

## POLYPHENOLIC COMPOSITION OF SPANISH CULTIVARS OF GLOBE ARTICHOKE (*Cynara cardunculus* L. var. *scolymus* (L.) Fiori)

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### ABSTRACT

Globe artichoke (*Cynara cardunculus* L. var. *scolymus* (L.) Fiori) is an edible herbaceous perennial plant that plays an important economic role in Mediterranean agriculture. In recent years, extensive research, which aimed to characterize the phenolic profile of the most important globe artichoke cultivars in Italy, has been conducted. However, very little information is available on the phenolic composition of cultivars traditionally grown in Spain. In this work, six cultivars ('Opal', 'Symphony', 'Concerto', 'Madrigal', 'Blanca de Tudela' and 'A-106') cultured in Spain were characterized according to their phenolic content. The phenolic profile differed between cultivars, and also between flower parts. The major phenolic compound in all the different cultivars was chlorogenic acid. Of the six studied cultivars, 'Madrigal' had the highest phenolic content.

**Key words:** globe artichoke, Spanish cultivars, phenolic content, chlorogenic acid, apigenin, cynarin

### INTRODUCTION

Globe artichoke (*Cynara cardunculus* L. var. *scolymus* (L.) Fiori) is an ancient perennial and cross-pollinated plant that belongs to the Asteraceae family. Unlike other plants, the edible part of artichokes (35–55% of fresh weight) is the immature inflorescence called capitula, buds or heads [Abu-Reidah et al. 2013], which is harvested in its early development stages with edible fleshy leaves (bracts) and a receptacle [Lombardo et al. 2010].

Artichoke has been known since ancient times as a food and herbal medicine. This native Mediterranean

Basin plant has been appreciated by ancient Egyptians, Greeks and Romans, who used it as both food and medicine (for its beneficial effects as hepatoprotectors, cholagogues, diuretics, liver-protectors and lipid-lowering agents) [Preziosi 1969, Gebhardt 1997, Lanteri et al. 2004, Lattanzio et al. 2009]. Currently, this vegetable is still an important component of the Mediterranean diet, and is consumed raw, boiled, steamed or fried. It is used in many recipes since it tastes good and is perceived as a healthy, nutritious vegetable [Pandino et al. 2011a]. The con-

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sumption of artichokes represents a diet source of fibre, inulin, vitamins and minerals [Orlovskaya et al. 2007, Lattanzio et al. 2009]. Apart from these nutrients, globe artichokes are a major source of bioactive compounds. In fact compared to other vegetables, artichoke is a promising source of polyphenols, hydroxycinnamates and flavones, whose therapeutic properties are well-documented [Brat et al. 2006, Pandino et al. 2011a].

Polyphenols are the most widely distributed class of plant secondary metabolites [Kähkönen et al. 1999] that play different roles in plant biology and human life, including UV protective agents, defensive compounds against herbivores, pathogens and parasites, as well as wound repair and protection from atmospheric pollution and extreme temperatures [Lombardo et al. 2012]. They also contribute to plant colours and the taste of food and drink [Haslam 1979, Hättenschwiler and Vitousek 2000]. Structurally, they range from simple molecules to highly polymerised compounds [Dewanto et al. 2002]. The most abundant phenolic substances reported in artichoke heads are the compounds that originate from the metabolism of phenylpropanoids such as mono- and dicaffeoylquinic acids, flavonoids like apigenin and different cyanidincaffeylglucoside derivatives. Of all the different caffeoylquinic acids, 5-O-caffeoylquinic acid (also known as chlorogenic acid) is the most important derivative [Lattanzio and Van Sumere 1987, Lattanzio et al. 1994, 2009]. Polyphenols are plant secondary metabolites that defend plants against biotic (i.e. bacteria, fungi, viruses) and abiotic (i.e. temperature, ultraviolet radiation) stress, and are also involved in plant growth and reproduction. Although they are not essential for growth and development in humans, their consumption has been related to a reduced risk of chronic diseases, such as diabetes, cancer, cardiovascular disease, and thus better quality of life [Pandino et al. 2011a]. These beneficial actions seem to be linked to their well-established dual role as a protective pool against oxidative damage caused by free radicals, and as substrates for oxidative browning reactions by both enzymatic and chemical mechanisms [Lombardo et al. 2010]. These data suggest that the edible part of artichoke heads might be an excellent source of diet

polyphenols and that artichoke could represent a renewed nutraceutical alternative to traditional phytopharmaceutical applications of leaf extracts.

Globe artichoke production reached 1.8 million of tons in 2013 worldwide [FAO 2016]. Of this amount, 51.7% came from Europe. Artichoke production in Africa, America and Asia represented 20.9%, 18.7% and 8.8%, respectively. In Europe, Italy (466508 Tm) is, besides being the major artichoke producer, the holder of the most important germplasm with numerous commercial and local varieties of globe artichokes that have adapted to different environments [Mauromicale and Ierna 2000, Fratianni et al. 2007]. Thus it not surprising that Italian cultivars (Catanese, Bianco di Pertosa, Carciofo di Aquara, Tondo di Paestum, C3, Violet de Provence, Romanesco, Tema, Tempo, Tondo di Paestum, Violetto di Sicilia) are the most studied for their composition and phenolic characterization [Lattanzio and Van Sumere 1987, Fratianni et al. 2007, Lombardo et al. 2010].

After Italy, Spain with 218 429 Tm in 2013 [FAO 2016] is the second largest artichoke producer and the first exporter of fresh and preserved artichokes. In Spain the main producing areas are located on the Mediterranean coast, especially Murcia, Alicante, and the Valle del Ebro. Despite the Spanish tradition in the production and consumption of this vegetable, artichoke production in Spain decreased from 306 Tm in 2003 to 166 Tm in 2010 [FAO 2016]. However, an increasing demand for functional foods with added value has led to a renewed interest in this crop, whose consequence has been the progressive recovery of its production capacity in recent years reaching a current production of 200 Tm. The main feature of Spanish production is its high industrial transformation rate. Although the importance of this crop in the Spanish agronomy, hardly any data on the polyphenol content of Spanish artichoke cultivars are available.

The aim of the study reported herein was to analyze the polyphenols of different parts (outer, intermediate and inner bracts, and receptacle) of heads in six artichoke cultivars, and to compare the phenolic content of these cultivars with those reported for Italian cultivars.

## MATERIALS AND METHODS

**Chemicals.** All the analytical reagents and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA) or Scharlab (Barcelona, Spain).

**Plant material.** Six different globe artichoke cultivars that are frequently cultured in Spain were included in this study: ‘Opal’, ‘Concerto’, ‘Symphony’, ‘Madrigal’, ‘Blanca de Tudela’ and ‘A-106’. Plants were cultured in the Cajamar fields (Paiporta, Spain) in 2013 under standard growth conditions and management practices.

‘Opal’, ‘Concerto’, ‘Symphony’ and ‘Madrigal’ are seed-propagated F1 cultivars of Nunhems, the seed brand of Bayer Crop Science. ‘Opal’ and ‘Concerto’ are purpled cultivars (tab. 1). ‘Opal’ is an early cultivar of medium colour, conical and is medium- or large-sized for autumn-winter-spring production, while ‘Concerto’ is deeper in colour, but is a late cultivar for winter-spring production, is less conical to cylindrical and smaller in size than ‘Opal’. ‘Madrigal’ and ‘Symphony’ are light green cultivars, ‘Madrigal’ is more conical in shape and has larger heads than ‘Symphony’, which is earlier and suitable for autumn-winter-spring production. ‘Blanca de Tudela’ is the main vegetative-propagated Spanish cultivar and represents more than 90% of total Spanish production.

The capitula for the analysis were obtained from the plants in a field experiment conducted at the Cajamar Field Station in Paiporta, SW Valencia (Spain). The seed-propagated cultivars were sown on 6 June 2012 and planted on 25 July 2012, as was the vegetative-propagated ‘Blanca de Tudela’ in sandy clay

loam soil (59% sand; 18% silt; 23% clay), pH = 8.4, organic matter = 1.29%; CE (1 : 5) = 0.168 dSm<sup>-1</sup>. Average temperatures between August 2012 and May 2013 ranged between 26.5°C and 11.2°C, maximum temperatures between 31.6°C and 16.5°C, and minimum temperatures between 21.4°C and 4.6°C.

Plants were arranged in a completely randomized manner with three replicates of eight plants per plot. Fertilization and irrigation were performed following Pomares et al. [2004]. Management of weed and pests was in accordance to standard commercial practices.

After reaching commercial maturity, 10–15 artichoke heads were carefully selected, manually recollected and transported to the laboratory at 4°C. At the laboratory, samples were washed, examined to eliminate damaged samples, cut into three pieces (stem [5 cm], external bracts [non-edible part] and receptacles [edible part]), freeze-dried, milled and stored in sailing bags until chemical analyses.

**Sample preparation for HPLC analyses.** The phenolic extract was obtained by solvent extraction with methanol (1 : 10) in a reflux condenser at the temperature of the solvent boiling point for 3 h. After percolation, the material was treated again with 80% methanol and was extracted twice for 2 h. Methanol extracts were joined, the solvent was evaporated, and the remains were eluted with hot water (50 ml). Water solutions were left in a refrigerator for 24 h. The separated tarry residues that contained ballasts were filtered and rinsed with distilled water. Having been obtained in this way, the filtrate was degreased by shaking 3 times with light petroleum (30 ml each). Then purified water solutions were extracted 10 times

**Table 1.** Colour, shape, weight and dimensions of the heads from different seeds cultivars with modification [Macua and Lahoz 2016]

Cultivar	Exterial colour	Head shape	Mean weight (g)	Height/diameter ratio	Mean heart thickness (mm)
B. Tudela	green	oval	119	1.26	11.7
A-106	green with violet tones	spherical	132	1.03	12.1
Concerto	dark violet with green tones	ellipsoidal	109	1.17	13.3
Madrigal	green	ellipsoidal	151	1.09	13.2
Symphony	green	oval	130	1.20	10.7

with diethyl ether (20 ml each). Joined ether extracts were concentrated to a 100-ml volume and shaken 10 times with a 5% water solution of NaHCO<sub>3</sub> (10 ml each) to transform phenolic acids into salts that were readily soluble in water. Bicarbonate fractions, including phenolic acids salts, were acidified with 35% HCl to pH = 3. In this way free phenolic acids were obtained, which were again extracted with diethyl ether by shaking with this solvent 10 times (10 ml each). Ether extracts were joined and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was then distilled until dry to give free phenolic acid fractions.

**HPLC determination of polyphenols.** HPLC separation was performed on a UFLC Shimadzu series instrument (Japan) coupled to a diode-array detector (DAD). Separation was performed in a Phenomenex Synergi Fusion-RP column (4 µm, 250 × 4.6 mm i.d.; Phenomenex) with a sample injection volume of 20 µL. The mobile phase was composed of acetonitrile (A) and water/formic acid (100/0.1, v/v) (B). A gradient programme was followed as so: 20% A (0 min), 25% A (10 min), 25% A (20 min), 50% A (40 min), 100% A (42–47 min), 20% A (49–55 min). The mobile phase flow rate was 1 mL/min; the chromatogram was recorded at 280 nm and 320 nm, and the spectral data for all the peaks were accumulated within the 190–400 nm range. Column temperature was controlled at 30°C [Gouveia and Castilho, 2012]. Apigenin, chlorogenic acid and cynarin were quantified according to the external standard method, in which a calibration curve of the peak area was used against the compound concentration. Total polyphenol

content was calculated as the sum of the identified phenolic contents: chlorogenic acid, apigenin, cynarin.

**Statistics.** The results of the polyphenolic content in the different artichoke head parts of all six cultivars were statistically processed by Statgraphics Centurion XV (Manugistics Inc., Rockville, MD, USA). Data were statistically processed using Statgraphics Centurion XVI (Statpoint Technologies, Inc., Warrenton, VA, USA). The influence of different cultivars and parts of the artichoke head on the content of a specific compound was analyzed by an analysis of variance (multifactor ANOVA). The LSD (least significant difference) procedure was used to test differences between averages at the 5% significance level.

## RESULTS AND DISCUSSION

**Total fresh weigh.** Total fresh weight of the non-edible and edible parts of the capitula ranged between 97 and 135 g·100 g<sup>-1</sup>. The highest value corresponded to the ‘Madrigal’ cultivar (tab. 2). Significant differences were observed in the average of fresh weight values of the stems, non-edible and edible parts among cultivars. For stem, weight values varied between 6 g·100 g<sup>-1</sup> for the ‘Symphony’ cultivars and 12 g·100 g<sup>-1</sup> for the ‘Madrigal’ cultivars. The weight values of the non-edible and edible parts of the capitula ranged from 50–71 and from 42–57 g·100 g<sup>-1</sup>, respectively. In both cases, the ‘Symphony’ cultivar obtained the lowest values. Higher values corresponded to ‘Madrigal’ and A106 for the non-edible parts, and to ‘Madrigal’ and ‘Opal’ for the edible parts.

**Table 2.** Fresh weight (mean ± SD) of different artichoke head parts (g)

	Symphony	Concerto	Madrigal	Opal	A106	Blanca de Tudela	Average
Stem	6 ±2 <sup>a</sup>	10 ±2 <sup>b</sup>	12 ±4 <sup>b</sup>	10 ±4 <sup>b</sup>	4 ±3 <sup>a</sup>	11 ±2 <sup>b</sup>	9
Non-Edible	50 ±11 <sup>a</sup>	53 ±14 <sup>a</sup>	71 ±13 <sup>b</sup>	53 ±10 <sup>a</sup>	68 ±19 <sup>b</sup>	54 ±18 <sup>a</sup>	58
Edible	42 ±9 <sup>a</sup>	44 ±11 <sup>ab</sup>	52 ±9 <sup>cd</sup>	57 ±8 <sup>d</sup>	46 ±8 <sup>abc</sup>	51 ±11 <sup>bcd</sup>	49
<b>Average</b>	<b>33a</b>	<b>36a</b>	<b>45b</b>	<b>40ab</b>	<b>39a</b>	<b>39a</b>	<b>39</b>
Dry matter (DM)	13	14	22	17	19	17	

Data are mean ± standard deviation of fresh weight for each head part of cultivars. Within rows, values bearing different letters are significantly different by ANOVA and Tukey’s multiple comparison test ( $p < 0.05$ ). Two-way ANOVA analysis of fresh weight by cultivar and part of the artichoke head is  $p < 0.001$  for cultivar, part of the artichoke head, and for their interaction

**Table 3.** Total measured polyphenols content in different parts of the artichoke head (mg·100 g<sup>-1</sup>DW)

	Symphony	Concerto	Madrigal	Opal	A-106	Blanca de Tudela	Average
Stem	1428 ±37 <sup>c</sup>	1285 ±62 <sup>b</sup>	2371 ±63 <sup>d</sup>	1191 ±54 <sup>b</sup>	699 ±62 <sup>a</sup>	1403 ±515 <sup>c</sup>	1396
Edible parts	1433 ±59 <sup>c</sup>	1220 ±77 <sup>b</sup>	907 ±64 <sup>a</sup>	1398 ±41 <sup>c</sup>	974 ±39 <sup>a</sup>	1192 ±71 <sup>b</sup>	1187
Non-edible parts	396 ±36 <sup>ab</sup>	468 ±58 <sup>bc</sup>	491 ±65 <sup>c</sup>	506 ±43 <sup>c</sup>	345 ±22 <sup>a</sup>	650 ±22 <sup>d</sup>	476
<b>Average</b>	<b>1086c</b>	<b>991b</b>	<b>1256d</b>	<b>1032bc</b>	<b>673a</b>	<b>1082c</b>	<b>1020</b>

Data are mean ± standard deviation of total phenolic content for each head part of cultivars. Within rows, values bearing different letters are significantly different by ANOVA and Tukey's multiple comparison test ( $p < 0.05$ ). Two-way ANOVA analysis of fresh weight by cultivar and part of the artichoke head is  $p < 0.001$  for cultivar, part of the artichoke head, and for their interaction

**Quantification of phenolic compounds in different morphological head parts.** Total polyphenolic content in the heads of all the varieties is shown in Table 3. The cultivar with the maximum total phenolic content was 'Madrigal' (1256 ±857 mg·100 g<sup>-1</sup> DW), closely followed by 'Blanca de Tudela', 'Symphony' and 'Opal'. The lowest content was found in A-106, which had half the polyphenol content of 'Madrigal' (672 ±276 mg·100 g<sup>-1</sup> DW).

When comparing the phenolic content in different parts of the artichoke capitula (tab. 3), it can be seen that total polyphenol content in the stem and edible parts is higher than in the non-edible parts ( $p < 0.001$ ). The non-uniform distribution of polyphenols in the different capitula parts has been described by different authors [Fратиanni et al. 2007, Lombardo et al. 2009, 2010, Pandino et al. 2011b].

The polyphenolic content in stems ranged between 2371 ±63 mg·100 g<sup>-1</sup> DW in the 'Madrigal' cultivars and 699 ±62 mg·100 g<sup>-1</sup> DW in A-106. In the edible parts, the highest content was found in 'Symphony' and 'Opal' (1433 ±59 and 1398 ±41 mg·100 g<sup>-1</sup> DW, respectively) and the lowest (907 ±64 mg·100 g<sup>-1</sup> DW) in 'Madrigal'. In the outer bracts, 'Blanca de Tudela' had the highest phenolic content (650 ±22 mg·100 g<sup>-1</sup> DW), followed by 'Opal', 'Madrigal' and 'Concerto' (506 ±43, 491 ±65, 468 ±58 mg·100 g<sup>-1</sup> DW, respectively). The lowest content was found in 'Symphony' (396 ±36 mg·100 g<sup>-1</sup> DW). According to this distribution, 'Symphony', Opal, 'Concerto' and 'Blanca de

Tudela' should be used for fresh consumption purposes for their high polyphenols content in edible parts [Lombardo et al. 2010]. Varieties with the lowest polyphenols content (i.e. A-106) should be used for food processing since it is supposed their tendency to browning is less during handling and storage [Lombardo et al. 2010]. In contrast, 'Madrigal' should be used for preparing pharmaceutical compounds thanks to its high content of polyphenol in stems and non-edible parts. Despite these differences, these results suggest that the studied Spanish cultivars represent an important source of dietary polyphenols.

The content in the most abundant phenolic compounds (apigenin, chlorogenic acid and cyanirin) distributed in the different globe artichoke head parts are shown in Tables 4–6. As observed, chlorogenic acid was the predominant phenolic species, followed by apigenin and cyanarin.

**Chlorogenic acid.** Chlorogenic acid content in the heads and stems of the six artichoke varieties cultured in Spain is displayed in Table 4. The analysis revealed that the content of this phenolic compound was higher in stems than in the edible and non-edible parts of heads ( $p < 0.01$ ). The stems of the 'Madrigal' cultivar had the highest content (1.314 ±32 mg·100 g<sup>-1</sup> DW), whereas the non-edible parts of A-106 contained only 165 ±9 mg·100 g<sup>-1</sup> DW. The chlorogenic acid content in the edible parts ranged from 388 ±22 mg·100 g<sup>-1</sup> DW in A-106, and 677 ±45 mg·100 g<sup>-1</sup> DW in 'Sym-

phony'. A comparison of these values with those reported in the literature for globe artichokes cultured in other territories revealed that the Spanish varieties are generally richer in chlorogenic acid. In the artichokes cultured in Italy, only the chlorogenic acid content in the receptacle and inner bracts of Violetto de Sicilia ( $471 \pm 26$  and  $1.484 \pm 25$  mg·100 g<sup>-1</sup> DW, respec-

tively) were at the same level as the Spanish cultivars [Lombardo et al. 2010]. The content in other varieties, such as 'Concerto', Harmony F<sub>1</sub>, 'Madrigal', 'Romanesco clone C3', 'Tema 2000', 'Tempo', 'Tondo di Paestrum' or 'Violet de Provence', was 10 to 100-fold lower than in the Spanish cultivars [Lombardo et al. 2010].

**Table 4.** Chlorogenic acid content in different parts of the artichoke head (mg·100g<sup>-1</sup> DW)

	Symphony	Concerto	Madrigal	Opal	A-106	Blanca de Tudela	Average
Stem	815 ±13 <sup>c</sup>	752 ±22 <sup>c</sup>	1314 ±32 <sup>d</sup>	577 ±27 <sup>b</sup>	343 ±38 <sup>a</sup>	781 ±12 <sup>c</sup>	764
Edible parts	677 ±45 <sup>c</sup>	570 ±45 <sup>b</sup>	410 ±34 <sup>d</sup>	610 ±18 <sup>b</sup>	388 ±22 <sup>a</sup>	567 ±39 <sup>b</sup>	537
Non-edible parts	194 ±12 <sup>ab</sup>	209 ±25 <sup>bc</sup>	246 ±36 <sup>c</sup>	249 ±18 <sup>c</sup>	165 ±9 <sup>a</sup>	336 ±28 <sup>d</sup>	233
<b>Average</b>	<b>562c</b>	<b>510b</b>	<b>657d</b>	<b>479b</b>	<b>299a</b>	<b>561c</b>	<b>511</b>

Data are mean ± standard deviation of chlorogenic acid content for each head part of cultivars. Within rows, values bearing different letters are significantly different by ANOVA and Tukey's multiple comparison test ( $p < 0.05$ ). Two-way ANOVA analysis of chlorogenic acid content by cultivar and part of the artichoke head is  $p < 0.001$  for cultivar, part of the artichoke head, and for their interaction

**Table 5.** Apigenin content in different parts of the artichoke head (mg·100 g<sup>-1</sup> DW)

	Symphony	Concerto	Madrigal	Opal	A – 106	Blanca de Tudela	Average
Stem	611 ±40 <sup>c</sup>	531 ±47 <sup>b</sup>	1054 ±32 <sup>d</sup>	612 ±29 <sup>c</sup>	355 ±26 <sup>a</sup>	664 ±24 <sup>c</sup>	638
Edible parts	741 ±37 <sup>d</sup>	640 ±33 <sup>c</sup>	468 ±35 <sup>a</sup>	778 ±27 <sup>d</sup>	579 ±25 <sup>b</sup>	614 ±34 <sup>bc</sup>	637
Non-edible parts	200 ±25 <sup>ab</sup>	258 ±35 <sup>c</sup>	242 ±30 <sup>bc</sup>	255 ±26 <sup>c</sup>	176 ±19 <sup>a</sup>	312 ±24 <sup>d</sup>	241
<b>Average</b>	<b>517bc</b>	<b>476b</b>	<b>588d</b>	<b>548c</b>	<b>370a</b>	<b>530c</b>	<b>505</b>

Data are mean ± standard deviation of apigenin content for each head part of cultivars. Within rows, values bearing different letters are significantly different by ANOVA and Tukey's multiple comparison test ( $p < 0.05$ ). Two-way ANOVA analysis of apigenin content by cultivar and part of the artichoke head is  $p < 0.001$  for cultivar, part of the artichoke head, and for their interaction

**Table 6.** Cynarin content in different parts of the artichoke head (mg·100 g<sup>-1</sup> DW)

	Symphony	Concerto	Madrigal	Opal	A – 106	Blanca de Tudela	Average
Stem	1.60 ±0.2 <sup>bc</sup>	1.54 ±0.18 <sup>bc</sup>	2.19 ±0.17 <sup>c</sup>	1.50 ±0.18 <sup>b</sup>	0.83 ±0.11 <sup>a</sup>	1.87 ±0.19 <sup>d</sup>	1.59
Edible parts	14.0 ±2 <sup>c</sup>	10.3 ±0.9 <sup>b</sup>	28.0 ±3 <sup>d</sup>	9.5 ±0.5 <sup>b</sup>	5.9 ±0.7 <sup>a</sup>	10.8 ±1.5 <sup>b</sup>	13.09
Non-edible parts	0.84 ±0.10 <sup>a</sup>	0.73 ±0.10 <sup>a</sup>	3.10 ±0.3 <sup>d</sup>	2.70 ±0.2 <sup>c</sup>	3.60 ±0.3 <sup>e</sup>	1.99 ±0.16 <sup>b</sup>	2.16
<b>Average</b>	<b>5.48c</b>	<b>4.19b</b>	<b>11.10d</b>	<b>4.57b</b>	<b>3.44a</b>	<b>4.89bc</b>	<b>5.61</b>

Data are mean ± standard deviation of cynarin content in each head part of cultivars. Within rows, values bearing different letters are significantly different by ANOVA and Tukey's multiple comparison test ( $p < 0.05$ ). Two-way ANOVA analysis of cynarin content by cultivar and part of the artichoke head is  $p < 0.001$  for cultivar, part of the artichoke head, and for their interaction

**Apigenin content.** Apigenin is an important flavonoid in globe artichokes. Flavonoids are known to inhibit low-density lipoprotein oxidation and reduce thrombotic tendency [Hertog et al. 1993]. The content of this phenolic compound in the non-edible parts of artichoke capitulas ranged from  $176 \pm 19$  mg·100 g<sup>-1</sup> DW for the A-106 cultivar and  $312 \pm 24$  mg·100 g<sup>-1</sup> DW for Blanca de Tudela (tab. 5). These values agree with those reported by other authors [Pandino et al. 2011a, Lombardo et al. 2012]. In the edible parts, ‘Madrigal’ had the lowest content ( $468 \pm 35$  mg·100 g<sup>-1</sup> DW), followed by A-106 ( $579 \pm 25$  mg·100 g<sup>-1</sup> DW), ‘Blanca de Tudela’ ( $614 \pm 34$  mg·100 g<sup>-1</sup> DW) and ‘Concerto’ ( $640 \pm 33$  mg·100 g<sup>-1</sup> DW). The highest contents were found in the ‘Symphony’ ( $741 \pm 37$  mg·100 g<sup>-1</sup> DW) and ‘Opal’ cultivars ( $778 \pm 27$  mg·100 g<sup>-1</sup> DW). These contents doubled those reported in the study of Pandino et al. [2011a]. If we bear in mind the presence of a large amount of apigenin in the edible parts of globe artichoke plants, and as consumers are really interested in functional foods, the excellent composition of artichoke in functional compounds may encourage consumers to eat this vegetable on a large scale [Lombardo et al. 2012]. Finally, apigenin content in stems ranged from  $355 \pm 26$  in A-106 to  $1,054 \pm 32$  mg·100 g<sup>-1</sup> DW in ‘Madrigal’. This high content indicates the potential of the Spanish cultivars for preparing apigenin-rich polyphenolic extracts from artichoke stems, which are generally discarded as waste.

**Cynarin.** Cynarin is a typical hydroxycinnamic acid in globe artichokes. Among different natural bioactive compounds, it is genuinely appreciated for its choleric action [Gebhardt 1997]. In the edible parts, the content of this compound ranged from  $5.9 \pm 0.7$  mg·100 g<sup>-1</sup> DW in A-106 to  $28.3 \pm 3$  mg·100 g<sup>-1</sup> DW in ‘Madrigal’ (tab. 6). The cynarin content in stems and outer bracts was 6-fold lower. In outer bracts, the highest content was found in A-106 ( $3.6 \pm 0.3$  mg·100 g<sup>-1</sup> DW), closely followed by ‘Madrigal’ ( $3.1 \pm 0.3$  mg·100 g<sup>-1</sup> DW). The stem parts of ‘Madrigal’ and ‘Blanca de Tudela’ contained 2.19 and 1.87 mg·100 g<sup>-1</sup> DW, respectively.

The lowest cynarin content was found in the A-106 cultivar stems ( $0.83$  mg·100 g<sup>-1</sup> DW). Comparing cynarin content with values reported in the literature for other cultivar, it can be concluded that the cynarin content in the Spanish cultivars was higher than in the Italian ones of the same varieties (i.e. ‘Concerto’ or ‘Madrigal’) [Lombardo et al. 2010]. This makes Spanish globe artichokes a good dietary source of flavonoids, whose presence is not widely distributed in food plants.

## CONCLUSIONS

The analysis of the most important polyphenols present in globe artichokes (i.e. chlorogenic acid, apigenin and cynarin) demonstrated the high content of polyphenols in six different Spanish cultivars. The most abundant species was chlorogenic acid, followed by apigenin and cynarin. While apigenin and cynarin accumulated mainly in the receptacle and inner bracts, chlorogenic acid predominated in stems. These data suggest the importance of these cultivars in not only the food industry, but also in the pharmaceutical one where industrial waste could be used to produce concentrated phenolic extracts. Finally, compared to globe artichokes cultured in other territories, the Spanish cultivars contained higher levels of all three analysed polyphenols than globe artichokes harvested in Italy. This evidence might be used to commercially promote Spanish varieties of globe artichokes, and to thus increase the consumption of this traditional crop in the context of a Mediterranean diet.

## REFERENCES

- Abu-Reidah, I.M., Arráez-Román, D., Segura-Carretero, A., Fernández-Gutiérrez, A. (2013). Extensive characterisation of bioactive phenolic constituents from globe artichoke (*Cynara scolymus* L.) by HPLC–DAD–ESI–QTOF–MS. Food Chem., 141(3), 2269–2277.
- Brat, P., Georgé, S., Bellamy, A., Du Chaffaut, L., Scalbert, A., Mennen, L., Arnault, N., Amiot, M.J. (2006). Daily polyphenol intake in France from fruit and vegetables. J. Nutr., 136(9), 2368–2373.

- Dewanto, V., Wu, X., Adom, K.K., Liu, R.H. (2002). Thermal processing enhances the nutritional value of tomatoes by increasing total antioxidant activity. *J. Agric. Food Chem.*, 50(10), 3010–3014.
- FAO (2006). Organic Agriculture and Food Security. <http://www.faostat.fao.org>.
- Fратиanni, F., Tucci, M., De Palma, M., Pepe, R., Nazzaro, F. (2007). Polyphenolic composition in different parts of some cultivars of globe artichoke (*Cynara cardunculus* L. var. *scolymus* (L.) Fiori). *Food Chem.*, 104(3), 1282–1286.
- Gebhardt, R. (1997). Antioxidative and protective properties of extracts from leaves of the artichoke (*Cynara scolymus* L.) against hydroperoxide-induced oxidative stress in cultured rat hepatocytes. *Toxicol. Appl. Pharmacol.*, 144, 279–286.
- Gouveia, S.C., Castilho, P.C. (2012). Phenolic composition and antioxidant capacity of cultivated artichoke, Madeira cardoon and artichoke-based dietary supplements. *Food Res. Int.*, 48, 712–724.
- Haslam, E. (1979). Vegetable tannins. In: *Biochemistry of plant phenolics*, Swain, T. (ed.). Springer US, New York, 475–523.
- Hättenschwiler, S., Vitousek, P. M. (2000). The role of polyphenols in terrestrial ecosystem nutrient cycling. *Trends Ecol. Evol.*, 15(6), 238–243.
- Hertog, M.G., Feskens, E.J., Kromhout, D., Hollman, P.C.H., Katan, M.B. (1993). Dietary antioxidant flavonoids and risk of coronary heart disease: the Zutphen Elderly Study. *Lancet*, 342(8878), 1007–1011.
- Kähkönen, M.P., Hopia, A.I., Vuorela, H.J., Rauha, J.P., Pihlaja, K., Kujala, T.S. (1999). Antioxidant activity of plant extracts containing phenolic compounds. *J. Agric. Food Chem.*, 47, 3954–3962.
- Lanteri, S., Saba, E., Cadinu, M., Mallica, G.M., Baghino, L., Portis, E. (2004). Amplified fragment length polymorphism for genetic diversity assessment in globe artichoke. *Theoret. Appl. Gen.*, 108(8), 1534–1544.
- Lattanzio, V., Van Sumere, C.F. (1987). Changes in phenolic compounds during the development and cold storage of artichoke (*Cynara scolymus* L.) heads. *Food Chem.*, 24, 37–50.
- Lattanzio, V., Cardinali, A., Di Venere, D., Linsalata, V., Palmieri, S. (1994). Browning phenomena in stored artichoke (*Cynara scolymus* L.) heads: Enzymatic or chemical reactions? *Food Chem.*, 50, 1–7.
- Lattanzio, V., Kroon, P.A., Linsalata, V., Cardinali, A. (2009). Globe artichoke: a functional food and source of nutraceutical ingredients. *J. Funct. Foods*, 1(2), 131–144.
- Lombardo, S., Pandino, G., Mauro, R., Mauromicale, G. (2009). Variation of phenolic content in globe artichoke in relation to biological, technical and environmental factors. *Ital. J. Agron.*, 4, 181–189.
- Lombardo, S., Pandino, G., Mauromicale, G., Knödler, M., Carle, R., Schieber, A. (2010). Influence of genotype, harvest time and plant part on polyphenolic composition of globe artichoke [*Cynara cardunculus* L. var. *scolymus* (L.) Fiori]. *Food Chem.*, 119(3), 1175–1181.
- Lombardo, S., Pandino, G., Ierna, A., Mauromicale, G. (2012). Variation of polyphenols in a germplasm collection of globe artichoke. *Food Res. Int.*, 46(2), 544–551.
- Macua, J.I., Lahoz, I., (2016). Seeds artichoke in Navarre. *Acta Hort.* 1147, 177–182, <https://doi.org/10.17660/ActaHortic.2016.1147.26>.
- Mauromicale, G., Ierna, A. (2000). Panorama varietale e miglioramento genetico del carciofo. *L'Informatore Agrario*, 56, 39–45.
- Orlovskaya, T.V., Luneva, I.L., Chelombit'ko, V.A. (2007). Chemical composition of *Cynara scolymus* leaves. *Chem. Nat. Comp.*, 43, 239–240.
- Pandino, G., Lombardo, S., Mauromicale, G., Williamson, G. (2011a). Profile of polyphenols and phenolic acids in bracts and receptacles of globe artichoke (*Cynara cardunculus* var. *scolymus*) germplasm. *J. Food Compos. Anal.*, 24(2), 148–153.
- Pandino, G., Lombardo, S., Mauromicale, G., Williamson, G. (2011b). Phenolic acids and flavonoids in leaf and floral stem of cultivated and wild *Cynara cardunculus* L. genotypes. *Food Chem.*, 126, 417–422.
- Pomares, F., Baixauli, C., Aguilar, J.M., Giner, A., Tarazona, F., Gomez, J., Albiach, R. (2004). Effect of water and nitrogen fertilization on seed-grown globe artichoke. *Acta Hort.*, 660, 303–309, DOI 10.17660/actaHortic.2003.660.43
- Preziosi, P. (1969). Valutazione farmacologica dei principi attivi del carciofo. In: *Atti del I Congresso Internazionale di Studi sul Carciofo*. Edizioni Minerva Medica, Torino, 237–281.