International Journal of Pharmacology

ISSN 1811-7775

science alert

ansinet
Asian Network for Scientific Information

OPEN ACCESS International Journal of Pharmacology

ISSN 1811-7775
DOI: 10.3923/ijp.2018.407.414

Research Article
Effect of Maturation Stages on Flavor Profile and Antioxidant Activity of Date Palm Fruits (*Phoenix dactylifera*) Grown in Saudi Arabia

[1,2]Hatem Ali, [1]Abdel Rahman Al-khalifa, [3]Amr Farouk and [3]Mohamed Shaheen

[1]Department of Food Science and Nutrition, College of Food Science and Agriculture, King Saud University, Saudi Arabia
[2]Department of Food Technology, National Research Center, Dokki, Cairo, Egypt.
[3]Department of Flavour and Aroma Chemistry, National Research Center, Cairo, Egypt

Abstract

Background and Objective: A number of studies have been published from a pharmaceutical and medicinal point of view, focusing on phenolic compounds and their biological activities in various date palm fruits from different date growing countries based on aqueous or alcoholic extracts. The present study was performed to identify the volatile constituents of date palm fruits cultivated in the Kingdom of Saudi Arabia at the besser, rutab and tamr maturation stages, as well as evaluating the total phenolic content in the volatile extracts and their antioxidant activity. **Materials and Methods:** Four varieties of date palm fruits *(Phoenix dactylifera* L.) cultivated in Saudi Arabia Khalas, Sokary, Seqah and Khenazy were analyzed for their aroma volatiles, total phenolic compounds and antioxidant activity at three maturation stage, besser, rutab and tamr. **Results:** The 71 aroma constituents were identified using the dynamic head space technique during the maturation stages. Alcohols were the major class of compounds present with 2.6-81.31% followed by carbonyls with 1.69-83.97% in Seqah rutab stage where esters accounted 2.66-49.89% of detected species. Total phenolic compounds were highest in the Khenazy rutab stage (9.23 μg GAE/100 g), which is in agreement with the radical scavenging activity (IC_{50} 1.45 μg mL^{-1}). **Conclusion:** The data obtained revealed that, the date palm cultivated in Saudi Arabia are rich in phenolic and antioxidant constituents and probably have use as nutraceutical and functional food additives.

Key words: Date palm fruits, stages of maturity, antioxidant activity, total phenolic content, aroma volatile compounds

Received: September 15, 2017 Accepted: November 09, 2017 Published: March 15, 2018

Citation: Hatem Ali, Abdel Rahman Al-khalifa, Amr Farouk and Mohamed Shaheen, 2018. Effect of maturation stages on flavor profile and antioxidant activity of date palm fruits (*Phoenix dactylifera*) grown in Saudi Arabia. Int. J. Pharmacol., 14: 407-414.

Corresponding Author: Amr Farouk, Department of Flavour and Aroma Chemistry, National Research Center, Cairo, Egypt Tel: +201092327777

Copyright: © 2018 Hatem Ali *et al.* This is an open access article distributed under the terms of the creative commons attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Date palm fruit (*Phoenix dactylifera* L.) is considered as high value product, that is produced in many arid regions of the world such as Middle Eastern countries especially, The Kingdom of Saudi Arabia, Iran, Algeria, Tunisia and Egypt. However, during the last three centuries, cultivation of dates has been introduced into South Africa, South America, Australia and North America. Dates have played significant roles in the economy, society and environment of the countries which cultivated this crop[1]. The Kingdom of Saudi Arabia which is one of the top three producers in the world, produce over 1 million tons of dates annually from about 23 million date palms over 400 cultivars, accounting for 17% of the total global production[2,3].

Many researchers have reported the nutritional value and main chemical composition of dates e.g., Al-Shahib and Marshal[4] who showed the following proportions in date palm fruits, carbohydrate (70-80%), fat (0.2-0.5%), protein (2.3-5.6%) dietary fiber (6.4-11.5%), minerals (0.1-916 mg/100 g date) and vitamins such as C, B1, B2, A, riboflavin and niacin. In addition, several investigations have been published from a pharmaceutical and medicinal point of view, focusing on phenolic compounds and their biological activities in various date palm fruits from different date growing countries based on aqueous or alcoholic extracts[5-7]. In spite of the importance of flavor as a key factor in consumer satisfaction and further processing of the fruits, only a few studies concerning aroma and volatiles of dates could be found in the literature. Jaddou *et al*.[8] extracted 38 compounds from an Iraqi Zahdi cultivar by vacuum distillation, whereas, Max *et al*.[9] and Torres *et al*.[10] have reported 36 and 25 aroma compounds respectively in three Tunisian dates cultivars extracted by headspace pentane method. More recently, El Arem *et al*.[11] identified 69 compounds in some Tunisian cultivars at different stages of maturation (besser, rutab and tamr) after extraction using Headspace Solid Phase Micro extraction/Gas Chromatography-Mass Spectrometry (HS-SPME/GC-MS). However, nothing could be found in the literature concerning volatiles or their bioactivity for dates cultivated in the Arab peninsula or the Kingdom of Saudi Arabia. During maturation, dates pass through many stages in which the chemical composition as well as the aroma can vary. Compounds are continuously synthesized and the total composition changes qualitatively and quantitatively during ripening[12].

The aim of the present study was to identify the volatile and aromatic constituents of date palm fruits cultivated in the Kingdom of Saudi Arabia at the besser, rutab and tamr maturation stages, as well as evaluating the total phenolic content in the volatile extracts and their antioxidant activity.

MATERIALS AND METHODS

Plant materials: Four different varieties of date palm fruit (Khalas, Sokary, Seqah and Khenazy) at different ripening stages (besser, rutab and tamr) were collected from the Station of research and agricultural experiments in Dirab, Faculty of Science of Food and Agriculture, King Saud University, Riyadh, KSA, during the 2013 harvest season. Uniformed fruits, free of defects were selected and stored at -20°C until analysis. Three replicate analysis were carried out for each type of date.

Chemicals and reagents: Diethyl ether and methanol were purchased from (Fisher Chemicals). Mixtures of n-alkanes C_6-C_{26}, authentic compounds, sodium bicarbonates, anhydrous sodium sulfate, linoleic acid (≥99%), Tween 40, β-carotene (≥97%), Folin-Ciocalteu reagent for total phenolic compounds, 2,2'-diphenyl-1-picrylhydrazyl (DPPH) and gallic acid were obtained from Sigma Aldrich Chemical Co. (St. Louis, MO, USA).

Extraction of volatile aroma compounds: The edible part of date palm fruits (100 g) was pitted, crushed and cut to small pieces with a sharp knife and dry-blended for 3 min in a blender (Moulinex, France). The tissue of date palm fruits was rapidly juiced and then the volatiles were isolated by using a dynamic headspace system (DHS). The samples were purged for 3 h with nitrogen gas (grade of N2>99.99%) at a flow rate 100 mL min^{-1}. the headspace volatiles were swept into cold traps containing diethyl ether and held at -10°C. The volatile extracts were dried over anhydrous sodium sulfate for 1 h and then reduced to 1 mL on a rotary evaporator (Heidolph, Germany).

Gas chromatographic-mass spectrometric analysis (GC/MS): The analysis was carried out by using a coupled gas chromatography Hewlett-Packard model (5890) and mass spectrometric detector (Hewlett-Packard5970). A fused silica capillary column DB-5 (60 m×0.32 mm, id) was used. The oven temperature was maintained initially at 50°C for 5 min. and then programmed from 50-250°C at a rate of 4°C min^{-1}. Helium was used as the carrier gas, at a flow rate of 1.1 mL min^{-1}. The injector and detector temperatures were 220 and 250°C, respectively. The ionization voltage was 70 eV and mass range m/z 39-400 amu. The identification of the compound was based on matching with the mass spectra library (NIST library version 2005), comparison with spectra of authentic compounds and published data[13]. The relative percentage of the oil constituents was calculated from the GC

peak areas. A linear retention was calculated for each compound using the retention times of a homologous series of C_6-C_{26} n-alkanes[13].

Antioxidant activity assays

β-Carotene bleaching assay: The antioxidant activity was determined by a β-carotene/linoleic acid system as described by Jayaprakasha *et al.*[14] in comparison to tert-butylhydroquinone (TBHQ). The absorbance was measured at 470 nm over a 60 min period.

DPPH radical scavenging assay: The potential antioxidant activities of volatile extracts were assessed according to Hatano *et al.*[15] in comparison to synthetic antioxidant used in food industry, TBHQ. The absorbance was measured at 517 nm using spectrophotometer (Evolution 300 Thermo UV-VIS), all tests were run in three replicates and averaged.

Determination of the total phenolic contents: The total phenolic content of the volatile extracts was determined using Folin–Ciocalteu reagent according to a modified method of Singleton *et al.*[16] with gallic acid as the standard. The reaction mixtures were incubated in a thermostat at 45°C for 45 min before the absorbance at 765 nm was measured.

Statistical analysis: Statistical analyses were performed using SPSS software version 16 (SPSS Inc., Chicago, IL, US). The variation in the results is expressed as mean±standard deviation (Mean±SD). The significance of the difference between samples was determined using t-test. The difference was regarded significant when $p<0.05$, where p is a level of significance.

RESULTS

Aroma volatiles of different date palm fruits varieties, Khalas, Sokary, Seqah and Khenazy, at different maturation stages, are reported in Table 1 and Fig. 1. Seventy one compounds were identified and classified into alcohols, esters, carbonyls (aldehydes and ketones), acids and hydrocarbons. The identified volatile compounds comprised about 90.04-99.15% of the total aroma compounds.

Twenty five alcohols were detected and constituted the major qualitative class of identified volatiles at 2.6-81.3% in all varieties and maturation stages. These were followed by 18 carbonyls (aldehydes and ketones) representing 1.69-83.97% of the detected species, 16 esters comprising 2.66-49.89% of the volatiles identified and finally 5 terpenes, 3 fatty acids and 4 long-chain hydrocarbons at 0-4.03, 0-23.84 and 0-5.19%, respectively.

According to Table 1 and Fig. 1, increases in alcohols could be noted in Khalas cultivar from the besser stage to the tamr stage (32.84-69.5%) as well as in Sokary (64.86-70.01%) and in khenazy (66.4-72.93%). In the Seqah variety, the besser stage had 35.41% of alcohols, which dropped dramatically to 2.6% in the rutab stage, before raising again to 35.91% in the tamr stage. The 2-Hexen-1-ol was the predominant alcohol identified, ranging from 0.8% in Khalas besser to 77.02% in the rutab stage of Khenazy, followed by 2-phenylethanol which found at 21.51% in besser stage of Khalas, while 1-hexanol was ranged from 1.45% in Khalas rutab stage to 3.88% in Sokary at tamr stage.

The concentrations of esters decreased from 30.36% at the besser stage to 16.21% in the tamr stage of Khalas cultivar and the changes in the Khenazy variety were from 19.78-17.24%. A slight increase was noted in the Sokary variety (16.89-19.32%) and a dramatic increase was seen in the Seqah cultivar from 13.9-49.89%. Ethyl nonanoate characterized besser stage in all cultivars, especially in Khalas (6.5%), in addition to another predominant fatty acid ester, hexadecenyl acetate which found at 21.32% in besser stage Khalas and 11.86% in tamr stage Seqah but was absent in other cultivars.

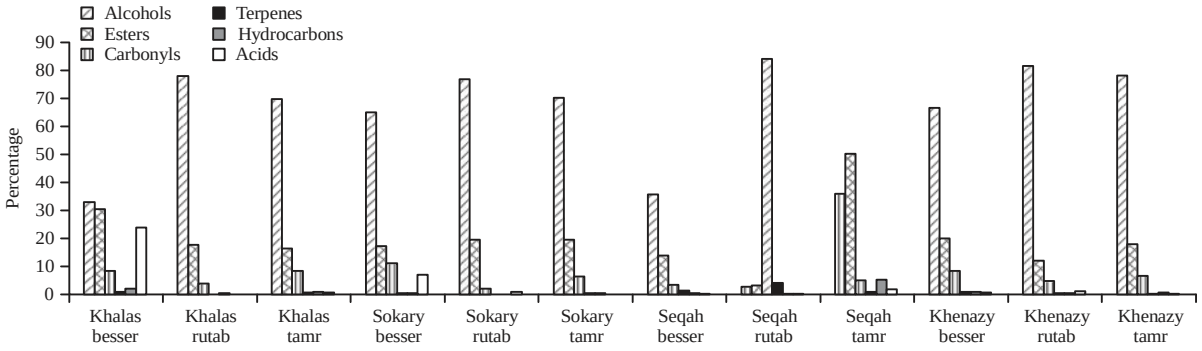

Fig. 1: Concentrations of different volatile classes along different maturation stages in date palm cultivars

Table 1: Volatile constituents of date palm fruits at different maturation stages

Identified compounds	KI[b]	Khalas besser	Khalas rutab	Khalas tamr	Sokary besser	Sokary rutab	Sokary tamr	Seqah besser	Seqah rutab	Seqah tamr	Khenazy besser	Khenazy rutab	Khenazy tamr
Esters													
Ethyl acetate	619		14.03±2.1	12.61±1.8	9.75±2.3	11.19±1.8	11.0±2.2	11.95±3.1		10.35±1.9	10.06±1.1	8.0±2.3	10.12±1.7
Methyl propionate	644		2.38±0.9*	2.49±0.63	3.74±0.4	4.44±0.87	6.53±1.7	1.3±0.36	0.61±0.04	0.8±0.09	2.99±0.99	2.3±0.56	2.41±0.63
Propyl acetate	721		0.55±0.05				0.14±0.06			0.85±0.05			
(E)-3-Hexenyl acetate	1017		0.25±0.1		0.81±0.02	0.71±0.06	1.51±0.28	0.52±0.05					0.47±0.04
Pentyl isobutyrate	1057			0.31±0.05	1.54±0.4	0.14±0.02					0.64±0.12		0.36±0.08
Ethyl octanoate	1199						0.14±0.08		0.66±0.01				
Isobornyl acetate	1286			0.14±0.07							0.3±0.02		0.12±0.01
Ethyl nonanoate	1297	6.5±0.96		0.2±0.01				0.13±0.01			0.39±0.03	0.11±0.01	0.16±0.02
Benzyl butyrate	1346	0.27±0.03							0.61±0.07				
(E)-Geranylacetone	1460								0.16±0.02			0.19±0.06	
Ethyl dodecanoate	1598	0.73±0.11								1.94±0.06			
Ethyl tetradecanoate	1796	0.78±0.13		0.12±0.01							0.16±0.04		
Isopropyl tetradecanoate	1830	0.36±0.02							0.12±0.06				
Ethyl (E)-11-hexadecenoate	1975	0.4±0.05		0.34±0.02		0.17±0.02			0.13±0.01		0.2±0.02		
(Z)-5-Hexadecenyl acetate	1989	21.32±3.6			1.05±0.45	2.7±0.87			0.37±0.08	11.86±2.2	5.04±0.42	1.38±0.17	
Ethyl hexadecanoate	1997									24.89±2.7			3.6±0.77
Total (%)[a]		30.36	17.21	16.21	16.89	19.35	19.32	13.9	2.66	49.89	19.78	11.98	17.24
Alcohols													
3-Methyl-3-buten-1-ol	629	6.06±0.88							0.83±0.08				
Butan-1-ol	676		0.84±0.09								0.43±0.06	0.73±0.04	0.43±0.03
Pentan-2-ol	690		0.11±0.02	0.17±0.02	0.14±0.03	0.41±0.02	0.82±0.01				1.19±0.28		1.24±0.41
Pentan-2-ol	730				0.15±0.01			0.78±0.1					
Isoamyl alcohol	747		0.44±0.03	1.44±0.39	2.05±0.54	1.99±0.22	1.22±0.33					2.58±0.77	1.58±0.33
1 –Pentanol	768				0.55±0.06	0.55±0.04	1.09±0.32	0.63±0.08		0.4±0.04	1.16±0.31	0.29±0.05	0.65±0.1
2,3-Butandiol	789		0.06±0.00					0.16±0.01				0.34±0.02	
(Z)-2-Hexen-1-ol	855	0.8±0.05	74.51±4.3	59.19±4.9	55.76±3.7	73.3±5.6	62.05±5.1	33.52±3.2	-	31.93±3.6	54.18±5.2	77.02±3.7	65.84±4.6
1-Hexanol	870		1.45±0.36	2.89±0.85			3.88±0.63				3.47±0.72		0.58±0.08
Heptan-2-ol	905		0.1±0.01	0.19±0.02							0.13±0.01		0.19±0.00
1-Octen-3-ol	975				0.14±0.01	0.15±0.02	0.23±0.02	0.14±0.00					
Phenylmethanol	1043			0.14±0.01	3.07±0.44	0.25±0.08	0.1±0.03	0.18±0.00			0.12±0.02	0.18±0.00	
1-Phenylethanol	1060	0.83±0.04		0.53±0.09	0.14±0.02		0.24±0.05			0.82±0.09	0.75±0.04		0.19±0.05
1-Octanol	1061				0.37±0.05						0.14±0.02		0.1±0.00
Octan-1-ol	1072			0.35±0.08					0.1±0.00		0.64±0.08		
3-Nonanol	1102			0.25±0.02							0.6±0.08		0.28±0.05
2-Phenylethanol	1116	21.51±3.9		0.31±0.02	0.17±0.05		0.14±0.05		0.32±0.08		0.49±0.03		0.16±0.00
Decan-1-ol	1277	0.38±0.09		0.27±0.07							0.43±0.07		0.23±0.01
p-Ethyl guaiacol	1280			0.21±0.06							0.2±0.05		
(E)-4-Dodecen-1ol	1462	2.62±0.23		1.69±0.17	0.19±0.01	0.37±0.07			0.82±0.08	0.27±0.02	1.12±0.02	0.17±0.01	0.65±0.04
1-Tridecanol	1575	0.52±0.05		0.51±0.07	0.13±0.02		0.24±0.01		0.41±0.02	0.74±0.04	0.45±0.06		
2-Propylphenol	1591	0.4±0.04		0.72±0.03					0.12±0.01		0.77±0.05		0.3±0.08
Hexadecan-1-ol	1894	0.52±0.06		0.24±0.02						0.27±0.02	0.62±0.04		0.17±0.04
Pentadecan-1-ol	1775		0.11±0.02	0.18±0.01						0.12±0.00	0.13±0.00		0.22±0.02
1,14-Tetradecanediol	1923			0.22±0.02						1.36±0.47	0.15±0.01		0.12±0.01
Total (%)[a]		32.84	77.62	69.5	64.86	77.02	70.01	35.41	2.6	35.91	66.4	81.31	72.93

Table 1: Continue

Identified compounds	KI[b]	Khalas besser	Khalas rutab	Khalas tamr	Sokary besser	Sokary rutab	Sokary tamr	Seqah besser	Seqah rutab	Seqah tamr	Khenazy besser	Khenazy rutab	Khenazy tamr
Carbonyls													
2-Methylbutanal	664		2.08±0.88	1.56±0.12	2.06±0.99	0.82±0.07	1.92±0.39					2.41±0.47	1.88±0.25
2-Ethylbutanal	770		0.27±0.04		7.45±1.6	0.87±0.10	1.78±0.17	0.58±0.08			0.2±0.02	1.42±0.18	0.47±0.02
Hexan-3-one	785			0.64±0.04			0.15±0.00				1.28±0.12	0.32±0.06	0.78±0.09
4-Heptenal	899		1.01±0.54	1.26±0.35	0.42±0.07		1.66±0.22				1.43±0.17		
Heptanal	902				0.57±0.01							0.18±0.01	
7-Octen-2-one	1055			0.54±0.02			0.1±0.00				0.15±0.05		0.6±0.07
(E)-2-Nonenal	1161	1.44±0.47		0.13±0.02					1.68±0.29		0.18±0.03		
4-Ethylbenzaldehyde	1181			0.13±0.03							0.1±0.00		0.18±0.02
(E)-2-Decenal	1266			0.48±0.04							1.05±0.14		0.44±0.06
Undecan-2-one	1294	0.31±0.02		0.13±0.01							0.14±0.02		
Undecanal	1308		0.31±0.03	0.63±0.09					2.19±0.85		0.99±0.06	0.11±0.00	1.01±0.19
(E)-2-Tridecene	1315			0.15±0.02							0.32±0.05		0.12±0.00
2,4-Dihydroxybenzaldehyde	1363						0.11±0.08	0.44±0.05	3.35±0.95	0.84±0.06			
(Z)-5-Dodecenal	1389	0.49±0.04							0.59±0.05	0.39±0.06			0.23±0.05
Dodecanal	1409	5.06±0.96		1.26±0.13	0.2±0.01		0.19±0.02		0.15±0.00	1.88±0.23	0.38±0.05		0.37±0.01
Tridecanal	1512			0.12±0.01							0.15±0.07		
1-Tetradecenal	1674	0.5±0.08		0.49±0.07	0.16±0.05		0.28±0.02	1.99±0.11		1.91±0.15	0.35±0.08		0.19±0.02
Pentadecan-2-one	1689	0.66±0.08							76.01±5.5		0.11±0.01		
Total (%)[a]		8.46	3.67	7.52	10.86	1.69	6.19	3.01	83.97	5.02	6.83	4.44	6.27
Terpenoids													
Borneol	1169							0.15±0.03	0.44±0.02				
Dihydrocarveol	1194							0.84±0.05		0.52±0.06			
β-Cyclocitral	1220				0.22±0.01				3.59±0.41				
β-Citronellol	1228	0.56±0.08					0.13±0.02						
(E)-β-Ionone	1486			0.41±0.05				0.28±0.04		0.28±0.04	0.76±0.02	0.17±0.01	0.3±0.02
Total (%)[a]		0.56	0	0.41	0.22	0	0.13	1.27	4.03	0.8	0.76	0.178	0.3
Hydrocarbons													
n-Pentadecane	1501	0.65±0.08		0.11±0.02				0.45±0.03	0.11±0.01	0.34±0.06	0.13±0.02	0.13±0.00	
1-Hexadecene	1578	0.98±0.1		0.75±0.06	0.18±0.05		0.28±0.06		0.11±0.01	0.43±0.07	0.74±0.09		0.27±0.02
n-Hexadecane	1600									4.42±1.1			
7-Ethylhexadecane	1728		0.19±0.02										0.28±0.05
Total (%)[a]		1.63	0.19	0.86	0.18	0	0.28	0.45	0.22	5.19	0.87	0.13	0.55
Acids													
Hexanoic acid	1020				7.1±1.8	0.71±0.02			0.22±0.01			1.12±0.4	
(Z)-9-Hexadecenoic acid	1953			0.21±0.06							0.36±0.07		0.14±0.01
(E)-9-Hexadecenoic acid	1960	23.84±2.9		0.37±0.02		0.11±0.01			0.16±0.02	1.36±0.47	0.31±0.04		0.15±0.03
Total (%)[a]		23.84	0	0.58	7.1	0.82	0	0	0.38	1.36	0.67	1.12	0.29

[a]Percentage obtained by MS peak area normalization, [b]Retention indices (kovats index). *Varying degree of the result is expressed as mean±standard deviation (Mean±SD)

Table 2: Antioxidant activity assays and total phenolic content of date palm fruit verities during different maturation stages*

Date palm varieties	Total phenolics[a] (mg GAE/100 g DW)	DPPH IC_{50}[b] (μg mL^{-1})	β-carotene ARE[c]
Khalas (b)	3.26±0.99	5.12±1.9	0.195±0.05
Khalas (r)	8.14±1.6	2.01±0.54	0.497±0.06
Khalas (t)	6.12±1.4	3.95±0.78	0.253±0.02
Sokary (b)	5.36±0.97	4.56±1.1	0.219±0.04
Sokary (r)	7.95±0.85	2.95±0.63	0.3389±0.06
Sokary (t)	6.58±0.76	3.64±0.79	0.274±0.03
Seqah (b)	5.12±1.2	4.68±1.6	0.213±0.07
Seqah (r)	2.47±0.22	5.44±1.1	0.183±0.06
Seqah (t)	4.25±0.37	4.98±1.7	0.200±0.08
Khenazy (b)	5.94±0.52	4.12±1.5	0.242±0.05
Khenazy (r)	9.23±1.4	1.45±0.41	0.689±0.11
Khenazy (t)	7.65±1.3	3.42±0.69	0.292±0.06

*Results are Mean±SD (n = 3), [a]mg gallic acid equivalents (GAE)/100 g dry weight (DW), [b]Efficient concentration (IC_{50}): Amount of antioxidant needed to decrease the initial DPPH-concentration by 50%, [c]Antiradical efficiency: 1/EC50

In addition to the aromatic aldehydes especially dihydroxy benzaldehyde and cyclocitral which found only in the rutab stage of Seqah (3.35 and 3.59%) with floral and fruity notes (Table 1), other aliphatic aldehydes were detected in some maturation stages, mainly 2-methylbutanal, heptanal, undecanal and dodecanal. Generally, carbonyls ranged from 1.69-10.86% in various maturation stages of the date cultivars under investigation, except for Seqah at the rutab stage (83.97%), due to the presence of 2-pentadecanone (76.01%).

Seqah variety at tamr stage was found to be the richest in saturated hydrocarbons especially n-hexadecane (4.42%), while no hydrocarbons could be detected in the rutab stage of sokary.

In addition to 9-hexadecenoic acid which represented a major component among the volatiles of Khalas besser, hexanoic acid was detected in besser stage of the Sokary with 7.1% and in rutab stage of Khenazy with 1.12%.

The determination of total phenolic content was based on the absorbance values of the various extract solutions after reaction with Folin-Ciocalteu reagent and compared with standard solutions of gallic equivalents as described in section 2, 5 and 3. The highest amount of total phenolics was in Khenazy at rutab stage followed by both Khalas and Sokary at rutab stage, while the lowest was in Seqah rutab stage.

In the present study, the relative antioxidant abilities of the date palm fruit extracts at different maturation stages were investigated through two *in vitro* models, antioxidant capacity by β-carotene linoleate system and radical scavenging activity using, DPPH method (Table 2). It was found that, the rutab stage of the Khenazy variety had the highest radical scavenging activity (IC_{50} = 1.45 μg mL^{-1}), followed by the Khalas type at rutab stage (2.01 μg mL^{-1}) and the rutab stage of Sokary (2.95 μg mL^{-1}), however, the rutab stage of the Seqah variety had the lowest radical scavenging activity (IC_{50} = 5.44 μg mL^{-1}). The β-carotene linoleate assay showed similar results to those found in DPPH assay (Table 2), where the rutab stage of the Khenazy variety again had the highest radical scavenging activity (0.689) in comparison to the other varieties at different maturation stages.

DISCUSSION

This study discovers the relation between maturity stages and the using of date palm fruits cultivated in Kingdom of Saudi Arabia, as a nutraceutical food based on their sensory compounds and phenolic content. It believed that, it will encourage the researchers to study and explore extensively the date palm fruits cultivated in arab peninsula. Stages of maturity have been shown to affect the aroma volatile constituents and the phenolic content of date palm fruits as well as their antioxidant activity. Alcohols have been found as the dominant class among the volatiles identified followed by carbonyls and esters. El Arem *et al.*[12] reported that, alcohols are the most important class formed during ripening as lipid oxidation products. Along with terpenes, alcohols are responsible for the herbaceous, fruity, citrus, floral and fungal aromas of dates[17]. With respect to the predominant alcohols identified in different cultivars at various stages, 2-hexen-1-ol, 1-hexanol and phenylethanol are probably contribute to the green, herbal and floral aroma notes of the dates fruits, respectively[17,18].

The concentrations of terpenes were found to be inversely proportional to the amounts of alcohols formed during all maturation stages (Table 1, Fig. 1). Terpenes e.g., borneol with a piney, camphor-like odor and dihydrocarveol with a floral and fruity aroma were detected only in the Seqah maturations stages, while cyclocitral, citronellol and β-ionone could be identified on other cultivars[18].

Esters are characterized by fruity, pineapple and apple odours[17]. Ethyl acetate and methyl propionate are the dominants of this class and seem to be similar for Degla, Horra and other varieties cultivated in Morocco and Tunisia as reported by Harrak *et al.*[19] and El Arem *et al.*[12]. Detection of ethyl nonanoate in besser stage of all studied cultivars, is in agreement to the findings of El Arem *et al.*[11] while the presence of hexadecenyl acetate as a dominant ester in Khalas besser and Seqah tamr, is in accordance to Torres *et al.*[10], who reported the formation of such esters as being due to lipid metabolism. Generally, like other volatile classes and as Max *et al.*[9] stated, the concentration of esters increased at the expense of alcohols (Fig. 1), since volatile esters are formed by esterification of alcohols during fruits ripening[20].

Aliphatic aldehydes are responsible for malt, aldehydic, green, citrus and sweet aroma notes especially in early maturation[19]. Short-chain aldehydes e.g., 2-methyl and 2-ethylbutanal were decreased over ripening, while the concentrations of other longer aldehydes e.g., 4-heptenal and dodecanal were found to be increased during ripening especially in Khalas, Sokary and Seqah varieties. Other aldehydes e.g., octanal, nonanal and tridecanal were reported by Jaddou *et al.*[8], El Arem *et al.*[12] and Harrak *et al.*[19], in other cultivars e.g., Zahdi in Iraq, Aziza, Bouskri and Jihel in Morocco and Allig, Degla, Gosbi and Horra in Tunisia.

Long-chain hydrocarbons increased considerably through different maturation stages, which is in accordance to El Arem *et al.*[12]. Jaddou *et al.*[8] and Harrak *et al.*[19] were reported the presence of hydrocarbons on different date cultivars, however, these compounds are not among the impact flavor of dates.

Hexanoic acid which has a pleasant fatty note reported by Burdock[18], seems to be the most important among fatty acids class from the sensory point of view. Many fatty acids were reported by Harrak *et al.*[19] e.g., C_6, C_8-C_{12}, C_{14}, C_{16}, C_{18}, $C_{18:2}$ and C_{20}, however, only C_6 and $C_{16:1}$ were identified in the varieties under investigation.

Wu *et al.*[21] have been suggested that date fruit may contain a higher level of total phenolic content than among other fresh and dried fruits. According, we have determined the amount of phenolic compounds in the tested extracts of different date varieties (Table 2). The results showed that the date palm fruits varieties under investigation had a similar level of phenolic content (2.47-9.23 mg GAE/100 g DW) to those of Algerian and Iranian cultivars[22-24]. However, Al-Farsi *et al.*[25] reported higher levels between 172 and 246 mg gallic acid equivalents/100 g fresh weight in Omani dates.

The antioxidant activity of the date palm fruits at different maturation stages were related to the phenolic contents of the species under investigation, whereas the rutab stage of Khenazy, Khalas and Sokary were presented the highest activity. The potential antioxidant activity recorded for the date palm fruits varieties under investigation at different maturation stages (1.45-5.44 μg mL^{-1}), favors their possible application as a nutraceutical food and natural antioxidant. Findings of the antioxidant activity are in agreement with Vayalil[26], who reported that, the amount of fresh extract required to scavenge 50% of superoxide radicals was equivalent to 0.8 mg mL^{-1} in the riboflavin photoreduction method and of 2.2 mg mL^{-1} for 50% hydroxyl radical scavenging activity in the deoxyribose degradation method. The antioxidant activity of the different date varieties under investigation depended on their phenolic content which is in accordance with Biglari *et al.*[23]. Presence of higher amounts of phenolic content in Khenazy, Khalas and Sokary rutab stage suggested their responsibility for the higher antioxidant activity of such varieties, which encourage the use of date fruits at various maturation stages as functional food ingredient.

CONCLUSION

The Khenazy, Khalas and Sokary varieties at rutab stage are good and easily accessible source of phenolic compounds in comparison with other maturation stages, which is in agreement with the antioxidant activities recorded for all samples under investigation. The 71 aroma volatiles identified in date palm fruits could be classified into alcohols, esters, carbonyl compounds, terpenes carboxylic acids and long-chain hydrocarbons. Qualitative and quantitative differences in compounds responsible for aroma were noted across maturation stages. While alcohols are the dominant species, there is an inverse relationship between concentrations of these and other classes of compounds present.

ACKNOWLEDGMENT

This project was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award Number (11-AGR 1600-2).

REFERENCES

1. Chao, C.C.T. and R.R. Krueger, 2007. The date palm (*Phoenix dactylifera* L.): Overview of biology, uses and cultivation. HortScience, 42: 1077-1082.
2. FAO., 2014. FAOSTAT database. Food and Agriculture Organization of the United Nations, Rome, Italy. http://www.fao.org/faostat/en/#data/QC

3. Anonymous, 2006. The Famous Date Varieties in the Kingdom of Saudi Arabia. Ministry of Higher Education, Riyadh, Pages: 39.
4. Al-Shahib, W. and R.J. Marshall, 2003. The fruit of the date palm: Its possible use as the best food for the future? Int. J. Food. Sci. Nutr., 54: 247-259.
5. Chaira, N., A. Mrabet and A. Ferchichi, 2009. Evaluation of antioxidant activity, phenolics, sugar and mineral contents in date palm fruits. J. Food Biochem., 33: 390-403.
6. Saleh, E.A., M.S. Tawfik and H.M. Abu-Tarboush, 2011. Phenolic contents and antioxidant activity of various date palm (*Phoenix dactylifera* L.) fruits from Saudi Arabia. Food Nutr. Sci., 2: 1134-1141.
7. Eid, N.M.S., B. Al-Awadi, D. Vauzour, M.J. Oruna-Concha and J.P.E. Spencer, 2013. Effect of cultivar type and ripening on the polyphenol content of date palm fruit. J. Agric. Food Chem., 61: 2453-2460.
8. Jaddou, H., M.T. Mhaisen and M. Al-Hakim, 1984. Flavour volatile analysis of Zahdi dates by gas-liquid chromatography. Date Palm J., 3: 367-380.
9. Max, R., M. Lebrun and P. Shaw, 1996. Identification of the Aromas of Three Varieties of Date. In: The date palm in the oasis agriculture of the Mediterranean countries, Michel, F., G. Didier, S. Bedrani and T. Jean-Philippe (Eds.)., CIHEAM, Paris.
10. Torres, P., R. Max, L. Marc and F. Michel, 1996. Volatile Constituent of Dates From Phoenix Dactylifera Grown in Elche. In: Le Palmier Dattier Dans L'agriculture D'oasis Des Pays Méditerraneens, Michel, F., G. Didier, S. Bedrani and T. Jean-Philippe (Eds.)., CIHEAM, Paris, Pages: 214.
11. El Arem, A., E.B. Saafi, G. Saafi, M. Issaoui and A. Ferchichi *et al*., 2012. Volatile and nonvolatile chemical composition of some date fruits (*Phoenix dactylifera* L.) harvested at different stages of maturity. Int. J. Food Sci. Technol., 47: 549-555.
12. El Arem., A., F. Guidob, S.E. Behijaa, I. Manelc and Z. Nesrine, 2011. Chemical and aroma volatile compositions of date palm (*Phoenix dactylifera* L.) fruits at three maturation stages. Food Chem., 127: 1744-1754.
13. Adams, R.P., 2007. Identification of Essential Oil Components by Gas Chromatography and Mass Spectrometry. Allured Publ. Corp, Carol Stream, IL, USA., pp: 18-43, 57-332.
14. Jayaprakasha, G.K., R.P. Singh and K.K. Sakariah, 2001. Antioxidant activity of grape seed (*Vitis vinifera*) extracts on peroxidation models *in vitro*. Food Chem., 73: 285-290.
15. Hatano, T., H. Kagawa, T. Yasuhara and T. Okuda, 1988. Two new flavonoids and other constituents in licorice root: Their relative astringency and radical scavenging effects. Chem. Pharm. Bull., 36: 2090-2097.
16. Singleton, V.L., R. Orthofer and R.M. Lamuela-Raventos, 1999. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. Methods Enzymol., 299: 152-178.
17. Richard, H., 1992. Connaissance de la Nature des Aromes. In: Les Aromes Alimentaires, Chapitre I: Generalites, Richard, H. and J.L. Multon (Eds.). Collection: Sciences et Techniques Agroalimentaires. Lavoisier TEC & DOC-Apria, Paris, France, pp: 22-73.
18. Burdock, G.A., 2016. Fenaroli's Handbook of Flavor Ingredients. 6th Edn., CRC Press, USA., ISBN: 9781420090864, Pages: 2159.
19. Harrak, H., M. Reynes, M. Lebrun, A. Hamouda and P. Brat, 2005. [Identification and comparison of volatile components of fruits of eight Moroccan date varieties]. Fruits, 60: 267-278.
20. Beaulieu, J.C., 2006. Volatile changes in cantaloupe during growth, maturation and in stored fresh-cuts prepared from fruit harvested at various maturities. J. Am. Soc. Hort. Sci., 131: 127-139.
21. Wu, X., G.R. Beecher, J.M. Holden, D.B. Haytowitz, S.E. Gebhardt and R.L. Prior, 2004. Lipophilic and hydrophilic antioxidant capacities of common foods in the United States. Agric. Food Chem., 52: 4026-4037.
22. Mansouri, A., G. Embarek, E. Kokkalou and P. Kefalas, 2005. Phenolic profile and antioxidant activity of the Algerian ripe date palm fruit (*Phoenix dactylifera*). Food Chem., 89: 411-420.
23. Biglari, F., A.F.M. AlKarkhi and A.M. Easa, 2008. Antioxidant activity and phenolic content of various date palm (*Phoenix dactylifera*) fruits from Iran. Food Chem., 107: 1636-1641.
24. Sadeghi, Z., J. Valizadeh and O.A. Shermeh, 2015. Antioxidant activity and total phenolic contents of some date varieties from Saravan region, Baluchistan, Iran. J. Med. Plants Res., 9: 78-83.
25. Al-Farsi, M., C. Alasalvar, A. Morris, M. Baron and F. Shahid, 2005. Comparison of antioxidant activity, anthocyanins, carotenoids and phenolics of three native fresh and sun-dried date (*Phoenix dactylifera* L.) varieties grown in Oman. J. Agric. Food Chem., 53: 7592-7599.
26. Vayalil, P.K., 2002. Antioxidant and antimutagenic properties of aqueous extract of date fruit (*Phoenix dactylifera* L. Arecaceae). J. Agric. Food Chem., 50: 610-617.