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THE EFFECT OF VARIETAL CHARACTERISTICS AND WEATHER FACTORS ON THE FORMATION OF ALPHA AND BETA ACIDS CONTENT IN AROMATIC AND BITTER HOP VARIETIES

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Introduction. Formulation of the problem

Hops (*Humulus lupulus* L.) are one of the primary and most expensive raw materials used in beer

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Abstract. The stability of the quality characteristics of brewing hop varieties under conditions of climate change that effect on the accumulation of bitter acids and the formation of beer's technological properties that is important for both producers and brewers. The aim of this study was to determine the impact of varietal characteristics and weather factors on the formation of alpha and beta acids content in aromatic and bitter hop varieties in the Zhytomyr region of Ukraine. Studies conducted from 2012 to 2022 established that the average alpha acids content in the cones of aromatic hop varieties was 4.0% and in bitter hop varieties was 7.7%, while the beta acids content was 4.9% and 4.8%, respectively. Inter-varietal differentiation was observed: among aromatic varieties, the highest accumulation of alpha and beta acids was characteristic of the Zagrava variety (5.4% and 6.2%) and the minimum was characteristic of the Klon 18 variety (2.5% and 3.3%); among bitter varieties, the highest values were found for the Ruslan (8.5% and 6.0%) and Xantha (8.6% and 5.6%) varieties and the lowest for the Promin variety (6.0% and 3.7%). It was established that the content of alpha acids is characterized by greater variability across the years of the study ($V_p=9.4-24.0\%$) compared to beta acids ($V_p=9.8-16.1\%$), that indicates their greater sensitivity to weather conditions. During the research period, the dominant influence of genotype on the formation of alpha acids content (53.2–66.3%) and beta acids content (67.1–72.0%) was demonstrated, while the contribution of weather conditions ranged from 12.4% to 20.9% and the interaction between varietal characteristics and weather conditions ranged from 17.5% to 32.4%. It was established that beta acids are characterized by higher genetic determination and stability, while alpha acids are more dependent on weather conditions during the growing season. The ratio of beta acids to alpha acids across the years of the study corresponds to typical ranges for the respective variety groups, with average values of 1.29 for aromatic varieties and 0.63 for bitter varieties, confirming the possibility of using this indicator as a criterion for the technological evaluation of hops. The most adaptable varieties were Zagrava and Ruslan, which combined high levels of alpha and beta acids accumulation with low variability across years. The study results provide valuable information on the characteristics of alpha and beta acids content formation in hops depending on genotype and weather conditions, which is the basis for predicting the quality of brewing raw materials.

Keywords: hops, alpha acids, beta acids, brewing, variety, genotype, weather conditions, variability, stability, beta-to-alpha acids ratio.

production therefore, the efficiency of the brewing process depends to a significant degree on the quality of the hop raw material. The use of hops in brewing is due to the presence of many components that belong to

biologically active compounds, which ensure the biological stability of beer, promote its preservation, create foam and produce a unique bouquet of taste and aroma properties [1, 2]. Among the complex of hop substances, the most valuable compounds, which create pronounced bitterness, a pleasant taste and antiseptic action are bitter substances [3]. In combination with other compounds, they contribute to the creation of foam, and thanks to their antibiotic properties, enhance beer's storage stability [4, 5]. The content and composition of bitter substances, particularly alpha and beta acids, are of great importance to the brewing industry [6]. Alpha acids are the main precursors of iso-alpha bitter acids, which are formed during the brewing process and play a key role in the formation of bitterness during the hopping of wort [7]. The alpha acids content in hops depends not only on growing conditions but also on varietal characteristics, therefore hop varieties are evaluated based on the content of these substances for their technological use [8]. With this in view, the alpha acids content in certain varieties is carefully controlled and is also a main price-determining factor in the evaluation of hops. Beta acids have a lower bitterness potential than alpha acids, but they have a very positive bioactive effect on beer [9]. They become more bitter due to oxidation during both storage and boiling [10, 11]. An increase in the content of alpha and beta acids indicates an improvement in the quality of hop varieties. Different hop varieties contain varying levels of alpha and beta acids [12].

The formation of alpha and beta acids depends not only on the genetic characteristics of the variety but also on external growing factors, particularly weather conditions, such as temperature, precipitation and water availability during the growing season [8, 13–18]. Current climate change, particularly trends toward rising average temperatures and irregular rainfall distribution, can lead to a decline in hop quality due to reduced alpha and beta acids content, that has direct technological and economic consequences for the brewing industry [15].

Hop production in Ukraine is concentrated in farms located in the Polissya and Forest-Steppe zones, where soil and climate conditions are best suited to the biological characteristics of the crop and enable the production of high-quality hop raw materials of aromatic and bitter varieties to supply the domestic brewing industry. At the same time, the industry is characterized by significant regional concentration: approximately 80% of the planted area and production volume is located in the Zhytomyr region, which determines its dominant role in the structure of the national hop industry [19]. Ukrainian hop varieties of the aromatic and bitter groups, thanks to the favorable natural climatic conditions, have long been famous for their high brewing qualities [20, 21]. Ukrainian breeders have offered growers over 30 domestically selected hop varieties, which differ in terms of growing season

length, productivity, cone quality indicators and other characteristics [22, 23].

Climate change may have significant consequences that will affect the quality of hop raw materials, necessitating a scientific basis for adapting varieties to local weather conditions and improving their technological properties. Existing domestic studies focus on evaluating the biochemical characteristics of individual hop varieties [20, 24–26], but complex studies combining the analysis of weather factors with the content of alpha and beta acids remain limited. Therefore, it is important to study the influence of varietal characteristics and weather conditions on the formation of alpha and beta acids in aromatic and bitter hop varieties under the conditions of the Zhytomyr region. The task of research in these conditions is to prepare the necessary information to make decisions.

Analysis of recent research and publications

The formation of alpha and beta acids content in hop cones (*Humulus lupulus L.*) is a complex biochemical process that determined by the interaction between the genetic characteristics of the variety and growing conditions. Alpha acids (humulones) are responsible for the bitterness of beer, while beta acids (lupulones) play a role in the formation of the aftertaste and aroma stability [27–30]. In current researches, increasing attention is given not only to the absolute content of these acids but also to their stability under various climatic conditions.

In a study [13], the authors established that temperature, precipitation, hours of sunshine and relative humidity during the growing season have a significant effect on the alpha acids content of the Aurora variety grown in Slovenia. Positive correlations between precipitation and alpha acids content were observed in the middle of the growing season, whereas high temperature and prolonged sunshine duration were negatively correlated with this parameter. Similar results were obtained by other researchers [31], which studied the influence of weather conditions, irrigation and plant age on yield and alpha acids content in the Czech hop varieties Žatecký, Sládek, Premiant and Agnus over a 25-year period in the Czech Republic. The authors established that precipitation was the main factor determining the yield of the Zhatetsky variety, whereas for other varieties, the level of moisture supply through irrigation was more significant. Elevated summer temperatures had a negative impact on the accumulation of alpha acids in the cones, reducing their content in most of the investigated varieties. At the same time, the Agnus variety was characterized by relative stability in alpha acids content independent of weather variations. These data indicate a complex interaction between weather factors and the genetic specificity of varieties.

The results of the research [15] indicate that not only alpha and beta acids, but also other secondary metabolites of hops, such as aromatic compounds and

polyphenols, have different sensitivity to weather conditions. The authors analyzed large consignments of samples from 11 German aromatic, 4 special-aroma and 5 bitter varieties grown over two subsequent years with very different climatic conditions. They found that alpha and beta acids were especially sensitive to unfavorable conditions (drought and high temperatures), with the effect noticeably stronger in aromatic varieties compared to special-aroma and bitter varieties. This indicates variety-specific sensitivity to abiotic factors, that has a direct impact on the bitterness of beer.

Researchers [8, 14] conducted over a 15-year period using various European hop varieties found that all hop varieties studied showed a tendency to decrease in alpha and beta acids content, a trend that correlates with long-term changes in climate and growing conditions. This confirms that not only short-term weather fluctuations but also long-term trends in global climate change can be important factors in the formation of hop quality indicators. These authors have demonstrated that the variability of alpha and beta acids differs significantly among varieties, while aromatic varieties are characterized by greater sensitivity to temperature fluctuations.

A large-scale interregional study on the impact of climate change on European hop growing has shown [32], that rising temperatures and reduced precipitation leads to a displacement of the phenological phases of hop development, an acceleration of the ripening period, a significant decrease in yield and a reduction in alpha acids content – the primary bitter components that determine the quality of raw material for brewing. A comparison of indicators before and after 1994 showed that production decreased by nearly 0.2 t/ha per year and the alpha acids content decreased by 0.6%. Model forecasts up to 2050 predict a further decline in hop yield of 4–18% and in alpha acids content of 20–31% due to rising temperatures and drought. These results underscore that climate variability is a significant risk factor for hop production and requires the implementation of adaptation practices in breeding, agronomic management and production planning.

Taking into account present and forecasted climate change trends [32–34], climate adaptation is necessary to enhance the stability and resistance of the hop-growing and brewing industries. In contrast to annual crops, for multi-year crops such as hops, hop growers and other stakeholders require more time to make decisions. Thus, the conducted research will combine evidence on the impact of environmental factors associated with climate change, as well as hop variety characteristics linked to climate adaptation, on the formation of alpha and beta acids in aromatic and bitter hop varieties, with the aim of informing hop growers and brewers and facilitating the adaptation of the hop-growing and brewing industries.

The aim and objectives of the study. The aim of the study was to determine the influence of varietal characteristics and weather conditions on the formation

of alpha and beta acids content in aromatic and bitter hop varieties under the conditions of the Zhytomyr region of Ukraine.

To achieve this aim, the following objectives were formulated:

- to determine the content of alpha and beta acids in aromatic and bitter hop varieties under the conditions of the Zhytomyr region and analyze their dynamics over the study period;

- to assess the level of inter-varietal variability in alpha and beta acids content and determine the features of their formation depending on the genotype;

- analyze weather conditions and investigate the influence of the main weather factors (temperature regime, precipitation, hydrothermal coefficient) on the accumulation of alpha and beta acids in the cones of aromatic and bitter varieties;

- determine the proportion of the influence of the factors “variety,” “annual weather conditions” and their interaction on the formation of alpha and beta acids content;

- determine the most adaptive varieties in terms of the stability of alpha and beta acids formation under the conditions of the study region.

Materials and methods.

Hop varieties. The studies were conducted during 2012–2022 using nine commercially important Ukrainian aromatic hop varieties: Klon 18, Zlato Polissya, Slovianka, National, Zagrava and bitter varieties: Alta, Promin, Ruslan and Xantha, which are included in the State Register of Plant Varieties Suitable for Distribution in Ukraine. The hops of the studied varieties were grown on specialized hop farms in the Zhytomyr region. The cultivation technology followed generally accepted recommendations, in accordance with which the full range of agrotechnical measures was carried out, namely: soil cultivation, fertilizer application and integrated plant protection against pests and diseases were performed at optimal times and post-harvest handling was carried out in a timely manner.

Weather conditions during the study period. The studies used meteorological data for the period from 2012 to 2022, provided by the Zhytomyr Regional Center for Hydrometeorology. The territory of Zhytomyr Oblast belongs to Ukraine’s traditional hop-growing region and is characterized by generally favorable soil and climatic conditions for hop cultivation [19]. The region is located in the Polissya zone and partly in the Forest-Steppe zone of Ukraine, which determines its temperate continental climate with relatively humid conditions and significant temperature fluctuations. The winter period continues approximately from the third ten-day period of November to the second ten-day period of March (about 111 days), while the lowest temperatures are observed mainly in February. Fluctuations in air temperature during all winter months lead to alternating periods of warming and frost. Warming typically begins in the third ten-day period of

April. The period with an average daily air temperature of 15 °C amounts to 106 days (from May 21 to September 4), with a sum of effective temperatures (above 10 °C) of 2,350–2,480 °C. The period with temperatures above +10 °C amounts to 150–155 days and the frost-free period –160–170 days, with a sum of temperatures of 2670 °C. Thus, based on long-term data, the growing season for hops in the Zhytomyr region amounts to approximately 160 days. In terms of precipitation, the Zhytomyr region is a zone of sufficient hydration. The average annual precipitation is about 540–650 mm. During the spring and summer period about 450–500 mm of precipitation falls, sometimes in the form of fairly heavy downpours, sometimes with hail. In recent years, there have been increasingly frequent periods of moisture deficit and uniform distribution of precipitation, with moisture deficit often occurring during critical phases of crop development. Long-term values of the hydrothermal coefficient (HTC) for the region range from 1.3 to 2.0.

Weather conditions during the study period deviated from the long-term average. During the hop growing season, the average daily air temperature exceeded the long-term average. On average, the increase over the study period was 2.4 °C. The largest increase in the average monthly temperature during the hop growing season was 3.7 °C in 2018 and 3.1 °C in 2015. Thus, there is a trend toward rising average monthly temperatures, indicating climate change toward warming. During the study period, a decrease in average monthly precipitation of 9.0 mm below the norm was observed. However, monthly precipitation exceeded the norm in May on the 28.5 mm and on the 5.8 mm in September. There is also a tendency for precipitation to be irregular during the growing season of hops. The largest amount of precipitation during the hop growing season falls in May–July (215.6 mm), which accounts for 60% of the total precipitation during the growing season. Over the years studied, the greatest deviation of the average monthly precipitation from the norm during the hop growing season was observed in 2015 (-34.0 mm), 2016 (-25.6 mm) and in 2017 (-26.7 mm). An analysis of the results of the soil moisture index (HTC) during the hop growing season indicated that only four of the 11 years (2013, 2014, 2020 and 2021) can be classified as wet. Other years were characterized as insufficiently moist and dry. On average, during the hop growing season over the study period, the HTC index was 1.13. Compared to the climatic norm (1.5), it decreased by 0.37. Thus, the moisture index of the region corresponds to insufficiently wet conditions, confirming the trend of gradual changes in the agroclimatic conditions of the Zhytomyr region, where the main hop plantations are concentrated.

Samples of hop cones were selected from industrial consignments of the corresponding varieties throughout the research period. Each year, 10 samples were analyzed from consignments of each hop variety. To determine the content of alpha and beta acids, spot

samples weighing at least 50 g were taken from three different locations within the bag (bale) selected for the test. The obtained spot samples were thoroughly mixed to form a composite sample weighing at least 1 kg. From this, an average sample weighing approximately 300 g was selected using the quartering method, which was used to determine the content of alpha and beta acids [35]. The determination of alpha and beta acids content was performed at the accredited laboratory of hop and beer biochemistry at the Polissya Institute of Agriculture of the National Academy of Agrarian Sciences of Ukraine using high-performance liquid chromatography in accordance with the international method EBC 7.7 [35, 36]. Hop bitter substances: alpha and beta acids were extracted from hop cones using the organic solvent methanol. The ratio of hop cones to extractant was 1:10. The amounts of alpha and beta acids were determined by high-performance liquid chromatography. Chromatography was performed using an Ultimate 3000 liquid chromatograph with a UV detector at a temperature of 35 °C. A 100 × 2.1 mm column filled by Pinnacle DV C18 3 µm sorbent was used. A solution of methanol, water and acetonitrile in a 38:24:38 ratio was used as the mobile phase. For the quantitative determination of alpha and beta acids, the international standard ICE-3 (International Calibration Extract ICE-3, manufacturer – Versuchsstation Schweizerischen Brauereien) was used [35]. All analyses were conducted in triplicate.

Statistical data analysis. In the analysis and processing of experimental data, methods of variational statistics were used: mathematical processing, determination of statistical characteristics, paired and multiple correlation analyses and analysis of dispersion (ANOVA) were performed using the computer programs “MS Office Excel 2016”, the “Statistica” software package (version 10.0) and a personal computer.

Results of the research and their discussion

The results of an 11-year study indicate that the average alpha acids content in hop cones grown in the analyzed region was 5.9%. The average alpha acids content in the cones of aromatic hop varieties was 4.0% (Table 1), that is 32.2% lower than the average varietal value. In hop cones of bitter-type varieties, the average alpha acids content exceeded the average varietal value by 30.5%.

Thus, among the studied groups of varieties, bitter-type hop cones were characterized by a higher alpha acids content compared to aromatic-type varieties. The observed trend of lower alpha acids content in aromatic hop varieties compared to bitter varieties corresponds to the results of studies by other researchers [8, 37, 38], which indicate that aromatic varieties generate less alpha and beta acids, whereas bitter varieties are characterized by significantly higher levels of these acids, which accounts for their main use in forming the bitterness of beer.

Table 1 – Alpha acids content in hop cones of different, % (2012–2022), $\bar{x} \pm s_x$, n=3

Hop variety	Average alpha acids content, %	<i>min</i> alpha acids content, %	<i>max</i> alpha acids content, %	Variation over the years, <i>Vp</i> , %
Aromatic hop type				
Klon 18	2.5±0.6	1.5	3.7	24.0
Zlato Polissya	2.8±0.4	1.9	3.2	14.3
Slovianka	4.1±0.9	2.2	5.2	22.0
National	5.1±1.4	3.3	7.7	27.5
Zagrava	5.4±0.8	4.1	6.8	14.8
Average	4.0±0.8	2.6	5.2	20.0
Alta	7.8±1.2	5.5	9.6	15.4
Promin	6.0±0.6	4.9	6.9	10.0
Ruslan	8.5±0.8	6.8	9.3	9.4
Xantha	8.6±1.4	6.6	10.5	16.3
Average	7.7±1.0	6.6	8.6	13.0

Among aromatic varieties, the lowest alpha acids content was observed in the cones of the Klon 18 variety (1.5%) from the 2015 harvest. This value was 62.5% lower than the average for the variety. The maximum alpha acids content of 6.8% was found in the cones of the Zagrava variety from the 2014 harvest. This exceeded the average variety value by 70.0%. The aromatic varieties that, according to the results of eleven years of research, accumulated the highest level of alpha acids were Zagrava and National, while the lowest was Klon 18. The Slovianka variety ranked in the middle.

Among the bitter-type varieties, the Promin variety harvested in 2018 had the lowest alpha acids content (4.9%). The alpha acids content was 36.4% below the average for the variety. The highest mass fraction of alpha acids was recorded in the 2019 harvest of Xantha hops (10.5%). This exceeded the average for the variety by 36.4%. Among the group of bitter-type varieties, the highest average alpha acids content was recorded in the cones of the Xantha and Ruslan varieties and the lowest in the Promin variety. The Alta variety ranked in the middle. The research results are consistent with the conclusions of German and Czech researchers [15, 39, 40], which note that weather conditions in some years are so different that they result in different alpha acid content levels. According to their data, different hop varieties react differently to the weather conditions of the year, which is reflected in the level of bitter acids accumulation in hop cones.

From a technological standpoint, hop varieties with cones characterized not only by a high alpha acids content but also by the stability of this parameter are particularly valuable for storage and use in brewing [8, 38, 41]. In our studies, we used the coefficient of variation *Vp* as an indicator of a variety's stability with regard to weather conditions across different growing years. It is known that when the coefficient of variation is less than 10%, the variability of the selection is considered insignificant or low; when it is between 10 and 20%, it is considered average; and when it is above 20%, it is considered significant or high [42].

The research results presented in Table 1 indicate an average variability in alpha acids content over the years of research in the aromatic variety group (*Vp* = 20.0%). The greatest influence of weather factors on the alpha acids content in the hop cones of this group was observed for the varieties National, Klon 18 and Slovianka, with coefficients of variation of 27.5%, 24.0% and 22.0%, respectively. The variability of these varieties under the influence of weather factors is considered significant. The most stable in terms of alpha acids content are the Zlato Polissya and Zagrava varieties, as evidenced by their coefficients of variation of 14.3% and 14.8%, respectively. The variability in alpha acids content over the years of research in the cones of the bitter-type hop variety group was also average (*Vp* = 13.0%). Among the bitter-type varieties, the most stable alpha acids content was found in the cones of the Ruslan variety (*Vp* = 9.4%), while the most variable was in the Xantha variety (*Vp* = 16.3%).

Thus, in terms of alpha acids content and the variability of their formation under the influence of weather factors in the region under study, the most perspective varieties from a technological standpoint were Zagrava (an aromatic type) and Ruslan (a bitter type). These varieties were characterized by a high content of alpha acids and low variability over the years of research.

Analysis of the research results showed that bitter-type hop varieties are characterized by a more stable level of alpha acids, whereas aromatic-type varieties show greater variability in this parameter. The results obtained are consistent with data from other researchers, which note that bitter hop varieties are characterized by a more stable alpha acids content compared to aromatic varieties. In particular, long-term studies of Czech varieties have shown that the variability in alpha acids content in bitter varieties over a 13-year period did not exceed 15% [14]. Similar results have been obtained in other studies of European hop varieties, where it was found that bitter varieties have lower variability in alpha acids, while aromatic varieties are characterized by

significantly greater variability in this parameter under the influence of growing conditions [8, 43].

Table 2 presents the results of a two-factor analysis of variance, which made it possible to assess the influence of weather conditions during the study years (factor A), hop variety characteristics (factor B), and their interaction (factor AB) on the formation of alpha acids content in aromatic and bitter hop cones.

It was established that for aromatic hop varieties, the dominant influence on the formation of alpha acids content was the variety (factor B), with a proportion of influence of 66.3%. Weather conditions during the study years (factor A) had a less significant influence - 20.9%. The interaction of factors (AB) had a middle impact - 12.5%. For bitter hop varieties, the dominant factor was also the variety (factor B) with a partial effect of 53.2%. The influence of weather conditions during the study years was 14.1%, which corresponds to the average influence. The interaction of study factors for bitter-type varieties accounted for 32.4% of the influence.

The results obtained indicate that, for both types of hop varieties, the variety is the determining factor in the formation of alpha acids content. However, for bitter varieties, a greater influence of the interaction between varietal characteristics and weather conditions during the growing season is also observed, which must be taken into account when selecting varieties for specific agroclimatic conditions. The results of our studies are supported by the conclusions of other researchers [15, 38, 40, 44, 45], which indicate that the formation of alpha

acids content in hops depends on the interaction between the genetic properties of the variety and growing conditions, particularly the meteorological parameters of the growing season. In particular, Brazilian researchers [46] also note in their studies that 30% of the variation in alpha acids content was observed among hop clones, while 47% was associated with environmental conditions.

During the studies, the dynamics of beta acids in the cones of aromatic and bitter hop varieties were examined over the period 2012–2022. The results of the studies allow us to conclude that the average beta acids content in hop cones grown in the analyzed region was 4.9%. The average content of beta acids in the cones of aromatic hop varieties was 4.9% (Table 3), which corresponded to the average varietal value. In the cones of bitter hop varieties, the average content of beta acids was 0.1% lower than the average varietal value.

Among the aromatic hop varieties, the lowest beta acids content was recorded in the cones of the Klön 18 variety (2.6%) from the 2015 harvest. It was 46.9% lower than the average for the variety. The maximum beta acids content of 7.6% was found in the cones of the Zagrava hop variety from the 2019 harvest. This exceeded the average variety value by 55.1%. Among aromatic-type varieties, Zagrava had the highest beta acids content as determined by eleven years of research, while Klön 18 had the lowest (Table 3).

Table 2 – Results of two-factor analysis of variance in the formation of alpha acids content in hop cones

Source of variation	Sum of squares	Degrees of freedom	Variance	F_{fact}	$F_{tab.095}$	Influence, %
Aromatic hop type						
Factor A (year)	72.4	10	7.2	786.1	1.9	20.9
Factor B (variety)	229.4	4	57.3	6224.4	2.5	66.3
Interaction AB	43.3	40	1.1	117.5	1.5	12.5
Factor A (year)	39.3	10	3.9	393.0	1.9	14.1
Factor B (variety)	148.1	3	49.4	4936.8	2.7	53.2
Interaction AB	90.1	30	3.0	300.4	1.6	32.4

Table 3 – Beta acids content in hop cones of different, % (2012–2022) $\bar{x} \pm s_x$, n=3

Hop variety	Average beta acids content, %	min beta acids content, %	max beta acids content, %	Variation over the years, V_p , %
Aromatic hop type				
Klön 18	3.3±0.5	2.6	4.3	15.2
Zlato Polissya	3.6±0.5	3.0	4.3	13.9
Slovianka	5.6±0.8	4.0	6.7	14.3
National	5.7±0.9	4.8	7.6	15.8
Zagrava	6.2±1.0	3.9	7.6	16.1
Average	4.9±0.7	3.7	5.7	14.3
Alta	4.1±0.4	3.4	4.6	9.8
Promin	3.7±0.5	2.6	4.7	13.5
Ruslan	6.0±0.9	4.1	7.4	15.0
Xantha	5.6±0.9	4.7	7.4	16.1
Average	4.8±0.7	3.9	5.7	14.6

In the group of bitter-type varieties, the Promin variety had the lowest content of beta acids in hop cones harvested in 2015. The beta acids content was 45.8% lower than the average for the variety. The highest beta acids content was recorded in the hop cones of the Ruslan variety from the 2016 harvest. In this case, the excess over the average for the variety was 54.2%. Among the group of bitter-type varieties, the highest average content of beta acids was recorded in the cones of the Ruslan variety and the lowest in the cones of the Promin variety.

The obtained results are consistent with data from other researchers, which also note significant inter-varietal variability in the content of bitter acids in hop cones. In particular, studies of European hop varieties have shown that the average beta acids content can range widely, from 2.7% to 7.3%, confirming the significant influence of a variety's genotypic characteristics on the chemical composition of hop cones [8]. Similar results were obtained during long-term studies of Czech bitter hop varieties, where the maximum content of beta acids was approximately 7.3%, while in some genotypes it did not exceed 3.6–3.7%, indicating significant inter-varietal differentiation of this parameter [14]. Furthermore, recent studies of aromatic hop varieties have noted that the level of bitter acids and their ratio significantly depends on the genetic characteristics of the variety and may also vary under the influence of growing conditions and the year of the study [47]. Thus, our results confirm the general trend according to which the content of beta acids in hop cones is largely determined by varietal characteristics and can vary significantly between genotypes even under similar agroclimatic growing conditions.

The stability of beta acids accumulation in hop cones is of great importance for predicting the technological properties of brewing raw materials [8, 14, 41]. Similar conclusions are presented in recent studies, which demonstrate the significant role of genotypic and climatic factors in the formation and stability of bitter acids in hops [48, 49]. The presented research results (Table 3) indicate the average variability of beta acids content across the years of study in the group of aromatic-type varieties. The greatest influence of weather factors on the content of beta acids in the cones of this group was

found for the Zagrava and National varieties, with coefficients of variation of ($V_p = 16.1\%$) and ($V_p = 15.8\%$), respectively. The Zlato Polissya variety had the most stable beta acids content, with a coefficient of variation ($V_p = 13.9\%$). The variability in beta acids content across the years of study in the cones of the bitter-type hop variety group was also average ($V_p = 14.6\%$). Among the bitter-type varieties, the content of beta acids was most stable in the hop cones of the Alta variety ($V_p = 9.8\%$) and most variable in the Xantha variety ($V_p = 16.1\%$).

In general, it was established that the studied hop varieties are characterized by higher stability in beta acids content over the years of the study compared to alpha acids content. This is consistent with the data of other researchers [15], which also note the lower sensitivity of beta acids to changes in climatic conditions.

To determine the influence of various factors on the formation of beta acids content in hop cones, a two-factor analysis of variance was conducted, taking into account variations in weather conditions across the years of the study (factor A), varietal characteristics (factor B) and their interaction (factor AB) (Table 4).

The obtained results showed that, for aromatic hop varieties, the variety (factor B) had the dominant influence on the formation of beta acids content, with an influence ratio of 72.0%. Weather conditions during the study years (factor A) had a less significant influence, at 12.4%. The interaction of factors (AB) provided an influence of 15.3%. For bitter-type hop varieties, the dominant factor was also the variety (factor B) with a contribution of 67.1%. The influence of weather conditions during the study years was 14.9%, which corresponds to an average influence. The interaction of study factors for bitter-type varieties accounted for 17.5% of the influence.

A comparison with the results regarding the influence of factors on the formation of alpha acids in hop cones showed that beta acids are characterized by a higher level of genetic determination and relatively lower dependence on weather factors compared to alpha acids. In contrast, alpha acids demonstrate greater sensitivity to variations in the growing year, which may be associated with the peculiarities of the regulation of their biosynthesis and accumulation.

Table 4 – Results of a two-factor analysis of variance for the formation of beta acids content in hop cones

Source of variation	Sum of squares	Degrees of freedom	Variance	F_{fact}	$F_{tab..095}$	Influence, %
Aromatic hop type						
Factor A (year)	39.9	10	4.0	399.3	1.9	12.4
Factor B (variety)	231.4	4	57.9	5786.2	2.5	72.0
Interaction AB	49.1	40	1.2	122.7	1.5	15.3
Factor A (year)	27.8	10	2.8	277.8	1.9	14.9
Factor B (variety)	124.9	3	41.6	4162.3	2.7	67.1
Interaction AB	32.6	30	1.1	108.8	1.6	17.5

As noted in studies [15], the mechanisms of the different reactions of hop chemical composition components to variable climatic conditions remain insufficiently studied. Probably, this is due to enzymatic processes occurring during the biogenesis of alpha and beta acids, which may differentially respond to environmental factors such as elevated temperature and drought. Further research into the regulatory mechanisms of the enzymatic pathways involved in the biosynthesis of alpha and beta acids is necessary to better predict their accumulation in hop cones, which will ensure the stable quality of brewing raw materials and optimize brewing parameters.

An important characteristic of the chemical composition of hop cones is the ratio of beta to alpha acids, which determines the technological properties of hops and their suitability for use in brewing. It is known that this ratio depends largely on the genotype of the variety and it is used as one of the indicators for classifying hops into aromatic and bitter types [8, 35]. Aromatic varieties are typically characterized by a high value of this indicator, close to a ratio of 1:1 or greater than 1, whereas in bitter varieties, the proportion of alpha acids is significantly higher, resulting in a beta-to-alpha acids ratio below 1 [1, 35]. This difference is of significant technological importance for brewing, as the ratio of bitter acids influences the formation of bitterness and the flavor profile of beer [30, 50]. Therefore, taking into account the actual and projected increase in average monthly temperatures during the hop growing season and the decrease in precipitation and its irregularity, it was important to understand how changing weather conditions affect the beta-to-alpha acids ratio in aromatic and bitter hop varieties (Table 5).

Our research conducted over a period of eleven years has established that the average ratio of beta acids to alpha acids in the hop cones of the studied varieties grown on hop farms in the Zhytomyr region was 1.29, which is consistent with literature data on the range of this ratio for aromatic varieties [23]. Among aromatic hop varieties, the lowest beta-to-alpha acids ratio was

measured in the cones of the National variety (0.91) from the 2020 harvest. The highest value of the beta-to-alpha acids ratio was found in the cones of the Klön 18 hop variety (1.95) from the 2016 harvest. Among the aromatic hop varieties, after eleven years of research, were characterized by the highest beta-to-alpha acids ratio, were Sloviianka and Klön 18; the lowest was Zagrava; the Zlato Polissya variety ranked in the middle.

For the group of bitter-type varieties, the average beta-to-alpha acids ratio in hop cones was 0.63. The highest beta-to-alpha acids ratio was observed in Xantha hop cones (0.97) from the 2015 harvest. The lowest beta-to-alpha acids ratio was determined in Alta hop cones (0.39) from the 2018 harvest. Among the bitter-type hop varieties, Ruslan had the highest beta-to-alpha acids ratio based on the research results, while Alta had the lowest; the Xantha and Promin varieties were in the middle.

The research results presented in Table 5 indicate the average variability of the beta-to-alpha acids ratio over the years of study among groups of aromatic and bitter varieties, with average coefficients of variation of 17.0% and 15.9%, respectively. The greatest influence of weather factors on the beta-to-alpha acids ratio in hop cones among aromatic varieties was found for the Klön 18 variety, with a coefficient of variation of 24.3%. The most stable variety in terms of the beta-to-alpha acids ratio was Zagrava, with a coefficient of variation of 12.3%. The variability of this variety under the influence of weather factors is considered average. Among the group of bitter-type varieties, the most stable beta-to-alpha acids ratio was found in the cones of the Promin ($V_p = 11.3\%$) and Ruslan ($V_p = 12.9\%$) varieties, while the most variable was in the Xantha variety ($V_p = 20.9\%$).

It was found that the ratio of beta-to-alpha acids in the aromatic and bitter hop varieties studied ranged depending on the year of the study; however, it generally remained within the values characteristic of their varietal specifications [23]/

Table 5 – Ratio of beta to alpha acids in hop cones of different hop varieties, % (2012–2022), $\bar{x} \pm s_x$, $n=3$

Hop variety	Average ratio of beta to alpha acids, %	<i>min</i> ratio of beta to alpha acids, %	<i>max</i> ratio of beta to alpha acids, %	Variation over the years, V_p , %
Aromatic hop type				
Klön 18	1.40±0.34	0.97	1.95	24.3
Zlato Polissya	1.31±0.22	0.97	1.57	16.8
Sloviianka	1.41±0.22	1.15	1.82	15.6
National	1.17±0.19	0.91	1.45	16.2
Zagrava	1.14±0.14	0.95	1.36	12.3
Average	1.29±0.22	1.03	1.53	17.0
Alta	0.53±0.09	0.39	0.76	17.0
Promin	0.62±0.07	0.52	0.75	11.3
Ruslan	0.70±0.09	0.58	0.92	12.9
Xantha	0.67±0.14	0.50	0.97	20.9
Average	0.63±0.10	0.54	0.72	15.9

Table 6 – Results of a two-factor analysis of variance for the beta-to-alpha acids ratio in hop cones

Source of variation	Sum of squares	Degrees of freedom	Variance	F_{fact}	$F_{tab..095}$	Influence, %
Aromatic hop type						
Factor A (year)	4.18	10	0.42	1077.93	1.9	41.8
Factor B (variety)	2.15	4	0.54	1385.37	2.5	21.5
Interaction AB	3.63	40	0.09	234.15	1.5	36.3
Factor A (year)	0.42	10	0.04	1217.77	1.9	23.3
Factor B (variety)	0.53	3	0.18	5118.28	2.7	29.4
Interaction AB	0.83	30	0.03	797.90	1.6	46.1

Similar trends have been noted in studies by other authors, which show that the alpha-to-beta acids ratio is largely determined by the variety's genotype, although it may vary under the influence of growing conditions and the growing season [8, 14, 15, 38, 51].

During the studies, a two-factor analysis of variance was conducted to assess the influence of weather conditions in the study years (factor A), hop variety characteristics (factor B) and their interaction (factor AB) on the beta-to-alpha acids ratio in aromatic and bitter hop cones. It was established that for both types of varieties, all studied factors had a statistically significant effect on the investigated indicator (Table 6).

For aromatic hop varieties, the greatest influence on the beta-to-alpha acids ratio was exerted by the weather conditions during the study years (factor A), which accounted for 41.8% of the total influence. The interaction of factors (AB) was also significant, accounting for 36.3%, indicating a complex reaction of varieties to changes in weather conditions. The influence of varietal characteristics (factor B) was somewhat lower, accounting for 21.5%, indicating a relatively lesser role of genetic control over this parameter in aromatic varieties compared to the influence of the growing year. For bitter-type hop varieties, a different character of the influence of factors was established. The greatest contribution to the variation in the beta-to-alpha acids ratio was provided by the interaction of factors (AB) – 46.1%, which highlights the significant dependence of the realization of the genetic potential of varieties on the specific weather conditions of the year. The proportion of the influence of varietal characteristics (factor B) was 29.4%, while the weather conditions of the study years (factor A) had a smaller, although statistically significant, influence - 23.3%.

The results obtained indicate that the ratio of beta-to-alpha acids is an integral indicator, the value of which is determined both by the genetic characteristics of the varieties and by the variability of weather conditions, with the degree of their influence depending

on the type of hop. Similar trends have been noted in recent studies, which show that the ratio of alpha-to-beta acids can vary significantly between varieties and growing years, reflecting both genotype characteristics and the influence of agroclimatic factors [8, 14]. In particular, studies by European researchers have established that the variability in the ratio of alpha-to-beta acids is determined by the interaction of varietal characteristics and environmental conditions and this indicator can be used as an important criterion for the technological evaluation of hop varieties [8, 14, 38]. In addition, it has been noted that different groups of varieties are characterized by different reactions to weather conditions, reflecting the characteristics of their adaptive potential [15, 38, 52].

Conclusion

Studies conducted in the Zhytomyr region during 2012–2022 showed that the dynamics of alpha and beta acids content were characterized by significant variability, which reflects the influence of varietal characteristics and weather conditions during the growing season. The average alpha acids content in hop cones of aromatic varieties was 4.0% and in bitter varieties - 7.7%. The beta acids content in aromatic varieties corresponded to the average varietal value of 4.9%, while in bitter varieties it was slightly lower - 4.8%. Significant inter-varietal differentiation was observed in the content of alpha and beta acids. Among aromatic varieties, the highest accumulation of alpha and beta acids was found in the Zagrava variety at 5.4% and 6.2%, respectively, while the lowest was in Klon 18 18 at 2.5% and 3.3%. Among the bitter varieties, the highest levels of alpha and beta acids content were found in the Ruslan variety at 8.5% and 6.0%, and in the Xantha variety at 8.6% and 5.6%, respectively, but the lowest levels were in the Promin variety at 6.0% and 3.7%.

The results of the studies showed that weather conditions during the growing season influenced the accumulation of alpha and beta acids, causing

variability in the indicators across the years of the study. Thus, for aromatic-type varieties, the coefficient of variation in alpha acids content ranged from ($Vp = 14.3\text{--}24.0\%$), and for bitter-type varieties, from ($Vp = 9.4\text{--}16.3\%$). The variability in beta acids content across the years of study in the aromatic-type variety group was within the range ($Vp = 13.9\text{--}16.1\%$), and in the bitter-type variety group within the range ($Vp = 9.8\text{--}16.1\%$). It was found that bitter-type hop varieties are characterized by a more stable level of alpha acids, whereas aromatic-type varieties are characterized by greater variability in this parameter. Alpha acids were characterized by higher sensitivity to weather factors, whereas beta acids were more stable, indicating different ecological plasticity of the components of bitter acids.

It was found that for aromatic and bitter hop varieties, the variety (factor B) had the dominant influence on the formation of alpha and beta acids content, with a contribution of 66.3% and 72.0% for the aromatic variety group, and 53.2% and 67.1% for the bitter-type group, respectively. The influence of weather conditions during the study years (factor A) was less significant for the studied indicators of the two hop variety types and ranges from 20.9% (alpha acids) to 12.4% (beta acids) for aromatic-type varieties and from 14.1% (alpha acids) to 14.9% (beta acids) for bitter-type varieties. The interaction between variety and weather conditions of the study years (AB factor), with a proportion of influence ranging from 17.5% to 32.4%, indicates a significant change in the varieties response to weather conditions across different years. In general, beta acids are characterized by a higher level of genetic determination and relatively lower dependence on weather factors compared to alpha acids. In contrast, alpha acids demonstrate greater sensitivity to changes in the growing year, which may be associated with the

specific mechanisms regulating their biosynthesis and accumulation.

The ratio of beta-to-alpha acids is a complex indicator, the value of which is determined by both the genetic characteristics of the varieties and the weather conditions of the year. For aromatic varieties, the influence of weather factors is more significant, whereas for bitter varieties, it is the interaction between varietal characteristics and weather conditions during the growing season. It has been shown that the ratio of beta-to-alpha acids over the years of research corresponds to the typical ranges for the corresponding groups of varieties, with average values of 1.29 for aromatic varieties and 0.63 for bitter varieties, confirming the possibility of using this indicator as a criterion for the technological evaluation of hops.

Taking into account the combined indicators of the content and stability of alpha and beta acids, the aromatic variety Zagrava and the bitter variety Ruslan were identified as the most adaptable to the conditions of the study region, as they combined high levels of alpha and beta acids accumulation with low variation over the years.

The results obtained highlight the necessity of further studying the mechanisms of alpha and beta acids biosynthesis and their regulation under the influence of weather factors. A prospective study involves investigating the interaction between varietal characteristics and weather conditions during the growing season to predict the quality of hop raw materials, with the aim of justifying the adaptive selection of varieties for specific agroclimatic conditions, which is of direct importance to producers and brewers, as it ensures the stability of high-quality raw materials and the controllability of bitterness and the sensory profile of beer.

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ВПЛИВ СОРТОВИХ ОСОБЛИВОСТЕЙ ТА ПОГОДНИХ ЧИННИКІВ НА ФОРМУВАННЯ ВМІСТУ АЛЬФА- І БЕТА-КИСЛОТ В АРОМАТИЧНИХ І ГІРКИХ СОРТАХ ХМЕЛЮ

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Анотація. Стабільність якісних показників сортів хмелю для пивоваріння в умовах кліматичних змін, що впливають на накопичення гірких кислот і формування технологічних властивостей пива є важливою як для виробників, так і для пивоварів. Метою роботи було встановити частку впливу сортних особливостей і погодних чинників на формування вмісту альфа- та бета-кислот у ароматичних і гірких сортах хмелю в умовах Житомирської області України. Дослідженнями проведеними у 2012–2022 рр. встановлено, що середній вміст альфа-кислот у шишках хмелю ароматичних сортів становив – 4,0 %, гірких – 7,7 %, тоді як вміст бета-кислот відповідно 4,9 % і 4,8 %. Виявлено міжсортну диференціацію: серед ароматичних сортів максимальне накопичення альфа- та бета-кислот характерне для сорту Заграва (5,4 % і 6,2 %), мінімальне – для сорту Клон 18 (2,5 % і 3,3 %); серед гірких сортів найвищі значення встановлено для сортів Руслан (8,5 % і 6,0 %) та Ксанга (8,6 % і 5,6 %), найнижчі – для сорту Промінь (6,0 % і 3,7 %). З'ясовано, що вміст альфа-кислот характеризується більшою варіабельністю за роками досліджень ($V_p = 9,4\text{--}24,0\%$) порівняно з бета-кислотами ($V_p = 9,8\text{--}16,1\%$), що свідчить про їх вищу чутливість до погодних умов. Впродовж періоду досліджень доведено домінуючий вплив генотипу на формування вмісту альфа-кислот (53,2–66,3 %) і бета-кислот (67,1–72,0 %), тоді як частка впливу погодних умов становила 12,4–20,9 %, а взаємодія сортних особливостей і погодних умов – 17,5–32,4 %. Встановлено, що бета-кислоти характеризуються вищою генетичною зумовленістю і стабільністю, тоді як альфа-кислоти є більш залежними від погодних умов вегетаційного періоду. Співвідношення бета-кислот до альфа-кислот за роками досліджень відповідає типовим діапазоном для відповідних груп сортів з середніми значеннями для сортів ароматичного типу – 1,29 та гіркого – 0,63, що підтверджує можливість використання даного показника як критерію технологічної оцінки хмелю. Найбільш адаптивними були сорти Заграва та Руслан, які поєднували високий

рівень накопичення альфа-кислот і бета-кислот із низкою варіативністю за роками. Результати дослідження дають цінну інформацію про особливості формування вмісту альфа-кислот та бета-кислот у хмелі залежно від генотипу і погодних умов, що є основою для прогнозування якості пивоварної сировини.

Ключові слова: хміль, альфа-кислоти, бета-кислоти, пивоваріння, сорт, генотип, погодні умови, варіабельність, стабільність, співвідношення бета-кислот до альфа-кислот.

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