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Metabolite and mineral profiling of "Violetto di Niscemi" and "Spinoso di Menfi" globe artichokes by ^{1}H-NMR and ICP-MS

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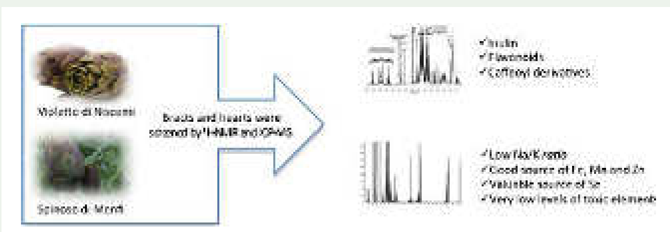
ABSTRACT
Globe artichoke has been long considered a nutraceutical food for its valuable content of bioactive compounds. However, beside a well-known polyphenol profile, poor information is available about its metabolite and mineral composition. The aim of this study was to investigate edible parts of Sicilian artichokes, 'Spinoso di Menfi' and 'Violetto di Niscemi', by ^{1}H NMR and ICP-MS for elucidating these compositional aspects. Although bracts and hearts of both artichokes shared a very similar metabolite pattern, 'Spinoso di Menfi' showed a higher number of metabolites, such as amino acids and polyphenols, than 'Violetto di Niscemi'. 'Spinoso di Menfi' was also marked by higher levels of macro- and microelements when compared to 'Violetto di Niscemi'. Also, artichoke heart demonstrated to accumulate higher mineral levels than bracts. ^{1}H NMR and ICP-MS successfully profiled metabolites and metals in such plant food, partially covering the lack of literature data about 'Spinoso di Menfi' and 'Violetto di Niscemi' artichokes.



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1. Introduction

Demand for food with benefits beyond basic nutrition has raised new commercial opportunities for food manufacturers. Indeed, functional foods containing bioactive compounds to prevent nutrition-related diseases and to increase physical and mental well-being of

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consumers are increasingly emerging in the marketplace (Siro et al. 2008). Among functional foods, a renewed focus on globe artichoke [*Cynara cardunculus* L. subsp. scolymus (L.) Hegi] has been recently reported (Lattanzio et al. 2009). Native to the Mediterranean area and cultivated worldwide, such herbaceous perennial plant has contributed significantly to the European agriculture and economy. In fact, in last 10 years, the Mediterranean Basin has accounted alone for the ~60% of the global artichoke production, with an estimated export value of 44.000 US dollars. Italy, in particular, has confirmed to be the major world producer with an average production of more than 500.000 tonnes, thanks to a wide genetic diversity of species, mainly distributed among Lazio, Tuscany, Apulia, Campania and Sicily (FAO 2016). In the latter region, 'Spinoso di Palermo' and 'Violetto di Sicilia' represent the two major cultivars, since they monopolise with different ecotypes the areas intended for globe artichoke culture, respectively, in the western and eastern side of the island, dominating the regional production (Mauromicale et al. 2004).

The edible part of globe artichoke is constituted by a large immature inflorescence, the so-called 'head', harvested in the early stages of plant development, and representing about the 30–40% of its weight. Typically characterised by fleshy bracts and a tender receptacle, known as 'heart', artichoke head is a precious food of the Mediterranean diet, because of its low-fat content (Lattanzio et al. 2009), and its richness in bioactive phenolic acids, flavonoids and inulin fibres, responsible for notorious hepatoprotective, antioxidant and anticarcinogenic effects (Lombardo et al. 2010; Pandino et al. 2011a). However, also by-products derived by globe artichoke processing, such as leaves and floral stems, are a precious source of health-promoting compounds (Pandino et al. 2013). Thanks to a valuable polyphenolic fraction, mainly composed of mono- and dicaffeoylquinic acids, flavonoids, as well as inulins, non-edible leaves, in particular, have long been appreciated in the phyto-medical area for their choleretic, diuretic, hepatoprotective properties, as well as antibacterial, antifungal and antioxidant activities (Rouphael et al. 2012; Colla et al. 2013; Lucini et al. 2016).

Although amount and types of constituents in plant food is typically linked to pre-harvest factors, such as environment and fertilisation, and genetic materials (e.g. cultivars) (Pantano et al. 2016; Tuttolomondo et al. 2015a, 2015b; Pandino et al. 2011b), experimental parameters, such as efficiency and reliability of the employed analytical method, may also qualitatively and quantitatively affect the compositional profile. Apart from some recent sensitive and sophisticated approaches (Shen et al. 2010; Farag et al. 2013), analysis of artichoke metabolites, mainly polyphenols, has been mostly based on HPLC, coupled with UV detection (Llorach et al. 2002), pulsed amperometric detection (Schütz et al. 2006), DAD detection (Sarawek et al. 2008), as well as DAD and MS detection (Schütz et al. 2004). In spite of the claimed low analytical sensitivity, proton nuclear magnetic resonance (^{1}H NMR) may be exploited as alternative approach to screen the entire metabolite profile of artichoke, including polyphenols, through a specific signal assignment, involving the identification of specific spin systems and fine structure coupled with labelled values for standard compounds (Mallamace et al. 2014; Cicero et al. 2015; Corsaro et al. 2015; Dugo et al. 2015). Furthermore, such an approach takes advantage of: (a) minimal sample preparation; (b) fast acquisition of a great amount of data; (c) non-destructive and non-invasive approach; and (d) high analytical reproducibility (Rotondo et al. 2011).

Contrary to the large amount of research devoted to the elucidation of bioactive polyphenols in artichoke, minor information about the metal profile of such a plant food is reported. To date, flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES) have been considered the techniques of choice for screening essential macro- and microelements of globe artichoke (Romani et al. 2006; Pandino et al. 2011b; Lombardo et al. 2012; Colla et al. 2013; Borgognone et al. 2016). However, inductively coupled plasma-mass spectrometry (ICP-MS) offers several advantages when compared to FAAS, including reduced spectral interferences, very low detection limits and a wider linear dynamic range, which allows the determination of major and trace elements at the same analysis. Additionally, ICP-MS provides valuable isotopic information and simpler spectral interpretation than ICP-OES (Nardi et al. 2009). Therefore, it is increasingly appreciated and routinely employed for fast and reliable food analyses (Bua et al. 2016; Di Bella et al. 2015; Lo Turco et al. 2012; Naccari et al. 2015; Salvo et al. 2016, 2014; Vadalà et al. 2016).

Within this context, the aim of the present work was to exploit high-throughput analytical approaches, such as ^{1}H NMR and ICP-MS, to explore the metabolite and metal composition of edible parts of two Sicilian artichoke, namely 'Spinoso di Menfi' and 'Violetto di Niscemi', belonging, respectively, to 'Spinoso di Palermo' and 'Violetto di Sicilia' cultivars. In particular, 'Spinoso di Menfi' received the 'Slow Food presidium', since it is the oldest and most precious globe artichoke produced in Sicily, which needs to be guaranteed and protected from other actual and more productive genetic material. The combination of ^{1}H NMR and ICP-MS could provide insights concerning the nutritional composition of edible parts of these two artichokes, yet not addressed in the literature, thus highlighting the close linkage between food and health, so that consumer's well-being, health and confidence could be improved.

2. Results and discussion

2.1. Metabolite fingerprints of 'Spinoso di Menfi' and 'Violetto di Niscemi' artichokes

^{1}H NMR was successfully applied for profiling the secondary metabolites of bracts and heart of the two investigated globe artichokes, since obtained extracts were characterised by the presence of numerous organic species belonging to different classes, namely amino acids, organic acids, carbohydrates, flavonoids and caffeoyl derivatives. Figure 1S and 4S report respectively the representative ^{1}H NMR spectrum of globe artichoke and the chemical structures of the main identified metabolites. Chemical shifts, coupling constants and related spectral peak assignments of detected metabolites are listed in Table 3S.

Different amino acids, such as valine, threonine, alanine, glicine, glutamate and tyrosine, were observed by ^{1}H NMR in both bracts and heart of the two Sicilian globe artichokes; while amino acids, such as tripthophan, leucine and isoleucine were only detected in bracts and heart of 'Spinoso di Menfi' (Table 3S). Although most of them are notoriously defined as essential aminoacids and result critical for whole metabolism, it becomes difficult to assess the value of such biocomponents in artichoke in absence of comparative studies and quantitative data. However, such screening could be a good starting point for further research.

An interesting organic acid pattern in bracts and heart of 'Spinoso di Menfi' and 'Violetto di Niscemi' artichokes was also elucidated. Indeed, the most common organic acids of plant foods, such as lactate, succinate, citrate and malate, were detected (Table 3S). They play an important role in metabolic activity, since they are mainly produced during the degradation of dietary constituents, such as carbohydrates, and often affect flavour, stability and keeping quality of food (Palmer & List 1973). Other organic acids detected by ^{1}H NMR were pyruvic acid, shikimic acid, quinic acid and gallic acid (Table 3S). In particular, the last three compounds take notoriously part in the shikimic acid pathway, involved in the biosynthesis of phenolic acids, such as gallic acid, characterised by valuable antioxidant properties (Ghasemzadeh & Ghasemzadeh 2011). The above-mentioned organic acids were detected in both bracts and heart with the exception of gallic acid, found only in heart of both globe artichokes.

^{1}H NMR analyses confirmed that artichoke is characterised by a limited presence of carbohydrates, mainly represented by monosaccharides and disaccharides (López-Molina et al. 2005). Indeed, simple sugars, such as fructose and glucose, and sucrose were identified in both bracts and heart of 'Spinoso di Menfi' and 'Violetto di Niscemi' artichokes (Table 3S). However, such sugars resulted to be also linked to several aglicones to form corresponding glicosides (Lombardo et al. 2009, 2010; Pandino et al. 2011a). The presence of few types of saccharides is counterbalanced by the presence of an alternative carbohydrate reserve, namely inulin (Lattanzio et al. 2009), detected in bracts and heart of both artichokes (Figure 1S, 4S and Table 3S). This fructan compound is considered as a diet fibre, since it is not digested in the small intestine, because of the lack of human enzymes required for fructan hydrolysis. One of the reasons explaining the renewed interest in globe artichoke has been just due to the fact that inulin positively affects the composition of the microflora gut, implying beneficial effects on mineral absorption and prevention of colon cancer. Furthermore, the valuable content of inulin linked to the scarce presence of non-fibre carbohydrates, makes artichoke an ideal food source to decrease blood glucose levels, as well as fat storage (Lattanzio et al. 2009).

Polyphenols are secondary metabolites commonly found in food and waste derived from plants (Alesci et al. 2014; Cacciola et al. 2016; Gervasi et al. 2016). In line with literature, globe artichoke head demonstrated to be a valuable source of two phenolic classes, namely flavonoids and caffeic acid derivatives, contributing considerably to its nutraceutical value, due to a well-know therapeutic activity (Pandino et al. 2011a; Lombardo et al. 2010, 2009; Fratianni et al. 2007).

Flavonoids occurred in both globe artichokes as aglycones and sugar conjugates, principally as *O*-glycosides. Luteolin and apigenin-7-*O*-β-D-glucoside were present in 'Violetto di Niscemi' and 'Spinoso di Menfi', while luteolin-7-*O*-β-D-glucoside was detected only in bracts and heart of 'Spinoso di Menfi' artichoke (Table 3S). Pandino and coworkers (2011a) elucidated the polyphenol content of different Italian artichoke cultivars by HPLC-DAD-MS/MS. Among them, 'Violetto di Sicilia' cultivar was considered, and the presence of luteolin and apigenin-7-*O*-β-D-glucoside was confirmed. However, several other works determined the phenolic profile of artichoke mainly by HPLC-MS approaches, and apigenin and luteolin flavones have always been identified in bracts and heart of the plant in form of glucosides and rutinosides (Fratianni et al. 2007; Lattanzio et al. 2009; Lombardo et al. 2009, 2010; Pandino et al. 2011a). In particular, globe artichoke constitutes a significant source of apigenin, which is not commonly found in other plant foods, because of its probable role in the biosynthesis of luteolin and, therefore its conjugates (Pandino et al. 2011a). On the other side, luteolin is also crucial for the nutraceutical effects of globe artichoke, since it inhibits *de novo* cholesterol biosynthesis (Fratianni et al. 2007). In general, all these flavonoids are well known to exhibit anticarcinogenic, vasomodulating, antioxidant and antimicrobial activities both *in vitro* and *in vivo* (Pandino et al. 2011a).

Conjugates derived from the reaction of caffeic acid with quinic acid are the most common constituents of the edible parts of globe artichoke (Lattanzio et al. 2009). In the present work,

^1H NMR allowed to detect three caffeic acid derivatives, namely 1,3-dicaffeoylquinic acid (in bracts and heart of both globe artichokes), 3,5-Di-O-caffeoylquinic acid (only in bracts and heart of 'Spinoso di Menfi' artichoke) and 5-O-caffeoylquinic acid (in bracts and heart of both globe artichokes) (Figure 1S, 4S and Table 3S). Obtained results are in line with previous works which have already explored the hydroxycinnamic acid derivative content of artichoke by HPLC coupled to PDA and/or MS/MS (Pandino et al. 2011a). In particular, 1,3-dicaffeoylquinic acid, also known as cynarin, shows typically higher contents in floral stem and leaves than head, and it is responsible for the choleretic properties of globe artichoke; while 5-O-caffeoylquinic acid, also known as chlorogenic acid and characterised by antioxidant and anticarcinogenic properties, is considered a typical metabolite of globe artichoke head, due to its potential involvement in many biochemical reactions producing different phenolic acids (Fratianni et al. 2007; Lombardo et al. 2010).

2.2. *Mineral composition of edible parts of 'Spinoso di Menfi' and 'Violetto di Niscemi' artichokes*

Although the intake of bioactive compounds is related to a lower incidence of chronic diseases, it is widely recognised that the lack of such substances in the diet does not induce human pathologies. Conversely, mineral deficiencies and imbalances give rise to many metabolic diseases, posing a serious threat to human health (Pandino et al. 2011b). The concentration of major elements, such as Na, K, Mg and Ca, and trace elements, such as Mn, Fe, Cu, Zn, Se, Cr, Ni, Ba, including potentially toxic trace elements, such as As, Cd Pb and Hg was determined in bracts and heart of 'Violetto di Niscemi' and Spinoso di Menfi" globe artichokes, employing a validated ICP-MS method. Overall, the artichoke head proved to be a good source of many mineral elements, but not heavy metals (Table 4S). However, the bioavailability of healthy metals is questionable since the chemical form of metals in food and/or nature of the food matrix, as well as the interaction between nutrients and other organic components (e.g. phytic acid, polyphenols, dietary fibres, oxalic acid, proteins, fat, ascorbic acid) can enhance or inhibit absorption (Gibson et al. 2006). Among macroelements, K and Ca were the main mineral constituents of bracts and heart of 'Spinoso di Menfi' and 'Violetto di Niscemi' globe artichokes, followed by Na and Mg. This trend was confirmed also in previous works focused on the mineral characterisation of 'Violetto di Sicilia', 'Violetto di Toscana' and 'Violetto di Provenza' cultivars (Romani et al. 2006; Lombardo et al. 2009; Pandino et al. 2011b), with the exception of 'Violetto di Toscana', where artichoke head showed bracts characterised by higher levels of Na than Ca. In the present study, the heart of 'Spinoso di Menfi' revealed levels of K and Ca equal to 6396.67 ± 129.61 and 4957.50 ± 183.73 mg kg^{-1}; while the heart of 'Violetto di Niscemi' was, respectively, characterised by K and Ca concentrations of 4093.72 ± 167.93 mg kg^{-1} and 4240.69 ± 103.94 mg kg^{-1}. Compared to heart, edible bracts showed slightly lower levels for both K and Ca in 'Spinoso di Menfi' (5754.08 ± 163.21 and 4153.55 ± 117.02 mg kg^{-1}, respectively) and 'Violetto di Niscemi' (3951.16 ± 145.05 and 3786.73 ± 125.70 mg kg^{-1}, respectively). The high levels of K could be explained by the fact that such macromineral is typically most absorbed by globe artichoke during its growing cycle (Pandino et al. 2011). Na and Mg represented ~19% and ~16% of the investigated major elements respectively in the head of 'Spinoso di Menfi' and 'Violetto di Niscemi', being more abundant in heart than bracts. Furthermore, Mg content showed the highest variation between the studied globe artichokes, since it varied of 51% and 56%, considering respectively bracts and heart. Although 'Spinoso di Menfi' revealed higher contents of all major elements, both Sicilian globe artichokes contributed significantly to the Recommended Dietary Allowances (RDAs) and adequate intakes (AIs) of macro-minerals established by the Food and Nutrition Board (Institute of Medicine 2005). Indeed, considering the assumption of 100 gr of 'Spinoso di Menfi' artichoke in an adult man (age comprised between 31 and 50 years), Na and K supplied respectively 9.30% and more than 100% of the relative AIs; while Ca and Mg respectively contributed to 45.56% and 34.22% of their RDAs. On the other side, the assumption of 100 gr of 'Violetto di Niscemi' showed to supply 6.61% of Na, 40.14% of Ca, 11.98% of Mg and more than 100% of K. Furthermore, both globe artichokes were characterised by a Na/K *ratio* well below the established counterpart (0.22 for 'Spinoso di Menfi' and 0.24 for 'Violetto di Niscemi' versus 0.3 of Food and Nutrition Board). Such an aspect represents an undeniable advantage from a nutritional point of view, since low levels of Na in food help to prevent hypertension and cardiovascular diseases.

As for trace elements, Fe, Mn and Zn constituted the most abundant microminerals in both 'Spinoso di Menfi' and 'Violetto di Niscemi' artichokes, thus, conferring them a high nutritional value. With the exception of Mn, Fe and Zn resulted slightly higher in heart than bracts of the two globe artichokes. This finding results partially in line with the work conducted by Pandino and colleagues (2011), where Fe and Mn resulted most abundant in bracts than heart. According to our results, Fe alone represented ~38% and ~32% of the investigated microelements respectively in 'Spinoso di Menfi' (bracts: 56.74 ± 2.16 mg kg^{-1}; heart: 67.33 ± 4.17 mg kg^{-1}) and 'Violetto di Niscemi' (bracts: 35.13 ± 1.16 mg kg^{-1}; heart: 38.39 ± 1.83 mg kg^{-1}), confirming to be the most abundant microelement in globe artichoke heads (Pandino et al. 2011); while Zn ranged from 45.07 ± 1.54 mg kg^{-1} to 48.85 ± 2.05 mg kg^{-1} in 'Spinoso di Menfi' and from 36.22 ± 1.95 mg kg^{-1} to 38.39 ± 1.83 mg kg^{-1} in 'Violetto di Niscemi'. Also, Mn resulted to be significantly more abundant in 'Spinoso di Menfi' (bracts: 33.43 ± 2.01 mg $kg^{-1;}$ heart: 32.14 ± 1.73 mg kg^{-1}) than in 'Violetto di Niscemi' (bracts: 17.19 ± 1.67 mg $kg^{-1;}$ heart: 16.01 ± 1.93 mg kg^{-1}). Considering the assumption of 100 gr of 'Spinoso di Menfi', Fe and Zn contributed to 34.46% and 46.96% of the respective RDAs; while Mn supplied more than 100% of its AI. On the other side, 'Violetto di Niscemi' supplied 47.41% of Fe, 37.30% of Zn and 72.17% of Mn.

Essential micro-nutrients such as Ni and Cu are cofactors of different enzymes, and play a fundamental role also in Fe absorption. Good levels of Ni and Cu were found in heart (10.51 ± 0.85 mg kg^{-1} and 9.11 ± 0.41 mg kg^{-1}, respectively) and bracts (8.67 ± 0.73 mg kg^{-1} and 8.15 ± 0.33 mg kg^{-1}, respectively) of 'Violetto di Niscemi'.

Among the trace elements, Se is another essential micro-mineral marked by a strong antioxidant activity, and, therefore, helpful in preventing oxidative stress-based diseases (Vadalà et al. 2016). Se showed the highest susceptibility to change between the two investigated globe artichokes, since its content varied between 81% and 94%, considering respectively bracts and heart. In particular, the highest content of such element was found in 'Spinoso di Menfi' artichoke, characterised by levels of Se equal to 0.85 ± 0.008 mg kg^{-1} in bracts and 1.24 ± 0.12 mg kg^{-1} in heart. Despite the lack of comparative literature data, investigated globe artichokes resulted to be a valuable source of Se, since it was calculated that 100 gr of 'Spinoso di Menfi' and 'Violetto di Niscemi' provided respectively more than 100% and 21.81% of Se. Just as with Se, determination of toxic elements in globe artichoke edible parts has not been yet carried out in other works. In the present study, toxic elements such as As and Cd were found in higher amounts in 'Spinoso di Menfi' (bracts: 0.33 ± 0.03 mg kg^{-1}

and 0.03 ± 0.002 mg kg^{-1} respectively; heart: 0.52 ± 0.09 mg kg^{-1} and 0.02 ± 0.002 mg kg^{-1}, respectively) than 'Violetto di Niscemi' (bracts: 0.01 ± 0.002 mg kg^{-1} and 0.02 ± 0.001 mg kg^{-1} respectively; heart: 0.01 ± 0.001 mg kg^{-1} and 0.01 ± 0.004 mg kg^{-1}, respectively); while Pb was more abundant in 'Violetto di Niscemi' (bracts and heart: 0.12 ± 0.07 mg kg^{-1} and 0.09 ± 0.002 mg kg^{-1} respectively) than 'Spinoso di Menfi' (0.04 ± 0.009 mg kg^{-1} in bracts and 0.04 ± 0.01 mg kg^{-1} in heart). Hg resulted inferior to LOQ in bracts and heart of both globe artichokes, confirming to be typically present at very low levels in plant foods (European Commission 2004). The Commission Regulation (EC) No. 1881/2006 established maximum levels of certain contaminants, including heavy metals such as Cd and Pb, in foodstuffs (EC no. 1881/2006). No maximum levels of Hg and As have been fixed for food plants, since the European Food Safety Autority (EFSA) affirmed that the chemical form in which such elements accumulate in vegetables, as well as relative contents, do not represent a risk to human health. According to the obtained data, levels of Pb equal and slightly below the safety limit (0.10 mg kg^{-1}) were detected respectively in bracts and heart of 'Violetto di Niscemi' artichoke; while Cd content were well below the regulatory level (0.10 mg kg^{-1}) in both Sicilian globe artichokes.

PCA performed on ICP-MS data of nutritionally important major and trace elements allow to reduce the entire data-set with a minimum loss of original information. Figure 5S shows the overlapped loading and score plots, explaining the major variability on PC1 (89.4%). The PCA loading plot reveals a clear clustering between K, Se, Fe and Zn, as well as a strong association between Mg and Na, which are characterised by the highest positive values on PC1. Overlapping the loading and score plots, it results that the content of such elements was higher in heart and bracts of 'Spinoso di Menfi' than 'Violetto di Niscemi', whose bracts and heart plot on the negative side of the PC score plot. From the loading and score plot, it can also be interpreted that hearts of 'Spinoso di Menfi' and 'Violetto di Niscemi' contain higher mineral levels than the respective bracts, since they show, respectively, the highest positive and lowest negative values on the PC1 space component.

3. Experimental

See Supplementary materials for: plant material, chemicals and standard solutions, instrumentation, sample preparation and analyses.

4. Conclusions

In the present study, the metabolite and mineral composition of two valuable Sicilian globe artichokes was investigated by high-throughput analytical techniques. Indeed, although several works already focused on the chemical composition of artichoke, ^{1}H NMR was employed as alternative technique to LC-based approaches for successfully elucidating the metabolite composition of such food plant, while ICP-MS helped to deepen the profile of minerals and toxic elements of globe artichoke, to date poorly addressed. Our data confirmed that the head of globe artichoke represents a valuable nutraceutical source of the Mediterranean diet. In fact, despite the lack of quantitative data, qualitative metabolite profiles delineated the presence of precious bioactive compounds, such as inulin, caffeoyl derivatives and flavonoids in both bracts and heart of 'Violetto di Niscemi' and 'Spinoso di Menfi'. Furthermore, ICP-MS confirmed not only that macro- and micro-minerals generally accumulated in heart in higher contents than bracts, but also that 'Spinoso di Menfi' is a more valuable mineral source, when compared to 'Violetto di Niscemi'.

Disclosure statement

No potential conflict of interest was reported by the authors.

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