultural trends and prompted farmers to culture Deglet-Nour variety, exposing the other varieties to danger of disappearing. In addition, dates are products which could be processed into various foods and non foods products with a high added value and easily marketable. Among such products: yeast, juice, syrup, vinegar and alcohol (Nancib et al., 1997; Espiard, 2002; Cheikh-Rouhou et al., 2006; Al-Farsi et al., 2007; Benamara et al., 2008).

Thus, the aim of this work is to study the morphological, physicochemical and antioxidant activity of dates in order to assess their qualities.

2. MATERIALS AND METHODS

A. Plant material

The selected dates for this study were: Mech-Degla, Degla-Beida and Deglet-Nour. They were originated from Algerian south east palms. These fruits were collected at "tamar stage" (full ripeness) and stored at 4°C until analysis.

B. Analytical Methods

a. Morphological characterization of dates

The morphological characteristics of dates were done on 20 fruits. The following characterizations were estimated:

- The dimensions of the entire fruit and its seed (length and width) using a electronic digital caliper with precision of 0.01mm.
- The weight of the entire date, pulp, and the seed using an analytical balance with precision of ± 0.0001mg.

b. Physicochemical characterization of dates

The moisture content was determined by drying a sample of dates in a vacuum oven at 70 ± 2 ° C until constant weight was reached (Reynes et al., 1994). The pH was determined according to AFNOR (1982) official method, using a pH meter type HANNA HI 2210. Sugars were extracted from date fruits (1g) with 70 ml of distilled water for 30 min. The extract was then filtered. Total sugars were determined by phenol-sulfuric acid reaction (Dubois et al., 1956) using a spectrophotometer (UV-VIS, Shimadzu). Reducing sugars were obtained using the acid method dinitrosalycilique (DNS) (Miller, 1959). The sucrose content was deduced by the difference between total sugars and reducing sugars. The protein content were determined by Kjeldahl method (AOAC, 1998), using a conversion factor of 6.25. The total ash was measured by the AOAC (1995). Minerals were determined according to the AOAC standards (1995), using an atomic absorption spectrometer (Perkin-Elmer AAnalyst 100) after nitro acid digestion (HNO_3:1M) and appropriate dilution.

Color was measured using a Color reader, Minolta CR 10 (Minolta Camera, Japan). Results were expressed according to CIELAB system (L^*, a^* and b^*).

c. Extraction and determination of polyphenols

The extraction of phenolic compounds was performed as follows: one gram of dates was crushed and macerated in 40mL of methanol with continuous stirring for 24 hours. The mixture was filtered through a standard filter paper. Then, the filtrate was evaporated to remove the methanol using a rotary evaporator, type: Heidolph.

The total polyphenols were determined using the method described by Meda et al. (2005): 500µL of dates extract were added to 2.5mL of Folin-Ciocalteu reagent (0.2N). The mixture was stirred for 5 min, then neutralized with 2mL of Na_2CO_3 (7.5%). The mixture was incubated during 1 hour at room temperature and in darkness. Then, the absorbance was performed at 760nm.The total phenolic content was expressed as mg gallic acid equivalents (GAE) per 100g of fresh weight.

d. Determination of antioxidant activity by DPPH radical

DDPH test is one of the most used methods to explore the antioxidant property.The method is based on the reduction of alcoholic solutions of DPPH (2,2-Diphenyl-1-picrylhydrazyl) in the presence of antioxidants in the reaction medium.

To 250µL of methanol extract, was successively added 1.75mL of methanol and

0.5mL of the solution of DPPH (0.2mmol). The mixture was placed in darkness at room temperature for 15min, then its absorbance was measured at 515 nm. A control sample, free from dates extract was prepared under the same conditions. The inhibition of the oxidation of DPPH was calculated using the following equation:

$$\text{Inhibition (\%)} = [(A_0 - A_1)/A_0] \times 100 \quad (1)$$

Where A_0 is the absorbance of the control and A_1 is the absorbance of the sample.

C. Statistical analysis

All analysis were determined in triplicate. Results were expressed as mean ± SD. Statistical analysis was performed using the software XLSTAT version 11.1.01 (Microsoft Office® 2009). The Duncan's test was usedto evaluate the significance differences between mean values, at the level of $p < 0.05$.

3. RESULTS AND DISCUSSION

A. Morphological characterization of dates varieties

Results of the physical properties of dates are presented in Table 1. Duncan's test revealed that the three dates varieties differed significantly ($p< 0.05$) for the entire weight of the fruit and the seed (Table 1). The weight of the date Deglet-Nour is heavier compared to Mech-Degla and Degla-Beida. In comparison with values cited by Mohammed et al. (1983), for Tamar-stage fruits weights for 50 dates varieties grown in Iraq were 2.01-17.00 g. The three studied dates, with fruit weight of 5.12-6.63g, could be classified as low or small varieties.

The weight of the of date pulp Deglet-Nour, is the highest (5.88g), with a significant difference ($p< 0.05$), compared to the weight of date pulp Degla-Beida and Mech-Degla, which is 4.15 and 4.65g, respectively. The weight of the date pulp Mech-Degla is the smallest one. These findings are similar to those of two Omani varieties (Sun dried dates varieties): Sellah and Um-Shahal, which are 3.85 and 4.97g, respectively (Al-Farsi et al., 2007).

The length of the dates are between 33.82 and 37.60mm. Widths are within the limits of 17.44 and 17.71mm, with a non significant difference ($p< 0.05$).These dimensions are similar to those reported in the literature (Amira et al., 2011). Fruits of Mech-Degla variety were the smallest in size, while those of Deglet-Nour and Degla-Beida were slightly higher but similar in size.

A significant difference is observed for the ratio: pulp/fruit, for the three dates varieties. This ratio highlights that Deglet-Nour is the highest one with a value equal to 88.65%. The ratio is only 77.38 and 80.90%, respectively for Mech-Degla and Degla-Beida. These values are in agreement with the results reported by Chibane et al.(2007) for the same varieties Degla-Beida and Mech-Degla, 79.15 and 82.77%, respectively. Amira et al. (2011) cited a ratio ranged between 86.75-92.25% for Tunisian dates varieties (Alig, Degla, Deglet-Nour, Gosbi and Horra). Differences between dates weight and dimension could be due to variety, soil, climatic and storage conditions.

Table 1. Morphological characteristics of dates varieties

Parameters	Mech-Degla	Deglet-Nour	Degla-Beida
Weight of date (g)	5.12 ± 0.65[a]	6.63 ± 1.07 [b]	5.99 ± 1.12 [c]
Weight of pulp (g)	4.15 ± 0.56 [a]	5.88 ± 0.99 [b]	4.65 ±0.97 [a]
Weight of seed (g)	0.97 ± 0.16 [a]	0.74 ± 0.16 [b]	01.34 ± 0.27 [c]
Length of date (mm)	33.82 ± 2.15 [a]	37.07 ± 2.51 [b]	37.60 ± 3.75[b]
Width of date (mm)	17.44 ± 0.86 [a]	17.71 ± 1.30 [a]	17.51 ± 1.35[a]
Ratio pulp/fruit (%)	80.90 ± 0.02 [a]	88.65 ± 0.02 [b]	77.38 ± 0.03[c]

All values given are means of twenteen determinations (n=20). Means in line with different letters are significantly different ($p< 0.05$).

Table 2. Physicochemical characterization of three dates varieties

Parameters	Mech-Degla	Deglet-Nour	Degla-Beida
Moisture (%)	11.98 ± 0.11 [a]	09.59 ± 0.10 [b]	11.63 ± 0.03 [c]
Dry matter (%)	88.01 ± 0.11[a]	90.41 ± 0.10 [b]	88.36 ± 0.03 [c]
pH	05.52 ± 0.00 [a]	05.30 ± 0.00 [b]	05.00 ± 0.00 [c]
Total sugars[1] (%)	63.10 ± 0.66[a]	69.29 ± 2.17 [b]	63.06 ± 0.87 [a]
Reducing sugars[1] (%)	14.29 ± 0.39 [a]	20.02 ± 0.22 [b]	46.27 ± 0.40 [c]
Sucrose [1](%)	48.80 ± 0.67 [a]	49.26 ± 2.36 [a]	16.79 ± 1.08 [b]
Proteins [2] (%)	01.95 ± 0.06 [a]	03.29 ± 0.02 [b]	03.95 ± 0.06 [c]
Ash[2] (%)	02.14 ± 0.07 [a]	02.50 ± 0.03 [b]	02.47 ± 0.01 [b]
K [2] (mg/100g)	714.27 ± 43.37 [a]	897.31 ± 10.92 [a]	798.32 ± 85.73 [ab]
Mg [2] (mg/100g)	38.53 ± 3.35 [a]	53.28 ± 3.65 [b]	43.84 ± 3.26 [a]
Ca [2] (mg/100g)	24.46 ± 0.10 [a]	21.31 ± 0.09 [b]	17.52 ± 1.04 [c]
Na[2] (mg/100g)	07.16 ± 0.72 [a]	08.39 ± 1.16 [a]	82.67 ± 3.02 [b]
Cu [2](mg/100g)	0.85 ± 0.007 [a]	0.99 ± 0.03 [b]	0.64 ± 0.01 [c]

All values are means of three determinations. Means in line with different letters are significantly different ($p < 0.05$).
[1]: on a fresh weight basis/ [2]: on a dry weight basis.

B. Physicochemical characterization of date pulp

The physicochemical characteristics of date pulp are presented in Table 2. Differences between biochemical composition of date fruits depend on several factors such as variety, soil conditions, agricultural practices, irrigation and environmental factors (Youssif et al., 1982; Booij et al., 1992; Ismail et al., 2006; Al-Farsi et al., 2007; Amira et al., 2011).

The moisture content of dates is between 9.58 and 11.98%, with a significant difference ($p<0.05$). These values are almost similar to those cited by Al-Hooti *et al*. (2002), with values of 11.53 and 11.55% for two Saudian varieties: Safri and Saudi Birhi, respectively.

The studied dates were characterized by the predominance of sugars. The rate of total sugar varies from 63.06 to 69.29% of the fresh weight. These levels show the richness of sugars in these dates with a significant difference ($p< 0.05$) between Deglet-Nour and the other two varieties Mech-Degla and Degla-Beida. Mohain Jain et al. (2011) reported that sugars ranged between 44 and 88%. The major fraction of sugars is mainly sucrose for the two varieties Mech-Degla and Deglet-Nour, with composition of 48.80 and 49.25%, respectively (not significant). However, Degla-Beida variety is characterized by high reducing sugars 46.27% (Table 2), with a significant difference comparing to the other two varieties. The high reducing sugar content of Degla-Beida dates appears to be due to invertase activity (enzymatic inversion of sucrose into glucose and fructose) during maturation (Barreveld, 1993; Cheikh-Rouhou et al., 2006; Awad et al., 2011).

The pH of dates is between of 5.00 and 5.52, with a significant difference ($p< 0.05$). These results partly confirm those given by Chibane et al. (2007), which are 5.05 and 5.54, respectively for the Algerian varieties: Degla-Beida and Mech-Degla. In comparison to other varieties, these results are similar to the pH of two Emirati varieties: Gash Gaafar and Bushibal, with values of 5.3 and 5.4, respectively (Al-Hooti et al., 1997). According to Reynes et al. (1994), the pH of Tunisian dates is between 5.3 and 6.3 for most of the studied varieties. These values indicate that dates are slightly acidic.

A significant difference was observed between the levels of proteins of the three dates varieties ($p< 0.05$). Degla-Beida is characterized by the highest protein content which is 3.95% of the dry weight, followed by Deglet-Nour and Mech-Degla, with values of 3.80 and 1.95 % respectively. Al-Farsi et al.(2007) gave values of 1.10 and 1.79 % for three Sun-dried Omani date varieties (Um-Mabseeli, Sellah and Shahal). The studied dates contained a non negligible protein content (1.95-3.95 %). Although dates are considered as a poor source of protein, it contains high quantities of some of the essential amino acids (Al-Hooti et al., 1997). Ahmed et al.(1995) confirmed that all the essential amino acids required for human nutrition were present in significant amounts in dates varieties of Oman.

The amount of the date pulp ash is between 2.14 and 2.50%, with a statistically significant difference between Mech-Degla and the two varieties: Degla-Beida and Deglet-Nour ($p< 0.05$). This value is compatible to those reported in the literature. Indeed, Sawaya et al. (1983) reported levels of 2.0, 2.20 and 2.60 % of the dry weight, respectively, for three Saudi dates: Sifri, Barni, and Ruzeiz, respectively. Besbes et al. (2009) reported ash values of 1.98 and 2.69% of the dry weight, respectively for the following Tunisian varieties: Allig and Deglet-Nour.

The mineral profile of the dates has shown that ahigh potassium content (K), characterizes the composition of dates (Table 2). This was confirmed by several studies (Youssif et al., 1982; Booij et al., 1992; Ahmed and Ahmed 1995; Cheikh-Rouhou et al., 2006). The maximum amount of potassium and magnesium was found in Deglet-Nour, followed by Degla-Beida and Mech-Degla. The variety Degla-Beida was characterized by a high sodium content (Na). This finding is compared to those cited by Ahmed and Ahmed (1995), with values between 55 and 287 mg of sodium per 100 g of the dry matter for Emirati varieties. In general, the findings of the mineral content agree with those reported by Al-Shahib and Marshall (2003) and Baliga et al. (2010). Date fruits are equally good sources of various minerals (Al-Hooti et al., 1997). According to Haas and Bliss, quoted by Reynes et al. (1994), the mineral elements of dates are classified into three groups according to their average levels, in decreasing order [K], [P, Mg, Ca] and [Fe, Cu, Zn, Mn].

C. Total polyphenols and antioxidant activity

The results of the polyphenls and DPPH scavenging activity of different varieties of dates are summarized in Table 3.

Polyphenols are known for their antioxidant and biological properties (Ben Thabet et al., 2009; Deshmukh et al., 2009; Kumar et al., 2012; Mibei et al., 2012; Gan et al., 2013; Kasote 2013). They contribute to the prevention of degenerative and cardiovascular diseases (Scalbert et al., 2002; Al-Mamary et al., 2011).

The total phenolic content of the studied dates varied from 116.74 to 189.60mg GAE/100 fresh weight (Table3).The results, showed that Degla-Beida contains higher total polyphenols than the other two dates varieties with a significant difference ($p< 0.05$). However, these values remained much higher than those reported by Mansouri et al. (2005), who reported that the phenolic content ranged between 2.49 and 8.36 mg (GAE)/100g fresh weight for varieties grown in Algeria.

Table 3. Content of total polyphenols and the inhibition percent of DPPH radical oxidation

Varieties of dates	Mech-Degla	Deglet-Nour	Degla-Beida
Total Polyphenols [1] (mg GAE/100g)	122.16 ± 11.46 [a]	116.74 ± 11.5[a]	189.60 ± 0.20[b]
Antiradical activity DPPH (%)	92.80 ± 2.90[a]	89.73 ± 0.92[a]	93.41 ± 2.56 [a]

All given values are means of three determinations (n=3). Means in line with different letters are significantly different ($p< 0.05$).
[1]: on a fresh weight basis.

Wu et al. (2004) obtained a high phenolic content ranged from 572 to 661mg GAE/100g fresh weight, respectively in Deglet-Nour and Medjol varieties. These were much higher than the results reported by Al-Farsi et al. (2007) with values of 172, 186 and 246mg GAE/100g fresh weight, respectively for the following Sun-dried Omani varieties: 'Shahal', Um-sellah and Mabseeli. Moreover, dates fruits have much higher phenol content than many fruits and vegetables consumed in US (Vayalil et al., 2012).

Many previous studies showed that fresh and dried date fruits varied quantitatively and qualitatively in their phenolic acids content (Mansouri et al., 2005; Allaith et al., 2008; Biglari et al., 2008).

The three dates varieties presented an interesting antioxidant activity (89.73-93.41%) with a non significant difference ($p< 0.05$). The percentage of the highest antioxidant activity was recorded for the Degla-Beida variety. Significant correlation was fond between the antioxidant activity and total phenolic content ($r=0.51$). The antioxidant properties of the dates fruits depend on the content of polyphenol compounds and other antioxidants such as vitamin C and α-tocopherol (Amorós et al., 2009; Al-Turki et al., 2010). Dates have a significant antioxidant potential, which has been reported in several previous studies (Vayalili, 2002; Mansouri et al., 2005; Al-Farsi et al., 2007; Allaith et al., 2008; Al-Turki et al., 2010). Indeed, dates are a good source of natural antioxidants (polyphenols) and could be considered as a functional food (Al-Farsi et al., 2005b; Biglari et al., 2008).

D. Color of date

Table 4 shows the L*, a* and b* values of dates, where Deglet-Nour variety presents the lowest luminosity and yellowness values. The values of parameter b* were significantly different ($p< 0.05$) between the three varieties. According to Zapata et al. (2011), the variability of CIELAB parameters (L*, a* and b*) depends on the variety and ripening stage of dates.

4. CONCLUSION

The morphological and biochemical study on dates presented more information about their nutritional, technological and market quality, which permits a better and appropriate use of dates varieties (fresh fruit marketing, storage and processing). The morphological characteristics of the three dates varieties showed that their weight differs significantly at $p< 0.05$. The results show that the pulp represents about 77.38- 88.65 %. The chemical composition of the dates showed that the studied varieties are of a noble quality, due to their richness in sugars (63.06-69.29%), minerals (K and Mg) and polyphenols. The detection of antioxidant activity of dates, contributes to a better market value of dates. Based these results, the common dates have a similar nutritional value compared to Deglet-Nour. Indeed, the transformed products of dates (flour, vinegar, syrup) into some food formulations could be classified as functional foods or functional ingredients. Hence, the valorization of common dates could help farmers of desert areas to find markets for their crops and also to preserve biodiversity of oasis ecosystem.

Table 4. Color of three dates varieties

Varieties of dates	Mech-Degla	Deglet-Nour	Degla-Beida
L*	57.93 ± 0.49 [a]	43.73 ± 1.36 [b]	57.06 ± 0.94 [a]
a*	13.50 ± 1.91 [a]	15.06 ± 0.15 [a]	12.03 ± 1.20 [b]
b*	37.43 ± 1.05 [a]	21.93 ± 1.04 [b]	32.23 ± 1.02 [c]

All values are means of three determinations. Means in line with different letters are significantly different ($p< 0.05$).

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