CHEMICAL PROPERTIES OF THE OIL EXTRACTED FROM FOUR VARIETIES OF DATE SEEDS GROWN IN AL-KHUMS, LIBYA

الخواص الكيميائية للزيت المستخلص من أربعة أصناف من بذورالتمرالمزروعة في الخمس بليبيا

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ABSTRACT

Date palm seedsare discarded as waste. Further, our Studies were conducted onfour cultivars date seeds ascultivated inLibya,which namely Omvitity, Taboni, Ami, and Raht. The oil yield was satisfactory at2 h extraction time and 0.5mm size of date seed powder by using soxhelt extractor and toluene as a solvent.The largest percentage of oil yield wasobtained from date seeds(8.9%) for Amicultivar .The acidvalue was ranged (2.02-2.4mg KOH/g)which showed Omvitity seeds had the highacid value(2.4 mg KOH/g)and highpercentage of free fatty acids (1.2 %FFA). While, the high saponification value was(527.434 mg KOH/g) of oil inTabonicultivar which that the highest of ester value (525.234 mg KOH/ g).

Keywords: Date seed, seed oil extraction,Soxhlet extraction, chemical characteristics.

الملخص

يتم التخلص من نواة نخيل التمركنفايات،لذلك أجريت دراساتناعلى أربعة أصناف من نواة التمرالمزروعة في ليبيا،وهي أم فيتيتي،طابوني،وعامي،ورهط. وتمت انتاجية الزيت المستخلص عند ساعتين من زمن الاستخلاص من حجم 0.5 مم من مسحوق نواة التمر باستخدام جهاز الاستخلاص (سوكسليت) (soxhelt extractor) والتولوين كمذيب. تم الحصول على أكبرنسبة من انتاجية الزيت من بذورالتمر لصنف أم فتيتي (8.9٪). وتراوحت قيمة الرقم الحمضي (2.02 -2.4 ملجمKOH / جم) مم اي دل على أن بذورالأوم فيتيتي لها قيمة رقم حمضي عالية (2.4 ملجمKOH / جم) ونسبةعالية من الأحماض الدهنية الحرة (1.2٪ FFA). بينما كانت قيمة رقم التصبن عالية (527.434 مجمKOH / جم) في زيت صنف الطابوني والتي كانت بها أعلى قيمة لرقم الاستر (525.234 مجمKOH / جم).

الكلمات المفتاحية: بذور التمر، استخلاص زيت البذور، سوكسليت، الخواص الكيميائية.

1. INTRODUCTION

Date palm(Phoenix dactylifera L.)is one of the most widely grown trees in the world, and widelycultivated on an area of (800000 hectare) distributed in 30 countries especially in Middle East and The Kingdom of Saudi Arabia[1].The date palm belongs to family of Arecaceae consisting of about 200 genera and more than 2,500 species. which have seeds with one institution(monocots)[2].which known as pit or stone of date fruitthat composed10-15% percentage of the of fruitand containcarbohydrate, protein, fat, fiber,water, oil,and ashand minerals(sodium, Potassium, Calcium, Iron, Copper, Magnesium, Manganese, Zinc and phosphorus[2.3].It is odorless and has a slightly bitter taste bland p, and it has a light and dark brown[3].In the last few years, the seed of date was considered as rubbish of date palm.Now days, various studies regarding seed of date have been published in order to determine the functional properties of date seed is used for food y for animal feeds in the cattle, sheep, and camel and non-food items such as a soil organic additive[4].Recently, date seed powderhas also been introduced to the market and as(Coffee Substitute),which available in two types plain and blended with coffeebased on physico-chemicaland functional properties of it [5].Many studies carried out on extracted oil from seed date and usedin cosmetics, pharmaceuticals, antimicrobial, antioxidantandandanti-inflammatorywhich is rich in phenolic acids [2,3].Many researches has been carried out on date seed oil and its composition invitamins, minerals, and fatty acids makes it valuable for foodformulations [2].Further more date seed oil can be utilized as a seasoning or cookingoil[6].

Several studies show the seed composition differences for different date varietiesBecause of the variety of varieties studiedso are the climatic conditions[7, 8].The lipid contentin dates seeds depend on the variety, origin and harvest Time and compost. However, carbohydrates and fatsthey are the main ingredients in date seeds. ProteinThe proportion of fat in date seeds is relatively highCompared to date meat (1.5-3% proteinand 0.1 - 1.4% for fat) [9].Dates seed protein contains the majorityEssential amino acids [10].The objectives of this study were to extend the work onfourcultivarsof date seeds which namelyOmvitity,Taboni, Ami, and Rahtfrom AL Khums-Libya and study some chemical characters of extract oil of its seeds.

2. MATERIALS AND METHODS

Samples

Date palmfruit were collected from the palm trees of AL-khums city of Libya. The seeds were isolated , washed and dried based on weather conditions and then were grinded to fine powder, next theywaskeptat room temperature in the tight container for required analysis. All chemicals in this study were purchased from BDH(ENGLAND) and Fisher chemical.

Soxhlet extraction method

Date seed oil wasextract bycontinuous extraction in a Soxhlet apparatus. This method based on the choice of solvent which have characteristics such as easy removal by evaporation from the extracts, high solvent–solute ratio،oil viscosity, and polarity. Also that method is the most common method used for extracting oil[2].Weights 15gof each seed powder. The extraction process continued for 6 hours usingtoluene as solvent (extract

solid-liquid), and then the solvent was evaporated on rotary evaporator under reduced pressure and the produced oil was stored in a dark container in the fridgeuntil subsequentanalysis

Determination of extraction yield

Extraction yield relates to the quantity of oil that can be derived from an oil seed which in the most represented as a percentage. The extract oil yield was determined as the ratio of the weight of oil recovered to the weight of the crushed seed sample before extraction [11]. This equation was used to determine the percentage of oil yield from date seed samples [12].

$$\%\ of\ yield = \frac{Woil}{Wcs} X\ 100$$

Where w_{Oil} is weight of oil obtained (g)and W_{CS} is the weight of crushed seed (g).

Chemical characteristics of oil

Acid value

Acid number (neutralization number) was defined as milligrams of alkali(KOH) required to neutralize the free fatty acids present in 1 g of oil or fat. Whereas, itrefers topercentageof free fatty acidsand releasing triglyceridesfound in oils which tend to the good quality of oil. Besides acid value provides informationabout the age of oil sample, also it signifies the effect of oil exposure to atmospheric oxygen[13].

The determination of acid value carried out based on a titration method ,accordingly, 20 ml ofdiethyl ether and ethanol (1:1) mixture was added 1 gram to each oil samplesin a 250ml conical flask and shacked well. After

adding 3-4 drops of phenolphthalein indicator,the solution was titratedwith 0.05N ethanolic potassium hydroxide (KOH) and shaking until theend point of the titration was confirmed (change from colorless to pink). The volume of 0.1 N ethanolic(KOH) consumed during the titration was recorded. The total acidity ofthe sample in mg KOH/g was calculated using the followingexpression[12].

$$AV = \frac{V\ x\ \ N\ x\ 56.11}{m}$$

Where AV= Acid value ,V= the volume (ml) of ethanolic KOH,*N*= the normality of ethanolic KOH used, 56.11 molecular weight of KOH, and m= the weight (g) ofoil sample.

Free fatty acids (%FFA)

The amount of %FFA is an indicator for acid value of fat or oil, and it provides information about how much generation of free fatty acids has taken place. Also, Thefree fatty acids in the oil sample is the result of the hydrolysis reaction between the oil and water during the treatment process[14, 15]. On the other hand, , thelow content offree fatty acidsin the oil that is usedin biodiesel production playsas an important role for cost saving, and it would become as an advantage for the date seed oil [8] . %FFA was calculated from the acid value of theoil using the following equation[12].

%FFA= AV/2

Saponification value

Saponification value is milligrams of alkali(KOH) required to saponifyone gram of oil or fat. Through this process is useful for comparative study of the fatty acid chain length in oils[14].Saponification value wasestimated by take 5 grams of oil from each oil samples by adding 50 ml of 0.05N ethanolic potassium hydroxide KOH in necked flaskequipped with reflux condenser and placed into water bath at 80°Cfor 2 h and then cooled at room temperature.At the end,the reaction was started by adding 3dropps of phenolphthalein indicatorand it was tittered with (0.05 N HCl)until end point was recorded the volume of acid.

The following equation can be used to calculate the saponification value:

$$SV = \frac{(\mathbf{Vo-V})\boldsymbol{X}\mathbf{N}\boldsymbol{x}\mathbf{56.11}}{\mathbf{m}}$$

Where :*SV* = saponification value , V=titter value of sample,V_o= titer value of blank, N normality of hydrolic acid,m = weight of the sample (g), and56.11= molecular weight of potassium hydroxide

From saponification value may estimateaverage molecular massof triacylglyceriedsM_{moy}^{TG} and average molecular mass of fat acid which formation triacylglyceriedsM_{moy}^{AT}as following equations

$$M_{moy}^{TG} = \frac{3\ X\ 56110}{SV}$$

$$M_{moy}^{AT} = \frac{M_{moy}^{TG}38}{3}$$

Ester number

Ester number is an amount of milligrams KOHrequired to saponificate esters contained in one gram of fat or oil[15] and calculate from expression

EV=SV-AV

Where EV= Ester number, SV= saponification value, and AV= acid value

3. RESULTS AND DISCUSSION

Oil extraction

Oil from Date palm seed wasextracted with toluenesolvent as it was mentioned[16].The extract oils from samples were liquid at room temperature and has a pleasant odor, yellowishin color. that refers to they contain unsaturated acid fat.From theobtainedresultsof oil extraction yield as shown in table 1.the yield of oil wasas following 8.9% Ami, 8%Omvitity, whereas the yield percentage of Taboniand Raht were 6.26 %.

TABLE.1 YIELD OF OIL EXTRACTION FROM DATE SEED

Parameter	Cultivars			
	Omvitity	Raht	Taboni	Ami
Sample weight(g)	15	15	15	15
Oil weight(g)	1.2	0.94	0.94	1.34
Yield of oil %	8	6.26	6.26	8.9

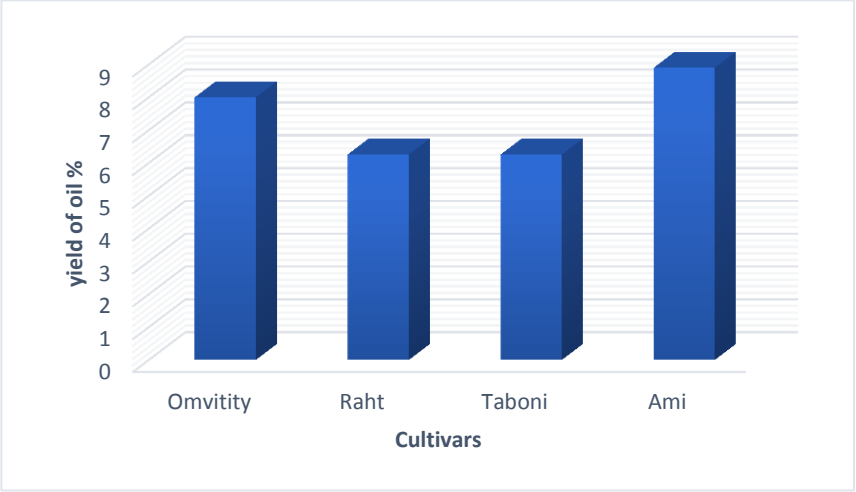

Figure1: yield of oil extraction from date seed

Chemical Characteristicsof Date Seed Oil

In current study,the following average characteristics have been reported for seed oil of four date cultivars (Omvitity , Raht , Taboni and Ami): acid value, Free fatty acids ,saponification value, andEster numberare shown in Table 2.

Acid Value

Acidity is another quality parameter [17] and isdefined as the number of milligrams of potassiumHydroxide is necessary to neutralize free acids in 1 g of sample. The acidity value is an indicatorThe free fatty acid content is also an indication of the viability of the oil and its suitability for industrial purposesBuhlali and others [18] indicated the value of the Moroccan acidity of date seedsThe oil was between 1.083-1.813 mg KOH / g, similar to the

olive oil analyzed by Borchani et *al*.(2010) [19], which means that date seed oil can be considered as an edible oil.

From the results, that shown in table. 2,the highest value was 2.4inOmvitityseed oilthat nearly obtained by*Guizani et al*[4] which may be attributed to its oils contain a small amount of freefatty acids, and could explain the decline in the acid value of oil perhaps due to the small exposure of the seeds to the air during the maturity of the fruits of the dates.

Free fatty acids (%FFA)

The difference in the percentage of free fatty acids (FFA%) is due to the difference in the moisture content of these oils, iron is important to accelerate the process of hydrolysis and release of free fatty acids, and the presence of free fatty acids in the oil is a measure of the quality of the oil and the important indicators that allow you to know the degree of cracking of oils And fats in the presence of acid, water, temperature or Laybiz enzyme and depend on their quality which depends on their purity and degree of decomposition, since their height indicates mantle oil. [20].

Free fatty acid contents are in Table 2. the highest value was 1.2% in Omvitity seed oil. Moreover, the low percentage of free fatty acids is an indication of the viability of the oil and its industrial suitability [2, 13]. Despite this, date seed oil has good potential for use in human and / or animal diets [21].

Saponification value

The saponification value is a measurement of the fatty acid molecular weight. It givesinformation about the nature of fatty acids and depends on the average molecular weight of these saponification valueofoils were in the range (201.996-527.434mg KOH /g) and the highest value was recorded in seeds oil ofTaboni, that indicates to low molecular weight triglyceridesand content low of molecular weight of fatty acids(319.149g/mol ,93.716 g/mol).Because ,there is an inverse relationship between saponification value and weight of fatty acids in the oils[21]. Moreover,The high saponification value of date seeds oil refers that the fatty acids present in the oil have high number of carbon atoms. This makes the date seeds oil after hydrogenationcould be substituted for some conventional oils[14].

Ester number

The ester values of studied date samples were shown in table 2, which wereranged between(199.596- 525.234mg KOH/g).

Parameters which are also important is the number of ester and acid. Ester number is an amount of mg KOHrequired to Saponification esters contained in one gram of fat or oil. The greater the number, the higher ester content ofester in the oil sample. While the acid number indicates the number of mg of KOH used to neutralize the free fattyacids in one gram of oil samples. Free fatty acids in the oil sample is the result of the hydrolysis reaction betweenthe oil and water during the treatment process. Based on SNI 06-2385-2006 [22], maximum number ester and acidvalue successively are 20 and 8 mg KOH/g.

TABLE 2. CHEMICAL CHARACTERISTICS OF DATE SEED OIL

Parameter	Cultivars				Refer.
	Omvitity	Raht	Taboni	Ami	
AV(mg KOH/g)	2.4	2.1	2.2	2.02	(1.35 - 1.38)[21]1.79 [23], (2,55,2.47)[24]
(%FFA)	1.2	1.05	1.1	1.01	-
SV(mg KOH/g)	201.996	460.102	527.434	471.324	(204.84-215.87)[21],(206.22)[23], (255,267) [24]
EV(mg KOH/g)	199.596	458.002	525.234	469.304	-
M_{moy}^{TG}(g/mol)	833.33	365.854	319.149	357.143	-
M_{moy}^{AT} (g/mol)	265.11	109.285	93.716	106.381	-

4. CONCLUSION

The study indicated thatdate seed oil is remarkable fors an agricultural byproduct of date palm.The extraction was achieved Soxhlet method.The chemical characteristics wereacid value,saponificationvalue, and ester number.Furthermore, these properties of the seed oil are of immense significant for feedstock selection relative to the production.Thus , the waste products such as seeds from date industry could use as a resource of edible oiland decrease pollution.Further research is suggested to extract compositions of date seeds and study its characteristics which could support the social development and economic of date fruit producing and manufacturing.

ACKNOWLEDGMENT

The authors wish to express sincere to Nemat Allah Moftah Al-Tunsi and Salima Ali Eddeif for their assistance in this work.

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