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EFFECT OF SHORT-TERM STORAGE ON WALNUT FRUIT QUALITY

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Two Hungarian and two introduced walnut cultivars were examined as fresh samples and under storage. Some important compositional data were determined in order to evaluate the differences between the cultivars and the changes after storage. The cultivars' oil contents were the same, but there was some difference in fatty acid composition; 'Alsószentiváni 117' had a higher mono-unsaturated fatty acid content than the others. Considering the oxidative stability, 'Alsószentiváni 117' contained good properties in all stages (induction time equals or higher than 10 h). Lower antioxidant capacity was measured in 'Chandler' samples compared to the others. 'Alsószentiváni 117' has higher α- and γ-tocopherol contents than the other cultivars studied. Two different drying methods were also compared in case of the Hungarian cultivars. The changes in compositional data showed no tendencies. We found that Hungarian cultivars were at least as valuable as the introduced ones.

Keywords: walnut, short-term storage, fatty acid composition, tocopherols, antioxidant capacity

The Persian walnut (*Juglans regia* L.) is harvested from early September till mid-October in Hungary. After the harvest, it is necessary to remove the husk, wash, dry, size and pack the fruits or crack and pack the kernels. The peak selling period of this fruit crop is in November or during Advent, therefore a short storage is needed for the prepared walnut. The Hungarian bred walnut cultivars have good compositional value (Bujdosó et al., 2010, 2014) as published before. Our aim is to save the good fruit quality (light shell and kernel colour, good taste) and the good compositional value of the dried in-shell walnut. There is no protocol for walnut storage in Hungary; the growers mainly keep the fruit between 2 and 10 °C in a dark room.

There are only a few papers on walnut storage. One study gives results on this topic, but focuses on evaluating the effect of low temperature (10 °C) on walnut fruit damage and reinfestation before shipping from California to avoid insect infections (Johnson et al., 2010). Whole walnut storage at 10 °C and relative humidity conditions of 60% gave the best results in order to save the original fruit quality (Lopez et al., 1995). Another research study stated that storage at 1 °C had a positive effect on saving total phenol compound content, total antioxidant content, and colour of the cultivars stored for 12 months compared to samples stored at 20 °C (Christopoulos & Tsantili, 2011). It has been found that tocopherol content of 'Franquette' and 'Hartley' stored at 4 °C decreased by 30% after less than 3 months (Lavedrine et al., 1997).

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According to some results, there is a positive correlation between the peroxide and lipoxigenase content of cultivars and their storability (Österberg et al., 2001; Kosáry et al., 2009). According to Österberg and co-workers (2001), 'Rex' and 'Vina' had the highest peroxidase content after three years storage among the examined cultivars, the 'Geisenheim 120' and 'Stanley' produced the lowest.

There is no ethylene production during the storage. Drying at 36 °C for 24 hours decreased the total phenol (TP) content as compared to fresh walnuts. TP and the total antioxidant capacity showed a 1.2- to 1.3-fold increase in the fresh kernels after the first 20 days of storage at 1 °C, and remained stable during the next 20 days. There was no growth in total phenol compounds (vanillic acid, protocatechuic acid, ellagic acid) at 8 °C, but an increasing tendency was observed at 1 °C (Miltiadis et al., 2012).

The aim of this paper is to study the effect of drying and low temperature storage on some Hungarian and introduced bred cultivars' fruit, as well as determination of oxidative stability and components of walnuts affecting rancidity (water content, antioxidant capacity, tocopherol content, fatty acid composition).

1. Materials and methods

1.1. Samples studied

Cultivars 'Milotai 10', 'Alsószentiváni 117', 'Chandler', and 'Franquette' were investigated. The fruit samples were taken from Juglans Hungaria Ltd.'s walnut orchard located in Lengyeltóti (Hungary) at optimal ripening time. The optimal ripening time means, when 50% of husks are open (FS=fresh samples). After harvest the husk was eliminated by hand and the fruit were washed and dried to 10% moisture content in the dryer machines at 35 to 37 ºC air temperature during 36 or 48 h, depending on the samples' moisture content. The samples were not bleached during the preparation process. After drying, half of the samples were examined in the lab (DS=dried samples), the other half was stored as dried in shell walnut at 8 ºC for two months. After the storage, in December, the samples were measured again (SS=stored samples), because this is the most important walnut selling period of the year.

In case of 'Milotai 10' and 'Alsószentiváni 117' two ways of drying were applied. The warm method written above and the cold method, which means air-dried samples (ADS=air-dried samples).

1.2. Determination of water content

Determination of water content was carried out at 103 °C (±2 °C) for 6 h at atmospheric pressure according to ISO (2000).

1.3. Determination of oil content

Oil content was extracted with petroleum ether and the solvent was removed in rotary vacuum evaporator according to Hungarian Standard (2000).

1.4. Determination of fatty acid composition

Fatty acids were analysed from the extracted oil by gas chromatography (Agilent 7890A GC System, Agilent Technologies, Santa Clara, CA, United States) of methyl esters of fatty acids

(Tóth-Markus & Sass-Kiss, 1993). Column was Supelco SP-2560 100 m×0.25 mm, 0.2 µm film thickness (Supelco, Bellefonte, PA, United States). Oven temperature program: 140 °C 5 min, 4 °C min^{-1} until 240 °C, 10 min on final temperature; injector temperature 220 °C, detector temperature 250 °C; carrier gas: hydrogen, column flow 1 ml min^{-1}; automatic injection, injected amount 1 µl. Oils were stored in deep freezer for a very short time until analysis.

1.5. Determination of oxidative stability

The oxidative stability of the freshly extracted oil was measured by Rancimat method (Rancimat 743, Metrohm, Herisau, Switzerland). With the Rancimat method, the sample is exposed to an air flow at a constant temperature between 50 and 220 °C (100 °C in our case). Highly volatile, secondary oxidation products (especially formic acid) are transferred into the measuring vessel with the air flow, where they are absorbed in the measuring solution (distilled water). Here the conductivity is continuously registered. The organic acids can thus be detected by increasing the conductivity. The time until occurrence of these secondary reaction products is referred to as the induction time (h) or induction period, which is a good indicator for the oxidation stability (Rancimat, 2009).

1.6. Determination of antioxidant capacity

Samples were extracted by methanol, stored at 4 °C for 24 h, and filtered after 30 min shaking. The colour reaction was carried out with 2,2-diphenyl-1-pycrylhydrazyl (DPPH) at 36 °C for 30 min in dark, and the absorbance decrease against blank sample was measured at 517 nm (ATI Unicam UV-Vis Spectrometer UV2, Unicam, England). The antioxidant capacity was given in Trolox equivalent per 100 g dry matter (TE/100 g d.m.) (Brand-Williams et al., 1995).

1.7. Determination of tocopherols

One gram ground walnut was saponified with 5 ml 30% KOH/MeOH, 20 ml MeOH, and 0.5 g ascorbic acid added, and boiled for 35 min on a sand bath. After cooling, 15 ml water containing 20% sodium chloride and 40 ml of *n*-hexane were added to sample. Tocopherols were separated in upper phase after a short shaking with a separating funnel. Another 40 ml of hexane was added to the lower phase and the separation was repeated. The lower phase was removed and the two upper phases were united in a separating funnel, washed twice with distilled water, and filtered through dry sodium sulphate. The filtrate was evaporated in rotadest and re-dissolved in 10 ml of HPLC grade hexane (Speek et al., 1985).

The HPLC system consisted of Shimadzu RF-535 Fluorescence HPLC Monitor Detector (Shimadzu, Kyoto, Japan), 250×4.6 mm, 5 µm, Nucleosil 100 Silica column (Macherey-Nagel, Düren, Germany). The eluent was *n*-hexane–abs. ethanol, 99.6:0.4 and the flow rate was 0.9 ml min^{-1}. The detection wavelength was set to EX: 295 nm, EM: 320 nm. α-tocopherol was used to identify the peaks.

1.8. Chemicals

All the chemicals were of analytical grade (VWR International LLC., Radnor, PA, United States), except for tocopherols, where HPLC grade chemicals were used (VWR International LLC., Radnor, PA, United States).

1.9. Statistical analysis

All analyses were carried out in triplicate. Data are given as mean±standard deviation and were analysed by *t*-test in Excel.

2. Results and discussion

'Alsószentiváni 117' and 'Milotai 10', the two main walnut cultivars in Hungary, were compared to two introduced cultivars, 'Chandler' and 'Franquette'. Compositional data determined from walnut samples are summarised in Tables 1 and 2.

The oil content is the lowest in fresh samples of all the cultivars. At this stage, the oil content of 'Chandler' was lower than of the others. The results show significant difference between the two ways of drying for the Hungarian cultivars ($P<0.05$).

The cultivars have a rather similar fatty acid composition. The difference between Hungarian cultivars and 'Chandler' and 'Franquette' was seen in the unsaturated fatty acids. 'Alsószentiváni 117' has lower PUFA (PUFA=polyunsaturated fatty acid) content, but its MUFA (MUFA=monounsaturated fatty acid) content is higher proportionally. The MUFA value (oleic acid, C18:1 content) is slightly lower in 'Chandler', but the PUFA content is higher than in the other cultivars. The difference in PUFA is caused by the higher α-linolenic acid (C18:3) content in 'Chandler, which makes it more sensitive to oxidation'. To compare the two drying methods, there was no difference between them.

Induction time, characterising the oxidative stability of oil extracted from walnut samples, differs for each sample. For cultivar 'Alsószentiváni 117', the induction time was increasing after drying and under storage. Comparing the two drying methods we found that air-dried samples showed rancidity 3 h later than the samples dried with warm air. For cultivar 'Milotai 10', the induction time of dried sample was higher than the fresh sample's, and decreased in the stored samples. The cultivar 'Chandler' was most inclined to rancidity. The induction time of dried sample of 'Chandler' was the lowest value of all the cultivars. Fresh sample of 'Franquette' had also low induction time (4.19 h), and there was no difference between dried and stored samples in oxidative stability for 'Franquette'. According to Vidrih and co-workers (2010), the correlation of oils' induction time and the PUFA content is negative, so the growth of induction time is caused by the decrease of linoleic and linolenic acids. Our results show the same tendency. In the induction time results we found significant difference between the two drying methods ($P<0.05$).

According to antioxidant capacity analysis, 'Chandler' had lower free radical scavenging ability than the other cultivars. Its fresh sample's antioxidant capacity was about third of the others and in the other two stages the values were lower than that of other samples. This can contribute to its lower oxidative stability. There is some tendency in the change of antioxidant capacity of samples. In case of 'Alsószentiváni 117', 'Milotai 10' air-dried, 'Chandler', and 'Franquette' the antioxidant capacity of dried samples is above the other stages, and under storage, all of the cultivars lose from their antioxidant capacity. Comparing the two ways of drying, in case of 'Alsószentiváni 117' there is no difference in antioxidant capacity, but for 'Milotai 10' the air dried samples (stored as well) have about 20% higher antioxidant capacity than the samples dried by warm air.

Table 1. Compositional data of the examined samples

		Dry matter (%) Mean±SD	Oil content (%) Mean±SD	Induction time (h) Mean±SD	TEAC (mmol/100 g d.m.) Mean±SD	α-Tocopherol (mg g^{-1}) Mean±SD	γ-Tocopherol (mg g^{-1}) Mean±SD	δ-Tocopherol (mg g^{-1}) Mean±SD
Alsószentiváni 117	GH	79.1±0.4	84.2±0.7	n.t.	20.2±1.2	25.2±0.6	345±8	12.8±0.6
	FS	86.8±0.3	85.5±2.0	7.39±0.04	21.4±0.8	15.0±0.1	257±2	14.1±0.3
	DS	96.6±0.0	77.0±0.1a	9.68±0.24a	24.0±0.6	21.0±0.1	333±8	13.9±0.2
	SS	95.4±0.0	74.9±0.2b	9.60±0.34b	21.6±0.6b	18.7±0.5b	338±9	14.7±2.4
	ADS	96.4±0.1	75.8±0.1a	10.65±0.48a	23.4±2.0	17.1±0.4	295±4	12.5±0.1
	AD SS	94.7±0.0	73.0±0.2b	12.41±0.06b	17.2±0.9b	10.6±0.2b	214±2	8.8±0.2
Milotai 10	GH	79.2±0.0	81.9±0.2	n.t.	20.3±1.5	9.9±0.1	239±1	12.6±0.1
	FS	80.8±0.3	78.4±0.5	6.64±0.08	30.8±1.3	10.3±0.4	257±5	15.3±0.7
	DS	95.9±0.1	73.1±0.1a	9.59±0.19	24.1±2.6	8.3±0.2	276±5a	16.3±0.3a
	SS	94.9±0.0	73.8±0.2b	7.76±0.14	23.0±2.0	8.7±0.1b	234±0b	10.9±0.1b
	ADS	95.5±0.2	74.4±0.2a	10.32±0.02	31.4±2.2	7.8±0.1	228±1a	8.9±0.3a
	AD SS	94.8±0.0	73.0±0.1b	6.57±0.17	27.4±1.8	9.5±0.0b	274±0b	13.4±0.3b
Chandler	FS	78.3±0.1	71.8±0.6	6.54±0.19	7.5±0.9	20.0±0.1	271±0	21.7±0.1
	DS	92.3±0.1	76.2±0.4	3.91±0.05	16.8±0.4	10.2±0.1	215±1	14.0±0.3
	SS	95.7±0.0	76.0±0.1	10.77±0.25	15.9±0.4	12.0±0.5	257±9	15.7±0.6
Franquette	FS	89.6±0.2	67.1±3.2	4.19±0.06	25.7±0.9	14.4±0.0	204±1	22.5±0.1
	DS	95.5±0.0	73.9±0.1	8.49±0.38	30.0±2.0	11.6±0.0	164±1	9.3±0.2
	SS	95.4±0.4	73.6±0.2	8.69±0.31	16.7±0.3	15.1±0.0	247±1	15.2±0.0

n.t.: not tested; GH: green husk sample; FS: fresh sample; DS: dried sample; SS: stored sample; ADS: air-dried sample; AD SS: air-dried stored sample; TEAC: Troloxequivalent antioxidant capacity
a,b: significant at $P<0.05$

Table 2. Fatty acid composition of the samples

		Palmitic acid C16:0 (%)	Stearic acid C18:0 (%)	Oleic acid C18:1 (%)	Linoleic acid C18:2 (%)	Linolenic acid C18:3 (%)	Saturated (%)	MUFA (%)	PUFA (%)
		Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD			
Alsószentiváni 117	GH	6.25±0.01	2.90±0.01	25.04±0.02	56.48±0.04	8.35±0.00	9.15	25.04	64.83
	FS	6.09±0.01	2.82±0.00	24.44±0.01	55.41±0.03	9.95±0.03	8.91	24.44	65.35
	DS	6.11±0.01	2.88±0.00	24.24±0.01	55.64±0.06	10.02±0.02	8.98	24.24	65.67
	SS	6.19±0.00	2.78±0.00	24.47±0.00	56.16±0.06	9.33±0.04	8.97	24.47	65.49
	ADS	6.03±0.00	2.86±0.00	24.44±0.01	56.03±0.05	9.29±0.02	8.88	24.44	65.31
	AD SS	6.20±0.01	2.72±0.01	28.08±0.02	54.67±0.02	7.27±0.02	8.92	28.08	61.94
Milotai 10	GH	6.99±0.00	2.53±0.00	21.30±0.01	58.49±0.05	9.59±0.04	9.52	21.30	68.08
	FS	6.78±0.00	2.67±0.01	21.74±0.00	57.93±0.02	9.38±0.01	9.45	21.74	67.31
	DS	6.88±0.00	2.69±0.02	20.93±0.01	58.36±0.03	9.62±0.03	9.57	20.93	67.98
	SS	6.78±0.00	2.66±0.00	22.47±0.00	57.36±0.05	9.33±0.00	9.43	22.47	66.68
	ADS	6.77±0.01	2.59±0.01	22.48±0.00	56.81±0.05	9.83±0.00	9.36	22.48	66.64
	AD SS	7.06±0.01	3.01±0.00	20.02±0.00	59.38±0.02	9.17±0.01	10.07	20.02	68.55
Chandler	FS	6.24±0.00	2.10±0.00	17.77±0.01	58.64±0.02	13.54±0.04	8.64	17.77	72.19
	DS	6.29±0.01	2.39±0.00	17.94±0.01	59.13±0.01	12.82±0.01	8.68	17.94	71.95
	SS	6.23±0.01	2.43±0.00	17.95±0.01	57.93±0.04	14.19±0.01	8.66	17.95	72.13
Franquette	FS	7.77±0.01	2.59±0.01	17.46±0.00	59.37±0.03	11.35±0.03	10.36	17.46	70.72
	DS	7.05±0.01	2.61±0.02	18.92±0.02	58.92±0.05	11.13±0.02	9.66	18.92	70.06
	SS	7.00±0.00	2.63±0.01	17.59±0.00	60.63±0.01	10.75±0.02	9.63	17.59	71.38

Saturated: C16:0+C18:0; MUFA (mono-unsaturated fatty acid): C18:1; PUFA (poly-unsaturated fatty acid): C18:2+C18:3
GH: green husk sample; FS: fresh sample; DS: dried sample; SS: stored sample; ADS: air-dried sample. AD SS: air-dried stored sample

Three tocopherol isomers were analysed: α-, δ-, and γ-tocopherols. The γ-tocopherol content is an order of magnitude higher than the α- and δ-tocopherol contents of the samples. 'Alsószentiváni 117's γ-tocopherol content is above the other cultivars in all stages, except in air-dried stored sample, because under storage this sample's γ-tocopherol content decreased to its two-third. Only 'Chandler' fresh samples have α-tocopherol content in the same level as 'Alsószentiváni 117'.

The α-tocopherol content of the other main Hungarian cultivar, 'Milotai 10', was about half of the α-tocopherol of the 'Alsószentiváni 117'. Under drying the α-tocopherol content of 'Chandler' decreased to half of the fresh sample and slightly increased under storage. For 'Milotai 10' there was no difference between the two drying methods, for 'Alsószentiváni 117' the warm air dried samples showed higher α-tocopherol content than the air dried samples, but there was no significant difference. The α-tocopherol content of the latter decreased by about half under storage.

There are larger differences in δ-tocopherol content between the drying stages and the cultivars. The 'Chandler' and 'Franquette' fresh samples are prominent, but their δ-tocopherol content decreased to around 70% under drying and storage. In the change of the δ-tocopherol content of 'Alsószentiváni 117' and 'Milotai 10' no such tendency was observed.

3. Conclusions

In our research the main two Hungarian and two foreign cultivars 'Chandler' and 'Franquette' were tested. The samples were examined in different stages (fresh, dried, stored) and some compositional data are presented. According to our data, the composition of traditional Hungarian cultivars is as valuable as or better than the foreign ones. The Hungarian cultivars have better position in global market because of their earlier harvest time.

We examined two kinds of drying method for the Hungarian cultivars, and according to the results, differences can be found in the parameters tested between these methods. Summarizing all the results there is no tendency in the effect of the drying methods.

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