L. F. Di Cesare[1],
R. Lo Scalzo[1],
C. Migliori[1],
G. Campanelli[2], V. Ferrari[2]

# Chemical and nutraceutical profile of italian onion (*Allium cepa* L.) organic-grown genotypes

Progress in Nutrition
Vol. 15, N. 4, 220-225, 2013

**Titolo**
Profili chimici e nutraceutici di genotipi di cipolla (*Allium cepa* L.) coltivati in biologico

**Key words**
Unsaturated sulfur volatiles, soluble sugars, vitamin C, quercetins, antiradical capacity, anthocyanins, GC-MS and HPLC analysis.

**Parole chiave**
Solfuri volatili insaturi, zuccheri solubili, vitamina C, quercetine, capacità antiradicalica, antociani, analisi GC-MS ed HPLC.

[1]Consiglio per la Ricerca e Sperimentazione in Agricoltura, CRA-IAA, Via G. Venezian, 26 - 20133 Milano, Italy
[2] Consiglio per la Ricerca e Sperimentazione in Agricoltura, CRA-ORA, Via Salaria, 1 - 63030 Monsampolo del Tronto (AP), Italy

Address for correspondence:
Dr. Luigi Francesco Di Cesare
E-mail: luigi.dicesare@entecra.it

Lavoro svolto nell'ambito del progetto "VALOR.BIO", MiPAAF (D.M. 314/2007), e presentato al IX Congresso di Chimica degli Alimenti (ChimALSI), Ischia (Na), 3-7 Giugno 2012.

**Summary**
The aim of this study was the evaluation of quality parameters in four onion genotypes named "Suasa" and "Precoce di Romagna", landraces typical from Marche and Emilia Romagna region, respectively; "Tropea", a commercial cv and "Density", a commercial hybrid. All genotypes have been cultivated in 2011 season on 11 years organic-converted soils. All samples, harvested at commercial ripening, have been subjected to some quality aspects as follows. Chemical quality: soluble sugars, unsaturated and saturated sulfur volatile compounds. Nutraceutical quality: unsaturated sulfur volatile compounds, ascorbic acid, quercetins, anthocyanins, polyphenols by Folin-Ciocalteau reaction, and antiradical capacity. The attention was particularly focused on unsaturated volatile sulfur compounds for their anti-carcinogenic effect. Moreover, quercetins are noted for their antiradical capabilities. The saturated sulfides content ranged 1282-1705 μg/100g dm for all genotypes, with the exception of Suasa (938 μg/100g dm). The unsaturated sulfur substances content ranged 3188-3716 μg/100g dm for Density, Tropea and Precoce di Romagna, while a lower amount for Suasa, 1917 μg/100g dm was ascertained. Quercetins, highly correlated with antiradical activity (rxy=0.94), revealed high content in Density and Tropea (43.3 and 30.6 mg/100g fw), and low amount in Precoce di Romagna and Suasa (13.1 and 11.4 mg/100g fw). The potential anti-tumor activity, given by unsaturated sulfur substances, resulted better in all genotypes than Suasa, with an high antiradical potential in Density and Tropea.

**Riassunto**
Lo scopo di questa ricerca è stato quello di valutare i parametri qualitativi di 4 cv di cipolla: Suasa e Precoce di Romagna, cv locali tipiche rispettivamente della regione Marche ed Emilia Romagna, Tropea cv commerciale e Density, ibrido commerciale. I genotipi sono stati raccolti nel 2011 in un terreno convertito alla coltivazione biologica da 11 anni. Tutti i campioni, al giusto grado di maturazione commerciale, sono stati sottoposti alla valutazione dei seguenti aspetti qualitativi. Qualità chimica: zuccheri solubili e solfuri volatili saturi ed insaturi. Qualità nutraceutica: solfuri volatili insaturi, acido ascorbico, quercetine, antocianine, polifenoli (reazione di Folin-Ciocalteau) totali

e capacità antiradicalica. La nostra attenzione è stata posta sulle sostanze solforate insature per il loro effetto antitumorale e sulle quercetine, dotate di una elevata capacità antiossidante rispetto agli altri composti polifenolici. I contenuti delle sostanze solforate sature oscillavano fra 1282 e 1705 μg/100g ss per tutti i genotipi ad eccezione della Suasa (938 μg/100g ss). Invece le sostanze solforate insature oscillavano tra 3188 e 3716 μg/100g ss per la Density, Tropea e Precoce di Romagna; valori più bassi, intorno a 1917 μg/100g ss erano rilevati nella Suasa. Le quercetine presentavano un'alta correlazione con la capacità antiradicalica (rxy = 0.94) e denotavano i maggiori contenuti nella Density e Tropea (43.3 e 36.6 mg/100 g pf) ed i più bassi nella Precoce di Romagna e Suasa (13.1 e 11.4 mg/100 g pf). Pertanto la potenziale attività antitumorale collegata alle sostanze solforate insature era elevata in quasi tutti i genotipi, ad eccezione della Suasa; mentre una alta potenziale attività antiradicalica era riscontrata nella Density e Tropea.

**Introduction**

Onion (*Allium cepa* L.) represents a food product significantly rich in healthy compounds. There are evidences that onion and garlic protect against cancer in humans. This effect is due, at first instance, to the organosulfur compounds that are represented by two different classes according to their side carbon chains (unsaturated or saturated ones). The unsaturated (diallyl disulfide, diallyl trisulfide, dipropenyl disulfide and trisulfide, allyl methyl trisulfide etc.) induce phase II detoxyfication enzymes as *quinone reductase* and *gluthathione transferase* in rat tissues. Diallyl disulfide, diallyl trisulfide and allyl methyl trisulfide were potent inducers of phase II enzymes. Dipropenyl disulfide and trisulfide were much less active among the unsaturated; while the other saturated sulfides (dimethyl disulfide, trisulfide and tetrasulfide, propylbutyl disulfide, dipropyl disulfide etc.) had a little or no effects on enzymes activities (1).

The same results were obtained with the unsaturated organosulfur compounds in the inhibitor effects on benzo[ ]pyrene induced neoplasia in forestomach and lung of female mice (2). Fukushima et al. (3) demonstrated as these unsaturated organosulfur compounds can be considered the potential inhibitors of colon and renal carcinogenesis in rats. Recently, Galeone et al. (4) showed an inverse association between the frequency of use of *Allium* vegetables and risks of common cancers in southern European populations.

The onion saturated and unsaturated organosulfur compounds are obtained by chemical transformation by cleavage of *S-(E)-1-propenyl cysteine sulphoxide* precursor by the allynase enzyme after cutting or chopping of the vegetable tissues (5-7).

Onion contains other nutraceutical substances as vitamin C and polyphenols (anthocyanins and quercetins). It's known the importance of these molecules in the prevention of cancer and cardiovascular diseases and in slowing down cellular aging, due to the high antiradical and antioxidant power (8-10).

It's evident that the content of healthy compounds in plants is influenced by a wide range of factors, among which the varietal difference and the crop management. Consequently, this study deals with the determination of chemical and nutraceutical profiles of

four onion genotypes named "Suasa", "Precoce di Romagna", "Tropea", and "Density".

## Experimental part

All genotypes have been cultivated in 2011 season on 11 years organic-converted soils, in the experimental field of CRA-ORA (Monsampolo del Tronto, Ascoli Piceno, Italy). All samples, harvested at commercial ripening, have been subjected to some quality aspects, performed at CRA-IAA (Milano, Italy) as follows. *Chemical quality:* soluble sugars by HPLC (11), unsaturated and saturated sulfur volatile compounds by GC/MS (12).
*Nutraceutical quality:* unsaturated sulfur volatile compounds, ascorbic acid by HPLC (13), total polyphenols index (Folin reaction) (14), quercetins and anthocyanins by HPLC and spectrophotometric analysis, respectively (15, 16), and antiradical capacity by DPPH* scavenging assay (17). Pyruvic acid representing the pungency, has been determined by HPLC according to Dhumal et al (18). The analysis were performed in triplicate for each sample. The Tukey's test was used to evaluate the dif-

**Tabella 1 - Organosulfur volatile compounds identified in four onion genotypes. Different letters indicated significant differences (p≤0,05).**

| | µg/100 g dm | | | |
|---|---|---|---|---|
| Organosulfur volatile substances | Suasa | Tropea | Precoce romagna | Density |
| Saturated sulfides | | | | |
| dimethyl disulfide | 328,03 a | 348,34 a | 287,24 a | 561,13 b |
| dimethyl trisulfide | 251,53 a | 710,77 c | 508,65 b | 878,73 d |
| dimethyl tetrasulfide | 289,74 b | 190,78 a | 378,02 c | 244,02 ab |
| propyl butyl disulfide | 58,34 a | 19,35 a | 50,01 b | 10,16 a |
| dipropyl trisulfide | 10,49 a | 12,61 a | 125,46 b | 11,50 a |
| Partial amount | 938,11 a | 1281,85 b | 1349,37 b | 1705,54 c |
| Unsaturated sulfides | | | | |
| propenyl methyl disulfide (E) | 249,12 a | 426,10 b | 616,40 c | 855,09 d |
| propenyl methyl disulfide (Z) | 349,07 a | 480,89 b | 530,65 b | 343,64 a |
| propenyl propyl disulfide (E) | 251,65 a | 566,05 c | 407,60 b | 175,37 a |
| propenyl propyl disulfide (Z) | 307,61 a | 572,34 b | 472,60 b | 262,63 a |
| propenyl propyl trisulfide (E) | 305,51 a | 307,37 a | 628,80 b | 578,48 b |
| propenyl propyl trisulfide (Z) | 283,72 a | 323,20 a | 867,46 b | 584,03 b |
| diallyl disulfide * | 106,91 b | 286,24 a | 127,86 b | 91,18 b |
| allyl methyl trisulfide * | 63,90 a | 579,00 b | 65,04 a | 298,19 b |
| Partial amount | 1917,49 a | 3541,19 b | 3716,39 b | 3188,61 b |
| Total amount | 2855,60 a | 4823,04 b | 5065,76 b | 4894,15b |

** Organosulfur compounds with the highest inducting power on phase II enzymes.*

ferences of quality parameters among four onion genotypes. Mean values were considered significantly different when $p \leq 0.05$.

## Results and discussion

Table 1 showed the onion volatile sulfur compounds divided into saturated and unsaturated sulfides. Both classes were responsible for the characteristic onion flavour, but a potential antitumor effect was ascertained to unsaturated ones, as reported above. In particular, the diallyl disulfide and allyl methyl trisulfide, considered the most biologically active organosulfur compounds, had the highest amounts in Tropea and the lowest in Suasa. Moreover, unsaturated sulfides were numerically and quantitatively (partial amount) superior with respect to saturated ones.

In Figure 1 the distribution of two classes of sulfur compounds were reported. Suasa genotype had the lowest content in saturated and unsaturated sulfides; while in the other genotypes the values ranged between 1281,9 and 1705.5 µg/100 g dm. for the saturated sulfides, and 3188,6 and 3716,4 µg/100 g dm. for the unsaturated ones.

Table 2 showed the content of other parameters that characterized the chemical (soluble sugars) and nutraceutical (all the other parameters) quality. The highest content of soluble sugars (glucose and fructose) was noted in Density genotype, followed by Precoce di Romagna and Tropea; while, a value lower than 5 g/100 g fw was found in Suasa. As concern nutraceutical parameters, ascorbic acid, even if its content in all the genotypes was quite low, showed the highest concentration in Suasa. Polyphenols in onions were mainly represented by quercetin glucosides and anthocyanins, belonging to polyphenols family. In Density, the highest level of total polyphenols was found. In this genotype, the only identified polyphenol were quercetins. In Tropea, total polyphenols were little lower than Density, but they were represented by quercetins and anthocyanins. Much lower content, but similar among them, were determined in Precoce di Romagna (quercetins) and Suasa (quercetins and anthocyanins). The anthocyanins contained only in the red onions showed the highest value in Tropea with respect to Suasa. The content in pyruvic acid, that reflected the pungency of onion, was clearly lower in Suasa and Precoce di Romagna, while Tropea and Density had the highest levels, in partial relationship with the presence of sulfur volatiles. According to the ranking of pungency determined by Dhumal et al. (18), low pungency onions were < 3 mmol/kg fw and medium (3-7 mmol/kg fw): the assayed genotypes resulted of low pungency for Suasa and Precoce di Romagna, while Tropea and Density resulted of medium pungency.

The highest antiradical capacity was showed by Density, followed by Tropea, about two-folds higher

**Figura 1** - Content of saturated and unsaturated sulfides in four organic onion genotypes.

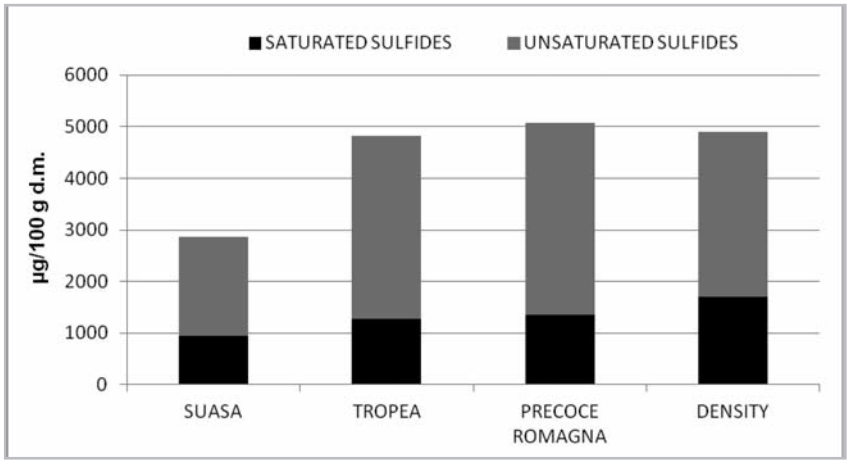


**Tabella 2 - Other chemical and nutraceutical parameters monitored in four organic onion genotypes. Different letters indicated significant differences (p≤0.05).**

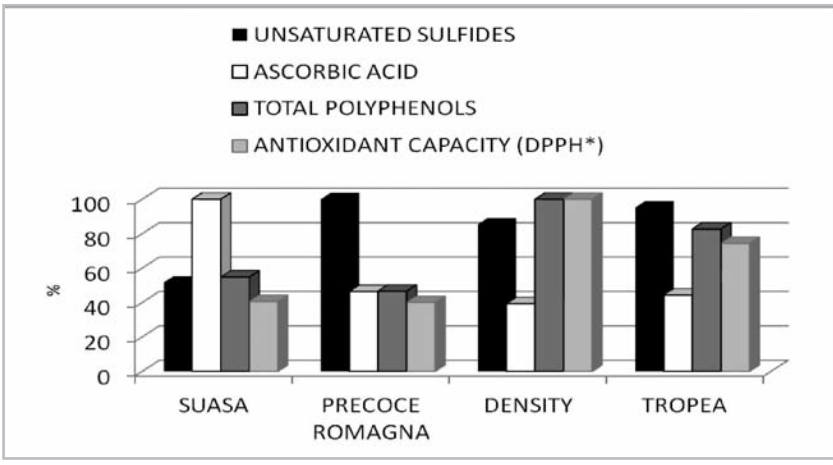
| | Suasa | Tropea | Precoce Romagna | Density |
|---|---|---|---|---|
| Soluble sugars (g/100 g fw) | 4,91 a | 5,45 ab | 5,47 ab | 6,21 b |
| Ascorbic acid (mg/100 g fw) | 9,99 a | 4,43 b | 4,63 b | 3,93 b |
| Total anthocyanins (mg/100 g fw) | 5,70 a | 16,61 b | - | - |
| Total polyphenols (mg/100 g fw) | 24,11 a | 36,35 b | 20,48 a | 43,96 c |
| Quercetins (mg/100 g fw) | 11,39 a | 30,60 c | 13,06 a | 43,34 d |
| Antioxidant capacity (DPPH*mg Trolox eq./100g fw) | 11,25 a | 20,60 b | 11,08 a | 27,70 b |
| Pyruvic acid (mmol/ kg fw) | 2.57 a | 4.95 b | 2.60 a | 6.00 c |

than Suasa and Precoce di Romagna, in full accordance with the data of total polyphenols index and quercetins (Tab. 2). The DPPH* *in vitro* tests highlighted that there were high correlations between the antiradical capacity and the total polyphenols and quercetins content (rxy=0,92 and 0.94, respectively), with a negative correlation index with ascorbic acid content, still confirming the interesting role of quercetins as powerful free radical scavengers in the present case of onion (8).

## Conclusions

The evaluation of chemical and nutraceutical parameters of four organic onion genotypes (Fig. 2) points out that Density, Precoce di Romagna and Tropea genotypes show not only a better chemical quality (aromatic profiles and soluble sugars content), but contemporary can have a stronger potential antitumor activity due to higher level of unsaturated sulfides (diallyl disulfide and allyl methyl trisulfide) with respect to Suasa. Moreover, Density has the highest antiradical capacity due to the highest content in polyphenols, in particular quercetins. Suasa genotype, instead, differs from the other genotypes for ascorbic acid content. In this context, ascorbic acid seems to have a low influence in the index of antioxidant capacity with respect to polyphenols.

**Figura 2** - Comparison of nutraceutical parameters of four organic onion genotypes, where the highest values of each parameter is = 100%.




## References

1. Munday R, Munday CM. Relative activities of organosulfur compounds derived from onions and garlic in in-

creasing tissue activities of quinone reductase and gluthathione transferase in rat tissue. Nutrition and Cancer 2001; 40 (2): 205-210.
2. Sparnins VL, Barahy G, Wattenberg LW. Effects of organosulfur from garlic and onions on benzo[α]-pyrene induced neoplasia and gluthathione-S-transferase activity in the mouse. Carcinogenesis 1988; 9 (1): 131-134.
3. Fukushima S, Takada N, Hori T, Wanibuchi H. Cancer prevention by organosulfur compounds from garlic and onion. J. Cell. Biochem. Suppl. 1997, 27: 100-105
4. Galeone C, Pilucchi C, Levi F, Negri E, Franceschi S, Talamini R, Giacosa A and La Vecchia C. Onion and garlic use and human cancer. The American Journal of Clinical Nutrition 2006; 84 (5): 1027-1032
5. Block E. The organosulfur chemistry of the genus Allium-Implications for the organic chemistry of sulfur. Angew. Chem. Int. Ed. Engl. 1992; 31(9): 1135-1178
6. Randle WM, Lancaster JE, Shaw ML, Sutton KH, Bussard ML. Quantifying onion flavour compounds responding to sulphur fertility- sulphur increases levels of alk(en)yl cysteine sulfoxides and biosynthetic intermediates. J. Am. Hort. Sci. 1995; 120(6): 1075-1081
7. Jones MG, Hughess J, Tregova A, Tomsett AB, Collin HA. Biosynthesis of the flavour precursors of onion and garlic. J. Exp. Bot. 2004; 55(404): 1903-1918
8. Rice-Evans CA, Miller NJ, Paganga G. Structure antioxidant activity relationships of flavonoids and phenolics acids. Free Radical Biol. Med. 1996; 20: 933-956.
9. Harris JR. Ascorbic acid: Biochemistry and Biochemical cell Biology. Subcellular Biochemistry. Plenum Press, New York, USA 1996; 25: 464.
10. Hou DX. Potential mechanism of cancer chemopreventions of anthocyanins. Curr. Mol Med. Mar 2003; 3 (2):149-159.
11. Forni E, Erba ML, Maestrelli A, Polesello A. Sorbitol and free sugar contents in plums. Food Chem 1992; 44: 269-274.
12. Di Cesare LF, Forni E, Viscardi D, Ferrari V. Valutazione della composizione aromatica e chimico-fisica di alcune cultivar di pomodoro da impiegare per il consumo diretto o per la trasformazione. Ind. Conserve 2003; 78: 195-206.
13. Lo Scalzo R, Bianchi G, Genna A, Summa C. Antioxidant properties and lipidic profile as quality indexes of cauliflower (Brassica oleracea L. var. botrytis) in relation to harvest time. Food Chem 2007; 100 (3): 1019-1025.
14. Singleton VL, Rossi JA. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am J Enol Vitic 1965; 16: 144-158.
15. Gennaro L, Leonardi C, Esposito F, Salucci M, Maiani G, Quaglia G, Fogliano V. Flavonoids and carbohydrate contents in Tropea red onions. Effects of homelike peeling and storage. J Agric Food Chem 2002; 50 (7): 1904-1910.
16. Swain T, Hillis WE.. The phenolic constituents of prunus domestica. I. The quantitative analysis of phenolic constituents. J Sci Food Agric 1959; 10: 63-68.
17. Brand-Williams W, Cuvelier ME, Berset C. Use of a free radical method to evaluate antioxidant activity. Lebesm-Wiss U-Technol 1995; 28: 25-30.
18. Dhumal D, Datir S, Pandey R. Assessment of bulb pungency level in different Indian cultivars of onion (Allium cepa L.). Food Chem 2007; 100: 1328-1330.