Triacylglycerols Profiles Established by UHPLC-ESI-MS in Developing Sweet, Semi-sweet and Bitter Seeds from Tunisian Oilseeds Apricot (Prunus armeniaca L.)

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Abstract: The aim of the present research is to investigate the effect of three harvest date on the composition of apricot seed. Indeed, triacylglycerols (TAGs) content and composition were studied in developing Tunisian apricot varieties bitter (Bargoug), semi-sweet (Oud Rhayem) and sweet (Chechi Bazza) cultivars at intervals of early (14 DAP), mid phase (28 DAP) and full phase (55 DAP) of oil accumulation by UHPLC-ESI-MS method. Eleven molecular species of triacylglycerols were detected and identified as LLL, LLO, LLP, LOO, LLS/LOP, LPP, OOO, LOS, OOP, POP and OOS. At 14 DAP, LLO was the major TAGs molecular species with 35.4-52.6% (maximum reached in semi-sweet apricot). Others major TAGs were founded at lower content as LOO (17.5-40.3%) and OOO (5.7-12.7%). However, among maturity, three distinct profiles of TAGs molecular species were observed: bitter apricot was significantly richer in OOO molecular species than cultivars one. However, semi-sweet and sweet cultivars were richer in LLO and LOO molecular species at different time-dates. These latter may provide a schedule for harvesting Tunisian apricot seeds with high quality of oil content.

Key words: wild apricot, cultivars apricot, UHPLC-ESI-MS, triacylglycerols, developing oilseeds

1 Introduction

Prunus L. (family Rosaceae; subfamily Prunoideae) consists of eight major species11. Among them, P. armeniaca L., commonly known as “apricot”. Its synonymous latin name is Armeniaca vulgaris L. supposedly originating from Armenia, where it has long been cultivated. The apricot tree is widely distributed across the five continents. Its gene centers originate in Turkey and it is cultivated for fresh or processed fruit consumption11.

Apricot is also a multipurpose tree species with ecological and economic value. It has a strong adaptation to stress that can be cultivated on marginal land12.

In Tunisia, apricot is a traditional fruit species, cultivated in various areas and adapted to different climates and soils. Two major apricot propagation strategies coexist, i.e. the asexual propagation by grafting from cultivars (semi-sweet and sweet apricot) and the sexual propagation by seeds from wild species or bitter apricot “Bargoug”33. The local apricot cultivars are only found in traditional plantations and are unknown outside of their area of origin, especially the cultivars of Testour (Northern Tunisia) namely “Chechi Bazza” designed as sweet apricot and “Oud Rhayem” or

Abbreviations: AprB: Apricot “Bargoug” (wild or bitter), AprC: Apricot “Chechi Bazza” (cultivar or sweet), AprO: Apricot “Oud Rhayem” (cultivar or semi-sweet), DAP: days after podding, EIC: extracted ion chromatogram, ESI-MS: electrospray-mass spectrometry, IS: immature stage (14 DAP), MMS: middle maturity stage (28 DAP), MS: full maturity stage (55 DAP), HPLC–MS: High pressure liquid chromatography–mass spectrometry, TAG: triacylglycerols, 1-linoleoyl-2,3-dioleyl (LOO), 1,2-dilinoleoyl-3-oleyl (LLO), 1,2,3-trioleyl (OOO), 1,2,3-trilinoleoyl (LLL), 1,2-dioleyl-3-palmitoyl (OOP), 1-palmitoyl-2-oleoyl-3-linoleoyl (POL), 1,2-dilinoleoyl-3-palmitoyl (LLP), 1,2-dioleyl-3-stearoyl (OOS), 1,2,3-trimyristoyl (MMM)

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semi-sweet apricot kernels\textsuperscript{3}). However, the wild "Bargougs", are an integral part of the oasis crop\textsuperscript{12}. Otherwise, authors\textsuperscript{3} have demonstrated by amplified fragment length polymorphism (AFLP), some molecular markers linked with climatic conditions and modes of cultivation that could impact considerably on the genetic variability of the apricot species in Tunisia. By the way, it has been proved that Tunisian cultivars "Oud Rhayem and Chechi Bazza" and wild "Bargougs" apricots are genetically different\textsuperscript{5, 4}. Moreover, many genetic variations were observed among semi-sweet and sweet cultivars on the same plantation\textsuperscript{5}. Bitter apricots are known to contain cyanogenic compounds such as amygdaline. Recently, many authors claim that amygdaline plays a supporting role in the treatment of atherosclerosis, immune suppression, diabetes and other diseases\textsuperscript{5}. Furthermore, amygdaline has been marketed as a cancer treatment (as "Laetril") with some clinical evidence for its efficacy\textsuperscript{5}.

Moreover, the seed of apricot was high in oil content (over 50\%)\textsuperscript{16} and has been to play an important role in human nutrition and health\textsuperscript{12}. Apricot oil is rich in mono- and polyunsaturated fatty acids such as oleic and linoleic acids as major constituents with presence of minor bioactive components, like tocopherols and phenolic compounds\textsuperscript{12}. Fatty acids and triacylglycerols composition are considered as prominent attributes in oil crops. However, fatty acids and triacylglycerols (TAGs) change in developing seeds\textsuperscript{23}. Therefore, the overall process to synthesize accumulating TAGs, ultimately in seed lipid droplets, begins with the de novo synthesis of fatty acids in plastids\textsuperscript{23}. After seven basic cycles 2 carbon additions in the Kennedy pathway, palmitylACP is produced which can be hydrolyzed to release palmitic acid or elongated using β-ketoacylACP synthase II(KAS II) to give stearoylACP. A very active \textit{Δ}\textsubscript{9} desaturase in plastids ensures that most plants produce a mixture of palmitic and oleic acids (in about a 1:4 ratio) as end products of de novo synthesis. Furthermore, diacetylglcerol acyltransferase (DGAT) enzyme is an important regulatory enzyme in TAGs synthesis. The over-expression of DGAT was shown to increase TAGs accumulation\textsuperscript{18}.

Moreover, edible oils triacylglycerols (TAGs) are usually used to evaluate the antioxidant or prooxidant activities of synthetic and natural antioxidants\textsuperscript{20}. In fact, Karabulut et al.\textsuperscript{20}, showed that the presence of antioxidants components in butter oils inhibits strongly lipid peroxidation and effectively protects TAGs profile.

Few researches on apricot kernel oil had been made and devoted to the analysis of apricot oils originating especially from Egypt, by thin-layer chromatography or TLC\textsuperscript{13}, or HPLC\textsuperscript{15} and from Turkey by RP-HPLC\textsuperscript{14}. To the best of our knowledge, TAG profiles of Tunisian apricot oils have never been investigated and this is the first report among maturity.

This present study aims to investigate TAGs profiles in three genetically different varieties of apricots grown in Tunisia by UHPLC with ESI-MS detection.

2 Materials and Methods

2.1 Chemicals

Methanol and \textit{n}-hexane, solvents for HPLC grade, were purchased from Pancreas Quimica SA (Barcelona, Spain), chloroform and petroleum ether is from Fisher Scientific SA (Loughborough, Spain). Ethanol was purchased from Scientific Limited (Northampton, UK), butan-1-ol (BuOH) and acetone (AcMe) from Merck (Darmstadt, Germany) and AgNO\textsubscript{3} from Sigma Aldrich (St Quentin Fallavier, France).

2.2 Samples and TAGs

\textit{Prunus armeniaca} L. seeds were collected in three stages of maturity (Immature stage; IS or 14 days after podding; DAP), mid phase (MMS or 28 DAP) and full phase (MS or 55 DAP) from April to June 2015 in two Tunisian regions (Testour and Gafsa). Three varieties of apricot (\textit{Prunus armeniaca}, \textit{L}) were analyzed. Two cultivated varieties of apricot or grafted cultivars "Chechi Bazza" (Apr C; sweet kernel) and "Oud Rhayem" (Apr O; semi-sweet apricot) originating from the Northern region of Tunisia (Testour), cultivated in 5 ha area (130 × 300 m). The Testour station is a small town located in the north of Tunisia and characterized by a typical Mediterranean climate with hot, dry summers and mild, wet winters. Tastour "Tastür" has a latitude of 36°32'59.64"N and a longitude of 9°26'32.16"E and is also located from 71.9 km WSW of Tunisia capital Tunis.

The third variety was a wild variety or a seed-propagated apricot "Bargougs" (Apr B; bitter kernel), originating from Gafsa oasis and cultivated in 2 ha area (40 × 40m). The "Bargougs" oasis population was genetically unknown and consequently had not been studied\textsuperscript{9}. The Gafsa oasis station is located in the South-West of Tunisia. Gafsa, the capital of the Gafsa province, has a latitude of 34°25'0"N and a longitude of 8°46'60"E and is also located from 294.3 km SSW of Tunisia capital Tunis. Gafsa has two different climates and is dominated by hot desert climates. Each sample was collected at three stages of maturity. There for, we focused our study on early stage (14 days after podding, DAP), mid (28 DAP) and late (55 DAP) phases of triacylglycerols accumulation in oilseed apricot.

2.3 Oil extraction

The total lipids were extracted by Bligh and Dyer method\textsuperscript{14}. Seeds (2.5 g) were washed with boiling water for 5 min to denature the phospholipases\textsuperscript{10} and then crushed in a mortar with a mixture of chloroform-methanol (2:1, v/v). The fixing water was added and the mixture was centri-
fuged at 3000 g for 15 min. The lower chloroform phase containing the total lipids was kept and dried under a stream of nitrogen.

2.4 Triacylglycerols analysis

2.4.1 Sample preparation

Oil samples were prepared on acetone to a concentration of 1.0 mg/mL. Standard solutions (LLL, PPLn, PLP, OLL, OOL, OOO and OSO) were also prepared on acetone at increasing concentrations (0.001, 0.010, 0.02, 0.05, 0.200 and 0.400 mg/mL). Samples and standards were than diluted (1/1, v/v) in the internal standard MMM (0.4 mg/mL) before injection of 1 or 5 µL into the chromatograph, as a function of the used detection mode\(^{18}\) (Ben Araf \textit{et al.}, 2017). For TAGs quantification, we used seven TAGs including LLL, PPLn, OLL, PLP, OOL, OOO and OSO; and we used MMM as internal standard. The acyl-homogeneous TAGs LLL, OOO, and MMM were purchased from Chuzeau (Sainte Foy la Grande, France), while the other ones came from Larodan (Malmo, Sweden). The purities of all TAGs are equal or higher than 99%.

2.4.2 UHPLC–ESI-MS

For UHPLC-ESI-MS, method validated by Cherif\(^{17}\) and Hmida\(^{18}\), we used an Ultimate 3000 UHPLC system (ThermoScientific, Courtaboeuf, France) for pumping the mobile phase connected (T connector) to a Varian 9010 (Aglient Technology, Santa Clara, CA, USA) pump for post-column AgNO\(_3\) delivery. As stationary phase, we used an ACQUITY UPLC HSS C18 column (100 × 2.1 mm, 18 µm) (Waters, St-Quentin-en-Yvelines, France). The mobile phase was a mixture of acetonitrile/butanol/1.0 mg/mL. Standard solutions of 0.25 mL/min 25 °C, the injection volume was 1 µL of standard or oil sample. In order to increase the sensitivity, 0.1-M AgNO\(_3\) methanolic solution was delivered at a flow rate of 0.15 mL/min into the LC effluent as described previously\(^{17-19}\).

For MS detection, the effluent was entirely directed to the H-ESI ion source of an Orbitrap Exact Mass spectrometer (Thermo Scientific, Courtaboeuf, France). Data acquisition and processing were performed using the X calibur data system (Woburn, MA, USA). The spray voltage was set at 5.5 kV, and the capillary temperature was 250 °C. The capillary voltage was 82 V, and the tube lens voltage was 190 V. Nitrogen was used both as sheath gas and as auxiliary gas at a flow rate of 5 and 5 (arbitrary units), respectively. The ESI source was in positive mode, and the mass range was set at 545-1250 amu. For high collision dissociation (HCD) analysis, collision energy was set at 53 eV.

2.5 Statistical analysis

Each oil sample was injected six times. Extracted ion chromatogram (XIC) of the parent ions, extracted from MS data were used to quantify TAGs. Mean values of the peak area percentages as well as standard deviations were calculated for each TAG. The differences between the means and medians composition of triacylglycerols and their components were measured using the Student (T) and Wilcoxon tests. All the statistical analysis was performed with the R software for statistical computing version 2.10\(^{20}\). Tests were deemed to be significant when \(p\)-value was ≤ 0.05.

3 Results and Discussion

3.1 Identification of TAGs by ESI-MS

The fatty acid composition can be used to evaluate the stability and nutritional qualities of fats and oils; however, in order to appreciate their physical and functional properties, determination of the type and amounts of TAG species existing in the oil is also important\(^{13}\). Indeed, recent studies tend to use the TAG profiles directly as important compositional markers in order to determine oils matrices and to solve authentic problems\(^{19}\). Actually, little information concerns the molecular species composition of TAGs in apricot oil and especially in the wild ones (bitter). In fact, Abd El Acel \textit{et al.}\(^{11}\) reported the fractionation of triglycerides by silicic acid silver nitrate thin layer chromatography (TLC) and revealed the presence of six parts on the chromatogram without any precision. Moreover, the separation and the identification of TAGs from vegetable oils seem to be a difficult task due to the presence of numerous TAGs species with similar physicochemical properties\(^{17}\). Indeed, Turan \textit{et al.}\(^{17}\), reported the identification of 6 TAGs in Turkish apricot oils by HPLC. Moreover, Hassanein\(^{13}\), also reported the presence of 11 TAGs in Egyptian apricot oils by RP-HPLC.

Interestingly, in our present work, TAGs were fully separated and identified by UHPLC-ESI-MS with silver cationization\(^{19}\). In order to improve the sensitivity and to assess TAGs present at trace levels, we used a previously described silver cationization technique coupled to ESI-MS detection\(^{17-19}\).

By this method and for each chromatographic peak, individual TAGs were identified on the basis of their positive ion ESI mass spectra by using the \(m/z\) ratios of the (TAG + Ag\(^+\)) and (TAG + Ag + AgNO\(_3\)) \(^+\) adducts for their molecular weight determination. Our previous biochemical experiments\(^{17-19}\) reported that silver addition has the advantage of improving the sensitivity of the detection\(^{17-19}\).

Figure 1 shows a typical TAG chromatogram extracted from bitter apricot (\textit{Bargouga}) at immature stage (IS) or 14 DAP. The identified TAGs species, their retention times and the mass of their TAGs adduct are given in Table 1. Eleven classes of TAGs were identified in our Tunisian apricots among development such as LLL, LLO, LLP, LOO, LLS/LO, LPP, OOO, LOS, OOP and OOS (Table 1). The TAGs composition of apricot oil is seen in Table 2. Seven major forms were quantified and expressed as LLO.
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LOO, OOO, LLL, LLS/LOP, OOP and LLP counting for more than 98% (% Fig. 2). While, OOS is counting for less than 1% of the total TAGs’ concentration. Thus, the major forms of TAGs molecular species contain primarily the three acyl groups oleate (C18:1) or O, linoleate (C18:2) or L and in lower content palmitate (C16:0) or P during seeds development. In addition, the presence of high levels of unsaturated bioactive fatty acids, given them high therapeutic values. In fact, researchers (8, 12) proved that diets rich in these compounds can decrease blood pressure, total blood cholesterol level and result many hepatoprotective effects.

3.2 Triacylglycerols distribution at three different stages of maturity

Triacylglycerols (TAGs) were the predominant lipid class in most oil seeds (23). It has been reported that the proportion of TAGs change during plant development and this is closely related to the rate of synthesized fatty acids (22). Moreover, it was shown that seed kernel oil content increased during immature stage. In fact, this synthesis of TAGs is governed especially by the enzyme diacylglycerol acyltransferase (DGAT) by the Kennedy pathway in the cotyledon tissues (23).

As represented in Fig. 2 (A, B and C) and Table 2 and among the major TAG species, LLO exhibited the highest contents at IS from the three varieties of apricot. During maturation, LLO decreases significantly until maturation (Fig. 2). The pattern of LLO accumulation is concomitant with the increase of LOO and especially OOO content in bitter and sweet apricots species (Figs. 2A and 2C). These results could be explained by the desaturation of oleic acid to linoleic acid via Δ9 desaturase during kernel development (24). As a result, LOO and OOO showed the same pattern of accumulation which consists in an increase of their contents.

Compared with LOO, LLO and OOO, the rate of accumu-

Fig. 1 Chromatogram of TAG by HPLC-ESI-MS from wild apricot or AprB at IS(14 DAP).

Table 1 The chemical composition of TAGs, their molecular masses, their structure as determined by mass spectrometry (MS) in the three apricot varieties (the retention times extracted from Fig. 1).

| tR[min] | Mass of TAG adduct (TAG + 107 Ag or 109 Ag) | Structure of identified TAG |
|---------|------------------------------------------|---------------------------|
| 6.78    | 985-987                                  | LLL                       |
| 8.96    | 987-989                                  | LLO                       |
| 9.65    | 961-963                                  | LLP                       |
| 11.90   | 989-991                                  | LOO                       |
| 12.90   | 989-991                                  | LLS/LOP                   |
| 13.97   | 937-939                                  | LOP                       |
| 16.13   | 991-993                                  | OOO                       |
| 16.86   | 991-993                                  | LOS                       |
| 17.54   | 965-967                                  | OOP                       |
| 18.89   | 939-941                                  | POP                       |
| 23.10   | 993-995                                  | OOS                       |
| tR: retention time, Stearic acid or S (M=283.3 g/mol), Oleic acid or O (M=281.2 g/mol), Linoleic acid or L (M=279.2 g/mol) and Palmitic acid or P (M=255.2 g/mol).
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The fatty acids’ synthesis, palmitic acid was converted to stearic acid in the TAGs’ synthesis. Therefore, we noted a decline in the LLP and LOP accumulation rate, whereas the TAGs containing oleic acid and palmitic acid such as OOP and OOS increased slightly during maturation (Figs. 2A, 2B and 2C). This presumably, reflects that during oil accumulation, the amounts of oleoyl-CoA and linoleoyl CoA increased significantly. As a result, these FAs were the major components of the acyl-CoA pool and their total level was doubled from 14 to 28 DAP.

### 3.3 Comparison of TAGs profiles during maturity

During maturity, distinct profiles of TAGs were observed. The major TAGs classes noted in the apricot oil were LLO, LOO, OOO with different contents. In fact, in bitter apricot, LLO (40.3% (w/w)), LOO (32.1% (w/w)) and OOO (max 37.5% (w/w)) were prominent during maturity (Fig. 2A). We noted a similar profile in sweet ones with LLO (35.4% (w/w)), LOO (33.9% (w/w)) and OOO (22.7% (w/w)).

![Fig. 2A](image1.png) Changes in the major forms of TAG (%) during sweet apricot or AprC kernel maturation. LLL, LLO, LOO, LOP, OOP, LLP and OOO.

![Fig. 2B](image2.png) Changes in the major forms of TAG (%) during semi-sweet apricot or AprO kernel maturation. LLL, LLO, LOO, LOP, OOP, LLP and OOO.

![Fig. 2C](image3.png) Changes in the major forms of TAG (%) during bitter apricot (wild) AprB kernel maturation. LLL, LLO, LOO, LOP, OOP, LLP and OOO.

### Table 2 Major Triacylglycerols composition and content\(^a\) (expressed in % of total triacylglycerol components) of AprB, AprO and AprC at three stages of maturity with ANOVA results.

| TAGs | AprB |     |     |     | AprO |     |     |     | AprC |     |     |
|------|------|-----|-----|-----|------|-----|-----|-----|------|-----|-----|
|      | IS   | MMS | MS  | IS  | MMS | MS  | IS  | MMS | MS  | IS  | MMS | MS  |
| LLL  | 14.8 ± 1.0 | 3.9 ± 0.8 | 1.6 ± 1.1 | 7.7 ± 1.1 | 9.7 ± 0.8 | 7.8 ± 1.2 | 8.1 ± 0.9 | 3.3 ± 0.8 | 10.9 ± 1.1 |
| LLO  | 40.3 ± 0.5 | 21.9 ± 0.9 | 18.8 ± 0.8 | 52.6 ± 0.6 | 38.1 ± 0.9 | 43.8 ± 1.1 | 35.4 ± 0.7 | 35 ± 0.8 | 26.8 ± 1.0 |
| LLP  | 3 ± 0.8 | 1.2 ± 0.7 | 0.8 ± 0.7 | 4 ± 0.4 | 4 ± 0.2 | 1.4 ± 0.1 | 2.4 ± 0.5 | 1.4 ± 0.7 | 0.9 ± 0.2 |
| LOO  | 25.7 ± 0.4 | 31.3 ± 0.6 | 32.1 ± 0.7 | 17.5 ± 0.9 | 29.6 ± 0.7 | 32.7 ± 0.9 | 31 ± 0.4 | 33.9 ± 0.7 | 33.4 ± 0.8 |
| LLS/LOP | 6.5 ± 0.7 | 5.6 ± 0.6 | 3.6 ± 0.6 | 8.1 ± 0.9 | 7.9 ± 0.6 | 4.3 ± 0.3 | 8.9 ± 0.5 | 5.8 ± 0.6 | 3.2 ± 0.5 |
| OOO  | 7.5 ± 0.5 | 30 ± 0.4 | 37.5 ± 0.4 | 5.7 ± 1.2 | 9.2 ± 0.4 | 7.8 ± 0.5 | 12.7 ± 0.9 | 17.8 ± 0.4 | 22.7 ± 1.1 |
| OOP  | 1.9 ± 0.1 | 5 ± 0.1 | 4.6 ± 0.3 | 3.8 ± 0.3 | 2.5 ± 0.3 | 2.0 ± 0.2 | 2.2 ± 0.3 | 2.5 ± 0.1 | 1.8 ± 0.1 |
| OOS  | 0.2 ± 0.4 | 1 ± 0.2 | 1 ± 0.1 | 0.2 ± 0.2 | 0.2 ± 0.2 | 0.2 ± 0.1 | 0.1 ± 1.2 | 0.2 ± 0.2 | 0.3 ± 0.3 |

\(^a\) Each value is a mean ± standard deviation (SD) of a triplicate analysis performed on different samples. AprB: bitter apricot; AprO: semi-sweet apricot; AprC: sweet apricot; IS: immature stage (14 DAP); MMS: middle maturity stage (28 DAP); MS: full maturity stage (55 DAP).
While, in the case of semi-sweet apricot only LLO (max 52.6% (w/w)) and LOO (max 32.7% (w/w)) were predominant. The abundance of these TAGs in apricot oil is a consequence of high levels of linoleic and oleic acids as concluded in our previous remarks.

At IS (14 DAP), Fig. 2B shows that semi-sweet apricot has a significant high value (p < 0.05) of LLO (52.6% (w/w)), compared to bitter (Bargoug) with 40.3% (w/w) and sweet (Chechi Bazza) with 35.4% (w/w). In addition, and at the lowest level, semi-sweet apricot (Oud Rhayem) is the richest (p < 0.05) in LLO (4.0%) (w/w) and OOP (3.8%) (w/w) contents too. Comparatively and at the same stage, bitter apricot seems to be (p < 0.05) the richest variety in LLO (14.8% (w/w)) but sweet apricot is distinguishable by its higher LOO (30.1% (w/w)), OOO (12.7% (w/w)) and LOP (8.9% (w/w)) contents.

During maturity, the TAGs’ content reached some fluctuations amongst the three apricot varieties (Figs. 2A, 2B and 2C). LLO seems to decrease in wild and sweet apricots. Presumably, it could result in a slight dilution of linoleic acid in favor of an increase of many fatty acids such as oleic acid. As a consequence, the content of TAGs changes during maturation. Precisely at the middle stage of maturity (MMS or 28 DAP), the two cultivars conserve the same major TAGs LLO and LOO. However, wild apricot reached the highest levels of OOO (30%) paralleled to the major TAGs LLO and LOO with a distinct profile compared to cultivars ones. (Fig. 2). Instead, at this same stage, cultivars apricot presents a distinct profiling of the two majors TAGs LLO and LOO. Indeed, semi-sweet apricot seems significantly (p < 0.05) to be the richest in LLO (38.14% (w/w)), LLL, LLP and LOP. While in sweet apricot; it was noted that LOO was significantly (p < 0.05) the major TAGs with 33.9% (w/w). Similarly, to bitter apricot, it was observed that the content of OOO TAG in sweet apricot increase during maturity too. (see Fig. 2). In point of fact, these results could be explained by the increase in the activity of diacylglycerol acyltransferase (DGAT) enzyme in favor of the incorporation of oleic acid in the TAGs skeleton. Furthermore, DGAT is the unique acyltransferase to the synthesis of TAG, and this step has received the most attention in terms of influencing the accumulation of TAG in plant tissues. As for the OOS content, it was remarkably the lowest one and still invariable during the development of the three apricot varieties and remained around 0.11% (Fig. 2).

At full maturity (MS or at 55 DAP), three distinct profiles were clearly observed among the three apricot varieties. Interestingly, wild bitter apricot still significantly (p < 0.05) the richest in OOO (37.5% (w/w)), OOP (4.6% (w/w)) and OOS (1%) contents. Semi-sweet apricot presents significantly (p < 0.05) a rich profile in LLO (43.8%) and LLP contents but with lower POL values. Finally, sweet apricot remained significantly (p < 0.05) the richest in LOO (33.4% (w/w)) and LLL (10.9% (w/w)) contents at this time date. The quantitative differences observed in the major TAGs’ composition of the three apricot varieties could be linked to differences in genetical origins and different enzyme activities. In fact, Chapman et al. reported that two classes of acyl-ACP thioestersases designed as FATA and FATB release newly synthesized 16:0 FA, 18:0 FA and 18:1 FA in the plastid stroma and are responsible for hydrolysis of unsaturated and saturated acyl-ACPs, and thus determine in large part the TAGs composition in oilseeds. Therefore, the differences in enzymes (FATA and FATB) modulation activities had possibly influenced our apricot TAG profile for the three varieties.

Qualitatively, these results mostly confirm previous ones showing that LLO, LOO and OOO are the majors TAGs present in apricot oil. Quantitatively, however, there are some significant differences independently on the apricot varieties. LOO do not differ significantly between the Turkish (32.6%) (w/w) and the Tunisian apricot oil varieties (29.6-33.4%) (w/w). However significant difference is noted between Egyptian (22%) (w/w) and Tunisian apricot oil for LOO. In the case of OOO TAGs, Tunisian apricot present the lowest values even bitter one (9.2-30%) (w/w) compared to Turkish (48.64%) (w/w) and Egyptian (43.8%) (w/w) apricot oils. Egyptian and Turkish apricot present a profile rich in OOO as major TAGs since bitter Tunisian apricot have this profile. Also, while LLO contents is about 7.6% (w/w) and 14.33% (w/w) respectively in Egyptian and Turkish apricot, they vary higher in Tunisian apricot with (21.9-38.1%) (w/w). Indeed, the richness of apricot in TAGS such as LOO (18.8 to 52.6%) (w/w), LLO (17.5 to 33.9%) (w/w) and OOO (5.7 to 37.5%) (w/w) is higher than sesame oil profile performed by the same method with respectively 14.94% (w/w), 32.89% (w/w) and 3.62% (w/w). Our results are similar to that in olive oil (25) with OOO (35%) (w/w) and LLLO (18%) (w/w), hazelnut oils with 32% (OOO) (w/w) and 15% (LLO) (w/w) 25.

4 Conclusion

Genetic diversity influenced the TAG composition in the three distinct apricot varieties. The profile of their distributions among maturity was found to differ substantially with different molecular species abundance. According to the results obtained by UHPLC method, Tunisian apricot varieties were founded to be rich in LLO, LOO and OOO TAGs compounds, whereas they contain lower amounts of LOP, OOP, LLP and OOS independently of the stage of maturity. Interestingly at full maturity, sweet cultivar apricot was found to be significantly the richest in LOO content, while LLO was the major TAGs content in semi-sweet apricot. However, bitter apricot was distinguishable by its higher
OOO content. The results show quite distinct molecular species distributions in TAGs classes among the three studied varieties and demonstrate the complex nature of metabolism during oil accumulation. This study could successfully indicate the best time to take advantages of each apricot varieties in TAGs compositions profiles and may provide a schedule for harvesting Tunisian apricot seeds with high quality of oil content. These TAGs compositions are established as a measurement of the quality and purity of apricot oils and can be used increasingly in the food industry to confirm authenticity and aid in disclosing apricot oil adulteration.

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