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Stability of the hop bitter acids during long-term storage of cones with different maturity degree

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Abstract. The aim of the study was to assess the dynamics of changes in the content of hop bitter acids during long-term storage of cones that vary in maturity degree under different temperature conditions. The impact of the degree of maturity of hop cones on the stability of bitter acids during storage is little known so far, and it is important, because due to the systematic increase of the hop growing area on individual farms, the cone harvesting period is extended beyond the optimal phase of technological maturity. Hop cultivars belonging to two groups were included in the study: bitter (Magnat, Magnum) and aroma (Puławski, Sybilla). Cones were collected on a few dates during vegetation season, starting from the phase in which they reached maximum size until the beginning of physiological maturity. The dried cones were stored at +5 °C and +20 °C for 12 months and tested every three months for alpha and beta acid content using HPLC. Studies have shown that too early a hop harvest adversely affected bitter acid content. Storage temperature had significant impact on the degradation of alpha and beta acids. At a higher temperature the decrease in the content of these compounds was greater. The tested hop cultivars were characterized by different stability of bitter acids. The highest stability of alpha acids was observed for Sybilla, while the lowest for Magnat. The stability of alpha and beta acids during long-term storage of the raw material, especially at + 20°C, depended on the degree of cones maturity. The aging rate of hop cones was not the same throughout the storage period. For the first 3–6 months at a temperature of +5°C, the bitter acid content remained at a level similar to the initial one, later a relatively rapid decrease in the content of these metabolites occurred. At higher temperatures, the bitter acid stabilization period was shorter.

Keywords: hop, alpha acids, beta acids, storage temperature, cones maturity

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INTRODUCTION

Hops are known as a perennial plant belonging to the *Cannabaceae* family. Its infructescences, called cones, are a raw materials used primarily in the brewing industry (Schönberger, Kostelecky, 2011). Ripe hop cones contain various secondary metabolites, of which the most significant groups of compounds are: hop resins, essential oils and polyphenols (Almaguer et al., 2014). Above mentioned substances are mainly accumulated in the lupulin glands produced by the epidermal cells. Most of the lupulin glands are formed at the base of the hop cones bracts, where they are recognisable in the form of a yellow, adhesive powder termed lupulin (Rybaček, 1991; Zanoli, Zavatti, 2008). The distinctive properties of hop secondary metabolites are applied in the brewing process to obtain the specific hop bitterness and aroma, stabilize the beer foam or extend durablity of the brew (Schönberger, Kostelecky, 2011; Almaguer et al., 2014). Hop resins exhibit the highest concentration of all active ingredients present in hop cones. Depending on the hop cultivar and plant growth conditions, the above compounds make up 15% to 30% of the dry matter of the cones (Almaguer et al., 2014). The chemical composition of hop resins is complex. They are divided into two basic groups of compounds, i.e. soft resins and hard resins, constituting 10–25% and 3–5% of the dry matter of hops respectively (Almaguer et al., 2014). The soft resins are the most important fraction for the brewing industry, as they are responsible for the typical hoppy bitterness of beer (De Keukeleire, 2000). This fraction contains, i.e. alpha and beta acids.

Alpha acids (humulones) are considered to be the most important components of hop resins. The content of these compounds in cones of individual hop cultivars varies greatly and ranges from 2–10% in the case of aromatic cultivars to about 12–18% in bitter ones (Hopsteiner, 2017). Alpha acids are a mixture of several homologues differing in the chemical structure of the isoprene system (Karabin

et al., 2016). Humulones are weak acids, poorly dissolving in water and do not taste bitter. During the brewing process of the beer wort, the alpha acids undergo isomerization in high temperature conditions, forming more soluble iso-α-acids (Almaguer et al., 2014). The alpha acid derivatives gain a bitter taste and are most responsible for the distinctive bitterness of the beer and foam stabilization (Schönberger, Kostelecky, 2011; Kunimune, Shellhammer, 2008). Alpha acids also exhibit antibacterial activity – mainly against Gram-positive bacteria, and have a high health-beneficial potential, such as regulating lipid metabolism, inhibiting inflammatory processes and reducing osteoporosis (Karabin et. al., 2016; Van Cleemput et al. 2009; Zanoli, Zavatti, 2008).

Beta acids (lupulones) are usually found in hop cones in smaller amounts than alpha acids, and their content is in the range of 3–8% (Almaguer et al., 2014). Lupulones, similarly to humulones, are not a chemically uniform fraction, but are a mixture of several homologues with a structure analogous to that of alpha acids (Steenackers et al., 2015). Due to their unique chemical structure and the absence of a tertiary alcoholic group in the aromatic ring, beta acids show a higher hydrophobicity compared to alpha acids, which translates into even lower solubility of these compounds in water (Steenackers et al., 2015). Beta acids, unlike alpha acids, are not isomerized, yet they are very susceptible to oxidation processes, resulting in oxidized derivatives – hulupones (Krofta, Mikyška, 2014). Oxidation of beta acids occurs mainly during drying and storage of hop cones and its rate depends considerably on temperature (Krofta et al., 2013). Initially, it was believed that beta acids do not have a greater influence on the formation of characteristic bitterness in beer, because 70–85% of these compounds remain in the waste fraction due to their very low solubility (Krofta, Mikyška, 2014). However, Haseleu et al. (2009) identified a number of beta acid derivatives that are released during beer brewing and affect bitterness. Krofta et al. (2013) have shown that beta acid oxidation products provide beer with a distinct, pleasant and short-lasting bitterness, and their bitterness potential is about 35–40% of the bitterness potential of iso-alpha acids. Beta acids are compounds with high biological activity. They exhibit antioxidant properties, inhibit the development of some cancers, and have a stronger antimicrobial activity compared to alpha acids or iso-alpha-acids (Bocquet et al., 2018; Van Cleemput et al., 2009).

The content and composition of bitter acids is a characteristic feature of the hop cultivars, but it also significantly depends on the climatic and environmental conditions of the harvest year and particular cultivation area (Almaguer et al., 2014; Krofta et al., 1997; Srečec et al., 2008). The hops are harvested at the stage of technological maturity, when the content of the most important metabolites reaches its highest level and stabilises (De Keukeleire et al., 2003). The stabilisation period lasts from a few to a dozen days, after which the bitter acid content gradually decreases and the quality of the aroma and physical characteristics of the cones also get worse (Migdal, Zaorski, 1996). Fresh hop cones quickly lose their properties, which is why they are dried immediately after harvesting in special dryers where the drying agent is air heated to +50°C (Migdal, Zaorski, 1996). The dried cones are packed using a press in hop bags and stored as dried for several months. During storage, the valuable secondary metabolites contained in the cones undergo chemical transformations which leads to a reduction in the brewing value of the raw material and is generally referred to as cones ageing. The rate of hops aging depends on a number of factors, the most important of which are the period and conditions of storage, i.e. temperature and oxygen and light availability (Krofta et al., 2013; Mikyška, Krofta, 2012; Skinner et. al., 1977; Stasiak, 2004). Stability of the hop bitter acids also depends on the hop cultivars (Mikyška, Krofta, 2012; Krofta et al., 2013). This parameter should therefore be determined for particular hop cultivars as it provides valuable information on the possibility of the long-term storage without substantial losses of valuable secondary metabolites used by the brewing industry.

The objective of this work was to evaluate the rate of change of bitter acids content in hop cones during long-term storage under various temperature conditions. Four hop cultivars were included in the study: two aroma (Sybilla and Puławski) and two bitter (Magnum and Magnat). The assessment of alpha and beta acids content was carried out in cones with different degree of maturity in order to determine the effect of this factor on the stability of the secondary metabolites useful for brewing technology purposes. The issue concerning the effect of hop cones maturity degree on the stability of bitter acids during storage is so far little known. These studies also have a functional aspect, since, due to the limited efficiency of hop machines and dryers, especially on farms with a large hop-growing area, the harvesting period for the cones sometimes extends beyond the optimum stage of technological maturity.

MATERIALS AND METHODS

The cones of four hop cultivars: two aroma (Sybilla, Puławski) and two bitter (Magnat, Magnum) were used in the study. The plants were cultivated under the same soil and climatic conditions at Experimental Station in Kepa, on medium-heavily alluvial soil. The research was conducted in 2017. The harvest of cones began in the BBCH 79 phase, i.e. when the cones reached their maximum size, but their bracts were open and the lupulin was poorly coloured. Harvest was repeated every 7–10 days until the BBCH 90 stage, i.e. until the beginning of physiological maturity, when the cones became brittle and lost their characteristic hoppy aroma. The cones of aroma cultivars were harvested at three terms, while those of ripened later bitter ones at

Table 1. Harvest dates of particular hop cultivars.

Harvest date	Sybilla	Puławski	Magnum	Magnat
I	25 August 2017		4 September 2017	
II	4 September 2017		13 September 2017	
III	15 September 2017		19 September 2017	
IV			26 September 2017	

four dates (Table 1). The cones of each cultivars were harvested from three plants, the same at all harvesting dates, which constituted three replications.

The cones samples were dried in the SLW 1000 TOP+ laboratory dryer from POL-EKO under a standard temperature for hop of 50 °C. Then the dried material was divided into two parts. One was stored at 5 °C and the other at 20 °C. The storage period took 12 months. During this time, the raw material was systematically analyzed for bitter acids (alpha and beta acids). The first analysis was performed immediately after harvesting and then examinations were repeated every 3 months throughout the whole period of cones storage.

The bitter acid content was determined by means of HPLC method. The modified EBC 7.7 method (Analytica EBC, 2006) was applied where toluene – methanol – 0.1 M HCl (100:20:40 v/v/v) solution was used as an extraction medium. High purity reagents for HPLC measurement purposes were used. Dried cones were ground, weighed about 10 g ± 0.001 and extracted for 40 minutes by shaking in 160 ml extraction solution. After the extraction, 5 ml of clear supernatant was taken and diluted in 50 ml of methanol, then the diluted extract was filtered by means of Acrodisc GHP 13 mm × 0.45 µm syringe filters. The compounds were separated using Agilent technologies 1200 chromatograph on EC 125/4 Nucleodur RP C18 5 µm × 250 × 4 mm column. The detection was carried out with UV/VIS detector at 314 nm wavelength. The volume of the injection was 5 µl, flow rate of mobile phase 1 ml min^{-1}, column temperature was 40 °C. Each sample was analysed in two replications. Individual alpha acid (cohumulone and n+adhumulone) and beta acid (colupulone and n+adlupulone) fractions were identified by comparing the retention times of the sample with the International External Standard (ICE 3, Labor Veritas, Switzerland) of known bitter acids composition. The quantitative analysis by comparing the peaks surface area corresponding to individual compounds in the analysed samples and the external standard was also carried out. The percentage content of individual alpha and beta acid compounds was calculated by summing up the content of particular fractions, i.e. cohumulone and n+adhumulone for alpha acids and colupulone and n+adlupulone for beta acids.

The results of the study were analysed statistically. Multifactor analysis of variance (ANOVA) with Tukey's confidence intervals was conducted to determine the relationships between the experimental factors, i.e. degree of cone maturity, temperature and storage time and bitter acids content. The calculations were made separately for aroma and bitter hop cultivars due to different number of replications.

RESULTS AND DISCUSSION

The content and composition of bitter acids is an individual cultivar feature, however it changes during the development and ripening of hop cones. Alpha and beta acids are detected in very small quantities as early as the flowering and their concentration gradually increases with the growth of the cones (De Keukeleire et al., 2003). The content of these valuable metabolites reaches a maximum during the technological maturity and then decreases as a result of the oxidation processes in the cones (Rybaček, 1991). The harvest time is therefore an important factor influencing the bitter acid content of hop cones. In the case of aromatic cultivars (Sybilla and Puławski), a significantly lower average content of these compounds (4.87%) was found in the earliest picked cones (Table 2). The alpha acids content increased at subsequent harvest dates. Sybilla reached the highest content of these compounds on the second harvest date and Puławski at the third. In the case of bitter hop cultivars, the lowest average alpha acids content (8.23%) was also recorded in the first harvest date. It was 28.3% lower than the maximum content (11.48%) that

Table 2. Alpha acids content in hop cones of aroma and bitter cultivars depending on harvest time [% d.w.].

Harvest date[#]	Sybilla	Puławski	Means of aroma cultivars	Magnum	Magnat	Means of bitter cultivars
I	4.25 a	5.48 a	4.87 a	7.08 a	9.37 a	8.23 a
II	5.40 c	7.27 b	6.34 b	9.96 c	11.34 b	10.65 c
III	4.87 b	7.44 b	6.16 b	10.39 d	12.57 c	11.48 d
IV				9.14 b	11.36 b	10.25 b
Mean	4.84 A	6.73 B		9.14 A	11.16 B	

[#] see Table 1

Small letters (a, b, c, d) denote significant differences between harvest dates, large letters (A, B) denote significant differences between cultivars within functional group

bitter hops obtained in the third harvest date. In the next, the latest date, a significant decrease in the content of these compounds to 10.25% was observed.

Similar relationships for beta acids were found (Table 3). The lowest content of beta acids (2.59%) was observed in cones of aroma cultivars harvested the earliest. In the next harvest date an increase in the content of these compounds was observed by 9.3% in Sybilla's cones and by as much as 39.7% in the cones of Puławski cultivar. Both aroma cultivars showed maximum beta acids content at this harvest date. The beta acids content in the cones of the bitter cultivars ranged from 3.72% at the second harvest date to 3.98% at the third date, with the difference between these dates being statistically significant. No significant differences in the beta acids content were observed at the other harvest dates of bitter hop cultivars.

During storage of the hops, the alpha and beta acids are oxidized, which leads to a gradual reduction of their content in the cones (Almaguer et al., 2014). Degradation processes are favoured by: increased temperature and unrestricted access to oxygen (Mikyška, Krofta, 2012; Skinner et al., 1977; Virant, Majer, 2003). In this study, the storage temperature had a great effect on the alpha and beta acids degradation (Table 4 and 5). In cones stored for 12 months at +5 °C, the decrease in alpha acids content was on average for all harvest dates as follows: 7.7% for Sybilla, 8.1% for Puławski, 19.6% for Magnat and 11.6% for Magnum (Table 4). In cones stored at the temperature of +20 °C during the same period, the decrease in alpha acids content was much greater and amounted for individual examined cultivars: 22.3%, 30.5%, 40.0% and 29.4% respectively. Forster (2001), stated that the percentage decrease in alpha acids content in relation to the initial value immediately after harvesting can be an indication of the hops' ageing. According to Forster's classification the raw material from tested hop cultivars stored for 12 months at a temperature of +5 °C can be defined as good quality (0–10% alpha acid loss) or showing a slight degree of ageing (11–20% loss). The raw material from the same hop cultivars stored at +20 °C should be considered as old (21–30% loss) or very old (31–40% loss).

The degree of beta acids degradation, similarly to alpha acids, depended on the storage temperature and the hop cultivar, with beta acids usually degrading to a greater extent than alpha acids (Table 5). Sybilla cultivar was characterized by the highest beta acids stability at +5 °C, while Magnum cultivar at +20 °C. The greatest decrease in the content of these compounds was found in cones of Magnat. Within 12 months of storage at +5 °C and +20 °C the decrease of beta acids content was 28.5% and 58.0% respectively. Beta acids are very easily oxidized. According to Krofta et al. (2013), these compounds, in their pure form, undergo 50% degradation after just one month at room temperature, while after six months the level of degradation reaches 90%. Beta acids present in hop cones are to some extent protected against oxidation by means of cell membranes of lupulin glands, which limits the degradation processes (Krofta et al., 2013).

The stability of bitter acids during storage depended not only on the hop cultivar but also on the date of harvesting of the cones and, consequently, on their degree of maturity. In the case of Sybilla, which was characterized

Table 3. Beta acids content in hop cones of aroma and bitter cultivars depending on harvest time [% d.w.].

Harvest date[#]	Sybilla	Puławski	Means of aroma cultivars	Magnum	Magnat	Means of bitter cultivars
I	2.45 a	2.72 a	2.59 a	5.22 b	2.38 a	3.80 ab
II	2.68 b	3.80 b	3.24 c	5.08 a	2.36 a	3.72 a
III	2.37 a	3.75 b	3.06 b	5.23 b	2.73 b	3.98 b
IV				4.95 a	2.67 b	3.81 ab
Mean	2.50 A	3.42 B		5.12 B	2.54 A	

[#] see Table 1

Small letters (a, b, c, d) denote significant differences between harvest dates, large letters (A, B) denote significant differences between cultivars within functional group

Table 4. Decrease of alpha acids content after 12 months of hop cones storage under different temperature conditions depending on harvest date [% rel.].

Harvest date[#]	Temperature + 5 °C				Temperature + 20 °C			
	Sybilla	Puławski	Magnat	Magnum	Sybilla	Puławski	Magnat	Magnum
I	-10.8	-11.0	-25.8	-17.7	-28.5	-18.6	-35.4	-38.3
II	-4.5	-6.4	-40.8	-4.5	-11.3	-35.3	-56.8	-25.7
III	-7.9	-6.8	-2.3	-12.9	-27.1	-37.6	-31.7	-28.9
IV			-9.3	-11.2			-36.0	-24.4
Mean	- 7.7	- 8.1	- 19.6	- 11.6	- 22.3	- 30.5	- 40.0	- 29.4

[#] see Table 1

by the highest alpha acid stability, the decrease in the content of these compounds during 12 months of storage at +5 °C temperature ranged from 4.5% in cones harvested at the second harvest date to 10.8% in cones harvested at the first date (Table 4). At the temperature of +20 °C, not only a greater decrease in alpha acids was observed, but also a higher variation in the stability of these compounds, depending on the date of cone harvest. The degradation of alpha acids was the slowest in cones harvested in the second term (11.3% loss in 12 months) and much faster in those harvested in the first and third term (28.5 and 27.1% loss respectively). Too early or delayed harvest of Sybilla cones therefore adversely affected the alpha acids stability, especially during storage at +20 °C.

In the case of Magnat, which was characterized by low alpha acids stability during storage, the second harvest date was the least favorable, when significant decreases in the content of these compounds were noted already after 3 months of cones storage (9.2% at +5 °C and 19.7% at +20 °C). After 12 months at low and elevated temperatures, the degree of alpha acids degradation increased to 40.8% and 56.8% respectively (Table 4). Considerably higher alpha acids stability was observed in cones of Magnat harvested at the third date. During 12 months of storage at +5 °C, the content of these compounds decreased only by 2.3%, while at +20 °C by 31.7%.

The cones of most of the examined hop cultivars, stored at +5 °C, were characterized by high alpha acid stability regardless of the degree of maturity. In cones stored at +20 °C the alpha acid stability was much lower and more dependent on the harvest date.

The stability of beta acids depended to a greater extent on the degree of cones maturity than that observed for alpha acids (Table 5). Only Sybilla stored at +5 °C was characterized by high stability of these compounds regardless of the date of harvest. However, at +20 °C, the same cultivar showed clear differences in beta acids stability depending on the degree of cone maturity. The lowest beta acid stability was reported for Magnat. During 12 months of storage at the temperature of +5 °C the losses of these compounds ranged from 21.1% to 37.2% depending on the harvest date, while at the temperature of +20 °C from 46.3% to 66.6%. The results of the study indicate that the appropriate date of cones harvest is of great importance for maintaining their quality during long-term storage, especially at room temperature.

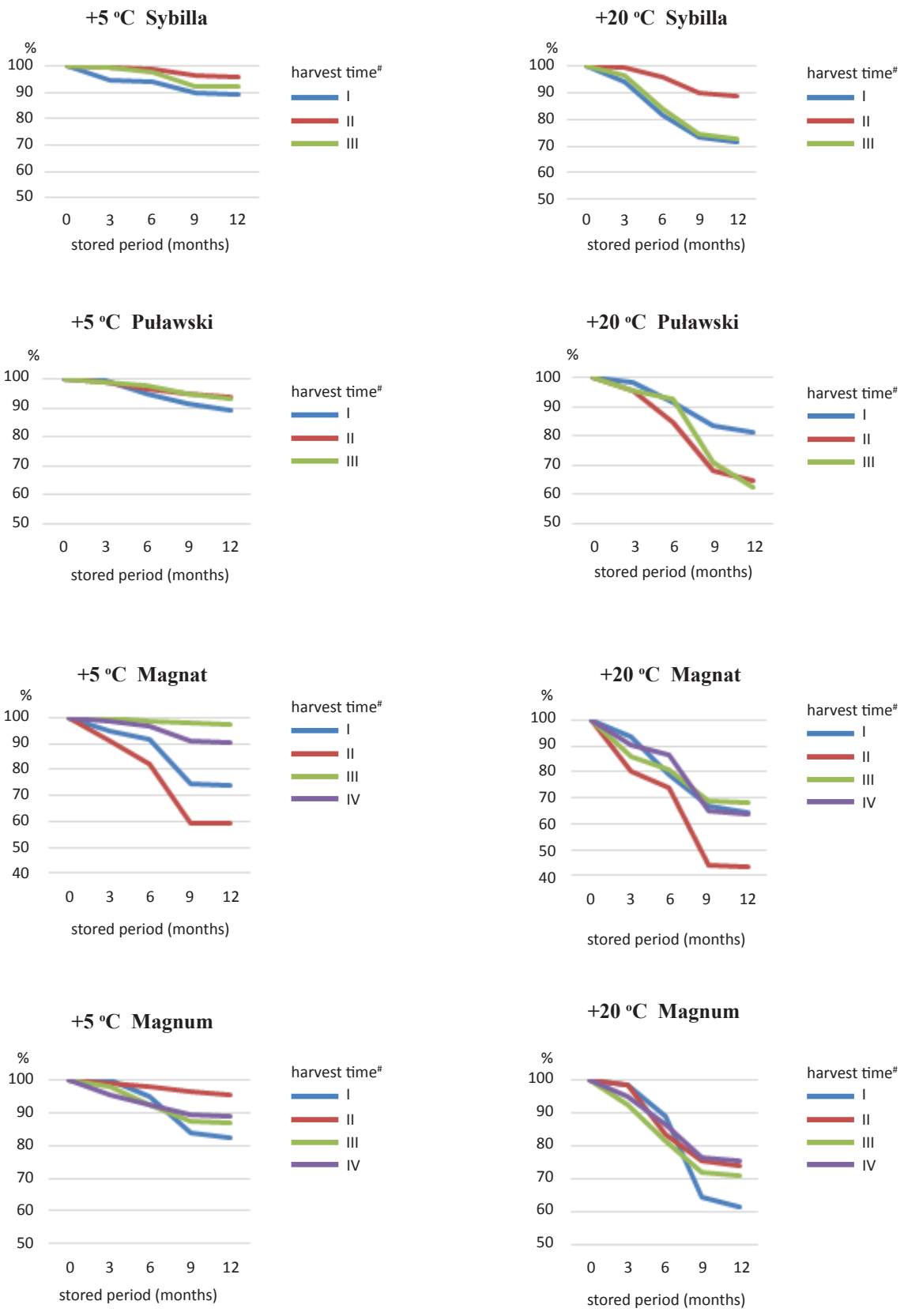
The rate of the hop cones ageing, expressed by the decrease in bitter acids content, was not uniform throughout the entire storage period. Initially, especially at lower temperature, a phase of relative stabilization was observed, in which the bitter acid concentration remained at a level close to the initial one (Fig. 1 and 2). This phase lasted for 3–6 months, according to the hop cultivar and the date of the cones harvest. The stabilization period was followed by a fairly rapid decrease in both alpha and beta acids. After that, the rate of degradation decreased in the last three months of storage. During storage of the cones at a higher temperature, the stabilization period was shorter (maximum 3 months) and in the case of Magnat the initial phase of stabilization was not observed but a dynamic decrease in alpha and beta acids content until 9 months of storage had place. The dynamics of changes in the content of bitter acids and polyphenols during storage of hops at +20 °C under air access conditions were also observed by Mikyška and Krofta (2012). These researchers concluded that the stabilization period, which lasted from 4 to 6 months, was followed by a rapid decrease in the concentration of the most important metabolites of hops. According to Likens and Nickerson (1971), the stability of hop resins during storage is affected simultaneously by two factors, i.e. the permeability of the lupulin gland epidermis to oxygen and the protective effect of natural hop antioxidants.

One of the indicators of hop cultivars' storage stability is a decrease in alpha acids content within 6 months at +20 °C (Krofta et al., 2017). Hop cultivars which lose less than 20% alpha acids under above mentioned conditions are characterized by very good storage stability, those with an alpha acids decrease between 20 and 40% have good storage stability, while those which lose more than 50% alpha acid are characterized by poor storage stability (Čerenak, Košir, 2009). Taking above classification into account, the cultivars Sybilla, Puławski and Magnum exhibited very good storage stability at all harvesting dates. In the case Magnat, the stability of cones harvested in the third and fourth date was very satisfactory, while cones harvested in the first and second date were characterized

Table 5. Decrease of beta acids content after 12 months of hop cones storage under different temperature conditions depending on harvest date [% rel.].

Harvest date[#]	Temperature + 5 °C				Temperature + 20 °C			
	Sybilla	Puławski	Magnat	Magnum	Sybilla	Puławski	Magnat	Magnum
I	-7.6	-28.1	-33.3	-28.1	-26.4	-43.3	-46.3	-53.7
II	-6.3	-10.9	-37.2	-7.6	-38.6	-45.7	-66.6	-28.1
III	-8.5	-17.0	-21.1	-3.9	-49.5	-54.1	-59.8	-16.8
IV			-22.3	-5.2			-59.2	-19.9
Mean	-7.5	-18.7	-28.5	-11.2	-38.2	-47.7	-58.0	-29.6

[#] see Table 1



see Table 1

Figure 1. Dynamics of changes in alpha acids content in hop cones stored for 12 months at +5 °C and +20 °C depending on the cultivar and harvest time.

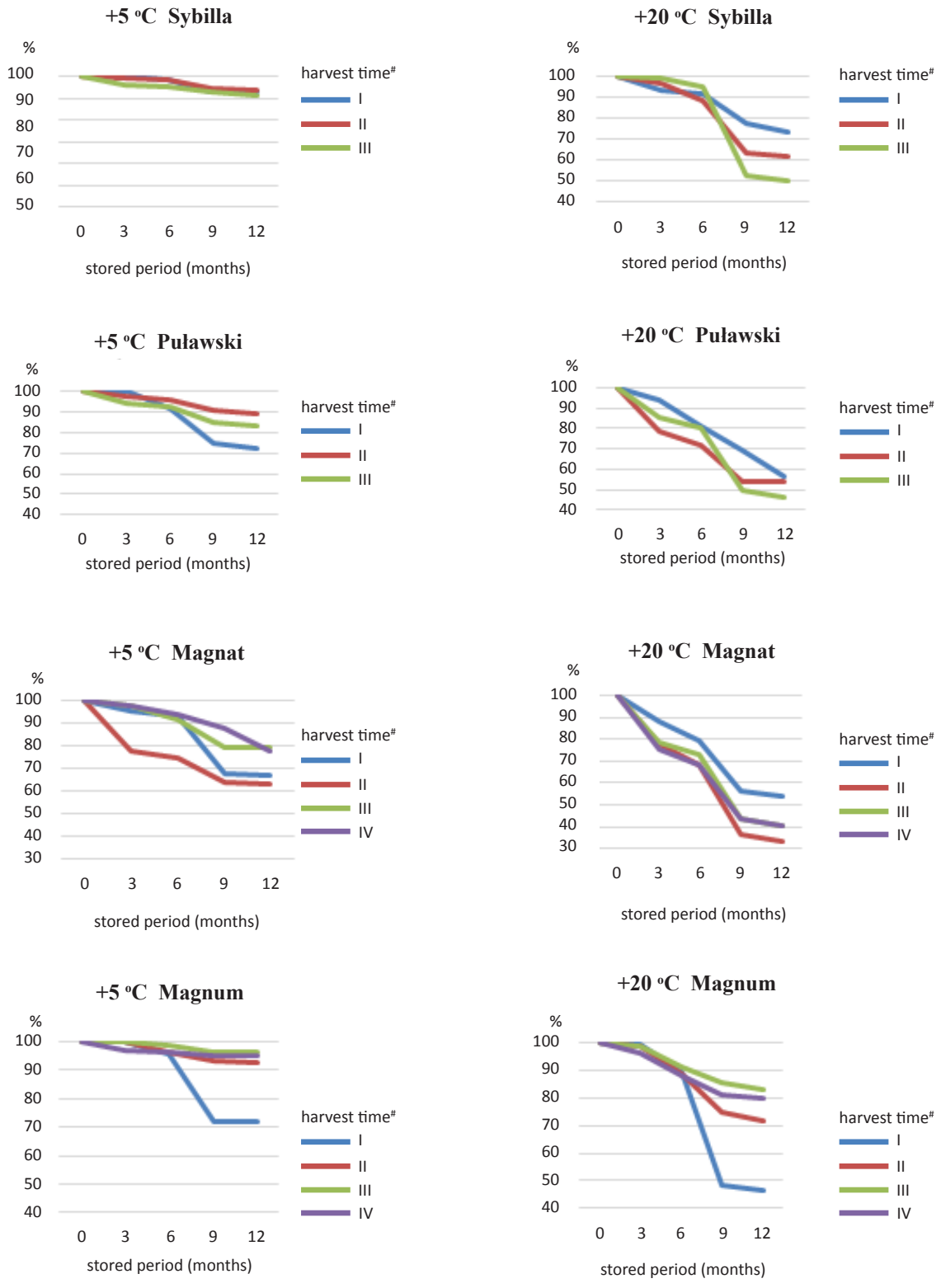
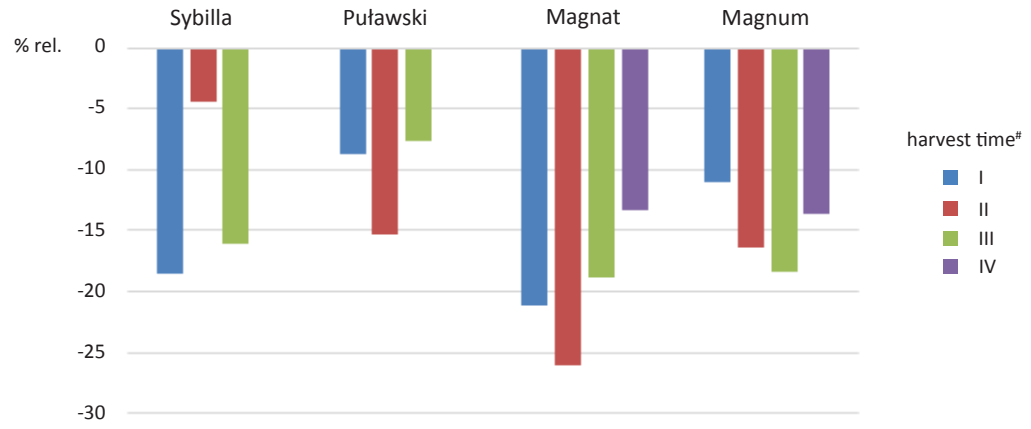


Figure 2. Dynamics of changes in beta acids content in hop cones stored for 12 months at +5 °C and +20 °C depending on the cultivar and harvest time.



see Table 1

Figure 3. Decrease of alpha acids content during 6 months storage of hop cones at +20 °C depending on the cultivar and harvest time [% rel.].

by lower stability, because during 6 months of storage at room temperature the decrease in alpha acid content was 21.2% and 26.1% respectively (Fig. 3).

CONCLUSIONS

1. The time of hop harvest significantly affected the alpha and beta acid content, whereby, due to the lowest alpha acid content, the earliest harvest before reaching the technological maturity stage was the least favourable for all the cultivars studied. The effect of the harvest period on the alpha and beta acid stability during long-term storage of hop cones was particularly evident during storage at +20 °C.
2. The storage temperature of hop cones had a considerable influence on the degree of alpha and beta acid degradation. In hops stored at the temperature of +20 °C, the decrease in alpha acids was on average 18.8 percentage points (p.p.) higher for all examined hop cultivars than at +5 °C. A similar correlation was observed for beta acids, with the degree of degradation of these compounds at +20 °C being 26.9 p.p. higher than at +5 °C.
3. The stability of bitter acids depended on the hop cultivar. The highest alpha acids stability at both +5 °C and +20 °C was characteristic for Sybilla. This cultivar was also found to have the highest beta acid stability at +5 °C, while at +20°C Magnum showed the lowest beta acid losses. Magnat was characterized by the lowest alpha and beta acid stability, regardless of the storage temperature.
4. The rate of hop cones aging was not uniform throughout the entire storage period. Initially, especially in cones stored at +5 °C, the bitter acid content remained approximately at the same level as the initial one. The stabilization phase lasted from 3 to 6 months, followed by a fairly rapid decrease in the content of these metabolites. At higher temperature, the period of bitter acid stabilization was shorter and amounted to maximum 3 months.

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