REVIEW ARTICLE



Phytochemical Composition and Potential Use of Rubus Species

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Abstract

Plants produce a number of compounds that are vital to the growth and development processes (primary metabolites) of cells and plant health. In addition to this type of metabolism, plants perform various processes that lead to taxonomically specific formation of compounds (secondary metabolites) that are a vital part of the human diet. Historically, plants have been used for their multiple benefits for the prevention and treatment of diseases. *Rubus* species are cultivated on all continents, at various altitudes, from temperate forests to tropical climates, and have edible and economically important fruits. The present review describes the polyphenols as the group of chemical substances that is most frequently found in species of the genus *Rubus*. Additionally, reference is made to nutritional components such as proteins, fats, calories, vitamins, fiber and minerals. Biochemical characteristics such as pH, total soluble solids and titratable acidity, and phytochemical compounds such as fatty acids, anthocyanins, total phenols, ellagitannis and saponins, among others, are presented. The uses of these compounds found in fruits, leaves, stems and seeds of *Rubus* species plants are considered, in regard to prevention and management of diseases and agroindustrial and pharmaceutical potential.

Keywords Polyphenols · Anthocyanins · Antioxidants · Nutrients · Phytochemicals



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Phytochemische Zusammensetzung und mögliche Verwendung von Rubus-Arten

Zusammenfassung

Pflanzen produzieren eine Anzahl von Verbindungen, die mit den Wachstums- und Entwicklungsprozessen (Primärmetaboliten) in Verbindung stehen, die für das Zell- und Pflanzenleben grundlegend sind. Parallel zu dieser Art von Metabolismus führen Pflanzen verschiedene Prozesse durch, die zu einer taxonomisch spezifischen Bildung von Verbindungen (Sekundärmetaboliten) führen, die ein wichtiger Bestandteil der menschlichen Ernährung sind. In der Vergangenheit wurden Pflanzen aufgrund ihrer vielfältigen Vorteile zur Vorbeugung und Behandlung von Krankheiten eingesetzt. *Rubus*-Arten werden auf allen Kontinenten, in verschiedenen Höhen, von gemäßigten Wäldern bis zu tropischen Klimazonen kultiviert und haben essbare und wirtschaftlich wichtige Früchte. Die vorliegende Übersicht beschreibt die Polyphenole als die Gruppe der chemischen Substanzen, die am häufigsten in Arten der Gattung *Rubus* gefunden wird. Zusätzlich wird Bezug genommen auf Nahrungsbestandteile wie Proteine, Fette, Kalorien, Vitamine, Ballaststoffe und Mineralien. Ebenso werden biochemische Eigenschaften wie pH, gesamtlösliche Feststoffe und titrierbare Säure und phytochemische Verbindungen wie Fettsäuren, Anthocyanine, Gesamtphenole, Ellagitannis und Saponine vorgestellt. Schließlich werden die Anwendungen dieser Verbindungen bei der Vorbeugung und Behandlung von Krankheiten in Betracht gezogen, wenn diese Substanzen in Früchten, Blättern, Stängeln und Samen von *Rubus*-Arten vorkommen. Auf diese Weise kann auf das agroindustrielle und pharmazeutische Potenzial dieser Arten geschlossen werden.

Schlüsselwörter Polyphenole · Anthocyane · Antioxidantien · Nährstoffe · Phytochemikalien

Introduction

Species belonging to the genus *Rubus* are grown on all continents, and have been identified at various altitudes, from temperate forests to tropical climates, however, only some species have edible and economically important fruits. The domesticated and wild species of this genus are characterized as rustic shrubs that have enormous genetic diversity (Cancino et al. 2011), recognized for the quality of their fruits. Various parts of the plant are consumed in different preparations for their medicinal and therapeutic properties.

Plants produce a wide range of compounds other than amino acids, simple sugars, polymers, nucleotides and fatty acids (primary metabolites), that are not directly related to the growth and development processes essential for cell life (Gershenzon and Dudareva 2007; Grajales-Conesa et al. 2011). In parallel, plants perform various processes similar to those of the primary metabolism that lead to the formation of compounds that are specific to taxonomic group and known as natural products or secondary metabolites (Gandhi et al. 2015). These compounds have no direct impact on photosynthesis, solute transport, respiration, differentiation, or carbohydrate formation, and plants can make use of secondary metabolites for their own defense, to attract pollinators, or to interact with their ecosystems (Taiz and Zeiger 2010; García 2004; Grajales-Conesa et al. 2011).

Secondary metabolites are produced in low quantities, and form depending on the phenological stage of the plant, the ecosystem services, and biotic or abiotic stress. In this sense, the secondary metabolism is responsible for biosynthesis, transformation and degradation of endogenous compounds through specialized proteins found in plants, and

constitute a valuable group of compounds with pharmacological, medicinal and phytosanitary functions (Bérdy 2005; Sepúlveda et al. 2003). According to Taiz and Zeiger (2010), there are three main types of chemically different secondary metabolites: compounds derived from nitrogen, terpenes and phenols.

In this review, polyphenols are described as compounds commonly found in plants of the genus *Rubus*. Also, descriptions of other compounds reported in the tissues of *Rubus* spp are discussed. Plant proteins, fats, vitamins, fiber, minerals, total phenols, ellagitannis and saponins are presented, and finally, some pharmaceutical and agroindustrial uses are proposed for these species. The study of secondary metabolites in *Rubus* species, their contributions to the human and animal diet, and their biological activity or function as phytosanitary products contribute to a significant pharmaceutical and agroindustrial potential. This review also proposes practices for the agronomic management of production chains of blackberries and raspberries, emphasizing quality raw materials and highlighting the challenges for industrial production.

Nitrogen-Derived Compounds

In plants, secondary metabolites containing nitrogen are biosynthesized from common amino acids, and are well known for their defensive action against herbivores and their toxic and medicinal properties. Among the compounds that have nitrogen are alkaloids, cyanogenic glycosides, non-protein amino acids and glucosinolates (Gandhi et al. 2015; Azcón-Bieto and Talón 2008).



$$\begin{array}{c} CH_3 \\ CH$$

Fig. 1 Rubupungenoside A, a terpene present in the species R. pungens

Fig. 2 Elagic acid, a polyphenol present in the species Rubus idaeus

Terpenes

In the plant kingdom, terpenes or isoprenoids form a huge group of secondary metabolites, which are insoluble in water, biosynthesized from acetyl-CoA or from glycolitic intermediates, and have an effect on plant growth. Terpenes are components of the cell membrane and act as complementary pigments. Examples of these compounds are gibberellins and abscisic acid (phytohormones), plastoquinone, chlorophyll phytol, carotenoids (tetraterpens), phytosterols, and dolichols (politerpens alcohols). Fig. 1 shows the pentacyclic triterpenoids and their glycosides, found in the species *R. pungens*, to which contraceptive and antibacterial properties are attributed in traditional Chinese medicine (Wang and Lin 2000).

Phenols

Phenols are compounds of aromatic structure with one or more hydroxyl groups, free or substituted, and can be found in a large part of the plant tissues of the *Rubus* species. The basic structure is phenol, however, most of these types of compounds are polyphenols, according to Rao and Snyder (2010).

At present, about 8000 phenolic compounds are known, among which are coumarins, phenolic quinones, stilbenes,

lignans, and flavonoids (anthocyanins), the latter characteristic of the reddish colorations of plants that act as antioxidants. Fig. 2 shows an example of elagic acid present in the fruits of the species *R. idaeus* (Rao and Snyder 2010). In addition, some phenolic compounds play an important role in the defense of the plant (phytoalexins), intervene in the processes of flowering, pollination and even in the fixation of nitrogen, and can act upon the growth of plants through a mechanism that changes the endogenous levels of 3-indolacetic acid. It should be noted that the anthocyanin that occurs most frequently among species of the genus *Rubus* is cyanidin (Markakis 1982; Taiz and Zeiger 2010).

In recent works, defined physiological functions have been found for many secondary metabolites, which have been fundamental for the promotion of many species as functional foods. In addition, these metabolites are no longer considered vegetable wastes. They are now considered natural compounds involved in plant defense processes (phytoalexins) and in ecophysiological strategies related to processes such as pollination, mainly due to the pigments that generate striking colours in the flowers for the attraction of pollinating insects, and the floral aromas generated as a communication strategy between herbivores, pollinators and some natural enemies (Grajales-Conesa et al. 2011).

Botanical Description

There are around 750 species in the world that belong to the *Rubus* genus, the genus with the highest number of species within the Rosaceae family. Fig. 3 describes the taxonomy of this plant genus with contributions of different authors regarding its enormous diversity, economic importance and geographic distribution. This genus is divided into 12 sub-genera, of which the sub-genera *Idaeobatus* (Raspberries) and *Rubus* (Blackberries) have been domesticated



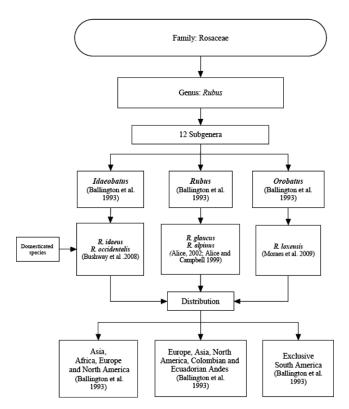


Fig. 3 Taxonomy and geographical distribution of some representatives of the *Rubus* genus

and make up a valuable group of raspberries, blackberries and strongly heterozygotic arctic fruit (Ayala et al. 2013; Bushway et al. 2008).

According to Ballington et al. (1993), the subgenus *Idaeobatus* has raspberry species that include *R. idaeus* and *R. occidentalis*, distributed in Europe, Asia, North America and Africa. The distribution of the subgenus *Rubus* is found in North America, Europe and Asia, and has taxa such as *R. glaucus* and *R. alpinus*, which were included in this subgenus after a phylogenetic analysis of nuclear ribosomal DNA with ITSs (internal transcribed spacer regions) (Alice and Campbell 1999; Alice 2002). The subgenus *Orobatus* is found only in South America: two such species are *R. loxensis* (threatened species) and *R. nubigenus* (Moraes et al. 2009). *Rubus, Orobatus*, and *Idaeobatus* are found in the Colombian and Ecuadorian Andes, demonstrating once again the enormous diversity that this genus of plants presents in the Andean mountain range.

Plants of the genus *Rubus* are characterized as being perennial subshrubs with reclining or scandent branches, they have prickles that are often erroneously called thorns, being thin to stout, straight or curved, and covered with simple white to red trichomes. Stems can be green, red or purple, leaves can have three or five leaflets, pinnate or simple, with simple or double serrate margins and persistent stipules, with terminal or axillary inflorescences, in clusters, panicles, or as solitary flowers (Kalkman 2004).

Pedicels or flowers can have flattened hypanthium, absent bracteoles, with five sepals persistent in the fruit and green plant parts with five white, pink or purple petals, numerous stamens, and a superior ovary, with 10 to 100 or more free, terminal style carpels. Fruits are in aggregates of drupes, either joined or free from the receptacle, and are yellow, orange, red or black-purple when ripe (Kalkman 2004).

Physiochemical Properties of Fruits

In 2014, according to the FAO (2017), in production of berries worldwide, Iran led with 313,880t, followed by Mexico with 152,922 and Vietnam with 136,529t respectively, while in 2016, 110,453t of blackberies were produced in Colombia (Agronet 2017). These figures are an indicator of the great importance of blackberries among *Rubus* domesticated species. These fruits are in great demand in international markets due to their taste, colour and their therapeutic properties. For these reasons, it is important to mention the physicochemical characteristics or organoleptic properties that determine the quality for marketing of fresh produce and processing for agroindustrial use.

Table 1 shows the physicochemical properties of berries in some Rubus species. According to Gómez-Romero et al. (2010), some of the physicochemical changes are possibly related to solar radiation, temperature, nutrition of the plant, among others, and these in turn directly influence the quality and taste of the fruits. For this reason, in countries such as Italy, Venezuela, Peru, Colombia and Brazil, clear differences in the content of total soluble solids (TSS) ranging from 7 to 13°Brix are reported. In the case of pH there are no marked differences between the different taxa and values are between 2.6 and 3.4. In the case of the total titratable acidity (TTA), marked fluctuations are evident in the different species which shows that agroindustrial processes for this type of fruit are successful, due to the organoleptic stability and the low microbial proliferation in juices and jam, due in part to pH and TTA values.

Nutritional Importance of the Species of the Genus *Rubus*

The daily requirement of nutrients in humans requires specific knowledge related to metabolism, digestion, absorption, retention, cellular transport and excretion, taking into account the storage capacity of each organ. Therefore, it can be stated that most of the fat-soluble vitamins and minerals are stored in adipose tissue, and in the liver and bones. On the contrary, water-soluble vitamins lack a specific deposit and only participate as enzymatic cofactors or active metabolites (Hernández 2004).



 Table 1
 Physicochemical characteristics of fruits in some Rubus species

Country Pro- ducer	Species	TSS (°Brix)	TTA	pН	Reference
			mg L ⁻¹		
Italy	R. ulmifolios cv. Black satin	10.8	30.1	3.2	Rotundo et al. (1998)
	R. ulmifolios cv. Smooth- stem	11.4	28.8	3.1	
	R. idaeus cv. Sumner	12	29	3.2	
	R. idaeus cv. Herbst gold	13	18.2	3.45	
Venezuela	R. glaucus Benth	7.5	13.05	3.1	García et al. (2003)
			%		
Brazil	Rubus spp cv. Brazos	7	1.74	2.88	Guedes et al. (2013)
	Rubus spp cv. Tupy	7.52	1.66	2.96	
Colombia	R. alpinus Macfad	8.18	1.81	2.77	Moreno-Medina and Deaquiz (2016)
	R. glaucus Benth	9.27	2.82	2.68	Rincón et al. (2015)
Peru	R. fructicosus L	10.55	0.93	3.4	Valencia and Guevara (2013)

TSS total soluble solids, TTA total titratable acidity (expressed as malic acid)

Table 2 Nutritional composition in fruits of the Rubus genus in 100 g of edible portion

Species	Producer country	% water	Energy (kcal)	Protein (g)	Total fat (g)	Carbohy- drates (g)	Total fiber (g)	Ash (g)	Source
Rubus spp	Central America and Panama	88.15	43	1.39	0.49	9.61	5.3	6.37	Instituto de Nutrición de Centro América y Panamá INCAP (2012)
Rubus glaucus Benth. (without prickles)	Colombia	83.7	-	1	0.1	14.5	-	0.6	Garzón et al. (2015)
Rubus idaeus. L	Canada	85.75	52	1.2	0.65	11.94	6.5	_	Rao and Snyder (2010)
Rubus fructico- sus L	Peru	82.98	66.43	0.93	0	13.19	2.48	0.42	Valencia and Guevara (2013)

Dietary patterns around the world suggest increasing the consumption of fruits and vegetables, as a sources of essential nutrients, fiber and some beneficial phytochemicals for health and reducing agents for chronic diseases (Seeram 2008). Table 2 and 3 show the nutritional composition of the fruits of different Rubus species and the importance in relation to other fruits, due to the high content of macro and micronutrients (calcium, potassium, phosphorus, magnesium, zinc, among others), and phytochemicals such as anthocyanins, tannins, flavonols, flavonoids and phenolic acids (Seeram 2006; Halvorsen et al. 2006). In addition to their striking colours ranging from red to purple or garnet, these fruits have a sweet acidified flavour, which exceeds 8-9 °Brix as reported by Rincon et al. (2015) for fruits of R. alpinus and R. glaucus. It is important to highlight that species such as raspberry (Rubus idaeus) contain ellagitannins and anthocyanins that differentiate them from other fruits (Rao and Snyder 2010), and it is precisely these type of characteristics that make berries foods with positive effects on the improvement and treatment of cardiovascular

diseases, neurodegenerative diseases, some types of cancer (gastrointestinal), aging and obesity (Seeram 2008).

Rubus species are a source of nutrients including essential minerals, fatty acids, vitamins and different phytochemicals. Table 2 and 3 show nutrient profiles and mineral contents in raspberries and blackberries (Rubus spp, Rubus glaucus Benth (without prickles), Rubus fructicosus, Rubus rosifolius, Rubus urticifolius, Rubus spp Brazos, Rubus spp cv Tupy and Rubus idaeus), reported in different countries. These species have dietary fiber contents between 3.0 and 6.5 g 100 g⁻¹ which aid in digestion (Bobinaité et al. 2016); they possess between 4 and 14 g of carbohydrates that intervene as a fast and profitable source of energy for the human body (Castellanos 2008). These berries contain a proportion of water close to 90% and less than 60kcal which places them in a group of fruits that do not substantially intervene in the increase of body weight, as water is the vehicle or transport of different substances within the body.

Rubus fruits are also a good source of vitamin C (26.5 mg $100 \,\mathrm{g}^{-1}$), an essential vitamin that in low intake induces health problems, and even death (Lee and Kader 2000). Vi-



Rao and Snyder (2010) Panamá INCAP (2012) Ferreira and Bergman Instituto de Nutrición de Centro América y Guedes et al. (2013) Garzón and Gómez Reference (2015)(2008)Magnesium Vitamin 0.055 0.03 I 0.23 16.3 22 15 20 Zinc 0.4 0.2 0.2 Vitamin Potassium 124 125 151 26.2 21 Niacin 0.598 Riboflavin 0.038 0.03 Thiamine Table 3 Content of minerals and vitamins in Rubus species, in 100 gr of edible portion 0.032 0.003 0.005 69.0 3.66 Calcium Phosphorouson 0.62 1.32 1.7 17.8 29 0.33 0.22 19.9 10 22 14.3 11.6 25 0.32 0.34 53 42 Central America and Panama Colombia Canada Brazil Brazil Rubus rosifolius Rubus idaeus L Benth (without Rubus glaucus Rubus spp. cv. Rubus spp cv. Sm. var Rosi-Rubus urtici-Rubus spp folius Poir prickles) Producer country folius

tamin C content depends on agronomic management and postharvest management as reported by Miret and Munné-Bosch (2016), in raspberry cv. Heritage. Additionally, these fruits are recognized as a good source of thiamine, riboflavin, niacin, zinc, magnesium, potassium (150–200 mg $100\,\mathrm{g}^{-1}$), phosphorus (10–40 mg), iron (0.5–1.5 mg $100\,\mathrm{g}^{-1}$), calcium (25–40 mg $100\,\mathrm{g}^{-1}$) and protein ($1\,\mathrm{g}\ 100\,\mathrm{g}^{-1}$ on average), the basic components of living cells involved in the construction of antibodies, hormones, enzymes, neurotransmitters, and nutrient transporters among others (Buttriss 2000).

In Rubus species around the world, there is a great potential for the utilization of their natural compounds found in different parts of the plant as shown in Table 4, the former perhaps influenced by the great genetic variability that occurs within the species. In the case of fatty acids the species R. glaucus shows potential for the cosmetic and pharmaceutical industry for its contents of palmitic, stearic, oleic, linoleic and linoleic acid, and in addition, these type of berries are notable for having considerable amounts of polyphenols, represented in compounds such as anthocyanins (pelargonidin and cyanidin in the species of R. idaeus) and ellagitannins, which can be found in fruits, leaves and stems of some species of blackberries and raspberries. These benefits are not popularly recognized, since the majority of consumers only attribute medicinal and bioactive properties to the fruits. The antioxidant potential of the other parts of the plant includes concentration in leaves of the species R. adenotrichos and R. coriifolius (values higher than $1.8\,\mu g\;EAG\,\mu L^{-1}$) and in stems with values higher than 0.5 µg EAG µL⁻¹ (Silva-Adame et al. 2013). At the same time there are other types of compounds such as triterpens in the aerial part of the plant, and glucans in roots. These compounds have important pharmaceutical uses for their antibacterial and immunological action (Wang et al. 2000; Weihua et al. 2009).

Fig. 4 reports investigations from various authors about how the increase in the consumption of fruit aids in prevention of diseases and reduction of stress, and lowers the risk of cardiovascular diseases and cancer (Trivedi et al. 2016; Law and Morris 1998). These positive effects are attributed to the presence of polyphenols (Van der Sluis et al. 2001; Silva-Adame et al. 2013). The total amount of secondary metabolites in plants depends on the agronomic management and environmental conditions where the crop is grown (Wang and Zheng 2001; Zheljazkov et al. 2009). Rubus species are used in traditional medicine for the management of diarrhea and the treatment of wounds and burns. The consumption of infusions of leaves can induce sedative effects, reduce kidney stones, and inhibit prostate and colon cancer. Additionally, these species are reported as useful plants in the recovery of natural resources in phytoremediation processes (Thinquino 1993; Wang and Lin



 Table 4 Chemical composition in some Rubus species

Producer country	Plant part	Species	Quantity	Component	Source
Country			%		
Colombia	Seeds	R. glaucus	11.24	Palmitic acid	Cerón et al. (2012)
			4.11	Stearic acid	
			9.42	Oleic acid	
			50.10	Linoleic acid	
			25.10	Linolenic acid	
			$mg 100 g^{-1}$		
United States	Fruits	R. ursinus G4 Bulk	211	Total content of anthocyanins	Moyer et al. (2002)
		R. ursinus G4-19	206		
		R. niveus Thumb	230		
		R. occidentalis cv. Early sweet	464		
		R. occidentalis cv Munger	627		
Canada	Fruits	R. idaeus	25.4	Cyanidin-3-sophoroside	Kassim et al. (2009);
			7.2	Cyanidin-3-glucosylrutinoside	Rao and Snyder (2010)
			3.9	Cyanidin-3-glucoside	
			2.3	Cyanidin-rutinoside	
			0.06	Pelargonidin-3-sophoroside	
			0.1	Pelargonidin-3-glucosylrutinoside	
			0.12	Pelargonidin-3-glucoside	
			0.005	Pelargonidin-3-rutinoside	
United States	Fruits	R. ursinus G4 Bulk	678	Total phenols	Moyer et al. (2002)
		R. ursinus G4-19	629		
		R. niveus Thumb	402		
		R. occidentalis cv. Early sweet	897		
		R. occidentalis cv Munger	980		
Lithuania	Fruits	R. idaeus. cv. Bristol	715	Total phenols	Bobinaité et al. (2012)
Hungary	Fruits	Rubus idaeus	226	Total phenols	Lugasi. et al. (2011)
Finland	Fruits	R. idaeus	76	Ellagitannins (sanguiin H-6 76 29)	Koponen et al. (2007)
			31	Ellagitannins (lambertianin C 31 29)	
			0.11	Ellagitannins (ellagic acid)	
Japan	Leaves	R. microphyllus	_	Esters and	Takashi et al. (1984);
		R. koehneanus		β-Glucosyl esters	Zhang et al. (2015)
		R. trifidus		of 19α-hydroxyursolic acid derivatives	
			$μ$ g EAG $μ$ L $^{-1}$		
Mexico	Leaves	R. adenotrichos	1.87	Polyphenols	Silva-Adame et al. (2013)
	Stems	R. adenotrichos	0.454	Polyphenols	
	Leaves	R. coriifolius	3.608	Polyphenols	
	Stems	R. coriifolius	0.761	Polyphenols	
China	Aerial plant part	R. pungens	-	Saponin triterpenoid (rubupungenoside A and B)	Wang et al. (2000)



Table 4 (Continued)

Producer country	Plant part	Species	Quantity	Component	Source
China	Aerial plant part	R. lambertianus	-	Triterpens and glucosides	Shu-Feng et al. (2015)
China	Root	R. crataegifolius Bge	-	Glucans	Weihua et al. (2009)

EAG Equivalents of gallic acid (Silva-Adame et al. [2013])

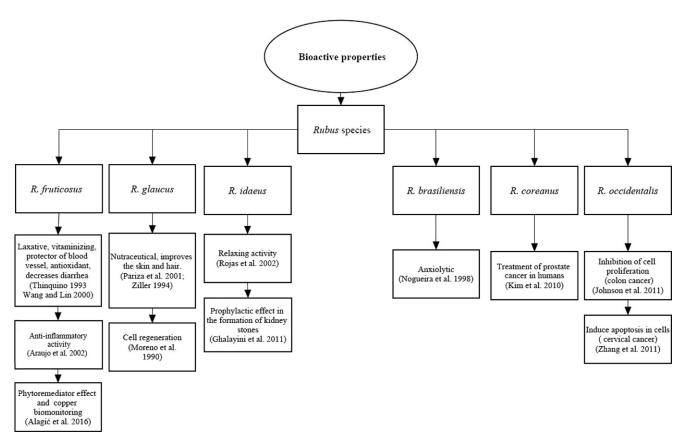


Fig. 4 Uses and bioactive properties in Rubus species

2000; Pariza et al. 2001; Ziller 1994; Moreno et al. 1990; Araujo et al. 2002; Rojas-Vera et al. 2002; Nogueiraa et al. 1998; Kim et al. 2010; Ghalayini et al. 2011; Alagić et al. 2016; Zhang et al. 2011). Fig. 4 shows the potential use of these species in different countries and their benefits to human health. Furthermore, the production and development of viable supply chains of blackberries and raspberries also contributes to increased income in rural communities.

Conclusions

There is a great potential for the use of various fruits of the *Rubus* species due to their high quantities of polyphenols, ellagitannins and anthocyanins, which provide an interesting source of natural antioxidants of vegetable origin. The nutritional benefits of the *Rubus* species include high dietary

fiber and water content, an adequate supply of calories and a good source of vitamin C. The agroindustrial potential of the different species of this genus depends on the agroecological conditions and the agronomic management of the regions where the crops are grown. Additionally, plants of this species are an important source of nutrients and phytochemicals that can influence the prevention and control of diseases in humans.

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Conflict of interest B.L. Moreno-Medina, F. Casierra-Posada and J. Cutler declare that they have no competing interests.



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