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Variability and stability of essential oil composition in Ukrainian hop varieties

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Abstract

The aim of the study was to evaluate the variation in essential oil content and composition within nine distinct Ukrainian hop varieties, with a particular focus on their genetic stability and suitability for brewing applications over 11 years of their cultivation. The hydrodistillation method (Analytica-EBC 7.10) was used to evaluate hop essential oil content and gas-liquid capillary chromatography (Analytica-EBC 7.12) to discern its qualitative composition. Variability was evaluated using statistical parameters. The essential oil content across the studied varieties spanned from 0.51 to 2.58 ml/100 g of dry hop cones. The highest content was measured in the bitter-aroma variety with a special aroma – Ruslan. The predominant essential oil components, including myrcene, caryophyllene, humulene, and farnesene, collectively constituted 70.0–84.2% of the total amount. The aroma varieties displayed myrcene content typical for European varieties (with the level up to 56.2% in the Ruslan variety). Farnesene content exhibited significant variation ranging from 0.3 to 17.6% with the highest content in Saaz-type varieties (Klon 18, Zlato Polissya, and National) and the bitter type Promin variety. Humulene content ranged from 13.2 to 32.6%. Among all studied varieties, Alta displayed the least variability for all parameters evaluated (Cv = 15.2%). This study underscores the genetic basis of essential oil composition in hops, emphasizing its potential as a biochemical criterion for identifying hop breeding varieties. The study revealed, that despite annual fluctuations, the essential oil content and composition remained within passport data declared for the variety. The findings provide valuable insight into a sustainable cultivation and optimal utilization of hops in the brewing industry.

Keywords: essential oil of hops; varieties of hops; variability; stability; biochemical criteria

1 Introduction

Hop (*Humulus lupulus* L.) is a perennial plant, the mature female fruits of which, known as hop cones, are widely used in the brewing industry. Hop cultivation is prevalent in countries with temperate climates across Asia, North America, and Europe, including Ukraine, which stands out due to its unique soil and climatic conditions (Afonso et al., 2021; Kovalev et al., 2020). Notably, hop cultivation in Ukraine is concentrated in the Polissya and Forest-Steppe zones, with the Zhytomyr region contributing up to 80% of hop cone production. This region plays a pivotal role in supplying high-quality hop for the domestic brewing industry and exportation (Kovalev et al., 2020). The development of hop production in Ukraine aligns with the preservation of centuries-old national brewing traditions, with a focus on valuable fine aroma hop varieties.

Globally, the brewing industry is the primary consumer of hop products, utilizing over 90% of worldwide hop production (Lamberti et al., 2021; Kovalev et al., 2020). Hops are renowned for contributing to the distinctive bitterness in beer, stemming from unique bitter compounds

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such as alpha and beta acids. These compounds set hops apart from other plants and also influence beer's colour, foam formation, and biological and colloidal stability during storage (Lamberti et al., 2021; Bocquet et al., 2018a).

In addition to bitterness, hops provide specific aromas, spiciness, and a subtle hop flavour to beer, which is attributed to aromatic substances found in hop resins and hop essential oils (HEO), synthesized in lupulin glands during hop cone formation and ripening (Afonso et al., 2021). The diverse composition of HEO imparts individual taste characteristics and aroma properties to beer, encompassing notes of citrus, floral, fruity, spicy, woody, herbal, and grassy fragrances (Carbone et al., 2021; Lamberti et al., 2021; Nance et al., 2011). Investigating the composition of bitter compounds and essential oils in hops is crucial for advancing brewing techniques, particularly in the context of craft brewing, where unique aroma and flavour profiles are actively pursued (Humia et al., 2019; Machado et al., 2019; Donadini et al., 2017). The nutritional features of special beers, and their proven or potential beneficial actions on one's health status and in preventing certain diseases, make hops a versatile resource with applications extending beyond brewing (Salanță et al., 2020).

The biologically active compounds in hop cones have drawn attention of the pharmaceutical industry for their antioxidant, anti-inflammatory, antitumor, and neuropharmacological properties (Paventi et al., 2020; Hrnčič et al., 2019; Karabín et al., 2016). Hop oils and resins also demonstrate antibacterial and antifungal activities (Bocquet et al., 2018b; Jirovetz et al., 2006), offering a potential natural alternative to synthetic insecticides (Aydin et al., 2017; Bedini et al., 2016; DeGrandi-Hoffman et al., 2012). Given the environmental concerns associated with synthetic pesticides, the use of hop extracts as natural insecticides holds promise (Pavela et al., 2016; Isman, 2006).

Assessing the composition of essential oils and bitter substances is essential for investigating hop properties. The quantity and composition of essential oils are influenced by various factors, including cultivation practices, fertilization methods, and weather conditions. However, the genetic characteristics of hop varieties play a predominant role in determining the quality and composition of HEO, making essential oil analysis valuable for hop variety identification and certification (Nesvadba et al., 2021; Olšovská et al., 2016).

Therefore, the evaluation of hop varieties may encompass various aspects, including yield, resistance to pests and diseases, and the stability of their biochemical characteristics under optimal cultivation and processing. This knowledge is vital in determining the suitability of hop varieties for long-term cultivation and their successful utilization in the brewing industry.

The primary aim of this study was to investigate the properties of hop essential oil, including its quantitative and qualitative composition as well as the stability of these two crucial parameters within Ukrainian hop varieties over an extended cultivation period (11 years).

2 Materials and methods

2.1 Plant material

The hops examined in this study comprised nine distinct aroma and bitter varieties of Ukrainian origin, cultivated at the "Elita-Hmyl" farm specializing in hop cultivation. The farm is situated in the Berdychiv district of the Zhytomyr region, recognized as the main centre of the Ukrainian hop production. The assessment of hop essential oil was conducted over a decade, spanning from 2011 to 2021.

2.2 Sampling

Each year, plant samples of every variety were meticulously selected at the phase of hop full technical ripeness. The sampling process involved selecting specimens from a minimum of twenty individual hop plants, typically from the middle tier of the plants. For purposes of identification and biochemical analyses, the weight of the average sample was maintained at a minimum of 1 kilogram of dried hop cones. Subsequently, these samples underwent drying at a controlled temperature of 55 °C until reaching a standard moisture content range of 9–12%. Afterward, they were hermetically sealed in bags crafted from multi-layer food-grade film, featuring an aluminium foil base, and stored under refrigeration conditions until the time of testing.

The study encompassed Ukrainian hop varieties classified into four distinct types based on their aromatic and bitter profiles that the most widespread in Ukraine:

- **Fine Aroma Varieties.** The varieties of the Saaz type, characterized by a delicate hop aroma: Klon 18 (registration in 1969) and Zlato Polissya (registration in 2002), with alpha-acid contents ranging from 3.0–5.5%, and Slovianka (registration in 1995) variety, with alpha-acid content of 4.5–7.5%.
- **Aroma Varieties.** These varieties are endowed with a distinctive hop aroma: National (registration in 2004) and Zagrava (registration in 1998), featuring alpha-acid content ranging from 5.0–9.0%.
- **Bitter Varieties.** This category includes varieties distinguished by a pronounced hop aroma: Alta (registration in 1996) and Promin (registration in 2001), characterized by alpha-acid levels ranging from 8.0–13.0%.

- **Bitter-Aromatic Varieties with a special aroma.** These varieties, exemplified by Ruslan (registration in 2003) and Xantha (registration in 2008), are known for their unique fruity-floral, citrus, and spicy tones, adding a special aroma to beers. Alpha-acid content in these varieties falls within the range of 8.0–11.0%.

The quantitative and qualitative data, encompassing the amount and composition of essential oil, for each of the studied hop varieties is detailed in Table 1 following their passport data.

2.3 *Content of Hop Essential Oil*

The content of hop essential oil was determined using a steam distillation technique following the procedure prescribed in Analytica-EBC 7.10 (2002). Briefly, 50 g of ground hops were weighed into a 2-l flask, and 1 l of distilled water was added. The flask was then attached to the distillation apparatus, and the trap was filled with water. Distillation was carried out for 3 h. The volume of oil was measured and reported as ml per 100 g of dry matter to two decimal places.

2.4 *Chemical composition of essential oil of hops by GC–FID*

The essential oil content was analysed by gas chromatography (GC). Four chosen components (myrcene, humulene, caryophyllene, and farnesene) were identified and quantified using a capillary gas chromatograph ("Crystall-2000M", Russia) equipped with a flame ionization detector (FID), following the official method in Analytica-EBC 7.12 (2006). Essential oils isolated from hop material were separated into individual compounds by GC on 50–60 m columns (Restek Stabilwax®, USA) using 20–30 cm^3 of nitrogen as the carrier gas. The temperature program was as follows: 60 °C (1 min hold), 60–190 °C (4 °C/min, 1 min hold), and 190–220 °C (40 min hold). The temperature of the injector was 200 °C, the volume of the injection was 0.3–0.4 µl, and the temperature of the detector was 250 °C. The results were expressed as the relative % of a particular compound in the total essential oil content. Processing of chromatographic results and chromatograph control were executed using computer software, ensuring the accuracy and reliability of the analytical findings.

Table 1 *The total amount of essential oil and its qualitative composition in the dried hop cones of Ukrainian varieties (passport data)*

Variety	The essential oil total content, ml/100 g of dried hope cones	% in the essential oil total content			
		Myrcene $C_{10}H_{15}$	Humulene $C_{15}H_{24}$	Caryophyllene $C_{15}H_{24}$	Farnesene $C_{15}H_{24}$
Fine Aromat Varieties					
Klon 18	0.4–0.8	20.0–35.0	25.0–35.0	8.0–12.0	15.0–20.0
Zlato Polissya	0.4–0.9	20.0–40.0	25.0–35.0	6.0–10.0	14.0–20.0
Slovianka	1.3–2.0	30.0–50.0	9.0–15.0	4.0–8.0	13.0–18.0
Aroma Varieties					
National	0.8–1.2	30.0–40.0	10.0–20.0	8.0–10.0	14.0–18.0
Zagrava	1.4–2.5	30.0–45.0	15.0–20.0	5.0–8.0	10.0–15.0
Bitter Varieties					
Alta	1.0–2.0	35.0–50.0	25.0–30.0	8.0–12.0	≤ 1
Promin	1.2–2.5	40.0–60.0	15.0–20.0	5.0–7.0	15.0–20.0
Bitter-Aroma Varieties with a special aroma					
Ruslan	2.0–3.0	40.0–60.0	15.0–20.0	5.0–8.0	≤ 1
Xantha	1.0–1.5	30.0–40.0	25.0–35.0	8.0–12.0	≤ 1

2.5 *Statistical Analysis*

To assess the variability in the accumulation of total essential oil content and its composition in hops, several statistical parameters were employed. These are crucial for understanding the fluctuations and trends in the essential oil characteristics over the years of research: the mean value (X) and the mean square deviation (SD), and the range (amplitude) of variation (R). The latter signifies the difference between the upper and lower limits of the characteristic being examined ($R = V_{max} – V_{min}$). It helps to assess the overall spread of values within the dataset. Since the research involved various hop varieties, each characterized by different values of the studied traits, the coefficient of variability or variation (*Cv*) was also employed for comparing statistical parameters. The *Cv* is especially useful when dealing with characteristics that have different levels and units of measurement across various hop varieties and years of study. It provides a more visually informative and biologically meaningful way to compare the variability of statistical parameters related to the content and composition of essential oil. The Coefficient of Variability (*Cv*) is calculated as the ratio of the mean square deviation expressed as a percentage to the average value of the characteristic content observed in the evaluated hop cone samples ($Cv = SD / X$). Typically, when the *Cv* is greater than 20%, it suggests a substantial degree of variability in the characteristic being studied (Blyznyuchenko, 2003). This statistical approach allows for a more nuanced and comparative assessment of essential oil characteristics across different hop varieties and throughout the research duration.

3 Results and discussion

The synthesis and accumulation of essential oil in hop cones predominantly occur within the lupulin glands as they progress through formation and ripening, reaching maximum levels at physiological ripeness. Table 2 provides detailed findings regarding the total accumulation of essential oil and its compositional variations over the 2011–2021 period.

The essential oil components in Ukrainian hop varieties are primarily hydrocarbons, including myrcene (monoterpenoid), caryophyllene, humulene, and farnesene (sesquiterpenoids), collectively constituting about 70.0% to 84.2% of the total essential oil content. The average essential oil content varies from 0.51 ml/100 g (Klon 18 variety) to 2.58 ml/100 g (Ruslan variety). The years 2011–2012 and 2017 showed the highest recorded essential oil amounts, possibly due to favourable weather conditions (not analysed). Figure 1 visually illustrates the variability in essential oil content across different Ukrainian hop varieties over the 11-year period.

Among fine aroma hop varieties, Klon 18 consistently exhibited the lowest essential oil content (0.40 to 0.70 ml/100 g), similar to the Zlato Polissya variety (0.43 to 0.78 ml/100 g), aligning with their respective lower limits declared in passport data (Table 1). In contrast, the Slovianka variety consistently showed higher essential oil content, nearing its upper limit, with an average content of 1.61 ml/100 g.

Within the aroma hop varieties, the Zagrava variety displayed the highest essential oil content at 2.82 ml/100 g. Among the bitter and bitter-aroma hop varieties with unique aromas, the Ruslan variety consistently exhibited high essential oil content, reaching up to 3.20 ml/100 g (Figure 1).

The data presented in Figure 1 indicate a noticeable trend: essential oil content tends to decrease over the years for varieties like Klon 18, Zlato Polissya, Alta, and Xantha, as their results consistently approach the lower limits. In contrast, the Zagrava and Ruslan varieties exhibit an increase in essential oil content, closer to the upper limits specified in passport data for oil content.

Additionally, the study revealed significant qualitative differences in hop essential oil composition among varieties. Chromatograms representing essential oils from Alta and Klon 18 (Figure 2 and Figure 3) illustrate a clear differentiation, particularly between the non-farnesene type found in Alta, Xantha, and Ruslan varieties and the farnesene type prevalent in Klon 18 and other examined hop varieties.

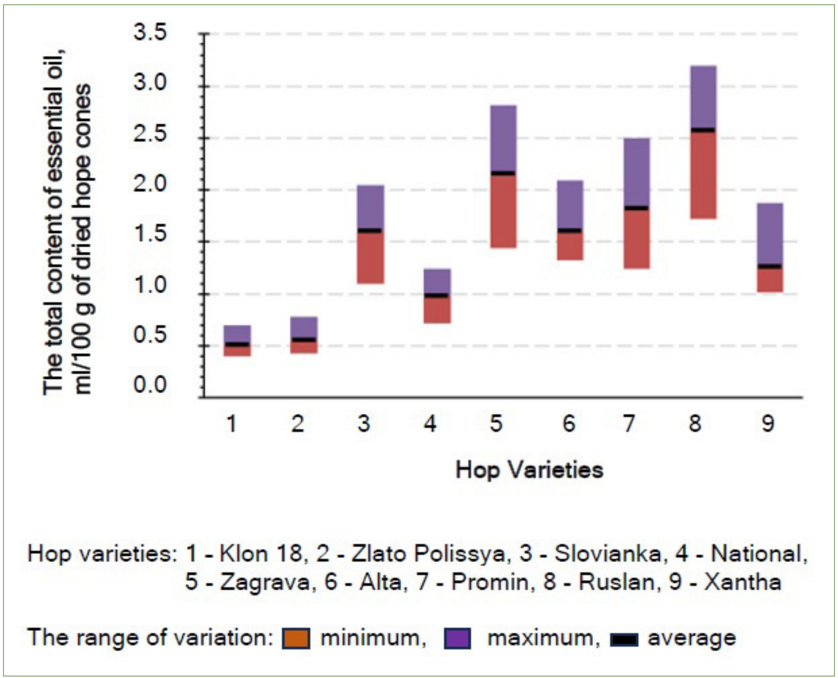

Figure 1 *Essential oil content variability in Ukrainian Hop varieties (2011–2021; n = 3, P ≥ 0.95)*

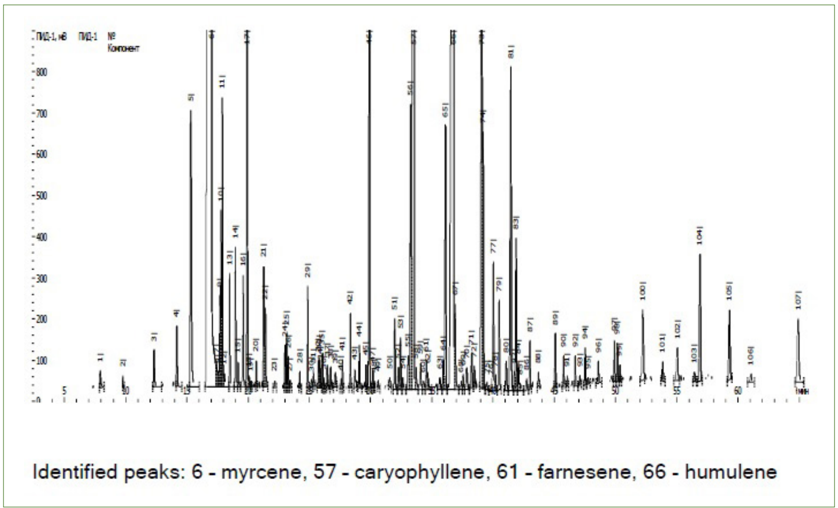

Figure 2 *Chromatogram of the essential oil composition of the Alta variety*

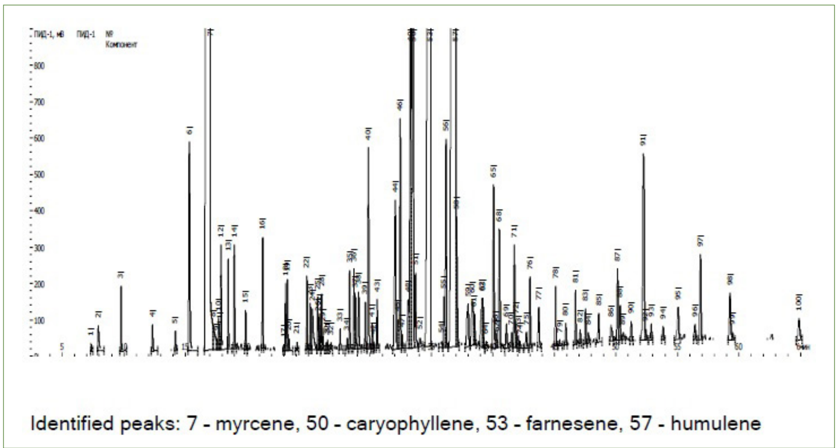

Figure 3 *Chromatogram of the essential oil composition of the Klon 18 variety*

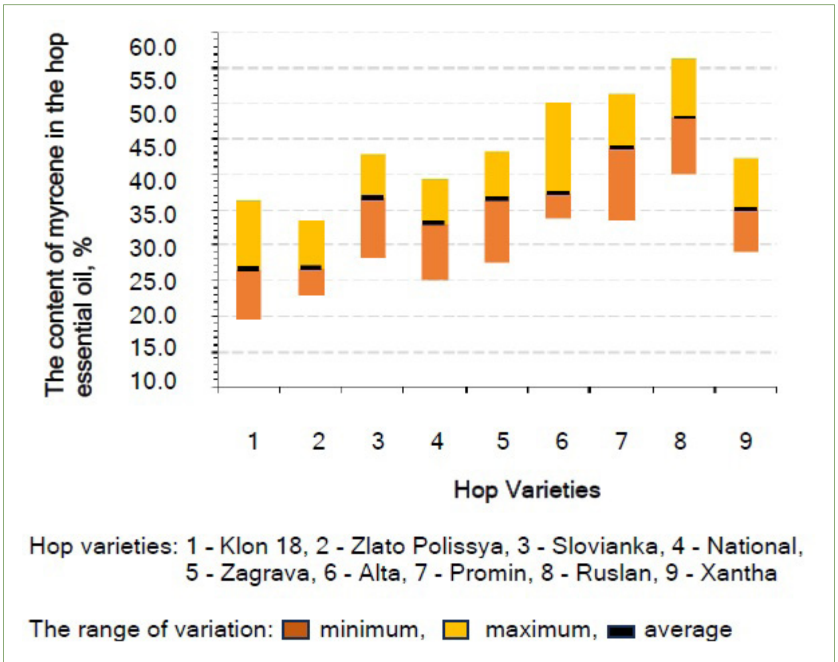

Figure 4 *Myrcene content variability in Ukrainian hop varieties (2011–2021; n = 3, P ≥ 0.95)*

Myrcene, a predominant component among monoterpenes, is a significant part of hop essential oil, varying between hop varieties. In American hop varieties like Cascade, Amarillo, Citra, and Simcoe, myrcene content typically ranges from 50% to 70% (Ting et al., 2017). European hop varieties, on the other hand, exhibit lower myrcene content, falling within the 20% to 40% range (Nesvadba et al., 2021). Myrcene contributes to a range of aroma properties, often described as green and hoppy with hints of pine and citrus, influencing modern brewing techniques like "dry hopping" (Hauser et al., 2019; Rettberg et al., 2018; Nance et al., 2011). Figure 4 displays the content and variability of myrcene in Ukrainian hop varieties studied.

The Ukrainian hop varieties categorized as aromatic display varying myrcene compositions within their essential oils. The content ranges from 19.5% in Klon 18 to 43.0% in Zagrava, aligning with the typical range seen in European hop varieties. Among the fine-aroma hop varieties, Zlato Polissya and Klon 18 consistently show lower myrcene content, around 26.6% and 26.8%, respectively. In contrast, Zagrava's essential oil consistently exhibits the highest myrcene content, averaging at 36.5%. Promin, among the bitter hop varieties, has the highest myrcene content, reaching 43.7%. However, Ukrainian varieties do not reach the myrcene levels of up to 70% found in some American hop varieties (Ting et al., 2017).

Humulene, another notable component of HEO, is typically associated with European fine aroma hop varieties and is recognized for its spicy and grassy aroma (Iannone et al.,

Table 2 *Total essential oil amount and composition in Ukrainian hop varieties (2011–2021; n = 3, P ≥ 0.95; mean ± SD)*

Variety	The essential oil total content, mL/100 g of dried hope cones	% in the essential oil total content			
		Myrcene	Humulene	Caryophyllene	Farnesene
Fine Aroma Varieties					
Klon 18 (control for the aroma varieties)	0.51±0.11	26.6±3.8	25.1±4.9	8.3±1.4	16.7±2.2
Zlato Polissya	0.55±0.12	26.8±3.8	24.7±3.8	8.1±0.9	15.6±2.2
Slovianka	1.61±0.26	36.7±5.9	13.2±2.6	7.5±1.0	14.3±2.0
Aroma Varieties					
National	0.97±0.17	33.0±6.3	16.4±2.9	8.4±1.2	17.6±2.0
Zagrava	2.16±0.39	36.5±6.1	19.4±2.7	7.3±1.3	14.2±2.1
Bitter Varieties					
Alta (control for the bitter varieties)	1.61±0.24	35.6±2.4	29.8±1.8	10.0±1.0	0.3±0.1
Promin	1.83±0.36	43.7±6.7	18.3±2.5	6.9±1.2	15.3±1.8
Bitter-Aroma Varieties with a special aroma					
Ruslan	2.58±0.40	47.9±6.6	16.7±2.3	7.0±0.9	0.8±0.1
Xantha	1.26±0.25	35.1±5.9	25.9±4.1	11.2±1.7	0.7±0.1

2022). Ukrainian hop varieties exhibit relatively high humulene content, ranging from 13.2% to 32.6%. The highest levels are found in Klon 18, Zlato Polissya, Alta, and Xantha varieties, making them distinctive for their delicate aromas (Figure 5). The first two varieties (Klon 18 and Zlato Polissya) also display the lowest content of myrcene in their essential oil and a substantial proportion of farnesene (as demonstrated below).

Caryophyllene, known for its woody, peppery, spicy, and earthy aromas, differs from humulene in taste and aroma characteristics (Rutnik et al., 2022a; Carbone et al., 2021; Rettberg et al., 2018; Nance et al., 2011). Caryophyllene is less prominent in European hop varieties but is found in English and American varieties such as Golding, Northdown, and Mount Hood (Ting et al., 2017). In Ukrainian hop varieties studied the content of caryophyllene falls within the range of 5.6% to 12.8% (Figure 6), a range characteristic of European varieties as well (Nesvadba, 2012).

Farnesene, contributing flavours reminiscent of green apple, as well as floral, citrus, and fruity aromas, is a distinctive feature of noble hop varieties (Nance et al., 2011). While it typically comprises less than 1% in European and American hop varieties (Rutnik et al., 2022b; Nance et al., 2011), farnesene plays a more significant role in European fine-aroma and aroma

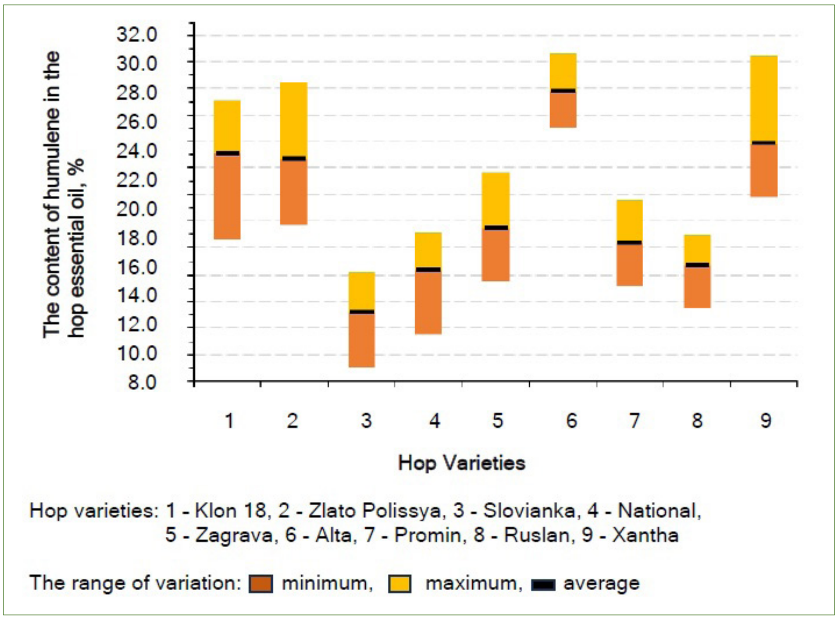

Figure 5 *Humulene content variability in Ukrainian hop varieties (2011–2021; n = 3, P ≥ 0.95)*

Ukrainian hop varieties, often exceeding 20% (Rutnik et al., 2022b; Nesvadba et al., 2020; Protsenko et al., 2020). Figure 7 provides insights into farnesene content and variability in Ukrainian hop varieties.

Ukrainian hop varieties with high farnesene content (12–20%) fall under the fine-aroma and aroma categories. Notably, Promin, a bitter variety, also contains a significant amount of farnesene, ranging from 13.3% to 18.2%. This unique composition contributes to Promin's high brewing qualities, despite being categorized as a bitter hop variety with a ratio of beta- to alpha-acids (from 0.5 to 0.6) and the low content of cohumulone in alpha acids (26–30%) (Protsenko et al., 2020). The National variety, with farnesene content ranging from 14.6% to 20.3%, is prized for its technological advantages, whereas Slovianka variety, belonging to the Saaz type, stands out as a valuable and fine aroma hop variety for brewing (Bober et al., 2020; Protsenko et al., 2020). Meanwhile, Alta, Ruslan, and Xantha hop varieties have minimal farnesene content, below 1.0% in their essential oil compositions.

The analysis of essential oil content and its components across the studied Ukrainian hop varieties reveals modest to moderate ranges of variation, as indicated in Table 3.

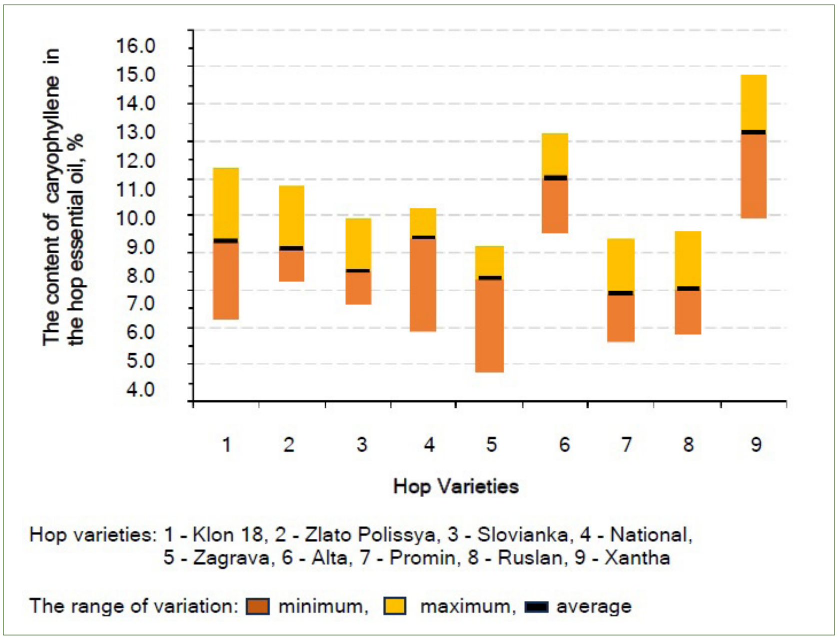

Figure 6 *Caryophyllene content variability in Ukrainian hop varieties (2011–2021; n = 3, P ≥ 0.95)*

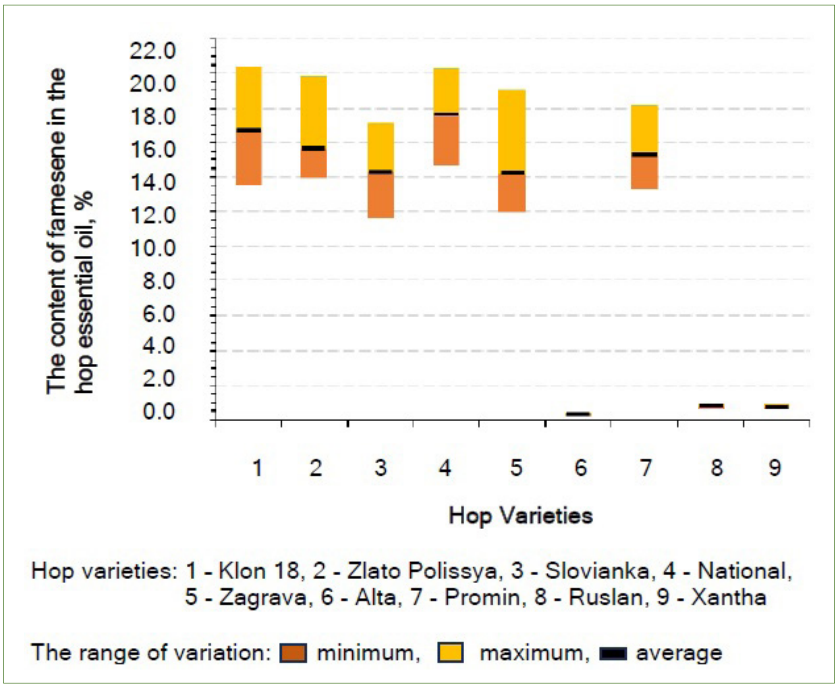

Figure 7 *Farnesene content variability in Ukrainian hop varieties (2011–2021; n = 3, P ≥ 0.95)*

Among the nine Ukrainian hop varieties examined, the early-ripening Alta variety exhibited the lowest variability in essential oil accumulation, with a coefficient of variation (*Cv*) of 15.15%, still considered moderate. The Slovianka, National, Zagrava, Promin, Ruslan, and Xantha varieties showed *Cv* values for essential oil content ranging from 15.52% to 19.72%, also within the moderate range. However, Klon 18 and Zlato Polissya displayed a slightly higher relative variability in essential oil content, with *Cv* values of 21.19% and 22.30%, respectively, just surpassing the 20% threshold for categorization.

The *Cv* values for myrcene in all varieties, except Alta, ranged from 13.8% to 18.9%, signifying moderate variability. Alta stood out not only with the lowest variability in myrcene but also in humulene content, with *Cv* values of 6.08% and 6.03%, respectively.

Table 3 *Coefficient of variability of essential oil and its components in Ukrainian hop varieties (2011–2021)*

Variety	Coefficient of variability (*Cv*), %				
	The essential oil total content	Myrcene	Humulene	Caryophyllene	Farnesene
Fine Aroma Varieties					
Klon 18	21.15	14.24	19.67	17.17	13.30
Zlato Polissya	22.25	14.00	15.29	11.10	14.10
Slovianka	17.17	16.30	19.36	13.31	13.90
Aroma Varieties					
National	18.23	18.90	17.65	14.81	11.68
Zagrava	18.04	16.81	13.72	17.81	13.91
Bitter Varieties					
Alta	15.15	6.80	6.03	9.76	17.09
Promin	19.20	15.39	13.47	17.59	11.98
Bitter-Aroma Varieties with a special aroma					
Ruslan	15.60	13.80	13.66	13.70	15.80
Xantha	19.90	17.04	15.92	15.28	14.08

The *Cv* values for humulene fluctuate from 13.47% to 19.67%, signifying a moderate degree of variability for all varieties studied.

The *Cv* values for caryophyllene, except for Alta, spanned from 11.10% to 17.59%, indicating a moderate level of variability. Remarkably, Alta exhibited the lowest relative variability in caryophyllene content among the studied varieties, with a *Cv* of 9.76%.

Hop varieties with high farnesene content (Klon 18, Zlato Polissya, Slovianka, National, Zagrava, and Promin) showed an average variability in this component, ranging from 11.68% to 14.10%. In contrast, varieties with less than 1% farnesene (Alta, Ruslan, Xantha) exhibited greater variability, ranging from 14.08% to 17.09%, primarily due to their very low absolute farnesene content.

In conclusion, the study highlights the Alta hop variety as the most consistent performer in terms of essential oil content and composition over the ten-year research period. Additionally, it's noteworthy that essential oil content variations across all varieties remained within the passport data range specified when these hop varieties were created, confirming their reliability for brewing applications. These passport data were established at different times, with Klon 18 dating back to 1969 and the remaining varieties developed between 1996 and 2008.

4 Discussion

The qualitative composition of hop essential oil is primarily determined by the hop variety itself, reflecting its genetic foundation (Olšovská et al., 2016). However, the quantitative content of essential oil can exhibit variations influenced by various agricultural practices, such as cultivation techniques, fertilizer applications, and prevailing weather conditions. Among these factors, temperature and precipitation patterns during the crucial phases of bitter substances and essential oil synthesis play significant roles in shaping the stability of hop variety characteristics.

Rising temperatures and a lack of precipitation, particularly during the essential oil synthesis phase, are key environmental parameters that can impact the stability of hop varieties. In recent years, increased temperatures and reduced precipitation have adversely affected hop cultivation (Krofta et al., 2019; Nesvadba et al., 2021). Acknowledging this challenge, a research project titled *"Application of New Hop Varieties and Genotypes Resistant to Drought in Hop Growing and Beer Brewing"* (Nesvadba et al., 2021) was initiated in the Czech Republic in 2021 to explore and utilize new hop genotypes that exhibit resistance to drought conditions, reflecting the industry's commitment to adapting to changing environmental conditions while ensuring stable beer quality.

As reported by Czech scientists (Nesvadba et al., 2021) the fine aroma hop varieties of the Saaz type, such as Saaz, Saaz Brilliant, Saaz Late, Saaz Shine, and Saaz Comfort, exhibit notably low levels of essential oil content, ranging from 0.43 to 0.83 ml/100 g of dry hops. This aligns with the outcomes of our own research, which revealed the lowest oil content in hop varieties of the Saaz type, specifically Klon 18 and Zlato Polissya, where oil content ranged from 0.40 to 0.78 ml/100 g of dry hop cones. The average values we obtained for these varieties, 0.51 and 0.55 ml/100 g of dry hop cones, respectively, closely approach the lower bounds of the values reported in their passport data, which indicate an oil content range of 0.4–0.9 ml/100 g.

Similarly, according to the Atlas of Czech hop varieties (Nesvadba et al., 2012), the essential oil content of Saaz varieties is reported to range from 0.4 to 0.8 ml/100 g of dry hops, consistent with the observations made decade later (Nesvadba et al., 2021). Furthermore, these Czech hop varieties are characterized by their high farnesene content, exceeding 20%, making them highly coveted among brewers for their aroma properties. Interestingly, these varieties also tend to have lower myrcene content, which aligns with our research findings.

While it is clear that the Czech aroma hop varieties like Bor, Sládek, Premiant, Harmonie, and Bohemie differ significantly from their Ukrainian counterparts in terms of essential oil composition, particularly in the case of farnesene content, other Ukrainian varieties like Slovianka, National, and Zagrava also display distinctive characteristics that set them apart. Notably, these Ukrainian varieties possess an average farnesene content ranging from 14.2% to 17.6%, making them stand out due to their particularly valuable farnesene component. In contrast, the Czech aroma hop varieties studied by Nesvadba et al. (2021) exhibit farnesene content of up to 1.5%. This pronounced difference highlights the unique aroma profiles and desirability of these Ukrainian varieties among brewers seeking specific flavour and aroma attributes in their beer.

Furthermore, it's noteworthy that some Ukrainian hop varieties, despite being classified as aroma or fine aroma hops, can be on par with Czech bitter hop varieties in terms of essential oil content and composition. For instance, Ukrainian aroma varieties like Ruslan and Xantha boast substantial essential oil content, ranging from 1.26 to 2.58 ml/100 g of dry hop cones, and a higher myrcene content (ranging from 35.10% to 47.90%). This places them in a unique category, as they surpass Czech varieties of a similar type, such as Kazbek and Mimosa, which exhibit lower essential oil content (ranging from 0.67 to 1.13 ml/100 g of dry hops) and comparatively less myrcene content (ranging from 30.55% to 34.93%) (Nesvadba et al., 2021).

The study reveals that the quantitative content of essential oil in certain hop varieties has changed over the course of their cultivation, likely due to the influence of weather conditions during critical phases of hop cone development. However, the impact of climate change on brewing qualities in Ukrainian hops remains inadequately explored and requires further research.

Future investigations will focus on assessing the influence of agro-climatic factors on brewing qualities in hops, particularly in aroma and bitter varieties, to better understand the relationship between various weather parameters and the commercial, as well as technological, quality indicators in this crop.

5 Conclusion

Significant variability in essential oil content, crucial for brewing, was observed across nine Ukrainian hop varieties, with contents ranging from 0.51 to 2.58 ml/100 g of dry hop cones. Ruslan, a bitter-aroma variety, exhibited the highest essential oil content (1.72 to 3.20 ml/100 g), while gentle aroma Saaz type varieties (Klon 18 and Zlato Polissya) had the lowest content (0.40 to 0.78 ml/100 g). Zagrava, among aroma varieties, stood out with 2.82 ml/100 g.

A significant portion of hop essential oil in these varieties consists of hydrocarbons, mainly myrcene and sesquiterpenoids (caryophyllene, humulene, and farnesene), collectively making up 70.0–84.2% of the total essential oil content.

Despite annual variations, the essential oil content and composition remained within passport data ranges, with moderate average variability. The Alta variety exhibited the least variability, with a coefficient of variation (Cv) of 15.2% in essential oil content and notably lower the *Cv* values for essential oil components, indicating their higher stability.

Our findings underscore that the qualitative composition of essential oil components and their relative ratios within hop cones are genetically determined, independent of the variety's chemical composition or group affiliation. This inherent genetic control at the genome level makes these characteristics an invaluable biochemical criterion for distinguishing and identifying hop breeding varieties.

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