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Sahar Ben-Youssef, Jawhar Fakhfakh, Cassandra Breil, Maryline Abert-Vian, Farid Chemat, et al.. Green extraction procedures of lipids from Tunisian date palm seeds. *Industrial Crops and Products*, 2017, 108, pp.520-525. 10.1016/j.indcrop.2017.07.010 . hal-02626282

HAL Id: hal-02626282

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Submitted on 26 May 2020

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Green extraction procedures of lipids from Tunisian date palm seeds

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A B S T R A C T

Keywords:

Date seeds
Oils
Alternative solvent
Hansen solubility parameter
Ultrasound
Micro-wave

This study was performed to compare, in term of quality and quantity, conventional and green lipid extraction procedures of three Tunisian date palm (*Phoenix dactylifera* L.) seeds cultivars (Deglet Nour, Allig and Belah). Extractions were performed using *n*-hexane and 2-methyltetrahydrofuran (MeTHF) as solvents. Identification and quantification of extracted fats and lipids were carried out by gas chromatography coupled with a flame ionization detector and high performance thin-layer chromatography.

Results showed that Deglet Nour presents the highest lipids extraction yield (7.24–5.97%) using the both solvents. Hansen solubility simulation demonstrated that MeTHF is a good alternative solvent for lipid date seeds extraction. In addition, extraction of oils from date pits with ultrasound and micro-wave were better in terms of extraction time (30 min versus 8 h) comparing to soxhlet procedure and of extraction yield comparing to maceration (about 6% versus 4%). Triglycerides represent almost the whole recovered oils composition with 99% and the fatty acids were mainly oleic (44.02–46.9%), lauric (20.00–23.10%), myristic (8.88–11.26%), palmitic (9.00–10.73%) and linoleic (6.13–9.21%) acids.

1. Introduction

The date palm tree (*Phoenix dactylifera* L.) is grown widely in arid and semiarid regions of the world. Date palm is the major fruit tree; it constitutes the basis of economy and the principal source of remuneration for the Tunisian people living in Sahara (Besbes et al., 2004a,b). Tunisia is the 10th producer and the first exporter of dates in the world. During five years, Tunisian production has attain about 127,000 tons per year with Deglet Nour variety constitute about 60% of the total production due to her good sensory quality and high commercial value (Besbes et al., 2009). In Tunisia, varieties of Deglet Nour, Allig and Bellah are much consumed. The large quantity of date seeds could be easily collected from the date processing industries or from the waste products (represent about 30% of the production in Tunisia) coming either directly from the gap-conditioning or from the stations palm grove. On an average, weight of date seeds is about 10–15% of date mass (Hussein et al., 1998) and contains between 4 and 13% crude oil (Biglar et al., 2012; Al-Farsi et al., 2007; Besbes et al., 2005). Though, these by-products are generally consumed either as a conventional soil fertilizer or as complementary feed materials for animals and poultry (Vandepopuliere et al., 1995). Also, they were used to make coffee in the Arabian Peninsula (Ali-Mohamed and Khamis, 2004) and to extract oil for pharmaceutical and cosmetic objects (Devshony et al.,

1992). Some reports were appeared in literature about fatty acid compositions and lipid classes of date seed (*Phoenix dactylifera* L.) oil cultivated in Tunisia (Besbes et al., 2004a,b; Hossain et al., 2014; Saafi et al., 2008) and in other countries as Saudi Arabia, Oman, Egypt, Iraq, Iran (Basuny and Al-Marzooq, 2011; Hossain et al., 2014). 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%) (Saafi et al., 2008). Lipids and oils were extracted with conventional soxhlet using petroleum solvents such as hexane and petroleum ether (Besbes et al., 2004b; Nehdi et al., 2010; Biglar et al., 2012; Kazemi and Dadkhah, 2012). Conventional solid-liquid extraction (SLE) techniques as maceration and soxhlet extraction methods consume time and use large amounts of solvents (Wang and Weller, 2006). Nowadays the development of the concept of green extraction, the environment friendly procedures are becoming more interesting. The application of new technologies, as microwave and ultrasound offer several advantages like reducing time, cost, solvent consumption and power to not affect the stability of extracted compounds, simplifying process and improving extraction quantitatively and qualitatively of extract (Arslan and Ozcan 2010; Chemat et al., 2008; Maskan, 2000; Tiwari, 2015). In this research, we applied the green extraction of oils and lipids in date seeds in which MeTHF was chosen as a good suitable solvent extraction due to its chemical and physical properties which are similar to hexane.

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This agro-solvent is produced from waste of corn cobs, oat hulls and sugar cane bagasse (Pace et al., 2012; Sicaire et al., 2015) and it has nocarcinogenic, mutagenic, and reprotoxic (CMR) properties (Antonucci et al., 2011). Several studies have been reported about the good yields of lipids compounds extraction using alternative methods and solvents (Sicaire et al., 2015; Virot et al., 2008; Dejoye Tanzi et al., 2013; Breil et al., 2016). This study deals for the first time with oils extraction from Tunisian date palm seeds using green extraction procedures as well as the determination of oils chemical compositions.

2. Material and methods

2.1. Plant material

In this study, about 100 g seeds of each date cultivar of Deglet Nour, Allig and Bellah were collected at "Tamr" stage (full ripeness), on November, January and September 2015 respectively, having all the same origin (Tozeur, Tunisia) with GPS position 33°55'6.722N/08°07'22.558E and pluviometry 8.9 mm. The seeds were immersed in water, washed to get rid of any adhering date flesh, air-dried within one week in shadow at ambient temperature and after dried in oven for 12 h at about 50 °C. Then seeds of each variety were grinded using the hammer mill with 1 mm Sieve and preserved at -20 °C until extractions.

2.2. Extraction procedures

Extractions of lipids from date palm seeds were carried out in triplicate with different procedures (Soxhlet, ultrasound, microwave and maceration) using hexane and MeTHF as solvents. Yield of the extracted oil was calculated according to the following expression:

$$\text{Oil Yield} = (W_{\text{oil}}/W_{\text{sample}}) \times 100$$

Where (W_{oil}): weight of oil obtained after extraction and (W_{sample}): weight of dry sample.

Conventional Soxhlet method (ISO 659-1988) was used for the extraction of oils from seeds of 3 different date palm cultivars. 15 g of powdered seeds were extracted using a 200 mL capacity Soxhlet apparatus in a 33 mm × 80 mm cellulose cartridge (Macherey-Nagel). The top of this latter was covered with cotton wool to avoid transfer of particles in the distillation chamber. All samples were extracted under reflux for 8 h using 300 mL of solvent placed in a 500 mL capacity flask which was putted under the soxhlet apparatus.

On the other hand, ultrasound, microwave and maceration procedures were applied for the extraction of oil from milled date palm seeds (10 g) with 100 mL of solvents (hexane and MeTHF) for 30 min.

- Ultrasound extraction was performed in a double envelope thermostatic glass reactor of 250 mL and a transducer of 6 mm, operating at a frequency of 20 kHz and a maximum input power of 130 W. The temperature was fixed at 40 °C.
- Microwave oven (Milestone NEOS-GR multimode) operating with a maximum input power of 450 W at 20 MHz was used for the extraction of lipids from date seeds. Microwaves heat up the solvent to boiling point. The solvent vapors penetrate via the dried date palm seeds and the condensation occurs on the condenser (extraction under reflux).
- Maceration was performed with mechanic agitation in a double envelope thermostatic glass reactor of 250 mL at 40 °C.

Samples extracted with MeTHF were filtered on 0.45 μm nylon filter and evaporated under reduced pressure. The obtained dry samples were re-extracted with hexane (150 mL); centrifuged (1000 rpm, 10 min, 25 °C) and then the hexane was evaporated under reduced pressure. The obtained dry extracts were stored in a freezer (-20 °C) for subsequent analyses.

2.3. Hansen solubility parameters

Hansen solubility parameters (HSPs) software (Hansen, 2007) was used to evaluate the solubility parameters of solvents. This software provides an efficient and convenient theoretical approach to characterize solute-solvent interactions according to the classical "like dissolves like" rule. HSPs are based on the concept that the total cohesive energy density is approximated by the sum of the energy densities required to overcome atomic dispersion forces (δ_d^2), molecular polar forces arising from dipole moments (δ_p^2) and hydrogen bonds (exchange of electrons, proton donor/acceptor) between molecules (δ_h^2), as given by Eq. (1):

$$\delta_{\text{total}}^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

where δ_{total} is the Hansen total solubility parameter, which is composed of three Hansen solubility parameters for dispersion (δ_d), polar (δ_p) and hydrogen bonding (δ_h). The Yamamoto (Y-MB) is the easiest method used to calculate HSPs (Benazzouz et al., 2013). Using JChemPaint version 3.3 (GitHub Pages, San Francisco, CA, USA), the chemical structures of the solvents and solutes were transformed to their simplified molecular input line entry syntax (SMILES) notations, then they were used to calculate the solubility parameters of the alternative solvent and constituents extracted from date seeds. The relative energy difference (RED) number is a simple composite affinity parameter, it has been calculated using (Eq. (2)) by HSP software to determine whether the alternative solvent and the solute are miscible:

$$\text{RED} = R_a/R_b \quad (2)$$

Where R_b is the radius of a Hansen solubility sphere, and R_a is the distance of a solvent situated within the Hansen solubility sphere.

In accordance with the classical "like to like" rule: smaller R_a is, greater affinity between solute and solvent (Filly et al., 2014). Signifies that a suitable solvent has a RED number smaller than 1, whereas unsuitable solvent has a RED number superior than 1. These solubility parameters were further modeled often using two dimensional HSP sphere for better visualization of the solute-solvent system, owing to the negligible differences between δ_D (HSPiP Version 4.0, Hansen-Solubility, Horsholm, Denmark).

2.4. High Performance Thin Layer Chromatography (HPTLC)

Two different HPTLC developments were applied to determine the classes of lipids through the separation of polar and neutral ones. Lipids were charring and quantified by a CAMAG 3 TLC scanning densitometer (CAMAG, Muttenz, Switzerland) with identification of the classes by comparison with known polar and neutral lipid standards. The extracted oils were loaded onto 20 × 10 cm HPTLC plates (Silica gel 60 F254; Merck KGaA, Darmstadt, Germany) by means of an ATS 5 automatic TLC sampler (CAMAG, Switzerland). The HPTLC silica gel plates were then developed with two eluents in an ADC2 automatic developing chamber (CAMAG, Switzerland): The first eluent (a mixture of methyl acetate/isopropanol/chloroform/methanol/KCl in a ratio of 25:25:25:10:9) running to a height of 7 cm from the origin; The second eluent is a mixture of *n*-hexane/diethyl ether/glacial acetic acid in a ratio of (70:30:2) running to a height of 7 cm from the origin. The dried plates were dipped for 6 s in a reagent (10 mg of primuline, 160 mL of acetone, 40 mL of water) and then scanned using a TLC Scanner 3 with a WinCATs software (CAMAG). Identification and quantification of lipids classes were carried out by comparison with lipid standards. The densitometry data are expressed as percent of lipid class in total date palm seeds oils.

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2.5. Analysis by gas chromatography (GC)

2.5.1. Preparation of fatty acids methyl esters (FAMES)

Acid-catalyzed transesterification was used in order to prepare fatty acids methyl esters (FAMES) from the extracted oil as described by Li et al. (Morrison and Smith, 1964). Briefly, a determined quantity of the extracted oil was mixed with 1 mL of a methanolic-sulfuric acid (5%) solution. Triheptadecanoin (C17:0 TAG) was used as internal standard. The obtained mixture was heated at 85 °C for 90 min. After that, the solution was cooled at room temperature and was mixed with 1.5 mL of sodium chloride (0.9%) solution and 1 mL of *n*-hexane; then it was shook vigorously for 30 s. The organic layer was recovered and transferred to a vial for a gas chromatography coupled with flame ionization detector (GC-FID) analysis.

2.5.2. FAMES analysis

Gas chromatography coupled with flame ionization detector (GC-FID) technique was used to analyze FAMES prepared from the extracted oils. This step was carried out by an Agilent (Kyoto, Japan) apparatus equipped with a BD-EN14103 capillary column (Agilent) 30 m × 320 μm × 0.25 μm. Helium was used as carrier gas at 33 cm s⁻¹. 2 μL of the analyzed sample were injected in the injector (kept at 250 °C) with a split mode (split ratio 1:20). The oven temperature varied as follows: Initially, it was kept at 50 °C for 1 min, then increased to 220 °C at a rate of 20 °C/min, then it continues increasing up to 280 °C at a rate of 2 °C/min. Finally the oven temperature was maintained at 230 °C during 10 min. The identification of FAMES was done according to the comparison of their retention times with those of authentic FAME standards (Sigma Co., USA).

3. Results and discussion

3.1. Hansen solubility parameters (HSP)

In theory, HSPs is a software that perform an evaluation of solubility potential of major components TAGs in the bio-sourced solvent (MeTHF) compared to *n*-hexane. Although, the molecules' structure have an influence on polarity, this software uses thermodynamic principles. These later are related to molecules and selection of solvents according to systems of solvent-solute based on parameters of solubility: Van Der Waals forces, hydrogen bonds and dipolar interactions. The calculated HSP values demonstrated that MeTHF may dissolve as an alternative solvents stated by the principle "like Dissolves like". The Yamamoto-Molecular Break (Y-MB) method was applied as the useful prediction method to calculate HSPs of solvents and constituents in extracts (Table 3) by putting SMILES on corresponding functional

Table 1

Yields (%) of fatty acid compositions and lipid classes extracted from date seeds using various solvents by soxhlet method.

	Allig		Bellah		Deglet Nour	
	<i>n</i> -hexane	MeTHF	<i>n</i> -hexane	MeTHF	<i>n</i> -hexane	MeTHF
Lipid Compositions and classes						
Triglycerides	100 ± 0	99.71 ± 0.12	100 ± 0	99.66 ± 0.04	100 ± 0	99.71 ± 0.02
Diglycerides	0	0.29 ± 0.12	0	0.34 ± 0.04	0	0.29 ± 0.02
Composition of fatty acids: Saturated						
Capric C10:0	0.48 ± 0.00	0.47 ± 0.04	0.40 ± 0.00	0.39 ± 0.01	0.47 ± 0.00	0.51 ± 0.03
Lauric C12:0	22.82 ± 0.01	22.62 ± 0.40	21.05 ± 0.09	20.05 ± 0.01	22.00 ± 0.01	22.64 ± 1.43
Miristic C14:0	10.09 ± 0.03	10.08 ± 0.22	11.27 ± 0.04	11.26 ± 0.06	10.14 ± 0.02	10.55 ± 0.67
Palmitic C16:0	8.59 ± 0.00	8.90 ± 0.03	9.92 ± 0.03	10.73 ± 0.11	9.00 ± 0.02	9.68 ± 0.49
Stearic C18:0 Mono-unsaturated	3.47 ± 0.00	3.43 ± 0.08	4.50 ± 0.05	4.59 ± 0.04	3.46 ± 0.02	3.59 ± 0.16
C18:1n9 Poly-unsaturated	44.67 ± 0.02	44.82 ± 0.99	43.65 ± 0.10	44.02 ± 0.26	45.71 ± 0.05	46.90 ± 2.44
C18:2n6	9.88 ± 0.00	9.66 ± 0.29	9.21 ± 0.02	8.97 ± 0.26	9.21 ± 0.02	6.13 ± 5.14
ΣSFAs	45.44	45.51	47.14	47.02	45.08	46.97
ΣUSFAs	54.56	54.49	52.86	52.98	54.92	53.03

ESFAs: Total saturated fatty acids, ΣUSFAs: Total unsaturated fatty acids.

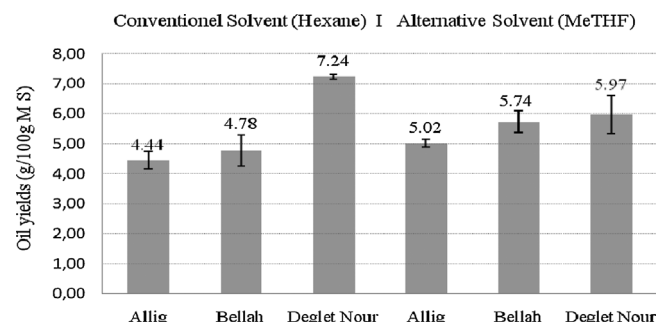


Fig. 1. Total lipid yields of the three cultivars date seeds extracted with different solvents.

groups and then evaluates several properties. The relative energy difference (RED) numbers were calculated for the selected solvents for the extraction of TAGs and resumed in Table 3. All solvents having an RED number smaller than 1 are considered as good solvents. *n*-hexane exhibit a RED value superior to 1 indicating that it is a poor solvent for TAGs extractions from date seeds as founding by Sicaire et al., 2015 for the extraction of rapeseed oil. Furthermore Table 3 showed that MeTHF have RED < 1. Thus, it has good solubility for the extraction of TAGs. Furthermore, two dimensional (2D) graph represented in Fig. 3 exhibits the solubility of different TAGs with MeTHF solvent. Then these solvents would be experimentally tested and compared with those calculated by HSPs.

3.2. Qualitative and quantitative comparison of oils

Seeds date (*Phoenix dactylifera* L.) Oils were extracted by green and conventional methods using MeTHF and *n*-hexane as solvents. All extracted lipids were converted into FAMES derivatives. Then, fatty acids were separated and identified by gas chromatography coupled with a flame ionization detector (GC-FID). Moreover, the extracts were analyzed using High Performance Thin Layer Chromatography (HPTLC) in order to obtain lipid classes. Tables 1 and 2 reported the chemical compositions and relative amounts of fatty acids in connection with solvents and extraction methods for each sample.

3.2.1. Extracted oils from three cultivars with different solvents

Date palm (*Phoenix dactylifera* L.) seeds of three cultivars (Deglet Nour, Allig, and Bellah) were extracted with different solvents (hexane, MeTHF) for 8 h by soxhlet. According to Fig. 1, variety of Deglet Nour was the richest in oils with a total yield ranging from 7.24 to 5.97 g of dry weight biomass followed by Bellah and Allig varieties (4.78–5.74 g/100 g and 4.44–5.02 g/100 g, respectively). Despite the extracted oil

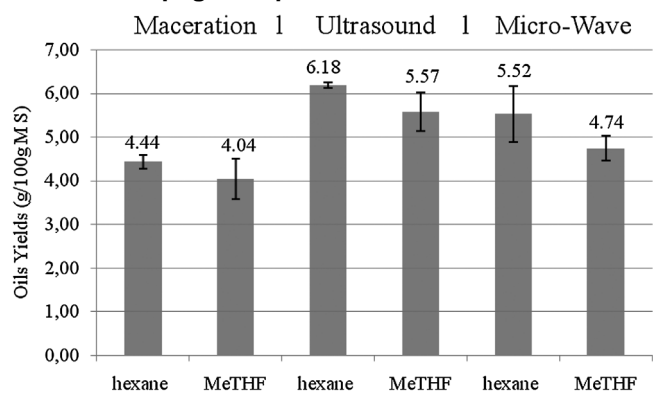


Fig. 2. Total lipid yields of date seeds “Deglet Nour” variety extracted with different solvents and methods.

yields from Deglet Nour by MeTHF was a little less than by *n*-hexane, MeTHF appears as a good alternative solvent for lipids extraction from Bellah and Allig. Fatty acids extraction yields from different date seeds varieties were reported in Table 1. The three cultivars seeds have the same main fatty acids. The highest percentages were found for oleic acid (C18:1) ranging between 43.65%–46.90% and lauric acid (12:0) between 20.05%–22.64%. Thus, all of the extracted date seeds oils were regarded as oleic-lauric oils. This result is in agreement with previous studies (Al-Hooti et al., 1998; Al-Showiman, 1990; Devshony et al., 1992). However, Besbes et al. (2004) founded that date seed oil from Allig variety can be considered as oleic–linoleic type because of its content in oleic acid 47.7%, linoleic acid 21% and lauric acid 5.8%. This difference can be explained either by differences in cultural and climatic conditions or/and region and period of harvest (Al-Shahib and Marshall, 2003). The both major fatty acids showed many benefits to health. Oils containing high amount of oleic acid showed frying stability and good flavor due to its low saturation level, its minimal trans–isomer level as well as its high oxidative stability and its capacity to reduce LDL cholesterol in the blood (Liang and Liao, 1992). On the other hand, De Roos et al. (2001) showed that lauric acid is a good substituent to the hydrogenate polyunsaturated in the preparation of margarine generating a favorable lipidic profile to reduce the risk of attack by the cardiovascular illnesses (Saafi et al., 2008). Other identified compounds in the extracted oils were myristic (14:0) palmitic (16:0) and linoleic acids (18:2) presenting respectively more than 11%, 10% and 9%. The least amount was related to stearic acid (C18:0) about 4% and traces of capric acid (C10:0) were detected between (0.39–0.51%). These amounts are approximately similar to those reported in others studies (Al-Shahib and Marshall, 2003; Besbes et al.,

2004b; Saafi et al., 2008). The saturated and unsaturated fatty acids contents in the three cultivar date seeds ranged from 45.08 to 47.14% and from 52.86 to 54.92% respectively. These values are similar to those reported by Saafi et al. (2008). High Performance Thin-Layer Chromatography (HPTLC) analysis of extracted oils showed only triglycerides (TAGs) (99.66%–100%) with traces of diacylglycerides (DAGs) (0.29–0.34%) detected only using MeTHF as solvent. This is in a good agreement with work of Besbes et al. (2004b) who founded about 97.26–96.90% of TAGs and 0.23–0.22% of DAGs in oils from Deglet Nour and Allig varieties. So far, all of the experimental results confirm that MeTHF is a good alternative solvent for lipids extraction from the three studied date seeds varieties.

3.2.2. Comparison of oils extracted from deglet nour in function of solvents and methods

As shown in Fig. 2, extracted lipids from Deglet Nour by Green extraction procedures, namely Ultrasound (US) and Micro-Waves (MW) were higher than maceration and slightly lower than soxhlet in only 30 min against 8 h. For all methods, MeTHF was found to be a good alternative solvent. No important differences were detected with the different used extraction methods and solvents. Results are similar in terms of quantitative and qualitative determination. As can be shown in Fig. 2, the extracted oil yields by US and MW had higher amounts than maceration (about 6% vs. 4%) under the same experimental conditions. Consequently, green extraction methods can be considered as interesting alternative technologies for conventional methods (Chemat et al., 2012). The most major compounds identified for both green methods were oleic acid (C18:1) and lauric acid (12:0), they represent together more than 67% of the total fatty acid composition of the extracted oils (between 44.84–45.56% of C18:1 and 22.19–23.10% of C12:0). As found with the conventional soxhlet, myristic (14:0), palmitic (16:0) and linoleic (18:2n6) acids were detected as minor compounds with the same lower amounts. Trace levels of stearic (C18:0) and capric (C10:0) acids were found respectively with maximum amounts of 5% and 0.51% respectively. Thus, it can be concluded that the profiles and proportions of saturated and unsaturated fatty acids have not been affected by experimental conditions used in all samples. Concerning lipid classes, results obtained by HPTLC analyses of both of the used green procedures were similar to those obtained by both conventional extraction methods using MeTHF as alternative solvent and *n*-hexane as reference. As shown in Table 2, all samples presented only TAGs with more than 99% of the total of lipids and trace of DAGs about 0.59–1%. All samples were almost similar in terms of profiles and yields for extraction of the fatty acids and TAGs. The practical results of fatty acid and lipid classes profiles were evaluated with the theoretical predictions by predictive software Hansen solubility parameters in order to

Table 2
 Yields (%) of fatty acid compositions and lipid classes extracted from date seeds (Deglet Nour) using various solvents and procedure extractions.

	Maceration		Ultrasound		Micro-Wave	
	<i>n</i> -hexane	MeTHF	<i>n</i> -hexane	MeTHF	<i>n</i> -hexane	MeTHF
Lipid Compositions and classes						
Triglycerides	99.35 ± 0.04	99.36 ± 0.05	99.26 ± 0.01	99.00 ± 0.09	99.41 ± 0.07	99.40 ± 0.02
Diglycerides	0.65 ± 0.04	0.64 ± 0.05	0.74 ± 0.01	1.00 ± 0.09	0.59 ± 0.07	0.60 ± 0.02
Composition of fatty acids: Saturated						
Capric C10:0	0.39 ± 0.01	0.51 ± 0.04	0.48 ± 0.01	0.48 ± 0.01	0.51 ± 0.02	0.49 ± 0.01
Lauric C12:0	20.05 ± 0.01	22.64 ± 1.23	22.19 ± 0.13	22.22 ± 0.29	23.10 ± 0.71	22.25 ± 0.27
Myristic C14:0	11.26 ± 0.06	10.55 ± 0.27	10.17 ± 0.01	10.20 ± 0.04	10.29 ± 0.10	8.88 ± 0.04
Palmitic C16:0	10.73 ± 0.11	9.68 ± 0.24	9.02 ± 0.03	9.03 ± 0.04	10.19 ± 0.07	9.07 ± 0.07
Stearic C18:0 Mono-unsaturated	4.59 ± 0.04	3.59 ± 0.16	3.47 ± 0.01	3.47 ± 0.03	3.42 ± 0.05	3.50 ± 0.03
C18:1n9 Poly-unsaturated	44.02 ± 0.26	46.9 ± 2.44	45.56 ± 0.12	45.49 ± 0.22	44.84 ± 0.59	45.40 ± 0.18
C18:2n6	8.97 ± 0.26	6.13 ± 5.14	9.11 ± 0.01	9.12 ± 0.05	8.96 ± 0.12	9.10 ± 0.03
ΣSFAs	47.02	46.97	45.33	45.39	46.20	45.50
ΣUSFAs	52.98	53.03	54.67	54.61	53.80	54.50

ΣSFAs: Total saturated fatty acids, ΣUSFAs: Total unsaturated fatty acids.

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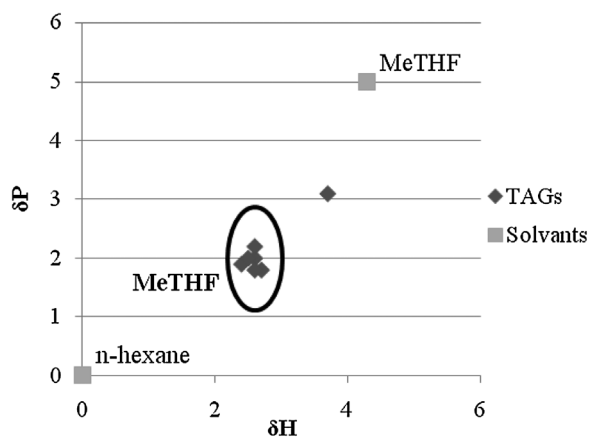


Fig. 3. Alternative solvent for solubilizing triglycerides (TAGs) via Hansen's settings. δ_P : parameter of polar, δ_H : parameter of hydrogen bonding.

Table 3

The relative energy difference (RED) values for HSP assisted selection of alternative solvent to *n*-hexane for the extraction of date seeds.

	TAG 1	TAG 2	TAG 3	TAG 4	TAG 5	TAG 6	TAG 7
<i>n</i> -hexane	1.11	1.21	1.1	1.04	1.12	1.04	1.06
MeTHF	0.90	1.16	0.93	0.91	0.93	0.96	0.92

TAG1 (R1: C12, R2: C14, R3: C14), TAG 2 (R1: C12, R2: C18:1n9, R3: C18:1n9), TAG 3 (R1: C16, R2: C18:2n6, R3: C18:2n6), TAG 4 (R1: C12, R2: C16, R3: C16), TAG 5 (R1: C14, R2: C16, R3: C18:2n6), TAG 6 (R1: C12, R2: C16, R3: C18:1n9), TAG 7 (R1: C12, R2: C14, R3: C16).

know if hexane can be replaced by MeTHF for oil extractions from seeds date palm (*Phoenix dactylifera* L.). MeTHF was a good candidate for the substitution whatever using green or conventional extraction methods. In previous studies, it was reported that green extraction procedures were cleaner than those obtained with conventional extraction methods (Chemat et al., 2012).

3.3. Comparison between experimental data and theoretical simulation

The theoretical results were compared to the experimental data. The Hansen method describes MeTHF as a promising alternative solvent to replace hexane for extraction of TAGs as was reported by Sicaire et al., 2015. Experimentally, the HPTLC analysis shows that solvent had no influence on the extraction of triglyceride yields. The lipid profiles of MeTHF extracts are similar to the hexane extracts. So the HSPs theory corroborates the experimental part. The 2-D graph of δ_P towards δ_H presented in Fig. 3 shows the different TAGs and the alternative solvent according to Hansen's method. Circles visualize the good simulation of MeTHF. This graph permits to see the good miscibility of TAGs with MeTHF. The experimental results were in coherence with those obtained by Breil et al., 2016 for *Yarrowia Lipolytica* IFP29.

4. Conclusion

This study shows that the date seeds would be an important edible and nutraceutical source of oils regarding to the high percentage of oleic (44.02–46.90%) and lauric (20.00–23.10%) acids which can prevent cardiovascular illnesses. Others fatty acids were detected myristic (8.88–11.26%), palmitic (9.00–10.73%) and linoleic (6.13–9.21%) acids. Triglycerides were the most recovered component oils with 99%. The aim of the present study was to evaluate the replacement aspects of petroleum-based solvents by bio-based and biodegradable solvent for its several economic and environmental advantages over conventional extraction techniques. The HSP prediction

of candidate solvent showed that MeTHF is a good suitable solvent to replace hexane due to its ability to dissolve triglycerides. Green extraction procedure and solvents lead to obtain high yield extractions by-products comparing to maceration (about 6% versus 4%) and in a less time (30 min versus 8 h) comparing to soxhlet procedure. Our study would encourage interest in date seed oils to be used in food, pharmaceuticals and cosmetics industries.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

The authors are grateful for the financial support of the Ministry of Higher Education and Scientific Research, Tunisia, granted to the Laboratory of Organic Chemistry, Natural Substances Team Faculty of Sciences of Sfax, [grant number LR17ES08].

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Ben-Youssef, S., Fakhfakh, J., Breil, C., Abert-Vian, M., Chemat, F., Allouche, N. (Auteur de correspondance) (2017). Green extraction procedures of lipids from Tunisian date palm seeds. *Industrial Crops and Products*, 108, 520-525. DOI : 10.1016/j.indcrop.2017.07.010

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