A. Forster, A. Gahr, F. Schüll and J. Bertazzoni

The impact of climatic conditions on the biogenesis of various compounds in hops

Climate influence on yield and α-acid content of hops is known. Systematic research on the biosynthesis of aroma substances and polyphenols in different hop varieties depending on the weather conditions are lacking. Pellet T90 samples from big lots of 11 German aroma, 4 special flavor and 5 bitter hop varieties were chosen for the study. In this respect the two consecutive crop years 2015 and 2016 were found to be very suitable for a comparison. Summer 2015 was hot and dry, so amount and alpha yield were rather poor, whereas the summer 2016 offered good conditions with enough rainfall and moderate temperatures. Subject to analysis were: α- and β-acids, xanthohumol, total polyphenols, low molecular polyphenols in five subgroups, total hop oil and 50 aroma substances that were grouped into their individual subgroups too. α- and β-acids were particularly sensitive to unfavourable conditions, in aroma varieties more than in flavor or bitter hops. However, the polyphenols were not. Aroma components show big differences in their sensitivity to climate, especially esters and epoxides. Terpenes turned out to be a bit more stable than the oxygenated fraction. Apparently, linalool content in flavour hops showed a higher resilience. The susceptibility of hop substances and hop varieties to climate conditions evidently is different. The aroma components of the bitter varieties were less affected than those of the flavour and the aroma hops especially. The knowledge, how hop compounds react differently on varying climatic conditions helps the brewers to minimize unwanted variations in aroma and beer bitterness.

Descriptors: climate change, hop compounds, climate tolerance, hop varieties, hop crop variability

1 Introduction

Substantiated by innumerable publications climate change meanwhile can be regarded as a fact. Representatively a comprehensive compendium here may be cited [1]. It is known for some time that climatic conditions affect hop yields as well as the formation of α-acids. The first unpleasant surprise for the European hop industry came in 1994, when that year's hot, dry summer resulted in poor yields and hops with a low α-acid content [2]. Almost all of the German hop varieties grown at that time posted 30 to 50 % lower α-acid yields (in kg of α-acids per hectare) compared to the average over many years. Hop cultivation suffered an even greater blow in 2003. This was the first summer of the century with weather conditions that were suspected to be a result of climate change [3]. In some cases, the α-acid yields shrank by two-thirds. This caused the following two phenomena to be addressed:

- Varietal differences with regard to climate sensitivity became apparent. Newer cultivars such as Hallertauer Tradition or Magnum exhibited a somewhat greater stability under these challenging conditions than the traditional landrace varieties or Northern Brewer and Perle.
- The quantity of the hop oil, determined volumetrically with the steam distillation method (EBC 7.10), exhibited less sensitivity to the factor hot/dry than the α-acids. The total polyphenols, determined according to EBC 7.14, showed an even lower degree of sensitivity.

A similar result has been found when investigating the variety Aurora grown in Croatia under hot and dry conditions [4]. Compared to the "good" year 2001 the α-acid yield in 2003 reached just 27 %. Furthermore, a model to predict the α-acid value of Aurora from the weather conditions has been developed [5].

In the Czech Republic, hop researchers began looking at the influence of climatic conditions for the first time in 2009 [6]. A review of the period spanning 1994 to 2006 revealed a positive correlation between the amount of rainfall from June to August and the yield in kg/ha. Moreover, a negative relationship between the α-acid concentrations in Saaz hops and the increase in the daily temperatures from April to August was established. In a later work, predictions about the harvest were able to be determined based on the weather patterns present during the growing season [7].

The increasing frequency of dry, hot summers was also underscored by the 2015 [8] and 2017 crop years in Germany [9]. Comments on this can be found in [10, p. 44] along with the implications for the hop market.

The effects of climate change with respect to α-acid yields

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(kg α/ha) for various German hop varieties over a longer period of time (from 2002) is the focus of a study in [11]. It was possible to derive a clear correlation between the weather conditions and α-acid yields and to establish the existence of distinct differences among individual hop varieties.

The relevant findings are summarized below:

- The three months from June to August represent the key growth period for hops. This becomes evident from the results when a climate factor is calculated, which is the sum of rainfall divided by the average temperature during these three months.
- The impact of climate change on hop cultivation is clear. Insights into the climate tolerance of hop varieties can be gained simply by comparing the α-acid yields in dry, hot years with those years when "normal" climatic conditions prevailed, e.g., in 2015 and 2016, respectively.
- The effects of climate change are portrayed even more clearly through the correlation between relative α-acid yields and climate factors. This correlation is highly significant for most hop varieties. Varieties exhibit considerable differences in their sensitivity to weather conditions. Classic aroma varieties, along with the variety Perle, show greater sensitivity compared to bitter hop varieties or "special flavor" varieties.

The differences among Czech varieties in terms of yield and their α-acid content can be found in two publications [12, 13], both of which reached comparable conclusions. The aroma varieties Saaz and Sladek are highly sensitive to climatic conditions in contrast to Agnus, a bitter variety.

An extensive pan-European study investigating the impact of the weather conditions on the hop production comes to similar findings. Drought and heat in 2015 and 2018 have been disturbing the α-acid formation particularly in aroma hops [14].

The question raises whether there is an explanation for the interrelation between weather conditions and the α-acid biogenesis. A study on this subject deals with the influence of drought stress on the growth of the hop plant under physiological and proteomic view [15]. Here a quote from the abstract: "We were able to connect proteome analysis results with physiological measurements for photosynthesis. Physiological measurements revealed a decreasing trend of photosynthesis with progressive drought. On the other hand the results of proteome analysis showed a decrease of proteins, important for photosynthesis, with more severe drought stress."

Table 1 **Average temperatures, rainfall, number of hot days and climate factors (amount of rainfall divided by the average temperature in the months from June to August): a long-term comparison for 1961 – 1990 and the years 2015 and 2016**

	Av. Temperature [°C]	Rainfall [mm]	Hot Days	Climate Factor
1961 – 1990	15.9	303	no data	19.1
2015	19.5	178	36	9.1
2016	17.7	334	7	18.9

Research findings to date have been focused on factors, such as yield and α-acids as well as these two factors in combination, α-acid yield. Hop oils and polyphenols have also been analyzed, but only marginally, using unspecific analytical methods. However, more detailed studies on individual hop compounds are lacking, which is the purpose of this research.

2 Material and methods

2.1 Sample selection

As already discussed in [11], two separate years of hop harvests were compared. The hops grew under distinctly different weather conditions and thus are a suitable choice for an analytical comparison. The conditions in the crop year 2015 (hot and dry) and the subsequent crop year 2016 (sufficient amounts of rainfall, moderate temperatures) offer the relevant contrast for this comparison. The data for the Hallertau hop cultivation region including the average temperature, total rainfall, number of hot days (temperature > 30 °C) and the calculated climate factors (amount of rainfall divided by the temperature in the months June to August) are listed in table 1. The two very different years of 2015 and 2016 were also compared with the average values from 1961 to 1990. This 30-year period is often considered to be the period before the onset of climate change was apparent. The weather during the crop year 2015 was the least favorable of the past 10 years with a climate factor of only 9.1. In the following year, the amount of rainfall was slightly above average, resulting in a climate factor of 18.9 for 2016. In addition, considerably fewer days of excessive heat were recorded in 2016, meaning that the weather conditions were significantly more favorable than those in 2015. Fortunately, this variation in weather conditions made it possible to compare two very different crop years in direct succession, which minimizes the variations that may have been caused by a longer time lag.

Original foils of pellets (type 90), packed under an inert atmosphere and stored at 2 °C, were used as samples in this study. Pairs of samples from the crop years 2015 and 2016 were each analyzed on the same day, which minimized the errors associated with repeatability. Samples were collected from three lots of each hop variety chosen for analysis. The lots ranged from a minimum of 3 metric tons to a maximum of 50 metric tons, all of which were processed between November and February of the following year. The pellets represent a homogeneous mixture of multiple lots of hops with a comparable degree of freshness. This mixture is therefore considered to be sufficiently representative.

The most relevant German hop varieties were selected as a basis for comparison for the two crop years.

Classic landrace aroma varieties:

- Hallertauer Mittelfrüh (HAL)
- Hersbrucker Spät (HEB)
- Spalter (SPA)
- Tettnanger (TET)

The following aroma hop varieties were developed at the Hop

Research Center in Hüll, Germany, except for Northern Brewer:

- Hallertauer Tradition (HTR)
- Opal (OPL)
- Perle (PER)
- Saphir (SIR)
- Smaragd (SGD)
- Spalter Select (SSE)
- Northern Brewer (NBR)

Special flavor hop varieties officially classified as aroma varieties, developed in Hüll, except for Cascade (from the USA):

- Cascade (CAS)
- Hallertau Blanc (HBC)
- Huell Melon (HMN)
- Mandarina Bavaria (MBA)

Bitter hop varieties developed in Hüll, except for Nugget (from USA):

- Hallertauer Magnum (HMG)
- Hallertauer Taurus (HTU)
- Herkules (HKS)
- Nugget (NUG)
- Polaris (PLA)

With the exception of Spalter and Tettnanger, both of which originated in their respective regions, all hops were grown in the Hallertau.

Varieties of minor importance, such as Brewers Gold, Hallertauer Merkur, Hersbrucker Pure or Huell Bitter, were not taken into consideration. Newer varieties, such as Diamant, Ariana and Callista, were not yet available in sufficient quantities during the 2015 and 2016 harvests.

The Northern Brewer hop was not originally an aroma variety. It was bred in England at the beginning of the 20th century and introduced to the Hallertau as the primary bitter variety in the 1960s. NBR has been officially listed as an aroma variety since 2017. Nevertheless, NBR is not included here when calculating the averages for cultivated aroma varieties, because some of its characteristics are not typical for an aroma hop.

In table 2 the harvest yields for 2015 and 2016 in tons per hectare are listed for the most important varieties and the relation between the two years. Relatively young cultivars with a high percentage of “young hops” remain unconsidered [9, 16]. Aroma hops yielded 39 % less in 2015 compared to 2016, bitter hops 24 %.

2.2 Analysis methods

The following analyses were performed on the samples of hop pellets:

- hop storage index (HSI) to check the degree of freshness of the selected samples; spectrophotometric method according to EBC 7.13 or ASBC Hops 12
- α-acids and β-acids, including the cohumulone ratio (co-α-acids : total α-acids × 100 %), as well as a specific determination of xanthohumol using HPLC according to EBC 7.7
- volumetric determination of hop oil by steam distillation according to EBC 7.10
- determination of individual aroma compounds by means of gas chromatography (GC-FID) with a method adapted from MEBAK [17]. Instead of the 34 mentioned aroma substances 50 components were quantified for this study.
- total polyphenol content (TPP) according to EBC 7.14, a non-specific, spectrophotometric, global method
- low molecular weight polyphenols (lmwPP) with an HPLC method [18]; formation of groups of compounds including hydroxycinnamic acids, flavanols, proanthocyanidines, quercetin flavonoids, kaempferol flavonoids and other flavonoids

In order to keep the numerical data from the analysis of the aroma compounds at a reasonably manageable level, not the total 50 single results are presented, but the following data are evaluated and discussed: the volumetric determination of total oils, the sum of all calibrated GC aroma compounds, the hydrocarbon fraction (sum of monoterpenes and sesquiterpenes), myrcene (quantitatively important monoterpene), α-humulene (quantitatively important sesquiterpene), the oxygenated fraction (compounds containing oxygen in the molecule and therefore more polar and better soluble in wort and beer), monoterpene alcohols (MTA); linalool (the most important representative of the MTA), the sum of the esters; 2-methylbutyl-2-methylpropanoate (the most important ester in terms of quantity), sesquiterpene alcohols, ketones and epoxides. In this respect the presentation of aroma compounds and lmwPP in substance groups is justified as the components within these groups behave similarly.

Due to limited access to analytical capabilities no results of thiols and other sulphur containing aroma substances can be presented.

Table 2 **Harvest yields of the most important German hop varieties in the years 2015 and 2016 and the relation 2015 : 2016**

	Variety	Crop year 2015 [to/ha]	Crop year 2016 [to/ha]	2015 : 2016 [%rel.]	
Aroma	Spalter	0.79	1.42	56	Ø 63
	Northern Brewer	1.21	2.08	58	
	Hallertauer Mfr.	1.11	1.87	59	
	Perle	1.40	2.33	60	
	Saphir	1.52	2.54	60	
	Hersbrucker	1.50	2.35	64	
	Hall. Tradition	1.45	2.28	64	
	Spalt Select	1.46	2.23	65	
	Tettnanger	1.18	1.48	80	
Bittter	Taurus	1.56	2.30	68	Ø 76
	Herkules	2.36	3.32	71	
	Hall. Magnum	1.73	2.14	81	
	Nugget	1.38	2.23	82	

Three samples of pellets were collected for each of the selected hop varieties. These were weighed out proportionally based on the size of the pellet lot for each individual analysis; each analysis was performed four times. The mean value, the standard deviation and the 95% confidence interval for the quadruple determinations was calculated. The absolute values for each of the compounds analyzed for both crop years were omitted from this report. The primary focus of this investigation was to compare two very different crop years in terms of climatic conditions and to address the following questions: how sensitive are hop compounds or groups of hop compounds in different varietal groups to changes in climatic conditions, how susceptible are they to drought and heat, and ultimately how adaptable are they to climate change?

The relationship between the crop years, expressed in terms of mean values for each year as a ratio, is of primary interest. The calculation is performed as follows:

$$\frac{\text{mean value for the crop year 2015}}{\text{mean value for the crop year 2016}} \times 100\ \% = \%\ (\text{rel.})$$

The result is the percent increase or decrease in the crop year 2015 compared to crop year 2016. Along with the comparisons of individual hop varieties, the mean values for four varietal groups are provided in the following tables:

Four landraces, six bred aroma hop vartieties without NBR, four special flavor varieties also described just as flavor hops and five bitter hop varieties.

The hop storage index (HSI) data for the pellets from both harvests were also compared in advance to ensure that there were no systematic differences in the degree of aging between the two harvests. If this was the case, an uncritical comparison could lead to incorrect conclusions.

3 Analysis results and discussion

3.1 Preliminary tests

3.1.1 Comparison of the α-acid content of selected pellets with published AHA values

In preparation for this study, the data regarding the α-acid content of the pellets was compared with the figures published by the “Arbeitsgruppe Hopfenanalyse” (Hop Analysis Working Group, AHA). The latter not only includes random samples but also the hop analysis data gathered for the entire crop year in 2015 and in 2016. The α-ratios of 2015 to 2016 for the hop pellets selected for this investigation are reasonably consistent with those of the AHA.

3.1.2 Comparison of HSI values of pellets from the crop years 2015 and 2016

The HSI is currently the most commonly employed method for describing the degree of freshness, or alternatively, of aging in samples of whole hops or pellets.

The average HSI values for all hop varieties in both crop years varied in average 0.02 with a maximum single deviation of 0.04. So, the HSI is comparable for both crop years. This ensures that the research results will not be subject to distortion due to different degrees of aging among the pellets from both crop years.

3.2 Primary investigation

3.2.1 Measurement error considerations

The distribution of the relative values for 2015 : 2016 were estimated as follows:

- determination of the standard deviations (SD) for the quadruple determinations and their 95 % confidence intervals
- calculation of a mean 95 % confidence interval (Ø CI) and the overall mean for all varieties for each analytical parameter considered

In the worst case, the mean 95 % confidence interval can double when comparing two values. In an effort to provide a simple overview, the maximum statistical error spread (MESmax) is calculated

Table 3 **Mean 95 % confidence interval for the quadruple determinations for all hop varieties; maximum error spread for the ratio of 2015 to 2016, expressed in % (rel.)**

	Dimension	Ø CI	MES$_{max}$ [%]
α-acids	% w/w	0.07	2.1
β-acids	% w/w	0.07	3.2
Cohumulone ratio	% rel.	0.7	5.8
Xanthohumol	% w/w	0.02	9.1
Total polyphenols	% w/w	0.15	7.0
Sum of low molecular weight polyphenols	mg/100g	360	8.8
Hydroxycinnamic acids / flavonols	mg/100g	61	9.8
Proanthocyanidins	mg/100g	75	10.4
Quercetin flavonoids	mg/100g	112	9.5
Kaempferol flavonoids	mg/100g	84	9.2
Other flavonoids	mg/100g	7	13.7
Hop oil volumetric	ml/100g	0.04	7.3
Sum of all GC compounds	mg/100g	48	11.1
Hydrocarbon fraction	mg/100g	32	8.7
Oxygenated fraction	mg/100g	6.5	10.7
Esters	mg/100g	4	13.6
Sesquiterpene alcohols	mg/100g	1.5	14.1
Ketones	mg/100g	1.6	14.5
Linalool	mg/100g	0.35	9.9
2-Methylbutyl-2-methylpropanoate	mg/100g	1.9	14.4
Epoxides	mg/100g	0.9	18.9

as follows and the results can be found in table 3:

$$\text{MES}_{\text{max}} = 2 * \text{Ø CI} : \text{overall mean} * 100\ \%$$

3.2.2 Comparisons of all analysis values for 2015 versus 2016

The analysis results are listed separately for the bitter compounds, including xanthohumol, the aroma compounds and the polyphenols as follows:

- The data are generally expressed in % (rel.) for the crop years 2015 to 2016.
- The values for all 20 varieties are further divided into the four groups mentioned previously: four landrace varieties, six aroma hop varieties (without NBR), special flavor hop varieties and five bitter hop varieties. The tables contain the mean values of the deviations in the ratios for 2015 to 2016 in percent for each of the four groups.
- Furthermore, the mean values for all 20 varieties (including NBR) are calculated.

Of the 20 varieties, 18 are grown in the Hallertau, along with Spalter in the Spalt region (90 km northwest of Hallertau) and Tettnanger in the Tettnang area (200 km southwest of Hallertau). Climatic conditions are different in these three growing regions. Table 4 contains the climate factors (CF) calculated for the crop years 2015 and 2016.

The highest and thus most favorable climate factor was determined for Tettnang, followed by the Hallertau. The climate factors in 2016 were twice as high for both regions compared to 2015 and therefore distinctly more favorable. In the Spalt region, the CF 2016 is almost 50 % higher, though at a considerably lower level. Approx. 20 % of these growing areas, particularly in the Hallertau and Spalt regions, are irrigated, which at least makes it possible to stabilize the yields per hectare. The following results do not take this into consideration.

Table 5 contains data on α-acids and β-acids, cohumulone ratios and xanthohumol. The latter as a prenyl flavonoid is grouped with the polyphenols, but it is biogenetically linked to the bitter acids and is found in the lupulin glands. According to [20], the biogenesis of bitter acids and prenyl flavonoids is initiated through a similar metabolic pathway. Analogous to the α-acids, xanthohumol also exhibits a low solubility in wort and beer.

While significant differences in the concentrations of α-acids and β-acids were observed in the ratios for crop years 2015 to 2016 among the hop varieties analyzed, the cohumulone ratio remained almost unchanged. The biogenesis of the homologs of the bitter acids remained unaffected by the climatic conditions, rendering any further discussion on this point unnecessary.

Table 4 **Climate factors (CF) of 2015 and 2016 calculated for the three main hop-growing regions in Germany: Hallertau, Spalt, Tettnang**

	2015	2016	2016 : 2015
Hallertau	9.6	18.9	2.0
Spalt	6.9	10.0	1.4
Tettnang	14.4	29.9	2.0

Table 5 **A comparison of relative concentrations of α-acids and β-acids, cohumulone ratio and xanthohumol in % (rel.) for the crop years 2015 and 2016. The color differentiation is also valid for table 6 and 7**

Variety	α-acids	β-acids	Cohumulone	Xanthohumol
HAL	54	64	105	71
HEB	68	69	100	88
SPA	60	78	100	90
TET	57	73	106	87
Ø Land races	**59.8**	**71.0**	**102.8**	**84.0**
HTR	76	59	112	91
SIR	63	59	100	81
SSE	64	63	95	75
SGD	75	73	111	87
PER	51	52	110	59
OPL	84	69	106	79
NBR	40	50	106	52
Ø Breeding varieties (without NBR)	**68.8**	**62.5**	**105.7**	**78.7**
MBA	79	103	97	102
HMN	82	94	99	96
HBC	75	84	95	88
CAS	69	106	92	80
Ø Flavor varieties	**76.3**	**96.8**	**95.8**	**91.5**
HMG	86	84	97	85
NUG	77	89	105	88
PLA	86	75	97	100
HTU	71	73	106	85
HKS	87	79	95	98
Ø Bitter varieties	**81.4**	**80.0**	**100.0**	**91.2**
Ø All varieties incl NBR	**70.2**	**74.8**	**101.,7**	**84.1**

< 55	🟥	55 – 65	🟥	65 – 75	🟥
75 – 85	🟨	85 – 95	🟩	> 95	🟩

Table 6 (see page 165) lists the relative concentrations of four individual, most important substances and nine groups of aroma compounds which serve as key indicators for hop aroma. An extensive review on occurrence and importance of hop aroma compounds in beer has been recently published [21], evaluating 174 publications. This forms the basis for a comparison between the crop years 2015 and 2016. Among the key indicators, extreme differences in climate sensitivity are evident, especially from variety to variety. This will be examined in greater detail later.

The data for the polyphenols (excluding xanthohumol) for a total of eight key figures are provided in table 7 (see page 166). At first glance, it is notable that the “bract polyphenols”, in contrast to xanthohumol, the “lupulin polyphenol”, show values approximately equivalent to 100 % for the ratio of the crop years 2015 to 2016,

Table 6 **Relative concentrations of aroma compounds and key indicators for aroma expressed in (% rel.) for the crop year 2015 as compared to crop year 2016 (1 = total oil by volume; 2 = sum of all calibrated aroma compounds; 3 = hydrocarbon fraction; 4 = myrcene; 5 = α-humulene; 6 = oxygenated fraction; 7 = monoterpene alcohols; 8 = linalool; 9 = sum of esters; 10 = 2-methylbutyl-2-methylpropanoate; 11 = sesquiterpene alcohols; 12 = ketones; 13 = epoxides)**

Variety	1	2	3	4	5	6	7	8	9	10	11	12	13
HAL	75	73	73	69	63	73	67	75	30	44	108	76	93
HEB	94	78	88	90	98	43	80	86	71	67	82	73	64
SPA	75	86	97	77	112	51	50	75	31	50	65	62	40
TET	88	81	83	63	102	67	63	75	50	50	75	71	88
Ø Land races	**83.0**	**79.5**	**85.3**	**74.8**	**93.8**	**58.5**	**65.0**	**77.8**	**45.5**	**52.8**	**82.5**	**70.5**	**71.3**
HTR	94	95	97	96	99	82	100	100	55	50	120	125	78
SIR	100	95	94	83	112	100	73	70	67	33	128	117	75
SSE	79	80	95	63	118	88	75	70	60	75	100	94	80
SGD	82	81	81	74	85	80	69	80	73	50	100	109	58
PER	72	72	72	63	77	74	78	75	57	53	108	94	73
OPL	77	80	75	84	66	72	100	100	61	55	94	94	35
NBR	58	58	58	44	76	53	86	74	41	35	84	55	77
Ø Breeding varieties (without NBR)	**84.0**	**83.8**	**85.7**	**77.2**	**92.8**	**82.7**	**82.5**	**82.5**	**62.2**	**52.7**	**108.3**	**105.5**	**66.5**
MBA	113	110	114	104	131	94	89	100	84	89	113	82	56
HMN	86	78	88	70	94	74	89	100	60	60	98	89	100
HBC	100	107	112	97	117	83	113	125	72	79	91	71	100
CAS	95	94	96	92	110	81	103	80	70	66	114	83	60
Ø Flavor varieties	**98.5**	**97.3**	**102.5**	**90.8**	**113.0**	**83.0**	**98.5**	**101.3**	**71.5**	**73.5**	**104.0**	**81.3**	**79.0**
HMG	91	82	82	84	80	79	60	71	76	94	96	100	63
NUG	83	70	70	58	88	70	61	53	63	61	100	83	64
PLA	104	95	102	103	100	66	85	88	60	49	95	105	45
HTU	78	76	76	67	111	72	73	59	83	59	77	69	40
HKS	71	77	80	64	100	63	73	71	57	51	100	75	67
Ø Bitter varieties	**85.4**	**80.0**	**82.0**	**75.2**	**95.8**	**70.0**	**68.4**	**68.4**	**67.8**	**62.8**	**93.6**	**86.4**	**55.8**
Ø All varieties incl NBR	**85.8**	**83.4**	**86.7**	**77.3**	**97.0**	**73.3**	**78.9**	**81.4**	**61.1**	**58.5**	**97.4**	**86.4**	**76.0**

< 55	🟥	55 – 65	🟥	65 – 75	🟥	75 – 85	🟨	85 – 95	🟩	> 95	🟩

indicating that the climatic conditions have no influence on these compounds. There are no obvious differences among the varieties analyzed except MBA which shows significantly lower TPP and lmwPP values in crop 2015.

3.2.3 A global comparison of the three groups of hop compounds

Figure 1 shows a comparison of the three major secondary metabolites present in all 20 varieties grown during the dry summer of 2015 with those grown under normal conditions in the summer of 2016:

- α- and β-acids, the most important of the bitter compounds
- sum of all calibrated GC aroma compounds
- total polyphenols

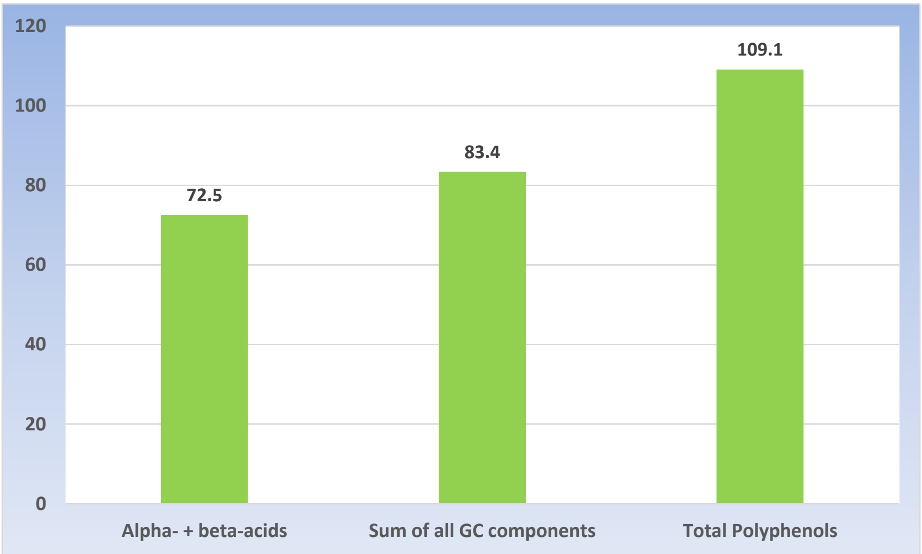

Fig. 1 **The ratio of secondary metabolites (α- and β-acids, sum of GC aroma compounds, and total polyphenols) for crop years 2015 and 2016 expressed in % (rel.), averaged for all 20 hop varieties**

Table 7 **Relative concentrations of polyphenols expressed in % (rel.) for the crop year 2015 compared with crop year 2016; total polyphenols (TPP), sum of low molecular weight polyphenols (lmwPP) and six groups of compounds within the lmwPP**

Variety	TPP	lmwPP	Hydroxy-cinnamic acids	Flavanols	Proantho-cyanidines	Quercetin flavonoids	Kaempferol flavonoids	Other Flavonoids
HAL	103	110	109	110	123	103	108	119
HEB	103	113	114	100	105	122	122	108
SPA	130	121	105	119	135	121	125	154
TET	110	99	90	94	98	99	111	135
Ø Land races	**112.5**	**110.8**	**105.5**	**105.8**	**112.0**	**111.3**	**116.5**	**129.0**
HTR	105	102	90	96	108	106	112	96
SIR	107	100	101	102	105	98	97	105
SSE	100	93	86	71	82	113	108	82
SGD	119	125	123	108	117	143	115	100
PER	107	108	122	108	101	109	102	109
OPL	111	110	101	98	110	113	117	147
NBR	136	141	132	131	141	155	145	129
Ø Breeding varieties (without NBR)	**108.2**	**106.3**	**103.8**	**97.2**	**103.8**	**113.7**	**108.5**	**106.5**
MBA	86	82	78	78	82	79	91	79
HMN	91	93	104	87	80	94	97	80
HBC	90	102	102	93	89	101	115	87
CAS	102	110	95	95	102	111	128	87
Ø Flavor varieties	**92.3**	**96.8**	**94.8**	**88.3**	**88.3**	**96.3**	**107.8**	**83.3**
HMG	110	110	97	98	108	115	123	138
NUG	108	124	112	124	149	119	123	108
PLA	114	133	107	117	118	130	152	115
HTU	136	152	153	127	162	161	163	106
HKS	114	151	149	120	169	155	155	120
Ø Bitter varieties	**116.4**	**134.0**	**123.6**	**117.2**	**141.2**	**136.0**	**143.2**	**117.4**
Ø All varieties incl NBR	**109.1**	**114.0**	**108.5**	**103.8**	**114.2**	**117.4**	**120.5**	**110.2**

< 55	🟥	55 – 65	🟥	65 – 75	🟥	75 – 85	🟨	85 – 95	🟩	> 95	🟩

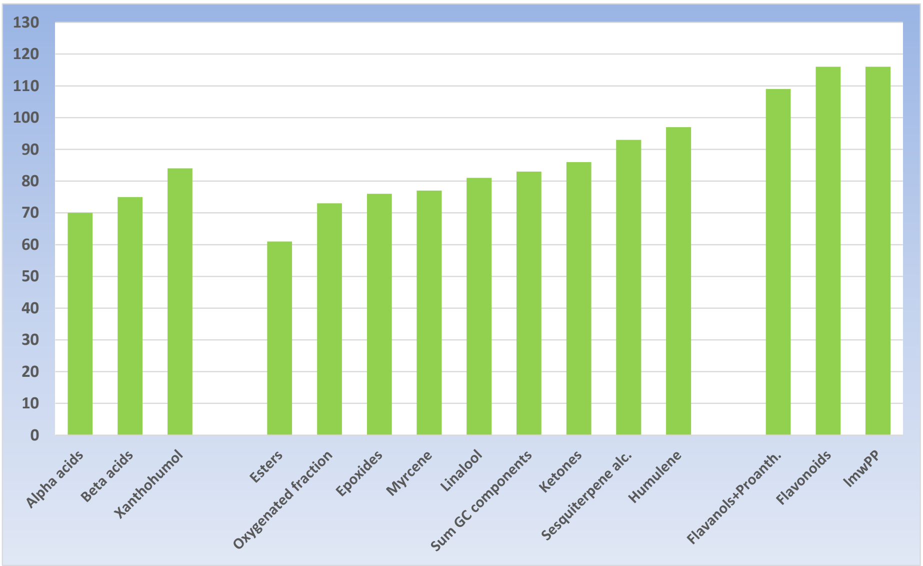

Fig. 2 **The ratio of 16 analytical parameters for the crop years 2015 and 2016 expressed in % (rel.), averaged for all 20 hop varieties**

This overall average of all 20 varieties shows that α- and β-acids are the most climate-sensitive metabolite with a 27.5 % reduction in quantity, followed by the sum of the aroma compounds (– 17 %), in the comparison of the crop years 2015 and 2016. Polyphenols were even slightly elevated in 2015 compared to 2016 (+ 9 %). Therefore, the bitter acids react most sensitively to the climatic conditions, followed by the aroma compounds; in contrast the polyphenols show no negative reaction.

3.2.4 A comparison of selected compounds and classes of compounds

A more detailed comparison of selected metabolites is provided in figure 2. The β-acids appear to be slightly less sensitive to drought conditions and heat stress than the α-acids.

The effect exerted by the climate varies among the aroma compounds and therefore must be examined group by group. The esters are the most sensitive (– 39 %). The epoxides and linalool, an important compound for hop aroma in beer, as well as the ketones were approximately 20 % lower in 2015 compared to 2016. The sesquiterpene alcohols remained surprisingly unaffected (– 3 %). These compounds belonging to the oxygenated fraction (– 27 %) may be relevant for hop aroma depending upon their solubility in wort and beer, which varies by compound. Myrcene and α-humulene are dominant aroma compounds in hops; however, their nonpolar character means that they are only found in small amounts in wort or beer, usually at concentrations below their flavor threshold [10, p. 215; 23]. Notable differences were observed between myrcene (– 23 %) and α-humulene (– 3 %).

The columns depicting the polyphenols are divided into non-specific total polyphenols (TPP) and the low molecular weight polyphenols (lmwPP), which can be determined by HPLC, in addition to the subgroups flavanols plus proanthocyanidines and the sum of all flavonoids. The polyphenols determined with this method are relatively good soluble in wort and beer, and their biogenesis is apparently not affected by climatic conditions. Only xanthohumol, which has a low solubility in beer, was negatively affected by the dry, hot weather conditions (see Table 5). As mentioned previously, it is enriched in the lupulin glands parallel to the bitter and aroma compounds [20] while the majority of the polyphenols are found in the bracts of the hop cones. It is unclear whether the location of biogenesis – in the lupulin glands or the bracts of the hop cones – is the reason why these metabolites react differently to differences in climate.

Additional information on the concentrations of polyphenols can be found in table 8. The ratios of the low molecular weight polyphenols (HPLC) to total polyphenols are calculated for the four varietal groups of hops in both crop years. The low molecular weight character decreased in both crop years from the landrace varieties to the bitter hop varieties. However, this relationship did not change from 2015 to 2016.

Table 8 **Ratio of low molecular weight polyphenols (HPLC) to total polyphenols for the crop years 2015 and 2016 expressed in % (rel.)**

	2015	2016
4 Land races	23.8	23.5
7 Bred aroma varieties (without NBR)	22.7	23.0
4 Flavor varieties	20.8	19.8
5 Bitter varieties	12.4	11.0

3.2.5 A comparison of the four varietal groups

In the next step, the four varietal groups were compared with one another. Figure 3 shows α-acids and β-acids, the low molecular weight polyphenols as well as four aroma indicators (oxygenated fraction, the sum of the esters, linalool and the epoxides).

The following observations can be derived from the analysis results:

- Among the varietal groups, the α-acids and β-acids did not respond in the same way. For example, only among the cultivated aroma hop varieties did the β-acids prove to be more sensitive than the α-acids, whereas they appeared to be quite stable among the flavor varieties.
- The aroma data for the flavor hops, compared to the other groups, were less affected by the hot, dry climatic conditions.
- The traditional landrace varieties proved to be exceptionally sensitive to any changes in the climatic conditions in terms of their oxygenated fractions and their ester content. The fact that the bitter varieties were also highly sensitive in this regard only plays a minor role, at least technologically, since they are most frequently used as bittering hops, added at the beginning of the boil. Their aroma compounds are therefore largely lost to the vapor rising from the wort during the boil.
- Compared to 2016, the results for the linalool content in the bitter varieties harvested in 2015 were also rather poor, followed by the landrace varieties and aroma hop cultivars. By contrast, the flavor hop varieties were quite interestingly unaffected by the different climatic conditions of the two crop years.
- Epoxides follow a similar pattern.
- No significant differences were discovered among the subgroups with regard to their polyphenol content. Thus, the sum of the low molecular weight polyphenols was sufficient for comparison. The bitter varieties harvested in 2015 showed notably higher values than those grown in 2016.

3.2.6 A comparison of the individual hop varieties

Tables 5 to 7 show comparisons of the hot, dry year of 2015 and the "normal year" of 2016 for the 20 varieties. Extreme differences

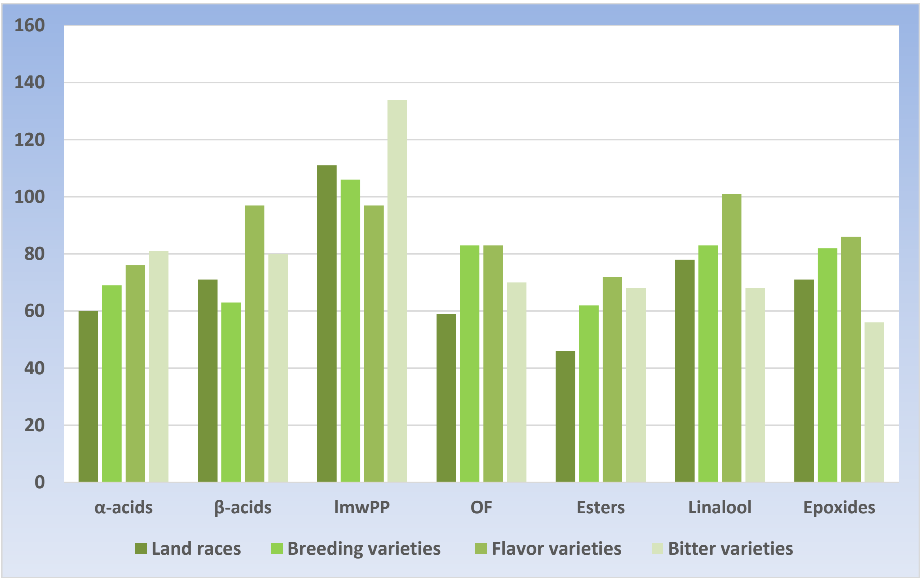

Fig. 3 **The ratio of α-acids and β-acids, lmwPP, oxygenated fraction (OF), esters, linalool, and epoxides for the crop years 2015 and 2016 expressed in % (rel.), divided into four varietal groups**

Table 9 **Ranges for the fluctuations in the fundamental attributes of the 20 varieties; data for the lowest value from the 2015 crop year compared to the data for the highest value from 2016 in % (rel.); ratio of max : min**

	min	max	max : min
α-acids	40	87	2.2
β-acids	50	106	2.1
Xanthohumol	52	102	2.0
Σ of all calibrated GC aroma substances	58	107	1.8
Myrcene	44	104	2.4
Oxygenated fraction	53	94	1.8
Linalool	71	125	1.8
Esters	31	83	2.7
Sesquiterpene alcohols	65	120	1.8
Ketones	55	117	2.1
Epoxides	35	100	2.9

Table 10 **Bitterness potential (α-acids) and aroma potential (Ø of six aroma attributes) of all 20 cultivars expressed as a ratio for the crop years 2015 and 2016 expressed in % (rel.); the mean values for these ratios was ranked from “hardly climate-sensitive” to “very climate-sensitive”**

Vartiety	Bitter potential	Aroma potential	Average	Ranking
MBA	79	91	85	1
PLA	86	76	81	2
HMG	86	76	81	2
HBC	75	97	81	2
HMN	82	80	81	2
HTR	76	81	80	3
OPL	84	72	78	4
HKS	87	67	77	5
SIR	63	89	76	6
SGD	75	74	75	7
CAS	69	79	74	8
HEB	68	72	70	9
NUG	77	63	70	9
HTU	71	67	69	10
SSE	64	74	69	10
TET	57	71	64	11
HAL	54	68	61	12
SPA	60	60	60	13
PER	51	67	59	14
NBR	40	58	49	15

< 55	🟥	55 – 65	🟥	65 – 75	🟥
75 – 85	🟨	85 – 95	🟩	> 95	🟩

between varieties were observed and these were significantly higher than the maximum error spread (3.2.1.). Table 9 lists the respective ranges for the deviations between the varieties as well as for the ratios between the maximum and minimum for each value, which mostly yield a factor of 2, meaning that the climate-sensitive hops were affected by the changes in the climatic conditions to almost twice the degree that the more climate-tolerant varieties were.

In order to gain a clearer and more concise overview when comparing the varieties, the following six attributes were selected from the 13 attributes analyzed for hop aroma presented in table 6, which most closely reflect the aroma potential of a variety:

- The sum of all compounds determined using gas chromatography.
- Despite its poor solubility in wort and beer, myrcene is capable of influencing the sensory characteristics of beer when the hops are added late in the brewing process but especially when the addition occurs through dry hopping [22, 23, 24].
- The oxygenated fraction encompasses the sum of all aroma compounds which contain an oxygen molecule and have a good solubility in wort and beer.
- Linalool as a key aroma compound [10, p. 288; 25].
- The sum of all esters which may be present above their flavor thresholds in beer is included [10, p. 215; 26, 27].
- The epoxides of β-caryophyllene and α-humulene may also contribute to the hop aroma in beer [28, 29].

Table 10 contains the ratios for bittering potential (α-acids) and aroma potential (Ø of six aroma attributes) for all 20 hop varieties, comparing the values from the 2015 and 2016 crop years. The mean for both values is given. This ratio allows the bittering and aroma potential to be ranked according to the following classification system: 1 = “hardly climate sensitive”- to 15 = “very climate-sensitive”.

- Mandarina Bavaria achieved the highest ranking at 85 %.
- Opal, Hallertauer Tradition, Herkules, Polaris, Hallertauer Magnum, Hüll Melon and Hallertau Blanc were even more stable (around 80 %).
- The next group in the ranking was Saphir, Smaragd and Cascade (around 75 %).
- Spalter Select, Hersbrucker, Nugget and Hallertauer Taurus reached approximately 70 %.
- The three landrace varieties, Spalter, Tettnanger and Hallertauer Mfr., follow with 60 – 65 %.
- Next to Northern Brewer in the ranking was the hop variety Perle (59 %), whose parentage, unsurprisingly, includes Northern Brewer.
- Northern Brewer ranked lowest by far among the varieties at 49 %.

It may still be of interest to explore the reasons behind the varying levels of sensitivity these compounds exhibit. Apparently, high temperatures during the day coupled with a lack of moisture have a negative effect on the biogenesis of bitter and aroma compounds as well as xanthohumol but not on the biogenesis of the other polyphenols in the bracts and bracteoles of the hop cones. According to [20, 30], the formation of bitter acids, terpenes, and prenyl flavonoids in the lupulin glands has a common origin and is controlled by a diverse set of enzymes. It is conceivable that extremely high temperatures and drought can disrupt this enzymatic activity. *Kolenc* et al. provide an initial assessment [15].

It remains unconsidered that the special flavor hops in particular originate from younger plant material. The area planted with younger special flavor hop plants averaged 37 % in crop 2015 and 29 % in 2016. Under this aspect a comparison of these two crop years is still justified. At the moment there are no references or own findings whether the climate sensitivity of a hop vine changes with its age.

4 Consequences for the quantity of hops added

The conclusions reached by this study shows that the ratio of compound groups to one another can shift significantly from crop year to crop year depending upon the climatic conditions. Thus, when a climate-sensitive variety is cultivated during a hot, dry growing season, double the amount of polyphenols and 30 to 80 % more of certain aroma compounds enter the beer while the quantity of α-acids remains the same. The effects of these shifts on the beer will not be discussed in detail here, but depending upon the target hop rate, they will have an impact on the beer.

Fluctuations in beer quality due to the growing conditions during individual crop years have the least effect if the hop addition occurs at the beginning of the boil with pure resin extract, which contains only negligible quantities of polyphenols. If the quantity of hop oil varies for an addition early during the boil, this also does not play a role, since almost all of the aroma compounds are lost to evaporation. However, if aroma hops are added towards the end of the boil, these fluctuations can indeed have an impact if the addition was based on the same α-acid content which is unfortunately still the case in a lot of breweries. A higher or lower amount of aroma compounds will, nevertheless, influence the intensity of the hop bouquet in beer. Fluctuations in the ratios of the polyphenols can affect the body and mouthfeel of the beer [10, p. 304]. The haze stability of beer also depends, at least in part, upon the quantity of polyphenols. Stabilization of the beer with PVPP may be necessary to manage these fluctuations.

Variable lupulin enrichment during the production of pellets offers one approach to contending with the issues of the ratios arising from fluctuations in the various groups of compounds. Depending upon the growing season, at least the ratio of alpha and hop oil to the polyphenols can be corrected with this kind of enrichment. While alpha and oil suffer significantly under drought conditions and high temperatures, for example, the polyphenols remain constant across the growing seasons, unaffected by climatic conditions. If type 90 pellets are employed in this situation, it is inevitable that significantly more polyphenols will be introduced to the beer compared to the alpha acid content in hops grown during hot growing seasons than in seasons with more favorable weather. Depending upon the beer style, a reasonably constant ratio of alpha to polyphenols is advantageous for beer quality. Flexible lupulin enrichment with the objective of securing a constant ratio of α-acids to polyphenols can therefore compensate for an extreme amount of polyphenols being added to the beer as a result of climatic conditions [10, p. 164; 31, 32].

Besides adding bitter compounds and polyphenols an important objective of a late dosage of aroma hops should be the introduction of a defined amount of aroma compounds. Additions according to the α-acid concentration cannot possibly meet the goal of maintaining a consistent aroma over years of fluctuating climatic conditions. Focusing on the hop oil, linalool or oxygenated fraction would be more beneficial [10, p. 279; 33] for achieving a reasonably constant hop aroma over successive crop years. Additions of aroma hops from hot, dry growing seasons according to their α-acid content for late additions or for dry hopping will result in an excessive quantity of hop polyphenols entering the beer along with some aroma compounds. Moreover, the issue also arises regarding fluctuations in the development of the relevant hop compounds among the various hop varieties.

Table 11 **A comparison of the factors affected by climatic conditions in sets of crop years, 2015 and 2016, 2019 and 2020, as well as 2019 and 2021**

	Hallertau	Tettnang	Spalt
2015 : 2016	9.4 : 18.9	14.4 : 29.9	6.8 : 10.0
2019 : 2020	10.7 : 17.9	17.6 : 27.1	8.7 : 14.7
2019 : 2021	10.7 : 23.3	17.6 : 37.5	8.7 : 20.5

5 New hop varieties

The data presented in this paper are based on the comparison of the 2015 and 2016 crop years, but new varieties are now being added at an increasing rate, up to five per year in Germany alone. The tolerance of new varieties with regard to changing climatic conditions is a constant concern, one that must be handled with increasing urgency. As shown here, the comparison of two different crop years is helpful in assessing the capacity for a variety to withstand different climatic conditions. Currently, it is useful to compare the 2019, 2020 and 2021 crop years, the climate data for which is presented in table 11. They show a distribution comparable to the crop years 2015 and 2016. The authors, therefore, intend to compare more recent varieties in these crop years, such as Ariana, Callista, Aurum and Diamant. However, it would be advantageous, as a guide for setting the parameters in new studies, to include the varieties Northern Brewer and Mandarina Bavaria, because in the present study, they have been identified as embodying opposite extremes with regard to climate sensitivity.

Another issue is that of targeted breeding of climate-tolerant varieties. Finding and selecting suitable breeding pairs will become increasingly important. Crossbreeding with hops from the USA to create a number of flavor and bitter varieties was originally intended to produce high alpha varieties or fruity aromas; however, these new varieties as a side effect have also exhibited more climate tolerance. One suspects that the poor climate tolerance of the variety Perle is due to its parentage. The extremely climate-sensitive mother Northern Brewer has likely had a negative impact on its offspring Perle.

6 Summary

Observations have made clear that yields with regard to quantity and the α-acid content of hops are dependent on climatic conditions. In hot, dry summers, α-acid yields (kg α-acids/ha) are reduced by

up to 70 % compared to “normal” summers. Nevertheless, little is known about the effects of climate on other hop compounds, which is the topic of the present study. For this purpose, 20 German hop varieties from the 2015 crop year (hot and dry) were compared to hops from the 2016 crop year (average rainfall and few excessively warm days). Type 90 pellets from large processing lots were analyzed to compare representative samples from both crop years. The analysis results from the poor 2015 harvest were counterbalanced to some extent by those from the higher yielding 2016 harvest. The deficit or excess of hop compounds in the 2015 harvest compared to 2016 is expressed in % (rel.) and can be summarized as follows:

- The reactions of the three secondary metabolites, α-acids (– 30 %), sum of the aroma compounds (– 17 %) and total polyphenols (+ 9 %), in the overall average of all 20 varieties exhibited significant differences.
- β-Acids fared slightly better (– 25 %) than α-acids. Groups of aroma compounds reacted very differently from one another. The most sensitive to climate were the esters at -39 %, followed by linalool at – 19 %, myrcene at – 23 %, and the sesquiterpene alcohols and α-humulene at only – 3 %.
- Among all of the attributes analyzed in this study, the polyphenols were surprisingly stable. Only xanthohumol showed any change (– 16 %).
- The most climate-sensitive varieties are the landraces, followed by the cultivated aroma hops and the bitter varieties. The flavor hops proved to be the most stable.
- Even individual varieties within a varietal group showed considerable variation in their climate sensitivity. For a simple and understandable classification, the bitter potential in the form of α-acids and the aroma potential as an average of six aroma attributes was employed. In the comparison of the 2015 and 2016 crop years, Northern Brewer was found to be the weakest regarding climate sensitivity at 51 %, followed by Perle (41 %). The landraces exhibited a change of 35 to 40 %. Saphir, Smaragd and Cascade showed an average variation of about 25 %. Opal, Hallertauer Tradition, Herkules, Polaris, Hallertauer Magnum, Hüll Melon and Hallertau Blanc proved to be even more stable (19 – 23 %). Mandarina Bavaria was even more stable with regard to the influence of climatic conditions, at only 15 %.
- Northern Brewer, being the mother of Perle, suggests that climate sensitivity is heritable.

Since compounds exhibit different levels of stability when subjected to more challenging conditions associated with climate change, the ratios of these groups of compounds to one another fluctuate depending upon the crop year, especially the ratio of the α-acids to the polyphenols. However, these ratios can be counterbalanced with the adoption of flexible enrichment strategies during pellet production.

At the very least, brewers should monitor these criteria and take them into consideration in hop additions. The ratio of bitter to aroma potential can shift depending upon the climate, which leads to changes in the aroma of the beer, if for example, late additions are weighed out according to their α-acid content. Aroma hop additions at the end of the boil, in the whirlpool, or especially on the cold side through dry hopping should be carried out logically according to the quantity of one or more aroma compounds present in the hops.

Why hop compounds react differently on differing climatic conditions is still unknown. It is predominantly a matter of the enzymatic processes that occur during biogenesis. It is conceivable that these enzymes respond differently to drought and heat.

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