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Influence of flower head order on phenolic content and quality of globe artichoke at harvest and during twenty-one days of cold storage

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A B S T R A C T

Artichoke is one of the vegetables with higher content in phenolic compounds, which are responsible for their taste, flavor and health beneficial effects. However, phenolic profile and concentration depends on many factors, such as genotype, harvest date, and environmental and agronomical conditions. The main aim of this study was to perform a phytochemical characterization of artichoke heads, based on their position on plant (main, secondary and tertiary head) and harvest date, during a complete growing season. Results showed that total identified polyphenol concentration was higher in tertiary heads than secondary and main heads, due to their higher concentration in hydroxycinnamic acid and luteolin derivatives. On the other hand, two postharvest storage experiments with main, secondary and tertiary artichoke heads, harvested in winter and spring, were performed. In addition, tertiary head showed the lowest weight, firmness losses and respiration rate during cold storage which could be attributed to their higher antioxidant compounds. In conclusion, tertiary heads have a greater aptitude to be stored at low temperature from harvesting to consumption since they maintained the quality properties for longer period of time and had higher content of bioactive compounds. However, main artichokes are the most appreciated by consumers due to their larger size.

1. Introduction

Globe artichoke [*Cynara cardunculus* L. var. *scolymus* (L.) Fiori] is a vegetable native to the Mediterranean region and its production and consumption has spread around the world in recent years. Artichoke is an immature inflorescence called *capitulum*, bud or head. Globe artichoke plant produce flower head at different order: at the apex of the central stem are formed the largest artichokes (named as primary or main head), while secondary and tertiary heads of smaller size, are developed on the central branches. The total area of artichoke cultivation in Spain is 13.862 hectares whose production is 196.965 tons (MAPA, 2020). Around 60% of production of globe artichoke heads is directed to the fresh market, and the remaining 40% is destined for the canning and freezing industries. For national market, artichokes are harvested with weight ranging from 140 to 160 g. However, largest calibers are chosen (200–500 g) when artichokes are destined for the export market (Baixauli et al., 2013). The edible fraction (receptacle and inner bracts) constitutes nearly 35–55% of the total head weight (Cecarelli et al., 2010). Vegetative propagation is the most common artichoke propagation method around the world (Grabowska et al., 2018). A common practice in Spain is planting lateral shoots with fully-developed roots that are separated from the mother plants, specifically in 'Blanca de Tudela' artichokes, which is the most cultivated cultivar in this country. 'Blanca de Tudela' is an early and re-flowering cultivar that has a large production throughout the year, which starts in autumn and continues until spring, even having two separate production peaks; the first one in winter, due to the first plant which emerges from the rhizome, and the second one in spring due to the second plant which emerges from the exhausted first plant.

Compare to other vegetables, artichokes contain the highest total polyphenol content and its intake provides benefits for human health and well-being (Brat et al., 2006). Specifically, artichoke metabolites provide hepatoprotection, cholesterol-lowering, diuretic, anti-inflammatory and antioxidative effects, and colon cancer protection (De Falco et al., 2015). Apart from having health-promoting properties, phenols are important in determining quality traits such as taste

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and flavor (Lattanzio, 2003). The major phenolic compounds in artichokes are phenolic acids (mono- and di-caffeoylquinic acids) and flavonoids (luteolin and apigenin derivatives) (Schütz et al., 2004; Lattanzio et al., 2009; Pandino et al., 2011; Lombardo et al., 2018). Nevertheless, the quantitative and qualitative profile of phenolic compounds in artichoke heads is influenced by genotype, part of the plant, harvest time, agronomic management and environmental and postharvest conditions (Lombardo et al., 2009; 2010; Cecarelli et al., 2010; Pandino et al., 2013; Scavo et al., 2019). Recently, the influence of artichoke head order and the effect of gibberellic acid treatment have been described in eight different artichoke cultivars (Giménez et al., 2021). This work concluded that tertiary head artichokes showed the highest individual phenolic content, followed by secondary and main heads, and this effect was cultivar-dependent. In addition, the gibberellic acid treatment affected the content of these bioactive compounds depending on the flower head order and artichoke cultivar. However, the effect of artichoke order on plant on crop yield and quality parameters during postharvest cold storage remains unclear.

After harvest, globe artichoke heads are very perishable due to its high respiratory and transpiration rate which could lead to some physiological changes such as weight and firmness losses, bracts hardening and opening, or color changes due to chlorophyll degradation and browning of the bracts apical parts (Ruíz-Jiménez et al., 2014). Furthermore, artichokes are hihgly susceptible to cold damage and several fungal diseases during postharvest storage, mainly caused by *Sclerotinia sclerotiorum* (white mold) (Marcucci et al., 2010) and *Botrytis cinerea* (gray mold) (Larran et al., 2004). For instance, the influence of genotype and harvest date on quality traits of ready-to-use globe artichoke slices during storage has been reported (Licciardello et al., 2017; Pandino et al., 2017a). These studies showed that artichoke cultivars with lower total phenolic concentration were more suitable for minimal processing uses, mainly due to their better color parameters and reduced browning, as well as early harvested artichokes in the growing season as compared with late harvest ones.

In order to maintain artichoke quality heads and to extend their shelf-life up to 3, 4 weeks, artichokes should be cooled after harvest as soon as possible and stored at 0, 1 °C and relative humidity of 90–95% (Gil-Izquierdo et al., 2002). During cold storage of artichoke heads, some changes in secondary metabolism occur and these changes have a direct influence on their quality. On the other hand, an induction of phenylalanine ammonia lyase (PAL) activity causing a biosynthetic increase of phenolics, especially in chlorogenic acid, had been reported by Lattanzio (2003). Significant increases on chlorogenic acid concentration in artichokes stored at 0, 2, 5 and 7 °C were also reported by Gil-Izquierdo et al. (2001). Previous works have showed that preharvest treatments with oxalic acid or methyl jasmonate led to artichokes with a higher phenolic content at harvest, which was related with a delay in the postharvest senescence process, maintenance of artichoke quality traits and extension of their shelf-life (Martínez-Esplá et al., 2017a; 2017b). Thus, the main aim of this study was to characterize 'Blanca de Tudela' artichoke production cycle and its influence on total and individual phenolic content and antioxidant activity of main, secondary and tertiary artichoke heads, as well as the effect of these variables on the artichoke quality maintenance under cold storage conditions. Based on these results, it could be recommended which are the artichokes head orders with the best aptitudes for fresh market or for the industrial processing.

2. Materials and methods

2.1. Plant material and experimental design

For the experiment, 'Blanca de Tudela' cultivar was studied along the developmental cycle from autumn 2017 to spring 2018, in an experimental plot of Miguel Hernández University (Alicante, southeast Spain). The local climate of the cultivation area is Mediterranean, with mild and humid winters and hot and rainless summers. According to historical meteorological data, the minimum monthly temperature ranges between 5 °C (January) and 21.2 °C (August) and maximum temperature between 16.2 °C (January) and 33.3 °C (July).Thus, 50 lateral offshoots from first-year artichoke plants for each replicate or block, were planted at the beginning of August, 0.8 m apart within a row and 1.2 m apart among close rows.Three replicates of 50 plants were used (150 plants in total), leaving a borderline between each block and at the edge of the plot. Crop management was performed according to the conventional agronomic practices. Fungicides and insecticides were used along the growth cycle, and fertilizers, composed of 250 kg N, 120 kg P_2O_5 and 300 kg K_2O per ha, were applied by drip irrigation system.

All the artichokes of each plant were harvested at commercial developmental stage based on head size and morphology when they were firm, tightly closed and ready-to-use. A total of 17 harvesting dates were performed from November 29th to May 24th. For each harvest date, yield (number of artichoke head per plant and kg per plant) of each artichoke head order (main, secondary and tertiary) was recorded. Then, 5 artichoke heads for each order and replicate were selected to analyze phenolic content and total antioxidant activity individually in each artichoke head. In addition, artichokes harvested on February 26th (winter harvest) and April 23rd (spring harvest) were used to performed two postharvest experiments. Immediately, main, secondary and tertiary artichoke heads without visual defects were selected and transferred to the laboratory. Then, head artichokes were sorted into 4 lots of 5 artichokes for each head order and replicate and stored at 2 °C and 85% of relative humidity. After 0, 7, 14 and 21 days of storage, one lot from each head order and replicate was taken at random and used to evaluate respiration rate and quality parameters. Beside, individual phenolic compounds and total phenolic content as well as total antioxidant activity were measured at harvest and during 21 days of storage.

2.2. Artichoke plant yield

Yield was quantified as kg per plant for each replicate of 50 plants ($n = 3$). Total number of harvested artichokes was recorded and artichoke heads were classified according to the flower head order: main, secondary or tertiary, for each harvest date. Yield (kg $plant^{-1}$) was recorded as well as the average weight of artichoke heads. Results were expressed as the mean ± SE.

2.3. Respiration rate and quality parameters during postharvest storage

Respiration rate was measured individually in 5 artichoke heads of each order (main, secondary and tertiary). Each artichoke head was closed in a 3 L glass jar, hermetically sealed, for 60 min and 1 mL from the jar atmosphere was withdrawn and injected in a gas chromatograph (Shimadzu, Kyoto, Japan) with thermal conductivity detector (GC-TCD) to measure CO_2 concentration according to Martínez-Esplá et al. (2017a). Respiration rate was expressed as mg CO_2 kg^{-1} h^{-1}. Weight loss (%) was determined by weighing individual artichokes at day 0 and after each sampling date during storage period and expressed as percentage with respect to weight at day 0. Firmness was determined individually in 5 artichokes of each order and replicate, the diameter of artichoke head was measured and then a force that achieved a 5% of deformation of the head diameter was applied (TX-XT2i Texture Analyzer Stable Mycrosystems, Godalming, UK) (Martínez-Esplá et al., 2017a). Results were expressed as the force/deformation ratio (N mm^{-1}) and were the mean ± SE.

2.4. Identification and quantification of phenolic compounds

Phenolic extraction was performed by using 5 g of edible fraction (internal bracts and receptacle) from each individual artichoke head, according to the protocol described by Martínez-Esplá et al. (2017a), by homogenizing artichoke samples with 15 mL of water/ methanol (2:8) containing 2 mM NaF. On the other hand, the identification and quantification of individual phenolics were made in the phenolic extract according to Gironés-Vilaplana et al. (2012) with slight modifications. HPLC-DAD-ESI /MSn and RP-HPLC-DAD systems were used for injection of 20 μL of the extracts, and chromatograms were recorded at 320 and 360 nm in an Agilent HPLC 1200 Infinity series, equipped with a photodiode array detector (Agilent Technologies, Waldbronn, Germany) and a mass detector in series (Bruker Daltonics Ultra HCT-ESI Ion Trap, Bremen, Germany). Mobile phases A and B were water/formic acid (99:1, v/v) and acetonitrile, respectively, with a flow rate of 1 mL per min. Compounds were identified by their mass and retention time using previous bibliography. A calibration curve of two standards, 5-*O*-caffeoylquinic acid and 3-luteolin-*O*-rutinoside (Sigma Aldrich, Germany), was used for the quantification of hydroxycinnamic acids and luteolin derivatives at 320 and 360 nm, respectively. The total identified polyphenols concentration was calculated as the sum of the individual phenolic concentrations. Results were expressed as g kg^{-1} of fresh weight (FW), and were the mean of 5 artichokes for each replicate ± SE.

2.5. Antioxidant activity

Total antioxidant activity (TAA) was quantified using the protocol described by Valero et al. (2011), which described TAA determination from both hydrophilic (H-TAA) and lipophilic (L-TAA) compounds in the same extraction. The extraction was performed for each artichoke individually by homogenizing 2 g of the edible part of each artichoke in 10 mL of 50 mM Na-phosphate buffer at pH 7.8 and 5 mL of ethyl acetate. The upper fraction after centrifugation was used to analyze L-TAA and the lower one for H-TAA. In both cases, TAA was determined by using the enzymatic system composed of the chromophore 2,2′-azino-bis-(3- ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), the horse radish peroxidase enzyme (HRP) and its oxidant substrate (hydrogen peroxide), in which $ABTS^{\cdot+}$ radicals were generated and monitored at 730 nm. Results were expressed as g equivalent of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) kg^{-1} FW and were the mean of 5 artichokes for each replicate ± SE.

2.6. Statistical analysis

Results were expressed as the mean of 5 artichokes ± SE from three replicates. Respect to field results, a *t*(MS) Student test was performed to show significant differences at $P < 0.05$ between two head artichoke orders (main and secondary heads), as well as between both harvest times (winter and spring). Data from the three head artichoke orders (main, secondary and tertiary heads) and days of storage at 2 °C were subjected to analysis of variance (ANOVA). Sources of variation were head artichoke order and storage days. Mean comparisons were performed using HSD Duncan's test to examine if differences were significant at $P < 0.05$. ANOVA assumptions were tested and found to be valid for this dataset. All analyses were performed with SPSS software package v. 17 for Windows.

3. Results and discussion

3.1. Growing season results

Yield (kg $plant^{-1}$) for each artichoke head order (main, secondary and tertiary) was evaluated for all harvest dates, from November 29th (2017) until May 24th (2018). Main heads began to be harvested at the end of November, secondary heads from December 11th, and tertiary heads at the end of February (Table 1). 'Blanca de Tudela' cultivar, the most produced one in Spain, is perfectly adapted to climate condition of Spanish southeast areas, being able to produce artichokes from November to May. Due to its earliness, the first plant to emerge from the rhizome become exhausted after 3 months and new plants develop leading to new productions. Thus, main heads showed two production peaks, in January and at the end of April, as well as the secondary heads, in February and May. Finally, the tertiary heads were harvested from February 28th to May 24th (Table 1). Taking into account the production of all the artichoke head orders along the complete growth cycle, a total yield of 4.23 kg per plant was obtained. This yield was slightly higher than the total yield obtained in other studies carried out with 'Blanca de Tudela' cultivar, in which yields between 3.14 and 3.75 kg per plant were achieved in November-April cycle (Martínez-Esplá et al., 2017b). The highest yield obtained in the present study could be related to the longest length cycle which lasted until May compared to Martínez-Esplá et al. (2017b). In a study with 'Blanca de Tudela' and others Italian and French cultivars, greater earliness and yield of 'Blanca de Tudela' was observed, due to a higher number of artichoke heads than other cultivars (Macua et al., 2005a). On the other hand, the physiological responses to differential irrigation rates in other study indicate that 'Imperial Star' artichoke plants subjected to deficit irrigation (50% ETc) exhibited a significant drought stress throughout the season, thus reducing vegetative growth and lowering yields (Shinohara et al., 2011). Others studies also showed a decrease in head number by deficit irrigation (Garnica et al., 2004; Pomares et al., 2004; Macua et al., 2005b). However, this is the first time that 'Blanca de Tudela' yield has been studied according to artichoke heads by order (main, secondary and tertiary).

3.2. Phenolic compounds at harvest

Total identified polyphenols and total antioxidant activity ranged from 5 to 12 g kg^{-1} FW and 1.5 to 3 g kg^{-1} FW, respectively, being dependent on artichoke head order. Thus, for all harvest dates, the highest total identified polyphenol content was observed for tertiary heads, followed by secondary ones, while the main artichoke heads showed the lowest total identified plyphenol concentration (Table 1). A similar trend was observed for total antioxidant activity which was significantly correlated (R^2=0.918) with total identified plyphenol content. On the other hand, an increasing general trend on total identified plyphenols among harvest dates was observed for each artichoke order (Table 1). Specifically, 1.35, 1.15 and 1.19-fold increase on this content was observed in main, secondary and tertiary heads from February 12th to May 24th.

A high phenolic content in artichoke heads has been related to their content in hydroxycinnamic acids and flavonoids (Schütz et al., 2004; Pandino et al., 2011; Martínez-Esplá et al., 2017a). The major hydroxycinnamic acids found in all artichoke heads were 5-O-caffeoylquinic acid (5-CQA, chlorogenic acid) and 3,5-di-O-caffeoylquinic acid (3, 5-diCQA), which had showed concentrations between 50 and 100-fold higher than the remaining hydroxycinnamic acids detected, leading to a total phenolic content (TPC) dependent of the concentration of these major acids. Chlorogenic acid presented an average concentration in the central flower head of 3 g kg^{-1} FW, the highest levels being observed in January. On the other hand, the secondary and tertiary heads showed an average chlorogenic acid (5-O-caffeoylquinic acid) concentration of 20.6% and 32.6%, respectively, higher than main artichoke head. Specifically, the highest content of chlorogenic acid (5 g kg^{-1} FW) was found in tertiary heads harvested at March 9th (Table 2). Respect to 3, 5-diCQA, the highest concentrations were reached in May for the central and secondary flower heads, while they were in March for the tertiary heads. Secondary heads showed an average concentration of 3, 5-diCQA ca. 3 g Kg^{-1} FW, 33% higher and 27% lower than main and tertiary flower head content, respectively (Table 2). Thus, no relationship was observed between concentration of these major hydroxycinnamic acids and harvet date, since the highest content on 5-CQA in tertiary heads was found in March 9th and in January 19th in main and secondary heads and for 3,5-diCQA the highest content was found at March 28th in main and secondary heads and at the last sampling date (May, 24th) for tertiary heads. Then, concentrations on these phenolic acids were not related with temperature changes along the growing

Table 1
Total yield (kg plant^{-1}), total number of harvested heads (n° heads in total), total identified polyphenols (g kg^{-1} FW) and total antioxidant activity (g kg^{-1} FW) in all harvest dates for different artichoke orders (main, secondary and tertiary heads). Data are the mean ± SE.

Harvest dates	Artichoke orders	Total yield	Total number of heads	Total identified polyphenols	Total antioxidant activity
2017–11–29 (1)	**Main**	0.029 ± 0.002	9.667 ± 0.333	0.066 ± 0.001	2.051 ± 0.026
	Secondary	–	–	–	–
	Tertiary	–	–	–	–
2017–12–11 (2)	**Main**	0.031 ± 0.003 a	5.667 ± 0.882 a	5.246 ± 0.090 b	1.729 ± 0.025 b
	Secondary	0.019 ± 0.002 b	5.333 ± 0.667 a	7.455 ± 0.001 a	2.152 ± 0.048 a
	Tertiary	–	–	–	–
2017–12–22 (3)	**Main**	0.053 ± 0.002 b	6.333 ± 0.186 b	6.316 ± 0.207 a	1.993 ± 0.032 b
	Secondary	0.079 ± 0.005 a	19.667 ± 0.882 a	6.723 ± 0.081 a	2.203 ± 0.042 a
	Tertiary	–	–	–	–
2018–01–08 (4)	**Main**	0.077 ± 0.006 b	13.000 ± 0.892 b	6.507 ± 0.122 b	1.976 ± 0.031 b
	Secondary	0.142 ± 0.007 a	43.333 ± 1.807 a	7.968 ± 0.216 a	2.588 ± 0.036 a
	Tertiary	–	–	–	–
2018–01–19 (5)	**Main**	0.098 ± 0.007 b	1.667 ± 0.333 b	7.581 ± 0.258 b	2.179 ± 0.025 b
	Secondary	0.198 ± 0.019 a	33.667 ± 1.207 a	8.894 ± 0.378 a	2.519 ± 0.049 a
	Tertiary	–	–	–	–
2018–01–30 (6)	**Main**	0.061 ± 0.003 b	9.667 ± 0.882 b	8.212 ± 0.346 a	2.940 ± 0.071 a
	Secondary	0.118 ± 0.005 a	50.000 ± 2.858 a	9.263 ± 0.237 a	3.147 ± 0.051 a
	Tertiary	–	–	–	–
2018–02–12 (7)	**Main**	0.038 ± 0.005 c	6.333 ± 0.602 b	5.834 ± 0.319 c	1.796 ± 0.042 c
	Secondary	0.121 ± 0.007 a	54.667 ± 2.186 a	8.299 ± 0.292 b	2.706 ± 0.062 b
	Tertiary	0.090 ± 0.006 b	0.333 ± 0.027 c	10.053 ± 0.164 a	3.085 ± 0.044 a
2018–02–26 (8)	**Main**	0.024 ± 0.002 c	64.333 ± 0.528 b	6.600 ± 0.162 c	2.315 ± 0.042 c
	Secondary	0.090 ± 0.003 b	77.333 ± 2.333 a	8.017 ± 0.184 b	2.539 ± 0.056 b
	Tertiary	0.174 ± 0.008 a	69.667 ± 2.452 ab	10.439 ± 0.223 a	3.105 ± 0.059 a
2018–03–09 (9)	**Main**	0.009 ± 0.002 c	3.667 ± 0.333 c	6.570 ± 0.204 c	2.247 ± 0.048 c
	Secondary	0.076 ± 0.005 b	52.000 ± 3.055 a	7.578 ± 0.265 b	2.522 ± 0.063 b
	Tertiary	0.290 ± 0.013 a	39.333 ± 2.372 b	12.210 ± 0.199 a	3.231 ± 0.090 a
2018–03–20 (10)	**Main**	0.008 ± 0.001 c	7.667 ± 0.728 b	6.958 ± 0.181c	2.291 ± 0.062 b
	Secondary	0.040 ± 0.003 b	33.333 ± 2.667 a	8.505 ± 0.167 b	2.407 ± 0.055 b
	Tertiary	0.335 ± 0.008 a	34.000 ± 2.215 a	10.303 ± 0.278 a	3.055 ± 0.056 a
2018–03–28 (11)	**Main**	0.016 ± 0.002 c	1.667 ± 0.333 c	8.182 ± 0.438 b	2.526 ± 0.063 b
	Secondary	0.044 ± 0.004 b	27.667 ± 0.856 a	8.923 ± 0.296 b	2.354 ± 0.071 b
	Tertiary	0.249 ± 0.009 a	20.000 ± 1.292 b	11.109 ± 0.388 a	3.001 ± 0.101 a
2018–04–11 (12)	**Main**	0.050 ± 0.004 c	2.333 ± 0.333 c	7.266 ± 0.239 c	0.224 ± 0.050 b
	Secondary	0.083 ± 0.009 b	23.667 ± 1.453 b	8.041 ± 0.154 b	2.469 ± 0.058 a
	Tertiary	0.198 ± 0.007 a	30.667 ± 2.219 a	8.998 ± 0.177 a	2.595 ± 0.056 a
2018–04–23 (13)	**Main**	0.103 ± 0.009 b	74.667 ± 1.410 a	6.665 ± 0.115 c	1.976 ± 0.053 b
	Secondary	0.171 ± 0.006 a	69.000 ± 0.786 b	8.079 ± 0.262 b	2.490 ± 0.071 a
	Tertiary	0.062 ± 0.002 c	69.333 ± 0.910 b	9.777 ± 0.193 a	2.546 ± 0.092 a
2018–05–02 (14)	**Main**	0.116 ± 0.007 b	28.667 ± 1.548 a	6.036 ± 0.248 b	1.815 ± 0.052 b
	Secondary	0.259 ± 0.008 a	22.000 ± 1.512 b	8.622 ± 0.160 a	2.487 ± 0.051 a
	Tertiary	–	–	–	–
2018–05–08 (15)	**Main**	0.070 ± 0.003 b	29.333 ± 1.667 a	7.943 ± 0.200 b	2.686 ± 0.071 b
	Secondary	0.227 ± 0.001 a	15.333 ± 0.860 b	10.214 ± 0.130 a	3.093 ± 0.065 a
	Tertiary	–	–	–	–
2018–05–15 (16)	**Main**	0.040 ± 0.004 b	17.000 ± 0.646 a	9.013 ± 0.184 a	2.536 ± 0.073 a
	Secondary	0.128 ± 0.002 a	15.333 ± 0.702 a	10.813 ± 0.717 a	3.113 ± 0.078 a
	Tertiary	–	–	–	–
2018–05–24 (17)	**Main**	0.038 ± 0.005 b	15.452 ± 0.241 a	7.877 ± 0.416 b	2.164 ± 0.053 b
	Secondary	0.079 ± 0.003 a	15.021 ± 0.104 a	9.532 ± 0.517 b	2.941 ± 0.068 a
	Tertiary	0.097 ± 0.006 a	14.984 ± 0.205 a	11.974 ± 0.337 a	3.041 ± 0.090 a

Different lowercase letters show significant differences ($P < 0.05$) among artichoke orders according to t(MS) Student (between main and secondary heads) or HDS Duncan's (among main, secondary and tertiary heads) tests within each harvest date and for each analyzed parameter.

cycle. Five minor hydroxycinnamic acids were quantified. 3-O-caffeoylquinic acid (3-CQA, neochlorogenic acid) showed levels around 0.04 g kg^{-1} FW, independently of head order and harvest date (Table 2). Similarly, 1,3-di-O-caffeoylquinic acid (1,3-diCQA, cynarin) concentration did not show significant differences among flower head orders (Table 3). However, 3,4-di-*O*-caffeoylquinic acid (3,4-diCQA) (Table 2), di-O-caffeoylquinic acid derivative (Table 3) and 4,5-di-*O*--caffeoylquinic acid (4,5-diCAQ) (Table 3) showed a 20% and 50% higher concentration in secondary and tertiary heads, respectively, compared to main heads, showing similar trends to those found in the major hydroxycinnamic acids.

On the other hand, the major luteolin derivatives was luteolin 7-O-glucuronide followed by luteolin 7-O-glucoside (Table 4), being luteolin 7-O-glucuronide-3-O-glucoside content 3-fold lower than the major one (Table 4). Tertiary heads showed average concentrations of 1 g kg^{-1} FW in the major luteolin derivatives; however, the main and secondary heads had 2-fold and 1.5-fold lower concentrations, respectively, than the previous ones. Finally, luteolin-7-O-glucuronide-3-O-glucoside presented an average concentration of 0.176 g kg^{-1} FW in main heads, and levels of 10 and 30% higher in secondary and tertiary heads, respectively.

Total identified polyphenols (as the sum of individual hydroxycinnamic acids and luteolin derivatives) in artichoke edible part from main, secondary and tertiary heads harvesting in winter and spring harvest times, are shown in Fig. 1. Significant differences were observed in phenolic content between head artichoke order within each harvest time. TPC was 27.6 and 22.4% higher in secondary heads for winter and spring harvest times, repectively, with respect to main heads. In the same line, tertiary heads showed an increase in TPC of 67.6 and 38.3% in winter and spring, respectively as compared with secondary heads. However, not significant differences were found between both harvest times for none of the artichoke heads.

Table 2
5-O-caffeoylquinic acid, 3,5-di-O-caffeoylquinic acid, 3-O-caffeoylquinic acid and 3,4-di-O-caffeoylquinic acid (g kg^{-1} FW) on the edible fraction of 'Blanca de Tudela' cultivar in all harvest dates for different artichoke orders (main, secondary and tertiary heads). Data are the mean ± SE.

Harvest dates	Artichoke orders	5-O-caffeoylquinic acid	3,5-di-O-caffeoylquinic acid	3-O-caffeoylquinic acid	3,4-di-O-caffeoylquinic acid
2017–11–29 (1)	**Main**	2.370 ± 0.059	1.772 ± 0.078	0.038 ± 2.70·10^{-3}	0.036 ± 9.00·10^{-4}
	Secondary	–	–	–	–
	Tertiary	–	–	–	–
2017–12–11 (2)	**Main**	2.374 ± 0.107 b	1.399 ± 0.066 b	0.009 ± 7.00·10^{-4} b	0.029 ± 6.00·10^{-4} b
	Secondary	3.332 ± 0.106 a	2.178 ± 0.049 a	0.014 ± 1.10·10^{-3} a	0.044 ± 6.00·10^{-4} a
	Tertiary	–	–	–	-
2017–12–22 (3)	**Main**	2.632 ± 0.277 a	1.484 ± 0.128 b	0.043 ± 3.70·10^{-3} a	0.030 ± 1.40·10^{-3} b
	Secondary	3.337 ± 0.116 a	1.869 ± 0.077 a	0.053 ± 5.20·10^{-3} a	0.038 ± 5.00·10^{-4} a
	Tertiary	–	–	–	–
2018–01–08 (4)	**Main**	3.317 ± 0.111 a	2.032 ± 0.109 b	0.061 ± 6.10·10^{-3} a	0.042 ± 1.10·10^{-3} b
	Secondary	3.747 ± 0.197 a	2.944 ± 0.163 a	0.035 ± 2.50·10^{-3} b	0.060 ± 1.60·10^{-3} a
	Tertiary	–	–	–	–
2018–01–19 (5)	**Main**	4.021 ± 0.339 a	2.317 ± 0.133 b	0.038 ± 5.70·10^{-3} a	0.047 ± 1.50·10^{-3} b
	Secondary	4.439 ± 0.331 a	3.186 ± 0.211 a	0.027 ± 2.60·10^{-3} a	0.065 ± 2.60·10^{-3} a
	Tertiary	–	–	–	–
2018–01–30 (6)	**Main**	4.029 ± 0.220 a	2.814 ± 0.087 a	0.058 ± 4.90·10^{-3} a	0.078 ± 2.60·10^{-3} a
	Secondary	4.476 ± 0.215 a	3.410 ± 0.183 b	0.052 ± 4.50·10^{-3} a	0.070 ± 2.30·10^{-3} a
	Tertiary	–	–	–	–
2018–02–12 (7)	**Main**	3.153 ± 0.359 a	1.710 ± 0.154 b	0.052 ± 4.70·10^{-3} a	0.035 ± 1.70·10^{-3} b
	Secondary	4.186 ± 0.298 a	2.727 ± 0.170 a	0.046 ± 2.70·10^{-3} a	0.056 ± 1.60·10^{-3} a
	Tertiary	–	–	–	–
2018–02–26 (8)	**Main**	2.987 ± 0.266 a	1.815 ± 0.095 c	0.053 ± 4.80·10^{-3} a	0.037 ± 1.02·10^{-3} c
	Secondary	3.683 ± 0.305 a	2.650 ± 0.087 b	0.041 ± 3.60·10^{-3} ab	0.054 ± 4.00·10^{-4} b
	Tertiary	3.676 ± 0.244 a	3.471 ± 0.263 a	0.036 ± 3.30·10^{-3} b	0.071 ± 3.70·10^{-3} a
2018–03–09 (9)	**Main**	3.000 ± 0.234 b	2.033 ± 0.175 c	0.047 ± 4.40·10^{-3} a	0.042 ± 1.70·10^{-3} c
	Secondary	3.589 ± 0.304 b	2.541 ± 0.086 b	0.041 ± 3.40·10^{-3} a	0.052 ± 3.10·10^{-3} b
	Tertiary	4.944 ± 0.224 a	4.465 ± 0.219 a	0.029 ± 2.20·10^{-3} b	0.091 ± 2.70·10^{-3} a
2018–03–20 (10)	**Main**	3.024 ± 0.233 b	2.284 ± 0.121 c	0.039 ± 3.75·10^{-3} a	0.047 ± 1.30·10^{-3} c
	Secondary	3.444 ± 0.206 ab	2.785 ± 0.135 b	0.042 ± 3.80·10^{-3} a	0.057 ± 1.50·10^{-3} b
	Tertiary	4.160 ± 0.270 a	3.860 ± 0.261 a	0.036 ± 2.90·10^{-3} a	0.079 ± 4.70·10^{-3} a
2018–03–28 (11)	**Main**	3.338 ± 0.320 ab	3.251 ± 0.175 b	0.045 ± 4.70·10^{-3} a	0.066 ± 3.60·10^{-3} b
	Secondary	3.178 ± 0.264 b	3.630 ± 0.126 ab	0.039 ± 3.40·10^{-3} a	0.074 ± 1.20·10^{-3} b
	Tertiary	4.538 ± 0.343 a	4.138 ± 0.261 a	0.036 ± 2.90·10^{-3} a	0.085 ± 2.50·10^{-3} a
2018–04–11 (12)	**Main**	3.090 ± 0.280 a	2.536 ± 0.120 b	0.030 ± 3.30·10^{-3} b	0.052 ± 2.20·10^{-3} c
	Secondary	2.951 ± 0.141 a	2.897 ± 0.194 ab	0.046 ± 2.90·10^{-3} a	0.059 ± 1.20·10^{-3} b
	Tertiary	3.263 ± 0.195 a	3.167 ± 0.163 a	0.039 ± 3.60·10^{-3} ab	0.065 ± 1.10·10^{-3} a
2018–04–23 (13)	**Main**	2.615 ± 0.106 b	2.481 ± 0.113 b	0.043 ± 2.80·10^{-3} a	0.051 ± 8.00·10^{-4} c
	Secondary	3.128 ± 0.308 ab	2.936 ± 0.182 b	0.051 ± 4.70·10^{-3} a	0.060 ± 1.24·10^{-3} b
	Tertiary	3.335 ± 0.214 a	3.759 ± 0.182 a	0.045 ± 3.60·10^{-3} a	0.077 ± 1.40·10^{-3} a
2018–05–02 (14)	**Main**	2.360 ± 0.206 b	2.130 ± 0.152 b	0.034 ± 3.60·10^{-3} a	0.044 ± 2.10·10^{-3} b
	Secondary	3.539 ± 0.213 a	3.123 ± 0.107 a	0.040 ± 4.00·10^{-3} a	0.064 ± 1.10·10^{-3} a
	Tertiary	–	–	–	–
2018–05–08 (15)	**Main**	2.976 ± 0.200 b	3.131 ± 0.152 b	0.049 ± 3.70·10^{-3} a	0.064 ± 1.80·10^{-3} b
	Secondary	4.099 ± 0.132 a	3.773 ± 0.115 a	0.046 ± 3.40·10^{-3} a	0.077 ± 2.60·10^{-3} a
	Tertiary	–	–	–	–
2018–05–15 (16)	**Main**	3.263 ± 0.191 a	3.497 ± 0.124 a	0.040 ± 3.90·10^{-3} b	0.071 ± 2.50·10^{-3} a
	Secondary	3.952 ± 0.363 a	4.148 ± 0.272 a	0.056 ± 4.66·10^{-3} a	0.085 ± 4.90·10^{-3} a
	Tertiary	–	–	–	–
2018–05–24 (17)	**Main**	2.730 ± 0.252 b	3.202 ± 0.154 b	0.039 ± 2.90·10^{-3} b	0.065 ± 3.35·10^{-3} b
	Secondary	3.114 ± 0.338 ab	3.813 ± 0.207 ab	0.055 ± 5.10·10^{-3} a	0.078 ± 3.90·10^{-3} ab
	Tertiary	4.084 ± 0.305 a	4.195 ± 0.256 a	0.063 ± 4.70·10^{-3} a	0.086 ± 3.10·10^{-3} a

Different lowercase letters show significant differences ($P < 0.05$) among artichoke orders according to t(MS) Student (between main and secondary heads) or HSD Duncan's (among main, secondary and tertiary heads) tests within each harvest date and for each analyzed compound.

In this sense, phenolic profile of artichoke has been widely studied, as well as the factors that affect the total phenolic content, such as genetic, environmental, edaphic, agronomic, among others (Schütz et al., 2004; Lombardo et al., 2018). For instance, differences on phenolic content have been reported among cultivars and harvest times, the early harvested artichoke having lower content than the latets ones (Licciardello et al., 2017; Pandino et al., 2017b). Furthermore, its correlation with total antioxidant activity has been previously confirmed (Bonasia et al., 2010; Ruíz-Jiménez et al., 2014). On the other hand, artichoke head order has been described as influencing total production, number of buds, head average weight, seed production, and phenolic content (Ortega 2002; Cappelletti et al., 2016; Gadliardi et al., 2020).

Previous works with different cultivars, including 'Blanca de Tudela', have identifed chlorogenic and 1,5-diCQA as major hydroxycinnamic acids (Pandino et al., 2011; 2017b). However, Gil-Izquierdo et al. (2002) indicated that using an HPLC-DAD-ultraviolet-visible (UV-vis), 3, 5-diCQA and 1,5-diCQA eluted together and could not be separated properly. Our results, therefore, are in agreement with recently published results in which 5-CQA and 3,5-diCQA stand out as the major hydroxycinnamic acids in several cultivars of globe and wild artichokes (Garbetta et al., 2014; Petropoulos et al., 2018). The phenolic profile obtained can be in influenced by both artichoke moisture content and extraction solvent (Martínez-Esplá et al., 2017a). Previous works carried out with purple artichoke cultivars, such as 'Violeto di Provenza', 'Romanesco C3', 'Apollo', 'Exploter' and 'Montelupone A', reported differences on phenolic content depending on flower head order (Cappelletti et al., 2016; Gagliardi et al., 2020), as also it has been observed in the present work, showing higher phenolic content in secondary and tertiary heads than in main ones. A previous research work has also reported this variability on the phenolic content and profile for white artichoke cultivar 'Blanca de Tudela' (Giménez et al., 2021), according to our results. Thus, this factor should be considered in order to

Table 3
1,3-di-O-caffeoylquinic acid, di-O-caffeoylquinic acid derivative and 4,5-di-O-caffeoylquinic acid (g kg^{-1} FW) on the edible fraction of 'Blanca de Tudela' cultivar in all harvest dates for different artichoke orders (main, secondary and tertiary heads). Data are the mean ± SE.

Harvest dates	Artichoke orders	1,3-di-O-caffeoylquinic acid	4,5-di-O-caffeoylquinic acid	di-O-caffeoylquinic acid derivative
2017–11–29 (1)	**Main**	$0.032 \pm 1.50{\cdot}10^{-3}$	$0.049 \pm 3.50{\cdot}10^{-3}$	$0.015 \pm 1.00{\cdot}10^{-3}$
	Secondary	–	–	–
	Tertiary	–	–	–
2017–12–11 (2)	**Main**	$0.018 \pm 8.00{\cdot}10^{-4}$ b	$0.016 \pm 1.40{\cdot}10^{-3}$ b	$0.013 \pm 7.00{\cdot}10^{-4}$ b
	Secondary	$0.025 \pm 1.00{\cdot}10^{-3}$ a	$0.024 \pm 1.40{\cdot}10^{-3}$ a	$0.019 \pm 8.00{\cdot}10^{-4}$ a
	Tertiary	–	–	–
2017–12–22 (3)	**Main**	$0.025 \pm 1.70{\cdot}10^{-3}$ b	$0.024 \pm 2.30{\cdot}10^{-3}$ b	$0.015 \pm 1.20{\cdot}10^{-3}$ a
	Secondary	$0.036 \pm 1.84{\cdot}10^{-3}$ a	$0.044 \pm 5.20{\cdot}10^{-3}$ a	$0.018 \pm 2.20{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–01–08 (4)	**Main**	$0.039 \pm 1.70{\cdot}10^{-3}$ a	$0.045 \pm 3.00{\cdot}10^{-3}$ a	$0.024 \pm 1.80{\cdot}10^{-3}$ a
	Secondary	$0.037 \pm 1.60{\cdot}10^{-3}$ a	$0.046 \pm 2.80{\cdot}10^{-3}$ a	$0.026 \pm 3.10{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–01–19 (5)	**Main**	$0.045 \pm 3.30{\cdot}10^{-3}$ a	$0.043 \pm 5.30{\cdot}10^{-3}$ a	$0.018 \pm 2.10{\cdot}10^{-3}$ a
	Secondary	$0.044 \pm 3.10{\cdot}10^{-3}$ a	$0.048 \pm 3.30{\cdot}10^{-3}$ a	$0.020 \pm 4.30{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–01–30 (6)	**Main**	$0.037 \pm 2.80{\cdot}10^{-3}$ a	$0.042 \pm 3.10{\cdot}10^{-3}$ a	$0.033 \pm 5.20{\cdot}10^{-3}$ a
	Secondary	$0.039 \pm 3.00{\cdot}10^{-3}$ a	$0.049 \pm 3.20{\cdot}10^{-3}$ a	$0.031 \pm 4.20{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–02–12 (7)	**Main**	$0.031 \pm 2.20{\cdot}10^{-3}$ a	$0.033 \pm 4.10{\cdot}10^{-3}$ b	$0.013 \pm 1.40{\cdot}10^{-3}$ a
	Secondary	$0.034 \pm 2.40{\cdot}10^{-3}$ a	$0.051 \pm 3.60{\cdot}10^{-3}$ a	$0.019 \pm 1.90{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–02–26 (8)	**Main**	$0.038 \pm 3.10{\cdot}10^{-3}$ a	$0.045 \pm 6.60{\cdot}10^{-3}$ b	$0.015 \pm 1.50{\cdot}10^{-3}$ b
	Secondary	$0.046 \pm 3.40{\cdot}10^{-3}$ a	$0.055 \pm 5.30{\cdot}10^{-3}$ b	$0.020 \pm 3.00{\cdot}10^{-3}$ ab
	Tertiary	$0.037 \pm 2.50{\cdot}10^{-3}$ a	$0.074 \pm 5.06{\cdot}10^{-3}$ a	$0.026 \pm 3.40{\cdot}10^{-3}$ a
2018–03–09 (9)	**Main**	$0.034 \pm 2.30{\cdot}10^{-3}$ b	$0.049 \pm 6.60{\cdot}10^{-3}$ b	$0.014 \pm 1.70{\cdot}10^{-3}$ b
	Secondary	$0.041 \pm 3.10{\cdot}10^{-3}$ ab	$0.051 \pm 5.50{\cdot}10^{-3}$ b	$0.016 \pm 2.10{\cdot}10^{-3}$ ab
	Tertiary	$0.047 \pm 3.10{\cdot}10^{-3}$ a	$0.084 \pm 5.40{\cdot}10^{-3}$ a	$0.024 \pm 2.90{\cdot}10^{-3}$ a
2018–03–20 (10)	**Main**	$0.042 \pm 2.90{\cdot}10^{-3}$ a	$0.056 \pm 5.50{\cdot}10^{-3}$ a	$0.020 \pm 2.10{\cdot}10^{-3}$ a
	Secondary	$0.047 \pm 3.80{\cdot}10^{-3}$ a	$0.063 \pm 5.10{\cdot}10^{-3}$ a	$0.018 \pm 1.00{\cdot}10^{-3}$ a
	Tertiary	$0.048 \pm 3.10{\cdot}10^{-3}$ a	$0.069 \pm 5.10{\cdot}10^{-3}$ a	$0.023 \pm 2.10{\cdot}10^{-3}$ a
2018–03–28 (11)	**Main**	$0.051 \pm 3.40{\cdot}10^{-3}$ a	$0.062 \pm 4.80{\cdot}10^{-3}$ a	$0.027 \pm 1.60{\cdot}10^{-3}$ a
	Secondary	$0.045 \pm 2.30{\cdot}10^{-3}$ a	$0.071 \pm 5.60{\cdot}10^{-3}$ a	$0.028 \pm 2.20{\cdot}10^{-3}$ a
	Tertiary	$0.051 \pm 4.00{\cdot}10^{-3}$ a	$0.075 \pm 6.90{\cdot}10^{-3}$ a	$0.024 \pm 3.00{\cdot}10^{-3}$ a
2018–04–11 (12)	**Main**	$0.040 \pm 2.50{\cdot}10^{-3}$ a	$0.057 \pm 4.60{\cdot}10^{-3}$ b	$0.020 \pm 2.00{\cdot}10^{-3}$ a
	Secondary	$0.042 \pm 1.40{\cdot}10^{-3}$ a	$0.057 \pm 3.90{\cdot}10^{-3}$ b	$0.030 \pm 4.40{\cdot}10^{-3}$ a
	Tertiary	$0.044 \pm 3.60{\cdot}10^{-3}$ a	$0.072 \pm 3.10{\cdot}10^{-3}$ a	$0.026 \pm 2.50{\cdot}10^{-3}$ a
2018–04–23 (13)	**Main**	$0.045 \pm 3.10{\cdot}10^{-3}$ a	$0.062 \pm 5.00{\cdot}10^{-3}$ a	$0.022 \pm 2.00{\cdot}10^{-3}$ b
	Secondary	$0.044 \pm 3.10{\cdot}10^{-3}$ ab	$0.075 \pm 9.30{\cdot}10^{-3}$ a	$0.020 \pm 3.80{\cdot}10^{-3}$ b
	Tertiary	$0.034 \pm 2.40{\cdot}10^{-3}$ b	$0.076 \pm 7.00{\cdot}10^{-3}$ a	$0.035 \pm 4.10{\cdot}10^{-3}$ a
2018–05–02 (14)	**Main**	$0.035 \pm 1.40{\cdot}10^{-3}$ b	$0.053 \pm 4.10{\cdot}10^{-3}$ b	$0.022 \pm 1.30{\cdot}10^{-3}$ a
	Secondary	$0.047 \pm 3.70{\cdot}10^{-3}$ a	$0.071 \pm 4.20{\cdot}10^{-3}$ a	$0.020 \pm 2.00{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–05–08 (15)	**Main**	$0.046 \pm 2.90{\cdot}10^{-3}$ b	$0.066 \pm 2.90{\cdot}10^{-3}$ b	$0.027 \pm 3.80{\cdot}10^{-3}$ a
	Secondary	$0.062 \pm 2.90{\cdot}10^{-3}$ a	$0.092 \pm 3.90{\cdot}10^{-3}$ a	$0.026 \pm 1.30{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–05–15 (16)	**Main**	$0.051 \pm 3.50{\cdot}10^{-3}$ a	$0.059 \pm 4.50{\cdot}10^{-3}$ b	$0.026 \pm 2.30{\cdot}10^{-3}$ a
	Secondary	$0.061 \pm 3.90{\cdot}10^{-3}$ a	$0.109 \pm 5.10{\cdot}10^{-3}$ a	$0.024 \pm 4.60{\cdot}10^{-3}$ a
	Tertiary	–	–	–
2018–05–24 (17)	**Main**	$0.047 \pm 3.60{\cdot}10^{-3}$ b	$0.049 \pm 4.10{\cdot}10^{-3}$ b	$0.033 \pm 5.20{\cdot}10^{-3}$ a
	Secondary	$0.046 \pm 3.50{\cdot}10^{-3}$ b	$0.060 \pm 4.70{\cdot}10^{-3}$ ab	$0.042 \pm 6.20{\cdot}10^{-3}$ a
	Tertiary	$0.063 \pm 4.20{\cdot}10^{-3}$ a	$0.080 \pm 6.60{\cdot}10^{-3}$ a	$0.048 \pm 7.00{\cdot}10^{-3}$ a

Different lowercase letters show significant differences ($P < 0.05$) among artichoke orders according to t(MS) Student (between main and secondary heads) or HDS Duncan's (among main, secondary and tertiary heads) test within each harvest date for each analyzed compound.

improve functional quality at harvest of globe artichoke crop.

3.3. Postharvest storage

As described in the experimental design section, two postharvest experiments were carried out, one in winter and another one in spring harvest time. Respiration rate at harvest was 3-fold higher in spring (182.7 ± 9.25 mg CO_2 kg^{-1} h^{-1}) than in winter (56.45 ± 4.08 mg CO_2 kg^{-1} h^{-1}), and main head showed a higher respiration rate than secondary and tertiary heads. These differences were also maintained during cold storage, although respiration rate decreased from day 0 to day 7 and increased afterward, for all artichoke head orders and both growing seasons. In general, tertiary heads showed lower respiration rate than main heads, with values of 16.2 and 10.2% lower at the end of the experiment in winter and spring harvest times, respectively (Fig. 2). It is well-known that shelf-life of fresh products is negatively correlated with intensity of respiration rate (Kader, 2002).

Thus, artichoke could be considered as a perishable product since it has a high respiration rate even under cold storage conditions, and has a short shelf-life under 20 °C (Gil et al., 2001; Sabi et al., 2013; Ruíz--Jiménez et al., 2014). For first time, a significant reduction on respiration rate in secondary and tertiary heads at harvest in both harvest times has been reported. As far as we know, there are not studies with similar results in respiration rate. However, experiments with treatments, such as ozone, modified atmosphere and oxalic acid, showed a reduction on respiration rate of artichokes and a quality maintenance during their postharvest cold (Gil et al., 2003; Restuccia et al., 2014; Lombardo et al., 2015) or room temperature (Ruíz-Jiménez et al., 2014) storage.

Weight losses showed significant differences among head orders in both postharvest experiments, being the highest weight losses observed from main heads, 23.16 ± 0.95 and 25.64 ± 1.03%, in winter and spring harvest time, respectively, after 21 days of cold storage at 2 °C.

Table 4
Luteolin derivatives content (g kg^{-1} FW); luteolin 7-O-glucuronide, luteolin 7-O-glucoside and luteolin 7-O-glucuronide-3-O-glucoside on the edible fraction of 'Blanca de Tudela' cultivar in all harvest dates for different artichoke orders (main, secondary and tertiary heads). Data are the mean ± SE.

Harvest dates	Artichoke orders	Luteolin 7-O-glucuronide	Luteolin 7-O-glucoside	Luteolin 7-O-glucuronide-3-O-glucoside
2017–11–29 (1)	**Main**	0.415 ± 0.024	0.637 ± 0.054	0.235 ± 0.015
	Secondary	–	–	–
	Tertiary	–	–	–
2017–12–11 (2)	**Main**	0.525 ± 0.036 a	0.612 ± 0.034 b	0.251 ± 0.015 a
	Secondary	0.641 ± 0.062 a	0.903 ± 0.047 a	0.275 ± 0.017 a
	Tertiary	–	–	–
2017–12–22 (3)	**Main**	0.614 ± 0.063 b	0.518 ± 0.050 a	0.129 ± 0.018 a
	Secondary	1.016 ± 0.083 a	0.527 ± 0.034 a	0.186 ± 0.013 a
	Tertiary	–	–	–
2018–01–08 (4)	**Main**	0.251 ± 0.039 a	0.513 ± 0.046 a	0.184 ± 0.016 a
	Secondary	0.358 ± 0.039 a	0.546 ± 0.033 a	0.214 ± 0.014 a
	Tertiary	–	–	–
2018–01–19 (5)	**Main**	0.283 ± 0.022 a	0.577 ± 0.052 a	0.192 ± 0.017 a
	Secondary	0.298 ± 0.028 a	0.552 ± 0.053 a	0.215 ± 0.010 a
	Tertiary	–	–	–
2018–01–30 (6)	**Main**	0.352 ± 0.057 a	0.573 ± 0.057 a	0.196 ± 0.004 a
	Secondary	0.464 ± 0.043 a	0.568 ± 0.052 a	0.185 ± 0.007 a
	Tertiary	–	–	–
2018–02–12 (7)	**Main**	0.259 ± 0.034 b	0.399 ± 0.038 a	0.150 ± 0.017 a
	Secondary	0.444 ± 0.039 a	0.588 ± 0.068 a	0.212 ± 0.018 a
	Tertiary	–	–	–
2018–02–26 (8)	**Main**	0.474 ± 0.052 b	0.608 ± 0.069 b	0.176 ± 0.016 a
	Secondary	0.743 ± 0.062 a	0.670 ± 0.077 b	0.224 ± 0.015 a
	Tertiary	0.810 ± 0.084 a	1.074 ± 0.093 a	0.222 ± 0.016 a
2018–03–09 (9)	**Main**	0.502 ± 0.076 b	0.540 ± 0.038 b	0.170 ± 0.018 b
	Secondary	0.624 ± 0.040 b	0.588 ± 0.062 b	0.238 ± 0.018 a
	Tertiary	1.056 ± 0.078 a	1.183 ± 0.089 a	0.294 ± 0.026 a
2018–03–20 (10)	**Main**	0.541 ± 0.065 b	0.606 ± 0.048 b	0.180 ± 0.017 a
	Secondary	0.902 ± 0.078 a	0.803 ± 0.073 ab	0.185 ± 0.017 a
	Tertiary	1.063 ± 0.105 a	0.888 ± 0.072 a	0.239 ± 0.019 a
2018–03–28 (11)	**Main**	0.358 ± 0.024 c	0.737 ± 0.048 b	0.249 ± 0.023 a
	Secondary	0.719 ± 0.071 b	0.950 ± 0.082 ab	0.188 ± 0.014 a
	Tertiary	1.008 ± 0.080 a	0.966 ± 0.075 a	0.189 ± 0.018 a
2018–04–11 (12)	**Main**	0.571 ± 0.052 b	0.687 ± 0.030 b	0.151 ± 0.015 a
	Secondary	0.818 ± 0.081 b	0.995 ± 0.102 a	0.211 ± 0.026 a
	Tertiary	1.261 ± 0.100 a	0.902 ± 0.080 ab	0.159 ± 0.005 a
2018–04–23 (13)	**Main**	0.496 ± 0.047 c	0.717 ± 0.048 a	0.133 ± 0.011 b
	Secondary	0.759 ± 0.076 b	0.843 ± 0.081 a	0.163 ± 0.012 b
	Tertiary	1.268 ± 0.079 a	0.907 ± 0.090 a	0.242 ± 0.018 a
2018–05–02 (14)	**Main**	0.545 ± 0.046 a	0.597 ± 0.057 b	0.117 ± 0.011 a
	Secondary	0.730 ± 0.066 a	0.835 ± 0.033 a	0.153 ± 0.012 a
	Tertiary	–	–	–
2018–05–08 (15)	**Main**	0.597 ± 0.054 a	0.772 ± 0.045 b	0.176 ± 0.016 a
	Secondary	0.737 ± 0.062 a	1.170 ± 0.113 a	0.203 ± 0.016 a
	Tertiary	–	–	–
2018–05–15 (16)	**Main**	0.718 ± 0.112 a	0.929 ± 0.072 a	0.140 ± 0.014 a
	Secondary	0.966 ± 0.094 a	1.242 ± 0.115 a	0.172 ± 0.012 a
	Tertiary	–	–	–
2018–05–24 (17)	**Main**	0.583 ± 0.076 b	0.958 ± 0.075 b	0.170 ± 0.016 b
	Secondary	0.861 ± 0.085 b	1.259 ± 0.101 ab	0.212 ± 0.018 b
	Tertiary	1.250 ± 0.111 a	1.497 ± 0.120 a	0.309 ± 0.018 a

Different lowercase letters show significant differences ($P < 0.05$) among artichoke orders according to *t*(MS) Student (between main and secondary heads) or HDS Duncan's (among main, secondary and tertiary heads) tests within each harvest date for each analyzed compound.

Nevertheless, secondary and tertiary heads showed significant ($P < 0.05$) lower weight losses than main heads during the whole storage period, although the greatest differences were observed at the end of the experiment (Fig. 3).

Firmness, measured at the equatorial diameter of each artichoke head, showed the artichoke compactness at harvest and during post-harvest cold storage. At harvest, firmness of main artichokes was 6.74 ± 0.21 and 7.28 ± 0.19 N mm^{-1} in winter and spring harvest time, respectively, and it was 37.8 and 29.1% higher in secondary heads than main ones in winter and spring harvest time, respectively. In addition, firmness values of tertiary heads were 21.7 and 105% higher than main heads for both harvest times, winter and spring, respectively. These differences were maintained during cold storage, despite of the decreasing on head firmness found in all artichokes, depending on the head order and showing a clear effect of this factor (Fig. 4).

Weight loss is an important quality parameter of artichoke heads during their postharvest storage. This quality trait is close related to the head compactness and, therefore, to the head firmness, leading to a withered appearance that could cause the non-acceptance of the product by the consumers, being the major reason of artichoke deterioration (Sabi et al., 2013). Weight losses and firmness are quality parameters directly related to respiration rate, and the effect of head order was observed at harvest and during cold storage, since tertiary followed by secondary heads maintained higher quality parameters and increased their shelf-life period as compared with main heads. On the other hand, postharvest treatments with oxalic acid or O_3-atmosphere decreased weight losses and maintained firmness levels, leading to overall quality maintenance during cold storage (Restuccia et al., 2014; Ruíz-Jiménez et al., 2014). Similar results have been reported with preharvest treatments with oxalic acid and methyl jasmonate as well as with irrigation with high quality water (Gil et al., 2001; Martínez-Esplá et al., 2017a; 2017b; Lombardo et al., 2018; Gagliardi et al., 2020). However, as far as

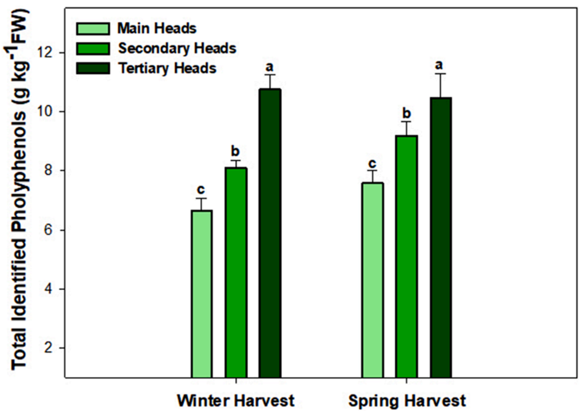

Fig. 1. Total identified polyphenols (g kg^{-1} FW) on the edible fraction of 'Blanca de Tudela' cultivar in two harvest times. Data are the mean ± SE. Different lowercase letters show significant differences at $P < 0.05$ among artichoke orders (main, secondary and tertiary heads). No asterisks found in spring harvest time bars for each artichoke order means that there were no significant differences ($P \geq 0.05$) between both harvest times.

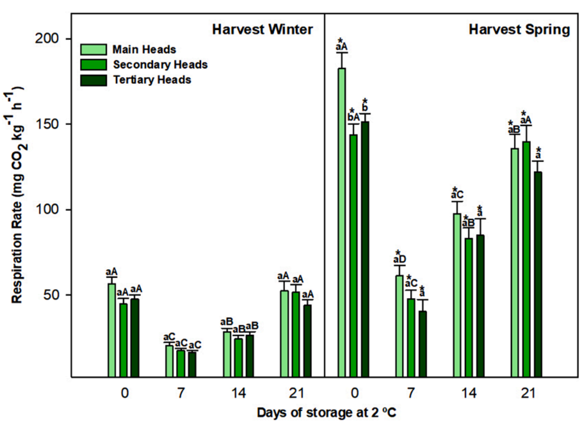

Fig. 2. Respiration rate (mg CO_2 kg^{-1} h^{-1}) of main, secondary and tertiary heads at harvest and during postharvest cold storage at 2 °C for winter and spring harvest times. Data are the mean ± SE. Different lowercase and capital letters show significant differences at $P < 0.05$ among artichoke orders (main, secondary and tertiary heads) and days of storage at 2 °C, respectively, for each harvest time. Asterisks found in spring harvest time bars for each artichoke order and storage day means that there were significant differences ($P < 0.05$) between both harvest times.

we know, this is the first report in which the effect of the artichoke head order in plant on quality traits during cold storage have been provided. Lombardo et al. (2015) concluded that the application of O_3 improved artickoke quality as a consequence of higher TPC which played a significant role in the detoxification process. In the present experiment, content of hydroxycinnamic acids and luteolin derivatives at harvest and at the end of cold storage in main, secondary and tertiary heads were analyzed (Table 5). In general, the concentration of these individual phenolics increased during cold storage, althouth it is important to note that differences among flower head orders observed at harvest were mainained during storage. Thus, chlorogenic acid content was 35.3 and 36.8% higher in secondary and tertiary artichokes, respectively, than in main heads harvested at winter time. In addition, an increase of 84.1 and 100% in secondary and tertiary heads, respectively, was observed in artichokes harvested at spring harvest time. On the other hand, 3,5-diCAQ increased in a similar trend than chlorogenic acid, which led to a 43.5 and 66.2% increase of total hydroxycinnamic acid content for secondary and tertiary heads, respectively, for artichokes harvested in winter time, and 41.9 and 73.7%, respectively, for those

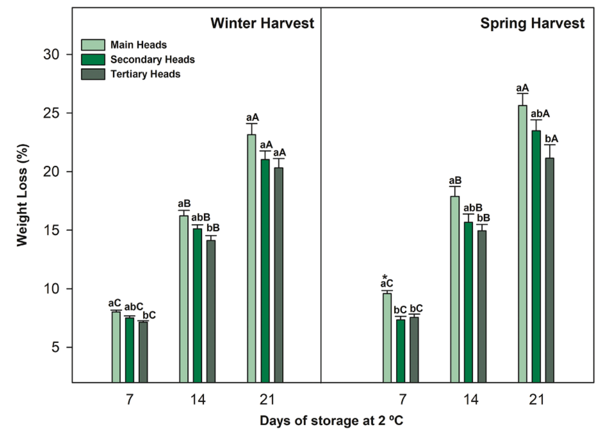

Fig. 3. Weight loss (%) of main, secondary and tertiary artichokes at harvest and during postharvest cold storage at 2 °C for winter and spring harvest times. Data are the mean ± SE. Different lowercase and capital letters show significant differences at $P < 0.05$ among artichoke orders (main, secondary and tertiary heads) and days of storage at 2 °C, respectively, for each harvest time. Asterisks found in spring harvest time bars for each artichoke order and storage day means that there were significant differences ($P < 0.05$) between both harvest times. No asterisks found in spring harvest time bars for each artichoke order means that there were no significant differences ($P \geq 0.05$) between both harvest times.

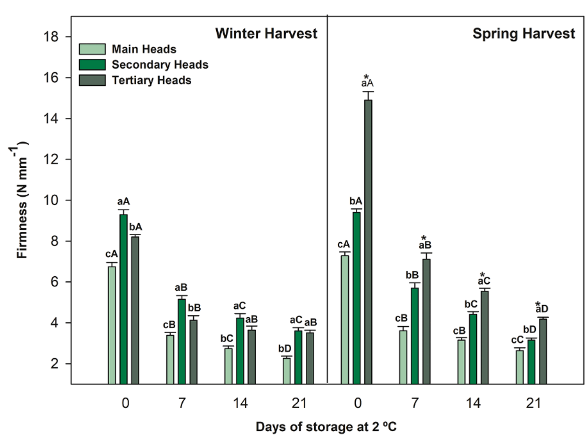

Fig. 4. Firmness (N mm^{-1}) of main, secondary and tertiary artichokes heads at harvest and during postharvest cold storage at 2 °C for winter and spring harvest times. Data are the mean ± SE. Different lowercase and capital letters show significant differences at $P < 0.05$ among artichoke orders (main, secondary and tertiary heads) and days of storage at 2 °C, respectively, for each harvest time. Asterisks found in spring harvest time bars for each artichoke order and storage day means that there were significant differences ($P < 0.05$) between both harvest times. No asterisks found in spring harvest time bars for each artichoke order means that there were no significant differences ($P \geq 0.05$) between both harvest times.

harvest in spring harvest time, at the end of the experiment. Luteolin derivatives showed a similar evolution during postharvest storage and especially after 21 days of storage at 2 °C, when they increased around 0.4 and 1 g kg^{-1} FW in secondary and tertiary heads, respectively, with respect to main heads in artichokes of both harvest times. This increase in phenolic content is due to the activation of phenylpropanoid biosynthetic pathways during cold storage as a defense mechanism against abiotic stresses such as high/low temperature (Saltveit, 2010; Smirnov et al., 2015; Handa et al., 2019).

Different lowercase letters show significant differences ($P < 0.05$) among artichoke orders according to Tuckey test for each analyzed compound and studied day. Significant differences between 0 and 21

Table 5
Individual phenolic compounds content (g kg^{-1} DW) on the edible fraction of different artichokes order (main, secondary and tertiary heads) at harvest and after 21 days of cold storage at 2 °C for winter and spring harvest times. Data are the mean ± SE.

		Head order	Winter Harvest		*t* (MS) Student	Spring Harvest		*t* (MS) Student
			Day 0[¥]	Day 21		Day 0[¥]	Day 21	
Hydroxycinnamic Acids	**3-*O*-CQA**	**Main**	0.441 ± 0.042	0.501 ± 0.075 a	–	0.358 ± 0.025	0.375 ± 0.025 a	–
		Secondary	0.342 ± 0.033	0.342 ± 0.017 a	–	0.425 ± 0.042	0.459 ± 0.025 a	–
		Tertiary	0.300 ± 0.025	0.342 ± 0.017 a	–	0.458 ± 0.033	0.434 ± 0.025 a	–
	5-*O*-CQA	**Main**	24.882 ± 2.216	30.199 ± 1.557 b	–	21.783 ± 0.883	18.473 ± 1.188 b	*
		Secondary	30.679 ± 2.541	41.600 ± 2.222 a	–	26.056 ± 2.566	35.409 ± 1.861 a	–
		Tertiary	30.621 ± 2.033	41.933 ± 2.331 a	–	27.781 ± 1.783	38.543 ± 2.543 a	–
	1,3-*O*-DCQA	**Main**	0.317 ± 0.025	0.242 ± 0.075 a	–	0.375 ± 0.025	0.392 ± 0.017 a	–
		Secondary	0.383 ± 0.025	0.400 ± 0.042 a	–	0.367 ± 0.025	0.334 ± 0.025 a	–
		Tertiary	0.308 ± 0.017	0.325 ± 0.033 a	–	0.283 ± 0.017	0.334 ± 0.025 a	–
	DCQA derivative	**Main**	0.125 ± 0.008	0.142 ± 0.017 b	–	0.183 ± 0.017	0.192 ± 0.017 b	–
		Secondary	0.167 ± 0.025	0.200 ± 0.017 ab	–	0.167 ± 0.033	0.225 ± 0.008 ab	–
		Tertiary	0.217 ± 0.025	0.217 ± 0.017 a	–	0.292 ± 0.033	0.275 ± 0.025 a	–
	3,4-*O*-DCQA	**Main**	0.308 ± 0.008	0.342 ± 0.008 c	–	0.425 ± 0.008	0.417 ± 0.008 c	–
		Secondary	0.450 ± 0.008	0.501 ± 0.008 b	*	0.500 ± 0.008	0.509 ± 0.017 b	–
		Tertiary	0.591 ± 0.033	0.701 ± 0.025 a	*	0.641 ± 0.008	0.751 ± 0.017 a	*
	3,5-*O*-DCQA	**Main**	15.119 ± 0.075	18.347 ± 0.626 c	–	20.667 ± 0.941	27.554 ± 0.794 c	*
		Secondary	22.075 ± 0.725	29.906 ± 0.936 b	*	24.457 ± 0.933	31.603 ± 0.526 b	*
		Tertiary	28.913 ± 1.358	41.517 ± 1.044 a	*	31.312 ± 1.516	44.575 ± 1.112 a	*
	4,5-*O*-DCQA	**Main**	0.375 ± 0.050	0.425 ± 0.067 b	–	0.516 ± 0.042	0.434 ± 0.869 a	–
		Secondary	0.458 ± 0.042	0.434 ± 0.050 b	–	0.625 ± 0.075	0.668 ± 0.058 a	–
		Tertiary	0.616 ± 0.042	0.676 ± 0.058 a	–	0.633 ± 0.058	0.601 ± 0.050 a	–
	Total HA	**Main**	41.567 ± 3.090 b	53.889 ± 2.613 b	–	44.299 ± 2.107 b	51.650 ± 0.200 c	–
		Secondary	54.562 ± 3.282 a	80.368 ± 3.604 a	–	52.596 ± 3.024 ab	76.347 ± 2.622 b	*
		Tertiary	61.592 ± 4.057 a	94.975 ± 3.246 a	*	61.400 ± 2.691 a	95.018 ± 2.028 a	*
Luteolin derivatives	**Lut 7-*O*-gluc 3-*O*-glc**	**Main**	1.466 ± 0.133	1.574 ± 0.092 a	–	1.108 ± 0.092	1.171 ± 0.108 c	–
		Secondary	1.866 ± 0.125	1.792 ± 0.108 a	–	1.358 ± 0.100	1.558 ± 0.075 b	–
		Tertiary	1.849 ± 0.133	1.674 ± 0.117 a	–	2.016 ± 0.150	1.944 ± 0.058 a	–
	Lut 7-*O*-glc	**Main**	3.948 ± 0.433	5.211 ± 0.693 b	–	4.132 ± 0.392	4.513 ± 0.836 b	–
		Secondary	6.189 ± 0.516	7.024 ± 0.643 ab	–	6.322 ± 0.633	6.719 ± 0.827 b	–
		Tertiary	6.747 ± 0.700	8.149 ± 0.576 a	–	10.562 ± 0.658	12.059 ± 0.526 a	–
	Lut 7-*O*-gluc	**Main**	5.065 ± 0.575	6.196 ± 0.359 b	–	5.973 ± 0.400	7.845 ± 0.760 a	–
		Secondary	5.581 ± 0.641	7.293 ± 0.492 b	–	7.022 ± 0.675	8.670 ± 6.571 a	–
		Tertiary	8.946 ± 0.775	11.811 ± 0.534 a	*	7.555 ± 0.750	9.383 ± 0.802 a	–
	Total Luteolins	**Main**	10.479 ± 0.392 c	13.305 ± 0.434 c	*	11.211 ± 0.183 c	13.875 ± 0.334 c	*
		Secondary	13.628 ± 0.300 b	16.550 ± 0.417 b	*	14.702 ± 0.325 b	17.479 ± 0.643 b	*
		Tertiary	17.535 ± 0.333 a	22.375 ± 0.760 a	*	20.125 ± 0.317 a	24.279 ± 0.684 a	*

[¥] Significant differences for values of day 0 have been previously included in Tables 2–4, depending on the analyzed compound on fresh weight (FW) basis, except for the total hydroxycinnamic acids and total luteolins content, which has been included in this table.

storage days for each harvest time are shown with * symbol when $P < 0.05$ performing a *t*-Student test. Not significant differences between these days are shown with – symbol.

In conclusion, our results showed that globe artichoke head order directly influences the content of individual phenolics, being higher for tertiary heads followed by secondary and main heads, respectively. These differences could lead to classify globe artichokes, not only based on their functional value, but also by their aptitude for postharvest storage, since artichokes with the highest TPC had a greater aptitude for their postharvest cold storage, extending their shelf-life period and, consequently, improving the consumer satisfaction or market value.

CRediT authorship contribution statement

María J. Giménez: Conceptualization, Methodology, Investigation, Writing – original draft. **Marina Giménez-Berenguer:** Investigation. **María E. García-Pastor:** Formal analysis, Validation. **Salvador Castillo:** Software. **Juan M. Valverde:** Methodology. **María Serrano:** Writing – review & editing. **Daniel Valero:** Writing – review & editing. **Pedro J. Zapata:** Conceptualization, Visualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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