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Antioxidant properties and lipidic profile as quality indexes of cauliflower (*Brassica oleracea* L. var. *botrytis*) in relation to harvest time

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Abstract

The cauliflower is considered as a food of high nutritional value and some authors indicate that its quality is related to stability of its fatty acids. Samples of 'Verde di Macerata' variety were analysed for their main quality parameters, fatty acid composition and stability, and for their antioxidant properties by using a test based on linoleic acid enzymatic degradation. Cauliflower buds were harvested early and late over three different years (2001, 2002 and 2003). The samples were evaluated both raw and after a defatting treatment with $CHCl_3$/MeOH 1:1 solution, in order to check the role of liposoluble substances. The main results were a very different composition profile for cauliflowers harvested in 2002 (increase of dry and fatty matter, polyphenols and antioxidant activity, decrease in ascorbic acid content), and a difference in fatty acid composition related to a relative increase in unsaturated fatty acids with respect to saturated ones in all late harvested samples. The difference shown in 2002 was probably due to environmental stress suffered by plants, like water loss and low temperature.

Keywords: Cauliflower; Quality indexes; Environmental stress; Fatty acids; Polyphenols

1. Introduction

Among vegetables for human consumption, the cauliflower has recently become popular as a food of high nutritional value, and according to Zhuang, Hildebrand, and Barth (1995, 1997), post-harvest senescence of cauliflower is correlated with lipid peroxidation by which polyunsaturated fatty acids are preferentially degraded. Some oxygen catabolites, commonly called 'reactive oxygen species', cause lipid peroxidation, whose degradation products contribute to the decrease in overall quality of a vegetable during senescence, especially with respect to nutritive value and flavour.

Lipid autoxidation is retarded by antioxidant substances, naturally present in vegetables or introduced with the diet; the selection of vegetable varieties rich in antioxidants is therefore a key to an high product quality.

The edible part of cauliflower and broccoli is a bud, and this probably causes a fast decrease in quality during their development, both pre- and post-harvest, owing to an high metabolism rate (Brennan & Shewfelt, 1989). Moreover, it is well known that harvest time is a very important factor to determine the quality of fruit and vegetables, and this fact assumes great importance for cauliflower, that has a narrow harvest window. In fact, some research on genetic amelioration of this species aim to obtain clones with a

Abbreviations: AA, Antioxidant Activity; C_6, with six carbon atoms; $CHCl_3$, chloroform; d.w., dry weight; FID, flame ionization detector; GC, gas chromatography; IVTPA, Istituto per la Valorizzazione Tecnologica dei Prodotti Agricoli; K, absorbance; MeOH, methanol; SSR, soluble solid residue; v/v, volume/volume.

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wider harvest time without significant loss in overall quality (Kanwar & Korla, 2002; Sharma & Behera, 2003; Stipic & Acciarri, 1998).

The aim of the present paper was to investigate some quality indexes of Italian-grown cauliflower (*Brassica oleracea* L. var. *botrytis*, cv. 'Verde di Macerata') such as common quality attributes, the antioxidant properties, the total polyphenol index, the lipidic profile and several indexes of lipid stability in relation to harvest time during three successive years.

2. Materials and methods

2.1. Plant material

Cauliflower (cv. 'Verde di Macerata', *Brassica oleracea* L., Botrytis group) heads were obtained from an experimental orchard of the 'Istituto Sperimentale per l'Orticoltura' at Monsampolo del Tronto, Ascoli (Italy) throughout 2001, 2002 and 2003 seasons. They were winter-grown to maturity under surveyed cultural practices by a conventional production, hand harvested at two different dates (10–20 December of the previous year for early and 20–30 January for late sampling – for example, 2001 season was represented by early harvest in December 2000 and late one in January 2001) and handled as in commercial practice. The heads (about 1 kg each), sorted and selected for uniform size, appearance and freedom from defects, were refrigerated at 3–5 °C and transported at IVTPA laboratories.

Once in laboratory, cauliflowers from each harvest were randomly divided into batches of 10 heads, comprising two samples of 5 heads each. Each head was carefully reduced to small florets by manual handling, separating florets from the main stem. The resulting pool of florets was immediately frozen at −50 °C in an air blast tunnel. An aliquot was frozen at −80 °C for solid soluble residue (SSR), pH and titratable acidity (TA) analyses and another aliquot was successively freeze-dried. After freeze-drying, each sample, comprising of a pool of florets from 5 heads, was homogenised at 0 °C and stored at −30 °C until analysed.

2.2. Biochemical quality attributes

Soluble solid residue (SSR), pH and titratable acidity were measured according to official methods (MAF, 1989) on an aqueous extract from frozen cauliflower florets previously subjected to homogenisation with a Waring blender at 0–2 °C (30 g with 30 ml of distilled water) and centrifuged at 25,000*g* for 30 min. Dry matter was determined according the AOAC method (1980).

Ascorbic acid was determined by a HPLC method already set up at IVTPA laboratories (Lo Scalzo, Iannoccari, Summa, Morelli, & Rapisarda, 2004), with the modification of sample preparation that comprised the treatment of 500 mg of freeze-dried material with 5 ml of metaphosphoric acid 6%, homogenisation of the resulting mixture and centrifugation at 25,000*g* for 30 min.

Fatty matter was determined by treating 300 mg of freeze-dried cauliflower with 6 ml of $CHCl_3$/MeOH 1:1, vortexing for 1 min, centrifuging at 10,000*g* for 10 min, and drying the supernatant under vacuum until constant weight, and stored under nitrogen at −30 °C for further analysis.

Total polyphenols index (Di Stefano & Guidoni, 1989, with some modifications) was measured on freeze-dried samples (50 mg) raw or defatted (see below), treated in sequence with 2 ml of bi-distilled water, 1.5 ml of Folin–Ciocalteu reagent, well mixed, 2 ml of Na_2CO_3 20% in water, well mixed, centrifuged at 10,000*g* for 10 min, kept in the dark for 2 h, read in a spectrophotometer against a blank at 730 nm after 10-fold dilution with water.

Each experiment was conducted two times and all analyses were made in quadruplicate and the results were expressed as amount per dry weight unit. The data analysis were submitted to analysis of variance and the averages were compared by Tukey test ($p < 0.05$). Significance of differences, are shown in each table with a different letter. Correlations between antioxidant properties and biochemical parameters were established using simple linear regression analysis, using Microsoft Excel 97 (Microsoft Office 97) and confirmed by Statgraphics-5-plus, Manugistics Inc., 2000.

2.3. Antioxidant properties

In this method, the enzymatic oxidation of linoleic acid was achieved by an external addition of lipoxygenase by modifying the method of Grossman and Zakut (1979), as in the paper of Pizzocaro, Gasparoli, and Ambrogi (1995). The oxidation of linoleic acid was analysed in absence (blank test) and in presence (sample test) of raw or defatted cauliflower aqueous extract by recording the linear increase in absorbance at 234 nm.

Raw cauliflower extract was prepared in quadruplicate by treating 300 mg of freeze-dried sample with 6 ml of bi-distilled water. The resulting suspension was vortexed for 30 s, centrifuged at 25,000*g* for 5 min, and the supernatant was used for analysis.

Defatted cauliflower extract was prepared in quadruplicate by treating 300 mg of freeze-dried sample with 6 ml of $CHCl_3$/MeOH 1:1 v/v. The resulting suspension was vortexed for 30 s, centrifuged at 25,000*g* for 5 min, and the supernatant was eliminated. The pellet was dried under vacuum, re-suspended in water and subsequently treated like the raw extract.

The substrate was prepared by dissolving under nitrogen 25 μl of linoleic acid (Sigma, St. Louis, USA) in 2.5 ml of absolute ethanol, with a further addition of 20 μl of Tween 20. The resulting solution was mixed, added with Na_2HPO_4 0.05 M and adjusted to pH 9.2 with NaOH 0.5 M to a final volume of 25 ml.

In the sample test, the lipoxygenase inhibition of cauliflower was measured in a solution made up of 2.5 ml of 0.1 M phosphate buffer (pH 7.0), 0.3 ml of substrate, 0.05 ml of cauliflower extract and 0.025 ml of the lipoxigenase solution made by dissolving 15 mg lipoxigenase standard extract of soybean (Sigma, St. Louis, USA) in 25 ml of 0.1 M phosphate buffer (pH 7.0). This solution was slowly shaken and stored at 2 °C until use.

In the blank test cauliflower extract was substituted with 0.05 ml of bi-distilled water.

Antioxidant activity (AA) was expressed as protection percentage from the enzymatic degradation of linoleic acid referred to the blank considered as 100% degradation.

2.4. Fatty acid profile and stability

The fatty acid profile was evaluated on the extract from freeze-dried cauliflower made by $CHCl_3$/MeOH 1:1 already obtained to calculate the yield of fatty matter (see above).

Dried extract was added under nitrogen with 4 ml of 0.5% KOH in MeOH; this solution was boiled under reflux for 6 min, then was methylated with 5 ml of 20% BF_3 · MeOH complex in absolute MeOH for another minute. The resulting mixture was cooled and 5 ml of *n*-hexane were added. The phase separation was obtained by adding 10 ml of saturated NaCl aqueous solution, the organic layer was dried on anhydrous Na_2SO_4 and concentrated under nitrogen to a small volume before GC injection.

Gas-chromatographic separation of fatty acids methyl esters from cauliflower extracts was made on a stainless-steel packed column (3 m × 3 mm i.d.) with fixed phase polyethylene-glycol-succinate on Chromosorb W 80-100, with nitrogen as gas carrier (40 ml/min) setted at 200 °C and with a flame ionization detection. The retention times of fatty acids methyl esters and their amount were evaluated by reference to commercial standards. The ratio unsaturated vs. saturated fatty acids was calculated considering the two main unsaturated fatty acids, i.e. linoleic and linolenic and the main saturated ones, i.e. palmitic and stearic.

The absorbance of conjugated trienes is commonly expressed by the ΔK value, a parameter commonly used in the quality evaluation of oils (Lotti & Galoppini, 1967) that represents the presence of conjugated trienes subtracted from the interferences at immediately lower and higher wavelengths: this value was obtained from the dried lipid extract of cauliflower dissolved in 5 ml isooctane and spectrophotometrically assayed in a 1 cm quartz cuvette. The absorbance (K) at 232 nm (conjugated dienes) and 268 nm (conjugated trienes) was measured and the ratio K_{232} vs. K_{268} was calculated.

The oxidative stability of fatty matter was also evaluated after treatment with Cu^{2+} ions at 80 °C, following a GC determination of the main fatty acids catabolites, like *n*-hexanal and *trans*-2-hexenal. Another important fatty acid catabolite is represented by *cis*-3-hexenal: this compound was separated by the used GC method (see the following paragraph, retention time 11.8 min), but it was not found in the cauliflower extracts, because it is spontaneously isomerised to *trans*-2-hexenal (Zhuang, Hamilton-Kemp, Anderesen, & Hildebrand, 1996).

These two aldehydes were quantified by a capillary GC-headspace technique, using an automatic headspace sampler, conditioning in a closed vial 5 ml of dried lipid extract added with 0.5 ml of Tween 20 0.5% and 0.1 ml of $CuSO_4$ 10 mM at 80 °C for 1 h. A 30 m Carbowax 20M column was used for headspace analysis with He as carrier at 0.8 ml/min, programmed at 40 °C for 5 min, then 30 °C/min and 150 °C for 5 min, injector was at 230 °C, FID was at 250 °C. In those conditions the retention time of *n*-hexanal was 9.0 min, and that of *trans*-2-hexenal was 14.0 min; their amount was calculated by the analysis of commercial standards, treated in the same way as the samples.

3. Results

3.1. Biochemical quality attributes

Commonly measured quality parameters are shown in Table 1. No difference was shown in 2001 and 2002 samplings between early and late harvest for SSR amount, with high values in 2002. In 2003 the content of SSR was significantly higher in late than in early harvested cauliflowers. The pH was around 6, with higher significant differences in late samples of 2003, while also titratable acidity was significantly higher in all late harvested samples, except in 2001.

Dry matter gave significant differences between early and late harvest only in 2003 samplings, with higher values in late harvest, resembling the SSR data. It could be due probably to the progressive cold, remembering that early harvest was in December, just at the beginning of winter, while late harvest was made at the end of January, in full winter season. In 2001, the value of dry matter was around 10%, while in 2002 it was much higher (12%); this fact

Table 1
Common quality parameters of 'Verde di Macerata' cauliflower during three years for early and late samplings

	Dry matter (%)	SSR (°Bx)	pH	Titratable acidity (mEq% NaOH)
2001				
Early	9.9 a	6.9 a	6.06 a	2.96 a
Late	9.6 a	6.6 a	6.17 a	3.08 a
2002				
Early	12.2 b	8.8 b	6.22 a	2.65 a
Late	12.6 b	8.7 b	6.29 a	3.57 b
2003				
Early	8.8 a	6.3 a	6.29 a	3.78 b
Late	12.3 b	9.1 b	6.44 b	5.09 c

Values are means, and different letters in each column mean statistically significant difference ($p < 0.05$).

Table 2
Biochemical quality attributes of raw and defatted samples of 'Verde di Macerata' cauliflower during three years and two harvest dates for each year

	Ascorbic acid (mg/100 g d.w.)	Fatty matter (mg/g d.w.)	Total polyphenols index (mg/kg d.w.)	Total polyphenols index on defatted samples (mg/kg d.w.)	Percent loss polyphenols after defatting
2001					
Early	474.7 c	170.7 b	4041.4 a	3745.5 b	7.3 a
Late	520.8 d	177.1 b	4221.9 a	3941.7 b	6.6 a
2002					
Early	360.7 a	209.0 c	6492.6 d	5143.4 c	20.8 b
Late	357.1 a	239.7 d	4905.6 c	3746.8 b	23.6 c
2003					
Early	375.0 b	189.8 c	4313.6 a	3339.8 a	22.6 c
Late	487.8 c	142.3 a	4748.0 b	3855.3 b	18.8 b

Values are means, and different letters in each column mean statistically significant difference ($p < 0.05$).

could be attributed to the very critical meteorological conditions during the samplings in 2002, very cold (average temperature was 3.6 °C vs. an historical value of 5.3 °C), snow-covered, and with little precipitation (29 mm against an historical value of 77), resulting in a partially compromised production.

As regards ascorbic acid (Table 2), the lowest amount was found in both samples of 2002, while the highest was in late heads of 2001. In 2002, no differences were found between early and late samples and in 2001 and 2003 a higher amount is present for late harvested samples.

All previously shown data came from analysis made on whole samples: the following take account for the presence of fatty matter, and will try to investigate the role of lipid fraction on some quality indexes of cauliflower.

The amount of fatty matter (Table 2), obtained by $CHCl_3$/MeOH 1:1 v/v extraction, did not give differences in 2001, about 170 mg/g d.w.. In the 2002 harvest, this amount was higher, arriving at values of about 220 mg/g d.w., especially in late samplings, thus confirming the different conditions encountered by plants in this year, already assessed by dry matter data.

The total polyphenols index data were obtained from raw and defatted samples. Raw samples showed no clear distinction between early and late harvest considering the three years together: the only clear information is that the amount found in 2002 is significantly higher than other two years, giving the chance to further confirm the different situation of 2002 cauliflowers. The polyphenol index on defatted samples had the same trend already examined, with lower amounts than in raw samples: this means that the treatment with the defatting solution made by $CHCl_3$/MeOH 1:1 decreases the value of Folin–Ciocalteu index. The percent loss after defatting treatment is very different according to the year of sampling: 2001 had a very low loss (about 7%) respect to 2002 and 2003, with a value of about 20%.

3.2. Antioxidant properties

Cauliflowers harvested in 2002 stood out for their higher antioxidant activity (AA) towards linoleic acid degradation with respect to the samples of 2001 and 2003 (Table 3): early harvested 2002 heads showed significantly higher activity than late harvested ones. In 2001 and 2003, the values of protection against linoleic acid degradation was higher in late than in early harvested samples, with statistical significance only in 2003 cauliflowers.

Table 3
Antioxidant properties (AA), measured by enzymatic (soybean lipoxygenase) linoleic acid degradation, as inhibition of diene formation at 234 nm referred to a blank, considered as 100% degradation of 'Verde di Macerata' cauliflower aqueous extracts from raw and defatted samples during three years and two different harvest dates

	AA raw (% inhibition)	AA defatted (% inhibition)	Percent loss AA after defatting
2001			
Early	30.7 a	8.9 a	71.0 c
Late	34.9 a	16.3 c	53.3 b
2002			
Early	66.8 d	30.9 e	53.7 b
Late	60.4 c	21.2 d	64.9 c
2003			
Early	32.2 a	12.9 b	59.9 b
Late	48.8 b	35.0 e	28.3 a

Values are means, and different letters in each column mean statistically significant difference ($p < 0.05$).

Defatted extracts gave low values of antioxidant activity respect to raw ones, which means that fatty matter exerts a significant contribution to the antioxidant activity, measured by the test used in the present study.

Late samples of 2003 showed the highest antioxidant activity in defatted extracts, while the difference between early and late harvested cauliflower exactly resembled the situation already examined for raw samples. Comparison of data from raw and defatted samples gave the chance to express the fatty matter contribution to the measured antioxidant activity, a significant percentage contribution was given by early samples harvested in 2001, with a lower value in late harvested cauliflower. This situation was repeated in 2003, while in 2002 the order of fatty matter contribution was reversed, giving a better value in late sam-

ples. This fact is consistent with the loss of polyphenols after defatting in 2002 samples compared to 2001 and 2003 (Table 2).

3.3. Fatty acid profile and stability

The main unsaturated fatty acid found in cauliflower was linolenic (C18:3) (Fig. 1), with an amount of 60–120 mg/g d.w., while the main saturated fatty acid was palmitic (C16:0), ranging from 30 to 60 mg/g d.w.. Those data, expressed as percentage presence, were confirmed by other authors (Pizzocaro, Senesi, & Monteverdi, 1986; Voisine, Vézina Louise, & Willemot, 1991).

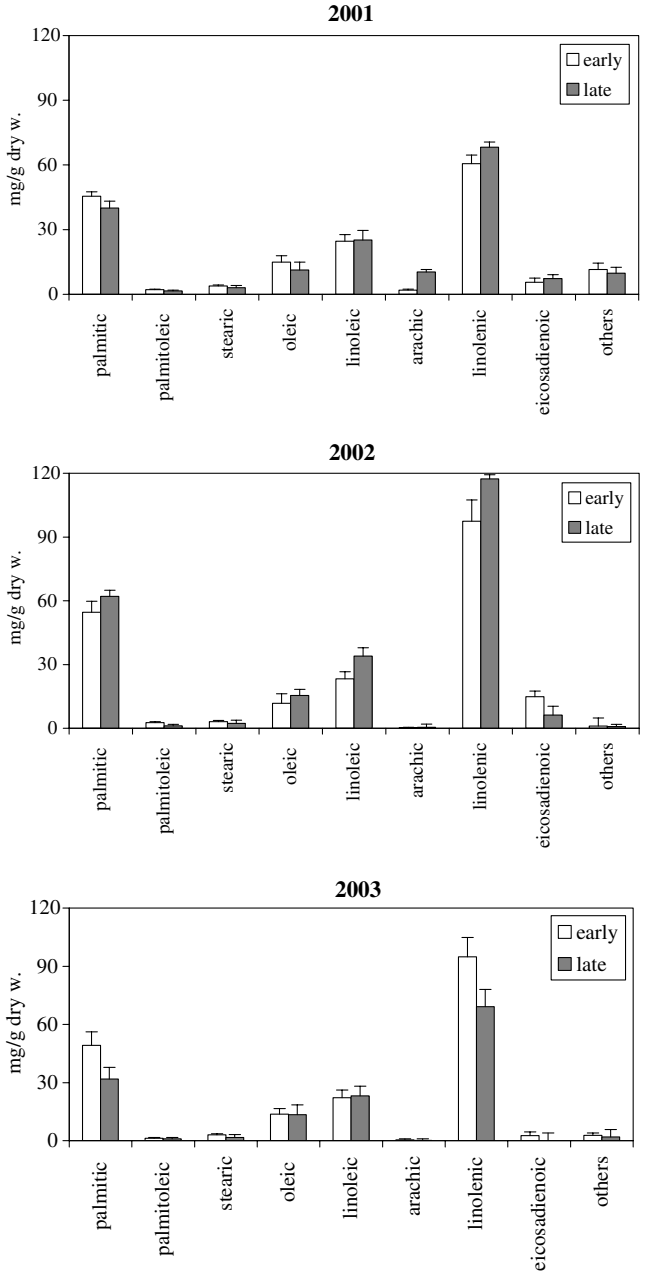

Fig. 1. Fatty acid composition from $CHCl_3$/MeOH 1:1 extract of 'Verde di Macerata' cauliflower in different years and in different harvest dates.

Table 4
Fatty matter quality and stability of 'Verde di Macerata' cauliflower in different years and harvest dates

	Unsaturated vs. saturated fatty acids	*n*-Hexanal (μg/g d.w.)	(*E*)-2-hexenal (μg/g d.w.)	ΔK	K_{232}/K_{268}
2001					
Early	1.7 a	4.85 c	1.82 b	0.0042 b	2.2 a
Late	2.2 b	5.42 c	1.25 b	0.0060 c	2.1 a
2002					
Early	2.1 b	3.85 b	1.64 b	0.0055 bc	2.9 c
Late	2.4 c	13.02 d	3.25 c	0.0065 c	2.6 b
2003					
Early	2.2 b	2.05 a	1.59 b	0.0067 c	2.6 b
Late	2.8 d	1.38 a	0.57 a	0.0028 a	2.2 a

Values are means, and different letters in each column mean statistically significant difference ($p < 0.05$).

The calculated ratio of unsaturated vs. saturated fatty acids (Table 4) showed the same difference between early and late harvest in all sampling years; early samplings gave lower ratios than late, averaging at 2.0 and 2.5, respectively, meaning a more pronounced presence of unsaturated fatty acids in late harvested cauliflowers. This different fatty acid composition could support a lower stability of samples with higher amount of polyunsaturated fatty acids, that could give a higher rate of deterioration during storage and processing, as already reported by other authors on broccoli (Murcia, Lòpez-Ayerra, & Garcìa-Carmona, 1999; Zhuang et al., 1995).

The affirmation that lipid profile of late harvested cauliflowers, evaluated by their fatty acid composition, could be less stable and induce an increased senescence rate was examined by some assays made on the fatty matter, whose results are showed in Table 4. In fact, an index of potential quality in fatty acids is the ratio of optical extinction at 232 nm (conjugated dienes) vs. 268 nm (conjugated trienes), with a high peroxidation potential. The higher is the ratio, the lower is the presence of polyconjugated compounds, more susceptible to peroxidation. This index was higher in all early with respect to late samples, with statistical significance in 2002 and 2003.

The ΔK index is a very useful quality index in oils, with low values around zero, indicating a high quality with a relative absence of conjugated compounds, susceptible to oxidative degradation. In 2001 and 2002 samples, the higher ΔK value was shown by late samples, in good agreement with the data of fatty acids' unsaturation degree and K_{232}/K_{268}. In 2003 the situation was unexpectedly reversed.

In another assay, fatty matter samples from cauliflower were treated with Cu^{2+} ions and heated in closed vials, to evaluate *n*-hexanal and *trans*-2-hexenal content in the headspace, which are among the most important degradation compounds from fatty acids (Table 4). The most abundant compound in the headspace was *n*-hexanal, which is a linoleic acid peroxidation product. However, as other author confirm (Zhuang et al., 1996), a high content of *trans*-2-hexenal was expected. It is the main peroxidation product of

linolenic acid, the most abundant fatty acid in cauliflower buds. The possible reason for the greater presence of *n*-hexanal in the headspace from cauliflower extract is that the reported pattern of C_6 aldehyde formation from fatty acid peroxidation is enzymatically mediated, while in the present method the formation of these aldehydes is chemically induced by Cu^{2+} ions and by the heating at 80 °C.

The *n*-hexanal content was significantly higher only in late samples of the 2002 harvest, and *trans*-2-hexenal was significantly higher in late samples of 2002, but there was no significant change between early and late samples of 2001 and 2003 both for *n*-hexanal and *trans*-2-hexenal.

These data were unexpected because it was more probable to find a higher amount of these aldehydes in all late samples, while this was shown only in 2002 harvest dates. It is possible that oxidation rate of fatty matter induced by an excess of Cu^{2+} ions is not only related to fatty acid composition.

4. Discussion

The AA data of raw and defatted samples were correlated with biochemical parameters (Table 5). Dry matter and SSR showed very high R^2 values. This is a very interesting result, since some discussions have been started on the possible role of simple carbohydrates in antioxidant activity towards some very reactive free radicals, like the hydroxyl radical (Gray & Mower, 1991; Morelli, Russo-Volpe, Bruno, & Lo Scalzo, 2003).

An interesting relation was found about total polyphenol index and AA; the statistical correlation made on these values, comprising the data obtained from defatted samples, was very high (0.88 and 0.69, respectively), demonstrating a very strong dependence of cauliflower AA on the polyphenol index. The correlation was higher for raw than for defatted samples, meaning that the role on AA of substances extracted by $CHCl_3$/MeOH 1:1 is significant. In fact, the value of polyphenolic index of defatted samples decreases with respect to raw ones (Table 2), and this is confirmed by the low values of R^2 between AA and total polyphenol index for defatted samples (0.70 and 0.57). The role of polyphenols as potential antioxidants is well known (Sanchez-Moreno, 2002), confirmed by many trials made at IVTPA laboratories, in which the total polyphenols index always fitted very well with antioxidant and free radical scavenging activities of different substrates, measured by different tests.

Unexpectedly, the correlation between ascorbic acid amount and AA values was not significant, meaning that the role of this compound on cauliflower's AA is not fundamental. To reinforce this hypothesis, some authors report that the antioxidant properties of fruits and vegetables are not solely attributed to ascorbic acid (Leonard et al., 2002).

Checking the correlations between AA data and the parameters related to fatty acid profile, it was found that a higher, but not significant, correlation existed between fatty acid matter and AA of raw samples (0.55), while the same correlation evaluated on AA data from defatted samples gave a lower, not significant value (−0.10). This could give the chance to attribute a role of fatty matter on AA. To establish this hypothesis, the correlation value was calculated also on the amount of the main fatty acids found in cauliflower: linolenic acid had the highest value (0.65), and this value is confirmed by the decrease in correlation value for defatted samples (0.18). Other fatty acids (palmitic and linoleic are shown) gave lower values than what found for linolenic acid, but every value is always greater than that found in the correspondent correlation with AA of defatted samples.

The absorbance ratios K_{232}/K_{268} are positively correlated with AA (0.68), meaning that the presence of conjugated trienes negatively influenced AA, and the role of liposoluble material is further confirmed by the absence of significance for defatted samples (0.30).

However, the most clear change between early and late harvested samples, evaluated in all sampling years, is related to the fatty acid composition; the late harvested cauliflower had an increased presence of unsaturated fatty acids with respect to saturated ones, giving the chance to assume that late harvested cauliflowers are less suitable for storage than early ones (higher ratio unsaturated vs. saturated). However, the AA data did not gave the same result, with higher values in early harvested cauliflower buds only in 2002, because other parameters, like polyphenols amount, are involved in this activity.

Table 5
Correlations coefficients of linear regression between the measurements of quality parameters to the antioxidant activity on extracts from raw and defatted samples from 'Verde di Macerata' cauliflower

	AA raw	AA defatted
Dry matter	0.89*	0.80*
SSR	0.87*	0.88*
pH	0.37	0.71*
Titratable acidity	−0.05	0.45
ΔK	0.04	−0.44
K_{232}/K_{268}	0.68**	0.30
Ascorbic acid	−0.58	−0.11
Total polyphenols index	0.88*	0.69**
Total polyphenols index on defatted samples	0.70**	0.57
Percent loss polyphenols after defatting	0.62	0.47
Fatty matter	0.55	−0.10
Unsaturated vs. saturated fatty acids	0.37	0.73*
n-Hexanal	0.37	−0.17
(*E*)-2-hexenal	0.33	−0.32
Linolenic acid	0.65**	0.18
Palmitic acid	0.49	−0.18
Linoleic acid	0.39	−0.07

* Significant at $p < 0.01$.
** Significant at $p < 0.05$.

5. Conclusions

Summarising, it could be inferred that quality parameters of cauliflower were subjected to great changes in rela-

tion to the years of harvest, especially in 2002, probably due to the environmental conditions with the most affected being dry matter, SSR, fatty matter and total polyphenolic index. Some parameters, like polyphenols and linolenic acid amount showed a good correlation with antioxidant properties, measured by the enzymatic inhibition of linoleic acid degradation.

This fact could be attributed to a higher water loss and low temperature stress suffered by plants in 2002, but it is only partially justified by the increased values in dry matter and SSR. The fatty matter and total polyphenols, whose measurements are referred to dry weight, maintain the differences between the samples previously evaluated by expressing the data on fresh weight.

The hypothesis of an environmental stress suffered by cauliflower plants during 2002 harvest season is reinforced by the comparison of precipitation and temperature data during the three examined years. The average precipitation during the harvest season (December 2001 and January 2002) of 2002 was 29 mm, while in 2001 and 2003 it was 114 and 146 mm, respectively; the historical average calculated over thirty years was 77 mm. The average temperatures during the same period were 3.6 °C in 2002, 7.1°C in 2001 and 6.2 °C in 2003, against an historical value of 5.3 °C.

This finding could be related to that of a previous paper (Hnilickova & Duffek, 2004) that discussed a significant decrease in photosynthetic rate suffered by cauliflower under water-stress.

Specifically, it has been established that environmental stress, like that for the harvest of 2002, enhances the fatty matter, the linolenic acid and polyphenols content, and decreases ascorbic acid amount.

At this point a question arises: could it be possible that a stress on plants is necessary to give products with an high nutritional quality? This fact is well known in the popular culture of agriculture; for example, in Italy there is the popular saying that 'a good wine comes from stressed grape', reflecting the well known fact that, to obtain a wine of high quality, it is necessary to have reduced yield in grape, and that a low yield in grape is obtained from stressed vines, for example the absence of irrigation, that is compulsory in 'controlled origin' productions.

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