The effect of long-term storage on quality of malting barley grain and malt

Vplyv dlhodobého skladovania na kvalitu zrna sladovníckeho jačmeňa a sladu

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Abstract

In the grain samples of five malting barley varieties harvested in 2011, the amount of basic components as well as physiological characteristics of barley were determined. These samples were micromalted and resulting malt was analyzed mainly according to the European Brewery Convention (EBC) and the Mitteleuropäische Brautechnische Analysenkommission (MEBAK) methodologies. The same samples of malting barley grain and also samples of malt were placed in polyethylene bags, from which the air was exhausted and they were further stored at 4 °C until 2016. In 2016, grain and malt samples were subjected to the same analyses as in 2011. Results were statistically evaluated by t-test of dependent samples. Most of the monitored parameters has remained at the same level as in 2011 or has slightly improved. The exception was statistically very highly significant decrease ($P \leq 0.001$) of friability and increase of amount of whole and partly unmodified grains. Under conditions described, long-term storage of malting barley grain has not significantly negatively affected its germination. Long-term storage of malt has had not a significant negative impact on its quality too.

Keywords: barley, malt, malting quality, storage

Abstrakt

Vo vzorkách zrna piatich odrôd sladovníckeho jačmeňa, zozbieraných v roku 2011, bolo stanovené množstvo základných obsahových látok a stanovené boli tiež fyziologické znaky jačmeňa. Vzorky zrna boli zosladované a následne vyrobený slad

bol analyzovaný najmä podľa metodík EBC a MEBAK. Tie isté vzorky zrna jačmeňa a vzorky sladu boli uložené do polyetylénových vreciek, z ktorých bol odsatý vzduch a boli ďalej skladované pri teplote 4 °C až do roku 2016. V roku 2016 boli vzorky zrna jačmeňa a sladu podrobené rovnakým analýzam ako v roku 2011. Výsledky boli štatisticky spracované pomocou párového t-testu. Väčšina sledovaných znakov zostala na rovnakej úrovni ako v roku 2011 alebo sa mierne zlepšila. Výnimkou bolo štatisticky veľmi vysoko preukazné zníženie ($P \leq 0,001$) hodnoty friability a zvýšenie množstva sklovitých a polosklovitých zŕn. Dlhodobé skladovanie zrna sladovníckeho jačmeňa nemalo za popísaných podmienok štatisticky preukazne negatívny vplyv na jeho klíčivosť. Taktiež dlhodobé skladovanie sladu nemalo výrazne negatívny dopad na jeho kvalitu.

Kľúčové slová: jačmeň, skladovanie, slad, sladovnícka kvalita

Introduction

Ensuring the supplies of malting barley of uniform quality for storage in the course of the whole year until the next harvest still appears problematic. Also, occasional differences in the technological quality of malting barley between individual years unfavorably show in the quality of produced malt, especially in years with adverse climatic conditions in the period of maturation and harvest (Sychra et al., 2001). Barley storage is an integral part of technology of its processing on malt with desired quality. The aim of malting barley storage is to keep or even improve its quality (Mikyška and Prokeš, 2009). Barley grain must be stored such as to maintain its ability to germinate rapidly and uniformly and at the same time must be protected from moisture and pests. In fact, it is very easy to turn premium grade cereal into animal feed with inappropriate storage practices (Fleurat-Lessard et al., 2005a). In this regard, several methods of storage may be distinguished. In the Slovak and Czech Republic, permanent structures as a flat stores or silos of different construction are used for this purpose, while the barley grain stores best if it is cool, dry and clean (American Malting Barley Association, 2007; Basařová and Basař, 2015; White et al., 1999). As a possibility to ensure uniform quality of malting barley supplies for storage appears the usage of long-term (multi-annual) storage of qualitative batches of malting barley (Sychra et al., 2001). In connection with the previously detected results (Briggs et al., 1994; Ochandio et al., 2010; Ruska and Timar, 2009; Sychra et al., 2001) can be assumed that ensuring the optimal storage conditions, it is possible to achieve maintenance of the same or slightly lower quality of the long term stored malting barley. Prerequisite for successful storage of malt is to keep highly hygroscopic malt cool and dry to avoid excessive intake of water. If the moisture content remains below 4%, malt can be stored under appropriate conditions for several months (Kreisz, 2009; Kunze, 2014; MacLeod, 2004). Generally, malts have moisture content below 5% and such content is not very favorable for fibrous micromycetes or insect pests. The variability of malt components during its storage depends mainly on temperature and water activity. Both of these factors should be as low as to preserve high quality of malt (Basařová, 2015; Kunze, 2014). The aim of this experiment was to evaluate, how the malting barley grain and malt quality may be altered by long-term storage.

Materials and methods

The experiment was performed on malting varieties of spring barley Blaník, Bojos, Kangoo, Sebastian and Xanadu (Psota and Horáková, 2006, 2007; Psota et al., 2005, 2008) harvested in 2011 at trial sites Jaroměřice nad Rokytnou, Lednice a Oblekovice (Psota et al., 2015).

Micromalting

Barley samples were micromalted in the Research Institute of Brewing and Malting (RIBM) in Brno. A standard method used in the RIBM (Psota et al., 2012), which is almost identical with the MEBAK (2011) methodology, was used for laboratory malting of samples. Malting parameters were as follows:
Steeping: 1st day - 5 hours, 2nd day - 4 hours, 3rd day - spraying or steeping to water content 45.5% in grain. Water and air temperature during the air rests was 14.5 °C.
Germination: total germination time was 144 hours at 14.5 °C.
Kilning: one-floor electrically heated kiln. Total kilning time was 22 hours. Pre-kilning was carried out at 55 °C and kilning at 80 °C for 4 hours (Dráb et al., 2013).

Determination of technological parameters

In barley grain, the contents of moisture, protein and starch were determined. Germinative energy, index, rate and homogeneity of germination were determined as well (EBC Analysis Committee, 2010; Finlay, 1960; Riis and Bang-Olsen, 1991). Technological parameters were subsequently determined in malt and sweet wort according to the Baxter and O'Farrell (1983), EBC Analysis Committee (2010) and MEBAK (2011) methodologies. List of the methods used is given in Table 1 and 2. Every test was performed on 3 samples of each variety from a specific year.

Table 1. Overview of parameters examined in barley grain
Tabuľka 1. Prehľad parametrov skúmaných v zrne jačmeňa

Parameter	Unit	Reference
Protein content in barley	% DM[a]	EBC 2010 - 3.13
Starch content in barley	% DM[a]	NIR
Moisture content in barley	%	EBC 2010 - 3.13
Germinative energy	%	EBC 2010 - 3.6.2
Germination index	-	EBC 2010 - 3.7
Germination rate	%	Finlay (1960)
Germination homogeneity	%	Riis and Bang-Olsen (1991)

[a] Dry matter percentage

Table 2. Overview of parameters examined in malt

Tabuľka 2. Prehľad parametrov skúmaných v slade

Parameter	Units	Reference
Moisture content in malt	%	EBC 2010 - 4.2
Wort viscosity (8.6%)	mPa·s	EBC 2010 - 4.8
Wort β-glucan content	$mg*l^{-1}$	EBC 2010 - 4.8
Friability	%	EBC 2010 - 4.15
Malt homogeneity[a]	%	Baxter and O'Farrell (1983)
PUG[b]	%	EBC 2010 - 4.15
WUG[c]	%	EBC 2010 - 4.15
Protein content in malt	% DM[d]	EBC 2010 - 4.3.1 , 4.3.2
Kolbach index	%	EBC 2010 - 4.9.1 , 4.9.3
Soluble nitrogen in wort	$mg*l^{-1}$	EBC 2010 - 4.9.1 , 4.9.3
Relative extract at 45 °C	%	MEBAK 2011 - 3.1.4.11
Wort saccharification rate	min	EBC 2010 - 4.5.1
Apparent attenuation limit	%	EBC 2010 - 4.11.1
Diastatic power	WK	EBC 2010 - 4.12
Extract content in malt	% DM[d]	EBC 2010 - 4.5.1
Wort clarity	-	MEBAK 2011 - 3.1.4.2.6
Wort haze at 12°	EBC	EBC 2010 - 9.29
Wort haze at 90°	EBC	EBC 2010 - 9.29
Wort colour	EBC	EBC 2010 - 4.7.2
Wort polyphenol content	$mg*l^{-1}$	EBC 2010 - 8.12

[a] (using the friabilimeter); [b] Partly unmodified grains; [c] Whole unmodified grains;
[d] Dry matter percentage

Storage of samples

After the analysis, samples of barley and malt were placed in polyethylene bags into laboratory warehouse, where they were stored at normal room temperature and humidity. In May 2012, these samples were sealed in bags, from which the air was exhausted. Additional storage was carried out in a warehouse with a constant temperature of 4 °C. In May 2016, samples were taken out from the warehouse and opened. Subsequently, the samples of barley and malt were subjected to the same types of analyses, as in 2011.

Statistical evaluation of results

To assess the differences between the results of analyses of barley grain and malt samples acquired in 2011 and subsequently in 2016, the t-test of dependent samples was used. Calculations were performed using the system STATISTICA version 8.0.

Results and discussion

Experimental storage of barley grain and malt was carried out 60 months under conditions that cannot be achieved in common practice. They were more similar to conditions used in gene banks when storing cereals. The aim was to limit the number of different factors, which obviously occur during normal storage (temperature and humidity fluctuation, ventilation, pest infestation of stored material, etc.) and also to find out the influence of storage on quality of barley grain and malt without the factors mentioned.

There are some storage systems used abroad (e.g. Argentina, Romania) just like hermetic storage system with a self-modified atmosphere (high-capacity plastic silo-bags) or the barley storage in the open air on a large concrete platform with low walls filled with barley and covered with PVC overliner and polyethylene underliner (Bartosik et al., 2012; Ruska and Timar, 2009). The use of modified atmospheres (e.g. low in oxygen, enriched in nitrogen or carbon dioxide) was also considered by Baxter et al. (1991) as an alternative way for the safe storage of barley. Similar airtight storage (under controlled atmosphere or not) provides protection against insect attack and limits the growth of fungal flora (Fleurat-Lessard et al., 2005a). The insect pests cannot become resistant to low oxygen atmospheres, which is an added advantage over conventional storage with the usage of fumigants and insecticides, which are trying to get rid of not only by malting industry (Baxter et al., 1991).

Characteristics assessed in barley grain

Kreisz (2009) states that grain moisture is the limiting factor and that barley should be stored in dry conditions with a maximum moisture content of 14%. According to Hřivna (2006), its further increase may result in a number of biochemical reactions that significantly reduce the storage period. Beyond this level were also 3 out of 15 samples from barley experiments in 2016. However, barley can be stored at slightly higher moisture content if it is kept cool. In addition, the allowable storage time is

approximately doubled for each 5.5 °C that the barley is cooled (American Malting Barley Association, 2007). Unmalted barley grain contained the same amount of moisture, protein and starch in 2011 as in 2016. In the barley grain was therefore no difference between the results of these analyses obtained from 2011 to 2016 (Table 3).

Table 3. Effect of storage on protein, starch and moisture content of barley grain

Tabuľka 3. Vplyv skladovania na obsah N-látok, škrobu a vody v zrne jačmeňa

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Protein content in barley	2011	10.6	0.678	0.007	0.110	14	0.913858	NS[g]
	2016	10.6	0.670					
Starch content in barley	2011	63.8	0.698	0.167	1.410	14	0.180313	NS[g]
	2016	63.7	0.699					
Moisture content in barley	2011	12.8	0.367	-0.367	-1.911	14	0.076737	NS[g]
	2016	13.2	0.827					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification; [g] No significance (P > 0.05).

In unmalted barley grains, the features characterizing the quality of germination were also determined. In the case of germinative energy, there were not any significant differences between the results obtained in 2011 and 2016 (Table 4). According to Woods et al. (2005), the germinative energy declines right after reaching its maximum during storage. However, if moisture content and temperature are low, the decline is very slow. No reduction in germinative energy was observed in the work of Fleurat-Lessard et al. (2005b) too, at the end of their long-term storage under hermetic conditions. The results of Baxter et al (1991) strongly indicate that barleys can be stored for extended periods in low oxygen atmospheres, without any deleterious effects, either on recovery from dormancy, germination performance, or malting quality.

However, in the case of parameters defining the speed and uniformity of germination, i.e. germination index, rate and homogeneity (Finlay, 1960; Riis and Bang-Olsen, 1991), very highly significant difference ($P \leq 0.001$) was proved. Long-term storage under these conditions had a positive effect on these characteristics (Table 4). Only a slight increase of germination index was recorded in airtight conditions of Fleurat-Lessard et al. (2005b). Mikyška and Prokeš (2009) also demonstrated a significant impact of conditions and time of barley storage on its physiological status.

Table 4. Effect of storage on barley grain physiological parameters

Tabuľka 4. Vplyv skladovania na fyziologické parametre zrna jačmeňa

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Germinative energy	2011	98.2	1.445	0.227	0.413	14	0.685756	NS[g]
	2016	97.9	1.513					
Germination index	2011	7.5	0.695	-1.113	-8.832	14	0.000000	***[h]
	2016	8.6	0.595					
Germination rate	2011	84.9	4.200	-6.707	-7.245	14	0.000004	***[h]
	2016	91.6	4.227					
Germination homogeneity	2011	51.9	5.982	-9.260	-5.388	14	0.000096	***[h]
	2016	61.1	8.694					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification;
[g] No significance (P > 0.05); [h] Very high significance (P ≤ 0.001).

Cytolytic modification

Among the values of wort β-glucan content and wort viscosity measured in 2011 and 2016, there were no significant differences, although some little increase in β-glucans was recorded. In parameters friability, malt homogeneity (Baxter and O'Farrell, 1983), partly and whole unmodified grains, however, there was statistically very high significant decrease (P ≤ 0,001) (Table 6). The reason for this deterioration was probably increase of the moisture content in malt from 4.35% to 7.45%, which most likely occurred during several months of its storage at laboratory warehouse (Table 5).

Table 5. Effect of storage on change of moisture content in malt

Tabuľka 5. Vplyv skladovania na zmenu obsahu vody v slade

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Moisture content in malt	2011	4.3	0.236	-3.103	-30.398	14	0.000000	***[g]
	2016	7.5	0.195					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification;
[g] Very high significance (P ≤ 0.001).

A slight increase in the malt water content during storage (typically ranging up to 0.5%) is not expected to affect its quality. But in poor storage conditions, where the water content increases by a few percent, the problems may occur (Basařová, 2015).

Similar results were recorded during the experiments of Fleurat-Lessard et al. (2005b). Under hermetic storage and high moisture content, the malt friability and modification decreased significantly. On the contrary, the β-glucan content and viscosity showed a large increase.

Table 6. Effect of storage on change of quality of cytolytic modification

Tabuľka 6. Vplyv skladovania na zmenu kvality cytolytického rozlúštenia

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Wort viscosity (8.6%)	2011	1.51	0.031	-0.007	-1.693	14	0.112495	NS[g]
	2016	1.51	0.032					
Wort β-glucan content	2011	253	98.913	-13.667	-1.009	14	0.330064	NS[g]
	2016	267	96.133					
Friability	2011	87	5.717	9.820	20.552	14	0.000000	***[h]
	2016	77	5.760					
Malt homogeneity	2011	98.3	2.067	3.833	6.138	14	0.000026	***[h]
	2016	94.3	4.072					
PUG	2011	1.6	1.952	-3.953	-6.040	14	0.000030	***[h]
	2016	5.5	4.072					
WUG	2011	0.1	0.161	-0.333	-2.184	14	0.046501	*[i]
	2016	0.5	0.720					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification; [g] No significance (P > 0.05); [h] Very high significance (P ≤ 0.001); [i] Significance (P ≤ 0.05).

Proteolytic modification

In the case of proteolytic modification, the changes observed may be caused by the change of analytical methods. In 2011, method by Dumas and in 2016, method by Kjeldahl was used. Kolbach index detected in 2016 was on average by 1.8% higher than in 2011. The protein content in malt in 2016 was by 0.4% lower than in 2011. In contrast, the content of soluble nitrogen in wort was in 2016 by 50 mg*l^{-1} higher than in 2011 (Table 7). Increase in the wort soluble nitrogen observed in stored malt Narziss (1976). According to Basařová (2015) and Kieninger and Narziss (1975), there should be also a slight increase in values of relative extract at 45 °C (RE45) during the maturing of malt. The experiment resulted in increased average value of RE45, but this increase was insignificant.

Table 7. Effect of storage on change of quality of proteolytic modification

Tabuľka 7. Vplyv skladovania na zmenu kvality proteolytického rozlúštenia

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Protein content in malt	2011	10.1	0.671	0.443	11.254	14	0.000000	***[g]
	2016	9.7	0.597					
Kolbach index	2011	40.2	2.550	-1.813	-6.675	14	0.000011	***[g]
	2016	42.0	2.574					
Soluble nitrogen in wort	2011	650	49.382	-51.533	-13.979	14	0.000000	***[g]
	2016	702	40.944					
Relative extract at 45 °C	2011	38.8	4.112	-0.553	-2.115	14	0.052870	NS[h]
	2016	39.3	3.707					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification;
[g] Very high significance (P ≤ 0.001); [h] No significance (P > 0.05).

Amylolytic modification

In the case of amylolytic modification, there was not any significant difference in monitored variables of values observed in 2011 and 2016. Storage under such conditions had no effect on these parameters (Table 8).
During the short-term maturing of malt, an adequate hydration of its colloidal substances takes place and subsequent activation of amylolytic enzymes is likely responsible for a slight increase in diastatic power (Basařová, 2015; Kieninger and Narziss 1975). On the contrary, the research carried out by Hoff et al. (2014) showed that during malt storage, the sugar content remains on the same level, showing that the major malt components and activities of starch degrading enzymes are almost intact. There was a small, statistically insignificant decrease in diastatic power within the experiment, which is in agreement with the results of experiments conducted by Fleurat-Lessard et al. (2005b).

Table 8. Effect of storage on change of quality of amylolytic modification

Tabuľka 8. Vplyv skladovania na zmenu kvality amylolytického rozlúštenia

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Wort saccharification rate	2011	10	1.056	0.200	0.564	14	0.581627	NS[g]
	2016	10	0.775					
Apparent attenuation limit	2011	81.7	1.349	-0.080	-0.530	14	0.604393	NS[g]
	2016	81.8	1.140					
Diastatic power	2011	414	51.600	6.267	0.740	14	0.471279	NS[g]
	2016	407	48.012					
Extract content in malt	2011	82.9	1.133	-0.040	-0.250	14	0.806570	NS[g]
	2016	82.9	0.883					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification; [g] No significance (P > 0.05).

Parameters of sensory quality of malt

Monitored samples provided both in 2011 and 2016 identically clear worts. Haze of wort showed statistically significant differences between the values measured in 2011 and 2016, but these differences are insignificant from a technological point of view. Wort colour has recorded highly significant decrease (P ≤ 0.01) between 2011 and 2016, but the decrease was from a technological point of view also negligible. During storage, the content of total polyphenols (that may affect some sensory characteristics of the final product) slightly decreased too, but the decrease was insignificant (Table 9).

Table 9. Effect of storage on change of malt sensory quality parameters

Tabuľka 9. Vplyv skladovania na zmenu znakov senzorickej kvality sladu

Parameter	Year	Mean	Std.Dv.[a]	Diff.[b]	t[c]	df[d]	p[e]	sign.[f]
Wort clarity	2011	1.33	0.617	0.200	1.871	14	0.082418	NS[g]
	2016	1.13	0.352					
Wort haze at 12°	2011	1.83	1.606	0.673	3.056	14	0.008548	**[h]
	2016	1.16	0.784					
Wort haze at 90°	2011	2.04	1.980	0.719	2.622	14	0.020102	*[i]
	2016	1.32	0.995					
Wort colour	2011	2.8	0.121	0.100	3.090	14	0.007996	**[h]
	2016	2.7	0.108					
Wort polyphenol content	2011	75.1	7.686	1.267	0.552	14	0.58389	NS[g]
	2016	73.9	6.106					

[a] Standard deviation; [b] Difference; [c] t-value; [d] Degree of freedom; [e] p-value; [f] Signification; [g] No significance (P > 0.05); [h] High significance (P ≤ 0.01); [i] Significance (P ≤ 0.05).

Conclusions

The results of the analyses after 5 years of storage pointed to very high significant improvement (P ≤ 0.001) in physiological characteristics of malting barley that define the speed and uniformity of germination, i.e. germination index, rate and homogeneity. Very high statistically significant improvement (P ≤ 0.001) occurred also in parameters of proteolytic modification - protein content in malt, soluble nitrogen in wort and Kolbach index. On the contrary, some characteristics of cytolytic modification - friability, malt homogeneity and partly unmodified grains - exhibited very high significant deterioration (P ≤ 0.001). In this case, the reason for this was probably the increase of moisture content in malt, which took place during several months of its storage at laboratory warehouse. Two parameters representing the sensory quality of malt - wort haze at 12° and wort colour - were highly significantly improved (P ≤ 0.01), and another one - wort haze at 90° - showed significant improvement (P ≤ 0.05). However, from a technological point of view, these differences can be considered as insignificant.

The experiment clearly demonstrated that barleys and malts can be stored long-term in cool atmosphere with low oxygen and without any adverse effect on germination or other significant parameters of malting quality.

Continuation of this study could be an experiment, in which the long-term stored barley will be also malted and resulting malt will be subsequently subjected to the relevant analyses.

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