Eur Food Res Technol (2014) 239:603–612
DOI 10.1007/s00217-014-2256-2

ORIGINAL PAPER

1-Methylcyclopropene postharvest treatment and their effect on apple quality during long-term storage time

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Received: 3 March 2014 / Revised: 3 May 2014 / Accepted: 12 May 2014 / Published online: 10 June 2014

Abstract The aim of this study was to evaluate the effect of the postharvest treatment by 1-methylcyclopropene (1-MCP) and storage time on the apple physicochemically quality. The effects of apple storage during 6 months on basic parameters such as dry weight, total soluble solids and titratable acidity, composition of phenolics, antioxidant activity and sensory evaluation were studied to evaluate the potential applicability of long-time stored apples for consumption and processing. Long-time storage of apples resulted in a higher dry matter but decreases total soluble solids and titratable acidity in all examined cultivars (cv.) of apples. The total phenolics determined by HPLC in fresh apples ranged from 1,243 mg in 'Idared' cv. to 1,435 mg/kg in 'Shampion' cv. During storage, the decrease of polyphenolic content has been observed, in 'Shampion' cv., it was higher than in 'Idared' cv. Similar effects were observed for antioxidant activity. Comparing quality of fruits just after harvest, it was found that cultivar affects most of the investigated sensory attributes with the exception of ripe apple smell, crispness, crunchiness and the overall texture score. In general, 'Shampion' cv. apples got higher ranks for sweetness, taste and the overall quality, whereas 'Idared' cv. were perceived as sourer, which is in arrangement with instrumental measurements. The results of presented study demonstrate that apples after storage, especially 'Shampion' cv., can be a valuable sensory attributes for food product and consumption. This study indicates that the use of 1-MCP treatment in long-term storage of apples is promising for maintaining the eating quality of fruits, however, in some extent may affect their antioxidant compounds content.

Keywords Storage · 1-MCP · Firmness · Phenolic compounds · Antioxidant activity · Sensory evaluation

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Introduction

There is a growing interest in food compounds with a possible health-protecting capacity. In epidemiological research, the intake of fruits and vegetables has been widely acknowledged to be inversely related to cancer incidence and cardiovascular diseases [1, 2]. About one-third of all cancer deaths could be avoided through appropriate dietary modification by increasing the consumption of fruits, vegetables and whole grains [3].

Phenolics, which play a crucial role in determining the sensory and nutritional quality of fresh apples, are an essential part of the human diet and are of considerable interest due to their antioxidant properties. Among the polyphenolic compounds found in apples, more than 50 % are procyanidins (tannins), responsible for the pungent and bitter taste of the fruit. The rest of the biologically active structures are phenolic acids, dihydrochalcones, quercetin glycosides, and anthocyanins. The main phenolic acid in apples is chlorogenic acid and among dihydrochalcones dominates phloridzin and phloretin-xyloglucoside [4, 5].

Total phenolic content of plant foods varies according to the extrinsic factors, such as geographic differences and different climate features, parts of plants analyzed, harvesting time, extraction and determination methods [6]. Besides, phenolic contents of plants depend on a number of intrinsic factors, such as genus, species and cultivars [7].

Apples have a relatively long storage life comparing with other fruits varieties. However, the main problem of apple storage is the fruit firmness. Fruit ripening is accompanied by softening, which is one of the most important determinants of fruit quality and consumer acceptability. Softening is generally considered an undesirable ripening process in apple fruit, as firmer apples tend to be juicier, crisper, crunchier and less mealy than softer ones [8]. One way of extending storage life of fruit is to control ethylene production and perception.

1-Methylcyclopropene (1-MCP) is a synthetic cyclic olefin capable of inhibiting ethylene action. It acts in very low concentrations as a competitor of ethylene, blocking its access to the ethylene-binding receptors [9]. 1-MCP is now used commercially in many parts of the world as a postharvest tool to maintain the quality of numerous horticultural products [10].

Despite the growing interest in the use of 1-MCP-based technology, still little is known about its effects on the nutritional properties of apples. Because of the increased interest in apple phenolics in the diet, it is important to document and understand their metabolism during long-term storage. Phenolic metabolism is a complex process, as phenolics undergo constant turnover and degradation [11, 12].

The aim of this study was to evaluate the effect of the postharvest treatment by 1-MCP and storage time on the apple quality. The effects of apple storage during 6 month on basic parameters such as dry weight, total soluble solids and titratable acidity, composition of phenolics, antioxidant activity and sensory evaluation were studied to evaluate the fruit composition, quality, sensory profile and potential applicability of long-time stored apples for further processing.

Experimentals

Chemicals

DPPH (1,1-diphenyl-2-picrylhydrazyl radical), ABTS (2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid), Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), TPTZ (2,4,6-tri(2-pyridyl)-s-triazine), acetic acid, phloroglucinol and methanol were purchased from Sigma-Aldrich (Steinheim, Germany). (−)-Epicatechin, (+)-catechin, chlorogenic acid, phloretin 2′-*O*-glucoside, quercetin-3-*O*-glucoside and procyanidins B_1, B_2, C_1 were purchased from Extrasynthese (Lyon, France). Acetonitrile and ascorbic acid were from Merck (Darmstadt, Germany).

Plant material

Apples of ‘Idared’ and ‘Shampion’ cvs (*Malus domestica* Borkh.) were used for the experiment. ‘Shampion’ apples were harvested from 15-year-old trees grown on M.26 rootstock and planted with 4 m × 1.5 m density in the orchard located in in Ostrowiec, near Lowicz—central Poland (52°09′36,2880″N 20°03′22,5720″E). ‘Idared’ apples were harvested from 13-year-old trees grown on P 60 rootstock and planted with 3.5 m x 1.5 m density in the orchard located in Kozietuły in Grójec region (51°45′04″N 20°45′50″E). In both orchards irrigation, training, mineral nutrition and orchard management system are used according to standard commercial practice. Crop protection programmes are applied in conformity with integrated fruit production rules. Fruits were harvested at optimum ripening stage recommended for long-term storage (based on internal ethylene concentration and starch index). After harvest, fruits were transported to Fruit Storage Laboratory of the Research Institute of Horticulture (formerly Research Institute of Pomology and Floriculture) in Skierniewice and were divided into two groups. Both groups were placed in cold room (temperature +2 °C). On sixth day, one group of apples were treated with 1-methylocyclopropene for 24 h at 2 °C at the commercial rate (1-MCP, 625 ppb, SmartFresh 0.14 %, AgroFresh Inc., wholly owned subsidiary of DOW Chemicals Company) according to Hoang et al. [13]. Then, both groups of fruits were stored for 2, 4 and 6 months under normal atmosphere at 2 °C with relative humidity ca 90 %.

Identification of polyphenols by the ultraperformance liquid chromatography–mass spectrometry (UPLC–MS) method.

Identification of apple polyphenols was determined using the ACQUITY Ultra Performance LC™ system with Micromass G2 Q-Tof Micromass equipped with an electrospray ionization (ESI) as described previously by Kolniak-Ostek et al. [14].

HPLC analysis of polyphenols

Polyphenolic compounds and polymer procyanidins by phloroglucinol method were determined using the HPLC method described previously by Wojdyło et al. [15].

Analysis of antioxidant activity

The total antioxidant potential of samples was determined using a ferric reducing ability of plasma (FRAP) assay by Benzie et al. [16] as a measure of antioxidant power. The

DPPH radical scavenging activity of samples was determined according to the method of Yen et al. [17]. The $ABTS^{+}$ activity of samples was determined according to the method of Re et al. [18]. For all analysis, portions (0.5 g) of freeze-dried apples were precisely measured into vials and mixed with methanol (80 %) acidified with HCL (1 ml/l). Standard curve was prepared using different concentrations of Trolox. All determinations were performed in triplicates using a Shimadzu UV-2401 PC spectrophotometer (Kyoto, Japan). The results were corrected for dilution and expressed in μM Trolox/kg.

Dry matter

The dry matter of fresh apples was performed by gravimetric method, according to Polish Norm [19]. Fresh apple samples (1.5 g) were precisely measured and dried at 70 °C in a vacuum (3 kPa), until a constant weight. The measurements were performed in triplicate and expressed as g of dry weight/100 g of fresh matter.

Total soluble solids

Percentage of total soluble solids was determined refractometrically, using electronic Pocket Refractometer PAL-1 (Atago, USA). The measurements were taken in triplicate and expressed in g of soluble solids/100 g of fresh matter.

Titrable acidity

Titratable acidity of samples was determined by using a pH meter (IQ's Scientific Instruments), according to Polish Norm [20]. The chopped apples were transferred to a volumetric flask (100 ml) and filled with water. Prepared samples were boiled and filtered after cooling down. About 10 ml of obtained filtrate was titrated with NaOH (0.1 mol L^{-1}) up to pH 8.1. The measurements were performed in triplicate and expressed in g of malic acid/100 g of fresh matter.

Sensory analysis

The quality of the fresh and stored apples was evaluated using a profiling method. The expert panel consisted of 15 persons, recruited from the staff of the Research Institute of Horticulture, trained and having extensive experience in performing sensory assessment of horticultural products. Before successive seasons the panelists participated in special training sessions, where particular attributes' definitions were discussed and clarified. For particular sessions, 10 available experts were invited. Sensory testing laboratory fulfilled the general requirements of the relevant ISO 8589:1998 [21] standard for sensory testing conditions. Each test booth was illuminated with white light (6,500 K) and equipped with a computerized system for data acquisition (Analsens v.4 software, Caret Systemy Cyfrowe i Oprogramowanie Sp. z o.o., Gdańsk, Poland). During one session, two combinations of fresh, and four combinations of stored apples were tested. Fruits were served peeled and placed in small plastic containers, which were covered for 5 min before sample presentation, to induce the aroma head space accumulation. Samples assigned with 3-digit codes were presented randomly. The experts assessed qualitative traits using an unstructured 100-mm linear scale anchored at their ends with relevant word description. The results were transposed into a 0–10 point scale, where '0' denoted lack of a given trait or a bad level, while '10' indicated an intensive sensation or a high quality. Other evaluated attributes included: ripe apple aroma, hardness, crispness, juiciness, overall texture, taste (sweet, sour, overall score) and the overall quality defined as the overall sensory impression of balance and harmony of all attributes and their interactions.

Fruit firmness

Fruit firmness was measured using at least 20 fruits, on the opposite sides of fruit (blushed and unblushed) using an EPT-1R pressure tester (Lake City Technical Products, Canada), equipped with 11.1 mm tip.

Statistical analysis

Results were given as mean ± standard deviation of three independent determinations. All statistical analyses were performed with Statistica version 9.1 (StatSoft, Poland). One-way analysis of variance (ANOVA) by Duncan's test was used to compare the means. Differences were considered to be significant at $P = 0.05$.

Results and discussion

Effect of 1-MCP on the basic parameters of fresh apples

The effect of postharvest treatment with 1-MCP and long-time storage of apples, on the total soluble solids, dry matter and titrable acidity was presented in Table 1. Storage of apples has increased the dry matter in all samples. In 'Idared' cv., dry matter varied from 15.6 g/100 g after 6-month storage for untreated fruits to 15.4 g/100 g after 1-MCP treatment. In 'Shampion' cv., after 6-month storage, apple dry matter increased from 14.7 g/100 g in fresh fruits up to 17.0 g/100 g in control sample and up to 16.0 g/100 g after 1-MCP treatment. Generally, after long-time storage, dry weight of apples treated by 1-MCP was about 3.5 % lower, compared with untreated fruits.

Table 1 The effect of long-time storage in control and after postharvest treatment by 1-MCP on the quality of apples

	Dry matter (g/100 g)	Total soluble solids (g/100 g)	Tritatable acidity (g/100 g)*
Idared (m)			
0			
Harvest	14.9 ± 0.1 e	14.0 ± 0.0 d	0.57 ± 0.0 a
2			
CONTROL	15.4 ± 0.0 d	13.4 ± 0.0 f	0.51 ± 0.1 b
1-MCP	15.3 ± 0.2 d	13.7 ± 0.2 e	0.52 ± 0.0 b
4			
CONTROL	15.4 ± 0.2 d	13.2 ± 0.1 g	0.38 ± 0.0 d
1-MCP	15.2 ± 0.1 d	12.9 ± 0.0 i	0.41 ± 0.0 c
6			
CONTROL	15.6 ± 0.3 d	12.9 ± 0.2 i	0.33 ± 0.1 e
1-MCP	15.4 ± 0.0 c	12.2 ± 0.0 j	0.38 ± 0.1 d
Shampion (m)			
0			
Harvest	14.7 ± 0.2 f	15.0 ± 0.2 a	0.29 ± 0.0 f
2			
CONTROL	16.4 ± 0.1 b	14.9 ± 0.2 ab	0.26 ± 0.1 g
1-MCP	15.5 ± 0.1 cd	15.2 ± 0.1 a	0.19 ± 0.1 h
4			
CONTROL	16.9 ± 0.1 a	14.8 ± 0.1 b	0.20 ± 0.1 h
1-MCP	15.6 ± 0.0 c	14.6 ± 0.2 c	0.16 ± 0.0 i
6			
CONTROL	17.0 ± 0.1 a	13.8 ± 0.1 e	0.15 ± 0.0 ij
1-MCP	16.0 ± 0.0 b	13.1 ± 0.1 h	0.14 ± 0.0 j

Values are mean ± standard deviation, $n = 3$; mean values within a verses with different letters (a, b, c…) are significantly different at $P < 0.05$

* Expressed as malic acid

After long-time storage of apples, decrease of total soluble solids was observed. In 'Idared' cv., total soluble solids varied from 12.9 g/100 g after 6-month storage for untreated fruits to 12.2 g/100 g after 1-MCP treatment. In 'Shampion' cv., after 6-month storage, total soluble solids decreased to 13.8 g/100 g in control samples and to 13.1 g/100 g after 1-MCP treatment. Generally, after 1-MCP treatment, total soluble solids of apple were about 5.0 % lower compared with untreated fruits. However, still, total soluble solids are much higher than the minimum requirements given by AIJN [X] for single-strength juice and do not restrict its processing into juice.

Long-time storage of apples resulted in a lower titratable acidity in all samples. In 'Idared' cv. after 6-month storage, titratable acidity decreased from 0.57 g/100 g in fresh samples to 0.33 g/100 g in control samples and 0.38 g/100 g after 1-MCP treatment. In 'Shampion' cv., after 1-MCP treatment, apple acidity decreased to 0.14 g/100 and to 0.15 g/100 g. This is below the minimum content for authentic juice which is 0.4 g/l [X] and indicates stored 'Shampion' fruits should be mixed or processed with cultivars with higher acidity.

Scientific data indicate that the composition and content of chemical compounds in fruits mainly depends on the species and variety [22]. The degree of ripeness of fruit has a significant influence on the content of sugars, minerals and acids. The sugar content in fully ripe apples is high due to complete hydrolysis of starch. Then, during storage, sugars content begins to decrease, as they are consumed in respiration process [23].

During ripening on the tree, the organic acid content in apples increases, reaches a maximum for a few days before harvest and then slightly decreases. However, acid content during storage has been gradually declining. It is thought that part of them, in addition to sugars, may be consumed in the process of respiration. Storage leads to softening of fruits, which is mediated by loss of cell-to-cell adhesion. Tissue from soft fruits has rounded cells, bigger cell separation and larger intercellular spaces [24, 25]. Analyses of pectin fractions have shown that apple softening is usually associated with the increased content of water-soluble pectin and reduced galactose and arabinose residues. A number of cell-wall-modifying enzymes that have been found in ripening apples may cause softening. The enzyme originally considered responsible for pectin solubilization, and therefore, softening was polygalacturonase (PG), with activities of both exo-PG and endo-PG detected in ripening apples [26]. Direct measurements of turgor showed that

Table 2 Retention time (R_t), λ_{max} and MS/MS fragmentation data of major phenolics detected in analyzed apples

Group of polyphenols	R_t (min)	λ_{max} (nm)	Compound	$[M–H]^-$ (m/z)	MS/MS (m/z)
Hydroxycinnamic acids	3.72	320	Chlorogenic acid	353	191
	5.05	320	Cryptochlorogenic acid	353	137
	5.71	305	*p*-Coumaryloquinic acid	337	163
Flavanols and procyanidins	2.47	275	Procyanidin B1	578	289
	2.81	280	(+)-Catechin	289	245
	5.47	275	Procyanidin B2	578	289
	5.90	280	(−)-Epicatechin	289	245
	5.98	280	Procyanidin C1	866	577, 289
Dihydrochalcones	6.99	285	Phloretin 2′-*O*-xyloglucose	567	273
	8.06	285	Phloretin 2′-*O*-glucose	435	273
Flavonols	6.23	355	Quercetin-3-*O*-galactoside	463	301
	6.56	350	Quercetin-3-*O*-glucoside	463	301
	6.69	350	Quercetin-3-*O*-xyloside	433	301
	7.12	355	Quercetin-3-*O*-arabinoside	433	301
	7.90	345	Quercetin-3-*O*-rhamnoside	447	301

cell turgor decreased in four apple cultivars during storage. There was a positive association between cell turgor and firmness after 6 months at 0–2 °C for cultivars with different softening rates. The dry matter content in fruit is variable and depends, i.e., on the type of soil, fertilization and the conditions prevailing during the growing season [27].

Qualitative analysis of polyphenolic compounds

As an initial step, apple samples were analyzed by LC–MS QTof and HPLC–DAD systems. Fifteen different polyphenolic compounds were identified as function of their retention times compared with the standard compounds in HPLC analyses and as function of their mass fragmentation compared with those of the standard compound during LC–MS QTof analyses. Qualitative analyses obtained by LC–MS QTof methods and by HPLC are summarized in Tables 2 and 3. Three hydroxycinnamates were detected: *p*-coumaroylquinic acid, chlorogenic acid and cryptochlorogenic acid. The compound that had a $[M–H]^-$ at *m/z* 337 was identified as *p*-coumaroylquinic acid. Chlorogenic acid and cryptochlorogenic acid have a characteristic mass spectral data as is produced on $[M–H]^-$ at *m/z* 353 and the fragmentation of the negatively charged molecular ion ($[M–H]^-$) at *m/z* 191 and 137, respectively. Five flavan-3-ols were detected: (+)-catechin, (−)-epicatechin and procyanidins B_1, B_2 and C_1. In the presence retention time (R_t) at 2.81 min, λ_{max} for 280 nm was identified as (+)-catechin with the fragmentation of the negatively charged molecular ion ($[M–H]^-$) at *m/z* 289. Procyanidin B_1 and B_2 (λ_{max}) 275 nm had a $[M–H]^-$ at *m/z* 578, but the retention time for procyanidin B_1 was R_t at 2.47 min and for B_2 was (R_t) 5.47 min. The compound with (R_t) 5.98 min, λ_{max} 280 nm that had the highest MW, with a $[M–H]^-$ at *m/z* 866 is procyanidin C_1. The compound that had the $R_t = 5.90$ min and λ_{max} 280 nm was identified as (−)-epicatechin. Dihydrochalcones were detected: phloretin 2′-*O*-xyloglucoside and phloretin 2′-*O*-glucoside. The peak with a $[M–H]^-$ at *m/z* 567 that had a $R_{t=}= 6.99$ and λ_{max} 285 nm is phloretin-2′-*O*-xyloglucoside. The peak at $R_t = 8.06$ min, λ_{max} 285 nm produced a $[M–H]^-$ at *m/z* 435 is the phloretin 2′-*O*-glucoside. Flavonols were detected as quercetin-3-*O*-galactoside, -3-*O*-glucoside, -3-*O*-arabinoside, -3-*O*-xyloside and -3-*O*-rhamnoside. Peaks with $R_t = 6.23$ and 6.56 min had λ_{max} values of 355 and 350, respectively. Both had a $[M–H]^-$ at *m/z* 463, and fragmentation yielded a quercetin ion at *m/z* 301. This fragmentation pattern and λ_{max} demonstrates that this peaks are quercetin-3-*O*-galactoside and -3-*O*-glucoside, respectively. A similar situation was found for quercetin-3-*O*-xyloside and -3-*O*-arabinoside that brought the same *m/z* 433 but different $R_t = 6.69$ and 7.12 min, respectively. The compound at $R_t = 7.90$ min, λ_{max} 345 nm that produced a [M- H]$^-$ at *m/z* 447 and a fragment at *m/z* 301 was identified as quercetin-3-*O*-rhamnoside. The obtained results were typical for apple polyphenols and in agreement with previously published results [28, 29].

Effect of 1-MCP on phenolic compounds of apples

The composition and characterization of polyphenolic compounds in fresh apples and after storage is summarized in Tables 2 and 3. The major polyphenolic groups in apples were hydroxycinnamic acids, flavan-3-ols/procyanidins, flavonols, dihydrochalcones and anthocyanins. The total phenolics determined by HPLC in fresh apples ranged from

Table 3 The effect of long-time storage in control and after postharvest treatment by 1-MCP on the concentration of phenolic compounds (mg/kg) in apples

	ChA	CA	*p*-CA	E	PB2	PC1	C	PB1	PXylo
Idared (m)									
0									
Harvest	78.9 ± 3.2 f	2.9 ± 0.2 a	11.7 ± 0.2 a	74.4 ± 1.3 a	163.3 ± 4.8 a	44.0 ± 1.8 a	10.8 ± 0.8 d	16.7 ± 0.9 f	17.2 ± 0.4 a
2									
CONTROL	45.5 ± 1.8 h	2.1 ± 0.3 e	10.5 ± 0.3 b	62.2 ± 2.2 b	120.0 ± 3.2 b	37.7 ± 4.2 b	9.2 ± 0.3 e	14.7 ± 1.1 g	14.6 ± 0.2 b
1-MCP	49.6 ± 2.6 g	2.0 ± 0.1 f	8.6 ± 0.2 c	57.1 ± 1.8 d	91.4 ± 2.5 e	23.4 ± 3.6 g	7.7 ± 0.8 g	12.8 ± 0.7 i	12.7 ± 0.6 c
4									
CONTROL	34.1 ± 3.3 i	0.9 ± 0.0 k	7.2 ± 0.1 d	59.0 ± 1.7 c	116.7 ± 2.0 c	30.1 ± 1.4 c	8.4 ± 0.2 f	13.5 ± 1.3 h	5.4 ± 0.1 e
1-MCP	44.9 ± 1.4 h	1.4 ± 0.1 h	8.6 ± 0.1 c	56.3 ± 2.3 e	90.3 ± 4.1 e	21.9 ± 2.5 h	7.5 ± 0.1 g	12.7 ± 0.8 i	12.6 ± 0.4 c
6									
CONTROL	33.4 ± 2.2 j	0.4 ± 0.0 l	5.2 ± 0.2 f	52.6 ± 3.6 g	109.4 ± 4.6 d	29.4 ± 2.0 d	5.1 ± 0.1 h	12.5 ± 0.8 j	4.8 ± 0.0 f
1-MCP	32.9 ± 2.5 k	1.3 ± 0.2 i	5.8 ± 0.0 f	47.8 ± 2.8 h	88.6 ± 3.9 f	23.5 ± 3.2 g	7.4 ± 0.1 g	12.5 ± 1.2 j	11.4 ± 0.5 d
0									
Harvest	152.5 ± 4.6 a	2.7 ± 0.3 b	7.1 ± 0.2 d	58.9 ± 4.0 c	86.7 ± 2.7 g	30.4 ± 2.1 c	13.4 ± 0.2 a	20.3 ± 0.9 a	2.3 ± 0.1 g
2									
CONTROL	149.3 ± 4.1 b	2.6 ± 0.2 c	6.2 ± 0.3 e	55.7 ± 3.7 f	79.9 ± 2.3 i	29.3 ± 2.3 d	12.4 ± 0.1 b	18.2 ± 0.6 d	1.9 ± 0.0 g
1-MCP	152.5 ± 3.9 a	2.5 ± 0.4 d	7.0 ± 0.2 d	58.5 ± 2.2 c	86.5 ± 1.6 g	30.4 ± 1.4 c	13.2 ± 0.3 a	20.1 ± 0.9 b	2.0 ± 0.1 g
4									
CONTROL	139.8 ± 2.8 c	2.1 ± 0.0 e	5.3 ± 0.1 g	39.7 ± 1.3 j	69.9 ± 3.0 k	20.4 ± 0.9 i	9.9 ± 0.1 e	15.0 ± 0.5 g	1.2 ± 0.1 h
1-MCP	132.9 ± 1.7 d	1.6 ± 0.1 g	6.3 ± 0.0 e	41.6 ± 3.4 i	82.1 ± 3.8 h	28.8 ± 1.1 e	11.2 ± 0.0 c	19.2 ± 1.0 c	1.5 ± 0.0 h
6									
CONTROL	126.8 ± 4.6 f	1.2 ± 0.0 j	3.2 ± 0.1 i	36.1 ± 2.5 l	63.8 ± 2.7 l	15.8 ± 1.9 j	8.1 ± 0.2 f	13.2 ± 0.3 h	0.5 ± 0.0 i
1-MCP	130.0 ± 3.0 e	1.4 ± 0.0 h	4.6 ± 0.1 h	38.3 ± 1.0 k	75.8 ± 4.1 j	26.2 ± 2.0 f	10.4 ± 0.3 d	17.2 ± 0.6 e	1.1 ± 0.1 h

	Pgluco	Qgala	Qgluco	Qara	Qxylo	Qrhamno	PP	Total
Idared (m)								
0								
Harvest	19.2 ± 1.0 a	6.5 ± 0.7 c	1.5 ± 0.3 a	4.8 ± 0.3 d	5.6 ± 0.3 f	5.4 ± 0.0 a	780.3 ± 5.9 d	1,243 ± 9.9 c
2								
CONTROL	17.5 ± 0.8 b	5.9 ± 0.9 d	1.2 ± 0.1 a	3.9 ± 0.2 f	4.9 ± 0.2 g	4.6 ± 0.3 e	832.5 ± 8.6 c	1,187 ± 8.3 d
1-MCP	14.0 ± 0.6 d	4.7 ± 0.3 e	1.3 ± 0.2 a	4.3 ± 0.6 e	4.6 ± 0.2 h	4.7 ± 0.2 d	667.3 ± 7.5 i	966. ± 9.8 h
4								
CONTROL	15.6 ± 0.1 c	4.4 ± 0.6 e	0.9 ± 0.0 b	3.7 ± 0.1 f	4.0 ± 0.0 j	3.7 ± 0.1 i	710.1 ± 9.1 g	1,017 ± 10.2 g
1-MCP	13.3 ± 0.7 e	4.7 ± 0.2 e	1.2 ± 0.0 a	4.3 ± 0.0 e	4.4 ± 0.1 i	4.9 ± 0.1 b	649.1 ± 2.2 j	938 ± 8.3 i
6								
CONTROL	8.6 ± 0.5 i	3.7 ± 0.1 f	0.8 ± 0.1 b	3.9 ± 0.2 f	4.4 ± 0.0 i	3.3 ± 0.3 k	689.4 ± 6.1 h	966 ± 11.5 h
1-MCP	9.8 ± 0.6 h	3.7 ± 0.2 f	0.8 ± 0.0 b	2.7 ± 0.1 g	4.4 ± 0.0 i	4.2 ± 0.0 h	629.1 ± 7.8 k	885 ± 10.9 j
0								
Harvest	14.5 ± 0.4 d	8.9 ± 0.5 a	0.8 ± 0.1 b	7.1 ± 0.3 a	17.4 ± 0.5 a	4.9 ± 0.2 b	1,008.0 ± 9.2 a	1,435 ± 12.8 a
2								
CONTROL	10.8 ± 0.2 g	6.7 ± 0.3 c	0.5 ± 0.0 c	6.7 ± 0.2 b	16.8 ± 0.4 b	4.8 ± 0.3 c	873.6 ± 4.8 b	1,275 ± 13.2 b
1-MCP	14.4 ± 0.7 d	8.9 ± 0.2 a	0.7 ± 0.0 b	7.0 ± 0.2 a	17.2 ± 0.1 a	4.8 ± 0.0 c	1,007.4 ± 9.9 a	1,433 ± 10.7 a
4								
CONTROL	8.9 ± 0.1 i	4.3 ± 0.3 e	0.3 ± 0.0 d	5.6 ± 0.0 c	11.7 ± 0.0 d	4.7 ± 0.1 d	762.7 ± 7.5 e	1,101 ± 11.6 e
1-MCP	12.9 ± 0.3 e	7.8 ± 0.0 b	0.4 ± 0.0 c	6.8 ± 0.1 b	15.8 ± 0.5 b	4.5 ± 0.1 f	873.6 ± 5.9 b	1,247 ± 8.8 c
6								
CONTROL	7.7 ± 0.5 j	3.7 ± 0.1 f	0.3 ± 0.1 d	4.7 ± 0.1 d	10.8 ± 0.3 e	4.3 ± 0.2 g	753.0 ± 4.3 f	1,053 ± 12.4 f
1-MCP	11.7 ± 0.6 f	6.3 ± 0.3 c	0.4 ± 0.0 c	6.8 ± 0.0 b	13.8 ± 0.4 c	3.6 ± 0.1 j	711.3 ± 6.6 g	1,059 ± 13.6 f

Values are mean ± standard deviation, $n = 3$; in columns, mean values with different letters (a, b, c…) are significantly different at $P < 0.05$

ChA, chlorogenic acid; CA, cryptochlorogenic acid; *p*-CA, *p*-coumaryloquinic acid; E, (−)-epicatechin; PB2, procyanidin B2; PC1, procyanidin C1; C, (+)-catechin; PB1, procyanidin B2; PXylo, phloretin 2′-*O*-xyloglucose; Pgluco, phloretin 2′-*O*-glucose; Qgala, quercetin-3-*O*-galactoside; Qgluco, quercetin 3-*O*-glucoside; Qara, quercetin-3-*O*-arabinoside; Qxylo, quercetin-3-*O*-xyloside; Qrhamno, quercetin-3-*O*-rhamnoside; PP, polimeric procyanidins; m, month

1,243 mg/kg in 'Idared' cv. to 1,435 mg/kg in 'Shampion' cv. Types and amount of polyphenolic compounds detected in these apple cultivar studies were similar to previous studies [4, 15, 30].

Analysis of nonstorage apples revealed a reasonably high content of polymeric procyanidins and flavan 3-ols, which represented 70.2 and 14.6 % of total polyphenols in 'Idared' cv. nonstorage apples and 70.1 and 20.5 % of total polyphenols in 'Shampion' cv. In fresh apples were also observed a high content of phenolic acids—11.3 % in 'Idared' cultivar and 6.2 % in 'Shampion' cv.

According to the literature data (X) during storage, reduction of polyphenolic content has been observed ($P = 0.05$). In 'Shampion' cv., reduction of polyphenolic compounds was higher after 1-MCP treatment. In case of 'Idared' cv., different trend was observed—apples treated by 1-MCP were characterized by a higher concentration of polyphenols. After 6-months of storage in 'Idared' cv., reduction of 26.2–26.6 % of polyphenolic content was observed. In 'Shampion' cv., decrease of polyphenols varied from 22.2 to 28.8 %.

In this study, phenolic compounds of analyzed cultivar of apples responded differently during storage with 1-MCP treatment. In 'Shampion' cv., hydroxycinnamic acids, flavan-3-ols, and procyanidins were significantly reduced after 1-MCP treatment. In 'Idared' cv., there was no such relationship. Decrease in the normal metabolism of phenolic compounds levels in fruits treated with 1-MCP may be caused by inhibition of ethylene production by 1-MCP. MacLean et al. [4] presented that the inhibition of polyphenols caused by 1-MCP depends on the fruit maturity—it was most dramatic in the early harvest maturity, less severe in the optimal harvest maturity and completely lost at the late harvest maturity fruits.

These results are similar to those obtained by Napolitano et al. [31]. After 4-month storage of 'Red Delicious' and 'Annurca' apples cv., they observed significant decrease of all polyphenolic classes concentrations. However, in apples 'Empire' and 'Golden Delicious,' they observed increase of total polyphenolics. Also Hoang, Golding and Wilkes [32] in 'Cripps Pink' apples after treated with 1-MCP and stored in normal and controlled atmosphere at 0 °C for up to 160 days observed that the level of phenolics decreased by 9 % in the peel.

The polyphenol concentrations of apples depend strongly on the cultivar [33–35]. Apple phenolics are mainly localized in the peel and in the seeds. Progressive depolymerization of the major classes of cell wall polysaccharide, such as pectins, cellulose and hemicellulose during apple storage, can lead to the excessive softening, resulting in heavy postharvest losses. For example, the content of (−)-epicatechin and (+)-catechin may decrease during storage due to polymerization and re-arrangement of procyanidins during storage. Similar effect was observed previously for strawberry jams [36] and drying sour cherries [37].

Decrease of total polyphenols during cold storage could be due to the 1-MCP action. Ethylene stimulates activity of phenylalanine ammonia lyase, a key enzyme in biosynthesis of phenolic compounds [38, 39]. The decrease of phenolic compounds observed in this study for 'Idared' and 'Shampion' cv. can be related to the inhibition of ethylene production by 1-MCP.

Effect of 1-MCP on antioxidant activity of apples

The effect of long-time storage of apples on antioxidant activity was measured as free radical scavenging activity (ABTS and DPPH methods) and ferric reducing capacity by FRAP method (Table 4). In this study, the results of the ABTS, DPPH and FRAP methods were expressed in the same unit, i.e., μMol of Trolox equivalent per kilogram of apple fresh matter.

The analysis revealed a statistically significant differences ($P = 0.05$) between apple cultivars. Among the fresh apples, DPPH antioxidant capacity varies from 3,818 μMol/kg in 'Idared' cv. to 4,299 μMol/kg in 'Shampion' cv.; ABTS capacity varied from 1,883 μMol/kg in 'Shampion' cv. apples to 1,923 μMol/kg in 'Idared' cv.; FRAP antioxidant activity ranged 3,388 μMol/kg in 'Shampion' cv. and 4,717 μMol/kg in 'Idared' cv. The study showed that after storage, antioxidant capacity decreased—the lowest antioxidant properties were characterized by apples stored for a period of 6 months. In the case of 'Idared' cv., fruit treatment by 1-MCP limited the reduction in DPPH, ABTS and FRAP antioxidant capacity by average 8.5, 13.5 and 10 %, respectively. In case of 'Shampion' cv., stored apples after treatment by 1-MCP have reduced DPPH activity by 25 %, ABTS activity by 17.5 % and FRAP capacity by 2.5 % in comparison with control apples (Table 4).

The differences in antioxidant activities between apple cultivars could be preliminarily attributed to their different contents and the type of polyphenols (Tables 2, 3). The data presented by Eberhardt et al. [33] and Salah et al. [40] show that the polymeric procyanidins have a high antioxidant activity. Also, Rice-Evans et al. [41] in their studies of antioxidant properties of polyphenolic compounds show that the compounds from the group of flavan-3-ols have strong antioxidative properties, while Horubała [42] argues that some polyphenols have antioxidant activity several times higher than ascorbic acid, such as quercetin is 4.7-fold more active and tannins as much as 3–30-fold.

Decrease in antioxidant activity is associated with the process of oxidation of polyphenolic compounds, formation of complexes with other food ingredients or transition of active polyphenols forms into inactive compounds

Table 4 The effect of long-time storage in control and after postharvest treatment by 1-MCP on the antioxidant activity (μMol Trolox/kg) of apples

	DPPH	ABTS	FRAP
Idared (m)			
0			
Harvest	3,818 ± 23 b	1,923 ± 25 a	4,718 ± 56 a
2			
CONTROL	3,216 ± 34 e	1,297 ± 13 g	3,812 ± 33 c
1-MCP	3,720 ± 26 b	1,405 ± 31 e	4,624 ± 54 b
4			
CONTROL	3,065 ± 18 g	1,027 ± 10 i	3,479 ± 25 d
1-MCP	3,135 ± 31 f	1,156 ± 25 h	3,806 ± 34 c
6			
CONTROL	2,429 ± 18 j	788 ± 9 k	3,112 ± 21 f
1-MCP	2,678 ± 39 h	998 ± 29 j	3,255 ± 30 e
Shampion (m)			
0			
Harvest	4,299 ± 12 a	1,883 ± 38 b	3,388 ± 29 e
2			
CONTROL	3,719 ± 13 b	1,743 ± 44 c	3,111 ± 47 f
1-MCP	3,438 ± 36 c	1,588 ± 22 d	3,002 ± 31 g
4			
CONTROL	3,338 ± 34 d	1,490 ± 19 e	2,933 ± 46 h
1-MCP	2,566 ± 22 i	1,213 ± 30 g	2,896 ± 32 i
6			
CONTROL	3,247 ± 27 e	1,383 ± 36 f	2,970 ± 28 h
1-MCP	1,827 ± 16 k	1,033 ± 24 i	2,886 ± 20 i

Values are mean ± standard deviation, $n = 3$; in columns, mean values with different letters (a, b, c…) are significantly different at $P < 0.05$

m month

[43]. Fruit with 1-MCP treatment was associated with lower lipoxygenase (LOX) and PPO activities, reduced $O2^{\bullet -}$ accumulation and maintenance of cell membrane integrity, decreased oxidation of polyphenols and thus retarded enzyme reactions involved in browning [44].

Effect of 1-MCP on fruit firmness and sensory attributes

Fruit firmness is one of the most important quality attribute for stored apple fruits [45]; therefore, all postharvest treatments that can control firmness are of great interest of fruit producers and researchers. 1-MCP due to specific ethylene action [9] can help to maintain fruit firmness but not in all cases. Generally, the firmness of apples declines when ethylene production or internal ethylene concentration increased. Apples treated at harvest with 1-MCP softened slower [10, 26, 46]. Presented results shows that in the case of 'Idared' cv. fruits with known good storability and with high initial firmness (8.5 kg), one can observe the decrease in stored fruits but no significant effect of neither storage nor 1-MCP treatment (Fig. 1). In the case of 'Shampion' cv. with 6.6 kg initial firmness on harvest time, fruits treated with 1-MCP significantly better retained firmness as compared with fruits stored without the treatment. It shows high usefulness of 1-MCP in 'Shampion' cv. storage.

The sensory characteristic of investigated fruits is given in Table 5. Comparing quality of fruit just after harvest, it was found that cultivar affects most of the investigated sensory attributes with the exception of ripe apple smell, crispness, crunchiness and the overall texture score. In general, 'Shampion' cv. got higher ranks for sweetness, taste and the overall quality, whereas 'Idared' cv. was perceived as

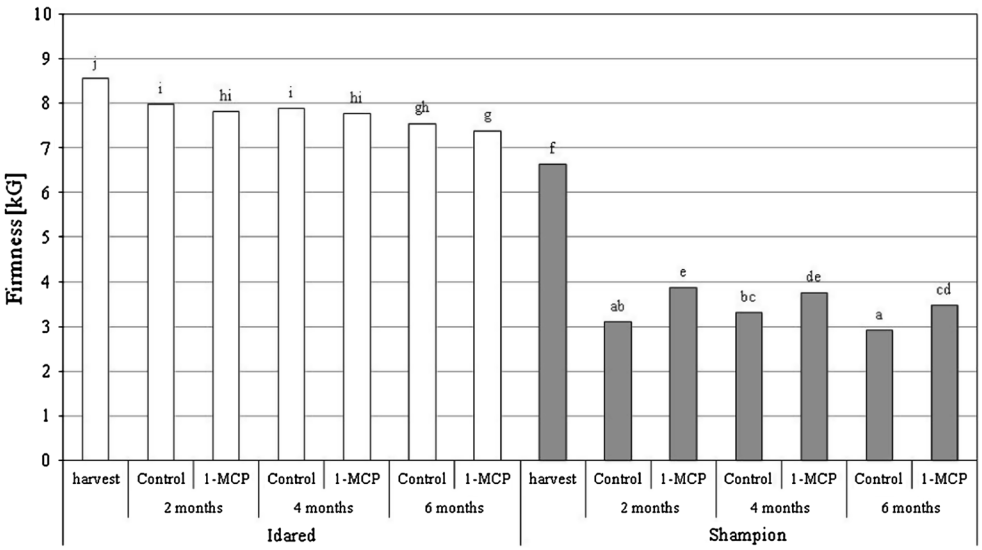

Fig. 1 Fruit firmness (kg) in relation to cultivar storage and 1-MCP treatment

sourer, which is in arrangement with instrumental measurements (Fig. 1).

As concerns quality of stored apple, sweetness scores were stable during apple storage for both cultivars, whereas sourness scores only for 'Idared' cv.; in 'Shampion' cv., the decrease was found; however, no significant effect of 1-MCP was observed.

The hardness evaluated by expert panel was much higher for 'Idared' cv. as it was for fruit firmness measured mechanically (Fig. 1); this difference between cultivars may originate from structural differences in cell walls [47].

During storage in normal atmosphere, no effect of 1-MCP treatment or storage time was found for ripe apple smell, crispness, crunchiness and sweetness score.

For hardness, in case of 'Idared' cv., no effect of 1-MCP treatment was found, whereas for 'Shampion' cv., retarding effect of 1-MCP was observed (Table 5). These observations were in close arrangement with firmness measurements; moreover, it was found the high correlation between sensory and instrumental ($R^2 = 0.963$). Fruit of 'Idared' cv. kept their juiciness and overall texture quality for 6-month storage but 'Shampion' cv. lost juiciness just after 2-month storage. It may be the indication of retarded harvest time for this cultivar as it may affect the storability [48]. However, 1-MCP significantly increased juiciness scores for fruits stored for 6 months, which probably influenced overall quality of fruits.

Overall texture for 'Shampion' cv. was lowest in all stored fruits without 1-MCP, while after 6-month storage, fruits with 1-MCP treatment got significantly better rank that all control samples.

Fruit flavor and the overall quality scores of 'Idared' cv. showed no effect of 1-MCP; this may be the effect of good storability of this cultivar. In the case of 'Shampion' cv., 1-MCP-treated fruit had better flavor and quality but the differences were not statistically significant.

Conclusion

The results of presented study demonstrate that treatment by 1-MCP is promising for the production of fruits rich in natural bioactive compounds. Apple storage after treatment by 1-MCP had positive effect on the quality of fruits by improving polyphenolic contents and antioxidant capacity.

The results of presented study demonstrate that apple after storage, especially 'Idared' cv., can be a valuable sensory attributes for food product. This study indicates that the use 1-MCP during long-term storage of apples is promising for the fruits designed for the direct consumption and also for the production of juices, rich in natural bioactive compounds.

Table 5 Sensory evaluation of fresh and stored fruits in control and after 1-MCP treatment

Cultivar	Storage (m)	Treatment	Ripe apple smell	Crispness	Hadness	Crunchiness	Juiciness	Textureoverall score	Sweetness	Sourness	Taste	Overall quality
'Idared'	0	harvest	4.9 ± 2.8 a	6.4 ± 1.8 cd	6.9 ± 1.4 d	6.1 ± 1.6 de	5.9 ± 1.5 f	6.6 ± 1.3 gh	4.6 ± 2.1 a	5.5 ± 1.4 f	5.9 ± 1.5 d	5.6 ± 1.9 d
	2	Control	3.8 ± 2.2 a	5.4 ± 1.4 bc	6.1 ± 1.2 cd	4.9 ± 1.7 cd	5.4 ± 0.9 ef	4.9 ± 1.8 d–f	4.3 ± 0.9 a	3.6 ± 0.9 de	4.9 ± 1.3 b–d	4.8 ± 1.9 cd
		1-MCP	2.9 ± 2.7 a	4.4 ± 1.3 b	5.8 ± 1.2 c	4.3 ± 1.7 bc	5.4 ± 1.2 ef	4.9 ± 1.3 d–f	3.6 ± 1.7 a	3.9 ± 1.1 de	4.9 ± 1.6 b–d	4.7 ± 1.3 cd
	4	Control	4.3 ± 1.5 a	5.1 ± 1.3 bc	5.9 ± 0.9 c	4.1 ± 1.7 bc	5.3 ± 1.2 d–f	5.5 ± 1.6 e–g	4.0 ± 1.6 a	4.6 ± 1.2 ef	5.1 ± 1.8 cd	5.1 ± 1.7 cd
		1-MCP	4.3 ± 2.0 a	4.8 ± 1.5 b	5.5 ± 0.6 c	4.3 ± 1.5 bc	5.3 ± 1.1 d–f	5.5 ± 1.3 e–g	4.2 ± 1.0 a	4.0 ± 1.0 de	4.8 ± 1.4 b–d	5.4 ± 1.5 d
	6	Control	3.4 ± 2.1 a	5.5 ± 2.2 bc	6.5 ± 1.0 cd	4.9 ± 2.1 cd	4.9 ± 1.3 c–f	5.0 ± 1.5 d–f	3.8 ± 1.3 a	3.8 ± 1.7 de	4.2 ± 1.4 a–c	4.7 ± 1.2 cd
		1-MCP	3.2 ± 2.1 a	5.3 ± 2.0 bc	6.0 ± 1.1 cd	4.9 ± 2.0 cd	5.3 ± 1.0 ef	4.7 ± 1.7 c–f	3.7 ± 1.3 a	3.8 ± 1.3 de	4.7 ± 1.7 b–d	5.1 ± 1.7 cd
'Shampion'	0	harvest	5.1 ± 1.9 a	6.9 ± 1.5 d	5.5 ± 1.1 c	7.2 ± 1.6 e	7.6 ± 0.9 g	7.8 ± 1.2 h	6.4 ± 1.8 b	3.5 ± 1.2 c–e	7.8 ± 1.2 e	8.0 ± 0.9 e
	2	Control	5.1 ± 2.3 a	1.9 ± 0.9 a	2.4 ± 0.7 ab	1.8 ± 0.9 a	3.3 ± 1.1 ab	3.1 ± 1.2 ab	4.3 ± 0.8 a	2.5 ± 1.0 bc	3.7 ± 1.1 ab	3.2 ± 1.2 ab
		1-MCP	3.8 ± 2.2 a	2.9 ± 1.2 a	3.3 ± 1.0 b	3.0 ± 1.1 ab	4.1 ± 1.6 b–d	4.3 ± 1.5 b–e	4.7 ± 1.2 a	2.4 ± 1.0 bc	4.6 ± 1.4 b–d	4.5 ± 1.2 b–d
	4	Control	4.7 ± 2.6 a	2.7 ± 0.9 a	3.0 ± 0.8 b	2.6 ± 0.8 a	3.9 ± 1.1 bc	3.4 ± 0.9 a–c	4.2 ± 1.1 a	2.0 ± 1.0 ab	3.6 ± 1.1 ab	3.3 ± 0.8 ab
		1-MCP	3.8 ± 2.1 a	3.0 ± 1.1 a	3.1 ± 0.7 b	2.4 ± 1.1 a	4.5 ± 1.7 c–e	3.9 ± 0.9 b–d	4.1 ± 1.2 a	2.4 ± 0.5 bc	3.7 ± 0.4 ab	3.8 ± 0.8 a–c
	6	Control	4.0 ± 2.2 a	2.3 ± 0.8 a	1.9 ± 0.7 a	1.9 ± 0.6 a	2.6 ± 0.8 a	2.5 ± 1.0 a	4.1 ± 1.1 a	1.1 ± 0.5 a	2.9 ± 1.2 a	3.0 ± 1.0 a
		1-MCP	3.9 ± 1.9 a	2.9 ± 1.0 a	3.0 ± 1.1 b	3.0 ± 1.4 ab	4.9 ± 0.9 c–f	4.1 ± 1.3 b–e	3.8 ± 1.7 a	2.0 ± 1.0 ab	3.6 ± 1.1 ab	3.9 ± 0.9 a–c

Acknowledgments This work was supported by the Ministry of Science and Higher Education of Poland (MNiSzW) under Grant MNiSzW NN312 199835.

Conflict of interest None.

Compliance with Ethics Requirements This article does not contain any studies with human or animal subjects.

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