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Article

Hops Across Continents: Exploring How Terroir Transforms the Aromatic Profiles of Five Hop (*Humulus lupulus*) Varieties Grown in Their Countries of Origin and in Brazil

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Abstract: *Humulus lupulus*, or hops, is a vital ingredient in brewing, contributing bitterness, flavor, and aroma. The female plants produce strobiles rich in essential oils and acids, along with bioactive compounds like polyphenols, humulene, and myrcene, which offer health benefits. This study examined the aromatic profiles of five hop varieties grown in Brazil versus their countries of origin. Fifty grams of pelletized hops from each strain were collected and analyzed using HS-SPME/GC-MS to identify volatile compounds, followed by statistical analysis with PLS-DA and ANOVA. The study identified 330 volatile compounds and found significant aromatic differences among hops from different regions. For instance, H. Mittelfrüher grown in Brazil has a fruity and herbaceous profile, while the German-grown variety is more herbal and spicy. Similar variations were noted in Magnum, Nugget, Saaz, and Sorachi Ace varieties. The findings underscore the impact of terroir on hop aromatic profiles, with Brazilian-grown hops displaying distinct profiles compared to their counterparts from their countries of origin, including variations in aromatic notes and α -acid content.

Keywords: *Humulus lupulus*; aromatic profile; terroir impact; volatile compounds; HS-SPME/GC-MS

1. Introduction

Humulus lupulus, commonly known as hops, is a species of flowering plant in the Cannabaceae family. It is native to Europe, Asia, and North America, and is primarily known for its use in brewing beer [1]. The plant is a vigorous, climbing vine with rough stems and serrated leaves arranged oppositely along the stem. Hops are dioecious, meaning there are separate male and female plants. The female plants produce cone-like structures called strobiles, which are used in brewing to impart bitterness, flavor, and aroma to beer. These cones contain lupulin glands, which contain essential oils and acids responsible for the characteristic bitterness and aroma of hops [2].

Apart from the most common compounds found in hop cones belonging to bitter acids (α - and β -acids) [3], there are at least several other bioactive compounds (essential oils and polyphenols) that make hop cones a feedstock with a broad range of microbiological properties [2, 3, 4]. Among various properties, hop cones contain compounds, such as prenylated flavonoids, which have been shown to possess sedative properties [5]. Certain compounds found in hops, such as phytoestrogens, have been investigated for their potential in hormone regulation. These compounds may have implications for conditions such as menopausal symptoms [6].

Hops offer health benefits due to their antioxidants, like polyphenols, which may reduce oxidative stress and chronic disease risk [7]. Compounds such as humulene and myrcene in hops are

believed to have relaxing effects [8, 9]. Besides, hundreds of aroma compounds are found in hop essential oils [10], though these oils constitute only about 0.5% to 3.0% of the hops' dry weight [3]. The complex composition of hop essential oil makes characterizing its aroma a challenging task.

Regarding volatile and aromatic compounds, Su and Yin [11] conducted a study aimed at analyzing five fresh samples of Cascade and Chinook hops from different locations in Virginia, using HS-SPME-GC-MS-O. They identified 33 aromatic compounds, including esters, monoterpenes, sesquiterpenes, terpenoids, an aldehyde, and an alcohol. Furthermore, the authors demonstrated how the cultivation location can significantly influence the aroma profiles of Cascade and Chinook hops [11].

Building on these principles, this study aimed to evaluate the aromatic profile of the hop varieties Hallertauer Mittelfrüher, Magnum, Nugget, Saaz, and Sorachi Ace. Except for Sorachi Ace, the study compared samples from their countries of origin with samples of the same varieties grown in Brazil, using the HS-SPME/GC-MS methodology (Headspace Solid-Phase Microextraction coupled with gas chromatography-mass spectrometry).

2. Material and Methods

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

2.1. Samples

For this study, 50 g samples of pelletized hops from five distinct strains were collected, with samples planted in their countries of origin, except for Sorachi Ace, which was compared with samples of the same strains planted in Brazil. Samples of Magnum and Hallertauer Mittelfrüher hops were obtained from Germany, Nugget and Sorachi Ace from the United States, and Saaz from the Czech Republic, all sourced from Barth Haas (Nuremberg, Germany). The Brazilian hops, Hallertauer Mittelfrüher, Nugget, and Saaz, were sourced from Dalcin (Taguaí, SP, Brazil), and the Magnum and Sorachi Ace hops from Brava Terra (Fortuna, SP, Brazil) (Table 1).

Table 1. Characteristics of the five hop (*Humulus lupulus*) varieties used in the present study.

Hop strain	Typical use	Company	Origin	Harvest	Alpha acid (%)
Hallertauer Mittelfrüher	Aroma	Dalcin	Brazil	2021	6.88
		Barth Haas	Germany	2020	4.50
Magnum	Bitter	Brava Terra	Brazil	2021	12.81
		Barth Haas	Germany	2020	14.70
Nugget	Bitter	Dalcin	Brazil	2021	9.66
		Barth Haas	United States	2018	9.50
Saaz	Aroma	Dalcin	Brazil	2021	5.67
		Barth Haas	Czech republic	2020	3.50
Sorachi Ace	Aroma/Bitter	Brava Terra	Brazil	2021	8.70
		Barth Haas	United States	2020	10.80

The samples were manually ground into a fine powder using a mortar and pestle for subsequent analysis. Ground hop samples (40 ± 0.5 mg) were placed in a 20 mL glass vial with an automatic sampler. The vials were sealed with PTFE/silicone septa and aluminum caps (Macherey-Nagel, Bethlehem, PA, USA).

2.2. Instrumentation

The volatile compound profiles were analyzed using headspace solid-phase microextraction (HS-SPME) combined with gas chromatography–mass spectrometry (GC–MS). This analysis employed the GCMSQP2020 NX system, incorporating the Nexis GC-2030 gas chromatograph, a quadrupole mass spectrometer, and the AOC-6000 Plus autosampler, all supplied by Shimadzu (Nakagyo-ku, Kyoto, Japan). For HS-SPME extraction, a DVB/CAR/PDMS (divinylbenzene/carboxen/polydimethylsiloxane) Smart Fiber (80 μ m) from Shimadzu was utilized.

Prior to analysis, the fiber was preconditioned at 240 °C, and two blank injections were performed according to the manufacturer's guidelines. Samples were equilibrated for 10 minutes at 50 °C in the autosampler's heat block. The extraction process involved exposing the SPME fiber to the sample headspace for 50 minutes. The fiber was then inserted into the GC injector port for 3 minutes at 230 °C in splitless mode (using an SPME glass liner with a 0.75 mm ID), enabling thermal desorption of the volatile compounds. GC separation was performed with a constant helium flow (1 mL/min) on a PEG capillary column (HP-INNOWAX, 30 m, 0.25 mm ID, 0.15 μ m) from Shimadzu. The oven temperature was programmed to increase from 40°C to 150°C at a rate of 5°C per minute, followed by a ramp to 225°C at 20°C per minute, with initial and final holding times of 5 minutes and 20 minutes, respectively as described by Su and Yin [11].

Mass spectrometry detection was carried out using electron impact (EI) ionization at 70 eV, in full-scan mode within the 40–350 amu range. The transfer line and ion source were maintained at 250 °C. Data acquisition was conducted in total ion current (TIC) mode.

2.3. Volatile Compounds Identification and Statistical Analysis

The detection of volatile compounds was conducted by comparing each peak's molecular fragmentation pattern against the mass spectra available in the 2020 NIST MS database library (National Institute of Standards and Technology, Gaithersburg, USA). A compound was considered identified if it displayed a similarity index (SI) exceeding 85. In cases of ambiguous identifications, retention indices were calculated using a series of n-alkanes (C8 - C23) as references for confirmation.

Chromatographic profiles from the samples were analyzed using chemometric classification methods. These methods aim to leverage experimental data to predict qualitative properties of the samples, referred to as categories or classes. Specifically, the goal was to determine the aroma characteristics of the hop samples. Given the multivariate nature of the experimental data (i.e., the chromatographic profiles), this study focused on employing partial least squares discriminant analysis (PLS-DA) to construct a classification model.

2.4. Database Software Analysis

Each identified compound was queried using its CAS Registry Number in the PubChem database (<https://pubchem.ncbi.nlm.nih.gov/>). Furthermore, the flavor and aroma profiles of these compounds were examined using the Perflavory database (<https://perflavory.com/search.php>).

2.5. Statistical Analysis

For statistical analysis, results were presented as mean $\pm$ standard deviation (SD). To quantify volatile compounds common in at least two of the analyzed styles, the identified peak areas were automatically converted into Area% using LabSolutions GCMSolutions software (Shimadzu). This quantification approach was adopted because, as per the manufacturer, employing a specific standard for quantification ensures consistent concentration levels across all samples. The Student's t-test was utilized for comparing two samples, given that normal distribution was confirmed. For comparing three or more samples, Analysis of Variance (ANOVA) was performed, followed by the Tukey test. Differences were considered statistically significant when $p \leq 0.05$ (5% significance level).

3. Results and Discussion

3.1. Classification by PLS-DA

To investigate data trends and sample correlations, multivariate analysis was utilized. A classification model was specifically created to highlight differences related to the production

method. Chromatographic profiles, illustrated as GC-MS total ion currents (TIC), were processed using PLS-DA to distinguish between hop varieties planted in Brazil and those in their countries of origin (Figure 1).

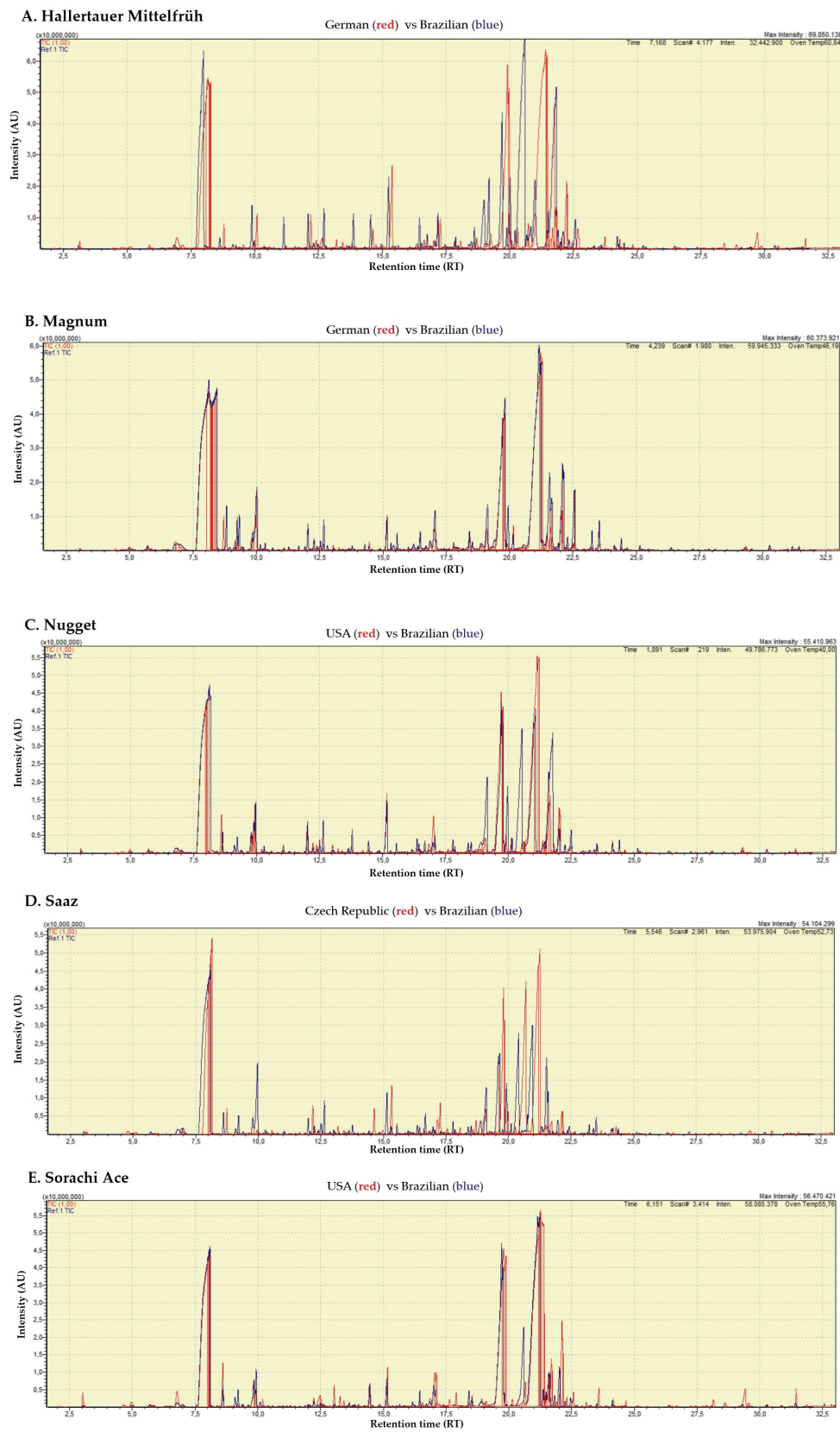


Figure 1. Chemical interpretation of the PLS-DA model discriminating between hops planted in their countries of origin (red) and the same varieties planted in Brazil (blue). Samples are based on VIP

scores and regression coefficients. The selected hop varieties were **A. Hallertauer Mittelfrüh**, **B. Magnum**, **C. Nugget**, **D. Saaz**, and **E. Sorachi Ace**. The chromatogram regions significantly contribute to the PLS-DA model.

To evaluate chemical differences between the beer groups analyzed, Variable Importance in Projection (VIP) scores were calculated from the PLS-DA model. VIP scores measure the contribution of individual variables to the model, with higher scores indicating greater importance. Normalized VIP scores greater than 1 are generally considered significant. By combining PLS regression coefficients with VIP scores, we can identify key compounds for distinguishing among sample types and gain insights into the direction of observed variations.

3.2. Aromatic Hop Profile

A total of 330 different volatile compounds were identified using HS-SPME/GC-MS across all hop samples (Table 2). Although several of these compounds exhibit distinct aroma and odor profiles, the suppliers of these hops, as well as Beer Maverick (<https://beermaverick.com/>), have already reported differentiated profiles (Figure 2).



Figure 2. Aromatic profiles according to the hop (*Humulus lupulus*) Strain Producers for the varieties used in this study, grown in their countries of origin (DE: Germany; USA: United States; and CZ: Czech Republic) and grown in Brazil (BR).

H. Mittelfrüh grown in Germany has a more spicy and herbal profile compared to the one grown in Brazil, which has a greener profile. Magnum grown in Germany has a spicier profile, whereas the one grown in Brazil features floral, berry, tropical fruit, citrus, and herbal notes. Nugget grown in the United States has a more herbal and woody profile, while the same variety grown in Brazil presents citrus, floral, and berry characteristics. Saaz grown in the Czech Republic has a slightly more woody and floral profile, while the same variety in Brazil exhibits more herbal, spicy, and citrus notes. Finally, Sorachi Ace grown in the United States shows almost the same pattern as the same variety in Brazil, except that the Brazilian variety is slightly more woody, tropical, citrus, herbal, and floral, but maintains a very similar sensory pattern. It is interesting to note that the same variety planted in its country of origin, in this case, Japan, and according to Beer Maverick (<https://beermaverick.com/>), also has the same profile, except for the absence of a woody profile. This may indicate a variety with little terroir effect.

3.3. Hallertauer Mittelfrüher

In terms of compound quantities, calculated by % Area, 14 compounds were more expressed in the variety planted in Germany, while 23 were more expressed in the variety planted in Brazil (Table 3). Among the 14 compounds more expressed in the German variety, 11 are related to aroma or odor. In the Brazilian variety, 13 of the 23 more expressed compounds are associated with aroma or odor. Regarding unique compounds, 64 were identified in the variety planted in Germany compared to the same variety planted in Brazil, with 28 of these related to aroma (Table 4). In the Brazilian HM, 45 unique compounds were found compared to the German HM, with 22 being related to aroma.

[illegible]

Methyl octanoate	111-11-5	Waxy	Green	
2-methylpropyl hexanoate	105-79-3	Fruity	Medium	Fruity
Benzaldehyde	100-52-7	Fruity	High	Fruity
Nonan-2-one	821-55-6	Fruity	Medium	Cheesy
4-hydroxyhexan-3-one	4984-85-4			
Octan-1-ol	111-87-5	Waxy	Medium	Waxy
3,7-dimethylocta-1,6-dien-3-ol	78-70-6	Floral	Medium	Citrus
Methyl 6-methyloctanoate	5129-62-4			
Heptyl propanoate	2216-81-1	Floral		Fruity
Heptyl 2-methylpropanoate	2349-13-5	Fruity		Berry
Methyl nonanoate	1731-84-6	Fruity		Winey
Hexanoic acid	142-62-1	Fatty	Medium	Cheesy
2-methylbutyl hexanoate	2601-13-0	Ethereal		
(1S,2R,6R,7R,8S)-1,3-dimethyl-8-propan-2-yltricyclo[4.4.0.0 ^{2,7}]dec-3-ene	1491-24-8			
(1R,2S,6S,7S,8S)-1,3-dimethyl-8-propan-2-yltricyclo[4.4.0.0 ^{2,7}]dec-3-ene	3856-25-5	Woody		
Decan-2-one	693-54-9	Floral	Medium	Fermented
Decyl trifluoroacetate	333-88-0			
7-Decen-2-one	3519-43-3			
7-methyl-3-methylideneoct-6-enal	5505-04-3	Aldehydic	Medium	
5-methylhexanoic acid	628-46-6	Fatty	Medium	
2-(2,4-difluorophenyl)-1-[4-[6-(4-methylpiperazin-1-yl)pyridazin-3-yl]piperazin-1-yl]ethanone	1191-2-2			

[illegible]

(1S,8aR)-4,7-dimethyl- 1-propan-2-yl- 1,2,3,5,6,8a- hexahydronaphthalene	483- 76-1	Herbal
Zonarene	4192 9-5-9	
1,6-dimethyl-4-propan- 2-yl-1,2,3,4,4a,7- hexahydronaphthalene	1672 8-99- 7	
1,2,4a,5,6,8a- hexahydro-4,7- dimethyl-1-(1- methylethyl)-, [1S- (1.alpha.,4a.beta.,8a.alp ha.)]-naphthalene	2440 6-5-1	
[(4S)-4-prop-1-en-2- ylcyclohexen-1- yl]methanol	1845 7-55- 1	
2-tridecanone	593- 8-8	
[(2E)-3,7-dimethylocta- 2,6-dienyl] propanoate	105- 90-8	Floral
(1S,4S)-1,6-dimethyl-4- propan-2-yl-1,2,3,4- tetrahydronaphthalene	483- 77-2	Herbal Spicy
[(2E)-3,7-dimethylocta- 2,6-dienyl] butanoate	106- 29-6	Fruity
(Z,Z)-1,8,11- heptadecatriene	5613 4-3-3 8163	
[(Z)-dec-3-enyl] acetate	4-99- 3	
Methyl ester 3,6- dodecadienoic acid	1610 6-1-7	
2-[(2R,5S)-5-ethenyl-5- methyloxolan-2- yl]propan-2-ol	5989 -33-3	Earthy
7-methyl-4- methylidene-1-propan- 2-yl-2,3-dihydro-1H- naphthalene	5027 7-34- 4	
Methyl (6Z,9Z,12Z,15Z,18Z)- henicososa-6,9,12,15,18- pentaenoate	6591 9-53- 1	
(9Z,12Z,15Z)-octadeca- 9,12,15-trien-1-ol	506- 44-5	
2-n-Butyl-2- cyclopentenone	5561 _5-7	
(1S,4R,4aS,8aR)-4,7- dimethyl-1-propan-2- yl-2,3,4,5,6,8a-	1991 2-67- 5	

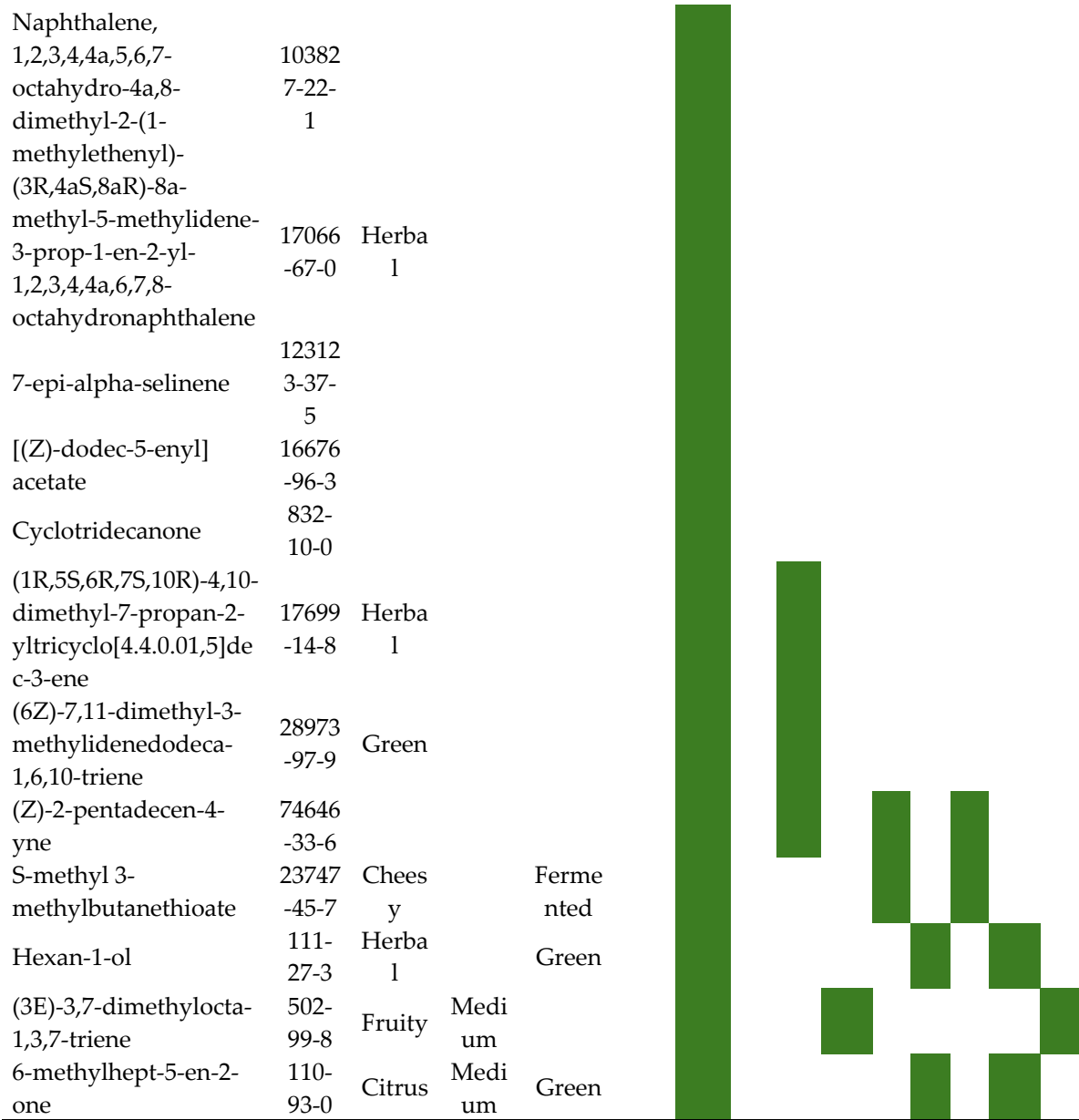
[illegible]

Hexahydro-1,1-dimethyl-4-methylene-4H-cyclopenta[c]furan [(4E)-11,11-dimethyl-8-methylidene-4-bicyclo[7.2.0]undec-4-enyl]methanol	34429 4-72-0 50277 -33-3			
Methyl 2-(3-oxo-2-pentylcyclopentyl)acetate	24851 -98-7	Floral	Medium	Floral
2,6,6-trimethylbicyclo[3.1.1]hept-2-ene	80-56-8	Herbal	High	Woody
2-methylpropyl 3-methylbutanoate	589-59-3	Fruity	Medium	Green
2,2,4,6,6-pentamethylheptane	13475 -82-6			
2-methylpropyl 2-methylpropanoate	97-85-8	Fruity		Fruity
3-methylbut-2-en-1-ol	556-82-1	Fruity		Fruity
(6Z)-7,11-dimethyl-3-methylidenedodeca-1,6,10-triene	28973 -97-9	Green		
(E)-oct-2-en-4-ol	4798-61-2			
(4aR,8aR)-5,8a-dimethyl-3-propan-2-ylidene-1,2,4,4a,7,8-hexahydronaphthalene	6813-21-4			
Trifluoroacetyl-lavandulol	28673 -24-7			
7-methyl-4-methylidene-1-propan-2-yl-2,3-dihydro-1H-naphthalene (5S,6R,7S,10R)-7-Isopropyl-2,10-dimethylspiro[4.5]dec-1-en-6-ol	50277 -34-4 72203 -99-7			
1-methyl-4-propan-2-ylidenecyclohexene (9Z,12Z)-octadeca-9,12-dien-1-ol	586-62-9 506-43-4	Herbal	Medium	Woody
2-methylbutan-1-ol	137-32-6	Ethereal	Medium	Ethereal
Methyl 2-methylpropanoate	547-63-7	Fruity		Ethereal
[(Z)-dec-3-enyl] acetate	81634 -99-3			

(Methyldisulfanyl)met	624-	Sulfur		Sulfuro					
hane	92-0	ous		us					
2-methyl-5-propan-2-	99-	Terpe	Medi	Terpen					
ylcyclohexa-1,3-diene	83-2	nic	um	ic					
1-methylidene-4-prop-	499-								
1-en-2-ylcyclohexane	97-8								
5-methyl-6-methylene-	75029								
decane	-95-7								
3-methylbutanoic acid	503-	Chees	High	Cheesy					
	74-2	y							
2,2-dimethyl-3-[(2E)-3-	28977								
methylpenta-2,4-	-57-3								
dienyl]oxirane									
4-hydroxyhexan-3-one	4984-								
	85-4								
Heptyl 2-	2349-	Fruity		Berry					
methylpropanoate	13-5								
5,5-dimethylfuran-2-	20019								
one	-64-1								
Methyl (2Z)-3,7-	1862-	Floral							
dimethylocta-2,6-	61-9								
dienoate									
(1S,4aS,8aR)-4,7-									
dimethyl-1-propan-2-	10208	Wood							
yl-1,2,4a,5,6,8a-	-80-7	y							
hexahydronaphthalen									
e									
2-[(2R,5S)-5-ethenyl-5-	5989-	Earth	Medi						
methyloxolan-2-	33-3	y	um						
yl]propan-2-ol									
(1R,3Z,7Z,11R)-1,5,5,8-	19888								
tetramethyl-12-	-34-7								
oxabicyclo[9.1.0]dodec									
a-3,7-diene									
Propan-2-one	67-	Solve	High						
	64-1	nt							
[(2E)-3,7-dimethylocta-	109-	Fruity	Medi	Green					
2,6-dienyl] 3-	20-6		um						
methylbutanoate									
3,7,7-	554-								
trimethylbicyclo[4.1.0]	61-0								
hept-2-ene									
(3Z)-3,7-dimethylocta-	3338-	Floral	Medi	Green					
1,3,6-triene	55-4		um						
2-methylbutyl 2-	2445-	Fruity							
methylpropanoate	69-4								
Hexyl acetate	142-	Fruity	Medi	Fruity					
	92-7		um						
Pentyl 2-	2445-	Fruity							
methylpropanoate	72-9								

5,9-dimethyl-, (E)-5,8-decadien-2-one	13087 6-99-2		
Nonan-2-ol	628-99-9	Waxy	Waxy
3,7-dimethylocta-2,6-dienyl acetate	16409-44-2		
(6E)-7,11-dimethyl-3-methylidenedodeca-1,6,10-triene	18794-84-8	Wood y	
(1R,2R)-1-ethenyl-1-methyl-4-propan-2-ylidene-2-prop-1-en-2-ylcyclohexane	29873-99-2	Green	Medi um
(3Z,6E)-3,7,11-trimethyldodeca-1,3,6,10-tetraene	26560-14-5		
4a,8-Dimethyl-2-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene (1R,4aS,8aS)-7-methyl-4-methylidene-1-propan-2-yl-2,3,4a,5,6,8a-hexahydro-1H-naphthalene (1S,4aR,8aS)-4,7-dimethyl-1-propan-2-yl-1,2,4a,5,8,8a-hexahydronaphthalene	473-14-3		
	39029-41-9	Wood y	Medi um
	523-47-7	Wood y	Medi um
[(2Z)-3,7-dimethylocta-2,6-dienyl] butanoate	999-40-6	Green	Green
(1S,4S)-1,6-dimethyl-4-propan-2-yl-1,2,3,4-tetrahydronaphthalene (9Z,12Z)-octadeca-9,12-dien-1-ol (1S,4R,4aS,8aR)-4,7-dimethyl-1-propan-2-yl-2,3,4,5,6,8a-hexahydro-1H-naphthalen-4a-ol (4Z,7Z)-1,5,9,9-tetramethyl-12-oxabicyclo[9.1.0]dodeca-4,7-diene (E,E,E)-2,6,10,14-hexadecatetraen-1-ol, 3,7,11,15-tetramethylacetate	483-77-2	Herba l Spicy	Medi um
	506-43-4		
	19912-67-5		
	19888-33-6	Herba l	
	61691-98-3		

3,7-Cycloundecadien-1-ol, 1,5,5,8-tetramethyl-(1R,4S,4aR,8aS)-1,6-dimethyl-4-propan-2-yl-3,4,4a,7,8,8a-hexahydro-2H-naphthalen-1-ol	118014-38-3	Herbal	Medium	
2-[(2R,4aR,8aR)-4a,8-dimethyl-2,3,4,5,6,8a-hexahydro-1H-naphthalen-2-yl]propan-2-ol	473-16-5			
Methyl (Z)-5,11,14,17-eicosatetraenoate	59149-1-8			
Methyl ester docosapentaenoic acid	108698-2-8			
Humulenol-II	19888-0-7			
2-methylbut-3-en-2-ol	115-18-4			
3,4-dimethyldecane	17312-45-7			
4,5-dimethylnonane	17302-23-7			
Ethyl hexanoate	123-66-0			
Oct-1-en-3-ol	3391-86-4			
S-ethyl hexanethioate	2450-12-6	Herbal	Medium	
Methyl ester 4-octenoic acid	1732-0-9			
3,5,5-trimethyl-2H-furan	23230-79-7			
6-methyl-7-octen-2-one	35215-49-7			
S-methyl heptanethioate	2432-82-8			
7-epi-sesquithujene	159407-35-9			
Prop-2-enyl 3-methylbutanoate	2835-39-4			
(1S,4aR,7R)-1,4a-Dimethyl-7-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydronaphthalene	52026-55-8			
(1S,2S,4R)-1-ethenyl-1-methyl-2,4-bis(prop-1-en-2-yl)cyclohexane	515-13-9			



The HM planted in Germany exhibit an aromatic profile rich in herbal, spicy, floral, fruity, and woody notes, whereas those from Brazil have an aromatic profile characterized by fruity, herbal, sweet, and woody notes. This aromatic profile aligns with the descriptions provided by the suppliers for both (Figure 2).

Among the compounds that are more highly expressed, we can highlight (4R)-1-methyl-4-prop-1-en-2-ylcyclohexene (citrus), also known as D-limonene. This compound acts against the cytoplasmic membranes of microorganisms, resulting in a loss of membrane integrity, altering its permeability, and leading to the loss of ions and proteins [13]. Benzaldehyde (fruity) is another significant compound, known as an inhibitor of quorum sensing for the opportunistic pathogen *Pseudomonas aeruginosa* [14]. Hexanoic acid (fatty) has been considered to have high sensory potential effects in Chinese 'Marselan' wines [15]. Additionally, undecan-2-one (fruity) is known for its antifungal activity against *Colletotrichum gloeosporioides* [16]. Another property of this compound is its ability to alleviate asthma by reducing airway inflammation and remodeling. This beneficial effect is achieved through the inhibition of the NF-κB pathway [17].

Among the unique compounds in the Brazilian HM, notable ones include oct-1-en-3-ol (earthy), known for its antioxidant and antimicrobial properties [18]. This compound acts as a defense mechanism in seaweeds [19], potentially enhancing food preservation and contributing to overall health. It is also associated with aging flavors [18]. Hexan-1-ol (herbal) is found abundantly in Pale

Ale and Lambic beer styles [20] and holds significant potential for applications in the food and cosmetic industries [21]. Ethyl hexanoate (fruity), providing flavors typical of apples and pineapples, is a maturity marker in pequi fruits (*Caryocar brasiliense*) and is the most predominant compound in this fruit [22]. Methyl 2-methylpropanoate (fruity) can be detected in numerous foods and beverages and has been identified as a key volatile compound in Hunan Changde rice noodles fermented with *Lactococcus* [23]. Hexyl acetate is frequently used as a flavoring agent in a variety of food products, including candies, baked goods, and beverages. It is also an ingredient in perfumes, soaps, and other personal care products [24]. Moreover, the hexyl acetate identified in the grape pomace of the investigated grape varieties can be used similarly, serving as a flavoring agent in various food items and as a component in perfumes, soaps, and other personal care products [21]. This ester is also known for imparting a fragrance known as 'Orange Beauty' [25].

Among the most expressed compounds in the Brazilian HM, noteworthy ones include methyl heptanoate (fruity), contributing to a fruity flavor and found in various fruits. Methyl octanoate (waxy) adds a smooth, sweet flavor, common in some fruits and wines, and is one of the main flavoring agents in foods, possessing a vinous, fruity, and orange-like odor [26]. Octan-1-ol (waxy) has a pleasant aroma that contributes to the complexity of flavors in foods and is common in various beer styles [20].

3.4. *Magnum*

Unlike H. Mittelfrüher, Magnum is a hop variety that showed a lower α -acid content when planted in Brazil, according to its suppliers (Table 1). Regarding the quantity of compounds, calculated by % Area, 26 compounds were more expressed in the variety planted in Germany, while 20 were more expressed in the variety planted in Brazil (Table 3). Of the 26 more expressed in the German variety, 17 are related to aroma or odor. Of the 23 compounds more expressed in the Brazilian variety, 11 are related to aroma or odor. Regarding the compounds found in the variety planted in Germany, 34 unique compounds were identified compared to the same variety planted in Brazil (Table 4). Of this total, only 22 are related to aroma. In the Brazilian Magnum, 7 unique compounds were found compared to the German Magnum, among them, 6 are related to aroma.

The German Magnum hop rofile characterized by a blend of herbal, terpenic, woody, citrus, fruity, floral, and fatty notes. The key compounds contributing to this profile include 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (herbal), 2-methyl-5-propan-2-ylcyclohexa-1,3-diene (terpenic), and [(2E)-3,7-dimethylocta-2,6-dienyl] butanoate (fruity), among others. The Brazilian Magnum exhibits a profile with fruity, floral, and woody notes. The key compounds responsible for this profile include 2-methylpropyl 3-methylbutanoate (fruity), methyl heptanoate (fruity), and (1S,8aR)-4,7-dimethyl-1-propan-2-yl-1,2,3,5,6,8a-hexahydronaphthalene (herbal). The aromatic profiles of the German and Brazilian Magnum hop varieties are influenced by the specific compounds present in each variety. The German variety is characterized by a complex mix of herbal, fruity, and woody notes, while the Brazilian variety is dominated by fruity, floral, and herbal aromas. These differences are due to the unique combination of compounds present in each variety, influenced by factors such as terroir and cultivation practices.

Beer flavored with total Magnum hop oil has a unique sensory profile, featuring strong "crushed grass, sap," "resinous," "earthy," and "musty" aromas. Magnum hop oil consists mainly of β -myrcene, β -caryophyllene, and α -humulene, making up to 80% of the oil. β -myrcene, the most abundant compound, can smell "spicy," "resinous," "metallic," or "geranium-like" at different concentrations. The aromas of β -caryophyllene and α -humulene are less distinct but are described as "rubber-like," "mouldy," "woody," and "spicy." These aroma characteristics are also found in sesquiterpene-flavored beer, but at lower intensities, indicating the total oil enhances them [27].

3.5. *Nugget*

Unlike In contrast to the hops mentioned in the previous sections, the α -acid content was the same in both the American and Brazilian Nugget (Table 1). Regarding the quantity of compounds,

calculated by % Area, 25 compounds were more expressed in the variety planted in the United States, while 19 were more expressed in the variety planted in Brazil (Table 3).

Among the 25 compounds more expressed in the American variety, 17 are related to aroma or odor. Among the 19 compounds more expressed in the Brazilian variety, 7 are related to aroma or odor. Regarding the compounds found in the variety planted in the United States, 42 unique compounds were identified compared to the same variety planted in Brazil (Table 4). Of this total, only 25 are related to aroma. In the Brazilian Nugget, 37 unique compounds were found compared to the American Nugget. Among them, 24 presented some relation to aroma.

Among the compounds most abundantly expressed in the variety planted in the United States, notable ones include (4R)-1-methyl-4-prop-1-en-2-ylcyclohexene (citrus), which is one of the primary compounds identified in the essential oil of Okoume (*Aucoumea klaineana*) [28], being studied for its bioactive constituents and antibacterial activities. 3,7-dimethylocta-1,6-dien-3-ol (floral) is commonly found in large quantities in Indian Pale Ale beers but in smaller amounts in Pale Ale (IPA) [20]. 3-Methylbutyl 2-methylbutanoate (fruity) is reported to occur in foods such as apple brandy (Calvados), banana (*Musa sapientum* L.), cider (apple wine), date (*Phoenix dactylifera* L.), grape brandy, passion fruit (*Passiflora* species), among others [29].

Among the compounds most abundantly expressed in the variety planted in Brazil, noteworthy is methyl octanoate (waxy), which, interestingly, was found in *Annona crassiflora*, known as marolo fruit from the cerrado biome. This species is one of the most consumed in the Brazilian Midwest, with this compound significantly contributing to its aroma [30].

Among the compounds found exclusively in the variety planted in the United States, methyl 2-methylpropanoate (fruity) was previously mentioned as a volatile compound in Hunan Changde rice noodles fermented by *Lactococcus* [23], and is also an exclusive compound of Brazilian HM hops. (Methyldisulfanyl)methane (sulfurous) adds a sulfurous character, which is interesting for certain aromatic profiles. It is also one of the most abundant compounds in microwave-cooked radish (*Raphanus sativus* L.) oils [31]. 3-methylbutanoic acid (cheesy) imparts a cheesy character and was exclusively found in Bock beers [20], being perceived by many individuals as a very strong odor impression [32].

Among the compounds found exclusively in the variety planted in Brazil, hexyl acetate (fruity) is also an exclusive compound of Brazilian HM hops. It is a flavoring agent in a variety of food products and an ingredient in perfumes, soaps, and other personal care products [24]. Methyl dodecanoate (waxy) adds a waxy and sweet flavor and is one of the most variable compounds for distinguishing wine cultivars, contributing significantly to their sensory characteristics [33]. It was also isolated from the ethyl acetate extract of the culture filtrate of the probiotic *Lactobacillus plantarum* H24 [34]. 3-methylbutyl 3-methylbutanoate (fruity) contributes a fruity flavor, enhancing the complexity of the aroma. It is the most abundant compound in all flowering stages of Asian skunk cabbage (*Symplocarpus renifolius*, Araceae) [35], and is present in the odors of ripe bananas, guavas, and oranges. It is also found among the compounds that attract both sexes of the invasive African fruit fly *Bactrocera invadens* [36].

3.6. Saaz

The Saaz hop exhibits an α -acid content of 3.5 for the Czech, compared to 5.67 for the Brazilian one (Table 1). Regarding the quantity of compounds, calculated by % Area, 17 compounds were more expressed in the variety planted in the Czech Republic, while 15 were more expressed in the variety planted in Brazil (Table 3).

Among the 17 compounds more expressed in the Czech Saaz, 10 are related to aroma or odor. Of the 15 compounds more expressed in the Brazilian Saaz, 9 are related to aroma or odor. Regarding the compounds found in the variety planted in the Czech Republic, 26 unique compounds were identified compared to the same variety planted in Brazil (Table 4). Of this total, only 18 are related to aroma. In the Brazilian Saaz, 28 unique compounds were found compared to the Czech Saaz. Among them, 18 were related to aroma.

The differences in the aromatic profiles of the Czech and Brazilian Saaz are largely due to the variation in the expression of specific compounds, which are influenced by factors such as climate, soil, and cultivation practices. The presence of more spicy, earthy, woody, and floral compounds in the Czech Saaz suggests a more traditional and balanced aroma profile, while the Brazilian Saaz higher expression of ethereal, herbal, fruity, and spicy compounds offer a unique and potentially more vibrant aroma.

These aromatic differences are crucial for brewers when selecting hops for specific beer styles, as the aroma profile of the hops can significantly influence the final product's flavor and aroma. Understanding the specific compounds responsible for these aromas allows brewers to tailor their hop selections to achieve desired sensory characteristics in their beers.

Regarding the compounds most expressed in Czech Saaz hops, 3,7-dimethylocta-1,6-dien-3-ol (floral) is commonly found in higher quantities in Indian Pale Ale beers [20]. Oct-1-en-3-ol (earthy), known for its mushroom-like aroma, is a byproduct of the enzymatic degradation of linoleic acid and ethanol [37] and previous studies have shown that it functions as a defense compound in marine algae [19, 38, 39].

Among the compounds most expressed in Brazilian Saaz hops, benzaldehyde (fruity) primarily manifests as a sweet note. Regarding the unique compounds in Czech Saaz hops, 3-methylbutanoic acid (cheesy) is noted for its sweaty-cheesy aroma and contributes to the sensory characteristics of Gouda cheese [40]. Hexanoic acid (fatty) plays a role in aromatic complexity and has been documented for its effects in Chinese wines [15].

For the unique compounds in Brazilian Saaz hops, hexyl acetate (fruity) is widely used in the food and cosmetic industries [24], is present in grape pomace [21], and is recognized for its distinct 'Orange Beauty' fragrance [25]. 3-Methylbutyl 3-methylbutanoate (fruity) contributes a fruity flavor and is the predominant compound in the flowering of *Symplocarpus renifolius*, Araceae [35].

3.7. Sorachi Ace

The Sorachi Ace (SA) hop exhibits an α -acid content of 10.8 in the American, while the Brazilian SA has an α -acid content of 8.7 (Table 1). Regarding the quantity of compounds, calculated by % Area, 24 compounds were more expressed in the variety planted in the United States, whereas 21 were more expressed in the variety planted in Brazil (Table 3).

Of the 24 compounds more expressed in the American SA, 13 are related to aroma or odor. Of the 21 compounds more expressed in the Brazilian SA, 12 are related to aroma or odor. Regarding the compounds found in the variety planted in the United States, 17 unique compounds were identified compared to the same variety planted in Brazil (Table 4). Of this total, only 13 are related to aroma.

In the Brazilian SA, 25 unique compounds were found compared to the American SA, among them, 17 have some relation to aroma.

The American SA tends to have a more diverse aromatic profile with herbal, citrus, and woody notes being dominant. The presence of compounds like 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene and (4R)-1-methyl-4-prop-1-en-2-ylcyclohexene significantly contribute to the herbal and citrus characteristics. The Brazilian SA exhibits a more fruity and spicy aromatic profile. Compounds such as 7-methyl-3-methylideneocta-1,6-diene and 3-methylbut-2-enyl 2-methylpropanoate are responsible for these attributes, providing a unique aroma compared to its American counterpart. The presence and concentration of specific volatile compounds influence the aromatic profile. Terpenes and esters are particularly important as they are responsible for the distinct aromas of hops, affecting beer's aroma and flavor. The unique environmental conditions and cultivation practices in the US and Brazil likely contribute to the differences in these aromatic compounds, resulting in variations in the hop profiles.

Sorachi Ace is a hop variety that imparts distinctive varietal aromas to the final beer, including woody, pine, citrus, dill, and lemongrass notes. Research concludes that the unique aroma of Sorachi Ace hops is due to the high levels of geranic acid, which acts synergistically with other hop-derived compounds to enhance the overall aroma. Sensory evaluations showed that late and dry hopping

resulted in beers with significantly higher scores for flowery, fruity, tropical, and lemon characteristics compared to kettle-hopped beer [41].

Regarding the compounds most expressed in the American SA, we can highlight (4R)-1-Methyl-4-prop-1-en-2-ylcyclohexene (citrus), which is a compound exclusively found in the Gose style compared to other sours [20]. It is found in the essential oil of okoume [28] and also acts against the cytoplasmic membranes of microorganisms [13]. Benzaldehyde (fruity) provides fruity notes. 3,7-dimethylocta-1,6-dien-3-ol (floral) is common in IPA. Regarding the compounds most expressed in the Brazilian SA, we can highlight 3-methylbut-2-enyl 2-methylpropanoate (fruity), which is one of the exclusive compounds found in the Farmhouse Ale beer style. Oct-1-en-3-ol (earthy) is known for being an antioxidant and antimicrobial [18], acting as a defense mechanism in marine algae [19], and is associated with the aging of flavors [18]. This compound is produced from 10-linoleate hydroperoxide [42] and is the most abundant alcohol found in soybeans cultivated in North America [43]. Nonan-2-one (fruity) is a bioactive compound capable of promoting rice growth [44]. It was identified in the volatilome of *Bacillus* sp. BCT9, showing the ability to increase lettuce biomass by up to 48% after 10 days of exposure [45]. Regarding the compounds exclusive to the American SA, we can highlight 3-methylbutanoic acid (cheesy), which, as discussed, is found exclusively in Bock beers [20] and has a strong impression on individuals [32]. Camphene (woody) is a component of rosemary (*Rosmarinus officinalis*) essential oil (Hendel et al., 2024). Hexan-1-ol (herbal) is found in Lambic and Pale Ale beers [20] and has potential applications in the food industry (Abreu et al., 2023). 6-Methylhept-5-en-2-one (citrus) is a compound that signals freshness in algae (*Cladostephus spongiosus*) [46]. *Hannaella* and *Neomicrosphaeropsis* showed a significantly positive correlation with this compound produced during the fermentation of Petit Manseng sweet wine [47].

Regarding the compounds exclusive to the Brazilian SA, we can highlight hexyl acetate (fruity), as discussed, it is an important compound for the food and perfume [24]. Octyl acetate (floral) is an exclusive compound found in Pilsen beers with hop extract [20], as well as in the Quadrupel beer style as an exclusive compound [20]. This compound is a useful marker for monitoring the fermentation process, as its post-fermentation concentration increases proportionally to the pre-fermentation concentration of the corresponding alcohol [48]. Large amounts of this compound have also been associated with potential antioxidant and anticancer effects in leaves of *Pittosporum* species (*Pittosporaceae*) [49]. Pentyl propanoate (fruity), which is a metabolic product derived from 1-pentanol, is an important flavoring ingredient formed by the condensation of pentanol and propanoic acid. The fruity smell of esters makes them unique, with wide applications in the flavor, fragrance, and solvent industries [50]. This compound is also found in truffles (*Tuber canaliculatum*) harvested in Quebec, Canada [51]. 2-Methyl-5-propan-2-ylcyclohexa-1,3-diene (terpenic) is a compound found in the industrial product Monash Pouch diet, although its role in the flavor of this product is still unknown [52]. 3-Methylpentanoic acid (animal) receives special attention due to its peculiar aroma and its importance for fermented beverages. Acids can be obtained by lipid oxidation or by conversion of aldehydes or ketones. Additionally, acids can react with alcohols to form esters and provide wine aroma, among them 3-methylpentanoic acid [53], which is also found in rice wine [54]. The presence of this compound seems to be stable in amounts in different wines [55] and has also been described in beers [56]. It is interesting to note that this aroma is present in the Brazilian SA, which can be very interesting for the country's scenario. Recently, Brazil developed its first beer style, the Catharina sour. This style has been studied [57-58], and has already shown complexity in its volatile compound composition [20]. Thus, this could be a good hop for the local production of Catharina sour-style beers, to even enhance the flavor.

3.8. The Brazilian Touch in Hops

Regarding hops cultivated in Brazil, we observed a pattern, specifically compounds that were present in higher quantities or exclusively in all Brazilian-cultivated varieties. All varieties showed a higher amount of methyl 6-methylheptanoate (unrelated to aroma) and lower amounts of 3-(4-methylpent-3-enyl) furan (woody), 3,7-dimethylocta-1,6-dien-3-ol (floral), and undecan-2-one (fruity). Concerning exclusive compounds, none were found common in all varieties planted in

Brazil; however, some are frequent in more than one hop. Pentyl propanoate (fruity), hexyl acetate (fruity), and 2-methylpropyl propanoate (fruity) were found in all hops except H. Mittelfrüher. [(2E)-3,7-dimethylocta-2,6-dienyl] propanoate (floral) was found in all except Magnum. Octyl acetate (floral) and octyl propanoate (fruity) were absent only in the German varieties H. Mittelfrüher and Magnum. [(Z)-hex-3-enyl] butanoate (green) and [(2E)-3,7-dimethylocta-2,6-dienyl] acetate (floral) were absent only in the varieties H. Mittelfrüher and Sorachi Ace.

Regarding hops cultivated in their places of origin, 3-methylbutanoic acid (cheesy) was the only exclusive compound found in all varieties. (Methyldisulfanyl)methane (sulfurous) was found in all except Sorachi Ace, while propan-2-one (solvent) was found in all except Magnum, and dodecane (alkane) in all except H. Mittelfrüher. Methyl hexanoate (fruity), (1R,4S,4aR,8aR)-1,6-dimethyl-4-propan-2-yl-3,4,4a,7,8,8a-hexahydro-2H-naphthalen-1-ol (herbal), and camphene (woody) were found in all American hop, possibly indicating a terroir effect.

H. Mittelfrüher and Magnum strains, which are German strains, have shown unique compounds compared to the German hop versus the Brazilian ones. Fourteen compounds are common between the H. Mittelfrüher and Magnum strains planted in Germany (Table 4), seven of which are aromatic, namely 2-methylbutan-1-ol (ethereal); methyl 2-methylpropanoate (fruity); (Methyldisulfanyl)methane (sulfurous); 2-methyl-5-propan-2-ylcyclohexa-1,3-diene (terpene); 3-methylbutanoic acid (cheesy); heptyl 2-methylpropanoate (fruity); and 2-[(2R,5S)-5-ethenyl-5-methyloxolan-2-yl]propan-2-ol (earthy); while 2 compounds are common between the H. Mittelfrüher and Magnum strains planted in Brazil, namely (1R,5S,6R,7S,10R)-4,10-dimethyl-7-propan-2-yltricyclo[4.4.0.0^{1,5}]dec-3-ene (herbal); and (6Z)-7,11-dimethyl-3-methylidenedodeca-1,6,10-triene (green).

Given that H. Mittelfrüher and Magnum are both cultivated in the same region in Germany, known as Hallertau in Bavaria, and our Brazilian hop also originate from the same region, the compounds indicated here could be the result of a terroir effect among the strains. The cultivation in Germany would suggest a hop with more fruity, earthy, and cheesy notes, while in Brazil it would suggest more herbal and green notes. Of course, further studies would be necessary to confirm this.

5. Conclusions

The study emphasizes the impact of terroir on the aromatic profile of hop varieties. Hallertauer Mittelfrüher and Magnum show distinct aromatic profiles depending on whether they are grown in Brazil or their country of origin (Germany). H. Mittelfrüher: variety has a more spicy and herbal profile when grown in Germany, whereas the Brazilian variety has a greener profile with increased α -acid content. The German Magnum variety is characterized by herbal, terpene, and woody notes, while the Brazilian variety is fruitier and more floral, with a decreased α -acid content compared to Germany. The American Nugget variety exhibits herbal and citrus notes, whereas the Brazilian counterpart shows more citrus, floral, and berry characteristics, maintaining similar α -acid levels. Interestingly, Sorachi Ace grown in the USA and Brazil shows minimal differences, suggesting a lesser terroir effect, with both having a tropical, citrus, and herbal profile.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: title; Table S1: title; Video S1: title.

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were created, or where data is unavailable due to privacy or ethical restrictions, a statement is still required. Suggested Data Availability Statements are available in section “MDPI Research Data Policies” at <https://www.mdpi.com/ethics>.

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