

Comparative Assessment of the Chemical Composition of Locally Cultivated and Imported Hops (*Humulus lupulus* L.) in Brazil Using Chemometrics

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ABSTRACT: The expansion of hop cultivation in Brazil highlights the need for studies on its chemical characteristics; however, such studies remain limited. This study compares three Brazilian hop cultivars (Comet, Cascade, and Sorachi Ace) with two major foreign brands, evaluating essential oil and α - and β -acids. Two-dimensional gas chromatography coupled with mass spectrometry (GC $\times$ GC–MS) revealed that the Brazilian hops essential oil composition was similar to that of imported hops of the same cultivar, although with lower essential oil content. Similarities were also observed for α -acids and β -acids contents. Hierarchical cluster analysis (HCA) and heat maps showed comparable characteristics between Brazilian and imported hops, clustering by cultivar. Partial least squares-discriminant analysis (PLS-DA) identified higher concentrations of myrcene and β -pinene in imported hops, while Brazilian hops exhibited higher levels of methyl (Z)-4-decenoate, α -selinene, β -selinene, selina-3,7(11)-diene, and β -cadinene. These specific chemical features indicate the potential of Brazilian hops that could benefit the brewing industry.

KEYWORDS: *brazilian hops, Humulus lupulus, essential oil, GC $\times$ GC, PLS-DA*

1. INTRODUCTION

Hops, responsible for imparting bitterness, flavor, and characteristic aroma to beer, have gained increased prominence in recent years, driven by changes in consumer preferences and the growing appreciation for beverages with differentiated sensory attributes.¹ In this context, hops have come to be used in much larger quantities than in traditional brewing methods, aiming to produce beers with more intense flavors and aromas. This increase in usage, along with the adoption of irrigation methods, genetic improvements, and the development of more efficient pesticides and fertilizers, has contributed to the global expansion of hop cultivation.^{2–4}

Hops are originally cultivated in temperate regions, with the United States and Germany being the largest producers, accounting for approximately 77% of global production. As cultivation has expanded, hop-growing regions have spread to various parts of the world, including Australia, New Zealand, South Africa, and Brazil. In Brazil, the growing number of breweries has driven higher hop consumption. As one of the world's largest beer producers, the country relies heavily on imports, which reached about 57 million USD in 2020. This high demand, coupled with the need to lower production costs, has fostered the development of domestic hop cultivation.^{5,6}

The first hop harvests in Brazil date back to 2017, and the crop has been expanding nationwide. In 2023, hop cultivation areas increased by 113% compared to 2022, totaling approximately 112 ha, with a focus on the southern and southeastern regions, because in some parts of the country, the shorter natural photoperiod requires the use of supplemental

lighting.^{7,8} This new scenario demands studies that evaluate everything from the genetic conditions of hop seedlings to the characteristics of hops used in brewing.

The quality and characteristics of hops can be influenced by several factors. Among the most relevant are the degree of ripeness at harvest, processing and pelletization methods, moisture control, and storage conditions. Additionally, chemical properties such as the content and composition of essential oils, as well as levels of α -acids and β -acids, are highly relevant to the aroma and bitterness attributes.⁹ These characteristics are directly related to hop quality and the attributes they confer to beer, with an intrinsic relationship between chemical composition and sensory properties. Thus, the use of techniques to determine chemical characteristics is a valuable parameter for evaluating hop quality, highlighting the importance of understanding their chemical composition.^{10–12}

Resins make up about 10 to 30% of hop dry matter and contain α - and β -acids that contribute to beer bitterness.^{13,14} On the other hand, essential oil imparts the characteristic hop aroma and flavor to beer and is composed mainly of hydrocarbons (50 to 80%) and oxygenated compounds (up to 30%).^{15–17}

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Considering the importance of hop chemical composition, hop quality can be comparatively assessed. The quality of Cascade hops grown in Sardinia was evaluated in comparison with hops cultivated in the United States and New Zealand. The levels of α - and β -acids and essential oil composition were assessed, and compatible proportions of these acids and oil compounds were found across the different samples.¹⁸ Hops from different cultivars cultivated organically and conventionally in Brazil were also compared in terms of essential oil composition and α - and β -acid levels. Minor chemical composition variations were observed among the different cultivars and within the same cultivar across the two cultivation methods.¹⁹ The essential oil composition of Cascade hops cultivated in Brazil was compared with samples of the same cultivar grown in the United States. The essential oils of the Brazilian samples showed lower levels of myrcene, humulene, and caryophyllene, and higher levels of *trans*- β -farnesene, β -selinene, and α -selinene than those from the U.S. samples.²⁰ In another study, cones of Cascade and Chinook cultivars grown in Brazil were compared with commercial pellets of the same cultivars imported from the United States, considering the content and composition of essential oils. The results showed that 40% of the Brazilian samples presented essential oil content within the expected range, and regarding composition, the hops were mainly differentiated by cultivar type, with no distinction between Brazilian-grown hops and commercial pellets.²¹

Additionally, the adaptation of some hop cultivars to the northeastern region of Brazil has been evaluated. When comparing bitter acids, xanthohumol, and essential oils from hop flowers to commercial hop pellets, a similar profile was observed among samples from different growing locations, despite being in different hop forms.²² Comparisons between hops grown in Brazil and imported cultivars have also been conducted using extracts obtained with dichloromethane²³ and through the volatile profile of the samples.²⁴ In both cases, differences were observed between Brazilian and imported samples, with compounds identified as being distinct among hops grown in different regions.

These findings demonstrate that hops of the same cultivar may exhibit different chemical characteristics depending on the cultivation region, resulting in site-specific properties and generating a regional identity.²⁵ However, considering the expansion of hop cultivation in Brazil, there are still few studies involving Brazilian hops and the evaluation of their chemical characteristics. Furthermore, there is a lack of studies assessing bitter acids and essential oils obtained through official methods, and comparing different hop cultivars cultivated and marketed in Brazil with the same imported cultivars, which are currently the most commonly used in beer production. Therefore, this study investigates the chemical characteristics of three hop cultivars (Cascade, Comet, and Sorachi Ace) produced and marketed in Brazil, comparing them with imported hops of the same cultivars.

2. MATERIAL AND METHODS

2.1. Samples. Samples of pelletized hops from the Comet, Cascade, and Sorachi Ace cultivars, harvested between 2021 and 2022, were acquired. At the time this study was conducted, hop cultivation in Brazil was still in an early stage, and few producers pelletized and commercialized their hops. Therefore, aiming to compare the same cultivars in the form most commonly used in beer production, the pellets, the study was limited to two Brazilian brands

for each cultivar. Thus, for each cultivar, two samples of hops grown in Brazil and two samples of imported hops were obtained, totaling 12 samples.

The hops grown in Brazil were purchased directly from producers and were cultivated in the state of São Paulo (SP), specifically in the cities of Fartura, Taguai, and Juquiá. The imported samples were from the brands BarthHaas (Nürnberg, Germany) and Yakima Chief (Yakima, USA), and were purchased from beer product Web sites. The country of cultivation for these samples is shown in Table 1.

Table 1. Description of Hops Samples

cultivar	typical use ^{23,32}	brand	abbreviation	origin	harvest
cascade	aroma	B1	cB1	Juquiá (SP, Brazil)	2021
		B3	cB3	Taguai (SP, Brazil)	2022
		I1	cI1	United States	2022
		I2	cI2	United States	2021
comet	aroma/bitter	B1	cmB1	Juquiá (SP, Brazil)	2022
		B2	cmB2	Fartura (SP, Brazil)	2022
		I1	cmI1	Germany	2021
		I2	cmI2	United States	2021
sorachi Ace	aroma/bitter	B2	sB2	Fartura (SP, Brazil)	2022
		B3	sB3	Taguai (SP, Brazil)	2022
		I1	sI1	Japan	2021
		I2	sI2	United States	2021

However, the specific city of cultivation could not be determined, as the brands only provide the country of origin, considering the hops may come from different producers in various regions within the same country.

All samples were shipped by carriers in light-impermeable packaging, either vacuum-sealed or in a modified atmosphere. Upon reception, the samples were stored under refrigeration until analysis, which was conducted immediately after opening the packages. The details of all hops acquired, according to origin and cultivar, are shown in Table 1.

2.2. Determination of Moisture, α - and β -Acids Content.

The moisture content, α - and β -acid contents were determined for each sample. Hop samples were analyzed in duplicate according to the official methods of the American Society of Brewing Chemists. To determine the moisture content, the Hop 4 method was used, and for α - and β -acid contents, the Hop 6 method was used.²⁶

2.3. Obtaining and Quantifying Essential Oils. The essential oils were obtained by steam-distillation as described in ASBC Hops 13.²⁶ The hydrolate obtained was centrifuged (Fanem Baby I model 260 BL, São Paulo, Brazil) at 965g for 15 min, and the essential oil was removed with the aid of a Pasteur micropipette and packed with magnesium sulfate in an amber vial sealed atmosphere of N_{2(g)}, which was stored under refrigeration until analysis.

The hop weight used in the hydrodistillation process was corrected according to the moisture content, and the calculation of the essential oil content of each sample was performed considering the volume of essential oil extracted.

2.4. GC $\times$ GC–MS and GC $\times$ GC–FID Analyses. To perform chromatographic analyses, essential oil samples were diluted to obtain 5% (v/v) solutions in hexane and were analyzed in triplicate. A GC $\times$ GC system was a TRACE 1300 chromatograph equipped with an FID and a transmission quadrupole mass spectrometer (QMS) (Thermo Fisher Scientific-Waltham, MA, USA). Samples were introduced using the TriPlus RSH autosampler, into which 1 μ L of sample was injected. The injector was operated at 250 °C with a split ratio of 1:10. The oven temperature program started at 60 °C, which was maintained for 3 min, and then the temperature was increased at 3 °C min⁻¹ to 210

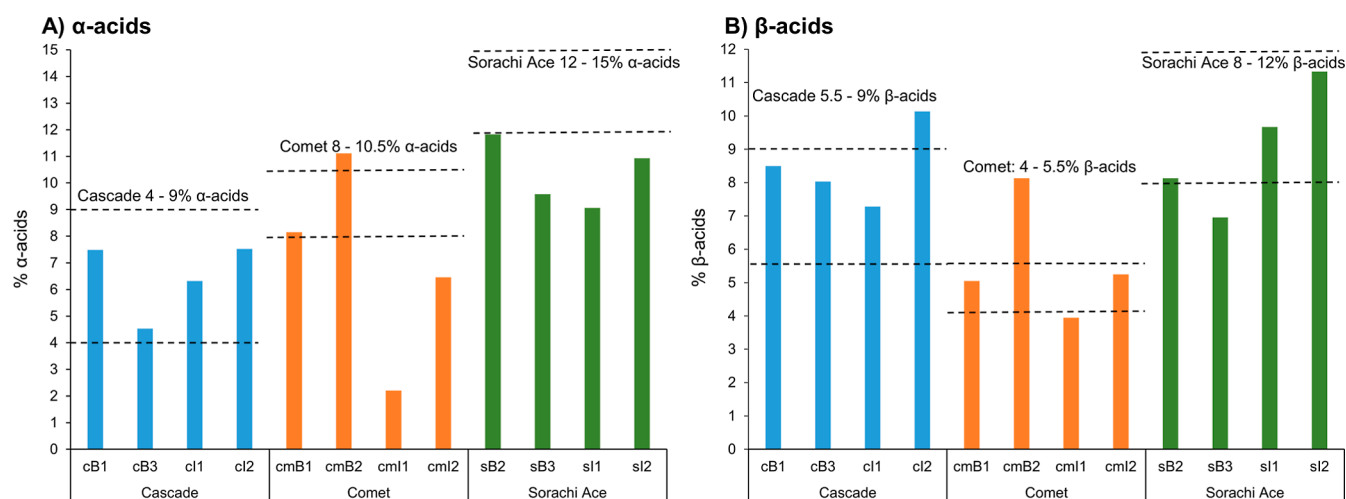


Figure 1. α -Acids e β -acids of hop samples. *Dotted lines indicate the range of reference values.

$^{\circ}\text{C}$. Helium was used as the carrier gas at a constant flow rate of 0.5 mL min^{-1} . The auxiliary gas was maintained at 20 mL min^{-1} . Flow modulation was performed using an INSIGHT modulator (SepSolve Analytical–Waterloo, Canada). The modulation period was 5 s. The columns used in the first and second dimensions were Rxi-5 ms of $30\text{ m} \times 0.25\text{ mm}$ ($0.25\text{ }\mu\text{m}$) and Rxi-17 ms of $5\text{ m} \times 0.25\text{ mm}$ ($0.25\text{ }\mu\text{m}$) columns, respectively. Further analytical details are provided in our previous papers.^{27,28} The FID temperature was $250\text{ }^{\circ}\text{C}$. For the mass spectrometer, the transfer line and ion source temperatures were 260 and $250\text{ }^{\circ}\text{C}$, respectively. Electron ionization (EI) was used to acquire the mass spectra in the m/z range of 50 – 350 .

For data acquisition, Xcalibur software (Thermo Fisher Scientific–Waltham, MA, USA) was used, and the data were processed with GC Image software (GCI, TX, USA), allowing for the integration of the chromatographic peaks to obtain the peak areas. To identify the essential oil compounds, the mass spectra of each compound were compared with those contained in the NIST database, with a minimum similarity of 80% between the spectra required for compound identification. Furthermore, by injecting a homologous series of n -alkanes from C_8 to C_{20} , the linear retention indices (LTPRI) of the compounds were calculated using the van den Dool and Kratz equation.²⁹ The calculated LTPRI were then compared with those reported in the literature (NIST and Adams), with tolerated deviations of up to ± 10 between the theoretical and experimental values.³⁰

2.5. Data Analysis. The composition of essential oils and the content of α - and β -acids were evaluated using analysis of variance (ANOVA) followed by Tukey's test. The analysis was performed using the Python programming environment in Google Colab, utilizing libraries such as `scipy.stats` and `statsmodels`. For each compound, when a significant difference was detected by ANOVA ($p < 0.05$), the means were compared using Tukey's test, and the results were represented by distinct letters. The results for the content of α - and β -acids, content of essential oils, and compounds identified in the essential oils are presented in Tables S1–S3 in the Supporting Information.

For chemometric analyses, the absolute areas obtained by GC $\times$ GC–FID for the identified compounds, the α - and β -acid contents, and the essential oil contents of the samples were used. The data were then organized into a matrix with 36 rows (12 triplicate samples) and 24 columns (areas of the 21 selected peaks and other chemical results). Using MetaboAnalyst 6.0, the data underwent a preprocessing stage in which they were autoscaled so that all variables had equal weights and contribution, and thereafter Hierarchical Cluster Analysis (HCA) with a heat map and partial least squares-discriminant analysis (PLS-DA) were performed.³¹ To evaluate the predictive capacity and robustness of the PLS-DA model, cross-validation was performed using the leave-one-out cross-validation (LOOCV) method. For the

first five latent variables, the accuracy, R^2 and Q^2 were obtained, with Q^2 being used to estimate the predictive capacity of the model based on cross-validation.

3. RESULTS AND DISCUSSION

3.1. α -Acids and β -Acids. Hop pellets were analyzed in triplicate, and the mean α - and β -acid contents are presented in Figure 1, along with the reference values reported by commercial brands of imported hops. The data were also subjected to statistical tests, and the results are shown in Table S1.

Based on the results presented in Figure 1, all Cascade cultivar samples showed experimental α - and β -acid values within the reference range, which represents a medium range over the last 4 years as reported by commercial brands of imported hops and can vary widely depending on the crop year.^{32,33} For Comet hops, the Brazilian samples had α - and β -acid values above the minimum, while imported samples cmI1 and cmI2 had α -acid values below the reference, with cmI1 also showing lower β -acid values. In the Sorachi Ace cultivar, all samples presented α -acid values below the reference, and the Brazilian sample sB3 also showed reduced β -acid values. To better evaluate these results, statistical tests were applied, according to the results of Table S1. When applying ANOVA to the Cascade hops data, a significant difference was observed in the α -acid and β -acid contents. This may be related to variations between harvests, considering that all of them present values above the reference values of international brands. Tukey's test revealed that sample cB3 differed significantly from the others about α -acid content. For β -acids, samples cI1 and cI2 differed from each other but were equivalent to the other samples. In Comet hops, significant differences were observed for both α -acids and β -acids, and Tukey's test indicated that all samples differed from each other, except cmB1 and cmI2, which did not present significant differences in β -acid content. For the Sorachi Ace cultivar, no significant differences were observed between the samples in α -acid content. However, for β -acids, a significant difference was observed between the imported sample sI2 and the two Brazilian samples, which can be explained by the higher content of these acids in the sI2 sample.

Despite the significant statistical differences observed, with these results no clear trends were identified that distinguish Brazilian hops from imported ones. Brazilian Cascade and

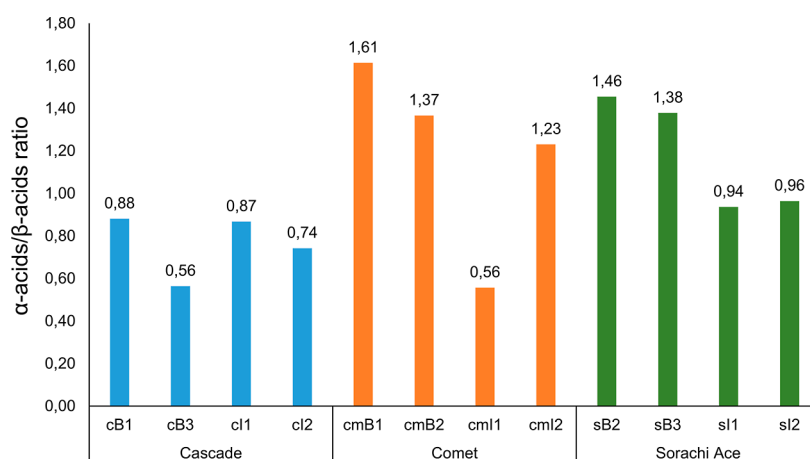


Figure 2. Ratio between α -acids and β -acids.

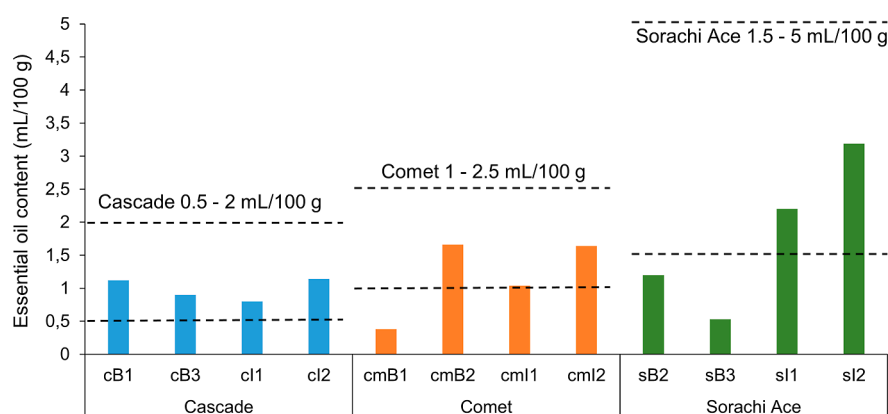


Figure 3. Essential oil content of hop samples.

Comet hops showed α - and β -acid values within the expected ranges according to the reference. For Sorachi Ace, although the Brazilian samples did not meet the reference values, they still presented higher α -acid levels than the imported samples. Therefore, based on these parameters, hops grown in Brazil meet the standards expected for commercialization, since they are compatible with imported hops.

To evaluate the bitterness characteristics that hops are expected to impart to beer, the ratio between α -acids and β -acids in the samples was also analyzed, as shown in Figure 2. Regarding the values, ratios close to 1 are typical of aroma hops, whereas higher ratios are characteristic of bittering hops.³⁴ Among the cultivars analyzed, Cascade exhibited the lowest α -acid/ β -acid ratios, indicating less pronounced bitterness characteristics compared to the other two. In contrast, the Comet and Sorachi Ace cultivars showed α -acid/ β -acid ratios close to or greater than 1. For the Brazilian samples of these two cultivars, this ratio was higher than that of their imported counterparts, which may suggest more intense bitterness characteristics. Samples cB3 and cmI1 showed the lowest ratio (0.56) among all those analyzed. These samples also had the lowest α -acid contents, which contributes to the lower ratio and may be associated with processing and storage conditions that favored the oxidation of these acids.

3.2. Essential Oils and GC $\times$ GC Analysis. In addition to α - and β -acids, essential oils are another parameter of great importance for hop quality, and their composition should be evaluated. Thus, the results of the essential oils of hops are

displayed in Figure 3, as well as the reference values for each cultivar reported by imported brands. The data were also subjected to ANOVA and Tukey's test and the results are presented in Table S2.

When comparing the obtained levels of essential oils with those expected according to the range reported by reference brands,³⁵ Brazilian hops Comet cmB1, Sorachi Ace sB2 and sB3 presented values below expectations, while imported hops presented levels compatible. The I1 brand packaging specified that the yields considered the average of the last harvests, and variations may occur. Lower essential oil contents in Brazilian hops could be due harvest variation, but this information was not available to the consumer. These variations may occur, for example, as a consequence of changes in climatic conditions, which have been reported to influence the composition of bitter acids and essential oils in hops cultivated within the same region across different years.³⁵ In addition, lower values can be also associated with factors related to the processing steps of Brazilian hops. After harvesting, several factors contribute to the reduction of the amount of essential oil in hops, such as the drying and pelletizing processes and storage conditions, especially when there is no control of temperature, since high temperatures contribute to the volatilization and loss of essential oil.^{11,17} The lower oil content of Brazilian hops may also be associated with plant age, as plants with less than three years of cultivation may not have reached sufficient maturity to produce the expected levels of essential oil.²¹ However, this information was not available for the samples analyzed as they

Table 2. Compounds Identified and Their Average Relative Areas ($N = 3$) for Essential Oils from Brazilian and Imported Hops^c

	compound	CAS-number	Lit. RI ^a	Exp. RI ^b	cB1	cB3	cI1	cI2	cmB1	cmB2	cmI1	cmI2	sB2	sB3	sI1	sI2
1	myrcene	123–35–3	991	985	50.62	44.58	44.43	51.86	19.44	58.90	34.64	52.34	50.60	36.80	43.48	55.58
2	α -humulene	6753–98–6	1452	1457	14.37	18.10	18.47	15.72	2.19	1.27	4.96	1.01	19.19	18.72	26.80	21.29
3	caryophyllene	87–44–5	1419	1421	7.54	7.69	8.15	7.66	23.64	11.15	14.75	16.06	9.37	9.31	12.25	8.92
4	δ -cadinene	483–76–1	1522	1516	1.14	1.08	1.26	1.11	1.24	0.31	0.69	0.50	1.10	2.04	1.86	1.22
5	(E)- β -farnesene	18794–84–8	1454	1449	8.18	10.43	9.34	8.65	0.00	1.27	0.00	1.01	4.21	6.33	1.65	1.66
6	(Z)- β -ocimene	3338–55–4	1038	1038	0.40	0.23	0.12	0.15	4.19	1.83	0.63	1.61	0.77	0.40	1.63	2.73
7	γ -muurolene	30021–74–0	1478	1472	0.89	0.74	1.10	0.81	2.44	0.77	1.71	1.22	0.78	1.57	1.29	0.84
8	γ -cadinene	39029–41–9	1513	1508	0.64	0.60	0.78	0.61	0.56	0.15	0.38	0.25	0.61	1.16	1.13	0.69
9	2-undecanone	112–12–9	1293	1275	0.14	0.26	0.20	0.17	0.54	0.24	0.45	0.26	1.14	1.10	0.83	0.47
10	α -selinene	473–13–2	1498	1495	3.08	1.57	2.61	1.94	12.18	4.82	9.45	7.67	1.52	3.68	0.72	0.46
11	β -pinene	127–91–3	974	972	0.59	0.53	0.59	0.46	0.23	0.77	0.92	0.65	0.62	0.32	0.59	0.44
12	β -phellandrene	555–10–2	1025	1022	0.48	0.39	0.51	0.66	0.29	0.60	0.41	0.62	0.53	0.46	0.56	0.69
13	α -copaene	3856–25–5	1374	1377	0.24	0.22	0.35	0.31	0.24	0.08	0.16	0.11	0.27	0.48	0.58	0.44
14	β -selinene	17066–67–0	1489	1484	1.81	0.97	1.40	1.20	10.98	3.95	8.97	6.87	1.12	2.96	0.38	0.23
15	2-methylbutyl 2-methylpropanoate	2445–69–4	1002	1002	0.91	1.81	1.11	0.57	0.07	1.10	1.78	0.48	0.98	0.28	0.24	0.15
16	methyl (Z)-4-decenoate	7367–83–1	1289	1291	0.31	0.58	0.06	0.24	1.89	0.80	0.67	0.25	0.17	2.24	0.00	0.00
17	selina-3,7(11)-diene	6813–21–4	1545	1542	0.18	0.35	0.20	0.17	4.09	0.94	1.49	1.52	0.25	0.22	0.00	0.00
18	linalool	78–70–6	1095	1084	0.59	0.40	0.53	0.59	0.36	0.62	1.18	0.57	0.51	0.93	0.39	0.30
19	β -cadinene	523–47–7	1529	1532	0.13	0.13	0.15	0.13	3.73	1.01	1.48	1.69	0.36	0.41	0.20	0.12
20	neryl acetate	141–12–8	1359	1361	1.69	1.45	0.00	1.01	0.19	1.07	2.29	0.14	0.16	0.08	0.00	0.00
21	unidentified			1639	0.38	0.75	0.61	0.61	1.46	0.73	1.10	0.87	0.39	0.61	0.15	0.00
	sum of % peak areas				94.28	92.86	91.97	94.64	89.95	92.38	88.11	95.70	94.65	90.13	94.74	96.23

^aLiterature retention index. ^bExperimental retention index. ^cIn bold the major compounds of each hop cultivar.

were currently available in the market, and the fact that hop cultivation in the country is recent suggests that some of them may have been obtained from plants younger than three years, resulting in pellets with essential oil content below the expected values.

Finally, when comparing the essential oil content for each cultivar, it can be observed that the Brazilian Cascade hops presented levels equivalent to their imported counterparts and to values reported in the literature.^{18,20,36} When applying ANOVA and the Tukey test (Table S2), it is noted that the two Brazilian samples are equivalent to the imported sample cI2, while the imported sample cI1, which presented a lower essential oil content, differs significantly from the samples cI2 and cB1. For the Comet cultivar, only the B2 brand was comparable to the imported samples, resending essential oil content equivalent to that of the imported sample cmI2. For Sorachi Ace, none of the Brazilian samples matched the essential oil content of the imported ones and all samples presented essential oil contents that differed significantly from each other. Given that Brazilian hops had α -acid levels compatible with the imported cultivars but some exhibited lower essential oil content, it was essential to evaluate the composition of these oils to determine if the chemical profile of Brazilian hops was comparable to that of imported hops. Additionally, it was important to investigate whether there was a trend toward the production of specific compounds that might differentiate Brazilian hops from imported ones.

To evaluate the composition of essential oils, a GC–MS is typically applied. However, the possibility of coelution of various isomers in essential oils emphasizes the need for greater separation capacity, which can be achieved with GC $\times$ GC. Therefore, analyses of the essential oils were performed in triplicate using two-dimensional chromatography and representative GC $\times$ GC–MS chromatograms comparing Comet cmB1 sample grown in Brazil and Comet cmI1 imported sample, with the name of the main compounds identified in each sample, are shown in Figure S1 (Supporting Information). A summary of all identified compounds and their average relative areas is provided in Table 2 (mean values and standard deviations detailed in Table S3 and Supporting Information).

Regarding the Comet hop cultivar, the four main compounds were myrcene, caryophyllene, α -selinene and β -selinene, which accounted for between 66 and 83% of the composition of these oils (highlighted in Table 2). For the Brazilian Comet samples, cmB1 and cmB2, the fifth most abundant compound was (*Z*)- β -ocimene (4.19 and 1.83%, respectively). For the imported samples, the fifth most abundant compound was α -humulene for sample cmI1 (4.96%), and β -cadinene for sample cmI2 (1.69%). For these compounds, similarities were observed between samples cmB2 and cmI2, which exhibited statistically equal values for myrcene, (*Z*)- β -ocimene and α -humulene. For the cmB1 sample, myrcene was the second most abundant compound, presenting a lower amount when compared to the other samples, for which this compound was the most abundant. In addition, this was the hop with the lowest yield, which possibly may be directly related to its processing and storage conditions, as these conditions can contribute both to the loss of essential oil and to changes in its composition.³⁷ Hydrocarbons are the main compounds with reduced concentrations in the essential oil, either by volatilization or oxidation. Among the hydrocarbons are monoterpenes, such as

myrcene, which, in addition to being very volatile, can easily oxidize into more than 40 different compounds, including perylene, linalool and geraniol.^{17,38} However, in the Comet cmB1 sample, no high concentrations of oxygenated compounds were found, which suggests that the low essential oil yield and low myrcene content arise from the loss of the most volatile compounds of the essential oil due to high temperatures in the process. Notably, when performing the analyses of the cmB1 sample, it was found that its pellets were less uniform, with a less intense green color than the other hops.

The Cascade cultivar is referred to as the “myrcene hop”, as myrcene constitutes 40–70% of the essential oil composition of this hop cultivar.¹⁸ Both Brazilian and imported hops exhibited similar myrcene contents, varying between 44.43% and 51.82%. Additionally, the four hop brands displayed myrcene, humulene, β -farnesene, and caryophyllene as the main compounds (highlighted in Table 2), collectively representing more than 80% of their essential oil compositions. For samples cB1, cI1 and cI2 the fifth most abundant compound was α -selinene, while for sample cB3 it was 2-methylbutyl 2-methylpropanoate. Similarities can also be observed between the samples, with compatible levels of some compounds. This similarity was confirmed for samples cB3 and cI1, which presented statistically equal values for myrcene and humulene. Furthermore, equivalent levels were also noted between Brazilian and imported samples for δ -cadinene, β -pinene, β -selinene, selina-3,7(11)-diene, linalool, and β -cadinene. These results indicate that the observed similarities and differences in the main compounds of these essential oils were not related to the origin of the hops, and that the Brazilian Cascade cultivar had a chemical composition similar to that of the imported hops.

The essential oils of the Sorachi Ace cultivar showed myrcene as the main compound, followed by α -humulene and caryophyllene in both Brazilian and imported hops. When β -farnesene and α -selinene, which were also present in all samples, were included, the sum of these compounds (highlighted in Table 2) accounted for 71–88% of the essential oil. These similarities between Brazilian and imported hops of the Sorachi Ace cultivar are notable. Based on ANOVA and Tukey's test, it was observed that, for some compounds, Brazilian hops had equivalent levels to imported hops, such as for caryophyllene, γ -cadinene, and 2-methylbutyl 2-methylpropanoate. Thus, considering all the evaluated essential oils, except for the Comet cmB1 sample, which had a low myrcene content, Brazilian hops demonstrated a chemical composition similar to imported hops, both in terms of compound composition and concentration of major compounds present.

In addition to the main compounds identified for each cultivar, other compounds were present in lower concentrations, showing variations both between samples of the same cultivar and across different cultivars. Thiols, which significantly influence flavor and are associated with characteristic aromas of blackcurrant, passion fruit, and grapefruit, have been reported at levels of $\mu\text{g kg}^{-1}$ in Cascade and Comet hops.³² Their detection via GC typically requires specific detectors or alternative sample preparation methods to hydrodistillation.³⁹ Consequently, none of the analyzed hop samples revealed the presence of thiols. In total, 21 compounds were identified across all hop essential oil samples. Through ANOVA and Tukey's test, it was observed that there is no clear trend of differentiation between Brazilian and imported samples, as

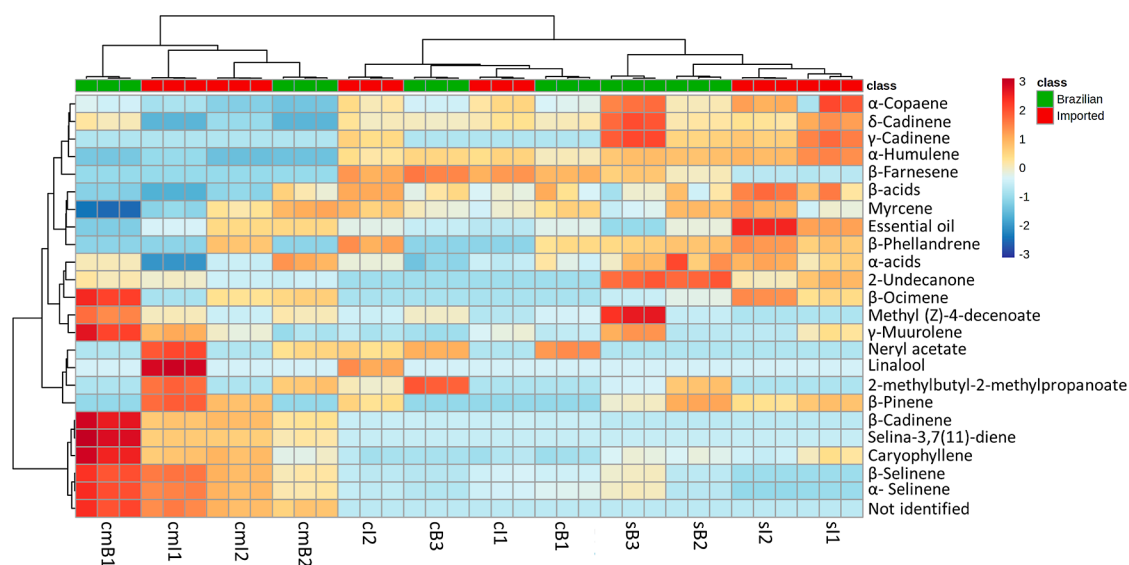


Figure 4. Heat map of the triplicate of hop essential oil of cascade (c), comet (cm) and sorachi ace (s) samples, and HCA of samples and compounds.

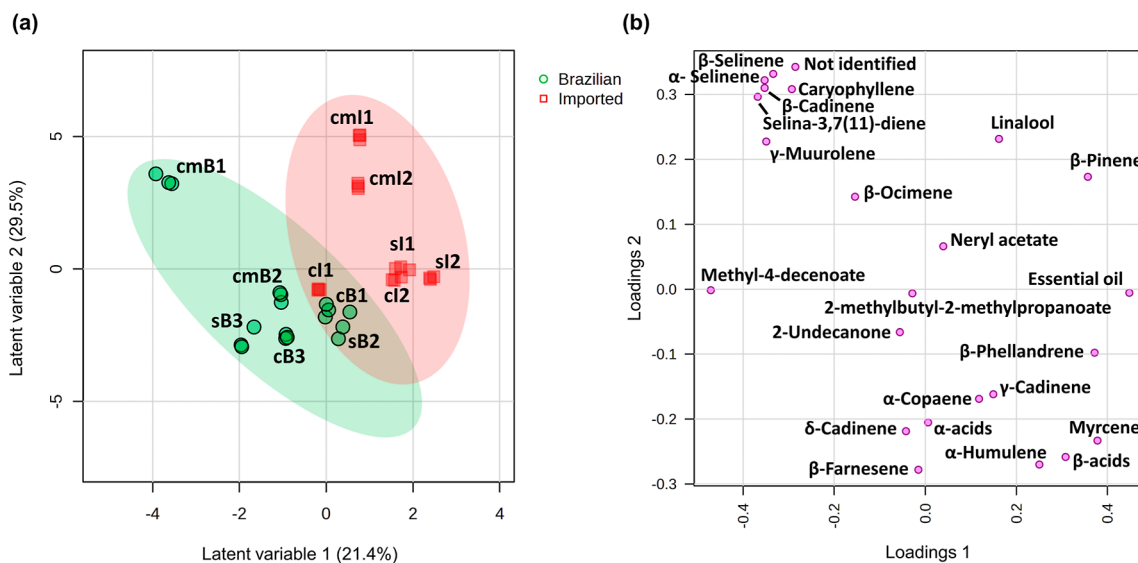


Figure 5. PLS-DA scores of Brazilian (green circles) and imported (red square) samples (a), and influence of the compounds in loadings graph (b).

some compounds show no significant differences between these samples, while others display significant differences even among imported samples.

3.3. Chemometrics. To gain a deeper understanding of these differences, an exploratory data analysis was conducted using unsupervised HCA and heat map construction. This analysis aimed to identify clusters among the samples. The HCA shown in Figure 4 reveals clustering based on hop cultivar, without distinctions related to sample origin. Additionally, it was possible to identify the most prominent variables for each cultivar, with a consistent pattern observed in samples of the same cultivar, regardless of their origin. Another notable finding is the clustering of both imported and Brazilian samples, observed in the I2 and B2 brand samples of the Comet cultivar, as well as in the I1 and B1 brand samples of the Cascade cultivar. For the Sorachi Ace cultivar, it is observed that the sB2 sample is grouped with the imported samples s11 and s12, indicating a greater similarity between their characteristics than the sB3 sample. Similarly, for the

Comet cultivar, the B2 brand sample also grouped with the imported ones, which may be evidence of the greater proximity of the samples of this brand with the imported hops. It is also possible to observe the clustering between the Sorachi Ace and Cascade samples, suggesting similarities between these two cultivars. Both have an aroma profile in which the sweet fruity and citrus characteristics stand out, which should contribute to this clustering.³²

The clustering of samples using HCA and the similar color patterns in the heat map indicates that, in general, Brazilian-produced hops are comparable to imported hops. Although a limited number of samples and hop cultivars were analyzed, and further studies are necessary in this area, these findings suggest that Brazil has the potential to produce hops main compounds similar to those of the major international producers.

Despite the similarities observed, there is the possibility that hops grown in Brazil produce unique minority compounds, which could confer a terroir to the national hops. Confirming

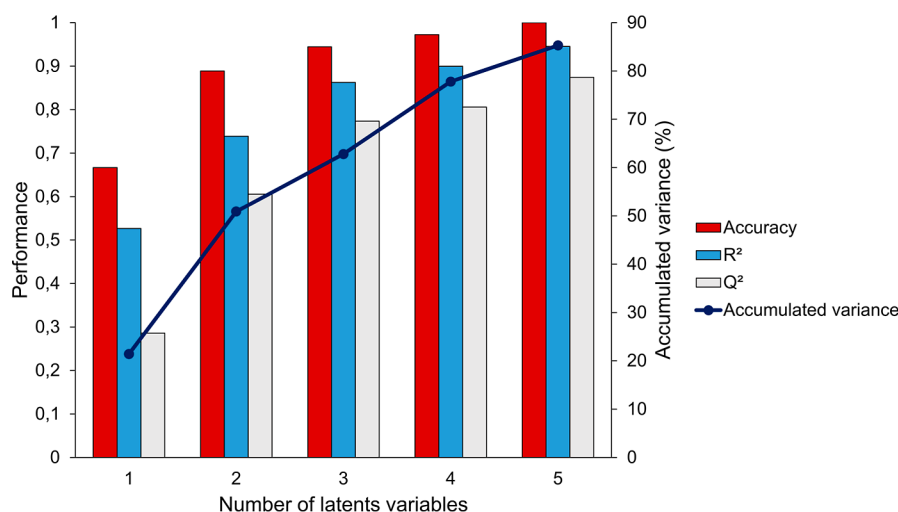


Figure 6. Accumulated variance and leave-one-out cross-validation for the PLS-DA model.

the presence of specific markers of Brazilian hops still requires more samples and complementary analyses, including sensory ones. Nonetheless, to verify whether there were specific characteristics of hops produced in Brazil that distinguish them from imported hops, PLS-DA, a supervised classification analysis, was performed. Although PLS-DA is originally a classificatory technique, in this study it was applied with an exploratory character, aiming to identify possible separations between classes. For this reason, the samples were not divided into training and test sets. The 36 samples were separated into Brazilian and imported groups, and the model was obtained, represented by two latent variables, according to the score chart illustrated in Figure 5a. Considering the region of the ellipses, which show 95% confidence, there is an overlap between the region represented by the imported samples and the region of the Brazilian samples, mainly due to the imported sample c11 of the Cascade cultivar, which is placed within the confidence area of Brazilian samples. However, the other samples were separated according to their origin, making it possible to investigate specific characteristics of hops cultivated in Brazil. For this, in the loading graph in Figure 5b, it is possible to observe which variables contributed to this separation.

With the PLS-DA model obtained, we aimed to establish a relationship between the hop composition data and its origin. For this purpose, the first two latent variables were selected, presenting 50.9% of the accumulated variance, as shown in Figure 6. Thus, with these two variables, there must be significant discrimination between classes based on the variables used to construct the model.⁴⁰ Therefore, to assess whether the data are suitable for discriminating between Brazilian and imported hops, the PLS-DA model was validated using leave-one-out cross-validation. As shown in Figure 6, the PLS-DA model with 2 latent variables—the number selected for the final model—yielded an accuracy of approximately 0.9, an R^2 of 0.74, and a Q^2 of 0.60. Although increasing the number of latent variables could raise these values and potentially improve the model's predictive capacity, it might also lead to overfitting and complicate the model's interpretation. Thus, the two components were deemed adequate for achieving good separation between hop classes, ensuring a good predictive capacity while minimizing complex-

ity, and allowing for meaningful relationships to be established between the variables and sample classification.

By a combined analysis of scores and loadings plots (Figure 5a,b), i.e., considering the spatial distribution of samples and variables on components 1 and 2, the imported hops were related to essential oil contents, β -pinene (piney, woody aroma), myrcene (herbaceous aroma, of fresh hops), β -phellandrene (mint aroma), α -humulene (woody aroma), γ -cadinene (herbal, thyme and woody aroma), α -copaene (woody aroma), linalool (floral-fruity aroma) and β -acids.^{10,41,42} Some imported hops showed a more intense peak area of these compounds, according to the analyses of essential oils by GC $\times$ GC, and had higher essential oil contents, justifying their contribution.

Among these compounds, considerable focus is directed toward linalool, which belongs to the terpene alcohol class, containing a hydroxyl group in its structure. This feature enhances its solubility in wort and beer, making linalool highly important to beer's flavor, which is characterized by fruity and floral aroma.¹⁰ β -pinene, another compound contributing to the differentiation of imported samples, is a monoterpene renowned for its herbal aroma. It can be naturally present in essential oils and can also be formed through the auto-oxidation process of myrcene.^{43,44}

In a similar way, the Brazilian hops were related to methyl (Z)-4-decenoate, caryophyllene (spicy aroma), γ -muurolene (woody aroma), α -selinene (pepper and orange aroma), β -selinene (herbal aroma), selene-3,7(11)-diene, β -cadinene (green and woody aroma), (E)- β -farnesene (woody aroma), (Z)- β -ocymene, 2-undecanone (fruity aroma), and an unidentified compound.⁴⁵ Methyl (Z)-4-decenoate, which is described with fruity characteristics and reported as an important marker to distinguish bitter hops from aromatic hops, presented the highest concentration in Brazilian hops (the greatest negative weight in loadings 1).^{45,46}

The isomers α -selinene, characterized by its pepper and orange aroma; β -selinene, with an herbal aroma;⁴³ and selene-3,7(11)-diene also showed an important contribution to discriminating the samples cultivated in Brazil. These compounds have already been identified in high concentrations in other studies of Brazilian hops, which may reveal a unique quality of these hops when compared to imported hops.^{19,20} However, no information on the odor threshold of selinene

isomers has been obtained to determine whether their concentrations in hops could significantly impact the aroma of both hops and beer.

In addition to the selinene isomers, β -cadinene and an unidentified compound showed higher concentrations in the essential oils of Brazilian hops (0.13–3.73% and 0.38–1.46%, respectively). When analyzing the chromatogram, compound unidentified, with a retention index of 1639, is actually the coelution of two compounds that were partially separated by two-dimensional chromatography. This coelution probably occurs recurrently in conventional GC. However, as GC $\times$ GC has peaks on the order of milliseconds, the number of spectra obtained was insufficient to perform the appropriate spectral deconvolution to individually identify the two coeluted compounds. One of the peaks could be tentatively identified as an isomer of eudesmol (contributes to the spicy character of hops).⁴⁷

In view of the results presented, there are similarities between hops grown in Brazil and their imported counterparts, which demonstrate great potential for Brazilian production. Nevertheless, there is a need for greater attention to the postharvest processing steps to ensure the integrity of essential oils and mitigate losses. Regarding the aromatic characteristics of hops, PLS-DA analysis revealed some differences for those grown in Brazil, with a higher concentration of some essential oil compounds, such as selinene isomers, than in imported hops, which may indicate specific characteristics of hops grown in Brazil. However, this conclusion cannot be definitively drawn due to the limited number of hop samples, batches and cultivars evaluated. Therefore, future analyses require a larger number of samples, including those from different batches and harvests, to confirm the evidence observed in this study. Furthermore, future work would also benefit from a more comprehensive evaluation of the chemical and sensory characteristics of hops, along with a sensory analysis of beers produced with these hops, to determine whether these compounds contribute unique attributes to Brazilian hops. Nevertheless, this study represents an important initial assessment of the quality of Brazilian hops and provides a basis for more comprehensive future investigations.

■ ASSOCIATED CONTENT

Data Availability Statement

Data and material are available upon request to the corresponding author.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsfoodscitech.5c00718>.

Additional tables containing detailed information and statistical data, as well as figures showing chromatographic profiles (DOCX)

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Notes

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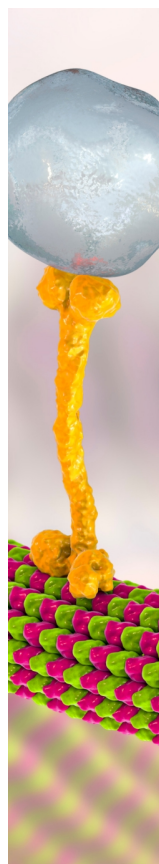
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