

## Chemical characterization and thermal properties of kernel oils from Tunisian peach and nectarine varieties of *Prunus persica*

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**SUMMARY:** A comparative study was conducted to determine the fatty acids, triacylglycerol compositions and thermal properties of Tunisian kernel oils from the *Prunus persica* varieties, peach and nectarine, grown in two areas of Tunisia, Gabes and Morneg. Qualitatively, the fatty acids composition and triacylglycerol species were identical for all samples. Oleic acid (67.7-75.0%) was the main fatty acid, followed by linoleic (15.7-22.1%) and palmitic (5.6-6.3%) acids. The major triacylglycerol species were triolein, OOO (38.4-50.5%), followed by OOL (18.2-23.2%), POO (8.3-9.7%) and OLL (6.3-10.1%). The thermal profiles were highly influenced by the high content of triolein due to the importance of oleic acid in these oils. Moreover, the fatty acids distribution in TAG external positions was determined as corresponding to an  $\alpha$  asymmetry coefficient that was between 0.10 and 0.12, indicating a high asymmetry in the distribution of saturated fatty acids in the position *sn*-1 and *sn*-3 in the TAG species of all samples.

**KEYWORDS:** DSC; Fatty acids; Kernel oils; Nectarine; Peach; *Prunus persica*; Triacylglycerols

**RESUMEN:** *Caracterización química y propiedades térmicas de los aceites de semillas de variedades tunecinas de melocotón y nectarina de Prunus persica.* Se ha realizado un estudio comparativo de aceites tunecinos obtenidos a partir de las semillas de variedades de *Prunus persica*, melocotón y nectarina, cultivadas en dos zonas de Túnez, Gabes y Morneg. Cualitativamente, la composición de ácidos grasos y de especies de triglicéridos fueron idénticas para todas las muestras. El ácido oleico (67,7-75,0%) fue el ácido graso principal, seguido del linoleico (15,7-22,1%) y el palmítico (5,6-6,3%). Las especies principales de triacilglicéridos fueron la trioleína, OOO (38,4-50,5%), seguida de OOL (18,2-23,2%), POO (8,3-9,7%) y OLL (6,3-10,1%). Los perfiles térmicos fueron muy influidos por el alto contenido de trioleína debido a la importancia del ácido oleico en estos aceites. Por otra parte, se determinó la distribución de ácidos grasos en las posiciones externas de los TAG correspondiendo a un coeficiente de asimetría  $\alpha$  entre 0,10 y 0,12, lo que indica una alta asimetría en la distribución de los ácidos grasos saturados en la posición *sn*-1 y *sn*-3 en las especies de los TAG de todas las muestras.

**PALABRAS CLAVE:** Aceites de semilla; Ácidos grasos; DSC; Melocotón; Nectarina; *Prunus persica*; Triacilglicéridos

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## 1. INTRODUCTION

In the last decades, developed countries have been trying to reduce their energetic dependence from fossil fuels and their derivatives. Vegetable oils, due to their chemical nature, have been the focus of a great part of the efforts directed to this purpose. Nevertheless, the main uses of the oleaginous crops produced worldwide (palm, soybean, canola, sunflower, olive, etc...) are limited to edible applications within the food processing industry. Since non-edible uses of these oils (fuel, lubricants or oleo-chemicals) would be problematic and unsustainable, research has been directed toward the use of oils from non-extensively cultivated species or the utilization of unusual sources, such as waste oils or by-products of the food processing industry.

Fruits from genus *Prunus* are qualified as drupes, membranous exocarp with an outer fleshy mesocarp. They are categorized as stone fruits because their seeds are inside a hard stone (Ram and Bhardwaj, 2004). *Prunus persica* is one of the species of the Rosaceae family that is widely distributed in most countries around the world. Peach and nectarine, a peach variety bearing fruits with smooth skin, are the second most important fruit crop in the European Union (EU) (approx. 3.8 million tons) after the apple (FAOSTAT, 2013), and the most important within the genus *Prunus* (Di vaio *et al.*, 2008). The pulp from peaches and nectarines is used directly for jams and canned food or diluted to prepare commercial or domestic juices (Bates *et al.*, 2001). In addition, the leaves of the peach tree are used for the treatment of irritated digestive tract and constipation (Gilani *et al.*, 2000).

The kernel is considered an important food source with a high nutritional value, mostly due to its oil and protein contents (Sabate and Hook, 1996; Socias i Company *et al.*, 2010), but they are usually destined to animal feed or used as fuel (Mezzomo *et al.*, 2009). The kernel has a slightly toxic effect due to its content in hydrogen cyanide, so any excessive human use can cause headache, blurred vision, palpitations, or even death from respiratory failure (Wu *et al.*, 2011). Its nutritional value is due to the high value of unsaturated fatty acids, mostly the monounsaturated fatty acids (MUFA). Several Clinical studies reported that an important consumption of monounsaturated fats in the diet reduce the prospect of cardiovascular diseases (Visioli *et al.*, 2002) by reducing the low density lipoprotein cholesterol levels in the blood (Sorci-Thomas *et al.*, 1989). However, each year, thousands of tons of stones (pericarp plus kernel) from peaches and nectarines are wasted as a by-product of the production of juices and jams.

Most oils and fats are mainly composed of a great variety of triacylglycerol (TAG) species, comprising of 96 to 99% of total lipids. In chemical

terms, TAGs consist of a glycerol molecule esterified to three fatty acids. Therefore, vegetable oils and fats can be further classified according to their fatty acids and TAG species compositions. The analysis of TAG composition is used as reference to characterize oils or fats because they contain structural information, such as the position of the fatty acid (FA) residues on the glycerol backbone. This information is lost in the transesterification reaction which is necessary for FA analysis by GLC (Tan and Che, 2000). Furthermore, oil industrial uses are influenced by the amount of tri-, di- and mono-saturated TAG species (Martinez-Force *et al.*, 2004). For this reason, an asymmetric  $\alpha$  coefficient was developed to explain the stereochemical distribution of fatty acids in the TAG molecule. This method is based on the data obtained from the fatty acid composition of TAG, the profile of TAG species, and the fatty acid content of the *sn*-2 position of TAG (Ruiz-Lopez *et al.*, 2003).

The phytochemical contents of fruits are influenced by numerous factors such as genotype, storage and climatic conditions, agronomic practices, harvesting time and post-harvest conditions (Cantin *et al.*, 2009). In addition, the physical, and nutritional properties of oils are affected by TAG species composition and their stereo-specificity (Ruiz-Lopez *et al.*, 2003). Until now, no one has characterized the oil quality from nectarine fruits, assuming that it is similar to peach in fatty acids and minor components. Due to their fatty acids compositions, peach and nectarine oils can be considered as valuable oils for industrial uses when compared with sunflower and rapeseed oils.

The aim of this work was to establish a comparative study between Tunisian peach and nectarine varieties of *Prunus persica*. A characterization of the physicochemical properties of the kernel oils was made to evaluate their nutritive value and to determine the environmental effect of two different production regions on kernel oil content and composition.

## 2. MATERIALS AND METHODS

### 2.1. Plant material

Peach (P) and nectarine (N) fruits were collected from trees growing wild in two Tunisian regions, Morneg (Mg) and Gabes (Gb), in July 2014. Morneg is located in the area of Ben Arous in the northeast of Tunisia, at 36°44'N latitude and 10°13'E longitude. The altitude above sea level is 12 meters. The station of Gabes is located in the south-east of Tunisia, at 33°52'N latitude and 10°05'E longitude. The altitude sea level is nine meters. From each station, fruits from each variety were collected, the mesocarp and stony endocarp were separated, and the kernels from the endocarps were mixed and

placed in an oven at 60 °C until dried and kept at a constant weight.

The dried samples were reduced in powder using a manual mortar. The oils were extracted by a Soxhlet apparatus for four hours using petroleum ether as solvent. This was evaporated under reduced pressure, using a rotary evaporator at 50 °C. The obtained oil was dried with a stream of nitrogen, weighed and stored in dark glass bottles at 4 °C until analysis. Samples from each crop were taken in triplicate.

## 2.2. Lipids analysis

The lipid fractions were determined by dissolving 6 mg of oil in 500 µL of chloroform. The resulting solution was fractionated in a Lichrolut 0.5 g silica gel cartridge (Merck) using a vacuum manifold and then equilibrated with 2 mL of chloroform (Nash and Frankel, 1986). The solution of total lipids was loaded onto the column which was then washed with another 15 mL of chloroform to elute neutral lipids from the column. Subsequently, the column was washed with 10 mL of methanol to recover the polar lipids quantitatively.

The fatty acids composition was determined by derivatizing 6 mg of the oil fractions to their corresponding fatty acid methyl esters for 1 h at 80 °C with 2 mL methanol/toluene/sulphuric acid (85/15/2.5, v/v/v) (Garcés and Mancha, 1993). Fatty acid methyl esters were extracted with 2 mL heptane and analyzed by gas chromatography (GC) on an Agilent 6890 gas chromatography system (Palo Alto, CA) according to the method used by Bootello *et al.* (2016).

The analysis of TAGs of the different oil fractions was carried out by injecting 1 µL aliquots of 5 mg of oil dissolved in 1.8 mL of heptane into an Agilent 7890 gas chromatograph (Palo Alto, CA) using the same chromatographic conditions as reported by Bootello *et al.* (2016).

For the positional analysis of TAG *sn*-2 fatty acids, 10 mg of purified TAGs were hydrolyzed with 2 mg of pancreatic lipase in 1 mL of a 1 M Tris-HCl buffer (pH8), 0.1 mL CaCl<sub>2</sub> (22%), and 0.25 mL deoxycholate (0.1%). The reaction was stopped when approximately 60% of the TAGs were hydrolyzed (1–2 min) by adding 0.5 mL of 6 N HCl. The lipids were extracted three times with 1.5-mL aliquots of ethyl ether, and the reaction products were separated by TLC. Free fatty acids and *sn*-2-monoacylglycerol bands representing the positions *sn*-1,3 and *sn*-2 of TAGs were scraped off the plate, trans-methylated and analyzed by GC. The validity of the procedure was confirmed by comparing the fatty acids composition of the original TAGs and those remaining after the partial hydrolysis. The distribution of saturated fatty acids between the *sn*-1 and *sn*-3 external positions of TAGs was calculated using the

coefficient of asymmetry  $\alpha$  as the quotient between subclasses Saturated-Unsaturated-Saturated and Saturated-Unsaturated-Unsaturated ( $\alpha$  SUS/SUU) (Martínez-Force *et al.*, 2009). Thus,  $\alpha$  can range between 0 and 0.5;  $\alpha = 0.5$  indicates a symmetrical distribution of saturated fatty acids in accordance with the Vander Wal theory (Vander Wal, 1960).

## 2.3. Calorimetric analysis by DSC

The melting and crystallization profiles of the different oils were determined by differential scanning calorimetry (DSC) using a Q2000 V23.5 scanner (TA instruments, New Castle, DE, USA). The results were processed using the TA analysis software provided by the manufacturer. This instrument was calibrated prior to use with indium, azobenzene, and undecane, purchased from Sigma-Aldrich (Madrid, Spain). Nitrogen was used to purge the system. Samples were prepared by pipetting 6–8 mg of the oils into aluminium pans, and weighing them using a Sartorius M2P electronic microbalance (Sartorius AG, Goettingen, Germany). The pans were then sealed and balanced calorimetrically, using an empty sealed capsule as the reference. The melting profile of the oils was determined by heating the samples at 90 °C and holding for 5 min (in order to delete the thermal memory), then cooling to -80 °C at a rate of 10 °C/min and holding for 20 min. Finally, a ramp of 5° C/min up to 90 °C was applied to obtain data from the melting thermogram. The crystallization profile was obtained by completely melting the oils at 90 °C for 5 min, and decreasing the temperature to -80 °C at a rate of 10 °C/min.

## 3. RESULTS AND DISCUSSION

### 3.1. Oil Content

The study of the oil content (% dry weight) of the two varieties of *P. persica* in the two locations, Morneg (Mg) and Gabes (Gb), revealed slight differences between the samples. Depending on their growth location, an oil content ranging from 51.4±0.2% for nectarine to 53.7±0.3% for peach was found in the Mg cultivar; and 49.4±0.1% and 50.5±0.3%, respectively, in the Gb cultivar. In both locations, the peach kernels exhibited the highest levels of oil content. As shown in Table 1, these results are within the values previously reported in the literature for the oil content of peach and nectarine dried kernels, ranging from 42.2% in Canadian fruits (Kamel and Kakuda, 1992) to 54.5% in Egyptian fruits (Rahma and Abd El-Aal, 1988). Furthermore, the oil contents were comparable with those of other oil crops of commercial interest, such as sunflower and rapeseed. The silica column fractionation of kernel oils from both *P. Persica* varieties showed that more than 98% of total lipids were

TABLE 1. Oil contents (%) and fatty acids compositions (mol%) of peach and nectarine kernels harvested in different countries described previously in the literature

	Oil (%)		Fatty acids composition (mol%)								Country											
			16:0	16:1	18:0	18:1	18:1A	18:2	18:3	20:0												
Peach	54.5	a	13.4	0.2	6.4	63.8		15.4			Egypt											
	48	b	6.3	0.4	1.7	69.0		22.0	0.1	0.1	Greece											
	42.2	c	8.1	0.4		58.5		32.8		0.3	Canada											
	43	d	4.6	0.6	1.3	64.5	1.4	27.3	0.1	0.1		Egypt										
													e	6.1		1.8	32.5		59.8			Russia
	50.4	g	6.0	0.5	2.1	74.6		15.7	0.1	0.2	Spain											
												g	6.2	0.6	2.1	72.2		18.1	0.1	0.2	Spain	
	44	h	6.2	0.3	2.4	70.5		20.5	0.0	0.2	Brazil											
												i	8.4	0.3	1.2	41.1		48.4	0.3	0.2	Brazil	
																						j
	39.5	k	5.9			57.5		25.4		6.2	Turkey											
Nectarine	43.8	c	6.1	0.5		66.3		26.8		0.3	Canada											
												e	6.1		4.5	38.6		50.6			Russia	

a, Rahma and Abd El-Aal (1988); b, Lazos (1991); c, Kamel and Kakuda (1992); d, Hassanein (1999); e, Deineka *et al.* (2002); f, Matthäus and Özcan (2009); g, Sánchez-Vicente *et al.* (2009); h, Mezzomo *et al.* (2010); i, Pelentir *et al.* (2011); j, Wu *et al.* (2011) and k, Özcan *et al.* (2015).

in the form of neutral lipids and only a very small amount corresponded to the polar fraction.

### 3.2. Fatty acids composition

The fatty acids profile, total saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) of nectarine and peach kernel oils can be found in Table 2. Six fatty acid species were identified in all the samples. Qualitatively, the fatty acids compositions in both varieties and provenances were similar. Both kernel oils are characterized by the predominance of MUFA, reaching its highest level (76.6%) for those grown in Mg. Oleic acid was the major FA in all the samples, accounting for 67.7% (N Gb) to 75.0% (N Mg), followed by linoleic acid and saturated fatty acids (palmitic and stearic). Thus, the location of cultivars influenced the fatty acids profile of *P. persica* kernel: nectarine and peach kernel oils from Mg contained more oleic acid than kernel oils from Gb. By contrast, higher levels of linoleic acid and palmitic acid were found for nectarine and peach from the Gb station.

In fact, these samples of kernel oils showed levels of oleic acid similar to high oleic sunflower oil (87.2%). Thus, *P. persica* kernel oils can be considered as high oleic oils. These results are in agreement with those reported in the literature (Table 1) such as Spanish *P. persica* kernels that showed a high content of oleic acid (74.6%), followed by linoleic acid (15.7%), and palmitic acid (6.0%) (Sánchez-Vicente *et al.*, 2009).

### 3.3. Triacylglycerol species composition

The analysis of the TAG composition showed variability according to the species and locations of the studied cultivars (Table 3). Fourteen molecular species of TAG were detected, with the predominant ones being those containing oleic, linoleic and palmitic acids. The results showed that OOO (triolein) was the main TAG species, followed by OOL, POO, OLL and POL in all *P. persica* kernel oils. Regarding the influence of the provenance, Table 3 shows that the nectarine oils grown in Mg exhibited the highest value of OOO and POO, according to the increasing oleic acid levels. When comparing both *P. persica* varieties, peaches vs nectarines, it was found that in the Mg location the peach kernel oil showed the highest content of TAGs species OOL, POO, OLL and POL compared to nectarine, which showed only an increase in OOO. For the Gb location, smaller differences were detected due to the very similar fatty acid compositions of their oils (Table 2). As observed in Table 3, *P. persica* kernel oils presented some similarities with high oleic sunflower oil, being OOO (69.2%) and POO (9.2%) the main TAG species. The TAG compositions of the *P. persica* oils were also similar to some rosaceae kernel oils, such as apricot (*P. armeniaca*), plum (*P. domestica*) and peach (*P. persica*) (Hassanein, 1999), which showed average contents of OOO (40.7%) and OOL (24.8%) as the major TAGs components.

The contents of the TAG subclasses di-saturated (SUS), mono-saturated (SUU), and tri-unsaturated (UUU) were obtained from the compositions of the

TABLE 2. Oil contents and fatty acid compositions of *Prunus persica* kernel oils from different varieties, nectarine and peach, grown in two locations (Morneg, Mg, and Gabes, Gb) and high oleic sunflower oil (HOSO). Data are the mean of independent samples with SD lower than 3% of the mean value

	Nectarine		Peach		HOSO
	Mg	Gb	Mg	Gb	
Oil content (% DW)	51.4	49.4	53.7	50.5	
Fatty acids (% w/w)					
16:0	5.7	6.3	5.6	6.1	4.0
16:1	0.4	0.4	0.4	0.4	0.0
18:0	2.0	2.0	1.9	1.9	3.8
18:1	75.0	67.7	73.6	69.3	87.2
18:1a	1.2	1.4	2.4	1.7	0.0
18:2	15.7	22.1	16.0	20.5	3.4
20:0	0.0	0.0	0.0	0.0	0.4
22:0	0.0	0.0	0.0	0.0	1.2
ΣSFA	7.7	8.3	7.5	8.0	9.4
ΣMUFA	76.6	69.5	76.5	71.4	87.2
ΣPUFA	15.7	22.1	16.0	20.5	3.4

DW, Dry weight; 16:0, palmitic acid; 16:1, palmitoleic acid; 18:0, stearic acid; 18:1, oleic acid; 18:1a, asclepic acid; 18:2, linoleic acid; 20:0 arachidic acid; 22:0 behenic acid. SFA, Saturated, MUFA, Monounsaturated, and PUFA, Polyunsaturated fatty acids.

TAG species and the coefficient  $\alpha$  (Martínez-Force *et al.*, 2009) was used to calculate the asymmetry of saturated fatty acids between the *sn*-1 and *sn*-3 TAG positions (Table 3). The coefficient  $\alpha$  varied between 0.10 and 0.12 (P Mg and N Mg, respectively) and between 10 and 12% saturated fatty acids were found in one external position and between 88 and 90% in the other position. This asymmetry is due to the enzymatic machinery responsible for the esterification of saturated fatty acids in the external positions, mainly glycerol-3-P acyltransferase and diacylglycerol acyltransferase. These results are similar to those reported for hazelnut and walnut oils, which exhibited low  $\alpha$  coefficients (0.17 and 0.04, respectively) and, therefore present a high asymmetry in their saturated fatty acids. However, the studied *P. persica* oils were quite different from soybean, high-stearic sunflower or rice which showed a higher  $\alpha$  coefficient value (0.29, 0.33, and 0.49, respectively), corresponding to more symmetrical distributions of saturated fatty acids in their TAG species (Martínez-Force *et al.*, 2004). The distribution of fatty acids in the three positions of TAG molecules has been studied in *P. persica* oils in the two locations (Table 4). These results confirmed that saturated fatty acid (palmitic and stearic acid) were mainly distributed in the external position (*sn*-1,3) of the TAG backbone; whereas the *sn*-2 position mostly contained unsaturated fatty acids, of which more than 80% corresponding to oleic acid. These data, together with the low values of  $\alpha$  coefficients can explain the strong asymmetrical distribution of

the fatty acids, and hence, the absence of di-saturated species of TAGs (SUS) in these oils. Therefore, *Prunus persica* oils are composed exclusively of TAG species with two or more unsaturated fatty acids in their molecules (SUU and UUU), something that would be reflected in their thermal properties.

### 3.4. Calorimetric analysis by DSC

The DSC thermograms of *P. persica* kernel oils can be found in Figure 1: heating curves or melting profiles (Figure 1A) and cooling curves or crystallization profiles (Figure 1B). In addition, Table 5 provides thermal parameters obtained from the thermograms depicted in Figure 1. Heating curves from -80 to 80 °C showed the melting profiles with an endothermic phase transition with a single and well-defined peak. The melting peaks in the DSC thermograms corresponding to *P. Persica* kernel oils exhibited an onset temperature with values between -46.9 to -33.6 °C for the nectarine Gb and peach Gb varieties, respectively. High oleic sunflower oil started to melt at higher temperature (-21.5 °C). The melting temperature for the peak ( $P_m$ ) showed values from -14.0 °C (nectarine Gb) to -9.4 °C (high oleic sunflower oil). For the temperature of end melting, it showed values ranging between -3.3 and 4.7 °C for the P Gb and N Mg varieties, respectively. Again, high oleic sunflower exhibited a higher temperature for end melting (5.2 °C). In general, it can be observed that for varieties with higher PUFA contents, lower melting temperatures were obtained.

TABLE 3. TAG species compositions (mol%) of *Prunus persica* kernel oils from different varieties, nectarine and peach, grown in two locations (Morneg, Mg, and Gabes, Gb) and high oleic sunflower oil (HOSO). Data are the mean of independent samples with SD lower than 3% of the mean value

	Nectarine		Peach		HOSO
	Mg	Gb	Mg	Gb	
POSt	0.0	0.0	0.0	0.0	0.5
POO	9.0	8.3	9.7	8.3	9.2
POL	5.5	8.4	6.5	7.9	0.7
PLL	1.2	2.1	1.4	2.0	0.0
StOO	3.5	2.7	3.5	2.9	8.9
OOO	50.5	38.4	47.3	39.6	69.2
StOL	2.8	3.5	2.9	3.0	1.8
OOL	18.2	22.3	19.8	23.2	3.8
StLL	1.5	2.3	1.3	1.4	0.0
OLL	6.3	10.1	6.7	9.7	0.9
LLL	1.5	1.7	0.9	1.9	0.3
StOA	0.0	0.0	0.0	0.0	0.4
OOA	0.0	0.0	0.0	0.0	1.4
OLA	0.0	0.0	0.0	0.0	0.5
OOB	0.0	0.0	0.0	0.0	2.4
SUS	0.0	0.0	0.0	0.0	0.9
SUU	23.6	27.4	25.3	25.6	24.9
UUU	76.4	72.6	74.7	74.7	74.2
$\alpha$ Sat	0.12	0.11	0.10	0.11	0.11

TAG were named with 3 letters. P, palmitic acid; O, oleic acid; St, stearic acid; L, linoleic acid; A, arachidic acid; and B, behenic acid. SSS, sum of trisaturated TAG; SUS, disaturated TAG; SUU, monosaturated TAG; and UUU, triunsaturated TAG. Peaks accounting for less than 0.3 % of total triacylglycerols were not integrated.

TABLE 4. Fatty acids compositions in TAG *sn*-1,3 and *sn*-2 positions (mol%) of *Prunus persica* kernel oils from different varieties, nectarine (N) and peach (P), grown in two locations (Morneg, Mg, and Gabes, Gb). Data are the mean of independent samples with SD lower than 3% of the mean value

		Fatty acids composition					
		16:0	16:1	18:0	18:1	18:1a	18:2
N Mg	<i>sn</i> -1,3	8.1	0.6	2.4	69.5	1.5	18.0
	<i>sn</i> -2	1.0	0.0	1.2	86.1	0.6	11.1
N Gb	<i>sn</i> -1,3	9.1	0.6	2.7	57.8	1.6	28.0
	<i>sn</i> -2	0.6	0.0	0.6	87.5	0.9	10.3
P Mg	<i>sn</i> -1,3	8.0	0.6	2.4	69.8	3.3	15.7
	<i>sn</i> -2	0.8	0.0	0.8	81.2	0.7	16.6
P Gb	<i>sn</i> -1,3	8.9	0.6	2.7	63.1	2.1	22.5
	<i>sn</i> -2	10.5	0.0	4.0	77.2	1.4	7.0

16:0, palmitic acid; 16:1, palmitic oleic acid; 18:0, stearic acid; 18:1 $\Delta$ 9, oleic acid; 18:1 $\Delta$ 11, asclepic acid; 18:2, linoleic acid.

The range of transition phase (R) for the melting curves (temperature difference between  $T_{\text{onset m}}$  and  $T_{\text{end m}}$ ) was higher for kernel oils compared to high oleic sunflower oil. Kernel oils contained higher amounts of the tri-unsaturated TAG species OOL and LLL, and of the mono-saturated TAG species

POL and PLL. Since these TAGs species exhibit lower melting points than other mono-saturated (StOO, OOA and OOB) and di-saturated (POSt and StOA) TAGs species, only present in high oleic sunflower oil, the melting range of kernel oil was lower. Regarding the melting enthalpy, kernel oils showed

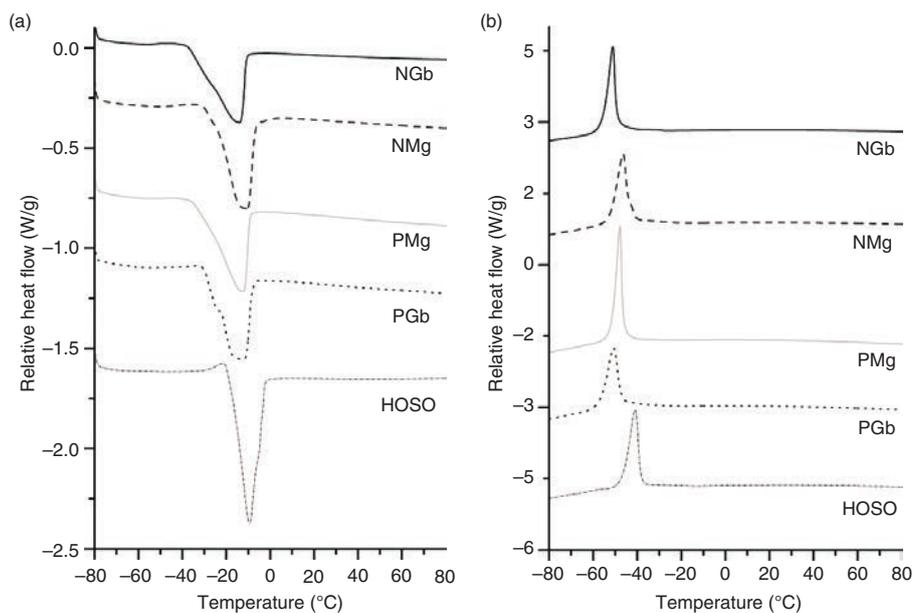


FIGURE 1. DSC thermograms of *Prunus persica* kernel oils from different varieties (Nectarine, N, and Peach, P) grown in two locations (Morneg, Mg, and Gabes, Gb) and high oleic sunflower oil (HOSO): (a) melting curves, and (b) crystallization curves

TABLE 5. DSC parameters obtained from the thermograms for *Prunus persica* kernel oils from different varieties, nectarine and peach, grown in two locations (Morneg, Mg, and Gabes, Gb) and high oleic sunflower oil (HOSO). Data are the mean of independent samples with SD lower than 3% of the mean value

	Nectarine		Peach		HOSO
	Mg	Gb	Mg	Gb	
Melting Curves:					
$\Delta H_m$ (J/g)	77.0	65.6	69.1	70.4	85.3
$P_m$ (°C)	-11.5	-14.0	-12.2	-12.1	-9.4
$T_{onset_m}$ (°C)	-35.9	-46.9	-43.7	-33.6	-21.5
$T_{end_m}$ (°C)	4.7	-2.9	0.3	-3.3	5.2
R (°C)	31.3	44.0	43.4	30.3	16.3
Crystallization Curves:					
$\Delta H_c$ (J/g)	63.7	59.2	62.6	57.0	60.5
$P_c$ (°C)	-46.2	-51.1	-47.9	-50.7	-41.0
$T_{onset_c}$ (°C)	-26.2	-29.5	-30.2	-29.5	-16.8
$T_{end_c}$ (°C)	-60.0	-64.0	-60.2	-64.2	-58.5
R (°C)	33.8	34.5	30.0	34.7	41.7

$\Delta H_m$ : 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,  $\Delta H_c$ : crystallization enthalpy,  $P_c$ : temperature of the major peak of crystallization,  $T_{onset_c}$  and  $T_{end_c}$ : initial and end temperature of the crystallization phase, R: range of the transition phase (temperature difference between  $T_{onset}$  and  $T_{end}$ ).

lower values compared to high oleic sunflower oil. As reported in the literature, lower melting enthalpy values indicate weaker crystalline structures. Thus, less energy would have to be absorbed to destroy the crystal network (Willie and Luton, 1966).

Cooling curves from 80 to -80 °C, showed the crystallization profiles corresponding to an exothermic event with a single and well-defined peak for both kernel and sunflower oils. For kernel oils, the crystallization peak in the DSC thermograms showed

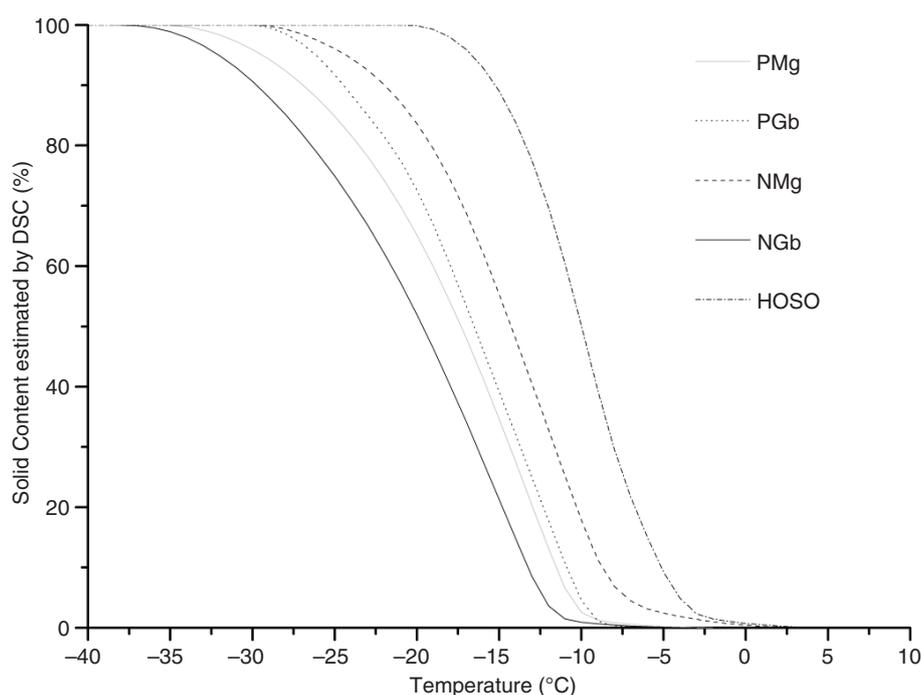


FIGURE 2. Solid contents estimated by DSC of *Prunus persica* kernel oils from different varieties (Nectarine, N, and Peach, P) grown in two locations (Morneg, Mg, and Gabes, Gb) and high oleic sunflower oil (HOSO)

an initial temperature of crystallization ( $T_{\text{onset c}}$ ) with values from  $-30.2$  to  $-26.2$  °C, whereas the peak for temperature crystallization ( $P_c$ ) reached values between  $-51.1$  and  $-46.2$  °C. High oleic sunflower oil exhibited higher values for  $T_{\text{onset c}}$  ( $-16.8$  °C) and  $P_c$  ( $-41$  °C). These differences for peak maximum and crystallization temperature ranges may be attributed to the higher levels of long chain saturated fatty acids (arachidic and behenic acids) and the SUS type TAGs present in high oleic sunflower oil. These di-saturated TAGs species crystallize at temperatures slightly higher than SUU and UUU TAGs, so for high oleic sunflower oil the crystallization took place at a higher interval of temperature than in kernel oils. The estimation of solid content (Figure 2) was calculated by integration of the melting thermograms using the analysis software provided by the DSC manufacturer. High oleic sunflower oil displayed a higher solid content and a sharper curve compared to kernel oils. So, at  $-20$  °C, kernel oils containing less OOO, displayed lower contents of solids (about 55% and 70% of solid content for N Gb and P Mg, respectively), whereas high oleic sunflower oil was 100% solid at that temperature. At  $-10$  °C, all kernel oils were melted except for N Mg, whose solid content was close to 20%. The kernel oil with the highest OOO content was N Mg, and was completely melted around  $0$  °C (similar to high oleic sunflower oil).

In summary, the melting and crystallization behavior of both *P. persica* varieties from different locations showed similar shapes with a unique peak

and DSC parameters with different values depending on the variety and provenance (Table 5). The small variations observed in the DSC profiles are in good agreement with the changes in TAG species found between varieties and locations (Table 3). Although the major peak observed for all samples was mainly due to the triolein content, the higher levels of linoleic acid present in the *P. persica* kernel oils also contributed to modifying their thermal behaviour compared with high oleic sunflower oil.

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