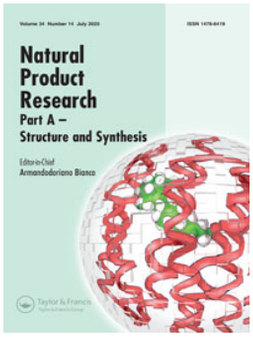

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SHORT COMMUNICATION

Phenolic compounds content and antioxidant capacity in cardoon achenes from different head orders

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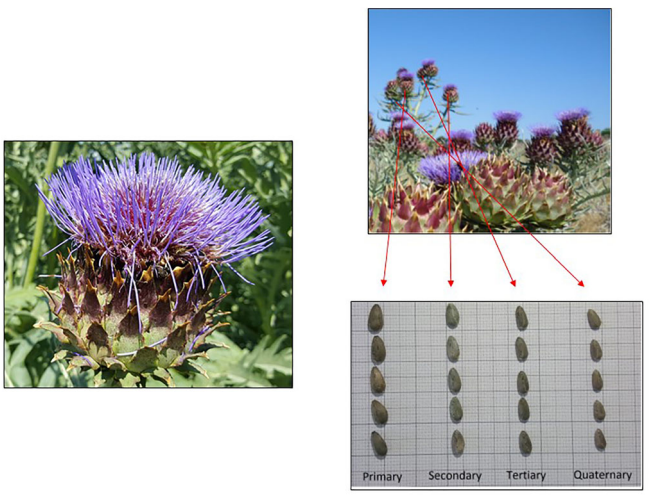
ABSTRACT

Cardoon inflorescences (heads) contain achenes, which are used for the production of edible oil and biodiesel but also represent a phenolic source. This research aimed at determining the level of bioactive compounds and antioxidant capacity of cardoon achenes and investigating their qualitative and quantitative variations in achenes harvested from heads having different insertion order on main stem. The head order significantly affected the number of achenes per head and one thousand weight but did not affect the achene values of antioxidant capacity and concentrations of total phenolic (107.7–117.4 g gallic acid equivalent kg^{-1} dry weight), as well as the concentration of chlorogenic and 3,5-di-*O*-E-caffeoylquinic acids. Conversely, the absolute amounts of these metabolites differed significantly among head order when referred to a single achene or head. About 75% of their absolute values per cardoon plant were produced by achenes belonging to secondary and tertiary heads.



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1. Introduction

The Mediterranean cardoon (*Cynara cardunculus* var. *altilis*) is a novel crop having interest for bioenergy, multipurpose uses, and industrial bio-based productions (Deligios et al. 2017; Gominho et al. 2018). Different plant fractions can support several productive exploitations of cardoon. The cardoon inflorescence is the *capitulum* (head), in which the florets are located on a flattened surface (receptacle), surrounded by bracts (Archontoulis et al. 2010a). The final number of heads (i.e. main stem head plus heads located on side branches of main stem) may reach 8–12 per plant (Archontoulis et al. 2010b). The cardoon fruits are achenes used for the production of edible oil, biodiesel and bioplastics (Raccuia et al. 2011).

According to Durazzo et al. (2013), cardoon achenes are rich in antioxidants, making this plant a potential useful source in nutritional field as well as agro-industrial applications. Among the various kinds of natural antioxidants, phenolic compounds play an important role in growth, reproduction and protection against abiotic and biotic stressors (Beckman, 2000), in pharmaceutical biology (Pejin and Bogdanović-Pristov 2012; Pejin et al. 2013; Glumac et al. 2017; Talevska et al. 2018) and exhibit a wide range of physiological effects when consumed by humans (Manach et al. 2004), such as anti-allergic, anti-atherogenic, anti-inflammatory, antimicrobial, antioxidant, anti-thrombotic, cardioprotective, and vasodilatory effects (Scalbert et al. 2005).

However, little information is still available regarding the overall phenolic composition and antioxidant properties of cardoon achenes as well as their contents in achenes belonging to heads having a different insertion orders on main stem (i.e. primary, secondary, tertiary and quaternary heads, respectively). Therefore, the main aims of this research were to (i) determine the level of bioactive compounds and antioxidant capacity of achenes, and (ii) investigate their qualitative and quantitative variations in achenes produced from primary, secondary, tertiary and quaternary heads, respectively.

2. Results and discussion

2.1. Total achene number per head, one thousand achene weight and estimation of achene yield

The total number of achenes was influenced by head order (Table S1) and the average number of achenes of the quaternary heads was approximately half than primary and secondary heads.

The one thousand achene weight differed significantly among head order and ranged from about 30 to 50 g in quaternary and primary heads, respectively. The recorded values were quite similar to those reported by Archontoulis et al. (2010b) who considered different ranges in cardoon seed from heads having different diameter and weight.

On average, the number of secondary, tertiary and quaternary heads per plant were 2.9, 3.4 and 1, respectively, and the achene yield per plant amounted to about 90 g (data not shown). Moreover, secondary and tertiary heads taken together represented about 75% of the total yield suggesting a preponderant role of these head orders on total achene production in cardoon plants. As we took into account only achenes normally ripened without any detectable damage, higher achene yields were

obtainable only in absence of insect damages, mainly caused by weevils, as reported in details from Sulas et al. (2018).

2.2. Antioxidant capacity, concentrations and absolute values of total phenolic, total flavonoids and individual phenolic compounds

Irrespective of head order, values of antioxidant capacity were in the range 16.0–16.8 and 16.0–16.1 mmol Trolox Equivalent Antioxidant Capacity (TEAC) 100 g^{-1} DW for 2,2′-azinobis (3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS) and of 1,1-diphenyl-2-picrylhydrazyl (DPPH), respectively (Table S2). Again irrespective of head order, total phenolic contents were in the range 107.7–117.4 g gallic acid equivalent (GAE) kg^{-1} DW, whereas total flavonoids varied from 16.8 to 20.1 g catechin equivalent (CE) kg^{-1} DW (Table S2).

Among the thirty individual phenolic compounds that were screened (Table S3), achenes were found to contain only two individual phenolic compounds, namely chlorogenic acid (1.18–1.40 g kg^{-1} DW) and 3,5-di-*O*-E-caffeoylquinic acid (3,5-DCQ, 12–13.2 g kg^{-1} DW) and their concentrations did not substantially differ in relationship to head order (Table S2).

On the contrary, when considering the absolute values for antioxidant capacity, total phenolic, total flavonoids, chlorogenic and 3,5-DCQ acids referred to a single achene (Table S4), marked differences were pointed out, indicating that variation was mainly caused by achene size. In addition, based on the achene number per head on Table S1, the corresponding absolute values were in the range 0.59–1.67 g GAE head^{-1} for total phenolic, 0.10–0.28 g CE head^{-1} for total flavonoids, 0.01–0.02 g head^{-1} for chlorogenic acid and 0.06–0.19 g head^{-1} for 3,5-DCQ acid, in quaternary and primary heads, respectively. At plant level, about 75% of investigated bioactive compounds were produced by secondary and tertiary heads.

There are only few studies dealing with the phenolic composition and antioxidant capacity in cardoon achenes. Khaldi et al. (2013) investigated several cultivars of wild and cultivated Tunisian cardoon and reported their total phenolic content of methanolic extracts (23.25 and 15.04 mg GAE g^{-1} DW, respectively), as also the total flavonoids (8.93 mg CE g^{-1} DW) contents of the wild cardoon seeds extracts lower than our results. In another study, Falleh et al. (2008) reported lower amounts of total phenolic (14.33 mg GAE g^{-1} DW) and flavonoids (9.78 mg CE g^{-1} DW) in seeds of Tunisian cardoon.

Durazzo et al. (2013) evaluated the TEAC in seeds of cultivated cardoon accessions and found values from 8.6 to 12 mmol TEAC 100 g^{-1} DW lightly lower than our results, probably due to the different genotype and extraction method.

As our results, Petropoulos et al. (2018b) identified in cardoon seeds only two phenolic compounds: chlorogenic acid and 3,5-DCQ detected at wavelength of 330 nm, with contents higher than our data but the concentration of 3.5-DCQ was tenfold higher than chlorogenic acid according to our results. These compounds were previously described in globe artichoke and wild cardoon head samples (Petropoulos et al. 2018a). The difference in the quantitative data could be explained with the different ripening stage of the heads and the different extraction methods. In fact, according to Petropoulos et al. (2018a), genotypic and growing conditions differences, as well as extraction method may play an important role in phenolic compounds profile and

could justify the contrasting results of the different studies. Raccuia et al. (2012) in a chemical characterization of cardoon achenes, after oil extraction, found three phenolic acids: chlorogenic acid (as our results), caffeic acid and catechin. On the contrary, we did not detect the last two compounds in our study.

To the best of our knowledge, our results represent the first information regarding antioxidant capacity, total phenolic, total flavonoids, chlorogenic acid and 3,5-DCQ specifically referred to achenes from different head order in cardoon. As about 75% of absolute values of total phenolic, total flavonoids, chlorogenic acid and 3,5-DCQ were produced by achenes belonging to secondary and tertiary heads, our results suggest the setting up an appropriate management aimed at maximize plant secondary and tertiary heads in order to enhance the production of bioactive compounds from cardoon achenes. Results also indicate the need to identify the best alternative uses (i.e. pharmaceutical, food, etc.) of achenes to enhance the added value of cardoon crop.

3. Conclusions

The number of achenes per head and achene size differed significantly among head order. Values of antioxidant capacity and concentrations of total phenolic and total flavonoids, as well as the concentration of chlorogenic and 3-5-DCQ acids were not affected by head order. Absolute values for antioxidant capacity, total phenolic, total flavonoids, chlorogenic and 3-5-DCQ acids contents referred to a single achene or head differed substantially among head order, they being mainly influenced by yield components such as achene size and number of achenes per head.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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