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Phytochemical compounds from the crop by-products of Tunisian globe artichoke cultivars

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Abstract

The phytochemical composition in two Tunisian globe artichoke cultivars (bracts, leaves and floral stems) was evaluated in the plant by-products. The results have indicated that the bracts contain the highest levels of total phenols, *o*-diphenols and flavonoids, whereas tannins seem to be more abundant in the leaves. Bracts from the 'Violet d'Hyéres' cultivar possessed more total phenols (160.8 mg g^{-1} DW), flavonoids (64.9 mg g^{-1} DW) and anthocyanins (15.3 µg g^{-1} DW) than the 'Blanc d'Oran' bracts (134.5 mg g^{-1} DW, 51.2 mg g^{-1} DW and 8.3 µg g^{-1} DW, respectively). Sixty-four volatile compounds were identified in the headspace of globe artichoke material, particularly in the bracts. The volatile profile showed that sesquiterpene hydrocarbons and non-terpene derivatives were the main volatiles emitted by the bracts in both cultivars. These results suggest that globe artichoke by-products might represent a potential source of natural compounds, which could be used as nutraceuticals or as ingredients in the design of functional foods.

Key words: globe artichoke, pigments, total phenols, volatile compounds.

Introduction

Secondary metabolites (i.e. phenolic acids, flavonoids, tannins) are compounds that are produced by plants and which are involved in the defence against biotic and abiotic stressors [1]. These compounds have also been found to provide a beneficial effect to human health, when they are consumed in the diet [2]. From the technological food point of view, these metabolites play an important role against oxidative damage, and thus prevent quality deterioration [3]. However, the continuous request from consumers for a sustainable source and environmentally friendly production has increased scientific interest in the search for potential natural compounds in plant materials and agro-industrial by-products [4].

The globe artichoke [*Cynara cardunculus* L. var. *scolymus* (L.) Fiori] is a herbaceous perennial crop that is widely cultivated in the Mediterranean area [5]. The heads, i.e., the large immature inflorescences with edible fleshy leaves and receptacles, are used worldwide and represent a fundamental ingredient of the Mediterranean diet. The by-products of globe artichokes (leaves, bracts and floral stems), which are rich in caffeoylquinic acids and flavones, constitute a huge amount of discarded material [6], [7]. These by-products have been studied to establish the possibility of using them for animal feedstuff [8]–[10], as fiber and a source of natural antioxidants [11], [12]. Peshel et al. [13] screened eleven fruit and vegetable by-products and two minor crops to establish the possibility of industrially exploiting their polyphenols by determining their extraction yield, total phenolic content and antioxidant activity. The extracts obtained from apple, golden rod and globe artichoke by-products resulted to have the highest antioxidant activity and phenolic content. However, to the best of the authors' knowledge, few studies have been conducted on the evaluation of the pigments and volatile compounds of globe artichoke by-products (bracts, leaves and floral stem).

In this context, the aim of this research was to define the volatile compound profile, and to quantify the total content of pigments in the crop by-products of two Tunisian globe artichoke cultivars, as well as their total amount in phenols, flavonoids and tannins. The polyphenol profile in the crop by-products of these cultivars has recently been reported [14].

Results and Discussion

Total phenol and o-diphenol contents

Significant differences ($p<0.05$) were observed among the different parts of the globe artichoke plants (Table 2). The bracts showed the highest values of total phenols (TP) for both cultivars (134.5 – 160.8 mg g^{-1} DW for 'Blanc d'Oran' and 'Violet d'Hyéres', respectively), and they were followed by the floral stems and leaves. This non-uniform distribution of the total phenols in the globe artichoke plant parts is in good agreement with a previous study [15]. In an earlier research, it was proved that globe artichoke plants accumulate more phenols in the flower heads than in the leaves [16]. Here, the lowest amount of TP was found in the leaves, as was also observed by Fratianni et al. [17]. However, it is also worth noting that the variation in TP within the parts of the globe artichoke was found to be cultivar-dependent. However, 'Violet d'Hyéres' did not report any statistical difference in TP and *o*-diphenols between the leaves and the floral stem, which on average showed a 47% lower TP content than the bracts (Table 2). Similar results were found for 'Blanc d'Oran', where no statistical difference was observed between the leaves and floral stems, in terms of TP and *o*-diphenols (Table 2). The highest amount of *o*-diphenols was observed in the bracts of both globe artichoke cultivars [88.3 and 76.8 mg hyroxytyrosol equivalents (HE) g^{-1} DW, respectively for 'Violet d'Hyéres' and 'Blanc d'Oran'] (Table 2). These results indicate that Tunisian globe artichoke by-products could represent an important source of polyphenols for therapeutic activities and phytopharmaceutical applications.

Total flavonoid content

As far as the total flavonoids (TF) are concerned, statistical differences were found between the bracts, floral stems and leaves (Table 2). The levels varied considerably, from 9.2 to 64.9 mg (catechin equivalent) CE g^{-1} DW for the floral stem and bracts of 'Violet d'Hyéres', and from 7.8 to 51.2 mg CE g^{-1} for the floral stem and bracts of 'Blanc d'Oran'. The leaves had an intermediate level of TF (16.7 and 18.9 mg CE g^{-1} DW for 'Violet d'Hyéres' and 'Blanc d'Oran', respectively) in both cultivars. These results are in contrast with previous ones [16] [18], which reported that leaves contained higher amounts of flavonoids, while they were very poor in the floral stem. Falleh [19] also recorded higher amounts of flavonoids in the leaves of a Tunisian cardoon type than in the flowers and seeds. On the contrary, Khaldi et al. [20] showed that the methanolic extract of floral stems contained higher levels of flavonoids (12.7 mg CE g^{-1} DW) than the seeds. Similarly, Fratianni et al. (2007) found a low content of flavonoids in the leaves. This discrepancy might be due to the different genetic backgrounds and growing conditions of the examined cultivars.

Total condensed tannin content

Tannins were recorded in all of the studied globe artichoke by-products, although they were found at a lower level than the other phenolic compounds. The highest total tannin contents were obtained in the leaves of both cultivars, with 8.9 mg CE g^{-1} DW for 'Violet d'Hyéres' and 12.3 mg CE g^{-1} DW for 'Blanc d'Oran' (Table 2). The total tannin contents in the bracts of both cultivars showed an analogous variation to that of the total phenols, *o*-diphenols and flavonoids. The lowest level of tannins was reported in the floral stems of both cultivars (Table 2). The present results are in agreement with a previous work, in which the lowest tannin content was reported in the floral stems of globe artichokes [20].

Total anthocyanin content

Significant differences were reported between the two cultivars for the bracts, leaves and floral stems (Table 2). The highest total anthocyanin content was found in the leaves of 'Blanc d'Oran' (20.5 µg g^{-1} DW). In addition, this cultivar displayed a greater variability, in terms of total anthocyanin content, than 'Violet d'Hyéres', and ranged from 5.9 (floral stem) to 20.5 µg g^{-1} DW (leaves). As mentioned above, for the flavonoid and tannin contents, these results suggest that the accumulation of anthocyanins within a cultivar varies over the different parts of a plant. Schütz et al. [21] reported that the anthocyanin content in the heads was significantly affected by the type of cultivar. However, it is difficult to make a comparison of the anthocyanin content in globe artichokes, due to the lack of available data in the literature.

Carotenoid and chlorophyll content

The results showed that the highest levels of total carotenoids were in the leaves of both cultivars (Table 3). This could be explained by considering the important role that the pigments play in plant tissues as photoprotectors and light energy receptors [22]. Since the leaf is the organ that is most exposed to the Sun, its photosynthetic membranes stimulate the production of pigments. In previous works, greater flavonoid and caffeoylquinic acid contents were reported in the leaves of globe artichokes, due to UV exposure [23], [24]. The consumption of carotenoids with the diet has been associated with a decreased incidence of cancer, due to their documented biological activities [25]. Pistón et al. [26] have recently demonstrated the nutraceutical value of the infusion of globe artichoke leaves. In this contest, the obtained data suggest that the leaves of these Tunisian globe artichoke cultivars could represent a good source of carotenoids for the Mediterranean diet. As expected, the

chlorophyll content was found to be higher in the leaves than in the other parts for both cultivars. However, to the best of the authors' knowledge, no data on the pigment contents of globe artichoke by-products are available in the literature that would allow the authors to draw inferences.

Volatile compounds

The results of the GC-MS analysis of the artichoke by-product volatiles are presented in Table 4. Overall, sixty-four compounds, representing 93 - 99% of the total volatiles, were identified, with 2,3-butandiol, hexanal, *(E)*-2-octenal, *(E,Z)*-3,5-octadien-2-one, *n*-undecane, nonanal, 2,6-dimethylcyclohexanol, β-caryophyllene, β-selinene and *(E)*-β-ionone being the main ones. Significant differences were observed, in the identified volatile compounds, in the different parts of the plants of both cultivars, with the highest levels being found in the bracts. Taking into account the chemical classes, sesquiterpene hydrocarbons (68 *vs* 74%) and non-terpene derivatives (25 *vs* 20%) were the main compounds of the 'Violet d'Hyères' and 'Blanc d'Oran' bracts, respectively. Non-terpene derivatives were more abundant in the leaves and floral stems of both cultivars, with the highest level being found in 'Blanc d'Oran'. Oxygenated sesquiterpenes were only detected in the bracts, while nitrogen derivatives were only found in the floral stems. Even though the emitted volatiles that are sampled by means of SPME are not directly comparable with essential oils, Nassar et al. [27] reported that mono- and sesquiterpenes are the main compounds (about 76%) of the oil obtained from the bracts. Other hydrocarbons (including heavily oxygenated hydrocarbons and lightly oxygenated hydrocarbons) represent 18% of the total amount of identified compounds in the head scales of globe artichokes. The same authors showed that cyclosativene, one of the sesquiterpene hydrocarbons that has been identified in the present study, but only in the floral stem of 'Blanc d'Oran', was the main active constituent in globe

artichokes. Furthermore, β-selinene, which exhibits an antioxidant activity [28], was the most abundant compound in the bracts of both cultivars. In contrast, Ghanem et al. [29] reported that β-selinene was the main compound of the leaves of globe artichokes. Other authors have reported that sesquiterpene hydrocarbons are the main group of components in globe artichokes, with β-selinene being the main constituent (about 32%) [30].

Conclusions

To the best of the authors' knowledge, this manuscript has reported a combined comparison of phenolic, pigment and volatile compounds in the by-products of globe artichoke for the first time. Significant differences in the level of total phenol concentrations, *o*-diphenols, flavonoids and tannins have been pointed out, depending on both the part of the plant and on the cultivar. Significant differences in the volatile compounds emitted by the different plant parts have also been observed in both cultivars, with the highest levels in the bracts. From the above results, it is possible to conclude that the bracts, leaves and floral stems, which are generally considered as waste products, could provide an added economic benefit through the extraction of possible natural antioxidants. In fact, these globe artichoke by-products contain powerful antioxidant substances, which may be responsible for its anti-inflammatory and chemoprotective properties. In addition, the presence of these compounds justifies the use of globe artichoke plant extracts as both folkloric remedies and as ingredients to functionalize foodstuffs (to decrease lipid peroxidation and to increase health-promoting properties) as well as a potential source for pharmaceutical industries.

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Experimental part

Plant Material, experimental field and management practices

The globe artichoke cultivars under study were 'Blanc d'Oran' and 'Violet d'Hyères', both native plants from northern Tunisia, which produce green heads from April to May. The experimental field was prepared during the 2011-2012 season and located at the experimental station of the Technical Center of Potato and Artichokes in Tunisia, in Jdaida-Mannouba (latitude 36°49'25.24" N, longitude 9°57'55.09"W, altitude 595 m), which is a typical area for the cultivation of globe artichokes in the Mediterranean Basin. The local climate is semi-arid-Mediterranean, with mild winters and hot rainless summers. The soil characteristics of the experimental field are presented in Table 1. The globe artichoke plants were cultivated with spacings (1.2 m * 0.6 m) of 13.888 plants ha^{-1} and (1.2 m * 0.8 m) of 10.416 plants ha^{-1} for the 'Blanc d'Oran' and 'Violet d'Hyères' cultivars, respectively. Crop management practices (irrigation, fertilization, pest management, weed control, etc.) were performed according to the local practices.

Extraction procedure

The plant residue parts of the globe artichoke were treated as described in a previous work [14]. An aliquot of the dried samples (50g) was dissolved in 500 mL of 95% ethanol, as reported by Harikrishnan and Balasundaram [31]. After filtration, the solvent was evaporated at reduced pressure, and all the resulting extracts were then transferred to vials and stored in the dark at 4°C to preserve them from photo-oxidation.

Phenolic compositions

Determination of the total phenols and o-diphenols

The total phenolic and *o*-diphenols contents of the extracts were determined according to the Montedoro et al. method [32], with minor modifications. An aliquot of 100 µL of each fraction, diluted with deionised water and 2.5 mL of diluted Folin–Ciocalteu reagent, was mixed for the total phenols. After 1-min of incubation, 2 mL of sodium carbonate (75g L^{-1}) was added and the mixture was incubated for 2h. The absorbance was measured at 765 nm. A1mL aliquot of a HCl (0.5N) solution, 1mL of a solution of a mixture of $NaNO_2$ (10g) and $NaMoO_4 \cdot 2H_2O$ (10g) in 100 mL H_2O and 1 mL of a solution of NaOH (1N) were added to 100 µL of the extract for the *o*-diphenols. After 30 min, the absorbance was read at 500 nm. The total phenols and *o*-diphenols were expressed as mg HE g^{-1} DW.

Determination of the total flavonoids

The total flavonoid contents of the extracts were determined according to the colorimetric assay developed by Zhishen et al. [33]. In brief, 250 µL of each extract or standard solution was mixed with 1.25 mL of distilled water. At zero time, 75 µL of a 5% (w/v) $NaNO_2$ solution was added. After 5 min, 150 µL of a 10% (w/v) $AlCl_3$ solution was added. At 6 min, 0.5 mL of a 1M solution of NaOH was added. Finally, the volume was immediately adjusted to 2.5 mL by adding 275 µL of distilled water. The mixture was shaken vigorously and the absorbance was read at 510 nm. The results were expressed as mg CE g^{-1} DW.

Determination of the condensed tannins

The condensed tannins were determined according to the Julkunen-tiitto method [34]. An aliquot (50µL) of each extract or standard solution was mixed with 1.5mL of a 4% vanillin methanol solution, and then 750µL of HCl was added. The well-mixed solution was

incubated in the dark at room temperature for 20 min. The absorbance against a blank was read at 500 nm. The results were expressed as mg CE g^{-1} DW.

Determination of the total anthocyanins

An amount (0.25g) of powder was extracted in the dark with 10 mL of acidified methanol (1% HCl), kept for 30 min at 37°C and then centrifuged for 15 min. The total anthocyanins were calculated from the methanolic extract as $[(A_{530}- (0.33* A_{657}))*V*DF]/w$, where V was the volume of the sample (mL); DF the dilution factor, w (g) the weight of the sample and A the absorbance. The results were expressed as µg cyanidin-3-glucoside per g DW [35].

Volatile compounds

Supelco (Bellofonte, PA) SPME (Solid Phase Micro-Extraction) devices coated with polydimethylsiloxane (PDMS, 100 µm) were used to sample the headspace of each sample inserted into a 5 mL glass vial and allowed to equilibrate for 30 min.

SPME sampling was performed using the same fiber, preconditioned according to the manufacturer's instructions, for all the analyses. Sampling was conducted in an air-conditioned room (22±1°C) in order to guarantee a stable temperature. After the equilibration, the fiber was exposed to the headspace for 50 min. Once sampling had been finished, the fiber 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 the relative peaks areas were performed for the same chemicals in the different samples.

GC–MS analyses were performed with a Varian (Palo Alto, CA) CP 3800 gas chromatograph equipped with a DB-5 capillary column (30 m x 0.25 mm x 0.25 µm; Agilent, Santa Clara,

CA) and a Varian Saturn 2000 ion trap mass detector. The analytical conditions were as follows: the injector and transfer line temperatures were 250 and 240 °C, respectively; the oven temperature was programmed from 60 to 240 °C at 3 °C/min; the carrier gas was helium at 1 mL/min; a splitless injector was used. The identification of the constituents was based on a comparison of the retention times with those of authentic samples, comparing their linear retention index relative to a series of n-hydrocarbons, and on computer matching against commercial (NIST 98 and Adams 95) and homemade library mass spectra, built from pure substances and MS literature data [36]–[41]. The results were expressed as percent values.

Pigment composition

The extraction of pigments was carried out in the dark with 25 mL of acetone (99.9%) and approximately 0.21 g of the powdered samples. The tissues were agitated in a water bath at 30 °C for 20 min and then filtered using Whatman No. 1 filter paper. About 1.0 g of anhydrous Na_2SO_4 was added to the filtrate [42]. The total volume of the extract was recorded. Absorbance readings were taken at 470, 645, 662 and 663 nm. The content of chlorophyll a and b (Ca and Cb) and that of the total chlorophylls (CTC), all of which were expressed as μg mL-1,were calculated according to the following formulas [43]–[45]:

$$C_a = (11{,}75 \times A_{662}) - (2{,}35 \times A_{645})$$

$$C_b = (18{,}61 \times A_{645}) - (3{,}96 \times A_{662})$$

$$C_{TC} = (7{,}06 \times A_{662}) + (18{,}09 \times A_{645})$$

The total carotenoid concentration (expressed as μg mL-1) was calculated as Cx+c = concentration of xanthophylls (x) and carotenes (c), using the following relationship [44]–[46]:

$$C_{x+c} = \frac{1000\ A470 - 1.90\ C_a - 63.14 C_b}{214}$$

where C = concentration, x = xanthophylls, c = carotenes, C_a = concentration of chlorophyll a, C_b = concentration of chlorophyll b, C_{TC} = concentration of total chlorophylls (all as µg mL^{-1}).

Statistical analysis

Significant differences between varieties were determined by means of the Students t-test, whereas significant differences between the globe artichoke parts were determined by means of the Duncan test (p<0.05), using the SPSS program, release 17.0 for Windows (SPSS, Chicago, IL, USA). All the data represent the mean values of three independent experiments (n=3).

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Table 1. Soil characteristics of the experimental site.

Soil characteristics	
Clay (%)	49.3
Silt (%)	32
Sand (%)	14.60
Retention capacity (mL/100g)	63
Na^{+} (ppm)	310
K^{+} (ppm)	516
Ca^{++} (ppm)	0.76
Mg^{+} (ppm)	680
CEC meq/100g	26.2
Total limestone (%)	26
pH 1/25	8.10
Active limestone (%)	18
Iron (ppm)	10
Carbon (%)	0.83
Organic matter (%)	1.43
Total nitrogen (‰)	0.86
P (ppm)	7.04
Salinity (g/L)	0.49
Exchangeable K_2O (ppm)	622
Available P_2O_5 (ppm)	16
Conductivity (ms/cm)	0.76

Table 2

Total phenols composition from bracts, leaves and floral stem of globe artichoke of the two cultivars grown in Tunisia

	Violet d'Hyères			*Blanc d'Oran*		
Phenols composition	**Bracts**	**Leaves**	**Floral stem**	**Bracts**	**Leaves**	**Floral stem**
Phenols (mg g^{-1} DW)	160.8±24.6 $^{(a,*)}$	84.5±2.3 $^{(b,*)}$	85.7±5.55^{b}	134.5±3.64$^{(x)}$	79.2±1.56$^{(y)}$	80.62±1.9 $^{(y)}$
o-diphenols (mg g^{-1} DW)	88.3±14.7($^{a)}$	58.8±2.0 $^{(b,**)}$	55. 6±9.8^{b}	76.8±4.1$^{(x)}$	47.8±3.4 $^{(y)}$	44.1±8. 7$^{(y)}$
Flavonoids (mg g^{-1} DW)	64.9±1.0($^{a,**)}$	16.7±0.6 $^{(b,*)}$	9.2±0.4$^{(c,**)}$	51.2±1.8 $^{(x)}$	18.9±0. 8$^{(y)}$	7.8±0.3$^{(z)}$
Tannins (mg g^{-1} DW)	4.7±0.4^{b}	8.9±1.8$^{(a)}$	1.52±0.2 $^{(c,**)}$	6.0±1.7 $^{(y)}$	12.3±1.3 $^{(x)}$	4.29±0.01$^{(y)}$
Anthocyanins (µg g^{-1} DW)	15.3±0.1$^{(a,**)}$	14.7±0.7$^{(b,**)}$	12.7±2.0$^{(c,**)}$	8.3±0.3$^{(y)}$	20.5±1.4$^{(x)}$	5.9±0.2$^{(z)}$

Mean composition of sampled globe artichoke from three replications ± standard deviation. Different letters (a–c) and (x-z), for the same parameter, within each row indicate significant differences ($p \leq 0.05$) among plant parts of each cultivar. Different symbols (*, **), for the same parameter, within columns indicate significant differences (*$p < 0.05$; **$p < 0.01$) among plant parts of each cultivar. DW: dry weight.

Table 3

Pigments composition (µg mL^{-1}) of bracts, leaves and floral stem of globe artichoke of the two cultivars grown in Tunisia

	Violet d'Hyères			*Blanc d'Oran*		
Pigment composition	**Bracts**	**Leaves**	**Floral stem**	**Bracts**	**Leaves**	**Floral stem**
Carotenoid						
total carotenoids	$0.1\pm0.01^{(b,**)}$	$0.9\pm0.07^{(a,**)}$	$0.1\pm0.01^{(b,**)}$	$0.2\pm0.01^{(y)}$	$0.6\pm0.01^{(x)}$	$0.1\pm0.01^{(z)}$
Chlorophyll						
chlorophyll a	$0.8\pm0.01^{(b,**)}$	$9.8\pm0.89^{(a,*)}$	$0.6\pm0.01^{(b,**)}$	$2.3\pm0.01^{(y)}$	$8.2\pm0.04^{(x)}$	$0.7\pm0.02^{(z)}$
chlorophyll b	$0.6\pm0.03^{(b,**)}$	$6.0\pm0.17^{(a,**)}$	$0.3\pm0.01^{(c,**)}$	$2.7\pm0.01^{(y)}$	$4.8\pm0.02^{(x)}$	$0.6\pm0.01^{(z)}$
total chlorophylls	$1.5\pm0.02^{(b,**)}$	$15.9\pm0.73^{(a,**)}$	$0.9\pm0.02^{(c,**)}$	$4.9\pm0.01^{(y)}$	$13.0\pm0.05^{(x)}$	$1.2\pm0.03^{(z)}$

Mean composition of sampled globe artichoke from three replications ± standard deviation. Different letters (a–c) and (x-z), for the same parameter, within each row indicate significant differences ($p \leq 0.05$) among plant parts of each cultivar. Different symbols (*, **), for the same parameter, within columns indicate significant differences (*$p < 0.05$; **$p < 0.01$) among plant parts of each cultivar

Table 4

Volatile compounds (expressed as percent) from bracts, leaves and floral stem of artichoke of the two cultivars grown in Tunisia

Volatile compounds	**LRI**	***Violet d'Hyères***			***Blanc d'Oran***		
		Bracts	**Leaves**	**Floral stem**	**Bracts**	**Leaves**	**Floral stem**
limonene	1032	1.8±0.7^{b}	4.5±0.1$^{(a,*)}$	3.5±0.7$^{(a,*)}$	1.6±0.1$^{(x)}$	2.4±1.0$^{(x)}$	1.8±0.5$^{(x)}$
Monoterpene hydrocarbons		**1.8±0.7**^{b}	**4.5±0.1**$^{(a,*)}$	**3.5±0.7**$^{(a,*)}$	**1.6±0.1**$^{(x)}$	**2.4±1.0**$^{(x)}$	**1.8±0.5**$^{(x)}$
camphor	1145	0.6±0.1$^{(a}$	2.2±0.1$^{(a,*)}$	4.2±3.1$^{(a}$	0.5±0.1$^{(y)}$	1.3±0.3$^{(x)}$	1.1±0.01$^{(x)}$
Oxygenated monoterpenes		**0.6**±0.1$^{(a}$	**2.2±0.1**$^{(a,*)}$	**4.2±3.1**$^{(a}$	**0.5±0.1**$^{(y)}$	**1.3±0.3**$^{(x)}$	**1.1±0.01**$^{(x)}$
α-longipinene	1352	0.9±0.1*	-	-	0.5±0.1	-	-
cyclosativene	1370	-	-	-	0.5±0.1	-	-
longicyclene	1372	-	-	-	3.3±0.1	-	-
α-ylangene	1373	0.8±0.2	-	-	-	-	-
α-copaene	1377	-	-	-	0.6±0.1	-	-
β-elemene	1392	0.5±0.2	-	-	0.4±0.01	-	-
longifolene	1404	-	-	-	2.2±0.1	-	-
β-caryophyllene	1419	12.7±1.3$^{(a}$	0.5±0.1$^{(b,*)}$	1.4±1.1^{b}	11.3±0.2$^{(x)}$	0.8±0.1$^{(y)}$	-
trans-α-bergamotene	1437	0.5±0.1	-	-	0.5±0.01	-	-
α-himachalene	1449	-	-	-	0.2±0.1	-	-
α-humulene	1455	0.8±0.1	-	-	0.7±0.01	-	-
α-acoradiene	1464	0.6±0.1	-	-	0.6±0.01	-	-
β-chamigrene	1477	0.2±0.1	-	-	-	-	-
γ-himachalene	1481	3.0±1.0$^{(a}$	-	0.5±0.1^{b}	-	-	-
β-selinene	1486	48.2±1.7$^{(a,*)}$	-	4.9±2.3^{b}	53.2±1.2$^{(x)}$	5.5±0.4$^{(y)}$	2.1±0.1$^{(z)}$
α-muurolene	1500	-	-	-	0.2±0.1	-	-

δ-cadinene	1524	-	-	-	0.3±0.01	-	-
Sesquiterpene hydrocarbons		**68.2±5.1**$^{(a)}$	**0.5±0.1**$^{(b,*)}$	**6.8±3.5**$^{(b,*)}$	**74.5±1.4**$^{(x)}$	**6.3±0.4**$^{(y)}$	**2.1±0.1**$^{(z)}$
caryophyllene oxide	1582	1.7±0.2$^{(*)}$	-	-	2.5±0.1	-	-
Oxygenated sesquiterpenes		**1.7±0.2**$^{(*)}$	-	-	**2.5±0.1**	-	-
safranal	1202	0.6±0.4$^{(b)}$	2.6±0.3$^{(a,*)}$	1.3±0.5$^{(b)}$	0.2±0.1$^{(y)}$	4.3±1.2$^{(x)}$	0.8±0.1$^{(y)}$
β-cyclocitral	1222	0.5±0.2$^{(b)}$	6.1±0.1$^{(a,*)}$	1.3±0.7$^{(b)}$	0.4±0.1$^{(z)}$	3.7±1.3$^{(x)}$	0.5±0.01$^{(y)}$
(E)-β-ionone	1487	-	9.2±0.50$^{(*)}$	-	-	2.4±0.4	-
dihydroactinolide	1536	0.2±0.1$^{(b)}$	2.5±0.1$^{(a)}$	0.3±0.1$^{(b)}$	-	1.8±0.6	-
Apocarotenoids		**1.3±0.6**$^{(b)}$	**20.4±0.2**$^{(a,*)}$	**2.9±1.4**$^{(b)}$	**0.6±0.01**$^{(y)}$	**12.2±2.6**$^{(x)}$	**1.3±0.1**$^{(y)}$
2,5-dimethylpyrazine	913	-	-	1.1±0.3$^{(*)}$	-	-	0.7±0.1
2-ethyl-3-methylpyrazine	1001	-	-	0.6±0.2	-	-	0.9±0.1
2,3,5-trimethylpyrazine	1003	-	-	0.9±0.2$^{(*)}$	-	-	1.4±0.1
2-ethyl-3,5-dimethylpyrazine	1088	-	-	0.9±0.2$^{(*)}$	-	-	2.3±0.2
Nitrogen derivatives		-	-	**3.5±0.6**$^{(*)}$	-	-	**5.3±0.1**
2,3-butandiol	790	1.8±0.2$^{(b)}$	-	30.6±3.6$^{(a*)}$	1.8±0.1$^{(z)}$	13.0±4.0$^{(y)}$	69.1±0.1$^{(x)}$
hexanal	804	5.4±0.8$^{(a)}$	3.4±0.5$^{(b)}$	4.4±0.9$^{(a,b)}$	3.7±0.4	-	-
2-methylbutanoic acid	852	-	0.8±0.1	-	-	-	-
(E)-3-hexen-1-ol	853	-	-	-	-	0.5±0.1	-
(E)-2-hexenal	856	0.4±0.1$^{(b)}$	2.6±0.4$^{(a)}$	-	-	-	-
1-hexanol	869	0.9±0.1$^{(c,*)}$	1.1±0.1$^{(b,*)}$	2.8±0.05$^{(a,*)}$	0.5±0.01$^{(y)}$	2.2±0.6$^{(x)}$	1.8±0.1$^{(x)}$
heptanal	902	-	0.5±0.1$^{(a)}$	0.6±0.1$^{(a)}$	-	-	-
benzaldehyde	962	0.2±0.1$^{(b)}$	2.4±0.2$^{(a,*)}$	0.1±0.06$^{(b)}$	-	1.4±0.2	-
1-octen-3-ol	980	1.1±0.1$^{(a,*)}$	1.2±0.2$^{(a)}$	0.6±0.1$^{(b)}$	0.3±0.1$^{(y)}$	-	0.6±0.01$^{(x)}$
hexanoic acid	985	-	-	-	0.6±0.1	-	-
6-methyl-5-hepten-2-one	987	0.2±0.1$^{(b)}$	1.7±0.1$^{(a)}$	-	-	1.0±0.1	-

2-pentylfuran	994	2.3±0.7$^{(a)}$	2.4±0.1$^{(a,*)}$	2.5±1.3$^{(a)}$	2.4±0.1$^{(x)}$	1.3±0.2$^{(y)}$	1.1±0.1$^{(y)}$
2,2,6-trimethylcyclohexanone	1034	-	1.3±0.1	-	-	1.1±0.3	-
3-octen-2-one	1043	1.7±0.3$^{(a,*)}$	2.2±0.1$^{(a,*)}$	2.1±0.9$^{(a)}$	1.2±0.1$^{(x)}$	0.4±0.1$^{(y)}$	1.1±0.1$^{(x)}$
(E)-2-octenal	1062	-	2.3±0.01$^{(b)}$	3.5±0.5$^{(a,**)}$	0.5±0.01$^{(z)}$	6.7±4.7$^{(x)}$	1.3±0.1$^{(y)}$
(E)-2-octen-1-ol	1071	-	0.8±0.01$^{(**)}$	-	-	3.2±0.4	-
(E,Z)-3,5-octadien-2-one	1076	3.6±0.1$^{(b)}$	13.8±0.1$^{(a,**)}$	7.6±4.7$^{(a,b)}$	3.0±0.5	3.9±1.1	3.2±0.2
2-nonanol	1086	-	-	-	-	0.4±0.1	-
1-undecene	1094	-	-	-	-	3.4±1.6	-
(E,E)-3,5-octadien-2-one	1095	1.0±0.01$^{(a)}$	1.6±0.6$^{(a)}$	2.0±0.9$^{(a)}$	0.8±0.1$^{(y)}$	2.5±1.0$^{(x)}$	1.1±0.1$^{(y)}$
n-undecane	1100	0.6±0.1$^{(b)}$	1.4±0.1$^{(a,**)}$	1.5±0.1$^{(a,**)}$	0.4±0.1$^{(y)}$	9.5±1.0$^{(x)}$	0.5±0.01$^{(y)}$
nonanal	1104	0.8±0.2$^{(b)}$	6.4±0.3$^{(a,**)}$	2.8±1.6$^{(b)}$	0.5±0.01$^{(z)}$	1.9±0.1$^{(x)}$	1.2±0.1$^{(y)}$
2,6-dimethylcyclohexanol	1110	1.7±0.2$^{(b)}$	16.3±0.6$^{(a)}$	3.9±1.7$^{(b)}$	1.3±0.01$^{(z)}$	13.7±0.3$^{(x)}$	1.8±0.2$^{(y)}$
isophorone	1120	-	-	0.3±0.05	-	-	-
3-nonen-2-one	1142	-	1.3±0.1$^{(**)}$	-	-	0.5±0.1	-
(E,Z)-2,6-nonadienal	1155	-	1.2±0.1	-	-	-	-
(E)-2-nonenal	1162	-	-	0.4±0.1	-	-	-
1-nonanol	1172	-	-	0.1±0.05	-	-	-
decanal	1206	0.6±0.2$^{(b)}$	2.7±0.01$^{(a,*)}$	2.8±1.2$^{(a)}$	0.4±0.01$^{(y)}$	1.7±0.6$^{(x)}$	1.9±0.4$^{(x)}$
1-decanol	1272	-	-	-	-	0.6±0.1	-
n-tridecane	1300	-	-	-	-	1.1±0.1	-
(Z)-2-tridecene	1314	-	-	-	-	0.5±0.1	-
2-butyl-2-octenal	1380	0.5±0.2$^{(a)}$	-	0.6±0.01$^{(a)}$	-	-	-
(Z)-jasmone	1394	-	-	1.4±0.4	-	-	-
1-pentadecene	1492	2.6±0.1$^{(a)}$	-	1.4±0.7$^{(b)}$	2.2±0.01$^{(x)}$	0.6±0.1$^{(y)}$	0.7±0.1$^{(y)}$
Non-terpene derivatives		**25.4±2.4**$^{(b,**)}$	**67.4±1.13**$^{(a,**)}$	**72.0±3.8**$^{(a,**)}$	**19.6±1.2**$^{(z)}$	**71.1±5.9**$^{(y)}$	**85.4±1.0**$^{(x)}$
Total identified volatile compounds		**99.0±1.2**$^{(a)}$	**95.0±1.3**$^{(a)}$	**92.9±4.3**$^{(a)}$	**99.3±0.1**$^{(x)}$	**93.3±2.3**$^{(y)}$	**97.0±0.1**$^{(x)}$

Mean composition of sampled globe artichoke from three replications ± standard deviation. Different letters (a–c) and (x-z), for the same parameter, within each row indicate significant differences ($p \leq 0.05$) among plant parts of each cultivar. Different symbols (*, **), for the same parameter, within columns indicate significant differences (*$p < 0.05$; **$p < 0.01$) among plant parts of each cultivar LRI: linear retention index.