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# Biochemical characterization and antioxidant activities of the edible part of globe artichoke cultivars grown in Tunisia

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#### **ABSTRACT**

A renewed interest has been observed recently in globe artichoke as a promising source of polyphenols, a heterogeneous class of secondary metabolites characterized by various well-documented healthy properties. However, only few studies have characterized Tunisian cultivars. Therefore, the present study aimed at evaluating the chemical parameters [fatty acids (FAs), volatiles, and phenolic derivatives content] in the edible part, the receptacle, of two globe artichoke cultivars ('Violet d'Hyéres' and 'Blanc d'Oran'), including their antioxidant activities. The FA profiles of the receptacles showed that the most abundant acids were linoleic and palmitic ones. Forty-one volatile compounds, accounting for 97.6-96.3% of the receptacle aroma emission, were identified. Sesquiterpenes hydrocarbons represented the main chemical class; in particular  $\beta$ -selinene, followed by  $\beta$ -caryophyllene, reached the highest levels in 'Violet d'Hyéres' (48.7% and 14.5%, respectively). Total phenols and tannins ( $p \le 0.05$ ), o-diphenols and flavonoids ( $p \le 0.01$ ) were significantly higher in the receptacles of 'Violet d'Hyéres' cultivar (73.0, 17.2, 15.4, and 12.2 mg 100  $g^{-1}$  of fresh weight, respectively). The antioxidant activity was notably phenolic derivatives content-dependent, where higher values were observed in the 'Violet d'Hyéres' cultivar. Results suggested that globe artichoke receptacles could represent a good source of health-promoting polyphenols with high antioxidant activity and this fact could encourage their consumption. Further investigations are needed to evaluate the variation of the considered compounds in other Tunisian cultivars.

#### **ARTICLE HISTORY**

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### **KEYWORDS**

Cynara cardunculus; Fatty acids; Phenols; Antioxidant activity; Volatile compounds

# Introduction

Cynara cardunculus var. scolymus L., popularly known as globe artichoke, is a tall thistle-like flower head with an edible part (receptacle) and it is an important component of the Mediterranean diet. [1] Its global production has risen to about 1.8 million tons per year. [2] According the Food and Agriculture Organization of the United Nations, [2] the leading producer country is Italy (548000 tons per year), followed by Egypt (391000 tons per year) and Spain (200000 tons per year). Globe artichoke has been appreciated since ancient times as a tasty food, in both its fresh and processed forms. In the literature, there are many reports on the composition and properties of globe artichoke concerning many cultivated and wild varieties. [3–5] Furthermore, it is a good source of natural antioxidants, such as vitamin C, hydroxycinnamic acids, flavones, and sesquiterpenes. [6,7] Hepatoprotection, choleretic,



lipid-lowering, and colon cancer protection are the main biological activities demonstrated by the artichoke metabolites. [8] The globe artichoke also appears as a source of volatile compounds, mainly sesquiterpenes and non-terpenes derivatives as reported by some authors. [9,10]

Recently, Claus et al. [11] chemically characterized the globe artichoke parts used for protection from oxidative stress in canola oil and reported their fatty acid (FA) content. Moreover, for the receptacle, they reported 88.4 g 100 g<sup>-1</sup> of moisture, 12.3 g 100 g<sup>-1</sup> of ash, 24.3 g 100 g<sup>-1</sup> of crude protein, 1.34 g 100 g<sup>-1</sup> of lipids, and 13.1 g 100 g<sup>-1</sup> of fibre. Instead, the receptacle was a good source of saturated FA (SFA; 359 mg 100 g<sup>-1</sup>) and polyunsaturated FA (PUFA; 963 mg 100 g<sup>-1</sup>). In Tunisia, globe artichoke production (18000 tons per year) is mainly concentrated in the north, where it provides an important contribution to the agricultural economy.<sup>[2]</sup> Nevertheless, few papers on the characterization of globe artichoke have been published, especially about their by-products. [10,12-14] Considering the scarcity of reports about the edible part of the globe artichoke cultivated in Tunisia, the aim of this study was therefore its valorization by studying the antioxidant capacity of the receptacle of two Tunisian globe artichoke cultivars ('Blanc d'Oran' and 'Violet d'Hyères') by means of three well-established colorimetric methods [2,2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid (ABTS), 1,1-diphenyl-2-picryl-hydrazyl (DPPH), and reducing power], and by evaluating their FA profile, phenolic composition, and volatile compounds.

# Materials and methods

# Standards and reagents

The methyl ester standards were obtained from Supelco (Supelco 37 Component FAME Mix, PUFA-1, and PUFA-3; Supelco, Bellefonte, PA, USA). The standards (limonene, camphor,  $\alpha$ -longipinene, longicyclene,  $\alpha$ -copaene,  $\beta$ -caryophyllene,  $\alpha$ -humulene,  $\beta$ -selinene, caryophyllene oxide, safranal, 2,3-butanediol, hexanal, 2-methylbutanoic acid, 1-hexanol, methyl hexanoate, 1-octen-3-ol, 2-pentylfuran, (E)-2-octenal, (E)-2-octen-1-ol, n-undecane, nonanal, 1-nonanol, (Z)-jasmone, and hydroxytyrosol) were purchased from Sigma-Aldrich and/or synthesized in the laboratory and verified by Nuclear magnetic resonance (NMR). The chemical reagents and solvents isopropyl alcohol, methyl acetate, sodium methoxide, sodium sulfate, oxalic acid, diethyl ether, ethanol, and methanol were of analytical grade and purchased from Sigma-Aldrich. ABTS, DPPH, trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), Folin-Ciocalteu, and sodium carbonate were obtained from Sigma (St. Louis, MO, USA).

# Experimental field, plant material, management practices, and sampling

Globe artichokes of 'Blanc d'Oran' and 'Violet d'Hyères' plants were grown in the experimental field "Technical Center of Potato and Artichoke of Tunisia" located in the Mannouba (northern of Tunisia) region, with spacing (1.2\*0.6); 13.888 plants per ha for the 'Blanc d'Oran' cultivar and (1.2\*0.8); 10.416 plants per ha for the 'Violet d'Hyères' cultivar. Crop management practices (irrigation, pest management, weeds control, etc.) were subsequently performed according to local practices. The samples were collected in April during the 2011-2012 season at the usual marketing stage, regardless of their size. At this stage, the length of the floral buds was ≤2 mm. [15] For each cultivar, five disease-free capitula per replicate (n = 3) were collected, washed with running water to remove impurities, air-dried, and the receptacles were taken. One portion of the receptacle was used as fresh material, while the remaining portion was freeze-dried and stored at -20°C until analysis.

# FA analysis

Lipid extraction from freeze-dried samples (1.5 g) and transesterification of the FA were performed according to Peiretti et al. [16] Briefly, the FA were analysed as their methyl esters by gas chromatography, using a Dani GC 1000 DPC (Dani Instruments S.P.A., Cologno Monzese, Italy), equipped with a Supelcowax-10 fused silica capillary column [60 m × 0.32 mm (i.d.), 0.25 μm film thickness]. The injector and detector ports were set at 240°C and 250°C, respectively. The oven temperature program was initially set at 50°C and then increased at a rate of 5°C min<sup>-1</sup> up to 230°C, where it remained for 24 min. The carrier gas was hydrogen. One microliter was injected using a Dani ALS 1000 auto sampler with a 1:35 split ratio. The peak area was measured using a Dani Data Station DDS 1000, where each peak was identified and quantified according to external methyl ester standards. The results were expressed as the percentage of total FA methyl ester.

# Volatile compounds analysis

Supelco (Bellefonte, PA) solid phase micro-extraction (SPME) devices coated with polydimethylsiloxane (PDMS, 100 µm) were used to sample the headspace of freeze-dried receptacles inserted into a 25 mL vial and allowed to equilibrate for 30 min. SPME sampling was performed using the same new fibre, preconditioned according to the manufacturer's instructions, for all the analyses. Sampling was accomplished in an air-conditioned room ( $22 \pm 1^{\circ}$ C) to guarantee a stable temperature. After the equilibration time, the fibre was exposed to the headspace for 50 min at room temperature. Once sampling was finished, the fibre was withdrawn into the needle and transferred to the injection port of the GC-MS system. All the SPME sampling and desorption conditions were identical for all the samples. Furthermore, blanks were performed before each first SPME extraction and randomly repeated during each series. Quantitative comparisons of relative peaks areas were performed between the same chemicals in the different samples. Gas Chromatography-Electron Impact Mass Spectrometry (GC-EIMS) analyses were performed with a Varian (Palo Alto, CA) CP 3800 gas chromatograph equipped with a DB-5 capillary column [30 m × 0.25 mm (i.d.) × 0.25 µm film thickness; Agilent, Santa Clara, CA] and a Varian Saturn 2000 ion trap mass detector. Analytical conditions were as follows: injector and transfer line temperatures were 250°C and 240° C, respectively; oven temperature was programmed from 60°C to 240°C at 3°C min<sup>-1</sup>; carrier gas was helium at 1 mL min<sup>-1</sup>; and split-less injection. The identification of the constituents was based on a comparison of the retention times with those of the authentic samples, comparing their linear retention indices (LRIs) relative to a series of n-hydrocarbons, and on computer matching against commercial and homemade library mass spectra, built from pure substances and MS literature data. [17-20] Moreover, the molecular weights of all the substances identified were confirmed by Gas Chromatography-Chemical Ionization Mass Spectrometry (GC-CIMS), using methanol as the ionizing gas. The results were expressed as percentage.

# **Phenols extraction**

Receptacle fresh sample (5 g) was ground in 20 mL of methanol 80% containing 1% hydrochloric acid for 2 min with an Ultra-Turrax T25 (Janke & Kunkel Ika-Labortechnik, Staufen, Germany) and stirred at room temperature for 1 h. Then, the homogenate was filtered through Whatman No. 4 filter paper and the filtrate was stored at -20°C until analysis. [4]

# Determination of total phenols and o-diphenols contents

Total phenols and o-diphenols compounds contents were determined according to the method of Montedoro et al. [21] In brief, an appropriate amount of extract was mixed with 10 mL of Folin-Ciocalteu reagent, diluted 10 times. After 1 min, 8 mL of sodium carbonate (75 g L<sup>-1</sup>) was added. The mixture was incubated for 2h and the absorbance was then read at 765 nm against a blank by a UV-Vis spectrophotometer (UV-VIS Beckman spectrophotometer DU 650, Beckman Instruments Inc., Fullerton, CA, USA). The results were expressed as mg hydroxytyrosol equivalents (HE)  $100 \, \mathrm{g}^{-1}$  of fresh weight (FW).



# **Total anthocyanins**

The fresh matter (1 g) was extracted with 25 mg mL<sup>-1</sup> of acidified methanol (1% HCl) for 2 h at room temperature in the dark, and then centrifuged at 450 g for 15 min. The absorbance was read at 530 and 653 nm by a UV-Vis spectrophotometer and the anthocyanin levels were calculated from the methanol extract as  $A_{530} - (0.24 \times A_{653})$  and the total anthocyanin content was expressed as mg cyanidin 3-glucoside equivalents per 100 g of FW, using an extinction coefficient (ε) of 26.900 L mol<sup>-1</sup> cm<sup>-1</sup> at the absorbance (Ab) of 530 nm and a molar weight (MW) of 449.2 g mol<sup>-1</sup>.<sup>[22]</sup>

$$\text{Anthocyanin} \left( \text{mg} / 100 \text{g} \right) = \frac{\text{Ab} \times \text{MW} \times \text{V} \times 100}{\varepsilon \times \text{G}}$$

# **Total flavonoid contents**

The method of Zhishen et al.<sup>[23]</sup> was adopted to determine the flavonoids content. An aliquot of 250 µL of each extract or standard solution was added with 1.25 mL of distilled water and 75 µL of 5% NaNO2 solution. After 6 min of incubation, 150 μL of 10% AlCl<sub>3</sub> solution was added. Five minutes later, 0.5 mL of 1 M NaOH solution was added and then the total volume was made up to 2.5 mL with distilled water. Subsequently, the obtained solution was mixed and the absorbance was recorded at 510 nm against a blank by a UV-Vis spectrophotometer. The flavonoid contents were calculated using a standard calibration curve, prepared from catechin. The results were expressed as mg catechin equivalents (CE) 100 g<sup>-1</sup> FW.

# Total condensed tannin contents

Total condensed tannins were determined by a spectrometric method described previously. [24] Around 50 µL of each extract or standard solution was mixed with 1.5 ml of 4% vanillin (prepared with methanol), and then 750 µL of HCl (12 M) was added. The well-mixed solution was incubated in the dark at room temperature for 20 min. The absorbance against the blank was read at 500 nm. The condensed tannin content was calculated from a calibration curve using a catechin as standard and expressed as mg CE 100 g<sup>-1</sup> FW.

## **Antioxidant activities**

The antioxidant capacities of the edible part of globe artichoke were determined by means of three different assays (ABTS, DPPH, and reducing power assays) described as follows. The antiradical DPPH activity of the extracts was determined using the method of Kontogiogis and Hadjipavlou-Litina. [25] Briefly, 20 µL of each extract, used for total phenols assay, was dissolved in absolute ethanol to a final volume of 1 mL and, then, added to 1 mL DPPH (0.1 mM, in absolute ethanol). The mixture was incubated at room temperature and then the absorbance was read at 517 nm by a UV-Vis spectrophotometer against a control after 20 min. The optical densities (ODs) of the samples in the absence of DPPH were subtracted from the corresponding ODs with DPPH. Inhibition of the free radical DPPH (I %) was calculated using the following equation:

$$I\% = \frac{A_{blank} - A_{sample}}{A_{blank}} \times 100$$

where A<sub>blank</sub> is the absorbance of the control reaction (containing all reagents except the tested compound) and A<sub>sample</sub> is the absorbance of the tested compound. A<sub>blank</sub> was read against absolute ethanol.

ABTS radical cation (ABTS\*+) was produced by the reaction of 7 mM of ABTS stock solution with 2.45 mM potassium persulfate (12-16 h, in darkness, at room temperature). [26,27] Afterward, the stock solution was diluted with ethanol (approx. 1:88) to obtain an absorbance of  $0.7 \pm 0.02$  at 734 nm by a UV-Vis spectrophotometer and equilibrated at 30°C. A reagent blank reading was taken (A0). For the assay, after the addition of 0.1 mL of sample to 3.9 mL of diluted (ABTS\*+) solution, absorbance readings were taken after 6 min of incubation in the dark at room temperature. The absorbance for each sample (ABTS\*+ solution plus compound, At) was measured at 734 nm and corrected for the absorbance of a control (ABTS\*+ solution without test sample, A0). Solutions of known concentration of trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) were used for antioxidant capacity equivalents calculations. [28]

The reducing power was determined using the method of Oyaizu. [29] An aliquot of each sample (250 μL) was mixed with 250 μL of sodium phosphate buffer (0.2 M, pH 6.6) and 250 μL of 1% K<sub>3</sub>Fe (CN)<sub>6</sub> incubated at 50°C for 20 min. After adding 250 µL of 10% trichloroacetic acid, the mixture was centrifuged at 3750 g for 10 min. The supernatant (100 μL) was taken out and immediately mixed with 100 µL of methanol and 25 µL of 0.1% ferric chloride. The absorbance was, finally, measured at 700 nm by a UV-Vis spectrophotometer after 10 min of incubation against a blank. Increased absorbance indicated increased reducing power.

# Statistical analysis

Significant differences between varieties were determined by the Students t-test using the SPSS program, release 17.0 for Windows (SPSS, Chicago, IL, USA). All data represent the average of three independent tests (n = 3).

# **Results and discussion**

# **FA** composition

The FA composition of both cultivars expressed as % of total FA methyl ester is shown in Table 1. The most abundant FAs were linoleic and palmitic ones; these findings are in good agreement with previous studies on globe artichoke grown in Italy and Brazil. [11,30] Significant differences were observed for capric, palmitic, oleic, and linolenic acid, monounsaturated FA, and n-6/n-3 PUFA ratio. In particular, oleic and linolenic acids predominated in 'Blanc d'Oran' (3.3% and 44.0%, respectively), while capric and palmitic acids were more abundant in 'Violet d'Hyères' (3.2% and 28.9%, respectively). The n-6/n-3 PUFA ratio was significantly lower in 'Blanc d'Oran' than in 'Violet d'Hyères'. No significant differences were observed for heptadecanoic, stearic, and linoleic acids, SFA, and PUFA between the two cultivars.

**Table 1.** Fatty acid composition (g 100 g<sup>-1</sup> of total fatty acid methyl ester) of the receptacle of two Tunisian globe artichoke cultivars.

|                       | Blanc d'Oran             | Violet d'Hyéres           |
|-----------------------|--------------------------|---------------------------|
| Capric (C8:0)         | 2.6 ± 0.12 <sup>b</sup>  | $3.2 \pm 0.05^{a^{**}}$   |
| Palmitic (C16:0)      | 27.6 ± 0.55 <sup>b</sup> | $28.9 \pm 0.37^{a^*}$     |
| Stearic (C18:0)       | $7.3 \pm 0.24$           | 8.1 ± 1.26                |
| Heptadecanoic (C17:0) | $4.5 \pm 0.64$           | $3.6 \pm 0.63$            |
| SFA                   | 42.0 ± 1.31              | $43.7 \pm 0.26$           |
| Oleic (C18:1n-9)      | $3.3 \pm 0.06^{a}$       | 2.9 ± 0.26 <sup>b*</sup>  |
| MUFA                  | $3.3 \pm 0.06^{a}$       | 2.9 ± 0.26 <sup>b*</sup>  |
| Linoleic (C18:2n-6)   | 44.0 ± 1.06              | $43.8 \pm 0.05$           |
| Linolenic (C18:3n-3)  | 10.8 ± 0.25 <sup>a</sup> | $9.7 \pm 0.04^{b^{**}}$   |
| PUFA                  | 54.8 ± 1.31              | $53.4 \pm 0.02$           |
| n-6/n-3 PUFA ratio    | 4.1 ± 0.01 <sup>b</sup>  | 4.5 ± 0.03 <sup>a**</sup> |

Values are expressed as means  $\pm$  standard deviation (n = 3). Different letters for the same parameter, within rows indicate significant differences (\* $p \le 0.05$ ; \*\* $p \le 0.01$ ) between cultivars. Saturated Fatty Acids, SFA; Monounsaturated Fatty Acids, MUFA, Polyunsaturated Fatty Acids, PUFA. n-6/n-3 polyunsaturated fatty acids ratio (n-6/n-3 PUFA ratio).

Table 2. Volatile compounds (%) evaluated by GC-MS for the dried receptacle of two Tunisian globe artichoke cultivars.

|                                   | L.R.I. | Blanc d'Oran                  | Violet d'Hyéres |
|-----------------------------------|--------|-------------------------------|-----------------|
| Limonene                          | 1032   | 1.9 ± 0.1                     | 1.7 ± 0.9       |
| Monoterpene hydrocarbons          |        | 1.9 ± 0.1                     | 1.7 ± 0.9       |
| Camphor                           | 1145   | $0.9 \pm 0.2$                 | $1.1 \pm 0.8$   |
| Oxygenated monoterpenes           |        | $\textbf{0.9}\pm\textbf{0.2}$ | 1.1 ± 0.8       |
| α-longipinene                     | 1352   | $0.7 \pm 0.1$                 | $0.8 \pm 0.1$   |
| Cyclosativene                     | 1370   | $0.6 \pm 0.1$                 | nd              |
| Longicyclene                      | 1372   | 5.2 ± 1.3                     | nd              |
| α-ylangene                        | 1373   | nd                            | $0.8 \pm 0.0$   |
| α-copaene                         | 1377   | $0.7 \pm 0.3$                 | nd              |
| β-elemene                         | 1392   | $0.7 \pm 0.1$                 | $0.2 \pm 0.3$   |
| Longifolene                       | 1404   | $3.7 \pm 0.7$                 | nd              |
| β-caryophyllene                   | 1419   | 12.2 ± 2.3                    | $14.5 \pm 3.5$  |
| <i>trans</i> -α-bergamotene       | 1437   | nd                            | $0.4 \pm 0.1$   |
| α-himachalene                     | 1449   | $0.6 \pm 0.1$                 | nd              |
| α-humulene                        | 1455   | $0.7 \pm 0.1$                 | $0.8 \pm 0.1$   |
| α-acoradiene                      | 1464   | $0.3 \pm 0.3$                 | $0.6 \pm 0.1$   |
| y-himachalene                     | 1481   | nd                            | $8.4 \pm 1.2$   |
| β-selinene                        | 1486   | $38.4 \pm 7.6$                | $48.7 \pm 0.4$  |
| α-selinene                        | 1495   | $1.0 \pm 1.0$                 | $1.3 \pm 0.2$   |
| δ-cadinene                        | 1524   | $0.5 \pm 0.1$                 | nd              |
| Sesquiterpene hydrocarbons        |        | 65.3 ± 14.0                   | 76.5 ± 1.9      |
| caryophyllene oxide               | 1582   | $1.3 \pm 0.0$                 | $1.6 \pm 0.6$   |
| Oxygenated sesquiterpenes         |        | $1.3 \pm 0.0$                 | 1.6 ± 0.6       |
| Safranal                          | 1202   | $0.7 \pm 0.1$                 | $0.9 \pm 0.1$   |
| Apocarotenoids                    |        | $0.7 \pm 0.1$                 | $0.9 \pm 0.1$   |
| 2,3-butandiol                     | 790    | $0.4 \pm 0.1$                 | nd              |
| Hexanal                           | 804    | 3.9 ± 1.1                     | $2.1 \pm 0.7$   |
| 2-methylbutanoic acid             | 852    | $0.5 \pm 0.1$                 | $0.3 \pm 0.1$   |
| 1-hexanol                         | 869    | $1.1 \pm 0.3$                 | $1.2 \pm 0.7$   |
| 3-methyl-1-hexanol                | 922    | $0.4 \pm 0.1$                 | $0.4 \pm 0.3$   |
| Methyl hexanoate                  | 929    | $0.5 \pm 0.3$                 | nd              |
| 1-octen-3-ol                      | 980    | $1.0 \pm 0.1$                 | $0.7 \pm 0.1$   |
| 2-pentylfuran                     | 994    | $1.3 \pm 0.0$                 | $1.0 \pm 0.6$   |
| 3-ethyl-1-hexanol                 | 1030   | $2.0 \pm 0.5$                 | $1.4 \pm 0.4$   |
| 3-octen-2-one                     | 1043   | $1.1 \pm 0.2$                 | $0.7 \pm 0.4$   |
| (E)-2-octenal                     | 1062   | $3.9 \pm 3.9$                 | $0.9 \pm 0.6$   |
| (E)-2-octen-1-ol                  | 1071   | $2.3 \pm 2.3$                 | $0.4 \pm 0.1$   |
| ( <i>E,Z</i> )-3,5-octadien-2-one | 1076   | 1.9 ± 0.5                     | $1.1 \pm 0.1$   |
| (E,E)-3,5-octadien-2-one          | 1095   | $1.6 \pm 0.7$                 | $0.9 \pm 0.2$   |
| <i>n</i> -undecane                | 1100   | $3.1 \pm 2.8$                 | $0.9 \pm 0.4$   |
| Nonanal                           | 1104   | nd                            | $0.4 \pm 0.1$   |
| (Z)-2-nonenal                     | 1150   | $0.8 \pm 0.8$                 | $0.4 \pm 0.3$   |
| 1-nonanol                         | 1172   | nd                            | $0.4 \pm 0.0$   |
| (Z)-2-tridecene                   | 1314   | nd                            | $0.3 \pm 0.1$   |
| 2-butyl-2-octenal                 | 1380   | $0.7 \pm 0.1$                 | $0.8 \pm 0.1$   |
| (Z)-jasmone                       | 1394   | $1.0 \pm 0.0$                 | $0.2 \pm 0.2$   |
| Non-terpene derivatives           |        | 27.5 ± 11.7                   | 14.5 ± 3.5      |
| Total identified                  |        | 97.6 ± 2.1                    | 96.3 ± 2.9      |

Values are expressed as means  $\pm$  standard deviation (n=3). L.R.I.: Linear Retention Index; nd: not detected.

# **Volatile compounds**

The volatiles spontaneously emitted and sampled by SPME from the samples of receptacles are shown in Table 2. Globally, 35 compounds have been identified for 'Blanc d'Oran' and 33 for 'Violet d'Hyéres' cultivars. They accounted for 97.6% and 96.3% of the total volatile compounds, respectively. The results showed that sesquiterpene hydrocarbons were detected with relatively higher concentrations in both cultivars (65.3% in 'Blanc d'Oran' and 76.5% in 'Violet d'Hyéres'), followed by non-terpene derivatives (27.5% and 14.5%, respectively). Although in different parts of the globe artichoke plant, these results confirmed the data obtained in our previous work. [14] The main identified compound was  $\beta$ -selinene, followed by  $\beta$ -caryophyllene, with higher levels in 'Violet



d'Hyéres' (48.7% and 14.5%, respectively). A previous study also reported  $\beta$ -selinene as the main compound. [31] Monoterpene hydrocarbons and oxygenated monoterpenes, reaching on average 1.8% and 1.0%, respectively, were less represented.

# Phenols composition

The levels of phenols and o-diphenols, flavonoids, anthocyanins, and condensed tannins in the fresh receptacle of both cultivars are summarized in Table 3. The total phenols content, measured by the Folin-Ciocalteu method, varied from 60 mg for 'Blanc d'Oran' to 73 mg HE 100 g<sup>-1</sup> of FW for 'Violet d'Hyéres'. With regard to the literature data, the total phenols content was lower compared with other globe artichoke varieties. [32,33] According to Fratianni et al., [34] receptacles and inner bracts exhibited the highest phenols concentration in five globe artichoke varieties than the intermediate and outer bracts and leaves. Similar trends were previously depicted by Romani et al., [5] who found that heads of the variety 'Violetto di Toscana', typical of the Tuscany region (Italy), were very rich in phenolic compounds and hence can be regarded as a functional food. Comparing the different parts of plants, Lombardo et al. [3] reported that the inner bracts contained a higher total phenolic content than the receptacle.

'Violet d'Hyéres' also recorded the highest content of both total flavonoids (12.2 mg CE 100 g<sup>-1</sup> FW) and total tannins (17.2 mg CE 100 g<sup>-1</sup> FW) contents. Pandino et al.<sup>[35]</sup> also reported that among the cultivated and wild cultivars studied, the flavonoids content was strongly affected by both cultivar and part of the plant. The contents of tannins found herein in the receptacles of globe artichoke were lower than those of the leaves, bracts, seeds, and stems found in C. cardunculus by other authors;-[10,13,36] nevertheless, no reports have been published on the content of tannins in the receptacles of globe artichoke cultivars in order to make possible a comparison. With regard to the anthocyanins levels, they were higher in 'Blanc d'Oran' (3.7 mg 100 g<sup>-1</sup> FW). Schütz et al. [37] found that the content of anthocyanins in heads was significantly affected by the cultivar. Overall, our results indicated that globe artichoke receptacles could represent an important source of polyphenols having useful antioxidant activities, [38] widely used in phytopharmaceutical applications. [39]

# **Antioxidant activities**

The reducing power, ABTS, and DPPH free radicals were used to evaluate the antioxidant activities of the fresh receptacle (Table 3). The values showed that the antioxidant capacity of globe artichokes was notably phenolic content-dependent. In fact, the higher antioxidant activities determined by the ABTS assay ( $p \le 0.01$ ) were observed in the 'Violet d'Hyéres' cultivar, which were the richest in phenols, o-diphenols, and flavonoids. However, no significant differences were observed between cultivars when the antioxidant activities were determined by DPPH and reducing power assays (Table 3).

Table 3. Phenolic composition and antioxidant activity of the receptacle of two Tunisian globe artichoke cultivars.

|  | Blanc d'Oran             | Violet d'Hyéres           |
|--|--------------------------|---------------------------|
| Phenolic composition   |                          |                           |
| Total phenols (mg 100 g <sup>-1</sup> FW) $o$ -diphenols (mg 100 g <sup>-1</sup> FW) | 59.6 ± 5.42 <sup>b</sup> | $73.0 \pm 4.11^{a^*}$     |
| o-diphenols (mg 100 g <sup>-1</sup> FW)  | 7.4 ± 1.17 <sup>b</sup>  | $15.4 \pm 0.49^{a^{**}}$  |
| Flavonoids (mg 100 $g^{-1}$ FW)  | $8.8 \pm 0.68^{b}$       | $12.2 \pm 0.96^{a^{**}}$  |
| Tannins (mg 100 g <sup>-1</sup> FW)  | 14.0 ± 1.04 <sup>b</sup> | 17.2 ± 1.37 <sup>a*</sup> |
| Anthocyanins (mg 100 g <sup>-1</sup> FW)   | $3.7 \pm 0.76$           | $2.5 \pm 0.09$            |
| Antioxidant activity   |                          |                           |
| Reducing power   | $0.59 \pm 0.04$          | $0.65 \pm 0.01$           |
| ABTS (mmol Trolox kg <sup>-1</sup> )   | $0.48 \pm 0.03^{b}$      | $0.56 \pm 0.02^{a^{**}}$  |
| DPPH (%)   | $62.9 \pm 1.46$          | $70.3 \pm 4.51$           |

Values are expressed as means  $\pm$  standard deviation (n = 3). Different letters for the same parameter, within rows indicate significant differences (\* $p \le 0.05$ ; \*\* $p \le 0.01$ ) between cultivars.



With respect to the literature, most authors have evaluated the antiradical activity of the globe artichoke extract using the DPPH free radical. Lombardo et al. [33] tested the DPPH activity in the receptacle of clones of two Sicilian globe artichokes landraces and found that 'Clone VI' had the highest antioxidant activity. In our findings, the highest antioxidant activities were linked to the highest phenols, tannins, and flavonoids contents. The antioxidant capacity measured using ABTS or reducing power of the methanolic extracts from globe artichoke by-products was evaluated by different authors [14,36,40] and the results obtained were higher than those in this study. These differences could be attributed to the quantitative and qualitative polyphenols profile characterizing the specific part of the plant under study.

# **Conclusion**

Data obtained herein suggested that receptacles of Tunisian globe artichoke cultivars represent a good source of health-promoting compounds, and therefore could encourage the consumption of this crop. In particular, 'Violet d'Hyéres' could be preferred for consumption, because of its major antioxidant activities. Indeed, this investigation showed that the receptacle of the studied cultivars has a good content of unsaturated FA, such as linoleic and linolenic acids, mainly in 'Blanc d'Oran', which are important hypocholesterolemic compounds. Significant differences in the volatile compounds were observed between the two Tunisian globe artichoke cultivars. Nevertheless, further investigations are needed to evaluate the variation of the considered compounds in other Tunisian cultivars.

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# References

- 1. Lombardo, S.; Pandino, G.; Mauromicale, G. The Nutraceutical Response of Two Globe Artichoke Cultivars to Contrasting NPK Fertilizer Regimes. Food Research International 2015, 76, 852-859.
- 2. FAOSTAT. Food and Agriculture Organization of the United Nations Statistics Division, FAO: Rome, Italy, 2013.
- 3. Lombardo, S.; Pandino, G.; Mauromicale, G.; Carle, R.; Knödler, M.; Schieber, A. Polyphenol and Mineral Profile of 'Violetto Di Sicilia', a Typical Italian Varietal Globe Artichoke. Acta Horticulturae 2012, 942, 445-450.
- 4. Lombardo, S.; Pandino, G.; Ierna, A.; Mauromicale, G. Variation of Polyphenols in a Germplasm Collection of Globe Artichoke. Food Research International 2012, 46, 544-551.
- 5. Romani, A.; Pinelli, P.; Cantini, C.; Cimato, A.; Heimler, D. Characterization of Violetto Di Toscana, a Typical Italian Variety of Artichoke (Cynara scolymus L.). Food Chemistry 2006, 95, 221-225.
- 6. Pandino, G.; Lombardo, S.; Mauromicale, G.; Williamson, G. Characterization of Phenolic Acids and Flavonoids in Leaves, Stems, Bracts and Edible Parts of Globe Artichokes. Acta Horticulturae 2012, 942, 413-417.
- 7. Ceccarelli, N.; Curadi, M.; Picciarelli, P.; Martelloni, L.; Sbrana, C.; Giovannetti, M. Globe Artichoke as a Functional Food. Mediterranean Journal of Nutrition and Metabolism 2010, 3, 197-201.
- 8. De Falco, B.; Incerti, G.; Amato, M.; Lanzotti, V. Artichoke: Botanical, Agronomical, Phytochemical, and Pharmacological Overview. Phytochemistry Reviews 2015, 14, 993–1018.
- 9. Nassar, M.I.; Mohamed, T.K.; Elshamy, A.I.; El-Toumy, S.A.; Lateef, A.M.A.; Farrag, A.R.H. Chemical Constituents and Anti-Ulcerogenic Potential of the Scales of Cynara scolymus (Artichoke) Heads. Journal of the Science of Food and Agriculture 2013, 93, 2494-2501.



- 10. Dabbou, S.; Dabbou, S.; Flamini, G.; Pandino, G.; Gasco, L.; Helal, A.N. Phytochemical Compounds from the Crop Byproducts of Tunisian Globe Artichoke Cultivars. Chemistry & Biodiversity 2016, 13, 1475-1483.
- 11. Claus, T.; Maruyama, S.A.; Palombini, S.V.; Montanher, P.F.; Bonafé, E.G.; Junior, O.D.O.S.; Matsushita, M.; Visentainer, J.V. Chemical Characterization and Use of Artichoke Parts for Protection from Oxidative Stress in Canola Oil. LWT-Food Science and Technology 2015, 61, 346-351.
- 12. Falleh, H.; Ksouri, R.; Chaieb, K.; Karray-Bouraoui, N.; Trabelsi, N.; Boulaaba, M.; Abdelly, C. Phenolic Composition of Cynara cardunculus L. Organs, and Their Biological Activities. Comptes Rendus Biologies **2008**, *331*, 372–379.
- 13. Khalid, S.; Chaouachi, F.; Ksouri, R.; El Gazzah, M. Polyphenolic Composition in Different Organs of Tunisia Populations of Cynara cardunculus L. and Their Antioxidant Activity. Journal of Food and Nutrition Research 2013, 1, 1-6.
- 14. Dabbou, S.; Dabbou, S.; Pandino, G.; Lombardo, S.; Mauromicale, G.; Chahdoura, H.; Gasco, L.; Helal, A.N. In Vitro Antioxidant Activities and Phenolic Content in Crop Residues of Tunisian Globe Artichoke. Scientia Horticulturae 2015, 190, 128-136.
- 15. Mauromicale, G.; Ierna, A. Characteristics of Heads of Seed-Grown Globe Artichoke [Cynara cardunculus L. Var. scolymus (L.) Fiori] as Affected by Harvest Period, Sowing Date and Gibberellic Acid. Agronomie 2000, 20, 197-204.
- 16. Peiretti, P.G.; Gai, F.; Tassone, S. Fatty Acid Profile and Nutritive Value of Quinoa (Chenopodium quinoa Willd.) Seeds and Plants at Different Growth Stages. Animal Feed Science and Technology 2013, 183, 56-61.
- 17. Davies, N.W.; Gas Chromatographic Retention Indices of Monoterpenes and Sesquiterpenes on Methyl Silicon and Carbowax 20 M Phases. Journal of Chromatography A 1990, 503, 1-24.
- 18. Adams, R.P.; Identification of Essential Oils Components by Gas Chromatography/Mass Spectroscopy; Allured: Carol Stream, IL, 2007.
- 19. Stenhagen, E.; Abrahamsson, S.; McLafferty, F.W. Registry of Mass Spectral Data; Wiley: New York, USA, 1974.
- 20. NIST. National Institute of Standards and Technology. PC Version 1.7 of the NIST/EPA/NIH Mass Spectral Library; Perkin Elmer: Norwalk, CT, 2014.
- 21. Montedoro, G.; Servili, M.; Baldioli, M.; Miniati, E. Simple and Hydrolyzable Phenolic Compounds in Virgin Olive Oil. 1. Their Extraction, Separation, and Quantitative and Semiquantitative Evaluation by HPLC. Journal of Agricultural and Food Chemistry 1992, 40, 1571-1576.
- 22. Mancinelli, A.L.; Yang, C.P.H.; Lindquist, P.; Anderson, O.R.; Rabino, I. Photocontrol of Anthocyanin Synthesis III. The Action of Streptomycin on the Synthesis of Chlorophyll and Anthocyanin. Plant Physiology 1975, 55, 251-257.
- 23. Zhishen, J.; Mengcheng, T.; Jianming, W. The Determination of Flavonoid Contents in Mulberry and Their Scavenging Effects on Superoxide Radicals. Food Chemistry 1999, 64, 555-559.
- 24. Julkunen-Tiitto, R.; Phenolic Constituents in the Leaves of Northern Willows: Methods for the Analysis of Certain Phenolics., Journal of Agricultural and Food Chemistry 1985, 33, 213-217.
- 25. Kontogiorgis, C.; Hadjipavlou-Litina, D. Biological Evaluation of Several Coumarin Derivatives Designed as Possible Anti-Inflammatory/Antioxidant Agents. Journal of Enzyme Inhibition and Medicinal Chemistry 2003,
- 26. Rice-Evans, C.A.; Miller, N.J.; Paganga, G. Structure-Antioxidant Activity Relationships of Flavonoids and Phenolic Acids. Free Radical Biology and Medicine 1996, 20, 933-956.
- 27. Re, R.; Pellegrini, N.; Proteggente, A.; Pannala, A.; Yang, M.; Rice-Evans, C. Antioxidant Activity Applying an Improved ABTS Radical Cation Decolorization Assay. Free Radical Biology and Medicine 1999, 26, 1231–1237.
- 28. Dabbou, S.; Brahmi, F.; Taamali, A.; Issaoui, M.; Ouni, Y.; Braham, M.; Zarrouk, M.; Hammami, M. Extra Virgin Olive Oil Components and Oxidative Stability from Olives Grown in Tunisia. Journal of the American Oil Chemists' Society **2010**, 87, 1199–1209.
- 29. Oyaizu, M.; Studies on Products of Browning Reaction: Antioxidative Activity of Products of Browning Reaction. Japanese Journal of Nutrition 1986, 44, 307-315.
- 30. Dosi, R.; Daniele, A.; Guida, V.; Ferrara, L.; Severino, V.; Di Maro, A. Nutritional and Metabolic Profiling of the Globe Artichoke ('Cynara scolymus' L.'capuanella' Heads) in Province of Caserta, Italy. Australian Journal of Crop Science 2013, 7, 1927–1934.
- 31. MacLeod, A.J.; Pieris, N.M.; De Troconis, N.G. Aroma Volatiles of Cynara scolymus and Helianthus tuberosus. Phytochemistry 1982, 21, 1647-1651.
- 32. Fratianni, F.; Pepe, R.; Nazzaro, F. Polyphenol Composition. Antioxidant, Antimicrobial and Quorum Quenching Activity of the "Carciofo Di Montoro" (Cynara cardunculus Var. scolymus) Global Artichoke of the Campania Region, Southern Italy. Food and Nutrition Sciences 2014, 5, 2053-2062.
- 33. Lombardo, S.; Pandino, G.; Mauromicale, G. Total Polyphenol Content and Antioxidant Activity among Clones of Two Sicilian Globe Artichoke Landraces, Acta Horticulturae 2013, 983, 95-101.
- 34. Fratianni, F.; Tucci, M.; De Palma, M.; Pepe, R.; Nazzaro, F. Polyphenolic Composition in Different Parts of Some Cultivars of Globe Artichoke (Cynara cardunculus L. Var. scolymus (L.) Fiori). Food Chemistry 2007, 104, 1282-1286.



- 35. Pandino, G.; Lombardo, S.; Monaco, A.L.; Mauromicale, G. Choice of Time of Harvest Influences the Polyphenol Profile of Globe Artichoke. Journal of Functional Foods **2013**, *5*, 1822–1828.
- Oliveira, G.L.D.S.; Souza, A.A.D.; Freitas, R.M.D.; Cavalcante, A.A.D.C.M.; Oliveira, F.R.D.A.M.; Gomes Junior, A.L.; Alencar, M.V.O.B.D. Evaluation of Antioxidant Capacity of the Aqueous Extract of *Cynara scolymus* L. (Asteraceae) in Vitro and in Saccharomyces Cerevisiae. African Journal of Pharmacy and Pharmacology 2014, 8, 136–147.
- 37. Schütz, K.; Persike, M.; Carle, R.; Schieber, A. Characterization and Quantification of Anthocyanins in Selected Artichoke (*Cynara scolymus* L.) Cultivars by HPLC-DAD-ESI-Msn. Analytical and Bioanalytical Chemistry **2006**, 384, 1511–1517.
- 38. Llorach, R.; Espin, J.C.; Tomás-Barberán, F.A.; Ferreres, F. Artichoke (*Cynara scolymus* L.) Byproducts as a Potential Source of Health-promoting Antioxidant Phenolics. Journal of Agricultural and Food Chemistry **2002**, *50*, 3458–3464.
- 39. Gebhardt, R.; Antioxidative and Protective Properties of Extracts from Leaves of the Artichoke (*Cynara scolymus* L.) against Hydroperoxide-induced Oxidative Stress in Cultured Rat Hepatocytes. Toxicology and Applied Pharmacology **1997**, *144*, 279–286.
- 40. Durazzo, A.; Foddai, M.S.; Temperini, A.; Azzini, E.; Venneria, E.; Lucarini, M.; Finotti, G.; Maiani, G.; Crinò, P.; Saccardo, F.; Maiani, G. Antioxidant Properties of Seeds from Lines of Artichoke, Cultivated Cardoon and Wild Cardoon. Antioxidants 2013, 2, 52–61.