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Article

Nutritional properties, aromatic compounds and *in vitro* antioxidant activity of ten date palm fruit (*Phoenix dactylifera* L.) varieties grown in Tunisia

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Phoenix dactylifera L. has traditionally been used as a medicine in many cultures. The aim of this study was to evaluate the nutritional properties, aromatic compounds, total phenolic content and the antioxidant activity of ten ripe date fruit varieties grown in Tunisia. Sugar profiles were analyzed by high performance liquid chromatography, while fatty acid compounds were detected by gas chromatography and aromatic compounds were analyzed by GC-Electron Impact Mass Spectroscopy. Total phenolic contents were measured using colorimetric methods, whereas antioxidant capacities were evaluated *in vitro* using DPPH and ABTS radicals. It has been found that total sugars are the predominant component in all date varieties, followed by moisture, along with moderate amounts of proteins, ash, and fats. Multivariate tests based on the volatile compounds profile showed significant differences among varieties. Between the sixty-two volatile compounds detected, alcohols, aldehydes and unsaturated hydrocarbons constituted the main chemical classes. The date varieties exhibited strong antioxidant potential that correlated with phenolic content. In conclusion date varieties can play a major role in human nutrition and health because of their wide range of valuable nutritional components and natural antioxidants that could potentially be considered as a functional food ingredient.

Keywords: Date palm fruits. Varieties. Chemical composition. Aromatic compounds. Phenolic content. Antioxidant activity

INTRODUCTION

The date palm (*Phoenix dactylifera* L.) constitutes for the Arab-Muslim countries a fundamental tree, not only for its economic importance but also for its integral part of their religious, historical and cultural heritage. It represents the pivot or the frame of the oasis system, which creates a favorable environment for men's lives and their livestock.

In Tunisia, this phoenicultural genetic heritage plays a very important role in the South especially in the regions of Djerid and Nefzaoua where it is the main vegetation on which almost the entire regional economy is based.

The Tunisian oasis cover an area of 46.000 ha and have approximately 4.231.000 tree (Crda, 2000) and

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ensure a production in clear evolution (46.800 Tons in 1981 and 241.666 Tons in 2017 (Gif, 2017)). The evolution of date production has mainly affected the Deglet Nour variety. This clearly reflects the orientation of the Tunisian phoeniculture towards the monovarietal culture stimulated by very favorable commercial circumstances.

The other cultivars, qualified as of inferior quality, have known a slight increase following the awareness of the selective orientation. Despite this consciousness, these varieties have not yet received the attention that they deserve such biochemical characterization and valorization of its by-products. Indeed, on more than 250 varieties, only about thirty have been studied and their nutritional quality determinated (Chaira *et al*., 2007; El Arem *et al*., 2012; Elleuch *et al*., 2008; Reynes *et al*., 1994).

Nowadays, the consumption of fruit and vegetables is regarded as important and beneficial for health. Indeed, recent studies revealed that consuming high amounts of fruit and vegetables would reduce the risk of a number of chronic diseases (Abuajah, Ogbonna, Osuji, 2015; Dal, Sigrist, 2016; Li *et al*., 2014; Zhang *et al*., 2015). This effect on people's health is attributed to the presence of a group of phytochemicals: dietary fibre, natural antioxidants, and other bioactive compounds.

Date fruit is renowned for the presence of many classes of bioactive components such as carotenoids, polyphenols (especially phenolic acids, lignans, and flavonoids and tannins), and sterols (Al-Farsi *et al*., 2005; Biglari, Al Karkhi, Esa, 2008; Mansouri *et al*., 2005). Some studies reported data about the chemical composition of different varieties of dates grown in different parts of the world (Elleuch *et al*., 2008; Ismail *et al*. 2006; Al-Farsi *et al*., 2007). However, studies pertaining to the detailed identification, characterization, and quantification of phytochemicals in different date fruit varieties are still insufficient. The present study was carried out to evaluate the nutritional quality of ten date varieties by analyzing various physicochemical characteristics, aromatic compounds profile, total phenolic content and *in vitro* antioxidant activity.

MATERIAL AND METHODS

Chemical reagents

2,2'-azinobis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS), Folin–Ciocalteu reagent (FC reagent), petroleum ether (40-60 ºC), methanol, gallic acid, glucose, fructose and sucrose, potassium persulphate, Trolox standard, and ethanol, were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals and reagents used were of analytical grade and were also obtained from Sigma-Aldrich.

Date Samples

The fruits were collected from ten date palm (*P. dactylifera* L.) varieties grown in south of Tunisia at the 'tamr' stage, the final stage of fruit ripeness, during the beginning of the 2015 harvest season. Nine of them (Allig, Bser Hlou, Deglet Nour, Fezzani, Hissa, Horra, Kenta, Khaltaia, and Okht Kenta) were collected in the oasis of Douz, Kebili, while the Kentichi variety in Tozeur. The ten varieties are identified by local cultivators and this identification is confirmed by Rhouma Abdelmajid, Tunisian National Coordinator of the project FEM/PNUD/IPGRI RAB98G31 of date palm in Maghreb. The voucher specimens were preserved with the code N° 4.9 for Allig, N° 6.10 for Bser Hlou, N° 5.8 for Deglet Nour, N° 10.10 for Fezzani, N° 3.2 for Hissa, N° 7.1 for Horra, N° 5.3 for Kenta, N°17.1 for Khaltaia, N° 5.4 for Okht Kenta, and N° 1.1 for Kentichi in the National Institute of Agronomic Research of Tunisia (INRAT).

Ripe fruits of uniform size, free of physical damage and injury from insects and fungal infection, were selected and used for all the experiments. Upon arrival at the laboratory, the samples (100–150 g portions) were packed in polyethylene bags, sealed and stored at -20 ºC until analysis.

Morphologic parameters and proximate composition

Samples were obtained randomly taking ten dates of each variety. Each fruit was then subjected to physical measurements. Fruit weight was first recorded, and the length and width dimensions of the fruit were then measured using a caliper micrometer. After pitting, the weight of the seed and pulp were measured.

Moisture, protein and fat were determined following the procedures described by Saafi *et al*. (2008). Briefly, the moisture content was evaluated by the weight difference before and after drying at 80 ºC; the total protein content was determined colorimetrically using the method of Lowry *et al*. (1951), the crude fat was determined by extracting a known weight of powdered sample with petroleum ether (40-60 ºC) in a Soxhlet apparatus; the

ash content was determined by incineration at 530 ºC using a muffle furnace.

Sugar analysis

Sugar levels were measured according to the high-performance liquid chromatography (HPLC) method of Chaira *et al*. (2007) with slight modifications. Sugars were extracted from date fruits (3 g) with 25 mL of ultrapure water for 10 min (stirring frequently to help dissolve the sugars). The extracts were then centrifuged at 8000 g for 15 min and the supernatants were collected. Each sample was filtered over 0.45-µm membrane filters and analyzed by liquid chromatography (LC).

LC separation was carried out at room temperature on Eurospher NH2 column, 100 Å pore size, 7 mm particle size, 250 × 4.6 mm I.D (Knauer, Germany). Prior to use, solvents were filtered over a 0.45-µm membrane filter and sonicated for 15 min in an ultrasonic Cleaner Model SM 25E-MT (Branson Ultrasonics Corporation, Danbury, USA). The mobile phase used was acetonitrile-ultrapure water (80%: 20%, v/v). The LC was connected to a refractive index detector K-2301 from Knauer (Germany). The flow-rate and the injection volumes were 1 mL/min and 20 µL, respectively. Identified sugars were quantified on the basis of peak areas of external standards consisting of glucose (2%), fructose (2%) and sucrose (1%) solutions. Total reducing sugars were obtained as the sum of glucose and fructose values. Each sample was analyzed in triplicate and quantification was carried out from integrated peak areas of the sample against the corresponding standard graph. Results were expressed as percentage of dry weight.

Fatty acid analysis

The oil fractions were converted into methyl esters using the Morrison and Smith method (1964). Then, fatty acid methyl esters were analyzed using the method described by Saafi *et al*. (2008). Briefly, the fatty acid methyl esters were analyzed in a Hewlett-Packard 5890 series II gas chromatography (HP, Amsterdam, Netherlands) equipped with a flame ionization detector and a Hewlett-Packard Innowax cross-linked polyethylene glycol (PEG) capillary column (dimensions: 30 m length × 0.32 mm internal diameter × 0.52 µm film thickness). The column temperature was programmed from 180 to 240 ºC at 5 ºC min^{-1} and the injector and detector temperatures were set at 250 ºC. Nitrogen was used as gas carrier at 1 mL min^{-1}. The identification of the peaks was achieved comparing their retention times with those of authentic standards analyzed under the same conditions. Peak areas of triplicate injections were measured with an HP computing integrator.

Volatile compound's analyses

Supelco (Bellefonte, PA) SPME devices coated with polydimethylsiloxane (PDMS, 100 lm) were used to sample the headspace of two date fruits inserted into a 10 mL glass vial and allowed to equilibrate for 30 min. After the equilibration time, the fiber was exposed to the headspace for 50 min at room temperature. Once sampling was finished, the fiber was withdrawn into the needle and transferred to the injection port of the GC–MS system. GC–EIMS analyses were performed with a Varian (Palo Alto, CA) CP 3800 gas chromatograph equipped with a DB-5 capillary column (30 m x 0.25 mm x 0.25 µm; Agilent, Santa Clara, CA) and a Varian Saturn 2000 ion trap mass detector. Analytical conditions were as follows: injector and transfer line temperatures were 250 and 240 ºC, respectively; oven temperature was programmed from 60 to 240 ºC at 3 ºC/min; carrier gas was helium at 1 mL/min; splitless injection. The identification of the constituents was based on a comparison of their retention times with those of authentic samples, comparing their linear retention indices (LRI) relative to a series of *n*-hydrocarbons, and on computer matching against commercial (NIST 98 and Adams) and homemade library mass spectra, and MS literature data (Adams, 1995; Davis, 1990). Moreover, the molecular weights of all the substances identified were confirmed by GC–CIMS, using methanol as ionizing gas (Flamini, Tebano, Cioni, 2007).

Determination of total phenolics and evaluation of antioxidant activity

Extraction of antioxidant compounds

The extraction of antioxidant compounds and total phenolics from the date varieties was carried out using two different solvents, as described by Al-Farsi *et al*. (2005). Two hundred milligrams of sample were extracted with 2 mL of H_2O or methanol/H_2O (50:50, v/v) at room temperature in an orbital shaker set at 200 rpm for 2 h. The mixture was centrifuged at 1000 *g* for 15 min, and the supernatant was decanted into 4 mL vials. The pellets were extracted under identical conditions.

Supernatants were combined and used for total phenolic assay and antioxidant activity.

Determination of total polyphenolics content

The total phenolic content (TPC) was determined using a colorimetric assay described by Al-Farsi *et al.* (2005) based on the reduction of the Folin Ciocalteu reagent by the samples and expressed as mg of gallic acid equivalents (GAE) per g fresh weight (FW).

Antioxidant activities assay

Antioxidant activity was evaluated using an improved ABTS (2,2'-azino-*bis*-3-ethylbenzthiazoline-6-sulfonic acid) method described by Re *et al.* (1999) and cited by El Arem *et al.* (2012). In brief, the ABTS radical cation ($ABTS^{\bullet+}$) solution was prepared through the reaction of 7 mM ABTS and 2.45 mM potassium persulphate, after incubation at 23 ºC in the dark for 12-16 h. The $ABTS^{\bullet+}$ solution was then diluted with 80% ethanol to obtain an absorbance of 0.700 ± 0.005 at 734 nm. $ABTS^{\bullet+}$ solution was added to the test sample and mixed. The reaction mixture was allowed to stand at 23 ºC for 6 min and the absorbance at 734 nm was immediately recorded. For quantification, a standard curve was obtained by using Trolox standard solution at various concentrations (measurements in triplicate), and the results were expressed in terms of Trolox equivalents (TE).

The antioxidant activity was also determined using the DPPH (2,2-diphenyl-1-picrylhydrazyl) test according to Brand-Williams, Cuvelier, Berset, (1995). Briefly, different dilutions of the phenolic extract were prepared for each variety. An aliquot of 25 µL of diluted sample was added to 975 µL $DPPH^{\bullet}$ solution (6×10^{-5} M). The decrease in the absorbance was determined at 515 nm at 0 min, and every 15 min until the reaction reached the plateau, using a UV spectrophotometer. The $DPPH^{\bullet}$ concentration in the reaction medium was calculated from the calibration curve, as determined by linear regression:

$$A_{515nm} = 5.7484\times ([DPPH^{\bullet}]\ (\mu g/mL)) + 0.0429\ (R^2=0.995)$$

For each sample concentration tested, the percentage of the remaining $DPPH^{\bullet}$, in the steady state, was calculated as follows:

$$\%\ \text{of remaining } DPPH^{\bullet} = \frac{[DPPH^{\bullet}] \text{ at: } t = T}{[DPPH^{\bullet}] \text{ at: } t = 0}$$

where T is the time necessary to reach the steady state.

For each concentration of total phenolic content in date variety extract tested, the reaction kinetic was plotted. From this graph, the percentage of $DPPH^{\bullet}$ remaining at the steady state was determined and the values transferred onto another graph showing the percentage of residual $DPPH^{\bullet}$ at the steady state as a function of the mass ratio of phenolic content to $DPPH^{\bullet}$. Antiradical activity was defined as the amount of antioxidant necessary to decrease the initial $DPPH^{\bullet}$ concentration by 50% (Efficient Concentration = EC_{50} ([phenolic] (µg/mL)/[$DPPH^{\bullet}$] (µg/mL)). For reasons of clarity, we will speak in terms of antiradical efficiency ($AE=1/EC_{50}$) or antiradical power (ARP), where the larger the ARP is, the more efficient the antioxidant is.

Statistical analysis

All parameters were determined in triplicate for each sample. Results were expressed as means ± standard deviation (SD). All the data were obtained with the Statistical Package for Social Sciences SPSS 18.0 for Windows (18th version, IBM Corporation, New York, USA). The results were analyzed using one way analysis of variance (ANOVA) followed by Duncan's multiple range test (DMRT) for comparison between varieties. Statistical significance was set at $p < 0.05$. Correlation analysis between phenolic content and antioxidant activity was performed with Pearson's test. Aromatic compounds were also discriminated by multivariate parametric methods where the principal component analysis (PCA) was carried out using XLSTAT 2010 software version 3.0 for Windows (Addinsoft, New York, NY, USA).

RESULTS

Chemical composition

The results of physical properties are shown in Table I. The average weight of the pulp part varied between 4.40 g (Kenta) and 10.43 g (Horra), with a relative percentage ranging between 81.22% for Kenta and 92.32% for Khaltaia. Based on this parameter, Khaltaia, Allig (91.46%), Deglet Nour (91.21%), and Horra (90.32%) varieties were similar and presented the highest percentage of pulp. On the contrary, Kenta, Kentichi, and Okht Kenta varieties were characterized by the lowest percentage of pulp.

TABLE I - Fruit weight and pulp physical properties of ten date varieties at the Tamr stage

Variety	Date weight		% Pulp	Dimensions (mm)	
	Fruit (g)	Pulp (g)		Length	Width
Allig	9.68±0.40^{ab}	8.86±0.39^{a}	91.46±0.56^{a}	44.07±0.35^{a}	16.93±0.53^{a}
Bser Hlou	8.74±0.18^{c}	7.45±0.15^{bc}	85.28±0.61^{b}	31.33±0.09^{bc}	15.60±0.32^{ab}
Deglet Nour	10.00±0.32^{a}	9.12±0.28^{a}	91.21±0.53^{a}	38.30±1.19^{d}	16.93±0.41^{a}
Fezzani	8.85±0.31^{bc}	7.75±0.28^{b}	87.57±0.32^{c}	42.10±0.21^{ae}	16.37±0.97^{a}
Hissa	7.73±0.22^{d}	6.81±0.27^{c}	87.94±1.02^{c}	39.00±0.58^{d}	14.33±0.67^{bc}
Horra	11.53±0.64^{e}	10.43±0.62^{d}	90.32±0.49^{a}	41.40±0.76^{e}	19.26±0.56^{d}
Kenta	5.42±0.13^{f}	4.40±0.11^{e}	81.22±1.01^{d}	30.73±0.82^{bc}	13.17±0.73^{c}
Kentichi	5.81±0.11^{fg}	4.74±0.12^{ef}	81.56±0.80^{d}	31.67±0.98^{b}	14.47±0.29^{bc}
Khaltaia	8.34±0.36^{cd}	7.70±0.32^{b}	92.32±0.27^{a}	36.93±0.35^{d}	16.60±0.40^{a}
Okht Kenta	6.46 ±0.35^{g}	5.38±0.33^{f}	83.00±1.03^{d}	29.00±1.26^{c}	16.03±0.07^{ab}
Average	**8.16±0.24**	**7.14±0.24**	**86.72±0.54**	**36.45±0.97**	**15.97±0.33**

Data are expressed as mean ± SD (n=10). Means ± SD followed by the same letter, in each column, are not significantly different according to Duncan's multiple range test (P> 0.05).

Table II presents the compositional characteristics of the ten date palm fruit varieties. On the average, date palm fruits of different cultivars contained 79.16% dry matter. Values varied from 71.85% of Khaltaia to 90.42% of Fezzani. Sugars were the most abundant components in all varieties, ranging from 28.08 g/100 g DW (in Bser Hlou) to 68.84 g/100 g DW (in Deglet Nour), followed by proteins. Ash and fat contents were low. The main sugar found in this plant material was sucrose, followed by Fructose and glucose (Table II). In the Deglet-Nour, Kentichi and Horra varieties, sucrose was the principal one, whereas in Allig, Fezzani, Kenta, Khaltaia, Khouet Kenta, Hissa, and Bser Hlou varieties, fructose and glucose were found in comparable proportions. Polyunsaturated fatty acids (PUFA) predominated over saturated fatty acids (SFA) and monounsaturated fatty acids (MUFA) (Table III). Eighteen fatty acids were detected. Eight of them were unsaturated, while the rest were saturated. The saturated fatty acids (SFA) include caprylic (C8:0), capric (C10:0), lauric (C12:0), myristic (C14:0), palmitic (C16:0), margaric (C17:0), stearic (C18:0), arachidic (C20:0), heneicosanoic (C21:0) and tricosanoic acids (C23:0). The detected unsaturated fatty acids (UFA) include palmitoleic (C16:1 *n*-7), C17:1 *n*-7, oleic (C18:1 *n*-9), vaccenic (C18:1 *n*-7), linoleic (C18:2 *n*-6), linolenic (C18:3 *n*-3), eicosanoic (C20:1 *n*-9) and eicosadienoic acid (C20:2 *n*-6).

TABLE II - Compositional characteristics of date palm fruit from ten varieties at the Tamr stage

Variety	Dry Matter[x]	Fat[y]	Protein[y]	Ash[y]	Fructose[y]	Glucose[y]	Fruc/Gluc	Sucrose[y]	Total sugar[y]
Allig	76.94±2.86^{a}	0.30±0.01^{a}	4.85±0.29^{ab}	2.83±0.11^{ab}	23.92±0.08^{a}	24.00±0.07^{a}	1.00	-	47.92±0.02^{a}
Bser Hlou	76.44±0.67^{a}	0.38±0.01^{b}	3.55±0.24^{cd}	2.61±0.10^{bc}	14.07±0.05^{b}	14.01±0.03^{b}	1.00	-	28.08±0.08^{b}
Deglet Nour	78.60±0.11^{ab}	0.23±0.01^{c}	5.60±0.49^{a}	1.72±0.10^{d}	12.19±0.02^{c}	11.63±0.19^{c}	1.05	45.02±0.04	68.84±0.25^{c}
Fezzani	90.42±0.69^{c}	0.29±0.01^{a}	2.46±0.05^{e}	3.63±0.12^{e}	26.29±0.07^{d}	29.76±0.52^{d}	0.88	-	56.04±0.59^{d}
Hissa	78.79±0.51^{ab}	0.76±0.01^{d}	4.15±0.08^{bc}	1.83±0.03^{d}	14.43±0.15^{b}	15.74±0.12^{e}	0.92	-	30.17±0.26^{e}
Horra	80.77±0.64^{bd}	0.75±0.01^{d}	2.86±0.32^{de}	3.83±0.08^{e}	18.68±0.13^{e}	15.86±0.18^{e}	1.18	24.07±0.02	58.61±0.29^{f}
Kenta	78.72±0.45^{ab}	0.43±0.00^{e}	4.41±0.30^{b}	2.16±0.06^{df}	25.05±0.03^{f}	26.88±0.02^{f}	0.93	-	51.93±0.04^{g}
Kentichi	82.79±0.38^{d}	0.25±0.00^{f}	5.55±0.26^{a}	2.04±0.17^{df}	6.75±0.09^{g}	6.64±0.14^{g}	1.02	37.00±0.06	50.36±0.29^{h}
Khaltaia	71.85±0.76^{e}	0.70±0.01^{g}	3.55±0.19^{cd}	3.12±0.33^{a}	23.41±0.73^{a}	26.55±0.28^{f}	0.88	-	50.00±0.45^{h}
Okht Kenta	76.26±0.28^{a}	0.25±0.00^{f}	5.66±0.18^{a}	2.35±0.55^{cf}	22.00±0.25^{h}	22.46±0.21^{h}	0.98	-	44.37±0.04^{i}
Average	**79.16±0.91**	**0.43±0.04**	**4.27±0.22**	**2.61±0.13**	**18.67±1.15**	**19.35±1.34**	**0.98**	**35.36±3.05**	**48.63±2.17**

Data ar e expressed as mean ± SD (n=3). Means ± SD followed by the same letter, in each column, are not significantly different according to Duncan's multiple range test ($P > 0.05$).
[x] results are expressed as g/100 g FM; [y] results are expressed as g/100 g of DM

As shown in Table III, significant differences (p<0.05) among the ten varieties were observed between the percentages of SFA and UFA. The percentage of SFA was lower than UFA for the majority of the varieties, with the exception of Fezzani and Hissa. The most abundant SFAs were palmitic (14.24-28.75%), lauric (1.25-15.30%), myristic (1.41-10.54%), and stearic (4.43-8.82%) acids, whereas UFA were represented mainly by oleic (19.39-38.06%), linoleic (4.56-31.84%), eicosadienoic (1.50-10.72%), and linolenic (0.14-5.15%) acids. Khouet Kenta Deglet Nour, and Kentichi varieties were characterized by the highest percentage of UFA (60.29%, 60.18% and 59.45% TFA, respectively), mainly due to their content of linoleic and linolenic acids, in addition to oleic acid.

TABLE III - Fatty acid composition of date palm flesh

Fatty acid	Allig	Bser Hlou	Deglet Nour	Fezzani	Hissa	Horra	Kenta	Kentichi	Khaltaia	Okht Kenta
C8:0	0.90±0.04^{a}	0.90±0.03^{a}	0.13±0.00^{bc}	1.72±0.02^{d}	0.18±0.01^{c}	1.91±0.06^{e}	0.07±0.01^{b}	0.19±0.02^{c}	0.85±0.06^{a}	1.05±0.03^{f}
C10:0	0.83±0.02^{a}	0.31±0.04^{b}	0.05±0.01^{c}	0.22±0.02^{bd}	0.10±0.00^{cd}	0.46±0.02^{e}	0.30±0.03^{b}	0.35±0.11^{be}	0.90±0.03^{a}	0.95±0.04^{a}
C12:0	15.30±0.06^{a}	3.67±0.21^{b}	1.25±0.17^{c}	3.77±0.13^{b}	11.51±0.28^{d}	8.91±0.52^{e}	9.21±0.14^{e}	2.68±0.10^{f}	10.08±0.15^{g}	2.55±0.17^{f}
C14:0	8.98±0.27^{a}	2.99±0.19^{b}	1.41±0.23^{c}	2.93±0.06^{b}	10.54±0.27^{d}	6.49±0.17^{e}	7.37±0.19^{f}	2.89±0.14^{b}	6.37±0.17^{e}	2.06±0.02^{g}
C16:0	14.24±0.24^{a}	21.80±0.01^{b}	18.20±0.18^{c}	28.75±0.15^{d}	20.70±0.13^{e}	21.84±0.10^{b}	21.60±0.12^{b}	24.29±0.14^{f}	16.33±0.12^{g}	22.72±0.11^{h}
C16:1 *n*-7	0.54±0.06^{a}	1.90±0.03^{b}	1.41±0.23^{de}	2.06±0.04^{c}	1.43±0.12^{de}	1.67±0.09^{bd}	1.54±0.17^{d}	1.33±0.06^{de}	2.98±0.02^{f}	1.13±0.01^{e}
C17:0	0.40±0.02^{a}	1.19±0.03^{b}	1.83±0.06^{c}	0.56±0.09^{a}	0.78±0.08^{d}	0.82±0.02^{d}	1.34±0.11^{b}	1.56±0.13^{e}	0.92±0.02^{d}	0.92±0.03^{d}
C17:1 *n*-7	0.13±0.01^{a}	0.47±0.05^{bc}	0.73±0.04^{d}	1.64±0.04^{e}	0.19±0.01^{a}	0.46±0.03^{bc}	0.61±0.01^{f}	0.39±0.02^{bg}	0.54±0.02^{cf}	0.30±0.03^{g}
C18:0	4.43±0.26^{a}	6.45±0.03^{b}	4.82±0.06^{cd}	8.82±0.11^{e}	6.41±0.11^{b}	5.02±0.01^{d}	5.82±0.10^{f}	4.52±0.14^{ac}	4.58±0.10^{ac}	4.97±0.09^{d}
C18:1 *n*-7	0.78±0.07^{a}	0.58±0.01^{b}	0.88±0.05^{a}	0.79±0.02^{a}	2.38±0.01^{c}	0.20±0.00^{d}	1.37±0.17^{e}	0.51±0.03^{b}	1.10±0.08^{f}	0.27±0.01^{d}
C18:1 *n*-9	38.06±1.11^{a}	25.76±0.11^{b}	19.39±0.21^{c}	23.84 ±0.11^{d}	30.15±0.55^{e}	27.86±0.09^{f}	30.99±0.61^{e}	19.49±0.03^{c}	32.86±0.08^{g}	27.51±0.27^{f}
C18:2 *n*-6	9.68±0.38^{a}	20.46±0.11^{b}	25.15±0.16^{c}	4.56±0.11^{d}	4.71±0.11^{d}	16.21±0.13^{e}	8.90±0.10^{f}	31.84±0.54^{g}	14.01±0.20^{h}	23.78±0.07^{i}
C18:3 *n*-3	0.79±0.04^{a}	2.70±0.03^{b}	5.15±0.11^{c}	0.84±0.04^{a}	0.14±0.00^{d}	1.95±0.05^{e}	1.05±0.29^{a}	3.98±0.03^{f}	0.97±0.01^{a}	3.88±0.04^{f}
C20:0	0.53±0.04^{ab}	0.61±0.04^{abc}	1.55±0.13^{d}	0.76±0.03^{c}	0.64±0.03^{bc}	0.48±0.04^{ab}	0.50±0.06^{ab}	0.43±0.04^{ae}	0.49±0.0.02^{ab}	0.27±0.06^{e}
C20:1 *n*-9	0.74±0.03^{ab}	2.58±0.18^{c}	3.22±0.12^{d}	3.53±0.33^{d}	2.40±0.24^{c}	1.69±0.07^{e}	2.42±0.13^{c}	0.42±0.02^{a}	0.95±0.02^{b}	0.73±0.01^{ab}
C20:2 *n*-6	2.17±0.10^{a}	3.40±0.09^{b}	4.25±0.15^{c}	10.72±0.17^{d}	4.31±0.17^{c}	1.95±0.03^{a}	4.50±0.23^{c}	1.50±0.23^{e}	3.21±0.09^{b}	2.69±0.03^{f}
C21:0	0.49±0.06^{a}	0.89±0.04^{b}	4.83±0.23^{c}	1.79±0.09^{d}	1.35±0.06^{e}	1.00±0.06^{bf}	1.49±0.11^{e}	1.23±0.12^{ef}	0.79±0.02^{b}	0.33±0.01^{a}
C23:0	1.01±0.06^{a}	3.35±0.06^{b}	5.75±0.42^{c}	3.31±0.12^{b}	2.06±0.05^{d}	1.07±0.12^{a}	0.93±0.03^{a}	2.39±0.10^{d}	2.08±0.05^{d}	3.89±0.03^{e}
SFA	**47.11±0.73^{a}**	**42.16±0.14^{bc}**	**39.82±0.17^{d}**	**52.02±0.74^{e}**	**54.28±0.93^{f}**	**48.00±0.29^{a}**	**48.63±0.89^{a}**	**40.54±0.48^{cd}**	**43.39±0.60^{b}**	**39.72±0.60^{d}**
MUFA	**40.25±1.08^{a}**	**31.27±0.40^{bc}**	**25.63±0.24^{d}**	**31.86±0.38^{c}**	**36.56±0.17^{e}**	**31.88±0.29^{c}**	**36.92±1.06^{ef}**	**22.14±0.00^{g}**	**38.43±0.22^{f}**	**29.94±0.34^{b}**
PUFA	**12.64±0.33^{a}**	**26.56±0.23^{b}**	**34.55±0.20^{c}**	**16.11±0.31^{d}**	**9.16±0.28^{e}**	**20.11±0.14^{f}**	**14.45±0.61^{g}**	**37.31±0.80^{h}**	**18.18±0.12^{i}**	**30.35±014^{j}**

Data are reported to mean ± SD (n = 3). Means ± SD followed by the same letter, within a row, are not significantly different according to Duncan's multiple range test (P>0.05)
SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids

Profiles of volatile compounds

The volatile compounds of the varieties of date palm fruit are reported in Table IV. A total of sixty-two volatiles were identified. The number of aromatic compounds differed according to the fruit variety. Fruits of Bser Hlou, Allig and Okht Kenta varieties produced the highest number of aromatic compounds (43, 40 and 40, respectively), whereas the lowest number of volatiles was detected for the fruits of Kentichi (35). Only 20 of the 62 identified compounds [2-propanol, isopentyl alcohol, 1-nonen-3-ol, 2-nonanol, 1-nonanol, dihydrocarveol, ethyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, octanal, nonanal, decanal, camphor, 4-terpineol, 6-methyl-5-hepten-2-one, *(E)*-geranylacetone, *n*-tetradecane, *(Z)*-2-tridecene, *(E)*-2-tridecene] were detected in all the samples. The sixty-two identifiable aromatic belonged to seven chemical groups, namely 14 alcohols, 8 esters, 12 aldehydes, 9 terpenoids, 6 ketones, 8 saturated hydrocarbons, and 5 unsaturated hydrocarbons. In percentage, alcohols and aldehydes were found to be the most important groups of volatiles of the different date fruit varieties. The percentage of alcohols varied from 20.9% of Horra to 44.9% of Allig. This class was characterized by the presence of appreciable relative percentages of 2-propanol and isopentyl alcohol in most varieties. In Allig, Deglet Nour and Bser Hlou, 1-octen-3-ol (6.1, 6.2 and 5.1% respectively) was the main alcohol, while 2,3-butandiol reached 7.4% in Fezzani. The fruits of Bser Hlou were characterized by the highest percentage of aldehydes (39.8%) in relation with the important relative percentages of nonanal (14.2%) and decanal (12.9%) (Table IV).

In addition to the above compounds, some esters, terpenoids, ketones saturated and unsaturated hydrocarbons contributed to the overall aromatic profiles of the date palm fruits. The main ester was represented by ethyl acetate, produced by all varieties in relative percentages ranging from 0.6 to 14.4% (Table IV). The highest relative percentage of terpenoids was found in Khaltaia (32.5%), with limonene (30.3%) as the most abundant component. This variety was also characterized by a low relative percentage of ketones (2.5%), saturated hydrocarbons (0.1%) and unsaturated hydrocarbons (3.5%). Ketones were the least represented chemical class (Table IV), with 6-methyl-5-hepten-2-one and *(E)*-geranylacetone as the main volatiles (detected in all varieties), and 3-octanone (detected in Bser Hlou variety at the highest relative percentage). Despite their low percentages (0.1-5.0%), saturated hydrocarbons were represented by eight different components. Among them, *n*-undecane, *n*-tridecane, *n*-tetradecane, and *n*-pentadecane were the most shared compounds. Date palm fruits were also characterized by the presence of some unsaturated hydrocarbon components. Horra exhibited the highest relative percentage (27.7%) of this group, mainly due to the presence of *(Z)*-2-tridecene (12.4%) and *(E)*-2-tridecene (14.5%).

TABLE IV - Volatiles compositiona of date palm fruits obtained from eight varieties at Tamr stage

Constituents	l.r.i.[b]	Allig	Bser Hlou	Deglet Nour	Fezzani	Horra	Kentichi	Khaltaia	Okht Kenta
Alcohols									
2-propanol	516	16.7	1.3	12.1	7.3	10.5	11.6	14.3	12.1
Isopentyl Alcohol	763	7.8	2.8	6.1	4.3	3.8	5.6	16.2	5.0
1,3-butandiol	788	–	–	–	0.1	–	–	–	–
2,3-butandiol	789	–	–	–	7.4	–	–	–	–

(continuing)

TABLE IV - Volatiles compositiona of date palm fruits obtained from eight varieties at Tamr stage (Cont.)

Constituents	l.r.i.[b]	Allig	Bser Hlou	Deglet Nour	Fezzani	Horra	Kentichi	Khaltaia	Okht Kenta
1-hexanol	873	1.2	3.4	2.7	–	0.1	0.4	0.4	0.6
1-octen-3-ol	980	6.1	5.1	6.2	–	tr[c]	tr	0.2	2.4
2-octen-1-ol	1071	2.8	2.3	2.4	–	–	–	–	1.4
1-octanol	1072	2.5	4.5	4.0	–	–	–	–	1.2
1-nonen-3-ol	1086	0.7	0.9	1.2	tr	2.4	1.5	0.5	1.8
2-nonanol	1088	0.6	0.9	1.3	0.8	2.8	1.8	0.6	2.5
3-nonanol	1106	–	0.1	–	–	–	–	–	–
Phenylethyl Alcohol	1110	5.6	2.1	1.4	tr	–	–	1.6	0.7
1-nonanol	1174	0.9	1.5	1.6	1.3	tr	0.6	0.5	1.6
1-dodecanol	1474	–	–	–	0.7	1.3	–	–	–
% Identified alcohols		**44.9**	**24.9**	**39.0**	**21.9**	**20.9**	**21.5**	**34.3**	**29.3**
Esters									
Ethyl Acetate	614	6.8	0.6	3.0	12.1	9.5	14.4	8.7	7.1
1-propyl acetate	710	–	–	–	–	–	–	1.2	–
Ethyl Hexanoate	1001	0.6	1.1	0.7	0.1	0.8	0.6	0.3	1.0
Ethyl Octanoate	1195	2.3	2.2	1.4	2.5	2.5	3.0	1.9	3.8
2-phenylethyl acetate	1258	0.1	–	–	–	–	–	–	–
Isobornyl Acetate	1287	–	0.7	–	–	–	–	–	–
Ethyl Nonanoate	1297	–	–	–	tr	0.4	0.6	0.3	0.6
Ethyl Decanoate	1395	1.2	0.7	0.8	0.9	0.6	0.8	1.6	1.5
% Identified esters		**11.0**	**5.3**	**5.9**	**15.6**	**13.8**	**19.4**	**14**	**14**
Aldehydes									
Hexanal	804	tr	2.4	0.6	–	–	–	–	–

(continuing)

TABLE IV - Volatiles compositiona of date palm fruits obtained from eight varieties at Tamr stage (Cont.)

Constituents	l.r.i.[b]	Allig	Bser Hlou	Deglet Nour	Fezzani	Horra	Kentichi	Khaltaia	Okht Kenta
Benzaldehyde	958	tr	1.4	0.1	0.8	tr	0.1	–	0.1
Octanal	1003	0.5	1.8	1.0	0.9	tr	0.5	0.2	0.6
(Z)-2-octenal	1052	1.8	3.6	3.5	5.1	1.5	0.2	–	1.6
(E)-2-octenal	1063	–	2.0	tr	–	1.2	0.9	–	1.0
Nonanal	1102	6.5	14.2	7.6	8.0	6.7	5.4	1.8	7.3
(E)-2-nonenal	1162	–	–	tr	tr	–	–	–	–
Decanal	1206	9.5	12.9	12.4	10.6	3.8	6.0	4.4	8.2
(E)-2-decenal	1266	–	–	–	0.9	–	–	–	–
Undecanal	1308	1.1	–	–	tr	–	–	tr	tr
Dodecanal	1409	0.6	0.8	0.7	1.2	tr	–	0.2	0.5
Tridecanal	1512	–	0.7	0.5	1.1	2.6	–	–	–
% Identified aldehydes		**20.0**	**39.8**	**26.4**	**28.6**	**15.8**	**13.1**	**6.6**	**19.3**
Terpenoids									
Limonene	1032	–	–	–	–	–	3.7	30.3	1.7
1,8-cineole	1035	2.1	–	–	–	1.5	1.0	0.5	–
Linalool	1099	0.7	0.7	–	–	–	–	0.9	–
Camphor	1147	1.2	tr	0.5	1.2	1.5	0.9	tr	1.4
4-terpineol	1179	1.1	0.7	0.5	1.8	0.8	0.7	0.2	0.9
α-terpineol	1191	–	–	–	tr	–	–	–	–
Dihydrocarveol	1193	1.7	1.2	0.7	3.0	1.3	1.2	0.3	1.3
β-cyclocitral	1222	0.8	0.9	0.8	–	–	1.9	0.3	0.6
Carvone	1245	0.8	2.7	–	–	–	–	–	–
% Identified terpenoids		8.4	6.2	2.5	6.0	5.1	9.4	32.5	5.9

(continuing)

TABLE IV - Volatiles compositiona of date palm fruits obtained from eight varieties at Tamr stage (Cont.)

Constituents	l.r.i.[b]	Allig	Bser Hlou	Deglet Nour	Fezzani	Horra	Kentichi	Khaltaia	Okht Kenta
Ketones									
6-methyl-5-hepten-2-one	987	0.6	2.3	1.4	0.8	0.4	2.0	0.5	0.5
3-octanone	989	–	2.1	1.8	–	–	–	–	0.6
Constituents	l.r.i.[b]	Allig	Bser Hlou	Deglet Nour	Fezzani	Horra	Kentichi	Khaltaia	Okht Kenta
3-octen-2-one	1044	–	tr	–	–	1.6	–	–	0.5
2-nonanone	1092	–	1.5	1.4	–	–	–	–	–
(E)-geranylacetone	1455	1.4	1.9	1.4	2.3	1.6	5.2	2.0	0.8
(E)-β-ionone	1486	0.9	–	0.5	2.1	0.5	1.3	–	–
% Identified ketones		**2.9**	**7.8**	**6.5**	**5.2**	**4.1**	**8.5**	**2.5**	**2.4**
Saturated hydrocarbons									
n-undecane	1100	–	–	1.0	tr	1.7	1.3	–	0.6
n-dodecane	1200	–	–	–	–	–	–	0.1	tr
n-tridecane	1300	0.6	0.8	–	0.9	1.4	0.9	–	1.0
n-tetradecane	1400	0.7	0.7	0.6	1.7	0.5	tr	tr	0.5
n-pentadecane	1500	0.8	0.7	0.6	1.5	1.4	0.6	–	–
n-hexadecane	1600	–	0.8	–	–	–	–	–	–
n-heptadecane	1700	1.3	–	–	–	–	–	–	–
n-octadecane	1800	0.5							
% Identified sat. hydroc.		**3.9**	**3.0**	**2.2**	**4.1**	**5.0**	**2.8**	**0.1**	**2.1**
Unsaturated hydrocarbons									
1-tridecene	1293	–	0.7	–	0.8	–	0.9	0.2	0.9

(continuing)

TABLE IV - Volatiles compositiona of date palm fruits obtained from eight varieties at Tamr stage (Cont.)

Constituents	l.r.i.[b]	Allig	Bser Hlou	Deglet Nour	Fezzani	Horra	Kentichi	Khaltaia	Okht Kenta
(Z)-2-tridecene	1304	1.1	3.8	4.2	4.8	12.4	7.5	1.6	7.6
(E)-2-tridecene	1315	1.9	3.4	4.0	4.6	14.5	8.3	1.5	9.1
1-tetradecene	1390	–	–	–	–	–	–	tr	–
1-pentadecene	1492	–	–	–	0.7	0.8	0.4	0.2	0.8
% Identified unsat. hydroc.		**3.0**	**7.9**	**8.2**	**10.9**	**27.7**	**17.1**	**3.5**	**18.4**
Total identified		**94.1**	**94.9**	**90.7**	**92.3**	**92.4**	**91.8**	**93.5**	**91.4**

[a] Relative percentages obtained by flame ionization detector (FID) peak area normalization (DB-5 column).
[b] Linear retention indices (DB-5 column).
[c] tr < 0.1%

To better understand the usefulness of the volatile profile to define and distinguish the eight date varieties, a principal component analysis (PCA) was also performed. This PCA was performed using all volatiles and was based on Pearson's correlations to standardize the data. The PCA reduced the number of variables to 7 principal components (data not shown). The first and second principal components (PC1 and PC2) represented 51.72% of the total variance (Figure 1(a)) and clearly separate all the eight varieties. The first component (PC1), explaining 30.10% of the variance, is correlated positively with Bser Hlou and Deglet Nour varieties, and negatively with Horra, Okht Kenta and Kentichi varieties. For the second principal component (PC2), explaining about 21.62% of the variance, the Allig and Khaltaia varieties showed positive values and Fezzani contributed to the negative side of same principal component.

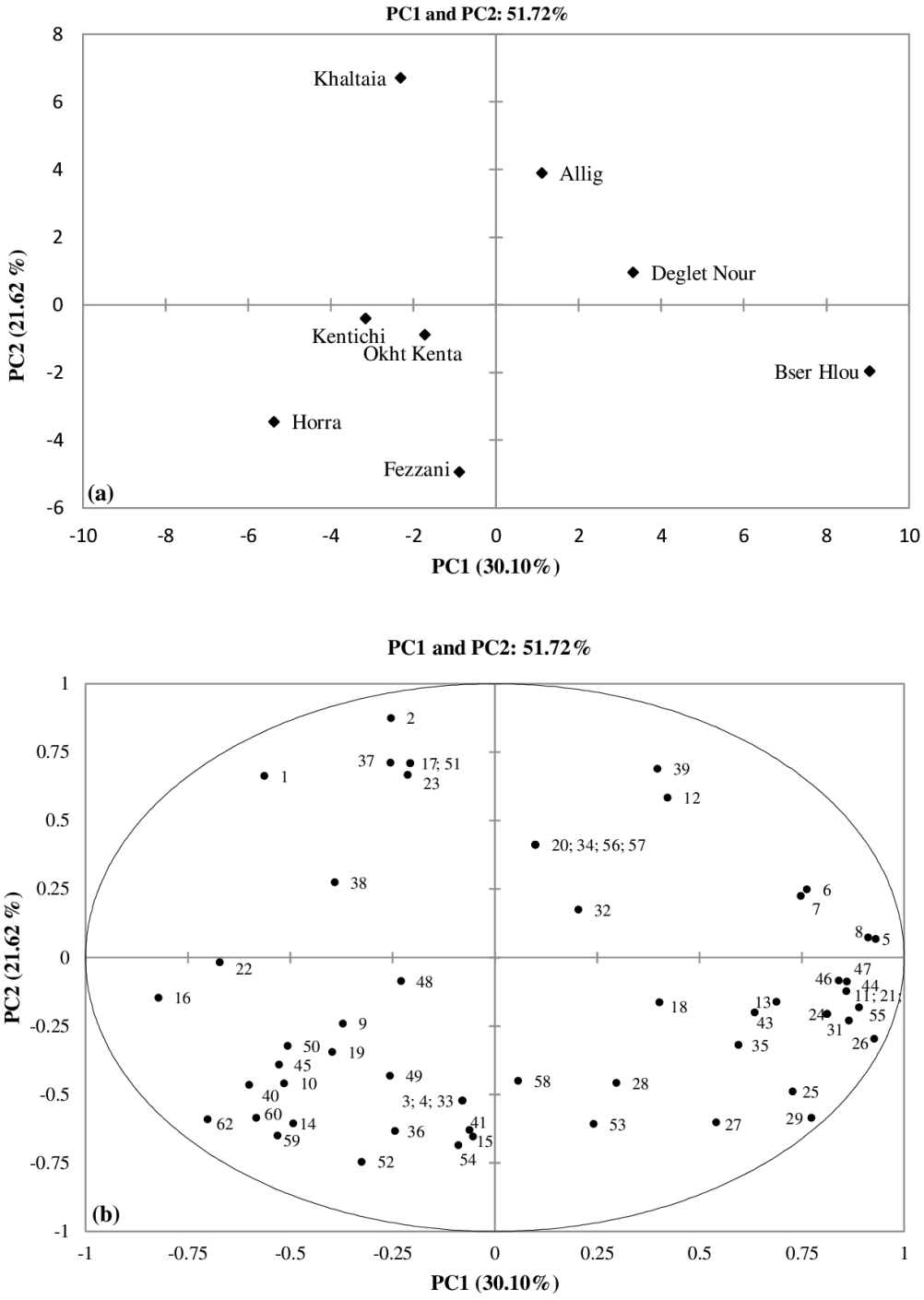

FIGURE 1 - (a) Principal component analysis (PCA) case scores date palm fruits based on first and second principal components. **(b)**: PCA variable loadings of date palm fruits volatile compounds based on first and second principal components. (see Table V for list of variables).

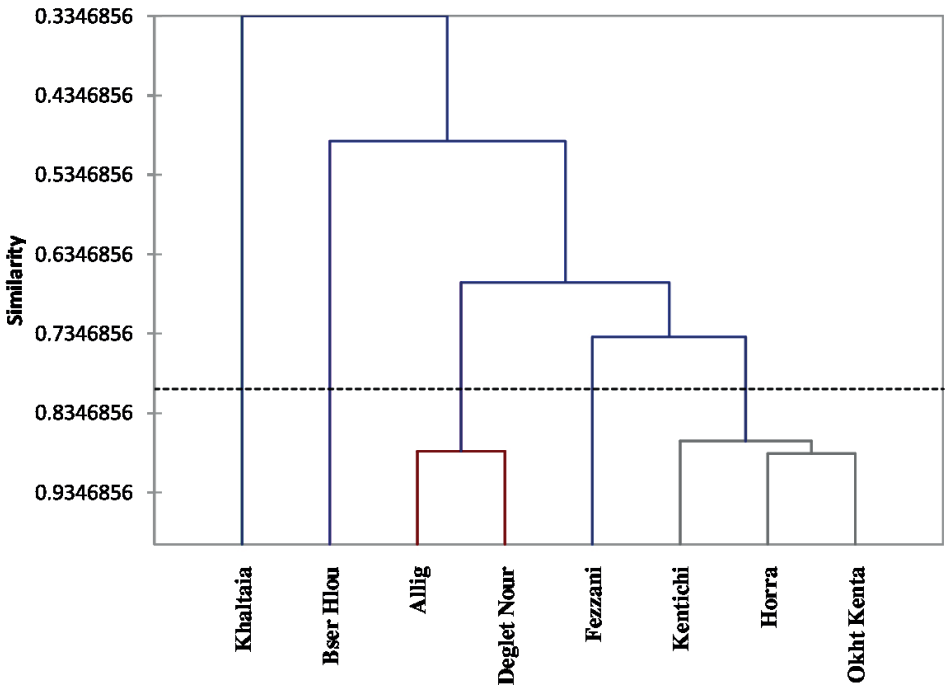

FIGURE 2 - Dendrogram showing hierarchical clustering of date palm varieties based on aromatic volatiles compounds.

Analysis of the loadings plot (Figure 1(b)) reveals the compounds responsible of the separation between samples. Volatile alcohols, namely 1-hexanol, 1-octen-3-ol and 1-octanol, were found in the upper right quadrant. These compounds were positively and highly correlated to PC1 and characterized Deglet Nour variety. In the same quadrant, phenylethyl alcohol, linalool, undecanal, *n*-heptadecane and *n*-octadecane showed a lower loading on PC1 axis and were more positively correlated to PC2. These compounds characterized Allig variety. In the lower left quadrant (*E*)-2-decenal, 1,3-butandiol, 2,3-butandiol, 4-terpineol, dihydrocarveol and *n*-pentadecane were grouped together and correlated negatively with PC2. These compounds were the dominant ones in Fezzani variety. Other compounds such as ethyl acetate, ethyl nonanoate and 1-pentadecene were highly negatively correlated with PC1 (-0.823, -0.673 and -0.703, respectively), while camphor and 2-nonanal were less negatively correlated with the same axis (-0.601 and -0.515, respectively). These compounds were found at important levels in Horra, Kenichi and Okht Kenta varieties, which are situated in this quadrant.

The scores plot in the PCA analysis illustrates that Bser Hlou and Khaltaia varieties were clearly different from the others due to their volatile profile (Table IV). Khaltaia variety was situated at the upper left side of PCA and was separated from the rest by its higher content of limonene, isopentyl alcohol, ethyl decanoate and its exclusive 1-propyl acetate and *n*-dodecane. However, Bser Hlou which was situated at the lower right side of PCA was characterized by its high content of nonanal, decanal, 1-octanol, 1-hexanol, carvone, hexanal, (*E*)-2-octenal, octanal, 2-nonanone, benzaldehyde and ethyl hexanoate. *n*-Hexadecane, isobornyl acetate and 3-nonanol were highly correlated (0.811) to PC1 and were detected only in this variety.

TABLE V - List of variables used for the multivariate statistical analysis

Codes	Volatile compounds	Codes	Volatile compounds	Codes	Volatile compounds
1	2-propanol	**23**	Ethyl Decanoate	**45**	3-octen-2-one
2	Isopentyl Alcohol	**24**	Hexanal	**46**	2-nonanone
3	1,3-butandiol	**25**	Benzaldehyde	**47**	Carvone
4	2,3-butandiol	**26**	Octanal	**48**	*(E)*-geranylacetone
5	1-hexanol	**27**	*(Z)*-2-octenal	**49**	*(E)*-β-ionone
6	1-octen-3-ol	**28**	*(E)*-2-octenal	**50**	*n*-undecane
7	2-octen-1-ol	**29**	Nonanal	**51**	*n*-dodecane
8	1-octanol	**30**	*(E)*-2-nonenal	**52**	*n*-tridecane
9	1-nonen-3-ol	**31**	Decanal	**53**	*n*-tetradecane
10	2-nonanol	**32**	β-cyclocitral	**54**	*n*-pentadecane
11	3-nonanol	**33**	*(E)*-2-decenal	**55**	*n*-hexadecane
12	Phenylethyl Alcohol	**34**	Undecanal	**56**	*n*-heptadecane
13	1-nonanol	**35**	Dodecanal	**57**	*n*-octadecane
14	1-dodecanol	**36**	Tridecanal	**58**	1-tridecene
15	Dihydrocarveol	**37**	Limonene	**59**	*(Z)*-2-tridecene
16	Ethyl Acetate	**38**	1,8-cineole	**60**	*(E)*-2-tridecene
17	1-propyl acetate	**39**	Linalool	**61**	1-tetradecene
18	Ethyl Hexanoate	**40**	Camphor	**62**	1-pentadecene
19	Ethyl Octanoate	**41**	4-terpineol		
20	2-phenylethyl acetate	**42**	α-terpineol		
21	Isobornyl Acetate	**43**	6-methyl-5-hepten-2-one		
22	Ethyl Nonanoate	**44**	3-octanone		

Biological activity

The mean total content of phenolics ranged from 160.03 to 449.94 mg of GAE/100 g FW and from 155.31 to 471.55 mg of GAE/100 g FW in aqueous and methanolic extracts of date varieties, respectively (Table VI). Among the varieties studied, Allig had the highest amount of total phenolics in both aqueous and methanolic extracts followed by Deglet Nour, Horra, and Kentichi, while the varieties Bser Hlou and Khaltaia presented the lowest values.

The average values indicating the antioxidant activity of date palm fruit evaluated by ABTS and DPPH assays are given in Table VI. Deglet Nour variety showed the highest level of antioxidant activity based on ABTS assay (1312.97 and 1308.94 µmol Trolox equivalent/100 g FW for aqueous and methanol extracts, respectively) and based on DPPH assay (1.75 and 2.17 for aqueous and methanol extracts, respectively). It is important to note that the methanol extract of Allig had a capacity to scavenge ABTS radical similar to Deglet Nour, reaching 1312.79 µmol Trolox equivalent/100 g FW. Conversely, Hissa variety exhibited the lowest level of antioxidant activity based on ABTS assay (304.49 and 94.24 µmol Trolox equivalent/100 g FW for aqueous and methanol extracts, respectively) and based on DPPH assay (0.70 and 0.41 for aqueous and methanol extracts, respectively). The order of antioxidant activity of the aqueous extracts based on ABTS assay was: Hissa < Khaltaia < Kenta < Kentichi < Fezzani < Allig < Horra <Bser Hlou < Deglet Nour and based on DPPH assay was: Hissa < Kenta < Bser Hlou < Kentichi < Fezzani < Allig < Horra < Khaltaia < Deglet Nour. As shown in Table VI, the results of the antioxidant activity of the methanol extracts evaluated with the same two methods did not provide the same order as above. In fact, for each antiradical assay a significant difference ($P < 0.05$) was revealed between the results of the two extracts in most varieties. These differences may be attributed to the different solubility of antioxidant compounds in methanol, water, or in their mixtures and to their capacity to scavenge free radicals.

TABLE VI - Total phenolic content and antioxidant activity of date palm fruit varieties at the Tamar stage, grown in Tunisia

Variety	Total phenolics content (mg of GAE/100 g FW)		Antioxidant activity by ABTS µmol equivalent Trolox /100 g FW		Antioxidant activity by DPPH			
					Aqu E		Met E	
	Aqu E	Met E	Aqu E	Met E	EC50	AE (1/EC50)	EC50	AE (1/EC50)
Allig	449.94±10.67^{a}*	471.55±5.32^{a}	1119.34±78.76^{a}*	1312.79±62.71^{a}	0.62±0.05^{a}**	1.62±0.11^{ab}**	0.91±0.01^{a}	1.11±0.02^{a}
Bser Hlou	160.03±3.67^{b}	175.25±4.81^{bc}	1230.94±23.03^{ab}	1095.50±61.20^{bc}	0.86±0.10^{b}	1.19±0.15^{bc}	0.99±0.10^{a}	1.03±0.11^{a}
Deglet Nour	359.46±8.13^{c}*	327.84±9.44^{d}	1312.97±7.75^{b}	1308.94±9.56^{a}	0.61±0.11^{a}	1.75±0.31^{a}*	0.46±0.01^{b}	2.17±0.04^{b}
Fezzani	200.58±6.00^{d}*	172.87±5.52^{bc}	565.95±71.17^{c}	602.27±26.33^{cd}	0.75±0.02^{ab}**	1.33±0.04^{ab}*	1.08±0.06^{a}	0.94±0.05^{a}
Hissa	180.96±3.01^{bd}	189.23±4.29^{c}	304.49±84.50^{d}**	94.24±10.49^{e}	1.43±0.00^{c}***	0.70±0.00^{d}	2.45±0.13^{c}	0.41±0.02^{c}
Horra	281.83±7.50^{e}**	240.72±3.57^{e}	1156.95±63.50^{ab}	1110.92±58.49^{b}	0.60±0.07^{a}***	1.71±0.19^{a}***	0.97±0.11^{a}	1.08±0.13^{a}
Kenta	161.85±1.35^{b}*	184.12±4.19^{c}	524.04±36.32^{c}	532.80±86.35^{df}	1.30±0.00^{c}***	0.77±0.00^{cd}*	0.88±0.04^{a}	1.14±0.06^{a}

(continuing)

TABLE VI - Total phenolic content and antioxidant activity of date palm fruit varieties at the Tamar stage, grown in Tunisia

Variety	Total phenolics content (mg of GAE/100 g FW)		Antioxidant activity by ABTS µmol equivalent Trolox /100 g FW		Antioxidant activity by DPPH			
					Aqu E		Met E	
	Aqu E	Met E	Aqu E	Met E	EC50	AE (1/EC50)	EC50	AE (1/EC50)
Kentichi	226.12±6.27^{f}	215.49±2.81^{f}	536.84±22.05^{c}*	727.35±35.65^{c}	0.86±0.13^{b}	1.25±0.19^{ab}	0.86±0.03^{a}	1.16±0.04^{a}
Khaltaia	170.91±9.42^{b}	155.31±13.42^{b}	523.72±38.08^{c}	419.03±3.17^{f}	0.58±0.01^{a}***	1.71±0.03^{a}***	1.00±0.07^{a}	1.01±0.07^{a}
Average	243.52±18.87	236.93±18.97	808.32±73.17	800.43±80.24	0.85±0.06	1.34±0.09	1.07±0.10	1.12±0.09

Data are expressed as mean ± SD (n=3) on a fresh weight basis. Means in the same column with different superscript differ significantly (p <0.05).

*, **, *** Significant difference between the different extract, for each variety, at p <0.05, p <0.01, p < 0.001, respectively.

Aqu E: Aqueous extract; Met E: Methanolic extract;

EC50: efficient concentration (µg phenolic sample/µg DPPH): amount of antioxidant needed to decrease the initial DPPH concentration by 50%.

AE: Antiradical efficiency: 1/EC50.

DISCUSSION

The physical properties of the varieties of date palm fruit was different from those reported by Ismail *et al*. (2006) and Al-Farsi *et al*. (2005). These variations in the physical properties could be attributed to the geographical origin, the normal variability of the cultivars and to the environmental factors and cultivation conditions, such as soil fertilization and irrigation modes (Basha, Abo-Hassan, 1982).

Regarding sugars composition, their amount was similar then previously studies (Ismail *et al*. 2006). This difference in sugar composition suggests the presence of relatively important invertase activity in the latter varieties, which convert their content in sucrose into reducing sugar at the tamr stage. The number of sugars identified and their levels were in good agreement with those previously published by most of the studies (Al-Farsi *et al*., 2007; Elleuch *et al*., 2008; Ismail *et al*., 2006). The sugar contents in Hissa and Bser Hlou varieties were very low. This result can be explained by non-enzymatic browning during storage (Maillard reaction). In fact, dates contain the required reactants, sugars and amine groups, in their proteins, to favor Maillard reaction during storage (Rinderknecht, 1959).

The sugars in dates are the most important constituents as they provide a rich source of energy. The fructose is twice as sweet as glucose; it induces a feeling of satiety and may also reduce the total calories intake compared to other foods (Shiota *et al*., 2002). Date palm may have an important agro-industrial future as a potential source of refined sugar.

Hitherto, based on the available evidence, it is apparent that some of the date fruit varieties belong to low Glycemic Index (GI) diet and may be included as a part of daily diet for the general population and possibly to patients with some chronic diseases (Vayalil, 2012). Furthermore, it has been proved that date fruit consumption had a dulled insulin response in healthy volunteers compared to dextrose (Famuyiwa *et al*., 1992), indicating a prospective advantage in preventing the development and evolution of chronic diseases.

Moreover, fatty acids composition depicted the high nutritional value for a healthy and for the prevention of cardiovascular diseases (Tapiero *et al*., 2002).

Among the available approaches, few studies have focused on the identification and quantification of volatile compounds. Harrak *et al*. (2005) have identified 47 volatile compounds in some varieties of Moroccan dates; Aziza, Boufeggous, Bouskri, Black Busthammi, Iklane, Jihel, Mejhoul and Najda. In Algeria, Mezroua *et al*. (2017), in their study, have shown that the 8 date varieties studied have 61 aromatic compounds with the predominance of (E)-Geranylacetone, Ethyl acetate, Isopentyl alcohol, Decanal and 2-Propanol (22.00%, 11.49%, 9.76%, 8.81% and 8.01% on average, respectively). In Tunisia, El Arem *et al*. (2012) identified a total of 69 compounds in three varieties of dates (Beidh Hmam, Khalt Ahmar and Rtob) at different ripening stage. The percentage of each compound varies from one variety to another and from one stage of maturation to another. The tamr stage is characterized by the abundance of alcohols and esters in all the varieties. These last results from literature prove that there are clear differences from those found in our study with some exceptions. Most of our varieties are characterized by a high percentage of alcohols and aldehydes, with the exception of the Khaltaia variety, which has a high percentage of terpenoids, in which limonene is the most abundant compound (30.30%). These discrepancies could be in part due to the difference in the varieties and/or the harvest locations, maturation stage and the detecting technique and its sensitivity.

This study presented the aroma composition of some date varieties of low market value (except Deglet Nour and Kentichi) and may attract processors attention to exploit its flavour in different products.

Total phenolic content showed that date palm fruit grown in Tunisia had a content of phenolics similar to those of Oman (Al-Farsi *et al*., 2015; Al-Farsi *et al*., 2007). However, Mansouri *et al*. (2005) and Biglari, Al-Karkhi, Easa (2008) reported that total phenolic content of Iranian and Algerian date palm fruit ranged, respectively, from 2.49 to 8.36 mg GAE/100 g of fresh and from 2.89 to 6.64 mg GAE/100 g of dry weight. These levels are much lower than those found in the present study, except for the Kharak date (Iranian dry date) that showed an average content of 141.35 mg GAE/100 g DW. Conversely, Wu *et al*. (2004), in a study on lipophilic and hydrophilic antioxidant capacities of common foods in the United States have observed that the varieties Deglet Noor and Medjool contained a high level on total phenolics (661 and 572 mg of GAE per 100 g FW respectively) as compared to our study. Various factors such as variety, growing condition, maturity, season, geographic origin, fertilizers, soil type, amount of sunlight received, and experimental conditions (storage, solvent extraction) among others might be responsible for the observed differences. The extraction with water gave the highest value for Deglet Nour, Fezzani, and Horra, whereas Allig and Kenta varieties offered the highest content in the methanol extract. Al-Farsi *et al*. (2005) studied the effect of the extraction methods on the total phenolics in sun-dried dates (Fard), using seven different solvents. These differences mainly depend on the solubility of phenolics in methanol, water, or in their mixtures.

The antioxidant properties were evaluated by two different tests as there is no universal method that can measure the antioxidant capacity of all samples accurately and quantitatively: DPPH and ABTS•+. Results showed that date palm fruit of Tunisia has a high level of antioxidant capacity compared to that of Iranian ones based on TEAC assay (Biglari, Al-Karkhi, Easa, 2008). Guo *et al*. (2003) measured the antiradical activity of the pulp of 28 fruits by FRAP assay, and found that dates had the second highest antiradical activity between the fruits consumed in China (6.9 mmol/100 g wet weight). The high antioxidant activity of dates is also supported by Vayalil (2002) and Al-Farsi *et al*. (2005, 2007). Vayalil (2002) stated that the powerful antioxidant and antimutagenic activities of dates implicate the presence of compounds with potent free radicals scavenging activity. Phenolic compounds, including *p*-hydrobenzoic, *p*-coumaric, *o*-coumaric, ferulic, gallic, cafeic, syringic, and vannilic acids and flavonoids, which have been identified in date fruits in our previous study (Saafi *et al*., 2010) may contribute to the antioxidant activity. A positive correlation was revealed between the antioxidant activity and the total phenolic content. The coefficients of correlation are 0.60 and 0.69 (P<0.01) based on the ABTS assay for the aqueous and the methanol extracts, respectively, and 0.49 (P<0.01) and 0.39 (P<0.05) based on the DPPH assay. Other water-soluble antioxidants, such as vitamin C, and minerals (Se, Cu, Mn, Mg, Zn) can participate and enhance the ability of date fruits to scavenge free radicals (Al-Farsi *et al*., 2007). In our previous studies, the aqueous date palm fruit extract revealed a strong capacity to heal the oxidative and cellular damage in rat liver and kidney; by

preventing excessive lipid peroxidation, by maintaining biochemical indicators, hepatic and renal antioxidant enzyme activities at near-normal concentrations, and by improving the liver and kidney's histopathology. It is reasonable to take for granted that the antioxidant portion present in this aqueous extract could play a most important role in preventing the oxidative stress induced by dimethoate (Saafi *et al*., 2011; 2012).

From our findings it was concluded that date palm fruit may serve up a real resource of several substances with nutritional and physiological properties of interest. On the basis of these findings, the common dates studied are similar to the Deglet Nour variety; they are characterized by important antioxidant capacities. This antioxidant capacity is strongly correlated with their polyphenol contents; responsible for this activity. It is therefore urgent to strengthen efforts and implement a strategy to protect and enhance this natural heritage. It would be interesting to exploit these properties in the fields of the agri-food, pharmaceutical and cosmetic industries.

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