



Valorization of agricultural byproducts from *Rubus glaucus* Benth (blackberry) as a natural source of high value-added ingredients

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Abstract

The sustainable utilization of agro-industrial waste and byproducts has gained increasing attention for its potential to generate value-added products. *Rubus glaucus* Benth (Andean blackberry) is particularly interesting because of its high content of antioxidant and volatile compounds. However, postharvest losses caused by diseases and fruit quality issues result in significant economic setbacks for farmers. This study aims to increase the value of *Rubus glaucus* Benth byproducts by characterizing their bioactive compounds and exploring their potential applications. Pruning residues, healthy fruits, and affected fruits were collected and analyzed. Solid-Phase Microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) was used to identify volatile compounds in the fruits, whereas antioxidant activity (DPPH and FRAP assays) and liquid chromatography–mass spectrometry (LC–MS) were employed to assess the phenolic composition of the pruning residues. A total of 45 volatile organic compounds were identified. The antioxidant capacity of the pruning extracts ranged from 13.854 ± 0.270 to 33.882 ± 0.628 mmol Trolox per 100 g, indicating a significant presence of phenolic acids and flavonoids. These findings highlight the potential of *Rubus glaucus* Benth agro-industrial residues as a sustainable source of bioactive compounds, with promising applications in food, pharmaceuticals, and cosmetics. This study demonstrates a viable pathway for waste valorization, contributing to the development of circular bioeconomic strategies and sustainable biorefinery processes.

Keywords Agro-industrial waste · Bioactive compounds · Biorefinery processes · Volatile organic compounds · *Rubus glaucus* benth. · Waste valorization

1 Introduction

Fruits belonging to the *Rubus* genus, one of the largest genera and with a wide geographical distribution, are considered healthy and nutritious due to their content of volatile organic compounds (VOCs), phenols, vitamin C, dietary fiber, α -tocopherol, tocotrienol, calcium, potassium, magnesium, and carotenoids, which provide potential health benefits [1]. Among the phenolic compounds found to be a new natural source of antioxidants in the food and

pharmaceutical industries are anthocyanins, phenolic acids, flavonoids, and ellagitannins [2].

Rubus glaucus Benth. is native to the tropical highlands of America, mainly Colombia, Ecuador, Panama, Guatemala, Honduras, Mexico, and Salvador. It is widely accepted for fresh and processed consumption because of its exquisite flavor, as well as easy agroindustrialization [3]. In Colombia, as in other Andean countries, the *Rubus* genus is found in cold and cold-moderate zones at altitudes of the Andes between 1,500 and 3,200 m above sea level; numerous species are used for human consumption in different ways, with *Rubus glaucus* Benth, known as “Mora de Castilla”.

Currently, blackberries (*Rubus glaucus* Benth.) present a great opportunity to supply domestic and export markets; both their production and their cultivated area show an increasing trend. For 2006, an increase of 94.31% in the cultivated area was expected, which would generate

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approximately 6,917 direct jobs [4]. In Colombia, this fruit is grown in 19 departments and is considered a competitive fruit because its national production is permanent. This plant is widely consumed, has applications in agribusiness, has export potential, and is highly economically important [5].

However, this production chain has weaknesses, such as little interest from food processors and chain stores in formalizing the market alliance. It is also susceptible to many diseases that result in significant losses for farmers. In this sense, fruits affected by different pathogenic fungi generate losses between 50% and 70% of production [6], generating a high percentage of byproducts in crops. Furthermore, the pruning process generates unused biomass, which, when not removed from the crop, favors the appearance of microclimates that contribute to the incidence of phytopathogenic fungi.

Therefore, fruits affected by phytopathogenic fungi are an important source of chemical compounds, mainly phenolic compounds such as phenolic acids, which exhibit various biological activities [7, 8]. Similarly, in the study by Lizcano et al. (2019) [9], the presence of different antioxidant compounds, such as vitamin C, anthocyanins, and flavonoids, was reported in the biomass of *Rubus glaucus* Benth.

These byproducts, including pruning residues and fruits affected by pathogenic fungi, are not intended for direct consumption but rather for the recovery of bioactive compounds. Molecules such as phenolic acids, flavonoids, anthocyanins, and terpenoids can be extracted and purified for use as natural antioxidants, antimicrobial agents, or aromatic ingredients in pharmaceutical and cosmetic formulations. This valorization approach aligns with current circular bioeconomic strategies, where plant waste is revalorized as a source of high-value compounds (Costa et al., 2022; López-Barrera et al., 2020).

Waste can be valorized, especially fruit and vegetable waste, as sources of natural and biobased products. The large-scale production of value-added biobased products from these sources could promote the investments needed to reduce the negative socioeconomic and environmental impacts caused by food waste [10].

The reuse of agroindustrial byproducts can represent a renewable source for some food additives that are already in use or even generate new value-added ingredients with functional compounds and properties, which will benefit the entire food system. Some of the food additives currently permitted within the scope of the European Commission Regulation [11] can be found in agrofood byproducts. These include anthocyanins from grape agroindustrial byproducts and chlorophylls that can be found in almost all plant byproducts, such as leaves or peels, together with all the waste resulting from pruning during agricultural production [12].

A potential use of berry byproducts is as color additives because they contain carotenoids, anthocyanins, porphyrins, and chlorophylls. Anthocyanins are a group of natural pigments responsible for the blue, red, violet, violet, and magenta coloration of various species in the plant kingdom [13].

Additionally, plants produce a wide range of volatile compounds, some of which are important quality factors in fruits, vegetables, spices, and herbs [14]. Plant volatiles have been widely used as food flavoring agents, and many are generally recognized as safe (GRAS), whereas synthetic chemical additives can generate chemical residues in food products [14].

In this sense, byproducts and biomass represent an interesting and economical source of active compounds that become a natural and renewable source of compounds with potential use in the food, pharmaceutical, and cosmetic industries, among others, promoting the concept of a circular economy. In the food industry, different compounds have been obtained from the byproducts of different agricultural crops, which are currently used as preservatives, antioxidant additives, colorants, texturizing agents, and emulsifiers, supported by European legislation [11], dietary fiber is incorporated as an ingredient in bread production [15], and volatile compounds can improve the sensory quality of the final product [16], in addition to the production of biopolymers for packaging development [17].

2 Materials and methods

2.1 Plant material

The samples were collected with a completely randomized block design in three municipalities of the Risaralda Department, Colombia, Guática, Pereira, and Santa Rosa de Cabal (Table 1). The fruits of *Rubus glaucus* Benth. The collected samples were healthy or affected by pathogenic fungi in stages 5 and 6 of maturity, according to the classification established in the Colombian technical standard NTC 4106.

Table 1 Georeferencing of the sampled areas in the municipalities of the Risaralda Department, Colombia

Municipality	Farm	Georeferencing	Altitude
Guática	“Santa Teresita”	N 05° 19' 7.41"	2101 ± 3 m
	Vereda La Unión	W 075° 47' 29.72"	
Pereira	“Añoranzas”	N 04° 44' 32.98"	1965 ± 3 m
	Corregimiento La Florida	W 075° 36' 58.11"	
Santa Rosa de Cabal	“El rubí”	N 04° 53' 24.1"	2085 ± 3 m
	Vereda Potreros	W 075° 33' 44.0"	

Furthermore, pruning samples were collected and stored in completely airtight plastic bags at 4 °C.

2.2 Extraction of volatile compounds via solid-phase microextraction

The extraction of volatile compounds was performed via 85 µm polydimethylsiloxane (PDMS) fibers, following the methodology proposed by D'Agostino et al. [18] with some modifications. Three grams of macerated fruits were placed in a 10 ml vial sealed with a screw cap with a Teflon septum. The vial was placed in a container at 45 °C in a water bath with a magnetic stirrer. Equilibrium was carried out for five minutes at 45 °C. Subsequently, the fiber was exposed to the headspace to adsorb the analytes for 30 min.

2.3 Analysis by gas chromatography–mass spectrometry

Solid-phase microextraction (SPME) fiber desorption was performed at 250 °C at the gas chromatographic injection port in split less mode. Chromatographic analysis was performed on a gas chromatograph (GC-2010 Plus) coupled to a mass spectrometer (QP-2020) equipped with a Shimadzu SH-Rxi-5MS capillary column (length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 µm). Helium was used as the carrier gas at a linear rate of 1.0 ml min⁻¹. The oven temperature was programmed at 40 °C (2 min), increased 8 °C min⁻¹ until 200 °C (8 min), maintained for 5 min, then increased at 10 °C min⁻¹ until 250 °C reached the final temperature and was maintained for 10 min. The mass spectrometer was operated in electron impact mode (70 eV) within the mass range of *m/z* 35–450. The transfer line and ionization source temperatures were set at 280 and 230 °C, respectively. The qualitative analysis was performed by comparison with spectra from the NIST mass spectral library.

2.4 Polar compound extraction from pruning

The stems and leaves collected by pruning were processed in a mill operated by cutting and impact. The extraction was carried out by acid hydrolysis using 80% ethanol, adjusting the pH to 2.6 with the addition of citric acid according to the methodology reported by Cardona-Hurtado et al. [7]. A sample–solvent ratio (1:8) with orbital mechanical shaking at 250 rpm was used for 2 h at room temperature. The extract obtained was filtered to remove solid particles from the fruit and diluted volumetrically with ethanol to 10 ml.

2.5 Total phenol content evaluation

The Folin–Ciocalteu method was used, following the methodology described in previous studies [19]. A gallic acid calibration curve was used as a reference standard at concentrations ranging from 5 to 80 mg/L. The absorbance was measured at 760 nm. The results are expressed per milligram of gallic acid equivalents per 100 g of sample (mg GAE per 100 g of sample).

2.6 Evaluation of antioxidant activity

2.6.1 Radical scavenging activity via the DPPH assay

Radical scavenging activity was determined following the methodology described in previous studies [19]. A calibration curve was generated using Trolox as the reference standard in a concentration range of 10–400 µM. The absorbance was measured at 517 nm. The results are expressed per micromole of Trolox equivalents per 100 g of sample (µmol TE per 100 g of sample).

2.6.2 Determination of reducing power (FRAP)

FRAP was determined following the methodology described in previous studies [7] with some modifications. Twenty microliters of the extract was mixed with 1.5 ml of FRAP reagent. The mixture was incubated at 37 °C for 30 min, the absorbance was measured at 593 nm, and a calibration curve was generated with Trolox as the reference standard. The results are expressed in millimoles of Trolox equivalents per gram of sample (mmol TE per 100 g of sample).

2.7 Chemical characterization by LC–MS

The analyses were performed via a Shimadzu HPLC–MS triple quadrupole system equipped with an electrospray ionization (ESI) source. The method was run in full-scan mode, configured in both positive and negative ionization. In positive mode, the scan range was set from 50 to 1000 *m/z* with an interface voltage of 4.0 kV, whereas in negative mode, the same range was applied with a voltage of –3.0 kV. The interface parameters for both modes were as follows: nebulizing gas flow, 3.0 L/min; heating gas flow, 10 L/min; drying gas flow, 10 L/min; interface temperature, 300 °C; and desolvation line temperature, 250 °C.

Chromatographic separation was achieved on a Phenomenex Kinetex EVO C18 core–shell column (100 Å pore size, 100 mm × 2.1 mm, 2.6 µm particle size) maintained at 30 °C, with a flow rate of 0.4 mL min⁻¹. The mobile phase consisted of solvent A (0.1% formic acid in water)

and solvent B (acetonitrile). The elution gradient started at 5% B and was maintained for 5 min, then increased to 15% B in 3 min, 20% B at 10 min, 22% B at 15 min, 25% B at 18 min, 30% B at 20 min, and 35% B at 23 min, which was maintained until 28 min; finally, the gradient reached 90% B at 34 min.

2.8 Statistical analysis

Statistical analysis of the data obtained from the assessment of the plant material was performed via R software version 4.2.1. Three replicates were averaged. One-way analysis of variance (ANOVA) was used to determine significant differences in VOCs and antioxidant activity between the municipalities sampled. Tukey's test was used for the comparison of means, with a significance level of 5% ($p < 0.05$). Multivariate analysis of variance (MANOVA) was performed to determine the significant compounds involved in the interaction between the place of cultivation and the type of material (healthy or diseased fruits). Principal component analysis (PCA) was performed to establish the relationships between the samples and volatile compounds. Ward's method and the squared Euclidean distance were used to determine the clusters.

3 Results and discussion

3.1 Identification of volatile organic compounds (VOCs)

A total of forty-five volatile organic compounds (VOCs), including 13 esters, one ketone, two aromatic hydrocarbons, six alcohols, 19 terpenes, and four aldehydes, were identified in *Rubus glaucus* Benth fruits. Among these compounds, 29 have been previously reported in other *Rubus* species [18, 20–22]. Although the remaining 19 compounds were not mentioned in other studies addressing *Rubus*, they are compounds found in other fruits and/or plants. On the other hand, the VOCs in *Rubus glaucus* Benth. extracted under the conditions described above corresponded mostly to terpenes, followed by esters and terpene alcohols.

Multivariate analysis, with 5% significance ($p < 0.05$), revealed that both the cultivation site and the plant material (healthy or pathogen-affected fruits) had significant effects on the VOC composition. Among the 45 compounds identified by GC–MS, only 27 had significant effects on the interaction between the site of cultivation and the material (Fig. 1).

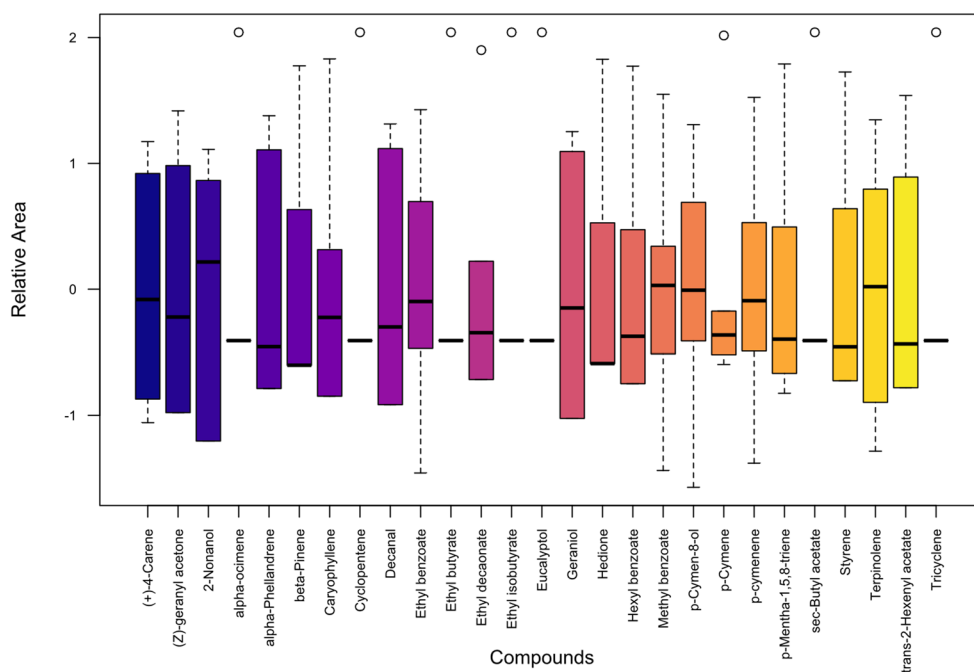


Fig. 1 Relative area of volatile compounds identified in *Rubus glaucus* Benth samples, including both healthy and pathogen-affected fruits collected from the municipalities of Guática, Pereira, and Santa Rosa de Cabal (Risaralda, Colombia). Each box represents the distribution of the relative abundance of a compound across biological replicates. The central line indicates the median, the box limits represent the

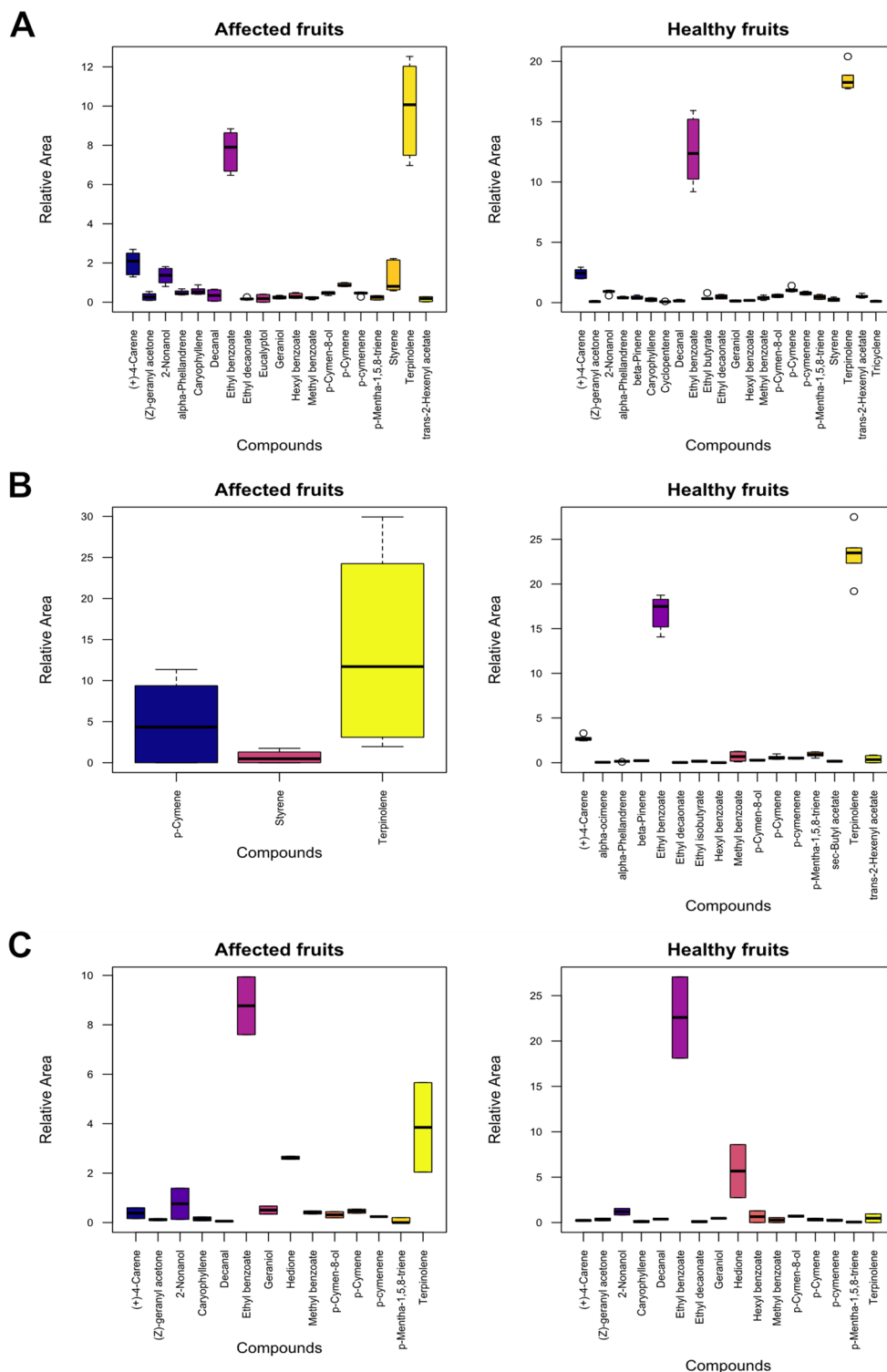
interquartile range, and the circles denote outliers. Colors distinguish groups of compounds according to their chemical class (terpenes, esters, alcohols, aldehydes, ketones, and aromatic hydrocarbons). Multivariate analysis ($p < 0.05$) revealed that both the cultivation site and the type of material (healthy or affected fruits) significantly influenced the volatile compound profile. according to their chemical class

Figure 2 shows the distribution of the significant VOCs identified in healthy and diseased fruits from the three municipalities of Guática, Pereira, and Santa Rosa de Cabal (Risaralda, Colombia).

As shown in Figs. 2A and 19 compounds were identified in pathogen-affected fruits, whereas 22 compounds

were identified in healthy fruits in the Guática municipality. The compounds identified in both materials were (+)-4-carene, geranyl acetate, 2-nonanol, ethyl benzoate, α -phellandrene, caryophyllene, decanal, ethyl decanoate, geraniol, styrene, hexyl benzoate, methyl benzoate, p-cimen-8-ol, p-cymene, p-cymene,

Fig. 2 Volatile compounds identified in healthy and diseased *Rubus glaucus* Benth fruits grown in the municipalities of (A) Guática, (B) Pereira, and (C) Santa Rosa de Cabal. Each boxplot represents the relative area of each compound across biological replicates. The central line indicates the median, the box limits correspond to the inter-quartile range, and the circles denote outliers. Colors distinguish groups of volatile organic compounds (VOCs) according to their chemical class



p-mentha-1,5,8-triene, styrene, terpinolene, and trans-2-hexenyl acetate.

Figure 2B shows that three compounds were identified in pathogen-infected fruits, whereas sixteen were identified in healthy fruits in the Pereira municipality; the reduced diversity is likely associated with metabolic alterations caused by pathogen infection. The compounds identified in both materials corresponded to p-cymene and terpinolene. As shown in Figs. 2C and 14 compounds were identified in pathogen-affected fruits, whereas 16 were identified in healthy fruits in the municipality of Santa Rosa de Cabal. The compounds identified in both materials corresponded to (+)-4-carene, 2-nonanol, geranyl acetate, caryophyllene, decanal, ethyl benzoate, geraniol, hedione, methyl benzoate, p-cimen-8-ol, p-cimenene, p-cymene, p-mentha-1,5,8-triene and terpinolene.

The crop that contained the greatest number of volatile compounds in the affected fruits was found in Guática municipality, whereas the lowest number of volatile compounds in these same fruits was found in Pereira municipality. With respect to healthy fruits, the greatest number of VOCs was identified in Guática, whereas Pereira and Santa Rosa de Cabal had the same number of compounds. On the other hand, the greatest difference between affected and healthy fruits was observed in Pereira.

With respect to the place of cultivation, ANOVA and Tukey's post hoc test were performed to determine the differences between the municipalities for each of the significant compounds. The results are shown in Table 2.

Beyond the compositional differences described above, it is important to consider their implications for the potential value and safe use of these byproducts. The significant

Table 2 Significant differences between cultivation sites

Compound	Guática		Pereira		Santa Rosa	
	Affected fruit	Healthy fruit	Affected fruit	Healthy fruit	Affected fruit	Healthy fruit
(+)-4-Carene	2.01±0.616 ^{aA}	2.42±0.39 ^{aB}	---	---	0.38±0.241 ^{cA}	0.23±0.088 ^{cB}
(Z)-geranyl acetone	0.278±0.204 ^{aA}	0.095±0.054 ^{aA}	---	---	0.12±0.044 ^{aA}	0.34±0.153 ^{aA}
2-Nonanol	1.343±0.426 ^{aA}	0.888±0.159 ^{aA}	---	---	0.76±0.69 ^{aA}	1.2±0.394 ^{aA}
alpha-ocimene	---	---	---	0.05±0.023 ^{aB}	---	---
alpha-Phellandrene	0.48±0.122 ^{aA}	0.42±0.07 ^{aA}	---	0.147±0.029 ^{bA}	---	---
beta-Pinene	---	0.43±0.124 ^{aB}	---	0.223±0.016 ^{aB}	---	---
Caryophyllene	0.568±0.19 ^{aA}	0.247±0.158 ^{aB}	---	---	0.15±0.088 ^{bA}	0.115±0.126 ^{bA}
Cyclopentene, 3-isopropenyl-5,5-dimethyl-	---	0.08±0.015	---	---	---	---
Decanal	0.347±0.318 ^{aA}	0.155±0.078 ^{aA}	---	---	0.055±0.027 ^{aA}	0.38±0.011 ^{aA}
Ethyl benzoate	7.74±0.996 ^{aA}	12.545±2.896 ^{aB}	---	16.882±1.9 ^{aB}	8.77±1.282 ^{bA}	22.595±4.902 ^{bB}
Ethyl butyrate	---	0.405±0.204	---	---	---	---
Ethyl decaonate	0.173±0.05 ^{aA}	0.483±0.183 ^{aB}	---	0.032±0.037 ^{bB}	---	0.105±0.115 ^{bB}
Ethyl isobutyrate	---	---	---	0.172±0.083	---	---
Eucalyptol	0.195±0.214	---	---	---	---	---
Geraniol	0.242±0.077 ^{aA}	0.147±0.05 ^{aA}	---	---	0.505±0.181 ^{bA}	0.47±0.044 ^{bA}
Hedione	---	---	---	---	2.62±0.066 ^A	5.67±3.199 ^B
Hexyl benzoate	0.315±0.134 ^{aA}	0.185±0.048 ^{aA}	---	0.008±0.01 ^{aA}	---	0.65±0.712 ^{aA}
Methyl benzoate	0.213±0.056 ^{aA}	0.402±0.165 ^{aB}	---	0.688±0.552 ^{aB}	0.41±0.066 ^{aA}	0.275±0.301 ^{aB}
p-Cymen-8-ol	0.462±0.075 ^{aA}	0.562±0.131 ^{aB}	---	0.288±0.049 ^{bB}	0.315±0.137 ^{aA}	0.715±0.115 ^{aB}
p-Cymene	0.883±0.089 ^{aA}	1.065±0.194 ^{aA}	4.9±5.439 ^{aA}	0.582±0.228 ^{aA}	0.46±0.088 ^{aA}	0.325±0.159 ^{aA}
p-cymenene	0.44±0.088 ^{aA}	0.783±0.138 ^{aB}	---	0.515±0.081 ^{bB}	0.24±0 ^{bA}	0.255±0.115 ^{bB}
p-Mentha-1,5,8-triene	0.232±0.113 ^{aA}	0.46±0.195 ^{aB}	---	0.912±0.282 ^{aB}	0.067±0.103 ^{bA}	0.055±0.06 ^{bB}
sec-Butyl acetate	---	---	---	0.17±0.041	---	---
Styrene	1.2±0.771 ^{aA}	0.262±0.157 ^{aB}	0.668±0.774 ^{aA}	---	---	---
Terpinolene	9.86±2.389 ^{aA}	18.55±1.004 ^{aB}	13.773±12.441 ^{aA}	23.338±2.692 ^{aB}	3.85±1.983 ^{bA}	0.48±0.526 ^{bA}
trans-2-Hexenyl acetate	0.16±0.123 ^{aA}	0.537±0.137 ^{aB}	---	0.387±0.427 ^{aB}	---	---
Tricyclene	---	0.117±0.05	---	---	---	---

Note. Different lowercase letters within the same element of volatile organic compounds indicate that they were significantly different between cultures ($p<0.05$). Different capital letters within the same item of volatile organic compounds indicate that they were significantly different between plant materials (affected and healthy fruits; $p<0.05$)

variations in the chemical profiles of healthy and pathogen-affected *Rubus glaucus* Benth fruits suggest that infection and environmental factors influence the biosynthesis of volatile and phenolic compounds. Although disease reduces the diversity of esters and terpenes, several alcohols and aldehydes remain abundant or even increase in concentration. From a valorization standpoint, these changes are acceptable and potentially useful because they modify rather than eliminate bioactive and aromatic compounds.

This variability can be advantageous for targeted applications: extracts rich in terpenes and esters may serve flavoring purposes, whereas those with higher alcohol or phenolic contents could be suited for antioxidant or antimicrobial uses. Although infected fruits are not suitable for direct consumption, the chemical integrity of their secondary metabolites supports their recovery and safe use after purification. Therefore, such differences represent an opportunity to diversify the industrial use of *R. glaucus* byproducts rather than a limitation.

3.2 Principal component analysis

The multivariate analysis based on the VOC data grouped the different sampling locations and types of material (healthy and diseased fruits), as illustrated in Fig. 3.

Five clusters are observed, namely, (1) diseased fruits sampled in the Pereira municipality; (2) diseased fruits sampled in the Guática municipality; (3) healthy and diseased fruits sampled in the Santa Rosa de Cabal municipality; (4) healthy fruits sampled in the Guática municipality; and (5) healthy fruits sampled in the Santa Rosa de Cabal municipality.

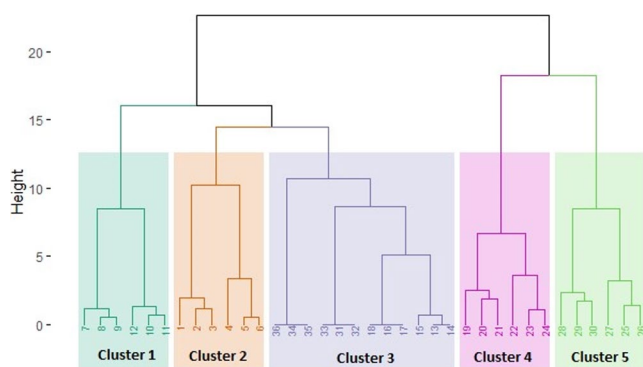


Fig. 3 Dendrogram obtained from hierarchical clustering analysis of volatile compound data. Samples 1 to 18 belong to the diseased fruits: Samples 1 to 6 were obtained in the municipality of Guática; samples 7 to 12 were obtained from the Municipality of Pereira; and samples 13 to 18 were obtained from the municipality of Santa Rosa de Cabal. Samples 19 to 36 were healthy fruits: samples 19 to 24 were obtained in Guática; samples 25 to 30 were obtained from Pereira; and samples 31 to 36 were obtained from Santa Rosa de Cabal. Height indicates the dissimilarity level at which clusters are joined; higher values represent greater differences between clusters

Cluster 3 included healthy and affected fruits from the Santa Rosa de Cabal municipality (Fig. 2C). The only difference between the materials assessed was due to two compounds, i.e., ethyl decanoate and hexyl benzoate, which are present in healthy fruits and absent in affected fruits.

According to the heat correlation map (Fig. 4), the compounds with the highest positive correlation that allowed the association of cluster 1 were p-cymene, styrene, and terpinolene. In cluster 2, the compounds with a positive correlation were geranyl acetate, 2-nonanol, decanal, styrene, α -phellandrene, caryophyllene, and eucalyptol.

For cluster 3, compounds such as hexyl benzoate, ethyl benzoate, p-cimen-8-ol, geranyl acetate, 2-nonanol, decanal, geraniol, and hedione were highly positively correlated. Cluster 4 was characterized by a positive correlation of compounds such as β -pinene, α -phellandrene, ethyl butyrate, p-cymene, ethyl decanoate, cyclopentene, 3-isopropenyl-5,5-dimethyl, methyl benzoate, trans-2-hexenyl acetate and α -phellandrene. Finally, cluster 5 presented positive correlations with the compounds methyl benzoate, trans-2-hexenyl acetate, α -ocimene, ethyl isobutyrate, sec-butyl acetate, terpinolene, (+)-4-carene and p-mentha-1,5,8-triene.

Finally, the heatmap revealed that there was variability in the volatile compounds of fruits collected in the different municipalities. Depending on the municipality, a positive correlation occurred with different groups of compounds, among which esters and terpenes stood out. A negative correlation occurred with alcohol and aromatic compounds.

3.3 Polar compound extraction from pruning

The total phenol contents of the blackberry crop pruning extracts are presented in Table 3.

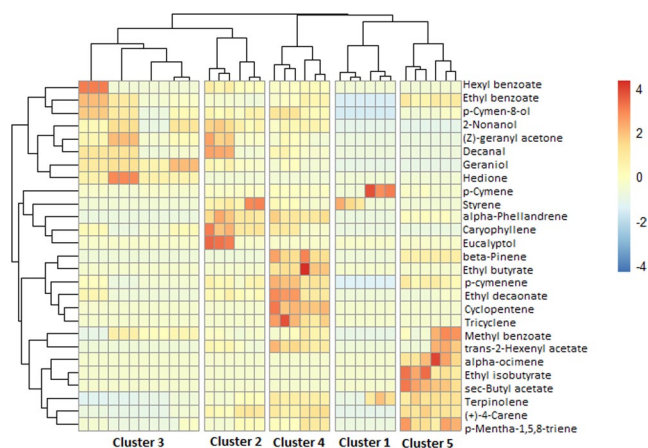


Fig. 4 Heat correlation map for the different volatile compounds according to cluster analysis by place of cultivation and material. Blue indicates negative correlations, red indicates positive correlations, and yellow indicates intermediate correlations

Table 3 Total phenol content of extracts obtained from the pruning of *Rubus glaucus* Benth. Crops in the Risaralda department

Municipality	Total Phenol Content (mg GAE per 100 g of sample)
Guática	19.888±4.636 ^a
Pereira	7.741±0.470 ^b
Santa Rosa de Cabal	24.725±1.382 ^a

Table 4 Antioxidant activity of extracts obtained from the pruning of *Rubus glaucus* Benth. Crops in the department of Risaralda

Municipality	DPPH (mmol Trolox per 100 g of sample)	FRAP (mmol Trolox per 100 g of sample)
Guática	21.074±0.201 ^a	19.243±0.927 ^a
Pereira	18.837±0.674 ^b	13.854±0.270 ^b
Santa Rosa de Cabal	33.882±0.628 ^c	25.989±1.026 ^c

Different lowercase letters within the same column indicate significant differences between growing sites at $p < 0.05$.

In terms of the total phenol content, values of 24.725 ± 1.382 and 7.741 ± 0.470 mg GAE per 100 g of sample were found in the different municipalities studied. According to the analysis of variance, there are statistically significant differences in means between the Pereira municipality and the Guática and Santa Rosa de Cabal municipalities. Therefore, Guática and Santa Rosa de Cabal have the highest content of phenolic compounds during pruning. Compared with previous reports, Rojas Ocampo [23] reported a value of 4.11 ± 0.01 mg GAE per 100 g of sample, attributed its low gallic acid value to the fact that bagasse extracts from Peruvian blackberry were obtained with water, a solvent with a lower extraction yield. Some authors have used other solvents for extraction; thus, comparisons do not accurately reflect the true richness of blackberry agro-industrial waste, and equal methods for comparison are necessary. Thus, Reátegui et al. [24] shows that the highest phenolic concentration (4.44 ± 0.30 mg GAE/g extract, Brazilian bagasse) was obtained with (CO₂) SFE at 20 MPa, 60 °C.

For ripe healthy fruits of *R. glaucus* (782 ± 0.06 to 1052 ± 0.07 mg GAE/100 g sample; Guerrero-Álvarez et al. [25], the pruning residues presented a lower total phenolic content overall, which is consistent with the expected decrease in extractable phenolic content due to tissue lignification, reinforcing its suitability for the recovery of bioactive molecules from agricultural byproducts.

The results obtained for the antioxidant capacity of *Rubus glaucus* Benth grown in the Risaralda department and evaluated via the DPPH and FRAP methods are shown in Table 4. Statistical analysis revealed significant differences in the antioxidant capacity of the pruning extracts obtained at the different cultivation sites according to the two methods evaluated.

Different lowercase letters within the same column indicate significant differences between growing sites at $p < 0.05$.

As shown in Table 4, the antioxidant capacity of the DPPH and FRAP methods was greater in Santa Rosa de Cabal municipality, with values of 33.882 ± 0.628 µmol TE per 100 g of sample and 25.989 ± 1.026 mmol Trolox per 100 g of sample, respectively, followed by the municipalities of Guática and Pereira.

When the antioxidant capacity of the *Rubus glaucus* Benth pruning biomass was compared with that of ripe fruits from the same cultivation sites, as reported by Guerrero-Álvarez et al. [26], notable differences were observed. After unit adjustment, the biomass DPPH values (210.7, 188.4, and 338.8 µmol Trolox/g for Guática, Pereira and Santa Rosa de Cabal, respectively) were comparable to or greater than those reported for ripe fruits (139.18, 162.32, and 50.69 µmol Trolox/g, respectively). These antioxidant capacity values of the Colombian blackberry biomass extracts were greater than the antioxidant capacity of the Peruvian or Brazilian blackberry bagasse extracts reported by Rojas Ocampo [23], which had AC values of 7.19 ± 0.06 µmol TE/g FW and 25.94 ± 0.57 µmol TE/g FW, respectively, as reported by Reátegui [24].

Similarly, the FRAP values were markedly greater for the biomass (19.24, 13.85, and 25.99 mmol Trolox/100 g) than for the fruits (2.16, 3.38, and 8.63 mmol Trolox/100 g). These results suggest that pruning residues retain or even increase antioxidant potential, possibly due to the presence of bound phenolic compounds such as tannins and hydroxycinnamic acids in lignified tissues. Therefore, the biomass of *R. glaucus* represents a promising and stable source of natural antioxidants for industrial recovery and valorization.

According to Pearson's correlation, a positive correlation of 0.93 (Pearson's correlation coefficient R), with a p value of 0.0002 (significance level), was observed between the total phenolic content and the antioxidant activity via the FRAP method, and a correlation of 0.78, with a p value of 0.01, was observed between the total phenolic content and the antioxidant activity via the DPPH method. The positive linear relationships between total phenolic content and antioxidant capacity values agree with the results of other authors, who confirmed that total phenolic compounds contribute largely to this activity [27].

Reactive oxygen species, including free radicals such as hydroxyl (OH·). In addition, superoxide (O₂·) and nonfree radicals such as hydrogen peroxide (H₂O₂) are produced by living organisms and environmental factors, which can damage cellular structures and alter their functions. To prevent oxidative stress, antioxidants in the form of polyphenols can restore redox balance, which is essential for cell viability, activation, proliferation, and organ function [28,

29]. In recent years, interest in the use and consumption of these compounds (polyphenols) from natural sources, which benefit humans and protect them from oxidizing agents, has increased [30–35].

3.4 Chemical characterization by LC–MS

Table 5 shows the possible phenolic compounds identified by LC–MS in the pruning extracts of *Rubus glaucus* Benth in the municipalities of Guática, Pereira and Santa Rosa de Cabal. The ionization type, possible chemical formula, m/z , neutral mass, and parameters used for identification are shown.

m/z : The most abundant parent ion in LC–MS is fragmented.

The neutral mass corresponds to the calculated molecular mass of the neutral compound on the basis of its chemical formula.

KEGG (Kyoto Encyclopedia of Genes and Genomes) and HMDB (Human Metabolome Database) were used for compound identification on the basis of MS fragmentation patterns.

Six phenolic-type compounds were tentatively identified, including five phenolic acid derivatives, including ellagic acid and its derivatives; ferulic and coumaric acid derivatives; and one flavonoid. These compounds have been reported in different species of the genus *Rubus*.

Hydroxycinnamic acids are linked mainly to quinic acid. 5-O-Feruloylquinic acid was identified ($[M-H]^-$ at m/z 367.104), which has been reported in several *Rubus* species, the most important being *Rubus matsumuranus* [36], *Rubus sanctus*, and *Rubus ibericus* [37].

Ellagic acid was identified due to the presence of the base peak at m/z 300.999 ($[M-H]^-$), which has been reported in different species of the *Rubus* genus [38, 39]. Ellagic acid arabinoside ($[M-H]^-$ at m/z 433.0397) comprises an arabinose attached to one of the phenolic hydroxyls of the ellagic acid core and has been reported in species of the *Rosaceae* family [40], *Rubus idaeus* [41], and different cultivars of the same species [42]. Ellagic acid acetyl-xyloside ($[M-H]^-$ at m/z 475.050083) has been described as a natural compound found in *Rubus idaeus* [43]. Ellagic acid 2-rhamnoside

($[M-H]^+ m/z$ 449.074) has been reported in *Rubus ulmifolius* [44]. Quercetin ($[M-H]^+ m/z$ 303.0494) was isolated from *Rubus fruticosus* [45], *Rubus idaeus* [46], and *Rubus glaucus* Benth [47].

Although these compounds have been reported in different species of *Rubus*, there are no studies that consider the chemical characterization of pruning residues. The differences in composition between healthy *Rubus glaucus* Benth fruits and pathogen-affected *Rubus glaucus* Benth fruits reflect adaptive metabolic responses to biotic and environmental stress. These variations, although they reduce the diversity of certain volatiles such as esters and terpenes, do not diminish the overall functional potential of the byproducts. In contrast, they reveal shifts toward compounds with antioxidant, antimicrobial, or preservative activity, such as alcohols, aldehydes, and phenolic derivatives.

From a valorization perspective, this chemical variability can be considered valuable rather than detrimental. It allows the differentiation of raw materials according to their predominant compound classes, facilitating targeted applications—aromatic or flavoring extracts from healthy fruit residues and antioxidant or antimicrobial ingredients from pathogen-affected material. Such differentiation supports the sustainable use of *R. glaucus* byproducts within circular bioeconomic approaches, where chemical diversity becomes an advantage for the development of multifunctional natural products.

4 Conclusion

This study demonstrated the potential of *Rubus glaucus* Benth pruning residues and pathogen-affected fruits as valuable agro-industrial byproducts. The pruning residues exhibited significant antioxidant activity, with values ranging from 18.837 ± 0.674 to 33.882 ± 0.628 mmol Trolox per 100 g of sample (DPPH) and 13.854 ± 0.270 to 25.989 ± 1.026 mmol Trolox per 100 g of sample (FRAP), highlighting the high bioactive potential of residues from Santa Rosa de Cabal. LC–MS analysis confirmed the presence of key antioxidant compounds, including phenolic acids and flavonoids, such as 5-O-feruloylquinic acid, ellagic acid derivatives, and

Table 5 Phenolic-type compounds identified in the pruning extract of *Rubus glaucus* Benth by HPLC–MS/MS (Shimadzu triple quadrupole, MRM mode)

Type of compound	Type of ionization	Main-Fragment Ions m/z	Tentative identification	Chemical formula	Neutral mass	Database
Phenolic acids	Negative ionization	367.10	Feruloylquinic acid	$C_{17}H_{20}O_9$	368.1107	KEGG
		300.99	Ellagic acid	$C_{14}H_6O_8$	302.0063	KEGG
		433.04	Ellagic acid arabinoside	$C_{19}H_{14}O_{12}$	434.0485	HMDB
		475.05	Ellagic acid acetyl-xyloside	$C_{21}H_{16}O_{13}$	476.0591	HMDB
	Positive ionization	449.07	Ellagic acid rhamnoside	$C_{20}H_{16}O_{12}$	448.0642	HMDB
Flavonoids	Positive ionization	303.05	Quercetin	$C_{15}H_{10}O_7$	302.0427	KEGG

quercetin—none of which have been previously reported in blackberry pruning residues.

Additionally, 45 volatile organic compounds were identified in healthy and affected fruits via SPME-GC-MS. Healthy fruits were positively correlated with esters and terpenes, whereas affected fruits were associated with aromatic compounds and alcohols. The Guática samples presented distinct volatile profiles, particularly for compounds such as p-cymene, styrene, and terpinolene.

Overall, the findings support the valorization of blackberry crop byproducts for the development of high value-added ingredients with potential applications in the chemical, food, cosmetic, perfumery, and pharmaceutical industries. This contributes to the circular bioeconomy and opens new commercial opportunities for farmers by transforming waste into sustainable, marketable products.

Author contributions Gloria E. Guerrero-Álvarez coordinated contact with local farmers to obtain sampling permission. Juan P. Arrubla-Vélez and Camila Correa-Henao carried out the sampling. Camila Correa-Henao and Valentina Santa-Grajales developed the SPME/GC-MS methodology, with technical support from Juan P. Arrubla-Vélez. The antioxidant activity assays were conducted by Camila Correa-Henao, with assistance from Nathalia Cardona-Hurtado. LC-MS analysis and statistical processing were performed by Nathalia Cardona-Hurtado under the supervision of Gloria E. Guerrero-Álvarez. Juan P. Arrubla-Vélez was also responsible for securing project funding. All the authors contributed to the conceptualization, methodology design, data collection and analysis, and writing, reviewing, and editing of the manuscript. All the authors have read and approved the final version of the manuscript for publication.

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Data availability All the data generated or analyzed during this study are included in this published article (and its supplementary information files).

Declarations

Conflict of interest The authors declare that there are no conflicts of interest related to the research or publication of this manuscript.

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