International Journal of Food Sciences and Nutrition,
February 2012; 63(1): 84–89

informa
healthcare

Physical and chemical properties, antioxidant activity, total phenol and mineral profile of seeds of seven different date fruit (*Phoenix dactylifera* L.) varieties

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Abstract
The physical and chemical properties of the date (*Phoenix dactylifera* L.) fruit seeds from seven date samples (Soukari, Soulag, Barhi, Khulas, Rozaiz, Soughi and Monaif) were evaluated. Energy values of dried and ground seeds were found between 4340 kcal/kg (Barhi cv) and 4795 kcal/kg (Rozaiz cv). Also, while crude oil content of seeds were established between 4.68% (Khulas cv) and 7.96% (Monaif cv), crude protein contents were found at the levels between 3.71% (Soulag cv) and 5.47% (Barhi cv). The antioxidant activity of seeds obtained from different date fruits changed between 78.03 (mg/ml) (Monaif cv) and 79.94 (mg/ml) (Barhi cv). In addition, the total phenol contents of seeds were found between 1.98 mg gallic acid equivalents (GAE)/100 g (Barhi cv) and 4.65 mg GAE/100 g (Soughi cv). The most abundant fatty acids of the date seed oils were oleic, lauric, myristic, palmitic and stearic acids. Ca, Mg, K and P contents of date seeds were found at the high concentrations.

Keywords: *date seeds, sugars, compositions, antioxidant activity, total phenol, minerals*

Introduction

The date palm (*Phoenix dactylifera* L.) is cultivated in dry and semi-arid regions in the world and is an important member of the family Palmaceae (Saafi et al. 2008; Al-Jasser 2009; Jamil et al. 2010). Palm trees are abundant all over the world, particularly in the Arab Gulf area. It is considered to be the most important tree in most of the Arabian countries (Mustafa et al. 1983; Jamil et al. 2010). On the other hand, fruit exploitation of date palm trees represents an important economical support for indigenous populations (Reynes et al. 1994). Dates are rich in certain nutrients and provide a good source of rapid energy due to their high carbohydrate content (70–80%). Most of the carbohydrates in dates are in the form of fructose and glucose, which are easily absorbed by the human body (Myhara et al. 1999; Al-Farsi et al. 2005; Mrabet et al. 2008). In most cases, date seeds end up as waste products of many date fruit-processing plants. Date seeds are also ground and added to the feed of some animals. In addition, date pits are used in making a caffeine-free drink that can substitute for non-caffeinated coffee when coffee-related flavour is desired. Such a drink has been used in the Arab world for centuries (Rahman et al. 2007; Habib and Ibrahim 2009). Habib and Ibrahim (2009) reported that Khulas and Barhe date seeds contained 8.64 and 10.64% moisture, 5.84 and 5.68% crude protein, 7.92 and 7.52% crude oil, 0.96 and 1.06% ash and 3.94 and 2.43% carbohydrate, respectively. Saafi et al. (2008) reported that the most abundant fatty acids of the date seed oil were mainly oleic acid and lauric acid, followed by linoleic acid, palmitic acid and myristic acid. Date pits could potentially be used as ingredients in the production of some functional foods for human consumption. Date pits could potentially be used as ingredients in the production of some functional foods for human consumption through enhancing the

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ISSN 0963-7486 print/ISSN 1465-3478 online
DOI: 10.3109/09637486.2011.598851

nutritional value of several food products (Habib and Ibrahim 2009).

The aim of this study was to determine the nutritional value, proximate analyses, fatty acid composition, sugar contents and bioactive properties of different date seeds provided from Riyadh in Saudi Arabia.

Materials and methods

Materials

Date fruits (Barhi, Khulas, Monaif, Rozaiz, Soukari, Soulage and Soughi) were purchased from local markets. About 100 g sample was taken and stored. The seeds were removed from date pulps and were preserved at −18°C until analyses. The seeds were washed to free them from any adhering date flesh and then air-dried. A portion of the seed mixture was ground by a hammer mill and the moisture content was established. The remaining part was dried at about 50°C and kept by using.

Physical properties of date seeds

Twenty-five date fruit seeds were taken randomly from each mass to determine fruit seed weight and fruit dimensions (length and diameter).

Chemical analyses of date seeds

The moisture content of pits were determined separately by drying a sample (about 5 g) in a drying oven at 100 ± 5°C during 24 h. Crude fat, crude fibre, crude ash, and values of samples were determined according to the Association of Official Analytical Chemists (AOAC 2000). The total fat content was determined in accordance with the AOAC (2000) method. The oil for fatty acid analysis was extracted from the kernels using a small hand-held cold press. The oil was placed in screw-capped test tubes and flushed with N_2 gas and stored at 4°C until analysis commenced the following day. Crude oil was obtained from finely crushed walnuts (ca. 20 g) extracted with petroleum ether (Merck–Darmstadt, Kyoto) in a Soxhlet apparatus; the remaining solvent was removed by vacuum distillation. The extracted oil was stored at 4°C in tubes. Energy value was measured by the IKA C2000 calorimeter. Protein content was determined by the Dumas Nitrogen Analyzer (DNA; Velp NDA 701, Italy). Protein was calculated using the general factor (6.25; Anonymous 2011).

Working conditions of DNA

O_2 flow rate: 400 ml/min
He flow rate: 195 ml/min
Combustion reactor: 1030°C
Reduction reactor: 650
Pressure (mbar): 881.0

Total phenol

Total phenolic contents were established using Folin Ciocalteu (FC) reagent as described by Yoo et al. (2004) with some modifications. About 0.5 ml aliquot of the aqueous date seed extract was mixed with 2.5 ml of 1:10 FC reagent and 1.5 ml of 20% Na_2CO_3. Absorbance was measured at 517 nm after 30 min standing at room temperature. Gallic acid was used as a standard and the total phenolics were expressed in mg/g gallic acid equivalents (GAE).

Radical scavenging assay

The free radical scavenging activity of the extracts was determined using 1,1-diphenyl-2-picrylhydrazyl or DPPH (Lee et al. 1998). One millilitre solution of the extract was mixed with 2 ml of 10 mg/l methanolic solution DPPH. The mixture was shaken vigorously and allowed to stand at room temperature for a minute and absorbance was recorded at 517 nm using spectrophotometer.

Sugar snalyses

Date seed powder, diluted with distilled water in 1/100 ratio, was kept for 1 h in a shaking water bath (Nüve) at 50°C and then filtered. One millilitre of extract was transferred to two tubes and 1 ml of phenol solvent (80%) was added to each tubes. In the mixture, 5 ml HCl (95.5%) was added at one time of quickly and then the tubes were left to cool for 30 min. The absorbance of the mixtures in the tubes was measured at 490 nm wavelength using a UV–vis spectrophotometer (Schimadzu, Japan). Calibration graphics of saccharose, raffinose, stachyose, galactose, fructose and glucose were prepared and by the use of the graphics the amounts of these sugars in the seed extracts were calculated (Dubois et al. 1956).

Determination of fatty acids

Fatty acid composition of olive oil was determined by the modified method defined by Hışıl (1998). Oil samples were converted to fatty acid methyl esters. Fatty acid methyl esters (1 μl) were analysed by 6890 Agilent branded gas chromatography with flame ion detector. The standard mixture of fatty acids (Sigma Chemical Co., Germany) was used for the identification of peaks.

Working conditions of GC. Name of GC: AGILENT 6890; Injection temperature: 260°C; Detector temperature: 250°C; Total flow rate (ml/d): 30 ml/min; The flow rate of Nitrogen (ml/d): Flow of Nitrogen 300 ml/min; Temperature programme: 250°C.

Determination of mineral contents

Collected date seed samples were dried at 70°C in a drying cabinet with air-circulation until they reached constant weight. Later, about 0.5 g dried and ground sample was digested using 5 ml of 65% HNO_3 and 2 ml of 35% H_2O_2 in a closed microwave system (Cem-MARS Xpress, Australia) at 200°C. The volumes of the digested samples were completed to 20 ml with ultra-deionized water and mineral concentrations were determined by inductively coupled plasma-optical emission spectroscopy (ICP AES; Varian-Vista, Australia). Distilled deionized water and ultrahigh-purity commercial acids were used to prepare all reagents, standards and samples. After digestion treatment, samples were filtered through Whatman No. 42. The filtrates were collected in 50 ml flasks and analysed by ICP-AES. The mineral contents of the date samples were quantified against standard solutions of known concentrations which were analysed concurrently (Skujins 1998).

Working conditions of ICP-AES

Instrument: ICP-AES (Varian-Vista)
RF power: 0.7–1.5 kw (1.2–1.3 kw for axial)
Plasma gas flow rate (Ar): 10.5–15 l/min (radial)
15″ (axial)
Auxilary gas flow rate (Ar): 1.5″
Viewing height: 5–12 mm
Copy and reading time: 1–5 s (max. 60 s)
Copy time: 3 s (max. 100 s)

Statistical analyses

Results of the research were analysed for statistical significance by analysis of variance (Püskülcü and İkiz 1989). This research was performed by three duplicates with a replicate.

Results

The physicochemical and bioactive properties of different date seeds are given in Table I. Date pit varieties showed significant ($p < 0.05$) differences among crude oil, crude fibre, fatty acids and mineral contents of the seven date pit varieties. These properties changed depending on date varieties. While ash contents changed between 1.02% (Rozaiz cv) and 1.26% (Soukari cv), crude fibre contents changed between 17.07% (Khulas cv) and 23.46% (Rozaiz cv). In addition, while diameter of whole date seeds changed between 6.85 mm (Monaif cv) and 9.02 mm (Soughi cv), the length of seeds ranged between 14.11 mm (Barhi cv) and 23.22 mm (Monaif cv). Energy values of grounded and dried seed powders were significantly ($p < 0.05$) found between 4340 kcal/kg (Barhi) and 4795 kcal/kg (Rozaiz). Also, while crude oil content of seeds were determined

Table I. Physicochemical properties of different date seeds.

Date varieties	Diameter (mm)	Length (mm)	Energy (kcal/kg)	Seed weight (Ağırlık g)	Moisture (%)	Crude protein (%)	Crude fibre (%)	Crude oil (%)	Ash (%)	Antioxidant activity (mg/ml)	Total phenol (mg GAE/100 g)
Soughi	9.02	18.25	4790	0.81	9.01	4.32	21.01	5.05	1.17	78.43	4.65
Monaif	6.85	23.22	4781	0.71	7.87	5.11	18.82	7.96	1.05	78.03	3.66
Soulag	8.81	17.29	4791	0.87	8.36	3.71	19.17	5.25	1.15	78.21	4.50
Soukari	6.99	19.49	4600	0.99	8.24	5.18	20.88	5.51	1.26	78.33	3.71
Barhi	6.89	14.11	4340	0.96	7.87	5.47	22.60	4.74	1.13	79.94	1.98
Khalas	7.85	21.61	4745	0.73	8.11	4.71	17.07	4.68	1.07	78.88	4.05
Rozaiz	7.43	17.45	4795	0.52	8.33	4.38	23.46	7.30	1.03	78.11	3.21

Table II. Sugar profile of date seeds.

Date varieties	Glucose (g/kg)	Fructose (g/kg)	Raffinose (g/kg)	Stachyose (g/kg)	Sucrose (g/kg)	Galactose (g/kg)
Soughi	3.52 ± 0.98*	3.84 ± 0.11	3.22 ± 0.09	3.76 ± 0.10	3.46 ± 0.10	2.27 ± 0.07
Monaif	3.60 ± 0.67	3.93 ± 0.75	3.29 ± 0.62	3.84 ± 0.69	3.54 ± 0.69	2.33 ± 0.50
Soulag	3.59 ± 0.05	3.91 ± 0.06	3.28 ± 0.05	3.82 ± 0.06	3.53 ± 0.06	2.31 ± 0.04
Soukari	3.56 ± 0.34	3.89 ± 0.39	3.25 ± 0.32	3.80 ± 0.35	3.50 ± 0.35	2.30 ± 0.26
Barhi	3.53 ± 0.14	3.85 ± 0.16	3.22 ± 0.13	3.76 ± 0.15	3.47 ± 0.15	2.27 ± 0.11
Khalas	3.13 ± 0.33	3.40 ± 0.37	2.85 ± 0.31	3.35 ± 0.34	3.06 ± 0.34	1.97 ± 0.25
Rozaiz	3.40 ± 0.16	3.70 ± 0.18	3.10 ± 0.15	3.63 ± 0.16	3.33 ± 0.16	2.17 ± 0.12

Note: *mean ± SD.

between 4.68% (Khulas cv) and 7.96% (Monaif cv), crude protein contents were established at the levels between 3.71% (Soulag cv) and 5.47% (Barhi). The antioxidant activity of seeds obtained from different date fruits changed between 78.03 (mg/ml) (Monaif) and 79.94 (mg/ml) (Barhi cv). In addition, the total phenol contents of seeds were found between 1.98 mg GAE/100 g (Barhi) and 4.65 mg GAE/100 g (Soughi cv).

The date seeds from seven samples (Barhi, Khulas, Monaif, Rozaiz, Soukari, Soulage and Soughi) were evaluated with respect to sugar compositions (Table II). Results partly changed depending on date seed varieties. The glucose contents of date seeds changed between 3.13 g/kg (Khulas) and 3.60 g/kg (Monaif cv). In addition, fructose contents were found between 3.40 g/kg (Khulas) and 3.93 g/kg (Monaif). Also, raffinose, stachyose and sucrose contents of date seeds were found to be similar. But, galactose contents of seeds were found at low levels. Their concentrations ranged between 1.97 g/kg (Rozaiz cv) and 2.33 g/kg (Monaif cv).

The fatty acid compositions of date seeds are given in Table III. In all of them, 14 fatty acids were present, six of which were unsaturated, whereas the others were saturated. The most abundant fatty acids of the date seed oils were oleic, lauric, myristic, palmitic and stearic acids. The seed oils contained between 40.51% (Soughi) and 45.74% (Rozaiz cv) oleic, between 17.95% (Rozaiz) and 25.01% (Soughi cv) lauric, between 12.07% (Rozaiz cv) and 13.94% (Soughi) myristic, between 9.75% (Khulas cv) and 11.00% (Rozaiz cv) palmitic and between 7.03% (Khulas cv) and 9.28% (Barhi cv) linoleic acids.

Macro- and microelement concentrations of different date seeds are presented in Table IV. Ca, Mg, K and P contents of seeds were significantly ($p < 0.05$) found at the high concentrations. Among the minerals, K was found at high levels. Its concentration changed between 3285 mg/kg (Rozaiz) and 4212 mg/kg (Soulag cv). Phosphorus values were established between 2101 mg/kg and 3063 mg/kg, followed by magnesium and calcium. Among the microelements, Fe was found at the high concentrations. Iron contents were established between 24.8 and 37.7 mg/kg. In addition, zinc contents of the seeds were determined between 8.48 mg/kg (Khulas cv) and 14.18 m/kg (Soukari cv), and followed by Mn, B, Cu, Cr and Ni.

Discussion

Habib and Ibrahim (2009) reported that 18 date pits contained 8.64 and 12.45% moisture, 4.81–5.83% crude protein, 5.71–7.92% crude oil, 0.82–1.14% ash and 2.43–4.65% carbohydrate. Khulas and Barhe date seeds contained 8.64 and 10.64% moisture, 5.84 and 5.68% crude protein, 7.92 and 7.52% crude oil, 0.96 and 1.06% ash and 3.94 and 2.43% carbohydrate, respectively (Habib and Ibrahim 2009). The same researchers determined micronutrients (Fe, Zn, Cu, Mn, Co, Mo and Se) and Fe was established at the highest levels. Fe ranged between 1.32 mg/100 g and

Table III. Fatty acid compositions of different date seed oils (%).

	Soughi	Monaif	Soulag	Soukari	Barhi	Khulas	Rozaiz
Caproic (C 6:0)	0.33	0.39	0.38	0.46	0.28	0.47	0.31
Caprylic (C 8:0)	0.44	0.30	0.47	0.44	0.34	0.85	0.25
Lauric (C 12:0)	23.53	21.31	22.69	23.40	19.21	25.01	17.95
Myristic (C14:0)	13.94	12.69	13.37	13.28	12.22	12.94	12.07
Palmitic (C 6:0)	10.33	10.45	10.16	10.21	9.95	9.75	11.00
Palmitoleic (C 6:1)	0.040	0.10	0.05	0.08	0.056	0.05	0.16
Stearic (C 18:0)	2.15	2.49	2.53	2.30	2.61	2.43	2.73
Oleic (C 18:1)	40.51	43.13	42.40	40.41	45.41	40.73	45.74
Linoleic (C 18:2)	7.97	7.72	7.27	8.66	9.28	7.03	8.76
Linolenic (C 18:3)	0.11	0.25	0.16	0.19	0.19	0.22	0.26
Arachidic (C 20:0)	0.09	0.36	0.03	0.06	0.08	0.18	0.09
Gadoleic (C 20:1)	0.33	0.35	0.34	0.28	0.28	0.21	0.34
Behenic (C 22:0)	0.08	0.22	0.06	0.05	0.06	0.07	0.09

Table IV. Mineral contents of different date seeds (mg/kg).

Dates	Minerals										
	Ca	Mg	K	P	Fe	Zn	Cu	Mn	B	Cr	Ni
Soughi	688 ± 4*	765 ± 11	3862 ± 91	2201 ± 135	37.7 ± 0.2	10.77 ± 0.48	4.82 ± 0.36	7.29 ± 0.34	6.2 ± 0.3	1.60 ± 0.03	1.4 ± 0.1
Monaif	358 ± 29	738 ± 25	3601 ± 166	2509 ± 11	28.1 ± 2.2	9.57 ± 0.33	4.11 ± 0.34	5.98 ± 0.08	6.1 ± 0.3	1.27 ± 0.16	0.8 ± 0.1
Soulag	323 ± 2	764 ± 15	4212 ± 103	2101 ± 8	24.8 ± 1.4	10.24 ± 0.28	4.71 ± 0.32	6.54 ± 0.21	5.7 ± 0.3	1.61 ± 0.14	1.4 ± 0.3
Soukari	405 ± 15	814 ± 36	4186 ± 211	2635 ± 88	36.2 ± 2.4	14.18 ± 0.36	8.48 ± 0.26	7.79 ± 0.32	6.1 ± 0.4	1.98 ± 0.07	1.2 ± 0.2
Barhi	207 ± 6	780 ± 7	3959 ± 81	2454 ± 93	34.4 ± 4.0	12.76 ± 0.12	6.18 ± 0.06	7.54 ± 0.44	5.2 ± 0.2	1.90 ± 0.07	1.2 ± 0.1
Khulas	264 ± 7	893 ± 10	3682 ± 14	3063 ± 6	27.7 ± 1.9	8.48 ± 0.25	3.93 ± 0.13	6.80 ± 0.26	5.5 ± 0.6	2.19 ± 0.15	0.9 ± 0.0
Rozaiz	399 ± 16	827 ± 1	3285 ± 97	2344 ± 220	30.5 ± 1.0	9.52 ± 0.33	3.42 ± 0.28	3.37 ± 0.15	6.2 ± 0.4	1.74 ± 0.29	1.6 ± 0.3

Note: *mean ± SD.

3.44 mg/100 g. While P contents of date seeds change between 110.09 mg/100 g and 173.07 mg/100 g (Habib and Ibrahim 2009). Habib and Ibrahim (2009) established that weight, length and diameter values of date seeds were between 0.60 and 1.26 g, 17.20 and 23.60 mm and 6.33 and 9.33 mm, respectively. Comparable levels of macroelements and trace elements were reported by Al-Hooti et al. (1998), Besbes et al. (2004), Rahman et al. (2007) and Habib and Ibrahim (2009) in date pits from various date cultivars. Minerals have many health benefits. They are generally important as constituents of bones, teeth, soft tissues, muscle, blood and nerve cells. Minerals are also vital to overall mental and physical well-being (O'Dell and Sunde 1997; Sardesai 1998; Habib and Ibrahim 2009). The proximate analyses values of date pits found in the current study are within the range of values presented earlier in the literature (Al-Hooti et al. 1998; Hamada et al. 2002; Aldhaheri et al. 2004; Besbes et al. 2004; Al-Masri 2005; Ismail et al. 2006; Al-Farsi et al. 2007; Rahman et al. 2007; Habib and Ibrahim 2009). The chemical composition of date pits from the mixture of common varieties called 'Khalti' at the 'Tamar' stage was determined by Saafi et al. (2008). Saafi et al. (2008) reported that date pit contained 6.88 g/100 g (FW) moisture, 8.12 g/100 g total sugars, 6.63 g/100 g (DW) reducing sugar, 1.49 g/100 g sucrose, 5.31 g/100 crude protein and 8.33 g/100 g fat. These results were in agreement with those reported by Devshony et al. (1992). Our results for protein were also similar to those of Hamada et al. (2002) and Habib and Ibrahim (2009). Date pits from these varieties contained a substantial amount of oil that needed to be characterized. We were interested in establishing the fatty acid composition. Date seed oil has a very intense yellow colour in comparison with other vegetable oils studied by Erol et al. (2011). This suggests the presence of a significant quantity of the yellow pigment, carotenoid. This pigment is responsible for the absorption of ultraviolet radiations measured by Besbes et al. (2004). Saafi et al. (2008) reported that the most abundant fatty acids of the date seed oil were mainly oleic acid (47.66%) and lauric acid (17.39%), followed by linoleic acid (10.54%), palmitic acid (10.20%) and myristic acid (10.06%). Besbes et al. (2004) showed that the date seed oil contained 47.7% oleic acid, 21% linoleic acid and 5.8% lauric acid. This result was in agreement with that reported by Saafi et al. (2008). Differences in the levels of minerals among different date pit varieties may be due to genetic differences, time of harvest, fertilizers, soil mineral availability, and climatic and environmental factors.

Conclusion

This general study also presents that the several date pits could represent an excellent source of food

ingredients with interesting technological functionality that could be used in food as an important source of protein, crude fibre and oil. They contain a high relative percentage of oleic acid, which is required in our nutrition and health to protect us from cardiovascular diseases. Date seeds could be a valuable source of edible and pharmaceutical oils (Saafi et al. 2008). Date pits could potentially be used as ingredients in the production of some functional foods for human consumption through enhancing the nutritional value of several food products, for example, increasing the fibre content of bakery products (Habib and Ibrahim 2009). They contain considerable amounts of some mineral and fatty acid compositions. Future studies will carried out on phenolic and bioactive compounds and the corresponding effects of date seeds.

Declaration of interest: This study was supported by Selcuk University Scientific Research Project (S.Ü.-BAP, Konya-Turkey). Also, the authors thank the ZADE Oil Company, GESAŞ A.Ş. and their researchers. The authors report no conflicts of interest. The authors alone are responsible for the content and writing of this paper.

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