Compositional Analysis and identification of bio-oil in Iraqi Date Pits

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Abstract
Iraq is known with the abundance of date palm trees. This can be an important source of food nutrients and agricultural waste for energy. Date pits represent 18-20% of the fruit weight, and are recognized for their oil content and other nutritional components. This agricultural waste can be of great importance as a source of biofuel or useful nutritional compounds. In this paper, date pits of the most common variety of dates in Iraq named Zahdi, was investigated for compositional analysis and biomass value assessment. Samples of dried pits were examined for sugars, wax & chlorophyll and total inorganic ash content. In addition, structural sugars were examined to assess the potential of producing biofuel from date pits. It is found that the total content of structural sugars was 62.16% mainly Arabinose (53.56%). This highly significant percentage of Arabinose in date pits has not been reported in literature till the present. Further analysis of the volatile organic compounds in the pits via pyrolysis, identified a rare sugar in nature named D-allose. It is believed that thermochemical conversion of polysaccharides has led to produce the monosaccharide d-allose sugar. It is the first time ever to identify this rare sugar in Iraqi date pits with a noticeable amount. The importance of this finding comes from the recent medical investigations that proved the inhibiting activity of D-allose on many carcinoma cells in the human body.

Keywords: date pits, Fatty acids, Arabinose, Biodiesel, D-allose.

1. Introduction

In spite of the importance and potential of this crop, research into date palm fruits and secondary products has not been plentiful till the present (Ismail, et al., 2006). There have been few investigation papers on dates chemical composition and physical characteristics, (Ahmed & Ahmed, 1995) (Al-Shahib & Marshal, 2003) (Ismail, et al., 2008; Khan, et al., 2008; Bendahou, et al., 2007; Rao, et al., 2008). Fresh fruits, leaves and pits of date palm were examined for sucrose, glucose, fatty acids and ash content. Also, previous studies have investigated the extractable value-added components such as monosaccharides for food functioning and nutrition (Booij, et al., 1993).

Research interest; in utilization of date pulp ingredients for pharmaceutical purposes have led to examine date fruits for minerals, proteins, antioxidant agents, and nutritive value (Chen, et al., 2015; Elgasim, et al., 1995; VANDEPOPULIERE, et al., 1995; PSZCZOLA, 1998; VAYALIL, 2002; Williams, et al., 2005; Mansour, et al., 2005; Dayani, et al., 2012). However, few studies on the chemical composition of the date pits are found in literature (Hamada, et al., 2002; Besbes, et al., 2004; Chiara, et al., 2007; Saafi, et al., 2008; Al-Farsi, et al., 2007). Moreover, fewer research papers on the potential of date pits for biofuel production are present. Jamil et al. (2016) extracted the oil from Omani date pits and converted it to biodiesel via transesterification with ethanol (Jamil, et al., 2016). Another investigation, extracted the oil from date pits of three date varieties through conventional soxhlet with a bio-based solvent and performed a qualitative analysis to determine the oil compositions (Ben Youssef, et al., 2017). (Abu-Jrai, et al., 2017) produced biodiesel from date pits using a synthesized KOH supported carbon catalyst, with a 91.6% yield. (Al-Muhtaseb, et al., 2018) extracted the oil of date pits then performed a transesterification step with the aid of C-CaO catalyst to convert the oil to biodiesel. Recently, oil from eight varieties of Moroccan date pits was extracted by (Ourradi, et al., 2021). Another recent work on biodiesel from date pits was performed by (Fadhil & Kareem, 2021). They extracted the oil from date pits via pyrolysis and optimized the pyrolysis conditions for the best yield at 500 ºC, 80 min time, 60 mesh particle size and 20 ºC/min heating rate. A new approach by (Elnajjar, et al., 2021) was to produce bio-syngas from date pits via microwave pyrolysis.

Date pits represent 14-20% of the fruit weight, and are recognized for their oil content and other nutritional components (Saafi, et al., 2008; Baker, 1931). This study aims to investigate the structural composition of the Iraqi date Zahdi variety pits due to its large annual production among other species in the country. In 2019, the Ministry of Planning report on dates' production (in Arabic) recorded 5,408,177 palm trees of Zahdi species combining 48.3% of the total number of producing palm trees (Agricultural Statistical Directorate, 2019). The annual yield of dates was 334,014 tons, and this is translated to 66,800 tons of pits per year. This fact encounters the abundance of this variety with not much consumption preference for food by the public has made it widely used in food processing such as vinegar and date molasses (Debis in Arabic). Due to their nutritional value, some of the date pits are used for animal food, and the rest of waste biomass is usually disposed to the landfill creating environmental issues. Thus, investigating the potential of biodiesel production from this waste biomass is of interest for an economic feasibility. In this study, chemical composition analysis "including extractive sugars, structural lignin, total solids and ash content" were examined on a dry weight basis. Furthermore, thermogravimetric analysis (TGA) was conducted to explore the production of fatty acids via pyrolysis with an inert gas. TGA is a convenient technique to control the thermal degradation conditions of biomass during pyrolysis (White, et al., 2011). In addition, qualitative analysis of the pyrolysis products is conceivable. Samples of condensable products from pyrolysis were analyzed with GC-MS to isolate fatty acids and other oil compounds possibly contained.

2. Materials and methods

2.1 Date fruit Source and Sample Preparation

For the purpose of this study, fruits of Iraqi date variety namely Zahdi at the tamer stage of less than 12 months harvest were collected from the local market of Baghdad area. Zahdi is the most common date variety in Iraq. It constitutes 48.3% of producing palm trees in the country.

Date pits were separated from pulp, rinsed carefully with water to remove any flesh adhering to them, then vacuum oven dried at 40 ºC overnight. The dried seeds were then milled with a heavy duty grinder to pass 0.599 mm (mesh 30) screen. Samples were stored at room temp for later analysis. Storage temperature was consistent with the usual postharvest practices of dates in the area. The relative humidity in the lab was kept on less than 50%.

2.2 Chemical Compositional Analysis

Chemical composition analysis was performed mainly for biomass evaluation from bio-energy perspectives represented by the percentage of structural sugars and lignin. The analysis included total solids, ash content, extractive sugars (sucrose and glucose), structural sugars and lignin in triplicates.

2.3 Total Solids & Ash Contents

Samples of 0.3 -1.0 g from DP were tested for total solid content by convection oven method, drying overnight at 105 ºC. At the same time, another set of samples were tested for inorganic ash content by placing them in a Carbolite CWF1200 muffle furnace at 550 ºC and heated to a final constant weight. The procedure followed BS No. CEN/TS 14775:2004.

2.4 Non-structural extractives

Measuring cellulosic, hemicellulosic and lignin constituents in biomass samples, required removing soluble materials such as sucrose, glucose, chlorophyll and waxes prior to structural composition analysis. Therefore, the same samples were maintained through consecutive testing procedures of non-structural then structural composition analysis. In literature, various methods are used to detect, measure or separate sugars from plant species. Methods such as High Performance Liquid Chromatography (HPLC) (Inoue, et al., 2011; Duarte-Delgado, et al., 2015; Llano, et al., 2017; Weiß & Alt, 2017; Talab , 2017; Zaky, et al., 2017), Ultra-Violet (UV) with capillary zone electrophoresis (Kaijanen, et al., 2015), and Spectrophotometric method (Borji, et al., 2017) are used to measure sucrose, glucose and fructose. In this study, the YSI2500 Biochemistry analyser was used to determine the water-soluble sugars and the HPLC method for structural carbohydrates analysis.

A 10.0± 0.001 g of date pits' sample is weighed into a soxhlet thimble for sugar extraction. The first step was heating to 70 ºC with 100 mL of HPLC grade water. After overnight air drying, the extractive-free residue was extracted with analytical grade ethyl alcohol to a temperature at 60 ºC. Each step of extraction continued for six hours. The extractive-free biomass was removed from extraction thimble and placed to air dry overnight for structural composition analysis.

A 5 ml sample of water-soluble extract solutions was removed to examine sucrose and glucose by YSI analyzer equivalent sucrose quantification method. The YSI uses two membranes, one that is reactive for Dextrose and one that is reactive for Fructose, the two sugars that form a dimer of glucose. Final calculations of Sucrose and Glucose are calculated based on a single point measurement of a calibration solution using a base line current established with a buffer salt solution prior to calibration. Standard solutions used to calibrate the instrument were 5% sucrose, 9% glucose and DIW.

The remaining of water-soluble extracts and ethanol-soluble extract tubes were placed in Nitrogen evaporator with water bath at 40 ºC for overnight drying. After 24 hrs, collection tubes were placed overnight in a vacuum oven at 40 ºC and 15 psi vacuum for further drying. The net weight of dried water extract represents sucrose and glucose content in the biomass. Conjunctively, ethanol-soluble extracts represent chlorophyll and wax content.

2.5 Structural composition analysis

2.5.1 Hydrolysis of extractive-free biomass

Structural carbohydrates and lignin combine a major part of a biomass. Cellulosic monosaccharides and hemicellulosic polysaccharides, including Glucose, a cellulose monomer, Xylose, Galactose, Arabinose, Fructose and mannose formulate with lignin structural carbohydrates. Those carbohydrates are extracted with a two-stage hydrolysis process after removal of extractive constituents. Samples of 300 mg portions from dried extractive-free biomass were placed in 100 ml glass pressure-tubes. A 3 ml aliquot of 72% w/w sulfuric acid from Fluka #00647 was added to each tube. Then reaction tubes were placed in 30 ºC water bath for 1 hour being stirred every five to ten minutes. The tubes were then removed and brought to a total volume of 87 ml with DIW bringing the acid concentration to 4%. Immediately, pressure tubes were sealed and put in one hour liquid cycle Autoclave at a temperature 121 ºC. A set of sugar recovery standards (SRS) were treated in the same manner and put into the autoclave cycle. The SRS provides for the calculation of a loss-factor which is used as an adjustment in the calculation of final structural sugars.

When the 4% acid hydrolyzates were cooled to room temperature, samples were filtered through a set of 2 µm filtering crucibles with vacuum. A 50 ml filtrate of each sample was stored at 4 oC for further analysis. Similar method was reported in literature (Wang, et al., 2016).

2.5.2 Lignin Determination

Acid soluble lignin content was measured by UV analysis of samples from hydrolyzates filtrate. Absorbance was measured with HP 8453 UV Vis at wavelength 240 using 1 cm quartz cuvette. Dilution ratio was determined when 0.7-1.0 absorption reading was obtained. DIW was used as calibration standard.

The acid insoluble residue collected in the filtering crucibles were dried overnight at a temperature 105 ºC in convection oven to determine the acid-insoluble solid percentage which represent the acid insoluble lignin, proteins and ash in the hydrolyzate solid residue. Ash content was calculated by weighing the remaining of the furnace dried solid residue at a temperature 550 ºC. Ash value was subtracted from the total lignin measurement.

2.5.3 Structural Sugars determination

Five ml samples of the 4% acid hydrolysis filtrate were neutralized with Calcium Carbonate $CaCO_3$, filtered with 2 µm filters and run on HPLC system equipped with refractive index detection using Biorad Aminex HPX-87H column. Sugar recovery standards of high purity were used for the analysis combining D-glucose, D-xylose, D-galactose, L-arabinose, and D-mannose. Weight and percentage of structural sugars were then determined using a set of correction factors giving a picture of the mono sugars contents in the cellulosic and hemi cellulosic parts of the pits.

2.6 Thermogravimetric analysis (TGA) of date pits

Samples of dry mater from date pits, were tested for oil composition by thermogravimetric analysis method (Fadhil & Kareem, 2021). A Mettler Toledo thermogravimetric analyzer was used to heat samples up to 500 ºC at two heating rates as of 20, and 100 ºC per minute. The carrier gas was nitrogen at flow rate 50 ml/min and the purge gas was Helium. Samples of date pits between 55 – 125 mg were placed in the furnace without any oxidation or catalyst addition. The resulting condensates were collected by a silica gel trap at the outlet of the heating tube. Different solvents were tried to dissolve the collected condensates. 2 ml of Methyl alcohol then Acetone each as polar solvents and Hexane as non polar solvent were used separately and sequentially to dissolve pyrolysis oil fractions for GC analysis.

Table 1. Chemical composition of Iraqi Zahdi date pits.

Composition	wt. %[a]	Total wt. %[a]
Total Water-extractives		**11.09±0.25**
Water-soluble sugars (sucrose)	3.77±0.18	
Total Fatty acid (ethanol) extractives		**9.79±0.07**
Total inorganic ash		**1.19±0.052**
Structural ash	0.26±0.07	
Total Structural Sugars		**62.16±4.61**
Glucose	5.59±0.40	
Xylose	0.97±0.13	
Galactose	2.04±0.12	
Arabinose	53.56±3.96	
Fructose	0.00	
Total Lignin		**15.32±0.99**
Acid-soluble lignin	2.76±0.19	
Acid-insoluble lignin	12.56±0.81	
Total Carbohydrates		**81.25±5.85**

[a] Based on dry matter.

2.7 Determination of solvent extractive compositions

A further GC-MS analysis for the carbohydrate composition of date pits was performed on the collected solvent extractives from pyrolysis test. HP 6800 Gas Chromatograph Mass Selective Detector was used with 30 m x 250 µm x 0.5 µm calibrated Inventory H Wax: J&W DB Wax column and FID detector for determination of oil products. Pure Acetone was used as the blank sample. Method parameters were; Helium as the carrier gas at 1.0 ml/min, and average velocity 36 cm/sec, oven temp 300 ºC and the sample volume was 1.0 µL. The programming software used to analyze results was GC/MS MS Top/ Environmental.

3. Results and discussion

3.1 Chemical Composition of date pits

3.1.1 Non-structural extractives and ash content

The amount of water-soluble extractives, ethanol-extractives (fatty acids) and inorganic ash content in samples of date pits (DP) are listed in Table (1). Water extractives formed 11.09% including 3.77% soluble sugars as sucrose. The remaining 7.32% of water-soluble extract composition was not analyzed in this study. It is most likely to be soluble proteins and nitrate/nitrite matter. Whereas, alcohol extractives namely fatty acids were 9.79% and the ash content was 1.19%.

These results are in agreement with the published data on date pits. (Chiara, et al., 2007) measured the reducing sugars (sucrose) in date pits and found them 3.16-3.47%. (Saafi, et al., 2008) reached to 8.12% total water extractives including 1.49% sucrose, 5.31% protein. They also measure total fats at 8.33%. Whereas, (Jamil, et al., 2016) reached to 16.5% fatty acids content in the Omani date pits. A recent work in 2021 reached to 6.05-10.25% oil content in eight Moroccan date pits (Ourradi, et al., 2021). (Hamada, et al., 2002) measured the protein and ash content in the pits of several Tunisian date varieties. Their results showed 5.2-6.0%, 1.0-1.4% of protein, and ash, respectively. (Besbes, et al., 2004) found 5.17-5.56%, protein in two date species pits. Similar results of ash content in date pits were found in literature (Besbes, et al., 2004) (Chiara, et al., 2007) (Al-Farsi, et al., 2007).

3.1.2 Structural Composition Analysis

Lignin Determination

Lignin is a complex phenolic polymer, bonds the cellulosic and hemicellulosic fibers together in plants. In biomass analysis, Lignin is quantified as acid-soluble and acid-non soluble fractions. Table (1) presents the soluble (2.76%) and insoluble (12.56%) lignin content measured for date pits as of total lignin content at 15.32%. No comparable data were found in literature for lignin in date pits.

Structural Carbohydrates (Cellulosic and hemicellulosic saccharides)

Dry matter of date (Phoenix dactylifera) pits, was examined for cellulosic and hemicellulosic sugars after removing non-structural sugars. The structural composition is shown in Table (1). Monosaccharides analysis showed 5.59% Glucose, 0.97% Xylose, 2,04% Galactose, and 53.56% Arabinose. No Fructose was found. This gives a total carbohydrates content as of 81.25%. This result is in agreement with the published data in literature. (Besbes, et al., 2004) reached to 81.0%-83.1% total carbohydrates. While (Al-Farsi, et al., 2007) measured the total carbohydrates of three date cultivar pits from Oman and found a slightly higher value in a range of 83-86% total carbohydrates.

To the best knowledge of the authors, it is the first time in literature to record this significantly high percentage of Arabinose in date palm pits, the sugar that is used in food industry as a sweetner (Krog-Mikkelsen, et al., 2011). (Ishrud, et al., 2001) have isolated polysaccharide glucomannan from date seeds in 93:7 molar ratio mannose to glucose. However, they did not quantify Arabinose sugar in the date pits, knowing that both sugars are derivatives of Arabinose as shown in Figure (1) (McMurry, 2000).

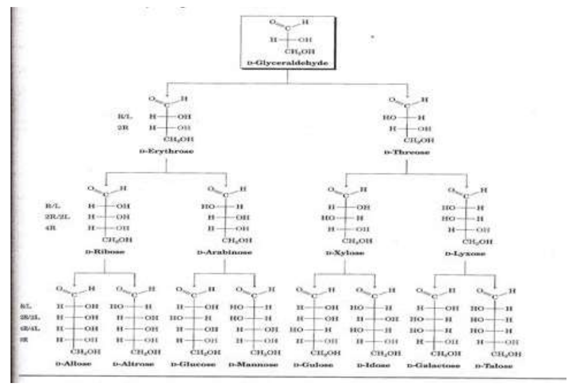

Fig 1. Configuration of aldohexose sugars (McMurry, 2000)

From Table (1), the total biomass compositional analysis of the date pits resulted into 81.25% total carbohydrates, 9.79% wax and 1.19% ash. The remaining 7.77% is suggested to be protein that we did not measure in this study.

3.2 Thermogravimetric (TGA)

The thermal profile of date pits was inspected via TGA to determine the volatile fraction. Samples were heated at two heating rates 20 ºC/min and 100 ºC/min to a maximum temperature at 500 ºC for one hour. Figures 2 and 3, show the loss in wt.% and degradation rate of dp with time. In general, thermal degradation of dp started with moisture evaporation between 25 ºC and 100 ºC. Afterwards, rapid loss in weight occurred due to decomposition of cellulose and hemicellulose between 275 ºC and 500 ºC. It can be seen that a weight loss of 74.05% - 77% from the sample weight as a volatile matter. This significantly high percentage of volatiles in date pits, entitles date pits for biofuel production. (Fadhil & Kareem, 2021) reached to 78% volatiles via TGA method and 83.98% volatiles via a bench scale pyrolysis setup for date pits. The higher yield of oil via pyrolysis method can be attributed to the larger sample and longer pyrolysis time.

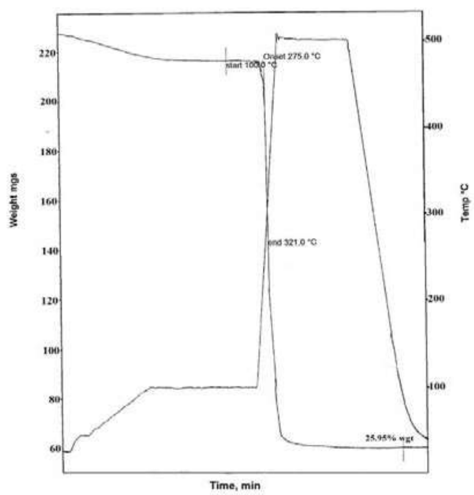

Fig 2. Pyrolysis profile of date pits via TGA at heating rates: (a) 20ºC/min

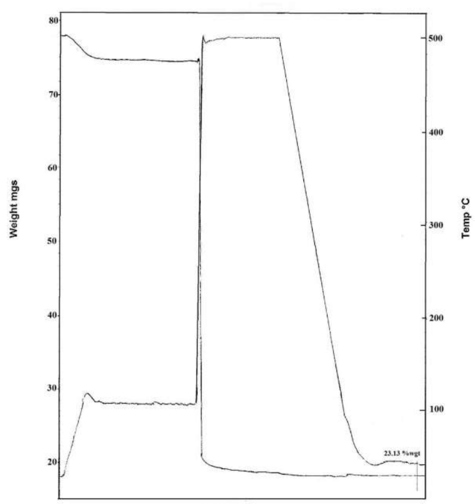

Fig 3. Pyrolysis profile of date pits via TGA at heating rate 100 ºC/min

3.3 GC-MS Analysis

The purpose of GC-MS analysis, was primarily qualitative determination of the structure and abundance of oil based constituents in the biomass (Abu-Jrai, et al., 2017). Using different solvents to collect the produced condensate showed different spectra pattern. The qualitative spectrum of samples dissolved with pure Methyl alcohol, Acetone and Hexane are shown in Figures (4, 5, and 6). Knowing that there was a remaining percentage of condensate on the silica gel particles, yet the GC-MS analysis revealed into very interesting composition as shown in Table (2). The rare sugar D-Allose was identified in a substantial estimated concentration in the Methyl alcohol extract (32.20%) at a retention time 14.84 min. Further, it was found in the Acetone and Hexane extracts in 3.8% at 14.75 min retention time and 0.1% at 14.73 min retention time, respectively. The total estimated concentration of D-Allose in three extracts was 36.1%.

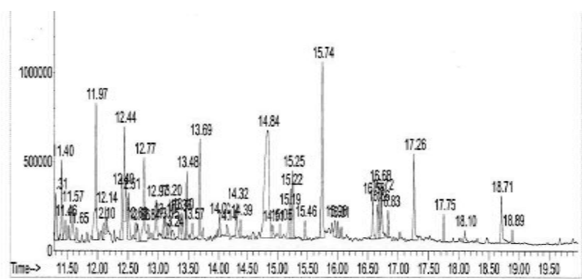

Fig4. GC-MS spectrum of pyrolysis condensate dissolved in Methyl alcohol

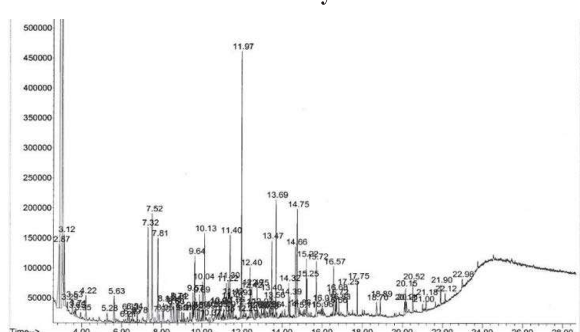

Fig 5. GC-MS spectrum of pyrolysis condensate dissolved in Acetone

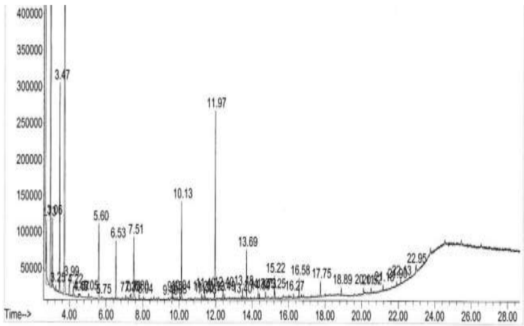

Fig 6. GC-MS spectrum of pyrolysis condensate dissolved in Hexane

Table 2. Tentative identified compounds of pyrolysis products of Zahdi date pits dissolved in sequential of solvents.

Solvent	TIC name	RT	Estimated Conc.%
Methanol	Furfural	7.35	25.95
	2-Furanmethanole	7.87	16.85
	γ-Hydroxybutyric acid	8.88	7.16
	2-Furanethanole	9.58	28.10
	Phenol	9.90	10.33
	Cyclopentasiloxane, decamethyl -	11.97	8.50
	Catechol	13.36	9.07
	Dodecane	12.40	5.09
	D-Allose	**14.84**	**32.20**
	Dodecanoic acid **(Lauric acid)**	**15.74**	**17.77**
	Tetradecanoic acid **(Myristic acid)**	**17.26**	**8.03**
	n-Hexadecanoic acid **(Palmitic acid)**	**18.71**	**5.23**
	9-Octadecenoic acid **(Oliec acid)**	**20.16**	**12.03**
Acetone	Furfural	7.33	1.65
	2-Pentanone, 4-Hydroxy-4-methyl-	7.52	3.10
	2-Furancarboxaldehyde, 5-methyl-	9.65	1.05
	Phenol	9.89	0.55
	Cyclopentasiloxane, decamethyl -	11.97	5.45
	D-Allose	**14.75**	**3.80**
	Lauric acid	**15.72**	**0.95**
	Myristic acid	**17.25**	**0.45**
	Palmitic acid	**20.52**	**0.90**
	Oliec acid	**21.03**	**0.60**
n-Hexane	Propane, 2,2-dimethoxy-	2.96	55.2
	Butane, 2,2, 3,3-tetramethyl-	3.47	4.3
	Heptane	3.72	21.5
	Toluene	5.6	2.1
	Octane	6.53	1.3
	2-Pentanone, 4-Hydroxy-4-methyl-	7.51	1.6
	Cyclopentasiloxane, decamethyl-	11.97	2.7
	D-Allose	**14.73**	**0.1**
	Palmitic acid	**20.52**	**0.1**

The importance of this finding comes from the significant pharmaceutical activity of D-Allose as an inhibiting agent to several carcinoma cells. D-Allose, is a rare existing monosaccharide in nature. It is one of the sixteen aldohexose sterioisomers that, only three of them normally occur in nature: D-glucose, D-galactose, and D-mannose. (See Fig. 1). The observation of this rare sugar in nature as a result of thermochemical conversion of date pits has not been reported in literature yet. There were few investigations on the synthesis of D-Allose derivatives from other aldohexose isomers such as D-glucose and D-mannose (Ishurd, et al., 2004) (D'Alonzo, et al., 2008) (Mariano, et al., 2009). (Ishrud, et al., 2001) have isolated a water soluble polysaccharide from date seeds that is (1- 4)-β-D-mannopyranosyl residues and carries a single (1_6)-α-linked D-galactopyranosyl residue. Recently, there have been few researches on the inhibiting effects of D-Allose on certain carcinoma cells such as; leukemia (Hirata, et al., 2009), head and neck carcinoma (Mitani, et al., 2009), hepatocellular carcinoma cells (Yamaguchi, et al., 2008) and others.

Furthermore, the chemical composition of the date pits oil is given by the GC-MS analysis. As shown in Table (2), saturated fatty acids were found mainly as Dodecanoic acid (Lauric acid) with estimated concentration at 17.77%, Tetradecanoic acid (Myristic acid) (8.03%), n-Hexadecanoic acid (Palmitic acid) (5.23%), in addition to the unsaturated fatty acid 9-Octadecenoic acid (Oleic acid) (12.03%). These fatty acids characterize the biodiesel composition from date pits. (Saafi, et al., 2008) reached to a similar fatty acid content in Tunisian date pits at 32.45% compared to 43.07% in this study. Also, (Abu-Jrai, et al., 2017) found the same fatty acids in addition to the stearic and linoleic acids in Omani date pits, dominated by oleic acid at 53.36%, however. Similar results for Omani date pits, were found by (Al-Muhtaseb, et al., 2018), as 55.36% of the date pits oil was oleic acid. (Ben Youssef, et al., 2017) found similar content of lauric acid, palmitic acid, and myristic acid in three Tunisian date varieties pits, a higher oleic acid content at 44-46% though. Recently, a study on Moroccan date pits showed the composition of fastty acids as 38.67-44.38% oleic acid, 21.72-26.66% lauric acid, 11.26-13.04% myristic acid, and 9.65-11.38% palmitic acid (Ourradi, et al., 2021). The variance between the oleic acid composition in these researches and the results of this study can be attributed to the different geographic area of the date origin. From above results, date pits can be a valuable source for production of second-generation biodiesel.

4. Conclusions

Structural Compositional analysis of Iraqi date pits was investigated in this work. Samples of Zahdi date pits were examined for soluble extractives, structural sugars and thermal degradation treatment. Obviously, date pits can be of a valuable biomass source that is rich with structural sugars (62.16%) mainly Arabinose with a highly notable percent at 53.56% of the seed weight, recorded for the first time in literature. In the same time, oil content in the date pits can be a promising source for biodiesel production. Thermal degradation of the date pits has produced a mixture of fatty acids that constitute primary oils for biodiesel production. On the other hand, Zahdi date pits can be an vital source for D-Allose sugar. This six carbon sugar was possibly formed from the thermochemical conversion of polysaccharides into monosaccharide d-Allose sugar. And, this is also the first time ever to identify this rare sugar in Iraqi date pits with a significant concentration. The importance of this finding comes from the recent medical investigations that proved an inhibiting activity of D-Allose on many carcinoma cells in the human body. Further investigation on the biodiesel production from date pits oil is highly recommended. Also, formation and separation of D-allose sugar from date pits via thermal conversion can be of a pronounced interest.

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