L. Sychra, V. Psota and J. Mareček

Effect of long-term storage of malting barley on malt quality

Long-term storage of qualitative batches of malting barley for gradual consumption is one of possibilities how to ensure the uniform quality of grain for storage. Changes were recorded in samples of long-term stored malting barley varieties Akcent, Kompakt, Krona, Olbram and Rubín by means of parameters of produced malt (extract, relative extract at 45 ºC, Kolbach index, diastatic power, apparent final attenuation, friability, β-glucan content in malt extract, protein content in malt) in regular intervals for two years. At the beginning of the storage period, the malting barley was subjected to controlled ventilation and then the malting barley grain was stored without any active ventilation. It follows from the analysis that the long-term storage results particularly in the decreased activity of amylolytic and cytolytic enzymes, which results in the deterioration of malt extract quality. By using regression equations it is possible – on the basis of the knowledge of initial quality of malt made of malting barley – to predict the quality development during storage.

BC 11 Barley

(Descriptors: Malting barley, malt quality, storage, active ventilation.

Deskriptoren: Braugerste, Malzqualität, Lagerung, aktive Entlüftung).

1 Introduction

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 unfavourably show in the quality of produced malt, especially in years with adverse climatic conditions in the period of maturation and harvest. The problem of quality that must be faced by growers reflects in the realization price. Another problem appears to be the maintenance of this quality in the processes of handling and warehousing until the moment of malt production.

A possibility to ensure uniform quality malting barley supplies for storage appears to be the use of long-term (several years) storage of qualitative batches.

With respect to the known results concerning the possibilities of using controlled ventilation at the storage of grains and regarding the results from analyses made to study the effects of storage methods on the quality of food grains (*Sychra* and *Hubík*, 1998), the authors went for the use of active ventilation in the first phase of storage to stabilize the grain, and then chose the method of storage without grain active ventilation during the storage in the silo chamber. In connexion with the formerly published results (*Briggs* et al, 1994; *Mareček* and *Sychra*, 1999) it can be assumed that an identical or only slightly lower quality of malt produced from malting barley can be maintained over a long-time (2-year) storage provided that optimum storage conditions are observed.

Dr. Ing. Luboš Sychra, Doc. Ing. Jan Mareček, CSc, Mendel University of Agriculture and Forestry Brno, Zemědělská 1, CZ 613 00 Brno, Czech Republic, sychra@mendelu.cz, Ing.Vratislav Psota, CSc., Brewery and Malting Research Institute (VUPS), Mostecká 7, CZ 614 00 Brno, Czech Republic

2 Material and method

To study the effect of long-term storage on the quality of malt produced from malting barley harvested in 1996 the authors made use of varieties most spread under the given conditions in the Czech Republic: Akcent (Selgen, CZ), Kompakt (Hordeum, SK), Krona (Semundo Saatzucht, D), Olbram (Hybritech Branišovice, CZ) and Rubín (Plant Select, CZ).

Samples of the above varieties – each of 1.5 kg – were placed into bags made of permeable plastic non-woven and inserted into the corn layer in the silo. The experiment included only grains with 2.5 mm above the seave. All samples of the mentioned varieties were stored in identical conditions and were taken for laboratory tests in regular month intervals for nearly two years (664 days).

The corn silo storage chamber where the samples were stored had a total warehousing capacity of 1000 tons, and a system of active ventilation was used in the chamber during the first phase of the storage (first three months) with the amount of air supplied to the storage chamber being $0.4375\ m^3.sec^{-1}$, storage chamber temperature maintained within a range from 8 – 12 ºC, and the grain kept at water content ranging from 13.5 – 15.4%. In the next phase of storage, i.e. until the end of the test, the grain was not subjected to any active ventilation. Relative grain moisture was 13.5 – 15.0% during the entire storage time and grain layer temperature ranged from 2 – 10 ºC in dependence on the measured layer's height.

The regularly collected samples were malted in the laboratory of the VUPS Malting Institute in the micro-malting plant. The malting procedure traditionally used in VUPS is identical with the procedure recommended by EBC (1999) the only difference being the total storage time that was only 144 hours (*Psota* and *Jurečka*, 2000). Technological parameters of malt (extract, relative extract at 45 ºC, Kolbach index, diastatic power, apparent final attenuation, friability, content of β-glucans and protein content in malt) were determined on the basis on EBC (1998) and MEBAK (1979) analytics.

The test results were subjected to the statistic analysis and determination of Pearson's correlation coefficient, which were used to analyze the dependence of studied qualitative parameters on the time of storage. The analyses were made on 95% significance level. The significance of effects (variety x storage time) on the qualitative indicators was determined by ANOVA analysis the results of which helped to assess which of the effects was more significant.

The regression analysis of time dependence for the given qualitative parameters made use of ordinary least squares regression by which regression equation coefficients were determined in the form $y = a + bx$, where x is storage time in days, and their standard errors and significance of coefficients. Standard deviations, coefficient correlation squares (R-squared) and significance were then determined for the final equation.

In order to make an analytic assessment of the effect of investigated varieties on the changes of studied parameters of malting barley in the course of the long-term storage a testing was performed of the regression test heterogeneity in all measured parameters of produced malt for the respective varieties with the time of storage of the malting barley of studied varieties being determined by the axis X.

3 Results and discussion

Long-term storage is naturally assessed particularly from a viewpoint of its impact on weight, and on mechanical and biological damage to the stored corn (HGCA, 1992). A key trait assessed within the storage experiments was barley germination (*Aastrup* et al., 1990; *Mareček* et al., 2000). A lesser attention was paid to the influence of long-term storage on other significant malting traits since it was assumed that if the germination can be maintained an acceptable level during the long-term storage, the same level would be maintained for other technological traits.

It follows from the achieved results (Tab. 1) that the time of storage and warehousing conditions used did not affect the values of extract in malt DM (Tab. 2). Based on the regression results we can assume that the extract values will not statistically significantly change under the given storage conditions in the course of two years (Tab. 3). It can be stated after the application of regression results for extract that there is only a mild and statistically insignificant decrease in the values of this trait. Both influencing factors (variety, time of storage) statistically very significantly affected the extract values in malt DM (with significance being at all times less than 0.0001). The effect of variety on the change of extract value was markedly greater than that of storage time.

Table 1 Summary malting barley quality index

Variety	Parameter	E	RE45	KI	DP	AFA	F	BG	P
Akcent	Minimum	83.00	43.50	46.80	250.00	80.80	81.00	212.00	10.00
	Maximum	84.70	52.10	51.70	350.00	84.30	90.90	371.00	10.40
	Average	83.66	48.73	48.94	308.21	82.75	87.69	259.07	10.19
	Std Deviation	0.47	2.93	1.44	30.62	1.11	2.21	37.52	0.10
Kompakt	Minimum	83.00	41.60	47.50	275.00	79.90	86.00	156.00	9.80
	Maximum	84.10	47.80	51.70	380.00	84.10	91.70	246.00	10.90
	Average	83.73	44.90	49.56	330.00	82.33	89.51	200.07	10.21
	Std Deviation	0.29	1.75	1.17	31.22	1.27	1.50	30.04	0.26
Krona	Minimum	80.70	38.80	40.70	335.00	82.20	80.00	115.00	11.50
	Maximum	82.70	49.20	52.80	435.00	84.70	87.00	252.00	12.00
	Average	81.56	43.53	46.20	385.00	83.29	82.99	184.29	11.76
	Std Deviation	0.51	2.94	3.03	29.76	0.84	2.45	35.37	0.14
Olbram	Minimum	81.80	40.40	44.70	190.00	79.30	87.00	149.00	9.70
	Maximum	85.60	47.10	52.80	285.00	84.70	94.10	293.00	10.40
	Average	84.94	44.99	50.14	242.14	82.54	92.53	210.14	10.09
	Std Deviation	0.91	2.24	2.16	24.11	1.54	1.65	48.50	0.16
Rubín	Minimum	81.60	38.10	43.20	200.00	79.10	72.00	257.00	10.50
	Maximum	83.40	45.80	47.70	285.00	83.40	80.10	466.00	11.10
	Average	82.49	42.02	45.54	250.71	81.79	78.55	338.21	10.89
	Std Deviation	0.41	2.21	1.37	24.56	1.18	1.95	67.11	0.18

Note: E – extract yield d.m. (%), RE45 – relative extract at 45 °C (%), KI – Kolbach index, DP – diastatic power (WK), AFA – apparent final attenuation (%), F – friability (%), BG – β-glucan content ($mg.dm^{-3}$), P – protein content in malt (%)

Table 2 Pearson's correlation coefficients (correlation of quality to storage time period)

Variety	Parameter	RE45	KI	DP	AFA	F	BG	P
Kompakt	-0.0586	-0.2918	-0.0252	-0.6530	-0.7388	-0.5618	0.8257	0.1896
Krona	-0.0704	0.2617	0.4555	-0.2319	-0.6858	-0.6994	0.4989	-0.0777
Olbram	-0.3808	-0.5899	-0.0990	-0.5909	-0.8849	-0.6437	0.8123	0.0820
Rubín	-0.4362	-0.8154	-0.0798	-0.6209	-0.8413	-0.7188	0.9499	0.0905

Note: E – extract yield d.m. (%), RE45 – relative extract at 45 °C (%), KI – Kolbach index, DP – diastatic power (WK), AFA – apparent final attenuation (%), F – friability (%), BG – β-glucan content ($mg.dm^{-3}$), P – protein content in malt (%)

Table 3 a Regression results – ordinary least squers regression y = a + bx (x = time period of storage)

	E				RE45			
	Intercept a	Slope b	R^2	Probability	Intercept a	Slope b	R^2	Probability
Akcent	83.8395	-0.0007	0.0734	0.3489	51.8206	-0-0114	0.5460	0.0025
Kompakt	83.7525	-0.0001	0.0034	0.8422	45.6297	-0.0027	0.0851	0.3115
Krona	81.6079	-0.0002	0.0050	0.8110	42.4307	0.0040	0.0685	0.3662
Olbram	85.4358	-0.0018	0.1450	0.1792	46.8804	-0.0069	0.3480	0.0264
Rubín	82.7401	-0.0009	0.1902	0.1190	44.5965	-0.0095	0.6648	0.0004

	Kolbach index				Diastatic power			
	Intercept a	Slope b	R^2	Probability	Intercept a	Slope b	R^2	Probability
Akcent	48.7321	0.0007	0.0098	0.7361	338.0271	-0.1095	0.4651	0.0072
Kompakt	49.6064	-0.0002	0.0006	0.9320	359.1068	-0.1069	0.4264	0.0113
Krona	44.2283	0.0072	0.2075	0.1017	394.8519	-0.0362	0.0538	0.4250
Olbram	50.4486	-0.0011	0.0098	0.7365	262.4777	-0.0747	0.3492	0.0261
Rubín	45.6915	-0.0006	0.0064	0.7862	272.4802	-0.0799	0.3855	0.0178

Table 3 b Regression results – ordinary least squers regression y = a + bx (x = time period of storage)

Variety	Apparent final attenuation				Friability			
	Intercept a	Slope b	R^2	Probability	Intercept a	Slope b	R^2	Probability
Akcent	84.0154	-0.0046	0.6405	0.0006	89.8293	-0.0079	0.4622	0.0075
Kompakt	83.6653	-0.0049	0.5459	0.0025	90.7096	-0.0044	0.3157	0.0365
Krona	84.1123	-0.0030	0.4703	0.0068	85.4353	-0.0090	0.4892	0.0054
Olbram	84.4862	-0.0071	0.7830	2.61E-05	94.0457	-0.0056	0.4143	0.0130
Rubín	83.2134	-0.0052	0.7077	0.0002	80.5530	-0.0074	0.5166	0.0038

Variety	Beta-glucan content				Protein content in malt			
	Intercept a	Slope b	R^2	Probability	Intercept a	Slope b	R^2	Probability
Akcent	221.1972	0.1391	0.5000	0.0047	10.1664	0.0001	0.0372	0.5086
Kompakt	164.6662	0.1300	0.6817	0.0003	10.1374	0.0003	0.0359	0.5163
Krona	159.0974	0.0925	0.2489	0.0694	11.7797	-0.0001	0.0060	0.7919
Olbram	153.8994	0.2065	0.6599	0.0004	10.0670	0.0001	0.0067	0.7806
Rubín	247.2122	0.3341	0.9024	2.04E-07	10.8702	0.0001	0.0082	0.7583

Regarding the fact that the content of N-substances in barley grain did not show any change in the course of storage (*Mareček* et al., 2000), no statistically significant change was recorded in the course of storage in protein content in malt either (Tab. 2), which was corroborated by the regression results (Tab. 3). Statistically highly significant was the influence of variety on the value of protein content (significance less than 0.001). On the other hand, statistically insignificant was the influence of storage time (significance 0.3001).

An important role in the case of relative extract at 45 ºC (hereinafter RE45) is played by the effect of variety (Tab. 1). The duration and conditions of storage did not affect the measured parameter in the varieties Kompakt and Krona. In the case of the varieties Akcent, Rubín and Olbram the trait exhibited a statistically significant to highly significant decrease (Tab. 2). Regression was affected by the variety as well. The RE45 values showed a statistically insignificant decrease in the variety Kompakt and a statistically insignificant increase in the variety Krona. In contrast, a significant to highly significant decrease in the RE45 values can be anticipated in the varieties Akcent, Olbram and Rubín (Tab. 3). Both influencing factors (variety and time of storage) statistically highly significantly affected the extract values in malt DM (with significance being at all times less than 0.0001). Variety showed a greater influence on the change of the RE45 value.

It follows from the achieved results (Tab. 1) that the time of storage and warehousing conditions used did not affect the values of Kolbach index (Tab. 2), whose changes in the course of the long-term storage are statistically insignificant in all varieties (Tab. 3). Both influencing factors (variety and time of storage) exhibited a statistically highly significant effect on Kolbach index (with significance being at all times less than 0.0001). Variety had a greater influence on the change of this value than storage time. A certain level of the decreased activity of proteolytic enzymes in modern varieties with the generally high level of proteolytic modification would be rather beneficial.

Amylolytic modification – given by the value of diastatic power – was also influenced by variety (Tab. l). Storage time did not statistically significantly affect the values of diastatic power in the variety Krona. In all other varieties the activity of amylolytic enzymes decreased significantly up to highly significantly with the increasing time of storage (Tab. 2). Also, the effect of variety on the value of diastatic power was recorded in regression. In the variety Krona the values of this trait will not show any statistically significant change in the course of storage; on the other hand, in all other varieties we can expect a significant up to highly significant decrease of these values (Tab. 3). It is possible to make a statement at the application of the regression results for diastatic power that the values of the trait decreased in the range 50 – 80 jWK for the assumed storage time of 750 days. This means that in the course of two-year storage, the activity of amylolytic enzymes will drop in some cases down to the minimum acceptable level (200 jWK). Both influencing factors (variety, storage time) statistically highly significantly affected the values of diastatic power in dry matter (with significance being at all times less than 0.0001). A markedly greater influence on the change of the trait was exhibited by variety.

Similarly, the activity of β-glucan reducing (Tab. 1) enzymes was decreasing with the increasing time of storage, which resulted in a statistically significant up to highly significant increase of the β-glucan content (Tab. 2). Based on the regression values an increasing β-glucan content can be expected in the course of long-term storage, which can even reach intolerable levels (over 200 mg.dm^{-3}) – also for the varieties Kompakt, Krona and Olbram. The increase is statistically highly significant in the varieties Akcent, Kompakt, Olbram and Rubín, and statistically insignificant in the variety Krona (Tab. 3). Both influencing factors (variety and time of storage) statistically highly significantly affected the values of β-glucan content in dry matter (with significance being at all times less than 0.0001). Variety had a greater influence on the change of the trait than the storage time.

The activity of cytolytic enzymes relates to the values of friability (Tab. 1). Malt friability decreased due to the decreasing activity of these enzymes during the long-term storage in all studied varieties (Tab. 2). Based on the regression values, a statistically significant up to highly significant decrease of friability can be expected in consequence of the long-term storage (Tab. 3). The regression results indicate that even this trait will exhibit decreased values after 750 days of storage, which are unacceptable in some cases (< 79%). Both influencing factors (variety and time of storage) statistically highly significantly affected the values of this trait (with significance being at all times less than 0.0001). A markedly greater influence on the change of friability was shown by variety.

The gradual deterioration of the activity of mainly amylolytic and cytolytic enzymes in the course of storage impaired the quality of unhopped wort, which showed in the statistically highly significant drop in values of apparent final attenuation (Tab. 2). It follows from the regression values that a statistically highly significant decrease can be expected in the quality of unhopped wort in the course of long-term storage (Tab. 3), which can reach a minimum acceptable level (79%) after 750 days. Both influencing factors (variety and time of storage) statistically highly significantly affected the values of apparent final attenuation (with significance being at all times less than 0.0001). A greater influence on the change of this trait had storage time.

It was found out in the previous work (*Mareček* et al., 2000) that the long-term storage did not affect the parameters of germination (germinative energy, germination index) by any conspicuous way. However, the results achieved in this work indicate that it is the enzymatic apparatus of the caryopsis, which exhibits ageing during the storage along with the decreasing activity of amylolytic and cytolytic enzymes. Future works dealing with the storage of malting barley should take into account not only the parameters of germination, but they should also study the ageing of the enzymatic apparatus of the caryopsis and find such a warehousing procedure that could reduce or slow down this negative process.

4 Conclusion

In the given experimental conditions the two-year storage did not affect the values of extract and protein contents in malt dry matter. In the course of storage, the activity of hydrolytic enzymes changed in dependence on the variety. The activity of proteolytic enzymes showed a tendency toward a slight decrease but statistically insignificantly. The activity of amylolytic enzymes was decreasing in all studied varieties with the exception of the variety Krona. The time of storage exhibited the heaviest impact on the activity of cytolytic enzymes. The quality of unhopped wort composition also worsened during the storage.

The experimental results indicate that the grain quality of some varieties of malting barley can be maintained on an acceptable level for use at malt production provided that suitable warehousing conditions are observed during the long-term storage. This particularly applies to the varieties capable of keeping the high activity of amylolytic and cytolytic enzymes over the entire time of storage.

In the above cases, the development of studied traits can be predicted with a certain measure of probability. The found out results further indicate that the differences in grain quality in the course of storage are first of all given by the variety, which is also documented by the ANOVA results.

It also follows out from the results that the most important period of time at keeping the grain under the optimum warehousing conditions and with using the grain at the stabilized moisture content is the very first stage of storage when the grain is subjected to a so called stabilization and conditioning. In this period of time, the use of active ventilation in grain stores is recommended. After the phase of stabilization, the active ventilation is not necessary provided that the temperature and moisture stabilization of grain was sufficient.

Acknowledgement

The issue was resolved with the financial support from the CR Ministry of Agriculture within the Project NAZV EP 0960006067 "Research and evaluation of the quality of food cereals". The authors also thank RNDr. Jana Gotthardová for her assistance at the statistic processing of measurements.

5 Zusammenfassung

Sychra, L., Psota, V., und Mareček, J.: Auswirkung langfristiger Lagerung der Braugerste auf die Malzqualität — Monatsschrift für Brauwissenschaften 54, Nr. 5/6, 114 – 118, 2001

BC 11 Gerste

Die langfristige Lagerung hochwertiger Lieferungen von Braugerste für einen schrittweisen Verbrauch ist eine der Möglichkeiten, wie die einheitliche Qualität des Korns für die Lagerung sichergestellt werden kann. Veränderungen wurden in Proben der langfristig gelagerten Braugerstenarten Akcent, Kompakt, Krona, Olbram und Rubin mittels Parametern des produzierten Malzes (Extrakt, relativer Extrakt bei 45°C, Kolbach Index, diastasische Kraft, augenscheinliche endgültige Vergärung, Reife, β-Glukan-Gehalt im Malzextrakt, Eiweißgehalt im Malz) in regelmäßigen Abständen über zwei Jahre hinweg aufgezeichnet. Zu Beginn der Lagerungszeit wurde die Braugerste kontrolliert belüftet, und danach wurde das Braugerstenkorn ohne aktive Belüftung gelagert. Aus der Analyse ergibt sich, dass die langfristige Lagerung insbesondere zur verringerten Aktivität der amylolytischen und der zytolytischen Enzyme führt, was wiederum die Abnahme der Malzextraktqualität mit sich bringt. Unter Anwendung von Regressionsgleichungen ist es möglich,

die Qualitätsentwicklung während der Lagerung vorherzusagen – auf der Basis der Kenntnis der anfänglichen Qualität des Malzes ohne Braugerste.

Sychra, L., Psota, V., et Mareček, J.: Répercussions d'un stockage prolongé de l'orge de brasserie sur la qualité du malt — Monatsschrift für Brauwissenschaften 54, No. 5/6, 114 – 118, 2001

BC 11 Orge

Le stockage prolongé de livraisons d'orges de brasserie de haute qualité pour une utilisation par étapes, représente une des possibilités pour assurer une qualité homogène du grain pendant le stockage. Les variations des échantillons d'orges Akcent, Kompakt, Krona, Olbram et Rubin, stockées sur longue période ont été enregistrées pendant des étapes régulières pendant deux ans sur les paramètres suivants du malt produit: extrait, extrait relatif à 45 °C, indice Kolbach, pouvoir diastasique, degré d'atténuation apparent, maturité, teneur en béta-glucane sur l'extrait de malt et teneur en protéines du malt. Au début du temps de stockage, l'orge de brasserie a été aérée de façon contrôlée, puis le grain d'orge a été stocké sans aération active. L'analyse fournie les résultats suivants: un stockage prolongé fait diminuer l'activité amylolytique et diminue les enzymes cytolytiques ce qui se répercute sur une diminution de la qualité de l'extrait de malt. Il est possible de prédire le développement de la qualité pendant le stockage en utilisant des calculs de régression sur la base des connaissances d e la qualité du malt au début et sans les orges de brasserie.

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(Manuskripteingang: 19. 1. 2001)

Leserbrief

An den Herausgeber der Monatsschrift für Brauwissenschaft

Der Grund unseres Schreibens ist, die in Ihrem Journal (1) und anderswo (2) erschienene Veröffentlichung einer modifizierten HPLC Methode für Hopfensäuren von Harms und Nitzsche, zur Diskussion zu stellen.

Beide Publikationen enthalten keinerlei Hinweise auf unsere vorangegangene Beitragsleistung zur besagten Methode (3, 4). Obwohl sie andeuten, dass man sich unserer Arbeit bewusst ist, haben Harms und Nitzsche die große Ähnlichkeit unserer Methoden weder diskutiert noch bestätigt. Die größte Ähnlichkeit in unseren Methoden ist der Einsatz einer Drei-Komponenten-Mobil-Phase, die sich aus Methanol, Aectonitrile und pH7 wässrigen Puffer zusammensetzt. Wir demonstrierten in unseren frühen Veröffentlichungen, dass diese Reagenzien-Mischung eine bedeutende Verbesserung der Sparierung von Cis- und Trans Iso-α-Säuren Isomeren in beiden, nämlich C8 und C18 Säulen ergibt (4).

Beim Vergleich unserer Methode mit der von Harms und Nitzsche finden wir eine beinahe identische Präzisierfähigkeit aller identifizierten Hopfensäuren (über 20 verschiedene Bestandteile).

Dies ist wirklich nicht überraschend da wie wir, so auch Harms und Nitzsche eine Alkyl Reverse-Phasen Säule benützen mit beinahe identischen Bedingungen der Mobil-Phase. Geringe Veränderungen in der relativen Halte zeit von Rho und Iso-α-Säuren resultieren wahrscheinlich aus der Einstellung der Methanol/ Acetonitrile Ratio im Lösungsmittelprogramm.

Veröffentlichte Chromatogramme zeigen, dass Harms und Nitzsche die Elutionszeit erhöhten und dadurch die Prägnanz (Ausdrucksgenauigkeit) der sechs Iso-α-Säure Bestandteile verbesserten.

Unsere Methode, die kürzer ist, ergibt anscheinend eine bessere Separierung des spät aufkommenden Rho und der früh aufkommenden Iso-α-peaks. Alleine unsere Publikation zeigt Separierung und Messung der Bestandteile von Hexahydro-Iso-α-Säure. Wir begrüßen und anerkennen die Identifizierung von Isoxanthohumol in der Methode von Harms und Nitzsche. Wir möchten klarstellen, dass ursprünglich einzig und allein unser sorgfältig entwickeltes Mobil-Phase-System eine Separierung von komplexen Hopfensäuremischungen ergab; dies mit konventionellen Reverse-Phase-Säulen. Wir begrüßen, dass Harms und Nitzsche unsere Anstrengungen als wertvoll empfanden bei der Verfeinerung ihrer Methode. Wir danken den Mitarbeitern der Monatsschrift für Brauwissenschaft für die Gelegenheit die Leser über unsere vorausgegangenen Arbeiten informieren zu können.

gez. *Dr. P. Douglas William*s

gez. *Louis J. Burroughs*

KALSEC, Kalamazoo, MI 49006/USA

Wir danken Herrn Rudy Held, unserem Marketing Manager für Hopfen weltweit, für die Übersetzung des Briefes.

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