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Chemical composition and thermal properties of Tunisian pecan nut [*Carya illinoinensis* (Wangenh.) K. Koch] oils

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SUMMARY: An investigation on fatty acid, triacylglycerol, tocopherol, and xanthophyll contents and thermal properties of pecan (*Carya illinoinensis*) kernel oils from two cultivars was carried out. The main fatty acids were oleic acid, followed by linoleic and palmitic acids. The predominant triacylglycerols were OOL, OOO, and OLL (where O stands for oleoyl and L for linoleoyl). Pecan kernel oil is a rich source of tocopherols, mainly γ-tocopherol. Two xanthophylls (lutein and zeaxanthin) were investigated, and lutein was found to be the major one. Thermal behavior was studied by differential scanning calorimetry (DSC). Pecan nut oil displayed melting and crystallization transitions at low-temperature zones. The difference between DSC parameter values provides a path for distinguishing among cultivars. These data promote pecan kernel oil as a potential source of bioactive compounds with nutraceutical properties (monounsaturated fatty acids, tocopherols, and xanthophylls) and reveal, for the first time, the thermal properties of *Carya illinoinensis* oil.

KEYWORDS: *Pecan nut; Fatty acids; Tocopherols; Triacylglycerols; Xanthophylls; Thermal properties*

RESUMEN: ***Composición química y propiedades térmicas de aceites de nuez de pecana* [Carya illinoinensis (Wangenh.) K. Koch] *tunecina.*** Se llevó a cabo una investigación sobre el contenido de ácidos grasos, triacilgliceroles, tocoferoles, xantofilas y propiedades térmicas de aceites de nuez de pecana (*Carya illinoinensis*) de dos cultivares. Los principales ácidos grasos fueron el ácido oleico seguido de los ácidos linoleico y palmítico. Los triacilgliceroles predominantes fueron OOL, OOO y OLL (donde O, oleoilo y L; linoleoilo). El aceite de nuez de pecana es una fuente rica en tocoferoles, principalmente γ-tocoferol. Se investigaron dos xantofilas (luteína y zeaxantina), la luteína fue la mayoritaria. Los comportamientos térmicos se estudiaron mediante calorimetría diferencial de barrido (DSC). El aceite de nuez de pacana mostró transiciones de fusión y cristalización en zonas de baja temperatura. La diferencia entre los valores de los parámetros de DSC proporciona un camino para distinguir entre cultivares. Estos datos presentan al aceite de nuez pecana como una fuente potencial de compuestos bioactivos con propiedades nutracéuticas (ácidos grasos monoinsaturados, tocoferoles y xantofilas) y revelan, por primera vez, las propiedades térmicas del aceite de *Carya illinoinensis*.

PALABRAS CLAVE: *Ácidos grasos; Nuez de pecana; Propiedades térmicas; Tocoferoles; Triacilgliceroles; Xantofilas*

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1. INTRODUCTION

The World Health Organization (WHO) has recommended the dietary consumption of nuts due to their high contents in unsaturated fatty acids which help to prevent cardiovascular diseases, obesity, diabetes, certain cancers, and other chronic diseases (WHO, 2019). Among all nuts, the world production of pecan (*Carya illinoinensis*) oil is promptly increasing. This oil is recognized as a healthy specialty oil. Indeed, pecan kernel oil has been reported to be a good source of fat-soluble bioactive compounds such as unsaturated fatty acids, tocopherols, phytosterols (Miraliakbari and Shahidi, 2008; Bouali *et al.,* 2013), and polyphenols (Kornsteiner *et al.,* 2006; Bouali *et al.,* 2020). Likewise, clinical studies have revealed that regular pecan nut supplementation ameliorates the lipid profiles that are related to cardiovascular risk (Atanosov *et al.,* 2017).

The potential health benefits of pecan kernel oil are often attributed to its high levels of monounsaturated fatty acids (MUFA) (Miraliakbari and Shahidi, 2008; Atanosov *et al.,* 2017), primarily oleic acid (60- 70% of total fatty acids) (Bouali *et al.,* 2013; do Prado *et al.*, 2013).

Pecan kernel oil contains triacylglycerols (96.4 g/100 g of oil) (Miraliakbari and Shahidi, 2008), which are the major components of most vegetable oils included in the human diet. They are considered an important factor in the evaluation of the oxidation of oils (Zeb, 2012). Moreover, triacylglycerols (TAG) are employed in the food industry to assess the authenticity of vegetable oils.

Emphasis has been given to the use of lipid-soluble antioxidants. Indeed, antioxidants such as tocopherols and carotenoids generally enhance oil stability, and consequently, consumers often value oils naturally rich in these compounds. Tocopherols are powerful antioxidants and scavengers of free radicals. They possess potent anti-cancer, anti-inflammatory, antiatherogenic, cardioprotective, and cholesterol lowering properties (Mathur *et al.,* 2015).

Carotenoids are fat-soluble compounds known for their provitamin A activity. Among the carotenoids, we primarily examined two xanthophylls which are lutein and zeaxanthin. They are present in the macula of the retina in the eye. They have protective effects against the evolution of age-related macular degeneration and cataracts (Ma and Lin, 2010). Likewise, many recent epidemiological studies have shown that lutein and zeaxanthin may reduce the risk of cancer and coronary heart disease (Ma and Lin, 2010).

It is important to monitor the thermal behavior of edible vegetable oils and fats in order to evaluate the changes in their comportments when exposed to thermal load disruptions, to verify their authenticity (Nilchian *et al.,* 2020), and to enhance the acquaintance concerning the influence of oil composition on their thermal behavior (Chambre *et al.,* 2019). Differential scanning calorimetry (DSC) is the most commonly used thermo-analytical tool for oils. Numerous studies have focused on the characterization of tree nut oils by DSC such as hazelnut (*Corylus avellana* L.) oil, walnut (*Juglans regia* L.) oil (Che Man and Tan, 2002), Almond (*Prunus dulcis* L.) oil (Beltrán *et al.,* 2011) and pistachio (*Pistacia vera* L.) oil (Ling *et al.,* 2015). So far, no complete research concerning the thermal behavior of pecan nut oil has been performed.

A comparative study of the different pecan cultivars is key for breeding programs and the food industry in the selection of cultivars with the maximum amount of high value-added compounds. In this context, our aim was to evaluate two Tunisian pecan cultivars (Mahan and Moore) through their fatty acids, TAG, tocopherol, and xanthophyll compositions and through their thermal behavior.

2. MATERIALS AND METHODS

2.1. Reagents and standards

Toluene, acetonitrile, methanol, dichloromethane, and hexane were supplied by Carlo Erba (Val de Reuil, France). Petroleum ether was obtained from Fisher Scientific SA (Loughborough, UK). Fatty acid methyl ester (FAME) standards were acquired from Nu-Chek-Prep (Elysian, MN, USA). Tocopherol standards, ammonium acetate, sodium bicarbonate, and 7% boron trifluoride in methanol (BF_3-MeOH) were provided by Sigma–Aldrich (Saint-Quentin Fallavier, France). Lutein and Zeaxanthin standards were generous gifts from Roche (Neuilly-sur-Seine, France).

2.2. Pecan samples

Pecan nuts from Moore and Mahan cultivars were harvested at complete maturity from a restricted

zone on the INRGREF experimental farm (National Institute for Research in rural engineering, water and forest), in Mateur, Northern Tunisia (Longitude: 09°48′ E; Latitude: 37°15′ N; Altitude: 5 m above sea level).

Husks were removed And the kernels were detached manually from the shell and dried in an oven at 60 °C. Using a mortar, the dry samples were finely ground for the extraction process.

2.3. Oil extraction

Oil was extracted from dry milled pecan kernels (5 g) using a soxhlet apparatus with light petroleum ether for 6 h at 42 °C. The solvent was removed from the resulting extract by rotary vacuum evaporation at 50 °C. The obtained oil was stored in dark glass bottles at 4 °C until analysis.

2.4. Fatty acid analysis

The fatty acid composition was determined as fatty acid methyl esters (FAME) prepared as described previously by Bouali *et al.* (2013). Twenty milligrams of oil were mixed with 0.7 mL boron trifluoride reagent (BF3/methanol, 7 %) and 0.3 mL toluene under nitrogen and the tube was heated at 95 °C for 2 h and then cooled to room temperature. FAMEs were extracted by adding 5 mL of sodium bicarbonate and 3 x 2 mL hexane. The obtained mixture was centrifuged for 3 min. The solvent was removed under a nitrogen stream. Then, the FAMEs were dissolved in hexane and analyzed on a Hewlett Packard Model 4890 gas-chromatograph (Palo Alto, CA, USA) with a CP-Sil 88 (100 m × 0.25 mm I.D. capillary column, 0.2 µm film, Varian, Les Ulis France). The injector and detector temperatures were 250 and 280 °C, respectively. The initial oven temperature was held at 60 °C for 5 min, increased to 165 °C at 15 °C/min and held for 1 min at this temperature; then increased to 225 °C at 2 °C/min, before being maintained at this temperature for 17 min. The peaks were identified based on their retention times using synthetic and commercial standards. Analyses were performed in triplicate.

2.5. Triacylglycerol analysis

The TAG analysis was performed by gas chromatography (GC) using the same chromatographic conditions as reported by Bootello *et al.* (2016). About 5 mg of pecan kernel oil were dissolved in 1.8 mL of heptane. One µL of this solution was injected into the GC, an Agilent 7890 gas chromatograph (Palo Alto, CA) equipped with a flame ionization detector (FID) and a Quadrex Aluminum-Clad 400-65HT chromatography column (30 m length; 0.25 mm diameter; 0.20 µm film thickness: Bellefonte, PA, USA). Hydrogen was used as the carrier gas at a linear gas rate of 50 $cm \cdot s^{-1}$ and a split ratio of 1:50. The detector and injector temperatures were 370 and 350 °C, respectively; the oven temperature was 335 °C, and a pressure gradient from 100 to 200 kPa was applied. Peak identification was performed by comparing their retention times with those of a standard mixture and known samples. Quantification of the peaks was made by internal normalization of the chromatographic peak area, and the results are expressed in relative percentage.

2.6. Tocopherol and xanthophyll analysis

The tocopherol and xanthophylls analysis was performed by reverse-phase high performance liquid chromatography (RP-HPLC) using the procedure previously described by Bouali *et al.* (2013). Samples (40 mg) were diluted in 1 mL of mixed HPLC mobile phase: acetonitrile/methanol containing 50 mM ammonium acetate/water/dichloromethane (700:150:50:100, V/V/V/V). Then, the mixture was vortexed.

The assays were carried out on a Jasco PU-1580 apparatus plus intelligent pump equipped with an automatic injector system AS300 (Thermo Finnigan, Les Ulis, France) and a Jasco MD-1510 plus multi wavelength detector (JASCO International Co., Ltd., Japan). Chromatographic separation was performed on a VIDAK C18 column (25 mm x 4.6 mm id, 5 µm particle size) connected with a Nucleosil C18 column (25 mm x 4.6 mm id, 5 µm particle size). The mobile phase was a mixture of acetonitrile/ methanol at 50 mM ammonium acetate/ water/ dichloromethane (700:150:50:100, V/V/V/V) at a flow rate of 2 mL/min. Samples of 18 µL were injected, the wavelengths were set at 298 nm for tocopherols and 450 nm for lutein and zeaxanthin. The identification was carried out by comparing the retention times and absorption spectra of unknown peaks to authentic standards and by adding α-, δ-, γ-tocopherol, lutein, and zeaxanthin standards to the sample for co-chromatography. The quantification was based on the external standard method.

2.7. Thermal analysis by DSC

Thermal properties of pecan kernel oils were carried out on a diferential scanning calorimetry (DSC) using a Q2000 V23.5 scanner (TA instruments, New Castle, DE, USA). Dry nitrogen was used as the purge gas at a rate of 20 mL/min. Oil samples (6-8 mg) were weighed directly into aluminium pans. An empty sealed pan was employed as control.

Samples were subjected to the following temperature program: 90 °C isotherm for 5 min, and then cooled to -80 °C at a rate of 10 °C/min, held for 20 min. Oil samples were then heated from -80 °C to 90 °C at a rate of 5 °C/min to acquire the data of the melting thermogram. The crystallization was achieved by heating the oils at 90 °C for 5 min and then decreasing the temperature to -80 °C at a rate of 10 °C/min.

Crystallization and melting parameters: the melting enthalpy ($\triangle H_m$), the temperature of the major peak of melting (P_m), the initial and end temperature of the melting phase (T onset $_m$ and T end $_m$), the crystallization enthalpy ($\triangle H_c$), the temperature of the major peak of crystallization (P_c), the initial temperature of the crystallization phase (T onset $_c$), the range of the transition phase (R: the temperature difference between T onset and T end) were determined.

2.8. Statistical analysis

The results were expressed as mean values and standard deviation and were analyzed using the statistical analysis system XLSTAT (version 2015). The differences between cultivars were analyzed using one-way ANOVA followed by Duncan's test ($P < 0.05$), and principal component analysis (PCA).

3. RESULTS AND DISCUSSION

3.1. Total lipid content

Oil contents, expressed in percentage of dry weight, are reported in Table 1. It can be deduced that the amount of lipids differs among pecan nut cultivars as has been observed previously (Ribeiro *et al.,* 2020). Moore kernels had lipid content significantly higher (72.57 %) than those of Mahan (69.64 %). The kernels investigated in this study exhibited a substantial fount of lipids for food with more than 69% of this macronutrient (Table 1). In the present study, the oil content of both cultivars was significantly higher than that of the Burkett cultivar (68.42% dry weight) as previously studied (Bouali *et al.,* 2013).

These values are similar to those published by Miraliakbari and Shahidi, (2008) but higher than those reported by do Prado *et al.* (2013) and Ribeiro *et al.* (2020). Differences in lipid content in pecans could be attributed to cultivar, geographic factors, ripening stage, and variations in extraction methods (Miraliakbari and Shahidi, 2008; Bouali *et al.,* 2013; Ribeiro *et al*., 2020). Most nuts contain high amounts of fat (almond 60.10%, pistachio nut 22.09%, and walnut 32.95%) (Rabadán *et al.,* 2019).

Table 1. Oil content (expressed as % dry weight) and fatty acid composition (% of total fatty acids).

	Cultivars	
	Mahan	**Moore**
Total oil content (%)	69.64 ± 0.24[a]	72.57 ± 1.02[b]
Fatty acids		
C14:0	0.06±0.017[a]	0.05±0[a]
C15:0	0.02±0.015[b]	0.013±0.005[a]
C16:0	6.37±0.06[a]	6.2±0.03[a]
C16:1n-9	0.03±0[a]	0.03±0[a]
C16:1n-7	0.09±0[b]	0.08±0[a]
C17:0	0.06±0[a]	0.06±0.005[a]
C18:0	2.61±0.005[a]	2.27±0.005[a]
C18:1n-9	55.16±0.28[a]	56.81±0.08[b]
C18:1n-7	1.05±0.04[a]	1.12±0.025[a]
C18:2n-6	32.73±0.24[a]	31.60±0.06[a]
C20:0	0.13±0[b]	0.12±0[a]
C20:1n-9	0.22±0[a]	0.26±0.006[b]
C18:3n-3	1.44±0.035[b]	0.3±0[a]
C22:0	0.03±0.005[a]	0.03±0[a]
Σ SFA	9.28	8.75
Σ MUFA	56.55	58.30
Σ PUFA	34.17	31.63
Σ UFA	90.72	89.93

Each value is a mean ± standard deviation (SD) of a triplicate analysis performed on different samples. Fatty acids detected: C14:0, myristic acid; C15:0, pentadecylic acid; C16:0, palmitic acid; C16:1n-9, palmitoleic acid; C17:0, margaric acid; C18:0, stearic acid; C18:1n-7, vaccenic acid; C18:1n-9, oleic acid; C18:2n-6, linoleic acid; C18:3n-3, α-linolenic acid; C20:0, arachidic acid, C20:1n-9, eicosanoic acid; C22:0, behenic acid; SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids; UFA, unsaturated fatty acids. Means with same letters in the same line were not significantly different according to the multiple range Duncan test at $P < 0.05$.

3.2. Fatty acid composition

Table 1 shows the fatty acid composition of Mahan and Moore cultivars. Fourteen fatty acids were detected. Oleic acid was the predominant one (55.16–56.81% of total fatty acids). Linoleic acid was the second in order of importance (31.60–32.73%). Among the remaining fatty acids only palmitic (6.20–6.37%) and stearic (2.27–2.61%) acids showed considerable amounts. The major fatty acids found in the present study are, in general, comparable to those reported in the literature (do Prado *et al.*, 2013; Ribeiro *et al*., 2020).

In the current study, the fatty acid composition of both cultivars was significantly different from the Burkett cultivar previously investigated, which showed a particular composition with very high oleic acid (69.04%) and low linoleic acid (20.69%) contents (Bouali *et al.,* 2013). This variation could be attributed to genetic differences.

In pecan kernel oil, saturated fatty acids (SFA) were the minor group (8.75–9.28% of total fatty acids): whereas monounsaturated fatty acids (MUFA) were the highest (56.55 – 58.30%) (Table 1). It is important to mention that the pecan nut oil is exceeded in monounsaturated fatty acids level by olive oil (58.07–71.13%) (Ouni *et al.,* 2011) but followed by other nut oils like pistachio nut (54.28%), cashew (57.54%) and walnut (19.16%) (Al Juhaimi *et al.,* 2018). Polyunsaturated fatty acids (PUFA) were present at high levels (31.63 – 34.17% of total fatty acids).

Overall, the obtained results (MUFA > PUFA > SFA) are similar to those observed in Brazilian pecan nuts (Ribeiro *et al*., 2020) and other geographical origins such as Mexico (Rábago-Panduro *et al.,* 2020).

3.3. Triacylglycerols composition

In a previous study, Miraliakbari and Shahidi (2008) reported that pecan nut oil contains 96.4% of triacylglycerols. Therefore, it was interesting to investigate the TAG compositions among pecan nut cultivars. The TAGs were identified and quantified by GC. Significant differences between the two cultivars were detected. As shown in Table 2, thirteen compounds were identified and quantified: POP, PLP, POS, POO, PLS, POL, PLL, SOO, OOO, SOL, OOL, OLL, LLL (where P, palmitoyl; S, stearoyl; O, oleoyl; and L; linoleoyl). The predominant TAG was OOL (28.05 – 28.54%) in both cultivars, followed by OOO (25.96%) and OLL (15.53%) in the Moore cultivar. In the Mahan cultivar, OLL (20.62%) was the second major TAG and OOO was the third (17.77%). The remaining TAGs had smaller percentages (Table 2). The amount of POS was the lowest in both cultivars. The variation, observed among cultivars, may be attributed to genetic causes, mostly acyltransferase activities during the TAG assembly. Several authors have emphasized the effect of genotype on TAG composition in other nuts (Bouabdallah *et al.,* 2014; Taş and Gökmen, 2015). The TAG composition is considered the most effective parameter for distinguishing cultivars (Bouabdallah *et al.,* 2014), which is confirmed by our findings.

Our results are different from those reported by Fernandes *et al.* (2017) for pecan nuts obtained from local grocery stores in Brazil. These same authors reported the predominance of PLP + OOO + PoPP. This difference could be attributed to cultivar and geographical variations, ripeness stages, storage conditions and differences in extraction methods and analytical procedures.

Table 2. Triacylglycerol composition (% of total triacylglycerols)

	Cultivars	
	Mahan	**Moore**
POP	0.49±0.12[a]	0.53±0.12[a]
PLP	0.44±0.1[a]	0.50±0.11[a]
POS	0.23±0.04[a]	0.28±0.04[a]
POO	5.63±0.7[a]	7.90±0.95[b]
PLS	0.53±0.1[a]	0.78±0.1[b]
POL	7.80±0.88[a]	8.20±0.83[b]
PLL	4.31±0.41[b]	3.03±0.25[a]
SOO	1.82±0.07[a]	2.03±0.05[a]
OOO	17.77±0.18[a]	25.96±0.07[b]
SOL	3.36±0.03[b]	2.00±0.00[a]
OOL	28.05±0.35[a]	28.54±0.73[a]
OLL	20.62±0 .82[b]	15.53±0.82[a]
LLL	8.97±0.5[b]	4.69±0.84[a]
Total	**100**	**100**

Each value is a mean ± standard deviation (SD) of a triplicate analysis performed on different samples. P, palmitoyl; S, stearoyl; O, oleoyl; and L; linoleoyl. Means with same letters in the same line were not significantly different according to the multiple range Duncan test at $P < 0.05$.

Table 3. Tocoperol and xanthophyll contents in pecan nut kernel oils (expressed as mg/kg of oil).

Cultivars	α-tocopherol	δ-tocopherol	γ-tocopherol	Total tocopherols	Lutein	Zeaxanthin	Total xanthophylls
Moore	6.31±0.5[b]	0.80±0.25[b]	259.82±10.35[b]	266.93	0.22 ± 0.01[a]	ND[a]	0.22
Mahan	4.64±0.42 [a]	0.50±0.1 [a]	197.30±7.54 [a]	202.44	0.23 ± 0[a]	ND[a]	0.23

ND: Not detected. Each value is a mean ± standard deviation (SD) of a duplicate analysis performed on different samples. Means with the same letters in the same column were not significantly different according to the multiple range Duncan test at $P < 0.05$.

For walnut (*Juglans regia*), a member of the same family as the pecan nut (the Juglandaceae family), 19 TAG compounds were detected in this oil, with LLL as the major one (Bouabdallah *et al.,* 2014).

3.4. Tocopherol contents

The amount of tocopherols is a fundamental parameter for assessing the quality of oils. The tocopherol composition is reported in Table 3. γ-Tocopherol was predominant in both analyzed oils, representing about 98% of total tocopherols. The highest amount was observed in the Moore cultivar (259.82 mg/kg of oil); whereas the lowest was detected in the Mahan cultivar (197.30 mg/kg of oil). γ-Tocopherol is considered the most frequent isoform of vitamin E in several nuts (Kornsteiner *et al.,* 2006). α-Tocopherol was the second predominant isoform, accounting for 2.36% and 2.29% of the total tocopherols in Moore and Mahan cultivars, respectively. Several investigations have revealed that γ-tocopherol possesses beneficial activities which are not common to α-tocopherol. γ-Tocopherol has, notably, stronger anti-cancer, anti-inflammatory, antioxidant, cardioprotective properties (Smolarek and Suh, 2011; Mathur *et al.,* 2015), greater detoxification of nitrogen oxides and higher inhibition of cyclooxygenase-2 (COX-2) (Mathur *et al.,* 2015) than α-tocopherol. In addition, γ-tocopherol, but not α-tocopherol, exerts an anti-proliferative effect on lung and prostate cancer cells (Jiang *et al.,* 2004).

Besides γ- and α-tocopherols, δ-tocopherol was also present in pecan kernel oil, with low amounts representing 0.3 and 0.25 % of the total tocopherols in Moore and Mahan cultivars, respectively.

These results indicated that pecan kernel oil provides natural antioxidants, with the Moore cultivar exhibiting the greatest tocopherol content (266.93 mg/kg of oil). In this study, the total tocopherol content of both cultivars was significantly higher than that of the Burkett cultivar previously investigated (Bouali *et al.,* 2013). Similar results have been found by other authors (do Prado *et al.*, 2013) implying that tocopherol content is highly cultivar-dependent.

The total tocopherol contents found in this study were higher than those reported by Kornsteiner *et al.,* (2006) and Fernandes *et al,*. (2017). In contrast, they were lower than those reported by Miraliakbari and Shahidi (2008). It is well-known that tocopherol content is strongly influenced by genetic differences, maturity (Bouali *et al.,* 2013), geographic and climatic conditions (do Prado *et al.*, 2013), as well as differences in extraction methods and analytical procedures (Miraliakbari and Shahidi, 2008).

Miraliakbari and Shahidi (2008) studied the tocopherol composition of oils extracted from several nuts by different solvents and found that the tocopherol content in pecan kernel oil ranges from 453.9 to 491.1 mg/kg oil, exceeded by the total tocopherol content in hazelnut oil. It has been pointed out that pecan kernel oil contains the greatest amount of γ-tocopherol among tree nut oils (Miraliakbari and Shahidi, 2008).

3.5. Xanthophyll contents

Both cultivars were also investigated for their levels of lutein and zeaxanthin. Among xanthophylls, lutein and zeaxanthin prevent the risk of several diseases (Ma and Lin, 2010). Thus, it is beneficial to assess the levels of these compounds in pecan nuts in order to select the cultivar which contains the greatest amount of xanthophylls.

The amounts of lutein and zeaxanthin as well as their sum are reported in Table 3. Concerning total xanthophylls, a similarity was found between the cultivars. In the present study, the total xanthophylls contents in both cultivars (0.22–0.23 mg/kg of oil) was significantly higher than that of the Burkett cultivar (0.14 mg/kg

Table 4. DSC parameters.

	Mahan		Moore	
	Peak 1	**Peak 2**	**Peak 1**	**Peak 2**
Melting Curves:				
$\triangle H_m$ (J/g)		66.2		70.2
P_m (°C)	-29.2	-21.2	-27.4	-19.4
T $onset_m$ (°C)	-41.7	-26.3	-37.5	-24.7
T end_m (°C)	-26.3	-7.6	-24.7	-4.5
R (°C)		34.1		33.0
Crystallization Curves:				
$\triangle H_c$ (J/g)		40.1		61.2
P_c (°C)		-63.3		-58.9
T $onset_c$ (°C)		-24.6		-24.8

$\triangle H_m$: melting enthalpy, P_m: temperature of the major peak of melting, T $onset_m$ and T end_m: initial and end temperature of the melting phase, $\triangle H_c$: crystallization enthalpy, P_c: temperature of the major peak of crystallization, T $onset_c$: initial temperature of the crystallization phase, R: range of the transition phase (temperature difference between T onset and T end).

of oil) already studied (Bouali *et al.,* 2013). It is important to highlight that *Carya illinoinensis* kernel oil is not a substantial source of dietary xanthophylls.

In pecan kernel oil, lutein was the predominant xanthophyll. Our findings are in disagreement with the previous study of Kornsteiner *et al.,* (2006) who did not detect any lutein. The same authors revealed that pecan nut oil was surpassed in lutein level by pistachio nut oil (15–96 mg/kg of oil) (Kornsteiner *et al.,* 2006). Indeed, pistachio nut oil contains the highest level of lutein among all nut oils; whereas almond, Brazil nut, cashew, hazelnut, macadamia and walnut oils do not contain any lutein (Kornsteiner *et al.,* 2006). Nonetheless, zeaxanthin was not detected in either cultivar of *Carya illinoinensis*.

3.6. Thermal properties

The thermal parameters supplied by the heating and cooling thermograms are given in Table 4. The melting thermograms of both cultivars displayed profiles with two not well-separated endothermic phase transitions. As shown in Table 4, the temperature of the first major peak of melting (P_m) was -29.2 ºC for Mahan cultivar and -27.4 ºC for Moore cultivar with an onset temperature (T $onset_m$) ranging between -41.7 °C (Mahan) and -37.5 °C (Moore) and an end temperature (T end_m) varying between -26.3 and -24.7 °C for Mahan and Moore, respectively. The temperature of the second P_m was -21.2 ºC for Mahan and -19.4 ºC for Moore with a T $onset_m$ ranging between -26.3 °C (Mahan) and -24.7 °C (Moore) and a T end_m varying between -7.6 °C (Mahan) and -4.5 °C (Moore). Mahan showed the lowest P_m. The non-significant difference in P_m values is attributed to the fact that the Mahan cultivar presents more unsaturated TAGs and fatty acids, and consequently, this leads to the appearance of a lower melting point (Mansor *et al.,* 2012) than that of the Moore cultivar. As explained in the literature, the first peak detected in both samples at a low-temperature region of the heating curve might be linked to the melting of the lowest stability polymorphic form of TAGs (Rezig *et al.,* 2012). The range of transition phase (R) varied between 33 and 34.1 °C for Moore and Mahan, respectively. The melting enthalpy ($\triangle H_m$) varied significantly among cultivars. The Moore cultivar had the highest value (70.2 J/g). The melting behavior of both cultivars revealed identical patterns but different DSC parameter values which confirm that the melting behavior was affected by cultivar. This difference is in concordance with the variation in TAG composition detected between the two cultivars.

Tan and Che Man (2002) investigated the melting behavior of walnut (*Juglans regia*) oil and reported a broad endothermic peak with smaller ones. These peaks were attributed to the melting of the predominant TAGs detected in this oil, namely LLL, LLLn, and OLL. The same authors also studied the melting behavior of hazelnut oil and found a large peak.

The crystallization profiles showed an exothermic phase transition with one well-defined peak for both cultivars. The temperature of the major peak of crystallization (P_c) was -63.3 for Mahan cultivar and

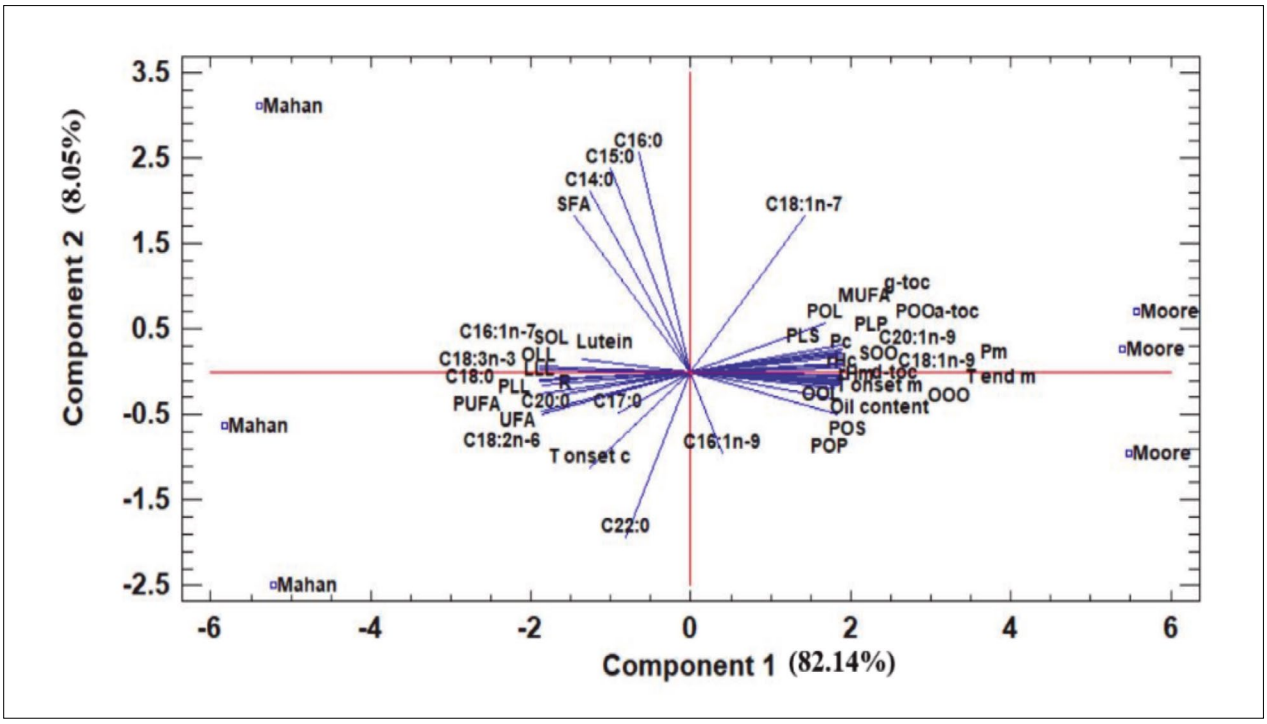

FIGURE 1. Graphical depiction of principal component analysis carried out for Mahan and Moore cultivars.

-58.9 ºC for Moore cultivar (Table 4). As explained previously, here too, the Pc observed for both samples at a low-temperature zone was mainly due to the high contents in OOL, OLL, and OOO, since these unsaturated TAGs are known to crystallize at lower temperatures (Yanty *et al.,* 2013). Both cultivars showed similar values for initial temperature of crystallization (T onset $_c$) (-24.8 – -24.6 ºC). The crystallization enthalpy ($\triangle H_c$) varied significantly among cultivars indicating that the genotype significantly influences the $\triangle H_c$ value.

The crystallization behavior of both cultivars exhibited identical patterns. However, different values for DSC parameters demonstrated that it was linked to cultivar. This significant variability (Table 4) may be explained by the dissimilarity of fatty acid and TAG compositions detected between cultivars.

The crystallization behavior in pecan nut oil differs remarkably from that of walnut oil. Indeed, a wide exothermic peak and two smaller ones were detected in walnut oil with a $\triangle H_c$ value of -57.4 J/g (Che Man and Tan, 2002). The major peak was attributed to the crystallization of the main TAGs found in this oil (Che Man and Tan, 2002).

The differences found in the thermal analysis supply a basic comprehension of the thermodynamic variations linked to the chemical composition. As indicated by the melting and crystallization parameters, the lowering of the transition temperatures is directly related to the high level of unsaturated TAGs present in pecan kernel oil. To our knowledge, no previous studies have investigated the thermal properties of pecan nut oil and hence, it was not possible to compare our findings with prior works.

3.7. Principal component analysis (PCA)

For a deeper investigation of the differences and similarities between the two studied cultivars, a principal component analysis was performed (Figure 1).

According to the PCA results, the first two components explained 90.19% of the total variance with the first one at 82.14% and the second one 8.05% of the total variance.

Moore and Mahan were different, located at the positive and negative sides of component 1. Moore was typified by great levels of oil content, C16:1n-9, C18:1n-9, C18:1n-7, C20:1n-9, MUFA, γ-tocopherol, α-tocopherol, δ-tocopherol, OOO, POO, POL, PLS, POP, POS, SOO, OOL, PLP, and high values for $\triangle H_m$, $\triangle H_c$, P_m, P_c, T end $_m$, T onset $_m$. Mahan was characterized by substantial levels of C14:0,

C15:0, C16:0, C17:0, C18:0, C20:0, C22:0, SFA, C16:1n-7, C18:2n-6, C18:3n-3, PUFA, UFA, SOL, OLL, LLL, PLL, lutein, and high values for T onset $_c$, R.

These findings confirm the great variability in chemical composition and thermal behavior between the two pecan cultivars.

4. CONCLUSIONS

Pecan kernel oil serves as a good source of natural antioxidants and bioactive compounds. The Moore cultivar showed a particular composition with a high level of tocopherols. Mahan was richer in xanthophylls than Moore. Pecan nut oil was found to be rich in TAGs containing oleic and linoleic acids. The pecan nut oil exhibited its main thermal transition at a low-temperature zone. Our DSC data revealed that three parameters, namely $\triangle H_c$ and P_c of the crystallization profile and $\triangle H_m$ of the melting profile are sensitive indicators for distinguishing between cultivars. The genotype appears to affect the chemical composition and thermal properties of pecan kernel oil.

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