Alicia Munoz-Insa, Bernhard Ramsauer and Mark Zunkel

Comparative study of packaged Citra® and Perle pellet storage stability over four years

This study evaluated the long-term storage stability of packaged T90 pellets of Citra® and Perle over 50 months under cold (3 °C) and ambient (25 °C) conditions without oxygen. Changes in α-acids, β-acids, Hop Storage Index (HSI), total oil content, and selected volatile compounds were evaluated descriptively. Cold-stored Citra® retained approximately 97 % and cold-stored Perle approximately 92 % of their initial HPLC-determined α-acid concentrations, whereas losses of approximately 37 % and 50 %, respectively, were observed at 25 °C. HSI changed moderately at 3 °C but increased markedly at 25 °C. Total oil content decreased in all samples, with larger losses at 25 °C. Individual volatile compounds showed compound- and cultivar-dependent changes; myrcene and several esters decreased, whereas other compounds remained comparatively stable or increased from low initial concentrations. Because no sensory evaluation or brewing trials were conducted, the potential effects of these compositional changes on aroma perception, beer quality, and brewing performance remain to be established. Overall, the results indicate that low-temperature, no oxygen present during storage greatly slows hop aging and can preserve both bittering potential and much of the aroma-relevant fraction for several years. The results provide a descriptive long-term dataset for the two investigated hop cultivars and storage conditions and provide practical guidance for brewers to interpret HSI in a variety-specific context and adjust hopping rates for older lots.

Descriptors: Hop storage stability, Citra®, Perle, Hop Storage Index, α-acids, hop aroma compounds

1 Introduction

A-acids and essential oils are the primary constituents that determine the brewing value of hops. Consequently, hop producers invest considerable effort in cultivation and harvesting practices aimed at maximizing the concentration of these compounds. Once hops are harvested, however, degradation processes begin immediately. The principal drivers of hop aging are oxygen exposure and temperature, both of which contribute to the chemical deterioration of α-acids and essential oils, thereby reducing the quality of the raw material supplied to brewers [1].

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Authors

Dr. Alicia Munoz-Insa (ORCID ID: 0009-0009-2172-7392), BarthHaas GmbH, Freiligrathstraße 7-9, 90482 Nürnberg; Dr. Bernhard Ramsauer, Hopfenveredlung St. Johann GmbH, Mainburger Str. 15, 93358 Train-St. Johann, Bernhard.Ramsauer@hopfenveredlung.de; Mark Zunkel (ORCID ID: 0009-0006-9458-7923), BarthHaas GmbH, Freiligrathstraße 7-9, 90482 Nürnberg, mark.zunkel@barthhaas.com; corresponding author: alicia.munoz@barthhaas.com

This study focuses on two of the most widely cultivated aroma hop varieties worldwide, Perle and Citra®, and examines their behavior of valuable bittering acids as well as hop oil composition during storage. Meaningful evaluation of hop storage requires a clear definition of storage conditions and handling procedures. The present investigation is limited to hops stored under commercially relevant conditions in oxygen-barrier hop packaging with no or very low residual oxygen levels.

From harvest onward, the chemical composition of hops may continue to change during post-harvest handling, processing, and storage. Depending on oxygen availability, temperature, and other storage conditions, α-acids and β-acids may undergo oxidative transformations, including the formation of humulinones from α-acids and hulupones from β-acids [1]. At the same time, the volatile fraction may change through losses and transformations of individual hop oil compounds. Such compositional changes may have sensory implications, although these cannot be inferred directly from chemical analysis alone.

Following cold storage, the raw hops will be produced into pellets following the process of bale breaking, blending, removal of foreign material, milling, homogenization of the resulting powder, and pellet pressing. After this process, the pellets are packed in oxygen-barrier foils under an inert atmosphere, typically nitrogen (N_2) or carbon dioxide (CO_2) or a mixture of both, reducing oxygen levels to below 5 %. However, an inert atmosphere minimizes rather than eliminates chemical changes during storage, and reactions involving hop constituents may continue despite the very low oxygen availability. Over the subsequent weeks, residual oxygen within the package is further consumed through oxidative

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processes, resulting in near-zero oxygen concentrations in the sealed packages.

In addition to oxidative degradation, α-acids may undergo isomerization to iso-α-acids during hop storage, including under inert conditions [2, 3]. This pathway is particularly relevant when interpreting changes in α-acid concentrations and the Hop Storage Index (HSI), since iso-α-acids absorb at 275 nm and may therefore contribute to an increase in HSI. Consequently, an increase in HSI does not necessarily reflect oxidative degradation alone. A further potential transformation pathway is enzymatic α-acid oxidation. Menary et al. demonstrated α-acid-oxidizing activity in hop bracts and bracteoles following damage to the lupulin glands; the reaction required oxygen and Mn^{2+} and increased with temperature [4]. However, as these observations were obtained from hop-cone tissues and enzyme preparations, the relevance of this pathway to long-term storage of kilned, pelletized hops under low-oxygen conditions remains uncertain.

This paper presents a comprehensive analysis of the aging behavior of Citra® and Perle hops to elucidate the effects of storage conditions and variety-specific characteristics on chemical degradation and the Hop Storage Index (HSI). The objective is to enhance brewers' understanding of hop freshness, support more accurate assessment of hop quality, and contribute to the development of best practices for hop storage and utilization.

2 Materials and methods

Hop Materials: T90 hop pellets of two varieties were used: Citra® (U.S., high-alpha, high-oil aroma variety) and Perle (Germany, widely cultivated aroma/dual-purpose variety) both from the 2018 crop year. Hops were pelletized within 3 months after harvest. Pellets were packaged in laminated foils with an aluminum layer as a barrier against diffusion of oxygen under inert gas (N_2 / CO_2). The residual oxygen content in the foil packs was less than 2 % by volume. The samples were stored at two temperatures: cold storage at 3 °C (37 °F) and ambient-temperature storage at 25 °C (77 °F) for 50 months. The storage time was selected to simulate long-term storage that might occur due to oversupply or strategic reserves as in a brewery cold storage or without cold storage.

The cold- and ambient-storage treatments consisted of separate packages originating from the same respective hop lot for each variety. At regular intervals samples were taken from sealed foil packs (opened immediately prior to analysis) and the following analyses were performed, in line with EBC (European Brewery Convention) and ASBC methods:

- Alpha and B-Acids: Measured by three methods for cross-validation.
  - ASBC Hops–6A/12: Spectrophotometric ultraviolet (UV) absorbance method for hop bitter substances, providing % α-acids, % β-acids, and Hop Storage Index (HSI).
  - EBC 7.5 (Lead Conductance Value): Conductometric titration method for bitter substances in hops/hop products providing % alpha acids.
  - EBC 7.7 (HPLC): High-Performance Liquid Chromatography method for separation and quantification of individual alpha (%) and β-acids (%) in hops.
- Total Hop Oils: Measured by steam distillation (EBC 7.10) to determine total oil volume, expressed in mL/100 g of hops.
- Essential Oil Composition: Extracted by means of a water steam distillation and quantified using gas chromatography with flame ionization detection (GC-FID) (inhouse method). A total of 21 individual volatile compounds were measured, including major terpenes (myrcene, humulene, caryophyllene, farnesene, etc.), ester compounds, oxygenated alcohols/ketones (e.g. linalool, geraniol, 2-undecanone), and terpene oxidation products (e.g. humulene epoxides) expressed in mg/100 g of hops.

The data was compiled to compare the degradation patterns of alpha acids, β-acids, and oils between Citra® and Perle under cold vs. ambient storage.

Analytical uncertainty and data treatment: At each sampling time point, one independently sealed bag per cultivar and storage condition was opened and used for analysis. A new, previously unopened bag was used at each time point; bags were not resealed or reused for subsequent measurements. Each sample was analyzed in duplicate (n = 2 analytical determinations), and results are reported as the mean ± standard deviation of the duplicate measurements. Small differences, particularly for compounds occurring at low concentrations, were interpreted with caution when they were comparable to the analytical uncertainty of the respective method.

Relative changes between the initial value (M0 = month 0) and the value after 50 months (M50 = month 50) were calculated as: Δrel (%) = [(M50 – M0) / M0] × 100. Accordingly, negative values indicate a decrease and positive values an increase.

3 Results

3.1 Bitter acids and hop storage index

The effects of long-term storage were evaluated by comparing the initial (M0) and final (M50) analytical values of Citra® and Perle pellets under cold and ambient storage. Separate packages from the same respective hop lot were assigned to each storage condition. Therefore, small differences between the M0 values reflect the individual initial measurements of these samples rather than a common baseline applied to both storage series.

Storage temperature had a dramatic effect on alpha acid stability (Table 1). In cold storage (3 °C), alpha acids in both varieties degraded slowly. Citra® lost only about 2.8 % of its HPLC-measured alpha acids over 50 months (retaining ~97 % of the initial alpha content). Perle cold-stored lost around 7.8 % of its alpha in the same period. These losses correspond to an extremely low degradation rate of roughly –0.02 % (Citra®) and –0.009 % (Perle) per month at 3 °C, practically negligible from a brewer's perspective (Figure 1). By contrast, at ambient temperature (25 °C) α-acids showed a pronounced decrease: Citra® lost about 37 % of its alpha over 50

Table 1 **Initial (M0 = month 0) and final (M50 = month 50) analytical values for Perle and Citra® T90 pellets stored at 3 °C (cold) and 25 °C (ambient) for 50 months. Relative change (Δ %rel) was calculated as (M50 – M0)/M0 × 100; negative values indicate decreases and positive values indicate increases**

	Perle						Citra®					
	cold M0	cold M50	cold Δ (%rel)	ambient M0	ambient M50	ambient Δ (%rel)	cold M0	cold M50	cold Δ (%rel)	ambient M0	ambient M50	ambient Δ (%rel)
Oil content (mL/100g)	1.31±0.13	1.10±0.11	–16.0 %	1.20±0.11	0.90±0.09	–25.0 %	2.33±0.09	2.15±0.21	–7.7 %	2.23±0.21	1.50±0.15	–32.7 %
α-acids % w/w (EBC 7.5)	6.3±0.14	6.0±0.13	–4.8 %	6.1±0.14	3.9±0.09	–36.1 %	12.3±0.27	12.0±0.27	–2.4 %	12.3±0.27	8.6±0.19	–30.1 %
α-acids % w/w (ASBC)	5.7±0.19	5.3±0.18	–7.0 %	5.4±0.18	2.2±0.07	–59.3 %	12.1±0.07	11.5±0.39	–5.0 %	12.2±0.39	5.8±0.19	–52.5 %
β-acids % w/w (ASBC)	3.7±0.30	3.7±0.30	0.0 %	3.7±0.30	3.7±0.30	0.0 %	3.2±0.30	3.1±0.25	–3.1 %	3.2±0.25	3.5±0.28	9.4 %
HSI	0.370± 0.012	0.391± 0.013	5.7 %	0.387± 0.013	0.695± 0.023	79.6 %	0.291± 0.023	0.316± 0.011	8.6 %	0.295± 0.011	0.638± 0.021	116.3 %
α-acids % w/w (EBC 7.7)	5.1±0.14	4.7±0.14	–7.8 %	4.9±0.14	2.4±0.07	–50.5 %	10.9±0.07	10.6±0.31	–2.8 %	11.0±0.31	6.9±0.20	–37.0 %
β-acids % w/w (EBC 7.7)	3.2±0.09	3.2±0.09	0.3 %	3.2±0.09	3.2±0.09	0.0 %	2.7±0.09	2.8±0.08	2.9 %	2.8±0.08	1.8±0.05	–34.5 %

months, while Perle lost roughly 50 % of alpha content. The implied degradation rates of α-acids at ambient are -0.11 % (Citra®) and -0.08 % (Perle) per month, an order of magnitude faster than in cold storage. These findings confirm that cold storage preserves α-acids. Practically, a brewer holding Citra® hops for 3+ years at cold temperatures will still get almost the full bittering value, whereas the same hops at room temperature could lose a third or more of their bitterness potential. Perle showed a similar trend; although it started with lower alpha percentage, it was even more sensitive to ambient storage (half of the alpha degraded in ~3 years at 25 °C).

Notably, different analytical techniques captured alpha decay similarly. The EBC 7.5 (lead conductance) method showed ~2–5 % alpha loss in cold vs ~30–36 % loss at ambient temperature for both varieties, and the ASBC 6A UV method (which also responds to oxidized alpha products) indicated slightly higher losses, especially at ambient temperature (e.g. ~5–7 % cold vs ~52–59 % ambient). These differences are expected as the UV method registers some oxidized alpha acids as lost bitterness, whereas HPLC measures the remaining intact alpha compounds.

The β-acid results depended on the analytical method. ASBC values showed little change for Perle and small changes for Citra®, whereas the HPLC results showed a decrease from 2.8 to 1.8 % in ambient-stored Citra®. B-acids are known to oxidize more slowly [5–8] and are not much utilized by brewers for bitterness. Their stability means aged hops still contain β-acids that could oxidize into bitterness over much longer periods (a factor not significant within 3 years given inert packaging).

HSI is an indirect measure of changes in hop bitter substances during aging. It is determined spectrophotometrically from the ratio of absorbance at 275 nm, associated with aged or transformed bitter compounds, to absorbance at 325 nm, associated predominantly with fresh hop bitter compounds (HSI = A_{275}/A_{325}). In the present study, HSI increased only moderately under cold storage but showed

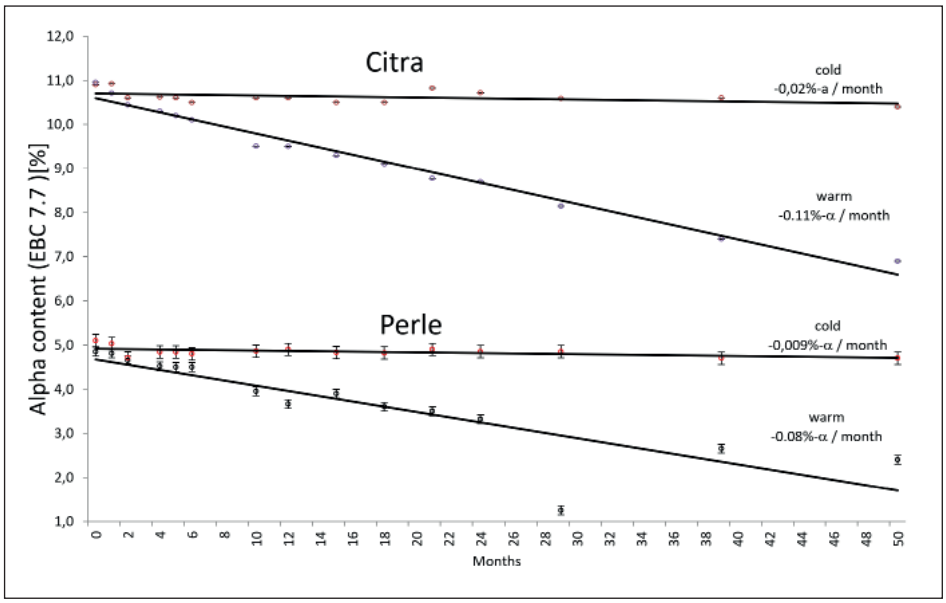

Fig. 1 **Alpha content (%) measured according to the EBC 7.7 of Perle and Citra® varieties during a period of 50 months**

a stronger increase at ambient temperature (Fig. 2). However, an increase in HSI should not be interpreted exclusively as evidence of oxidative degradation. Iso-α-acids also absorb at 275 nm and their formation during storage can therefore contribute to an increase in HSI. This is particularly relevant for hops stored under an inert atmosphere, where conversion of α-acids to iso-α-acids may occur in parallel with a decrease in α-acid concentration [2, 3]. Since iso-α-acids were not quantified in the present study, their contribution to the observed increase in HSI cannot be determined. Consequently, the HSI results are interpreted as an indicator of changes in bitter compounds during storage rather than as a direct measure of oxidation [2]. Citra® stored cold saw HSI increase only from ~0.290 to ~0.310 (+8.6 % relative). Perle stored cold went up from ~0.370 to ~0.390 (+5.7 %). These changes indicate that the measured HSI remained comparatively stable under cold storage. At 25 °C, HSI increased by approximately 80 % in Perle and 116 % in Citra® over 50 months.

The comparatively high initial HSI values of Perle (0.370 and 0.387) reflect the condition of the raw hop material before the start of the storage trial. Initial HSI can be influenced by pre-storage factors, including harvest conditions, weather conditions, maturity at harvest, post-harvest handling, and processing. Therefore, the initial HSI should not be interpreted solely as an indicator of the quality of the 2018 crop year as a whole, but rather as a characteristic of the specific Perle lot used in this study.

Moreover, these results highlight for brewers that keeping hops cold is the single most effective way to preserve bitterness potential. Even without the presence of oxygen (inert gas-filled packs), ambient temperatures accelerate chemical reactions that could have been resulted in a decomposition of alpha acids or isomerization of those to iso-α-acids. Brewers storing hops at room temperature for multiple years should therefore expect substantially lower α-acid levels than stated at harvest and might need to adjust their hopping rates accordingly.

3.2 Total Oils and Key Aroma Compounds

Both varieties showed a decline in total oil content over 50 months, with greater losses at ambient temperature, which is to be expected. In cold storage, Citra®'s total oil (initially ~2.3 mL/100g) dropped by about 8 %, and Perle's oil (initial ~1.3 mL/100g) dropped by ~16 % (Figure 3). When stored at 25 °C, losses roughly doubled: Citra® lost about 33 % of its oil, and Perle about 25 % of total oil volume. Interestingly, the most rapid oil loss occurred in the early months of storage, especially at ambient conditions. After the initial 6–12 months, the rate of oil loss slowed and levels plateaued, particularly for Perle, which showed little change after an initial drop. Citra® continued a more gradual decline over the first year before plateauing.

Detailed gas chromatographic analysis by GC-FID was used to monitor 21 individual volatile compounds. Table 2 and Table 3 present the initial and final concentrations of selected compounds in Perle and Citra® under cold and ambient storage. Small differences, particularly for compounds occurring at low concentrations, were interpreted with caution when their magnitude was comparable to the analytical uncertainty of the GC-FID method.

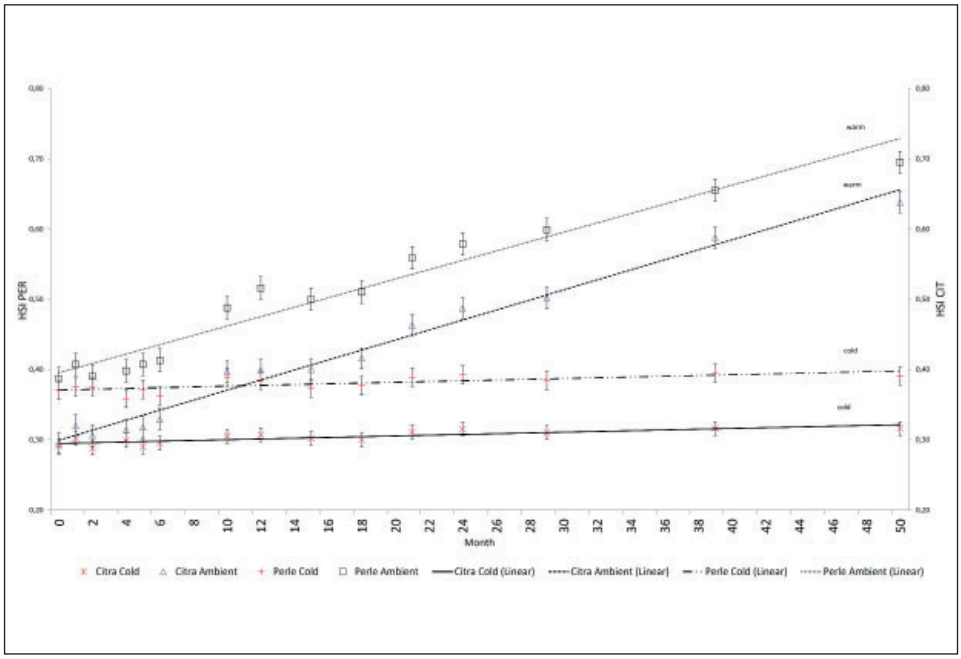

Fig. 2 **Results of HSI measures for Perle and Citra® under cold and ambient conditions over a period of 50 months**

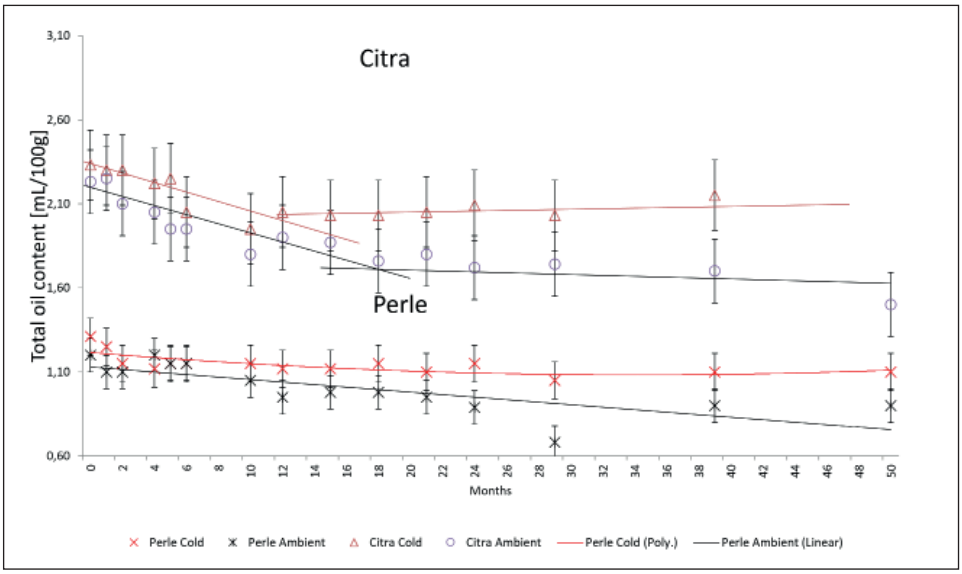

Fig. 3 **Total oil content according to EBC 7.10 of Perle and Citra® varieties for a period of 50 months under cold and ambient conditions**

Several clear patterns emerge from these data. For example, the total oil content decreased in all samples, more so at ambient temperatures. However, not every individual compound followed a simple linear decrease. Myrcene, which is a dominant monoterpene hydrocarbon dropped substantially under both conditions (especially in Perle at ambient temperature: –75 %).

Notably, limonene concentrations increased in both hops over time. For example, Citra®'s limonene more than tripled. These increases might reflect chemical transformations or release of bound forms rather than new synthesis. One possibility is that oxidative or enzymatic processes degraded other compounds (like other sesquiterpenes) into limonene, or that some terpene glycosides hydrolyzed to free limonene among others as suggested by some authors [9–12].

Moreover, esters and oxygenated compounds tend to decrease, especially at ambient storage. The analyzed esters (2-methylpropyl 2-methylpropanoate, 3-methylbutyl propanoate, 3-methylbutyl 2-methylpropanoate, 2-methylbutyl 2-methylpropanoate, methyl decanoate, methyl 4-decenoate, and methyl geranate) were present at relatively low concentrations in Perle at the beginning of storage, whereas higher initial concentrations were observed in Citra®. Overall, the measured ester concentrations tended to decrease during storage in both varieties. However, because the absolute concentrations of several esters in Perle were low, the corresponding relative changes should be interpreted with caution. Notably, some highly volatile short-chain esters essentially vanished under ambient conditions (for example, 2-methylbutyl 2-methylpropanoate in Perle decreased 100 % and in Citra® to 90 % at 25 °C).

Among the oxygenated compounds, linalool showed variety- and storage-dependent behavior. In Perle, linalool was present at very low concentrations. In Citra®, where linalool concentrations were higher, a decrease was observed under cold storage, whereas the concentration remained comparatively stable under ambient storage. Geraniol was present only at low concentrations in Perle and showed a decrease of 30–36 % in Citra® at cold and ambient conditions. This indicates some aroma compounds are

Table 2 Changes in selected aroma compounds for Perle after 50 months of storage at 3 °C (cold) vs 25 °C (ambient); initial (M0 = month 0) and final (M50 = month 50). Relative change (Δ %rel) was calculated as (M50 – M0)/M0 × 100; negative values indicate decreases and positive values indicate increases

Compound	Cold M0 (mg/100 g)	Cold M50 (mg/100 g)	Cold Δ (mg/100 g)	Cold Δ (%rel)	Ambient M0 (mg/100 g)	Ambient M50 (mg/100 g)	Ambient Δ (mg/100 g)	Ambient Δ (%rel)
Myrcene	274±73.4	189±25.31	-85	-31 %	237±63.49	59±7.09	–178	–75 %
Limonene	1±0.27	2±0.26	1	100 %	1±0.2	3±0.4	2	200 %
β-Caryophyllene	141±12.59	133±10.69	–8	-6 %	120±10.72	89±7.15	–31	–26 %
Farnesene	1±0.10	3±2.41	2	200 %	1±0.13	7±5.63	6	600 %
α-Humulene	402±26.92	443±39.56	41	10 %	348±23.31	338±30.18	–10	–3 %
2-Methylpropyl 2-methyl-propanoate	3±0.8	1±0.08	–2	-67 %	2±0.54	0	–2	–100 %
3-Methylbutyl propanoate	1±0.27	0	–1	-100 %	1±0.30	0	–1	–100 %
3-Methylbutyl 2-methylpro-panoate	1±0.30	0	–1	-100 %	1±0.20	0	–1	–100 %
2-Methylbutyl 2-methylpro-panoate	17±4.55	3±0.25	–14	-82 %	16±4.29	0	–16	–100 %
Linalool	3±0.67	2±0.18	–1	-33 %	3±0.66	3±0.27	0	0 %
Methyldecanoate	2±0.50	0	–2	-100 %	2±0.54	0	–2	-100 %
2-Undecanone	5±1.34	4±0.40	–1	-20 %	5±1.30	4±0.36	–1	–20 %
Methyl dec-4-enoate	1±0.27	1±0.08	0	0 %	0	1±0.09	1	n.a.
Methylgeranate	2±0.54	1±0.08	–1	-50 %	2±0.54	2±0.18	0	0 %
Citronellol	0	0	0	0 %	0	0	0	0 %
Nerol	0	0	0	0 %	0	0	0	0 %
Geraniol	1±0.26	1±0.09	0	0 %	1±0.27	1±0.09	0	0 %
Caryophyllene oxide	3±0.8	1±0.1	–2	-67 %	2±0.54	0	–2	–100 %
Humulene epoxide I	2±0.54	1±0.09	–1	-50 %	2±0.54	1±0.09	–1	–50 %
Humulene epoxide II	8±2.14	1±0.09	–7	-88 %	7±1.88	0	–7	–100 %
Humulene epoxide III	1±0.25	0	–1	-100 %	1±0.27	0	–1	–100 %

Table 3 **Changes in selected aroma compounds for Citra® after 50 months of storage at 3 °C (cold) vs 25 °C (ambient); initial (M0 = month 0) and final (M50 = month 50). Relative change (Δ %rel) was calculated as (M50 – M0)/M0 × 100; negative values indicate decreases and positive values indicate increases**

	Cold M0 (mg/100 g)	Cold M50 (mg/100 g)	Cold Δ (mg/100 g)	Cold Δ (%rel)	Ambient M0 (mg/100 g)	Ambient M50 (mg/100 g)	Ambient Δ (mg/100 g)	Ambient Δ (%rel)
Myrcene	1236±331.1	1001±134.07	–235	-19 %	1252±335.39	807±108.09	–445	-36 %
Limonene	3±0.8	16±2.14	13	433 %	4±1.07	21±2.81	17	425 %
β-Caryophyllene	131±11.7	130±10.54	–1	-1 %	114±10.18	105±8.44	–9	-8 %
Farnesene	0	10±8.04	10	n.a.	0	18±14.47	18	n.a.
α-Humulene	224±15.0	220±19.64	–4	-2 %	178±11.92	175±15.63	–3	-2 %
2-Methylpropyl 2-methyl-propanoate	2±0.54	2±0.18	0	0 %	2±0.54	1±0.09	–1	-50 %
3-Methylbutyl pro-panoate	5±1.30	3±0.27	–2	-40 %	5±1.34	0	–5	-100 %
3-Methylbutyl 2-methyl-propanoate	10±2.68	3±0.27	–7	-70 %	9±2.41	1±0.09	–8	-89 %
2-Methylbutyl 2-methyl-propanoate	39±10.45	35±3.13	–4	-10 %	40±10.72	4±0.36	–36	-90 %
Linalool	15±3.30	15±1.34	0	0 %	15±3.40	16±1.43	1	7 %
Methyldecanoate	25±6.7	18±1.61	–7	-28 %	25±6.7	12±1.07	–13	-52 %
2-Undecanone	18±4.82	18±1.61	0	0 %	17±4.55	22±1.96	5	29 %
Methyl dec-4-enoate	43±11.52	30±2.68	–13	-30 %	42±11.25	12±1.07	–30	-71 %
Methylgeranate	21±5.63	22±1.96	1	5 %	21±5.63	23±2.05	2	10 %
Citronellol	0	0	0	0 %	0	0	0	0 %
Nerol	0	1±0.09	1	n.a.	1±0.27	1±0.09	0	0 %
Geraniol	11±2.95	7±0.63	–4	-36 %	10±2.68	7±0.63	–3	-30 %
Caryophyllene oxide	1±0.27	0	–1	-100 %	1±0.27	0	–1	-100 %
Humulene epoxide I	1±0.3	1±0.09	0	0 %	0	1±0.09	1	n.a.
Humulene epoxide II	3±0.8	2±0.18	–1	-33 %	2±0.54	1±0.09	–1	-50 %
Humulene epoxide III	0	0	0	0 %	0	0	0	0 %

inherently more storage-stable, especially in inert atmosphere (likely because they are less volatile than myrcene and not easily oxidized without oxygen present). Nerol and citronellol were not present in the samples.

The measured caryophyllene oxide and humulene epoxides did not show consistent accumulation during storage and decreased in several samples. For example, caryophyllene oxide and humulene epoxides I–III all showed either low concentrations or clear decreases in concentration over time. The decrease in humulene epoxide II does not necessarily indicate the absence of oxidative transformations, since humulene epoxides can undergo subsequent conversion to other oxygenated compounds.

The results also show that the heavier hydrocarbon fraction (sesquiterpenes like humulene and caryophyllene) was relatively stable. Importantly, β-caryophyllene and α-humulene did not drastically degrade: for instance, humulene in Citra® at cold temperature remained almost constant (from 224 to 220 mg/100g), and in Citra® at ambient temperature it was essentially unchanged (~178 mg); in Perle, humulene ended at a slightly higher level as it started in cold temperature (~443 mg), and only slightly down at ambient temperature (from 348 to 338 mg).

Some measured oxygenated volatile compounds increased during storage, although the magnitude and direction of change differed among compounds, cultivars, and storage conditions. Overall, Citra® had higher initial oil content and higher concentrations of most aroma compounds compared to Perle, yet both varieties exhibited more similarities than differences in their storage behavior. The higher oil content of Citra® meant it still retained a higher absolute concentration of aroma compounds than Perle after storage (relevant for brewers relying on Citra®'s intense aroma), but proportionally each compound class shifted in similar ways for both hops.

From a brewer's point of view, the key practical implications regarding aroma are:

I Cold storage is beneficial not just for bitterness but also for preserving delicate aroma components.

II Even cold-stored hops will have an oxidized aroma profile different from fresh hops having notably less of the vivid green/myrcene and fruity ester notes. If using aged hops in late-hop or dry-hop applications, brewers might find the aroma slightly softer or shifted toward more herbal/spicy tones because humulene/caryophyllene remain while bright top-notes diminish.

III The absence of harsh oxidation products in these well-stored hops means even 3-year-old hops can produce clean flavors, however somewhat reduced in intensity. This is good news for inventory management.

4 Discussion

Hop freshness is crucial for preserving the full bittering power and desirable aromas that brewers seek. This comprehensive study shows that by controlling storage conditions and understanding hop chemistry, one can store hops for longer than previously expected and make informed decisions about hop usage.

The findings indicate that strict cold, oxygen-free storage dramatically slows hop aging. After 50 months at 3 °C in inert atmosphere, both Citra® and Perle retained ~84–97 % of their α-acids and total oils (HSI increases ~0.020), whereas at 25 °C they lost roughly 37-50 % of α-acids and 25-37 % of their oil content. These values agree well with Rutnik et al. [8], who showed that storage under anaerobic conditions at 4 °C provided the best preservation of hop quality, with α-acid losses typically ranging from about 10–35 % over two years, whereas aerobic storage at room temperature resulted in much greater α-acid losses (63–99 %) and oil losses (approximately 72–91 %), accompanied by substantial increases in HSI. Chenot and Shellhammer [12] reported that Citra® hops stored for four years under commercial cold-storage conditions remained remarkably stable, showing only minimal changes in α-acids, HSI, and oil content, while oxygen-exposed samples exhibited a numerical degradation of all measured quality parameters. Such consistency across studies underlines that temperature and O_2 exposure are major determinants of hop deterioration during storage [1, 6, 7, 12].

Notably, both this work and earlier studies emphasize that compounds are lost or formed during aging is as important as overall losses. The 25 °C storage trial shows that myrcene (the most volatile terpene) decrease by 36-75 % in content, far outpacing the modest 0-30 % declines in less volatile aroma terpenoids like linalool and geraniol. This is consistent with previous observations that monoterpene hydrocarbons, particularly myrcene, are among the most storage-sensitive components of hop essential oil [9, 13]. Foster and Nickerson [9] observed myrcene losses in all 20 varieties after six months at room temperature, with the extent of loss related to initial composition. Additionally, Chenot and Shellhammer [12] reported that oxidative storage promoted the accumulation of specific sesquiterpene oxidation products, particularly humulenol II, although the extent of these changes depended on hop cultivar and storage conditions. The absence of such accumulation in the present study may therefore reflect the oxygen-restricted conditions maintained by the barrier packaging. Interestingly, it was observed that in Citra® linalool held relatively steady and geraniol only declined moderately, likely because some loss via volatilization was offset by oxidation of other precursors (e.g. myrcene) into the same alcohols. This supports the mechanism proposed by Rutnik et al. [11, 14], who showed that as myrcene oxidizes during storage, it yields oxygenated compounds like linalool and geraniol, partially compensating their net decline even as total oil falls. Overall, our findings are consistent with previous studies [9, 11, 13] showing that monoterpene hydrocarbons, particularly myrcene, are highly susceptible to losses during hop storage, whereas less volatile sesquiterpenes may persist longer or undergo transformation into oxygenated derivatives.

A key practical question is how well the hop storage index (HSI) captures these chemical changes. This study tracked alpha acid loss reasonably (e.g. HSI roughly doubled in hops that lost ~50 % α-acids at 25 °C) and reflected strong oil oxidation. This is consistent with decades of research establishing HSI as a convenient indicator of resin oxidation [5]. However, the results also underscore HSI's limitations as a universal aroma predictor. This study found that Citra® maintained an HSI <0.32 even after prolonged cold storage, whereas an older stock of Perle reached HSI ~0.38 in the same period. Chenot and Shellhammer [12] similarly reported that HSI is not a reliable predictor of aroma quality, noting that Centennial hops often start with a higher HSI than Cascade, yet sensory analysis revealed that aroma quality after aging is variety-dependent and not directly correlated with HSI values. Varieties have different baseline HSI stability and aroma sensitivities. This variability explains the statement of variety-specific HSI benchmarks. As an example, fresh Perle pellets showed HSI ~0.38 versus ~0.29 for fresh Citra® (owing to cultivar differences in oil/resin makeup), so an aged sample reaching HSI 0.45 may be acceptable for one hop but signifies advanced oxidation in another. It is therefore advisable to compare an aged hop's HSI to its known fresh value for that same variety [15]. Many German aroma hops can still be used for brewing with an HSI up to ~0.40 (roughly +0.1–0.2 from harvest value) but begin to show sensory decline beyond ~0.45. It is therefore advisable to compare a stored hop's HSI with its value at processing or packaging, where available, and interpret the change in a variety-specific context [15–17].

From a brewer's perspective, the implications of these aging patterns are clear. First, proper storage can dramatically extend hop usability. In this study, cold-stored hops remained fresh in bitterness and aroma potential for well over a year, consistent with numerous studies [11, 15] and with traditional guidelines that pellets in foil can last 3–5 years at 0–5 °C. Conversely, even a few months of ambient storage can greatly accelerate hop degradation.

Second, when using aged hops, brewers should consider changes in hop chemistry when determining their application. Humulinones formed through oxidation of α-acids can contribute to beer bitterness and have been reported to exhibit approximately 66 % of the bitterness intensity of iso-α-acids [18]. Sensory consequences of hop aging may also depend strongly on cultivar. Chenot and Shellhammer [12] found that beers brewed with aged Cascade hops were sensorially distinguishable from those brewed with younger hops;

beers produced with younger Cascade were perceived as fruitier, whereas those produced with aged Cascade were more frequently characterized as bitter and grassy/resinous. Similarly, Foster and Nickerson [9] demonstrated substantial changes in hop essential-oil composition during aging, accompanied by a decrease in hoppiness potential. More recent brewing trials [12, 15, 19] have shown that the sensory consequences of hop aging depend on cultivar and storage history and may not be reliably predicted by HSI alone. Consequently, the suitability of aged hops for late or dry-hopping applications should be evaluated using HSI in combination with storage history, chemical composition, and sensory assessment rather than by applying a universal HSI threshold. Brewers should instead reserve such material for bittering additions. If moderately aged hops must be used in dry hopping, one can partly compensate by increasing the hop dosage, but there are diminishing returns; beyond a point, no amount of oxidized hop will equal the aroma of a smaller batch of fresh hops. A practical strategy is blending: e.g. combining an older hop lot with a fresher variety in dry hop, so that the fresh hops supply the lost volatile top-notes while the aged hops contribute background bitterness or flavor. In any case, routine sensory evaluation of stored hops is advised.

5 Conclusion

In summary, this study reinforces and quantifies the prevailing understanding [1, 11] of hop storage: cold, oxygen-free storage is paramount to preserve hop acids and oils. Under such conditions, even aroma-rich hops can maintain quality for years, whereas high temperatures or, in the worst case, oxygen ingress rapidly erodes both bitterness potential and aroma quality. The chemical markers like HSI, α-acid retention, and oil composition (for example myrcene loss) observed in aged hops closely mirror those reported [9, 13].

By combining HSI data with periodic sensory checks, brewers can make informed decisions such as diverting an older hop lot to kettle additions or increasing its dosage, while reserving the freshest lots for late hopping. All these measures help ensure beer flavor remains consistent.

Ultimately, these results and these comparative data all drive home the same message: "Hops don't like to get old" [1]. However, by rigorously controlling storage conditions and understanding a hop's chemistry, one can significantly slow down the aging clock. Brewers equipped with both analytical indicators (HSI, oil content) and sensory awareness can confidently leverage older hops in appropriate ways (e.g. bittering) and allocate the freshest ones to where aroma impact is paramount. This strategic use of hops ensures beer quality is maintained while maximizing the usable lifespan of hops. In conclusion, careful hop storage and judicious usage of aged hops allow brewers to mitigate the detrimental effects of time, thereby preserving the precious flavors and aromas that high-quality hops impart to beer.

Conflict of interest

The authors declare there are no conflicts of interest.

CRediT authorship contribution statement

Munoz-Insa, Alicia: formal analysis, writing – first draft, review & editing, visualization; Ramsauer, Bernhard: conceptualization, investigation, formal analysis, visualization; Zunkel, Mark: conceptualization, formal analysis, investigation, writing – review & editing, visualization.

Use of AI

Microsoft 365 Copilot, based on OpenAI technology, was used during manuscript preparation. AI-generated content was used as an initial basis for selected passages involving literature synthesis and scientific discussion. AI-assisted editing was also used to improve grammar, clarity, readability, and organization of text written by the authors. All AI-generated content was critically reviewed, verified against the cited original publications and the authors' experimental data, and substantially revised by the authors before inclusion in the manuscript. The final manuscript and its scientific conclusions were reviewed by the authors, who take full responsibility for its content.

6 Literature

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