



Phenolic compounds in acerola fruit and by-products: an overview on identification, quantification, influencing factors, and biological properties

João C. Vilvert^{1,2} · Sérgio T. de Freitas² · Luana F. dos Santos² · Tiffany da S. Ribeiro^{2,3} ·
Cristiane M. Veloso^{1,4}

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Abstract

Acerola (*Malpighia emarginata* DC) is a cherry-like tropical fruit well-known for being a rich source of ascorbic acid (vitamin C) and phenolic compounds. This review provides a complete overview on aspects related to phenolic compounds of acerola fruit and by-products, comprising the identification and quantification of phenolic compounds, influencing factors, and biological properties. Scientific evidences suggest that the acerola is a promising superfruit with great potential in the food and pharmaceutical industries. At least 76 phenolic compounds were identified using high performance liquid chromatography in acerolas, including 55 flavonoids (anthocyanins, flavan-3-ols, flavonols, flavones, flavanones, isoflavones and chalcones) and 21 non-flavonoids (phenolic acids, stilbenes and lignans). Phenolic compounds in acerola show several biological properties, including antioxidant, antibacterial, antihyperglycemic, antihyperlipidemic, anti-inflammatory, and hepatoprotective activities. However, studies are further required to assess the seasonal and genotypic influence on the phenolics of acerola and their bioaccessibility. Acerola is an anthocyanin-rich fruit with high potential for pigment extraction, but stabilization of anthocyanins in juice and pulp should be further elucidated and improved.

Keywords *Malpighia emarginata* DC · Polyphenols · Phytochemicals · Antioxidant activity · Biological properties

Introduction

In recent years, global demand for fruit and vegetables is steadily increasing, as a result of healthier eating behavior and lifestyle by consumers, since their consumption have been associated with lower incidence of mortality caused by non-communicable chronic diseases [1, 2]. Red fruit, also called berries, are very popular due to their attractive appearance, pleasant taste and aroma and high nutritional value, as sources of vitamins,

carotenoids, phenolic compounds, fibers, phytosterols, and other bioactive compounds with well-known biological properties, including antioxidant, anti-inflammatory, anti-cancer, antimutagenic, antimicrobial, antiproliferative, anti-neurodegenerative, antiglycemic, hypolipidemic, cardio-protective, and neuroprotective properties [3–6].

In tropical countries, there are several native red fruit species that are underexploited when compared with traditional ones such as strawberry, grape, blueberry, raspberry, and blackberry, but which have high potential for use in food and pharmaceutical industries [7]. One of these species is acerola (*Malpighia emarginata* DC), a cherry-like tropical fruit that is one of the richest natural sources of ascorbic acid (AsA, or vitamin C) in the world, representing up to 100 times the levels found in orange and lemon [8].

AsA together with phenolic compounds such as flavonoids, phenolic acids, and stilbenes are the main responsible for the high antioxidant activity of acerolas, which can help reducing the oxidative damages of free radicals to human body and strengthening the immune system.

✉ João C. Vilvert
jcvilvert@gmail.com

¹ Graduate Program in Agronomy, State University of Southwest Bahia, Vitoria da Conquista, BA 45083-900, Brazil

² Tropical Semi-Arid Embrapa, Brazilian Agricultural Research Corporation, Petrolina, PE 56302-970, Brazil

³ University of Pernambuco, Petrolina, PE 56328-900, Brazil

⁴ Process Engineering Laboratory, State University of Southwest Bahia, Itapetinga, BA 45700-000, Brazil

In spite of its high nutrient profile and appeal for functional food, acerola is underutilized worldwide and information related to bioactive compounds and the factors that influence the synthesis of these compounds are still scarce [9]. This review provides a complete overview on aspects related to phenolic composition of acerola fruit and by-products, comprising identification, quantification, influencing factors and biological properties.

Research methodology and data collection

A search was performed on the Scopus database including the keywords *acerola* OR *Barbados cherry* OR *West Indian cherry* OR *Guarani cherry* OR *Surinam cherry* OR *Malpighia* OR *Malpighia emarginata* OR *Malpighia glabra* OR *Malpighia puniceifolia* AND *phenolic compounds* OR *polyphenols*, resulting in 171 published documents between January 2002 and December 2022 (Fig. 1). The main results were related to identification and quantification of phenolic compounds in whole fruit (skin and pulp), juice or residuals from pulp processing (seeds), extraction methods of phenolic compounds, and influencing factors. We addressed and discussed results from articles published in high impact scientific journals between 2013 and 2022.

Information on phenolic compounds studied in this review, as well as the 2D structures of the main phenolics in acerola fruit and by-products, were based on PubChem (<https://pubchem.ncbi.nlm.nih.gov/>).

Botanical description and cultivation of acerola

Acerola, also known as Barbados cherry, West Indian cherry, and Guarani cherry, is a tropical fruit belonging to the Malpighiaceae family. It is native from Central America, South

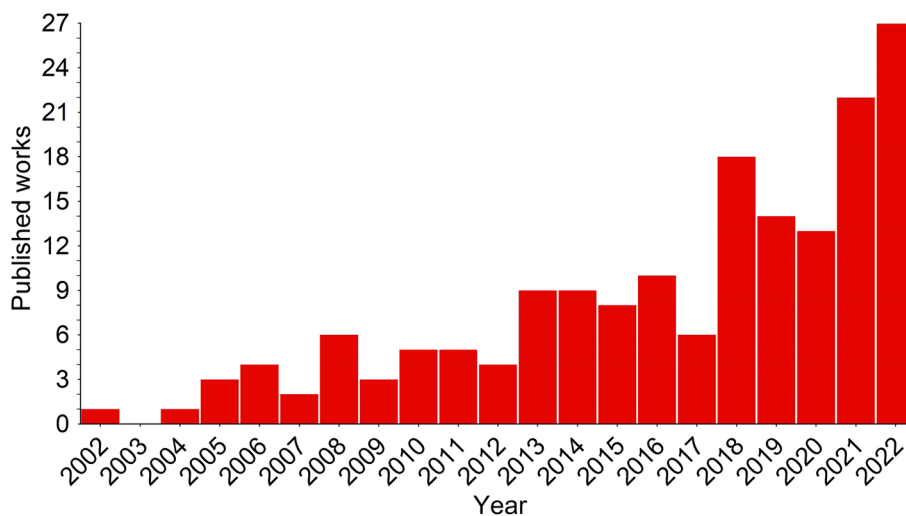
American and the Caribbean islands, and is also found in tropical and subtropical areas of Asia and Africa [10].

The taxonomic classification of acerola is not well established in the literature, since some researchers defend that the acerola originates from two species, *Malpighia puniceifolia* and *M. glabra*, while others argue that both are not distinct species, but different botanical forms. In Brazil, acerola orchards were established from *M. puniceifolia* seeds imported from Puerto Rico in the 1950s, characterized by causing strong skin irritation due to the presence of hairs on the leaves, but the presence of *M. glabra* is also confirmed due to the occurrence of glabrous plants (without hairs), which do not cause irritation [11]. Gomes et al. [12] indicate *M. emarginata* as the proper nomenclature for designating acerola. The Integrated Taxonomic Information System establishes *M. glabra* and *M. emarginata* as accepted nomenclatures for acerola, while *M. puniceifolia* is considered misapplied (non-accepted) [13].

Acerola (Fig. 2) tree is a shrub with small to medium height (2–3 m), the leaves are oval to elliptical-shaped with dark and glossy greenish color and height of 2.5–7.5 cm, and the inflorescences are sessile or have short peduncles, with five-fringed light or dark pink petals [10]. Ripe fruit is a globose drupe with 1–4 cm of diameter, a thin and fragile pericarp of reddish or dark purplish color, a mesocarp (pulp) that represents around 60–80% of total fruit weight, and one seed surrounded by a reticulated, tri-lobbed endocarp [14].

Acerola is a juicy, acid to sub-acid (0.46–1.10% malic acid, 0.05–0.09% succinic acid, titratable acidity of 0.87–1.97 g of malic acid 100 g⁻¹) and sweetish fruit (1.23–1.87% fructose, 1.24–1.83% glucose, 0.06–0.13% maltose, soluble solids of 6.03–13.87%), whose flavor is highly dependent on genotype [15, 16]. Acerola is well-known for its high AsA content, with ranges from 400 to 2,800 mg 100 g⁻¹ in red-ripe fruit and up to 4,000 mg 100 g⁻¹ in unripe green fruit [17, 18].

Fig. 1 Number/year of published works on phenolic composition of acerola fruit and by-products



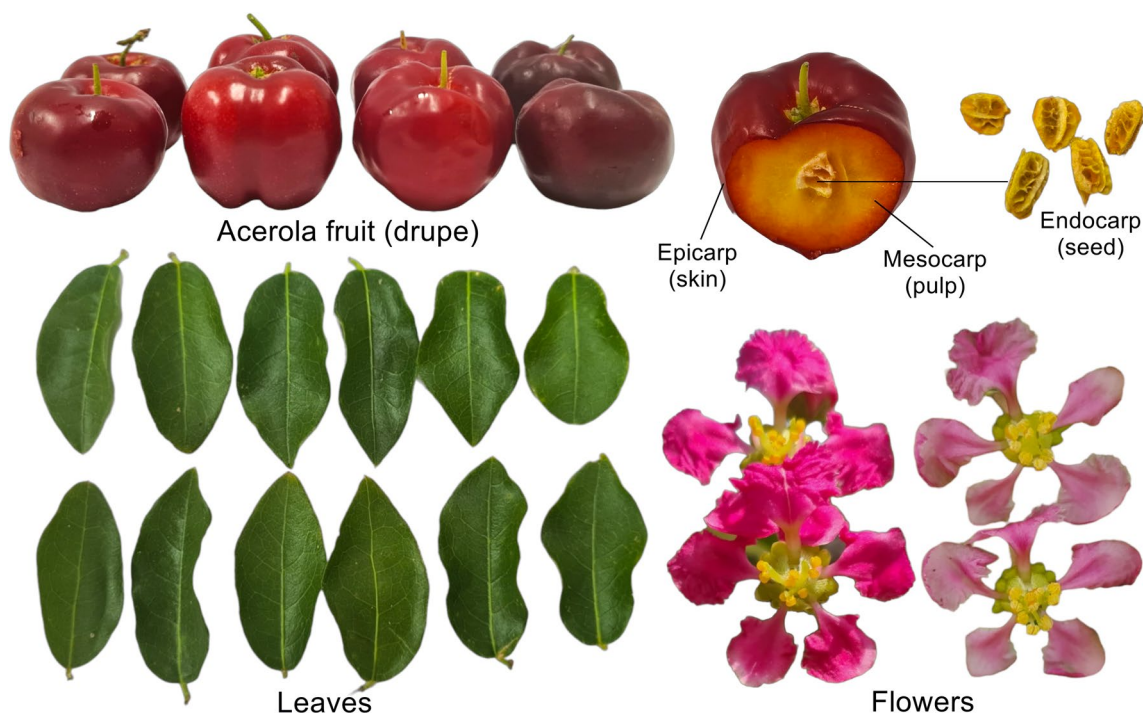


Fig. 2 Leaves of the tree and structure of the acerola (*Malpighia emarginata* DC) fruit

Acerola flowering and fruiting can occur concomitantly when temperatures are close to or greater than 26 °C and the season is rainy or water is made available through irrigation [10]. Fruit formation occurs very quickly, with an average period of 17–25 days between anthesis and harvest, which may vary depending on the genotype, temperature, solar radiation, and water availability.

Short production cycle of acerola enables the occurrence of up to eight harvests per year in irrigated orchards in the Brazilian Northeast under Semi-arid climate conditions, between August and April, when climatic conditions are favorable for fruit growth and development. Furthermore, acerola has little damage from pests and diseases when compared to other fruit species, which reduces the use of pesticides and enables the production of organic fruit, whose value is up to 50% more than that paid for fruit produced in the conventional system [11].

The commercial cultivation of acerola in Brazil has been growing every year, with a planted area of 5,753 hectares and production of 60,966 tons of fruit in 2017, according to official data by the Brazilian Institute of Geography and Statistics [19]. Acerola market is divided in two main purposes: green fruit for AsA extraction and red fruit for fresh consumption or processing.

The great AsA content in green acerolas motivated their use for the production of concentrates for food enrichment or pharmaceuticals, as an alternative to synthetic AsA in

dietary supplements [20, 21]. In Brazilian Northeast, several plantations are exclusively destined for AsA extraction in green fruit through partnerships between rural producers and multinational companies [22]. The acerola extract market is steadily expanding, with an expected market value of US\$ 17.5 billion until 2026 [23], as a result of higher absorption of acerola AsA by human body when compared to synthetic AsA, besides its ability to act as a food preservative.

Acerolas at red maturity stage are commonly commercialized for fresh consumption or for processing of value-added products, including frozen pulp, juice, marmalade, frozen concentrate, jam, yoghurt, and liquor [20]. As a naturally very acidic fruit, new acerola varieties have been developed in order to reach a higher consumer acceptance of fruit, characterized by high diameter, mass, firmness and sugar content, and low acidity [16]. Even though, high natural perishability and intense metabolic activity can limit the shelf life in acerolas, making processing an alternative to avoid postharvest fruit losses.

Scientific investigations on phenolic composition and health-promoting properties of native and exotic fruit as yet unknown or under-exploited species is important for their adding value, serving as a basis for social and economic development of local population and future source of income for small farmers [24].

Phenolic compounds in acerola: identification, quantification, and influencing factors

Phenolic compounds are phytochemicals produced by plants as secondary metabolites, i.e., compounds not required for plant growth or development but produced for its defense against biotic and abiotic stresses, such as salinity, exposure to high-energy radiation, drought, extreme temperatures, flood, attacks of insects, nematodes and phytopathogenic fungi, bacterial infection, and disease progression. In addition to defense responses, phenolic compounds perform a wide array of antioxidant, structural, attractant, ultraviolet (UV) screen, and signal functions in plants [25]. These compounds are synthesized by the shikimate and phenylpropanoid pathways, and are characterized by their structures with at least one aromatic ring, with single or multiple hydroxyl (–OH) and methyl (–CH₃) groups linked, ranging from simple structures to highly polymerized compounds [25–27].

From the discovery of phenol in 1834 to the present day, more than 10,000 phenolic compounds are known, and many of them have been studied in relation to their functional properties [28]. The interest on phenolic compounds is mainly related to their antioxidant activity, preventing and reducing oxidate damages by free radicals to vital cellular constituents such as lipids, proteins and nucleic acids. Free radical scavenger potential of a phenolic compound depends on its reducing properties as hydrogen- or electron-donating agents, which in turn varies according to the number of hydroxyl groups and their position in relation to the carboxyl functional group [29, 30].

Phenolic compounds are categorized according to their structural differences, source of origin, and biological activity [28]. In general, they can be divided in two major classes, flavonoids and non-flavonoids. Flavonoids are the main group of phenolic compounds, characterized by a polyphenolic structure (C₆–C₃–C₆) constituted of two aromatic rings (A and B) linked by a three-carbon bridge (frequently as a heterocyclic ring, named C). Flavonoids are subdivided into different subgroups, according to the substitution pattern (degree of unsaturation and oxidation) in C rings. Additionally, the sites of hydroxyl and methyl groups attached to flavonoid structure can result in glycoside modifications, thus flavonoids are found in both aglycone and glycoside forms. The main subgroups of phenolic compounds are anthocyanidins, flavan-3-ols, flavonols, flavones, flavanones, isoflavones, and chalcones [30–32].

Biosynthesis of phenolic compounds is regulated by several intrinsic and extrinsic factors, including plant hormones, developmental phase, water, temperature, minerals, salinity, UV radiation, and visible light, and can be stimulated by agricultural practices such as the application of plant growth

regulators and the postharvest application of UV radiation [33–35].

Many flavonoids are often responsible alongside the carotenoids for color pigmentation of fruit and flowers in most angiosperm families [31, 36]. In red fruit and berries, major flavonoids are composed of anthocyanins, water-soluble pigments with pink, red, blue and purple hues [4]. The color provided by anthocyanin depends on its hydroxylation, methylation, and glycosylation; higher number of hydroxyl groups attached to B-ring increases blue coloration, while methylation results in reddish hues [37].

The use of fruit anthocyanins to enhance and provide color to food products has been increasing, since natural ingredients are associated by consumers with the health benefits and improvement in life quality, in contrast with critics to synthetic dyes and their insecurity for human health [38]. However, anthocyanins are highly susceptible to degradation, depending on temperature, pH and light, which leads to changes in their color to yellow or even colorless degradation under these conditions [37].

Methods for assessment of acerola phenolics: from spectrophotometry to smartphone-based sensor and high-performance liquid chromatography (HPLC)

Classical method

Folin-Ciocalteu colorimetric method is the most widespread analytical technique for estimation of total phenolic compounds (TPC) content in plant extracts by the oxidation-reduction reaction of phenols with a mixture of phosphomolybdate and phosphotungstate (Folin-Ciocalteu reagent) to form a blue complex able to be quantified by spectrophotometry [39].

Since the first study on quantification of phenolic compounds in acerola, using the classical colorimetric Folin-Ciocalteu method [40], this fruit has shown to have an incredibly high content of these compounds. A comparative study of 18 non-traditional fruits from Brazil was carried out by Rufino et al. [41] and demonstrated that this fruit had the second highest content of polyphenols [1063 mg of gallic acid equivalents (GAE) per 100 g of fresh mass (fm)], slightly lower than that observed in camu-camu (*Myrciaria dubia*, Myrtaceae) (1,176 mg GAE 100 g⁻¹ fm), a little known Amazonian fruit also recognized as one of the richest natural sources of AsA worldwide.

Acerola (593.77 mg GAE 100 g⁻¹ fm) presented together with the panã (*Annona crassiflora*) (902.18 mg GAE 100 g⁻¹ fm), açai (*Euterpe oleracea*) (708.22 mg GAE 100 g⁻¹ fm) and jabuticaba (*Myrciaria cauliflora*) (626.57 mg GAE 100

g^{-1} fm) the highest TPC content in frozen pulps between 44 traditional and exotic Brazilian fruit species [42].

Innovations on Folin–Ciocalteu-based approaches for assessment of phenolic content in acerola

As alternatives to the use of spectrophotometer in determination of TPC content, which has high cost and little portability and that is limited to the laboratory routine, some innovative approaches have been proposed using acerolas. These new techniques mainly aim to make the assessment of plant-based phenolic content cheaper and more accessible, ceasing to be exclusive to the laboratory and accessible to industries.

Miranda et al. [43] designed a low-cost system for measuring the concentration of TPC and flavonoids in twelve fruit species, including acerola. Briefly, the system consists of an optical sensor, which requires a light emitting diode, an optical filter, a cuvette holder, a photodiode, an electronic board and a mechanical structure. Measurements were collected in transmittance and compared with those from a commercial spectrophotometer. The results did not indicate significant ($p > 0.05$) differences between the methods for determination of TPC ($48.16 \mu\text{g} \mu\text{L}^{-1}$ for the spectrophotometer and $60.27 \mu\text{g} \mu\text{L}^{-1}$ for the sensor) and flavonoids ($71.41 \mu\text{g} \mu\text{L}^{-1}$ for the spectrophotometer and $68.61 \mu\text{g} \mu\text{L}^{-1}$ for the sensor) in acerola, as well for the other fruit evaluated in the study.

Martins et al. [44] developed a simple and fast system based on colorimetry for quantification of phenolic compounds in acerola using acquisition of images by mobile devices followed by image conversion into the quantifiable RGB color system, i.e., a mathematical model that represents simultaneously red (R), green (G) and blue (B) colors as number values. Both spectrophotometry and smartphone-based method were in close agreement (145.0 and $146.0 \text{ mg GAE g}^{-1} \text{ dm}$, respectively). Additionally, the proposed method reduced in five times the reagent consumption and waste generation, being an efficient and greener approach for determination of the phenolic content.

HPLC: detailed phenolic composition of acerola

Recently, technological advances on food composition analysis have allowed an efficient and sensible separation, identification and quantification of phenolic compounds, whose biological and health properties are structure-dependent [45]. HPLC and mass spectrometry (MS) are undoubtedly recognized as the most advanced techniques for the elucidation and determination of phenolic compounds by the scientific community [46].

Phenolic compounds in acerola were separated by chromatography for the first time by Vendramini and Trugo

[47]. The authors identified nine phenolic compounds in red-ripe acerolas including three anthocyanins (malvidin-3,5-diglucoside, cyanidin 3-glucoside and pelargonidin), four phenolic acids (*p*-coumaric acid, ferulic acid, caffeic acid and chlorogenic acid), and two flavonols (kaempferol and quercetin). Since this period, at least 76 phenolic compounds were identified using HPLC in acerolas, including 55 flavonoids (anthocyanins, flavan-3-ols, flavonols, flavones, flavanones and isoflavones) (Table 1) and 21 non-flavonoids (phenolic acids, stilbenes and lignans) (Table 2). Different classes of phenolic compounds previously reported in acerola are discussed in the next topics.

The sensitivity of HPLC in detection of phenolic compounds is generally based on their purification and pre-concentration from matrices of plant extracts (i.e., acerola fruit and by-products). Furthermore, HPLC combined with MS detectors is highly sensitive and show high power for identification achieve high specificity due to the mass selectivity of detection [36].

The column selection also influences the success of the processes of identification and quantification of phenolic compounds in plant extracts. In studies with acerola and by-products, as with other fruit crops, a normal phase C_{18} or reversed phase (RP- C_{18}) column is employed, with 10–25 cm of length, 2.1–4.6 mm i.d., and 3–5 μm particle size [15, 48–53]. New types of columns, with 10 cm length, 2.1 mm i.d., and 1.7–1.8 μm particle size have been used in advanced HPLC methods of phenolic compounds identification, such as UPLC (ultra performance liquid chromatography) [54, 55]. Identification of acerola phenolic compounds has been carried out with ambient column temperature (30–40 °C), although higher temperatures can be adopted to new columns and techniques [36]. The running time is another crucial factor that influences the HPLC determination of phenolics, ranging from 15 to 90 min in studies with acerola. The flow rate varied between 0.35 and 1 mL/min and the volume injected was 4–40 μL .

Successful and accurate identification and quantification of acerola phenolic compounds with HPLC are confirmed by validation parameters, including calibration curves from external standards of the analyzed phenolics with excellent adjustment of linear regression, as well as low values for limit of detection (LOD) and limit of quantification (LOQ). Ferreira et al. [15] quantified 17 phenolic compounds in acerola fruit of seven varieties using HPLC–DAD, with $\text{LOD} < 0.0027 \text{ mg}/100 \text{ g}$, $\text{LOQ} < 0.0102 \text{ mg}/100 \text{ g}$, and $R^2 > 0.996$ for all evaluated compounds. In another study with acerola fruit using HPLC–DAD, low LOD ($0.0039 \text{ mg}/100 \text{ g}$) and LOQ ($0.0128 \text{ mg}/100 \text{ g}$) were found for nine phenolic compounds in fruit of three maturity stages [49].

In recent years, sophisticated systems of liquid chromatography combined with modern detectors have been employed

Table 1 Individual flavonoids (anthocyanins, flavan-3-ols, flavonols, flavones, flavanones, isoflavones and chalcones) reported in acerola fruit and by-products

| Flavonoid | PubChem CID | Fruit fraction | Fruit maturity stage | Identification method | Extraction solvent | Content (mg 100 g ⁻¹) | Reference |
|----------------------------|-------------|----------------|----------------------|-----------------------|--------------------|-----------------------------------|-----------|
| Anthocyanins | | | | | | | |
| Cyanidin 3-rhamnoside | 102601165 | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 14.99–68.23 ^a | [15] |
| | | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 47–1152 ^b | [50] |
| Cyanidin 3-rutinoside | 29231 | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 12–67 ^b | [50] |
| Cyanidin 3,5-diglucoside | 441688 | By-product | Ripe | HPLC–DAD | Ethanol | 0.7 ^a | [58] |
| Delphinidin | 68245 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Malvidin 3-glucoside | 11249520 | By-product | Ripe | HPLC–DAD | Ethanol | 8.9 ^a | [58] |
| Pelargonidin | 440832 | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 0.4–7.0 ^b | [50] |
| Pelargonidin 3-glucoside | 443648 | By-product | Ripe | HPLC–DAD | Ethanol | 1.3 ^a | [58] |
| Pelargonidin 3-rhamnoside | 44256696 | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 25–155 ^b | [50] |
| Peonidin-3-xylopyranoside | NL | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 6–156 ^b | [50] |
| Petunidin 3-glucoside | 443651 | By-product | Ripe | HPLC–DAD | Ethanol | 14.7 ^a | [58] |
| Phloretin | 4788 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Tulipanin | 5492231 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Flavan-3-ols | | | | | | | |
| <i>Monomeric catechins</i> | | | | | | | |
| (±)–Catechin | 9064 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.64 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.8 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.68–2.51 ^a | [15] |
| | | Skin and pulp | Ripe | HPLC–DAD | Methanol | 871 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 396 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Methanol | 115 ^a | [49] |
| | | Seed | – | UPLC–MS | Ethanol | 1.57 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 3.12 ^b | [48] |
| | | Seed | – | HPLC–UV | Water | 1.09 ^a | [59] |
| | | Seed | – | HPLC–UV | Methanol | 1.13 ^a | [59] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 35.1 ^a | [58] |
| | | Non–pomace | Green | UHPLC–MS/MS | Water | 1.26–22.08 ^b | [54] |
| | | Juice | Ripe | HPLC–DAD | NS | 0.15 ^a | [52] |
| | | Juice | Green | UHPLC–MS/MS | Water | 0.42 ^a | [54] |
| (±)–Epicatechin | 72276 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.63 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.7 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.003 ^a | [15] |
| | | Skin and pulp | Ripe | HPLC–DAD | Methanol | 704 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 253 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Methanol | 521 ^a | [49] |
| | | Seed | – | UPLC–MS | Ethanol | 159.5 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 33.1 ^b | [48] |
| | | Seed | – | HPLC–UV | Water | 1.17 ^a | [59] |
| | | Seed | – | HPLC–UV | Methanol | 9.19 ^a | [59] |

Table 1 (continued)

| Flavonoid | PubChem CID | Fruit fraction | Fruit maturity stage | Identification method | Extraction solvent | Content (mg 100 g ⁻¹) | Reference |
|--------------------------------|-------------|----------------|----------------------|-----------------------|--------------------|-----------------------------------|-----------|
| (-)-Epicatechin gallate | 107905 | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 0.25–0.72 ^a | [15] |
| (-)-Epigallocatechin gallate | 65064 | Skin and pulp | Green | HPLC-DAD | Ethanol | 5.83 ^b | [60] |
| | | Seed | – | HPLC-UV | Methanol | 0.91 ^a | [59] |
| | | By-product | Ripe | HPLC-DAD | Ethanol | 3.8 ^a | [58] |
| <i>Proanthocyanidins</i> | | | | | | | |
| Procyanidin A2 | 124025 | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 0.52–0.93 ^a | [15] |
| | | By-product | Ripe | HPLC-DAD | Ethanol | 3.8 ^a | [58] |
| Procyanidin B1 | 11250133 | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 0.09–1.78 ^a | [15] |
| | | By-product | Ripe | HPLC-DAD | Ethanol | 20.9 ^a | [58] |
| Procyanidin B2 | 122738 | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 0.25–0.81 ^a | [15] |
| | | By-product | Ripe | HPLC-DAD | Ethanol | 39.1 ^a | [58] |
| <i>Flavonols</i> | | | | | | | |
| Isoquercitrin | 5280804 | Skin and pulp | Fully ripe | HPLC-MS/MS | Methanol | 33.2 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC-MS/MS | Methanol | 43.2 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 1.31–3.29 ^a | [15] |
| | | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 0.5–2.8 ^b | [50] |
| Isorhamnetin | 5281654 | By-product | Ripe | HPLC-DAD | Ethanol | 15.8 ^a | [58] |
| | | Skin and pulp | Fully ripe | HPLC-MS/MS | Methanol | 0.62 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC-MS/MS | Methanol | 0.99 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 2.08–4.70 ^a | [15] |
| Isorhamnetin 3-galactoside | 13245586 | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 1.1–1.3 ^b | [50] |
| | | Skin and pulp | Green | HPLC-DAD | Ethanol | 10.13–11.41 ^b | [60] |
| | | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 2.7–3.0 ^b | [50] |
| | | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 17–43 ^b | [50] |
| Kaempferol | 5280863 | Skin and pulp | Fully ripe | HPLC-MS/MS | Methanol | 2.39 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC-MS/MS | Methanol | 1.61 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC-DAD | Methanol | 162 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC-DAD | Methanol | 231 ^a | [49] |
| | | Skin and pulp | Green | HPLC-DAD | Ethanol | 6.18–6.30 ^b | [60] |
| | | Skin and pulp | Green | HPLC-DAD | Methanol | 125 ^a | [49] |
| | | Seed | – | UPLC-MS | Ethanol | 2.30 ^b | [48] |
| | | Seed | – | UPLC-MS | Methanol | 3.26 ^b | [48] |
| | | Seed | – | UPLC-MS | Acetone | 4.15 ^b | [48] |
| | | Juice | Ripe | HPLC-DAD | NS | 0.37 ^a | [52] |
| Kaempferol 3-galactoside | 44258992 | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 1.5–5.5 ^b | [50] |
| | | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 1.5–5.5 ^b | [50] |
| Kaempferol 3-glucoside | 5282102 | Skin and pulp | Ripe | HPLC-DAD | Ethanol | 0.34–0.83 ^a | [15] |
| | | Skin and pulp | Green | HPLC-DAD | Ethanol | 8.50–32.68 ^b | [60] |
| Kaempferol 7-neohesperidoside | 5483905 | By-product | Ripe | HPLC-DAD | Ethanol | 12.0 ^a | [58] |
| | | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 3.1–7.0 ^b | [50] |
| Kaempferol 3-arabinofuranoside | 5318717 | Skin and pulp | Intermediate | HPLC-MS/MS | Methanol | 10.5–18.1 ^b | [50] |
| Myricetin | 5281672 | Juice | Ripe | HPLC-DAD | NS | 0.09 ^a | [52] |

Table 1 (continued)

| Flavonoid | PubChem CID | Fruit fraction | Fruit maturity stage | Identification method | Extraction solvent | Content (mg 100 g ⁻¹) | Reference |
|---------------------------|--------------|----------------|----------------------|-----------------------|------------------------------|-----------------------------------|-----------|
| Myricetin 3-glucuronide | 44259442 | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 0.1–14.3 ^b | [50] |
| Myricetin 3-glucoside | 44259426 | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 0.1–25.1 ^b | [50] |
| Myricetin 3-rhamnoside | 5352000 | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 74–196 ^b | [50] |
| Quercetin | 5280343 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 12.0 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 12.1 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–DAD | Methanol | 118 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 113 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Methanol | 601 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Ethanol | 6.63–8.13 ^b | [60] |
| | | Seed | – | HPLC–UV | Water | 0.007 ^a | [59] |
| | | Seed | – | HPLC–UV | Methanol | 0.03 ^a | [59] |
| | | Juice | Ripe | HPLC–DAD | NS | 1.36 ^a | [52] |
| | | Quercitrin | 5280459 | Skin and pulp | Ripe | HPLC–DAD | Methanol |
| Skin and pulp | Intermediate | | | HPLC–DAD | Methanol | 580 ^a | [49] |
| Skin and pulp | Green | | | HPLC–DAD | Methanol | 193 ^a | [49] |
| Quercitrin-2''-O-gallate | NL | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 0.8–1.9 ^b | [50] |
| Rutin | 5280805 | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.06–0.48 ^a | [15] |
| | | Skin and pulp | Ripe | HPLC–DAD | Methanol | 1657 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 1034 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Methanol | 1018 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Ethanol | 2.35 ^b | [60] |
| | | Seed | – | UPLC–MS | Ethanol | 3.62 ^b | [48] |
| | | Seed | – | UPLC–MS | Methanol | 7.07 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 8.29 ^b | [48] |
| | | Non–pomace | Green | UHPLC–MS/MS | Water | 1.54–2.48 ^b | [54] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 1.2 ^a | [58] |
| Juice | Green | UHPLC–MS/MS | Water | 0.28 ^a | [54] | | |
| Flavones | | | | | | | |
| Acacetin | 5280442 | Seed | – | UPLC–MS | Ethanol, methanol or acetone | <LOQ | [48] |
| Apigenin | 5280443 | Skin and pulp | Ripe or fully ripe | HPLC–MS/MS | Methanol | <LOQ | [51] |
| | | Seed | – | UPLC–MS | Ethanol, methanol or acetone | <LOQ | [48] |
| Chrysin | 5281607 | Seed | – | UPLC–MS | Ethanol, methanol or acetone | <LOQ | [48] |
| Luteolin | 5280445 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.05 ^b | [51] |
| | | Juice | Ripe | HPLC–DAD | NM | 0.04 ^a | [52] |
| | | Seed | – | UPLC–MS | Ethanol, methanol or acetone | <LOQ | [48] |
| Malonylapiin | 5280803 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Pinobanksin | 73202 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.15 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.32 ^b | [51] |
| Vitexin | 5280441 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| 7,8,4'-Trihydroxy-flavone | 688853 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Flavanones | | | | | | | |
| Hesperetin | 72281 | By-product | Ripe | HPLC–DAD | Ethanol | 32.6 ^a | [58] |

Table 1 (continued)

| Flavonoid | PubChem CID | Fruit fraction | Fruit maturity stage | Identification method | Extraction solvent | Content (mg 100 g ⁻¹) | Reference |
|--------------------------------|-------------|----------------|----------------------|-----------------------|------------------------------|-----------------------------------|-----------|
| Hesperidin | 10621 | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 1.02–3.26 ^a | [15] |
| Naringenin | 932 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.11 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.28 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.22–1.73 ^a | [15] |
| | | Seed | – | UPLC–MS | Ethanol | 47.88 ^b | [48] |
| | | Seed | – | UPLC–MS | Methanol | 33.73 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 118.82 ^b | [48] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 16.7 ^a | [58] |
| Naringin | 442428 | Skin and pulp | Ripe or fully ripe | HPLC–MS/MS | Methanol | <LOQ | [51] |
| 2,4',7-Trihydroxy-isoflavanone | 13953272 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Isoflavones | | | | | | | |
| Biochanin A | 5280373 | Seed | – | UPLC–MS | Ethanol, methanol or acetone | <LOQ | [48] |
| Daidzein | 5281708 | Seed | – | UPLC–MS | Ethanol, methanol or acetone | <LOQ | [48] |
| 6,7,4'-Trihydroxy-isoflavone | 5284649 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Formononetin | 5280378 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Genistein | 5280961 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Chalcones | | | | | | | |
| Naringenin chalcone | 5280960 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |

NL not listed on PubChem; NS not shown; LOQ limit of quantification

^aExpressed in fresh mass basis; ^bExpressed in dry mass basis

for the identification of acerola phenolics, including UPLC–q-TOF–MS (ultra performance liquid chromatography coupled to a quadrupole-time-of-flight mass spectrometer) [54, 55]. This system consists in a powerful and reliable analytical approach to trace qualitatively and quantitatively the phenolic profile of plant extracts, outperforming the conventional HPLC method, which may present limitations in the detection of compounds in very small amounts, besides disturbance of high background noise [56]. However, these systems are still very expensive and limited to a few labs around the world, which justifies the wide use of DAD coupled to the liquid chromatography in the identification of phenolics, as a low cost, sensitive, efficient, and flexible system [57].

Identification and quantification of flavonoids in acerola

Anthocyanins

The majority of polyphenols found in acerola are anthocyanins, responsible for the reddish/purplish fruit color, similarly to other red fruit. The anthocyanin profile of acerola

includes cyanidins, delphinidins, malvidins, pelargonidins, peonidins, and petunidins (Table 1). These anthocyanin subclasses are the six most widespread in nature [61]. Cyanidin is the main anthocyanin found in acerolas, corroborating with Olivas-Aguirre et al. [62] as the most widely distributed anthocyanin in red and blue fruit.

Anthocyanins are a large class of water-soluble pigments with a wide range of color diversity, present in vacuoles of different plant tissues, including the fruit [63]. Fruit color is not only the main indicator of sensory quality, but also correlated with nutritional quality [64]. Anthocyanins isolated from acerola show strong ability as free radical scavengers [65] and exhibit several health-promoting effects.

Anthocyanins extracted from fruit are promising for use as food colorant. However, they are unstable and highly susceptible for degradation, depending on conditions such as pH, light, oxygen, and temperature. In this sense, techniques can be adopted for anthocyanin stabilization. In acerola, the stability of anthocyanins seems to be severely compromised by the very high AsA content in the fruit, which condensates on carbon 4 of anthocyanins, resulting in losses of both compounds [66].

Table 2 Individual non-flavonoids (phenolic acids, stilbenes and lignans) reported in acerola fruit and by-products

| Non-flavonoid | PubChem CID | Fruit fraction | Fruit maturity stage | Identification method | Extraction solvent | Content (mg 100 g ⁻¹) | Reference |
|------------------------------|-------------|----------------|----------------------|-----------------------|--------------------|-----------------------------------|-----------|
| Phenolic acids | | | | | | | |
| <i>Hydroxybenzoic acids</i> | | | | | | | |
| Ellagic acid | 5281855 | Skin and pulp | Ripe | HPLC–DAD | Methanol | 253 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 172 ^a | [49] |
| Gallic acid | 370 | Skin and pulp | Green | HPLC–DAD | Methanol | 130 ^a | [49] |
| | | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.4 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.38 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–DAD | Methanol | 536 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 1.3–2.9 ^b | [50] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 451 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Methanol | 470 ^a | [49] |
| | | Seed | – | HPLC–UV | Water | 0.47 ^a | [59] |
| | | Seed | – | HPLC–UV | Methanol | 0.33 ^a | [59] |
| | | Juice | Ripe | HPLC–DAD | NS | 0.07 ^a | [52] |
| Protocatechuic acid | 72 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.39 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.31 ^b | [51] |
| Salicylic acid | 338 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.24 ^b | [51] |
| Syringic acid | 10742 | Seed | – | HPLC–UV | Water | 4.61 ^a | [59] |
| | | Seed | – | HPLC–UV | Methanol | 3.72 ^a | [59] |
| Vanillin | 1183 | Skin and pulp | Ripe | HPLC | Methanol | 0.24 ^a | [53] |
| <i>Hydroxycinnamic acids</i> | | | | | | | |
| Caffeic acid | 689043 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.73 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.95 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.07–0.29 ^a | [15] |
| | | Skin and pulp | Ripe | HPLC–DAD | Methanol | 682 ^a | [49] |
| | | Skin and pulp | Intermediate | HPLC–DAD | Methanol | 563 ^a | [49] |
| | | Skin and pulp | Green | HPLC–DAD | Methanol | 459 ^a | [49] |
| | | Non–pomace | Green | UHPLC–MS/MS | Water | 1.36–3.44 ^b | [54] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 0.9 ^a | [58] |
| | | Juice | Green | UHPLC–MS/MS | Water | 0.49 ^a | [54] |
| | | Juice | Ripe | HPLC–DAD | NS | 0.05–0.10 ^a | [52] |
| Caftaric acid | 6440397 | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.34–0.45 ^a | [15] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 19.4 ^a | [58] |
| Chlorogenic acid | 1794427 | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.17–0.38 ^a | [15] |
| | | Seed | – | UPLC–MS | Methanol | 0.28 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 4.25 ^b | [48] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 6.5 ^a | [58] |
| <i>m</i> -Coumaric acid | 637541 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| <i>p</i> -Coumaric acid | 637542 | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.79 ^b | [51] |
| | | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 0.98 ^b | [51] |
| | | Skin and pulp | Green | HPLC–DAD | Ethanol | 28.87 ^b | [60] |
| | | Seed | – | UPLC–MS | Ethanol | 4.22 ^b | [48] |
| | | Seed | – | UPLC–MS | Methanol | 6.06 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 8.34 ^b | [48] |
| | | Seed | – | HPLC–UV | Methanol | 0.12 ^a | [59] |
| | | Seed | – | HPLC–UV | Methanol | 0.24 ^a | [59] |

Table 2 (continued)

| Non-flavonoid | PubChem CID | Fruit fraction | Fruit maturity stage | Identification method | Extraction solvent | Content (mg 100 g ⁻¹) | Reference |
|------------------------------------|-------------|----------------|----------------------|-----------------------|--------------------|-----------------------------------|-----------|
| <i>p</i> -Coumaroylquinic acid | 441280 | Juice | Ripe | HPLC–DAD | NS | 0.33–0.84 ^a | [52] |
| | | Skin and pulp | Intermediate | HPLC–MS/MS | Methanol | 3.9–8.1 ^b | [50] |
| Ferulic acid | 445858 | Skin and pulp | Ripe | HPLC–MS/MS | Methanol | 1.27 ^b | [51] |
| | | Skin and pulp | Fully ripe | HPLC–MS/MS | Methanol | 0.62 ^b | [51] |
| | | Skin and pulp | Green | HPLC–DAD | Ethanol | 0.34–1.63 ^b | [60] |
| | | Seed | – | UPLC–MS | Ethanol | 4.10 ^b | [48] |
| | | Seed | – | UPLC–MS | Methanol | 5.41 ^b | [48] |
| | | Seed | – | UPLC–MS | Acetone | 6.53 ^b | [48] |
| | | Non-pomace | Green | UHPLC–MS/MS | Water | 2.96–5.44 ^b | [54] |
| | | Juice | Green | UHPLC–MS/MS | Water | 0.61 ^a | [54] |
| | | Juice | Ripe | HPLC–DAD | NS | 0.04–0.45 ^a | [52] |
| Isochlorogenic acid | 6436237 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| <i>n</i> -Feruloylglycine | 5280527 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Stilbenes | | | | | | | |
| <i>trans</i> -Resveratrol | 445154 | Skin and pulp | Ripe | HPLC–DAD | Ethanol | 0.23–0.38 ^a | [15] |
| | | Juice | Ripe | HPLC–DAD | NS | 0.34 ^a | [52] |
| | | By-product | Ripe | HPLC–DAD | Ethanol | 8.1 ^a | [58] |
| <i>cis</i> -Resveratrol | 1548910 | By-product | Ripe | HPLC–DAD | Ethanol | 2.5 ^a | [58] |
| Coumarin | 323 | Skin and pulp | Green | HPLC–DAD | Ethanol | 1.69–4.06 ^b | [60] |
| Lignans | | | | | | | |
| Lariciresinol | 332427 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Sesaminol | 94672 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |
| Secoisolariciresinol monoglucoside | 101138945 | Skin and pulp | Green and ripe | UPLC–MS/MS | Methanol | NS | [55] |

NS not listed on PubChem; NS not shown; LOQ limit of quantification

^aExpressed in fresh mass basis; ^bExpressed in dry mass basis

The use of inorganic host materials as additives to increase stability of acerola anthocyanins was suggested by Ribeiro et al. [67]. These authors demonstrated that the incorporation of montmorillonite (Mnt) clay into clarified acerola juice at 4% (dry basis) was enough for intercalation of major anthocyanins into Mnt interlayers, resulting in variations from pale red to darker and redder shades after 60 days, and thus preserving the red color of the juice.

Innovative and advanced approaches for stabilization of anthocyanin have been proposed, including co-pigmentation, acylation with various organic acids, complexation metal ions, and microencapsulation, but their application in acerola is still incipient.

Flavan-3-ols: monomeric catechins and proanthocyanidins

(+)-Catechin and (–)-epicatechin were the major flavan-3-ols previously reported in acerola, besides the isomers (–)-epicatechin gallate and (–)-epigallocatechin gallate were also observed in fruit and by-product (Table 1). Catechin content in acerola is comparable to that found in other fruit such as grape [68], apple [29, 69], pear [70], and cherry [71, 72], known as some of major sources of catechin in the world.

Catechins are colorless and astringent, responsible for the fruit bitter taste. Their extraction in different plant tissues is a hard task, due to polymerization with other molecules and high susceptibility to degradation by oxygen, high temperature, light and alkaline conditions. In this way, encapsulation and protected coating are strategies to stabilize catechin molecules [73].

Several beneficial properties has been attributed to catechin and derivatives, including anticancer, anti-obesity, antidiabetic, anticonvulsant, anti-infectious, hepatoprotective, and neuroprotective effects [74]. Furthermore, the antioxidant activity of catechins occurs through the scavenge of free radicals, chelation of redox active transition-metal ions, inhibition of redox active transcription factors, inhibition of pro-oxidant enzymes, and induction of antioxidant enzymes [75]. Studies with catechin from apple after ingestion have shown that this phenolic compound remains stable during gastric digestion, besides being rapidly absorbed from the small intestine [76].

Concerning the presence of proanthocyanidins (or condensed tannins) in acerola fruit and by-products, three were previously reported, namely procyanidin A2, procyanidin B1 and procyanidin B2 (Table 1). These compounds, together, accounted for 1.7–6.0% of total phenolic compounds analyzed by RP–HPLC/DAD in ripe acerolas of different cultivars [15].

Proanthocyanidins are synthesized by the polymerization or oligomerization of flavan-3-ols units (catechins and/or epicatechins). Proanthocyanidins are formed in the flavonoid pathway, sharing the same upstream pathway with anthocyanins, including the function of the anthocyanidin synthase as key role in the biosynthesis of both [77].

Proanthocyanidins are mainly produced in fruit at earlier maturity stages and are responsible for their bitterness [78]. They are synthesized as end products of the flavonoid pathway and are involved in the browning of plant tissues, including fruit, as substrates of polyphenol oxidases, causing higher browning than other phenolics [79, 80].

Flavonols

Flavonols were the phenolic class with the highest diversity of compounds in acerola, with 17 flavonols previously found, including the aglycones kaempferol, myricetin, quercetin, quercitrin, isoquercitrin, isorhamnetin, and rutin, as well as some of their glycosylated forms (Table 1). Glucose was the most frequent sugar type linked to flavonols in acerola, but other mono- and di-saccharides were also found, such as galactose, arabinofuranose, robinobiose, neohesperidose, and rhamnose. Other compounds attached to flavonols in acerola were glucosiduronic acid (in myricetin-3-O-glucuronide) and gallic acid (in quercitrin-2''-O-gallate).

Flavonols is usually the main class of phenolic compounds in acerolas at green maturity stage, when the anthocyanins are absent [60]. In that case, kaempferol, isorhamnetin, and quercetin have been reported as the main flavonols in unripe green fruit [49, 51, 60].

Flavonols are flavonoids with a ketone group and a hydroxyl at 3-position on the C ring, where glycosylation

generally occur [31]. Quercetin and kaempferol are the major classes of flavonols, differing from each other by one extra OH group at the C3 of the B ring in quercetin (Fig. 3) [81]. Both were the flavonols reported with the greatest variety of glycosylations in acerola, with five distinct forms besides aglycone for quercetin, considering isoquercitrin, quercitrin, and rutin are glycoside derivatives of quercetin, and four distinct glycosylated forms for kaempferol (Table 1). At least 347 and 279 different glycosidic combinations are possible for kaempferol and quercetin, respectively [82].

Flavonol glycosides and aglycones are involved in several functions in plants, including UV photoprotection, reproduction, and internal regulation of cell physiology, besides acting as a free radical scavenger and contributor to plant immune system [83].

Flavones and flavanones

Eight flavones (acacetin, apigenin, chrysin, luteolin, malonylapiin, pinobanksin, vitexin and 7,8,4'-trihydroxyflavone) and five flavanones (hesperetin, hesperidin, naringenin, naringin and 2,4',7-trihydroxyisoflavanone) were found in acerolas (Table 1). These classes have less participation in the phenolic composition of acerolas than other flavonoid classes [15, 51].

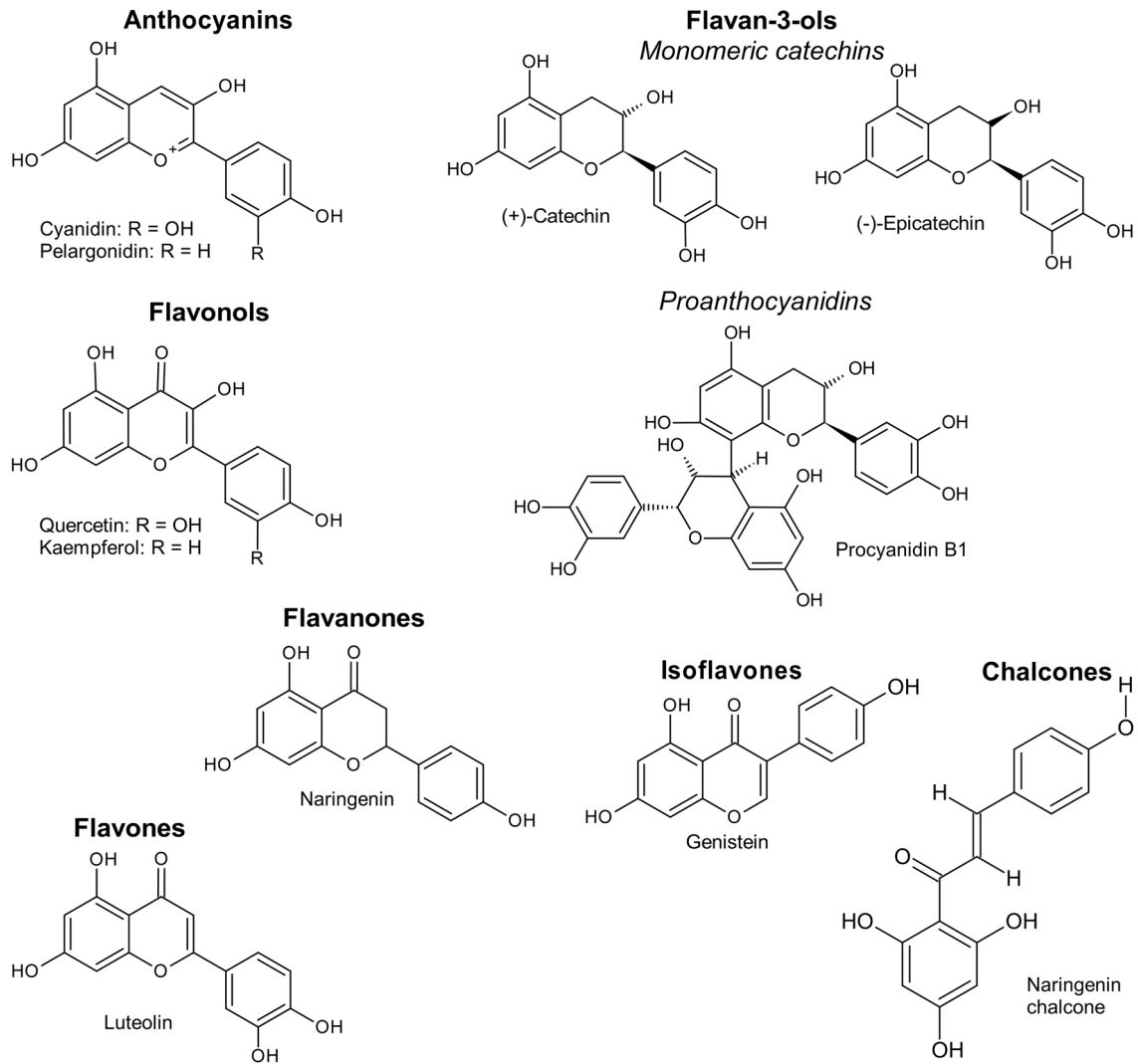
Flavones and flavanones are generally colorless or pale yellow. Flavones are structurally similar to flavonols, with a double bond between positions 2 and 3 and oxidized at position 4 of the C ring, differing only in the absence of hydroxy group at C3 in flavones. The flavanones, in turn, have a similar structure to the flavones, but with the absence of double bond between C2 and C3 (Fig. 3) [27, 80, 84].

Naringenin was the major flavanone reported in acerola (Table 1). Naringenin is the first product resulted from the synthesis of flavonoids, from which many other flavonoids are formed [78].

Isoflavones and chalcones

The literature search indicated that, so far, at least five isoflavones and one chalcone have been identified in acerola fruit, but without quantification of these phenolic compounds. The isoflavones biochanin A and daidzein were reported in seed of acerola agro-industrial residues [48], while formononetin, genistein, 6,7,4'-trihydroxyisoflavone and the chalcone 2',4,4',6'-tetrahydroxychalcone (naringenin chalcone) were found in skin and pulp of green and red-ripe acerolas [55].

Flavonoids



Non-flavonoids

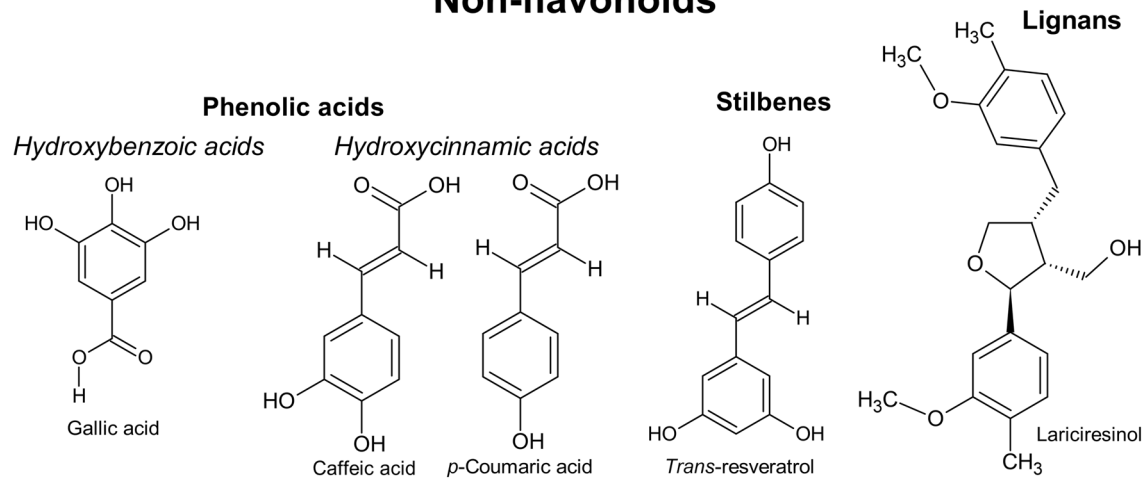


Fig. 3 Chemical structures of representative phenolic compounds in acerola fruit and by-products

Identification and quantification of non-flavonoids in acerola

Phenolic acids

Phenolic acids are classified in two major substituted acid derivatives, hydroxybenzoic and hydroxycinnamic acids. The main differences between both classes of phenolic acids are related to the methoxylation and hydroxylation positions of their aromatic rings and the number of carbons: C6–C1 basic skeleton for hydroxybenzoic acids, and C6–C3 basic skeleton for hydroxycinnamic acids [71].

A total of six hydroxybenzoic (ellagic, gallic, protocatechuic, salicylic and syringic acids, and vanillin) and nine hydroxycinnamic acids (caffeic, caftaric, chlorogenic, *m*-coumaric, *p*-coumaric, *p*-coumaroylquinic, ferulic and isochlorogenic acids, and *n*-feruloylglycine) were found in studies with acerola fruit and by-products (Table 2).

Stilbenes and lignans

Stilbenes described in acerola fruit and by-products include resveratrol and coumarins (Table 2). Resveratrol was reported for the first time in acerola in its *trans* form by Nowak et al. [52], in cold-pressed juices prepared from whole fruit without addition of water and sugar, in a level of 0.34 mg 100 mL⁻¹. Afterwards, *trans*-resveratrol was found in the skin and pulp of ripe fruit (0.23–0.38 mg 100 g⁻¹ fm) [15] and in by-products of fruit pulp processing (8.1 mg 100 g⁻¹ fm) [58], where *cis* form of resveratrol was also observed (2.5 mg 100 g⁻¹ fm).

Stilbenes are characterized by two aromatic rings joined by an ethylene bridge. Resveratrol has one of the simplest structures among the stilbenes, and present two forms: *trans* form is not sterically hindered, while *cis* form is sterically hindered and therefore less stable [68, 80]. Resveratrol is an antimicrobial and antifungal phytoalexin produced in the plants as a response to injury or infection [26]. It is the most studied stilbene and one of the most popular phenolic compounds, especially for its high concentration in wines, whose moderated and continuous ingestion plays a key role on the prevention of chronic heart diseases [57].

Even if the skin of red grapes (and consequently red wines) are the most known sources of resveratrol in human diet, its presence was also stated in several red fruits other than acerola, such as açai (0.38 mg 100 g⁻¹ fm), blackberry (6.48 mg 100 g⁻¹ fm), blueberry (1.58 mg 100 g⁻¹ fm) and raspberry (1.12–3.85 mg 100 g⁻¹ fm) [4].

A total of three lignans (lariciresinol, sesaminol and secoisolariciresinol monoglucoside) were identified in the

skin and pulp of both green unripe and red ripe acerolas, but without quantification [55]. Lignans are less common and less studied in fruit and vegetables when compared to flavonoids, but are involved in important pathways of cell signaling, which arouses the interest in future investigations about its usefulness [26, 27].

Bioavailability and bioaccessibility of phenolic compounds in acerola

In recent years, the importance of research related to the bioavailability and bioaccessibility of phenolic compounds was raised, once the biological activities and health-promoting properties of these compounds are not only based on the absolute quantity of intake, but also their behavior in the gastrointestinal system [76]. The ambiguity in the concepts and the undifferentiated use require clear definitions of both terms [85]. Bioavailability is defined as the fraction of a phenolic compound (or any phytochemical or nutrient) that is absorbed, i. e. that reaches the bloodstream, and is available for use in metabolic processes. Bioaccessibility refers to the amount of phenolic compounds released from the food matrix during digestion, becoming absorbable (available for intestinal absorption) [86]. Bioavailability is part of the bioaccessibility, thus the bioaccessible fraction is always equal to or higher than the bioavailable fraction [85].

Studies on bioavailability and bioaccessibility of phenolic compounds of acerola are scarce. For the best of our knowledge, there are no reports in the literature related to the assessment on phenolic content of acerola fruit after gastrointestinal digestion. Bioaccessibility in acerola was previously reported only in frozen pulp, which was compared with other Brazilian fruit pulps. Stafussa et al. [87] found that acerola pulp exhibited remarkably high content of phenolic compounds (13,890.90 mg GAE 100 g⁻¹ dm) and high antioxidant activity by DPPH (727.86 μM Trolox g⁻¹ dm) and DPPH (958.20 μM Trolox g⁻¹ dm) methods, outperforming other phenolic-rich fruit such as açai and jaboticaba. Furthermore, a considerable reduction of phenolic content and antioxidant activity occurred for frozen pulp of all species after *in vitro* digestion in gastric and intestinal stages; bioaccessibility of phenolic compounds in acerola after both phases was 13.74%, while 8.35% of antioxidant activity was bioaccessible after gastrointestinal digestion [87].

Assis et al. [88] assessed seven flavonoids, three phenolic acids and two stilbenes in acerola purees after oral, gastric, and intestinal digestion and found great variations; *cis*-resveratrol (6.79%) and chlorogenic acid (7.18%) presented the lowest bioaccessibility, while rutin (52.24%) and catechin (52.19%) were the most bioaccessible. Additionally, fermentation with probiotic cultures (*Lactobacillus* spp.) increased

the bioaccessibility of all phenolic compounds, except *cis*-resveratrol and kaempferol 3-glucoside.

In acerola juices prepared with frozen pulps diluted in water (1:3, w/v), Fonteles et al. [89] reported a bioaccessibility of 13.3% for phenolic compounds, which was increased with high-temperature short time (22.8%) or ultra-high temperature (22.3%) processing. Acerola by-products (skins and seeds) extracted with water were assessed for phenolic compounds, and presented a bioaccessible fraction of 10.2% [90]. Additionally, the authors found a reduction in bioaccessibility to 4.8% when samples were ultrasonically extracted.

Factors affecting phenolic composition of acerola

Genotype/cultivar

It is very clear that the genotype of acerola plant greatly influences the fruit postharvest quality and chemical composition [16–18, 91]. Likewise, the phenolic composition of acerola fruit is also affected by the choice of cultivar. In the last decade, first studies were accomplished by research groups in different regions of Brazil to investigate genetic influence on the phenolic compounds in edible portion of acerola fruit by the classical Folin-Ciocalteu method [92–94].

‘Flor Branca’, one of the major acerola cultivars produced in the Brazilian Northeast Region due to high production regularity, showed less phenolic content when compared to other acerola varieties [92, 94]. The cultivar ‘Okinawa’ was compared to other varieties in at least three studies, and has been noted for its high content of AsA, but not of phenolic compounds [92, 93, 95].

Studies by Mariano-Nasser et al. [93] and Ferreira et al. [15] assessed the same four acerola cultivars (Apodi, Cereja, Roxinha and Frutacor) and conducted similar results; ‘Cereja’ acerola stood out in terms of phenolic compounds, in addition to its high AsA content, and is a great choice for processing and production of frozen pulp, once its high acidity and low sugar content is not recommended in fruit for fresh consumption.

Recently, the use of HPLC revealed both quantitative and qualitative variations on acerola phenolic composition, depending on the genotype. In seven Brazilian acerola varieties, the sum of phenolic compounds quantified individually ranged between 237.02 mg kg⁻¹ fm (cv. Jaburu) and 845.89 mg kg⁻¹ fm (cv. Roxinha), which represents a difference of almost four times between the varieties with the highest and lowest phenolic concentration [15]. The study also revealed that variation in types of phenolic compounds is genotype-dependent, like the 16 phenolic compounds found in ‘Apodi’ acerolas, in contrast to 11 found in ‘BRS Cabocla’. Furthermore, only five of the 17 studied phenolic compounds were reported in all genotypes.

In the same way, the anthocyanin content is also influenced by the genotype, which reflects in diversity of skin color in acerola cultivars, from dark orange/light-red to dark-purple fruit. Cyanidin content in ‘Flor Branca’ ripe acerolas was 520.76 mg 100 g⁻¹ dm, 262% higher than that found in ‘Jaburu’ in the same study [94]. Besides that, pelargonidin content was 97.04 mg 100 g⁻¹ dm in ‘Flor Branca’, but this anthocyanin was absent in ‘Jaburu’ acerolas.

Fruit maturity stage

Throughout acerola maturity stages, several physical, biochemical, and physiological changes are accomplished in the fruit, visually represented by color shift from light green to final reddish hues, which serve as an indicator of harvest time. Thus, a large increase is observed in the anthocyanin content during acerola ripening, in the same way as observed in most red fruit crops [96]. In acerolas harvested at four maturity stages, cyanidin content was 0.49–1.15 mg 100 g⁻¹ dm in small-green fruit, increasing in big-green (9.47–21.63 mg 100 g⁻¹ dm) and intermediate (44.87–111.84 mg 100 g⁻¹ dm) stages and reaching maximum levels in red-ripe fruit (143.65–520.76 mg 100 g⁻¹ dm) [94].

Nascimento et al. [49] assessed phenolic acids and flavonols in green, intermediate and red acerolas by HPLC–DAD, and reported rutin as major phenolic compound in green (101.8 mg 100 g⁻¹ fm) and ripe (16.57 mg 100 g⁻¹ fm) fruit, in contrast to quercetin (11.27 mg 100 g⁻¹ fm) as the main polyphenol in fruit at intermediate stage.

Most of anthocyanins and flavones, as well as chlorogenic and isochlorogenic acids, one flavanone, one lignan, and one chalcone predominantly accumulated in the red acerola fruit rather than in green unripe ones [55]. Meanwhile, ferulic acid, *n*-coumaric and feruloylglycine were found in higher amounts in unripe fruit than in ripe ones.

Betta et al. [51] determined phenolic composition of acerolas in two red stages, named ripe and fully ripe. Most of the phenolic acids, flavan-3-ols, flavonols, and flavanones assessed individually showed highest concentrations in the ripe stage rather than in fully ripe. A decrease in flavonol content throughout fruit ripening was also related in blueberries, strawberries and cranberries (*Vaccinium macrocarpon* Ait.) [97]. This behavior may be a consequence of the use of phenolics from other classes for biosynthesis of anthocyanins in late ripening stages, like the conversion of flav-2-en-3-ol 3-O-glucoside (a flavonol glycoside) to cyanidin 3-rutinoside as a probable phenomenon in the seed-coat of black soybean (*Phaseolus vulgaris* L.), a cyanidin-rich crop [98].

Extraction methods

Extraction is the first procedure to obtain bioactive compounds from fruit or other parts of plants. Different approaches have been applied to separate phenolic compounds from acerola fruit and by-products [99]. Considering the diversity on structure of phenolic compounds, the extraction method influences directly on the recovery rate of phenolic compounds from fruit samples [5, 100]. The use of different organic solvents such as acetone, ethanol, methanol, and their aqueous solutions affect the extraction efficiency, based on the solubility, polarity, and affinity to the solute. Furthermore, the application of physical forces and thermal treatment may optimize the phenolic extraction [4].

Conventional extraction methods such as maceration and Soxhlet methods have been applied in the extraction of phenolic compounds in fruit crops, for their low cost, high accessibility in most laboratories and satisfactory recovery. However, the high volume of solvents and manual procedures required in conventional methods, as well as the concernment about solvent toxicity and environmental pollution, led to the development of emergent extraction approaches [101, 102].

Emergent unconventional extraction techniques reported in acerola include subcritical water extraction (SWE), enzyme-assisted extraction (EAE) and ultrasound-assisted extraction (UAE), as described below.

SWE is an eco-friendly technique that uses only water in a liquid state at a temperature between 100 and 374 °C, under high pressure. In acerola by-product (seeds and pomace), SWE had a higher extraction efficiency and AOX in fresh and dry samples when compared to Soxhlet method. Additionally, an increase in temperature of SWE from 70 to 130 °C improved the extraction yield, phenolic content, and antioxidant activity [99].

EAE involves the use of cell wall degrading enzymes to weaken cell wall and ensure the extraction of cellular content. In acerola residues, the combination of skin and EAE method using the protease/peptidase enzyme showed the best result of total phenolics when compared to conventional method and seed [103].

UAE method applies ultrasound energy by implosion of cavitation bubbles, resulting in damages to cell wall with increased contact between phenolic compounds and solvents. This process reduces the processing time, energy and solvent consumption [100]. Carvalho Gualberto et al. [48] assessed the combination of extraction methods (UAE and conventional shaking) and solvents (ethanol, methanol and acetone), and found that UAE and acetone were the best conditions for extraction of phenolic compounds in acerola residues. In acerola wastes evaluated by Silva et al. [104], the UAE yielded better results than those obtained with the conventional solid-liquid extraction.

Biological activities and health benefits of phenolic compounds in acerola fruit and by-products

The first study on biological activity of acerola was published in 2005 by Hanamura et al. [105]. These authors isolated three phenolic compounds (cyanidin 3-rhamnoside, pelargonidin 3-rhamnoside and quercetin-3-rhamnoside) from acerola fruit and reported effects of these compounds on in vitro O₂⁻ scavenging activity, as well as an inhibitory effect on diabetes-related molecules (α -glucosidase and advanced glycation end products).

Since then, several health-promoting properties have been attributed to phenolic compounds extracted from acerola. Most of the works published about phenolic compounds in acerola in the 2000s and early 2010s were focused on quantification of antioxidant activity in fruit, juice and frozen pulp by the widely used methods ABTS and DPPH [106–108]. In the last ten years, residues generated as by-products from acerola processing industry, including seeds and residual skin and pulp, began to be investigated as a source of antioxidants for food and nutraceutical applications [109, 110].

Antioxidant activity

In vitro antioxidant activity is the most evaluated biological property attributed to phenolics of acerola fruit and by-products, due to remarkable advances in analytical methods and tools for its quantification during the last few decades. It is known that acerola is rich in various bioactive compounds with antioxidant properties, although phenolic compounds and AsA have the strongest antioxidant capacity [108].

Antioxidants acts in different cellular processes, including direct scavenging of ROS, activation of antioxidant enzymes, metal-chelating activity, increase in levels of α -tocopherol and uric acid, inhibition of NADPH oxidases, mitigation of oxidative stress by NO, and increase in the antioxidant properties of low-molecular-weight antioxidants [32].

Antioxidant potential is variable between different phenolic compounds, depending on substitutions in aromatic rings and arrangements in molecules related to hydrogenation, hydroxylation, methylation, malonylation, sulfation, and glycosylation [31]. The presence of two hydroxyl groups in the ring tends to improve the antioxidant potential of a phenolic compound, since hydrogens and electrons are donated to stabilize free-radicals. C2=C3 double bonds associated with 4-carbonyl groups also increase antioxidant activity by providing planarity, electron expansion,

and displacement between adjacent rings. Conversely, the presence of 3-OH in a phenolic compound tends to suppress its antioxidant action. Furthermore, *O*-glycosylation seems to reduce the free radical scavenger property of a flavonoid when compared to its corresponding aglycone [30, 111].

In vitro antioxidant activity of natural extracts can be determined by a range of assays with different mechanisms of action, whose results may vary between them. The lack of consensus on the most convenient and applicable method reflects the need for multiple assays to consistently determine the antioxidant capacity of a plant material. In acerola fruit and by-products, most used methods are based on the capacity of plant extract to neutralize the organic free radicals 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) (Table 3). These colorimetric assays are widely disseminated in scientific research worldwide due to their low cost, easy operation and good reproducibility when compared to other methods, despite depending on a spectrophotometer [112].

A very high antioxidant activity was observed in green acerola fruit (skin and pulp) assessed by the DPPH assay, in both ethanolic (1,910.87–2,154.93 $\mu\text{M Trolox g}^{-1} \text{ dm}$) [60] and methanolic (95.0–251.0 $\text{mM Trolox kg}^{-1} \text{ fm}$) [113] extracts. Advancement in ripening results in a small reduction in antioxidant activity of acerola, as observed in ripe (1120.4 $\text{mg Trolox g}^{-1} \text{ dm}$) and fully ripe (963.3 $\text{mg Trolox g}^{-1} \text{ dm}$) fruit [51]. Poletto et al. [22] evaluated the composition of by-products generated in the acerola processing of acerola and reported the following DPPH free radical scavenging activity (IC_{50}): 38.17 $\mu\text{g mL}^{-1}$ for bagasse (seed and peel), 6.87 $\mu\text{g mL}^{-1}$ for non-pomace (from the juice clarification step), and 4.24 $\mu\text{g mL}^{-1}$ for juice powder. Additionally, DPPH assay was also adopted for measurement of antioxidant activity of acerola juice prepared with green (67.4 $\mu\text{M Trolox mL}^{-1}$) [54] and ripe (5149.0 mg Trolox L^{-1}) [52] fruit (Table 3).

Results of antioxidant activity in fruit skin and pulp using ABTS assay corroborated with the DPPH method, reflecting the reduction on antioxidant activity during acerola ripening, from 3,628–14,004 $\mu\text{M Trolox } 100 \text{ g}^{-1} \text{ fm}$ in green fruit, to 4,104–4,617 and 3,293–4,236 $\mu\text{M Trolox } 100 \text{ g}^{-1} \text{ fm}$ in intermediate and ripe stages, respectively [94]. In agro-industrial residues of acerola composed of seeds, the antioxidant activity showed oscillations depending on the solvent and extraction method, ranging from 5,556.22 $\mu\text{M Trolox } 100 \text{ g}^{-1} \text{ dm}$ (using methanol and ultrasonic bath) and 25,493.45 $\mu\text{M Trolox } 100 \text{ g}^{-1} \text{ dm}$ (using acetone and shaker) [48]. In addition, the antioxidant activity of a water extract of acerola juice prepared with ripe fruit was also reported in the literature (21.4 mM Trolox) [52] (Table 3).

The Ferric Reducing Antioxidant Power (FRAP) is other colorimetric method that has also been considered

for determining the antioxidant capacity of acerola [15, 51, 53, 60]. FRAP is a single electron transfer method based on the measurement of the reduction in the colorless complex of ferric iron and tripyridyltriazine (TPTZ) (Fe^{3+} -TPTZ) to the intensely blue ferrous complex (Fe^{2+} -TPTZ) by the plant extract containing antioxidants [114].

Ethanolic and methanolic extracts of ripe acerola evaluated by the FRAP assay presented antioxidant activity of 29.3–53.5 $\text{mM Fe}^{2+} 100 \text{ g}^{-1} \text{ fm}$ [15] and 2.2 $\text{mM Fe}^{2+} 100 \text{ g}^{-1} \text{ fm}$ [53], respectively. Antioxidant capacity of acerola seeds showed a variation between 17,105.57 and 86,045.58 $\mu\text{M ferrous sulfate } 100 \text{ g}^{-1} \text{ dm}$ by the FRAP assay, depending on the extraction method and solvent [48] (Table 3).

The Oxygen Radical Absorbance Capacity (ORAC) assay was also adopted in previous reports for determination of antioxidant capacity in acerola [22, 60, 113]. ORAC is based on the ability of the radical chain reaction by antioxidants through monitoring the inhibition of peroxy radical-induced oxidation [114]. ORAC method showed a slight reduction in antioxidant activity of fruit (skin and pulp) from green (43.5–79.0 $\mu\text{M Trolox kg}^{-1} \text{ fm}$) to intermediate (36.5–62.0 $\mu\text{M Trolox kg}^{-1} \text{ fm}$) and ripe (36.2–53.0 $\mu\text{M Trolox kg}^{-1} \text{ fm}$) stages. In addition, Poletto et al. [22] used ORAC assay for determining antioxidant capacity (IC_{50}) of by-products generated in the acerola processing, and reported 2.13 $\mu\text{g mL}^{-1}$ for non-pomace from the juice clarification step, 7.86 $\mu\text{g mL}^{-1}$ for bagasse, and 2.44 $\mu\text{g mL}^{-1}$ for juice powder (Table 3).

Antibacterial activity

Acerola bagasse flour was tested against the microorganisms *Listeria monocytogenes* ATCC 19117, *Escherichia coli* ATCC 11229, *Pseudomonas aeruginosa* ATCC 15442, and *Salmonella choleraesuis* ATCC 6539 [115].

Staphylococcus aureus was inhibited by contact with acerola puree extract [minimum inhibitory concentration (MIC) = 6.25 mg mL^{-1}], which was attributed to the high content of anthocyanins, especially pelargonidin, and rhamnosides of cyanidin and pelargonidin [87]. Phenolic compounds extracted from different portions of acerola fruit were tested against *S. aureus* by Delva and Goodrich-Schneider [113]. The antimicrobial activity of flavonoids from the edible fraction (skin and pulp) was clear in green fruit and moderate in red fruit, while the non-edible fraction (seeds) had a clear activity against *S. aureus*. Additionally, phenolic acids from seeds also showed moderate antimicrobial activity.

In several plant species, the antimicrobial activity has been attributed to their secondary metabolites, including phenolic compounds and alkaloids [116].

Table 3 Antioxidant activity measured by different assays (DPPH, ABTS, FRAP and ORAC) in acerola fruit and by-products

| Method | Contents | Fruit fraction | Maturity stage | Extraction solvent | References |
|---|--|---|----------------|--------------------|------------|
| DPPH | 1,910.87–2,154.93 μM Trolox g^{-1} dm | Skin and pulp | Green | Ethanol | [60] |
| | 38.33 μg fm g^{-1} DPPH (IC_{50}) | Skin and pulp | Green | Methanol | [49] |
| | 95.0–251.0 mM Trolox kg^{-1} fm | Skin and pulp | Green | Methanol | [113] |
| | 54.7–142.0 mM Trolox kg^{-1} fm | Skin and pulp | Intermediate | Methanol | [113] |
| | 39.57 μg fm g^{-1} DPPH (IC_{50}) | Skin and pulp | Intermediate | Methanol | [49] |
| | 1120.4 mg Trolox g^{-1} dm | Skin and pulp | Ripe | Methanol/acetone | [51] |
| | 138.1–200.0 mM Trolox kg^{-1} fm | Skin and pulp | Ripe | Ethanol | [15] |
| | 3,276.67–7,738.03 g fm g^{-1} DPPH (IC_{50}) | Skin and pulp | Ripe | Methanol/acetone | [95] |
| | 40.4–101.0 mM Trolox kg^{-1} fm | Skin and pulp | Ripe | Methanol | [113] |
| | 46.20 μg fm g^{-1} DPPH (IC_{50}) | Skin and pulp | Ripe | Methanol | [49] |
| | 40.0 μg fm g^{-1} DPPH (IC_{50}) | Skin and pulp | Ripe | Methanol | [53] |
| | 963.3 mg Trolox g^{-1} dm | Skin and pulp | Fully ripe | Methanol/acetone | [51] |
| | 2,226.24–2,305.27 μM Trolox 100 g^{-1} dm | Seed | – | Ethanol | [48] |
| | 2,221.39–2,305.83 μM Trolox 100 g^{-1} dm | Seed | – | Methanol | [48] |
| | 2,214.16–2,242.86 μM Trolox 100 g^{-1} dm | Seed | – | Acetone | [48] |
| | 67.4 μM Trolox mL^{-1} | Juice | Green | Water | [54] |
| | 5149.0 mg Trolox L^{-1} | Juice | Ripe | Not mentioned | [52] |
| | 88–299 μM Trolox g^{-1} | Non-pomace | Green | Water | [54] |
| | 6.87 μg mL^{-1} (IC_{50}) | Non-pomace (pressure) | Green | Ethanol | [22] |
| | 38.17 μg mL^{-1} (IC_{50}) | Bagasse (seed and peel) | Green | Ethanol | [22] |
| 4.24 μg mL^{-1} (IC_{50}) | Juice powder | Green | Ethanol | [22] | |
| ABTS | 7,475.86–8,613.54 μM Trolox g^{-1} dm | Skin and pulp | Green | Ethanol | [60] |
| | 3,628–14,004 μM Trolox 100 g^{-1} fm | Skin and pulp | Green | Methanol/acetone | [94] |
| | 4,104–4,617 μM Trolox 100 g^{-1} fm | Skin and pulp | Intermediate | Methanol/acetone | [94] |
| | 3,293–4,236 μM Trolox 100 g^{-1} fm | Skin and pulp | Ripe | Methanol/acetone | [94] |
| | 2.72–5.84 μM Trolox g^{-1} fm | Skin and pulp | Ripe | Methanol/acetone | [95] |
| | 135.7–208.3 mM Trolox kg^{-1} fm | Skin and pulp | Ripe | Ethanol | [15] |
| | 5,556.22–12,055.18 μM Trolox 100 g^{-1} dm | Seed | – | Ethanol | [48] |
| | 7,943.29–16,752.68 μM Trolox 100 g^{-1} dm | Seed | – | Methanol | [48] |
| | 14,404.44–25,493.45 μM Trolox 100 g^{-1} dm | Seed | – | Acetone | [48] |
| | 21.4 mM Trolox | Juice | Ripe | Not mentioned | [52] |
| | 204–380 μM Trolox g^{-1} | Non-pomace | Green | Water | [54] |
| | FRAP | 824.23–1,447.97 μM Trolox g^{-1} dm | Skin and pulp | Green | Ethanol |
| 29.3–53.5 mM Fe^{2+} 100 g^{-1} fm | | Skin and pulp | Ripe | Ethanol | [15] |
| 501.8 μM Trolox g^{-1} dm | | Skin and pulp | Ripe | Methanol/acetone | [51] |
| 2.2 mM Fe^{2+} 100 g^{-1} fm | | Skin and pulp | Ripe | Methanol | [53] |
| 338.3 μM Trolox g^{-1} dm | | Skin and pulp | Fully ripe | Methanol/acetone | [51] |
| 23,789.66–86,045.58 μM FS 100 g^{-1} dm | | Seed | – | Ethanol | [48] |
| 17,105.57–64,941.90 μM FS 100 g^{-1} dm | | Seed | – | Methanol | [48] |
| 33,480.00–57,171.28 μM FS 100 g^{-1} dm | | Seed | – | Acetone | [48] |
| ORAC | 1,950.10–2,454.42 μM Trolox g^{-1} dm | Skin and pulp | Green | Ethanol | [60] |
| | 43.5–79.0 μM Trolox kg^{-1} fm | Skin and pulp | Green | Methanol | [113] |
| | 36.5–62.0 μM Trolox kg^{-1} fm | Skin and pulp | Intermediate | Methanol | [113] |
| | 36.2–53.0 μM Trolox kg^{-1} fm | Skin and pulp | Ripe | Methanol | [113] |
| | 2.13 μg mL^{-1} (IC_{50}) | Non-pomace (pressure) | Green | Ethanol | [22] |
| | 7.86 μg mL^{-1} (IC_{50}) | Bagasse (seed and peel) | Green | Ethanol | [22] |
| 2.44 μg mL^{-1} (IC_{50}) | Juice powder | Green | Ethanol | [22] | |

FS ferrous sulfate

Antihyperglycemic, antihyperlipidemic, anti-inflammatory and hepatoprotective activities

A methanolic extract of bagasse flour from acerola agro-industrial residue containing phenolic compounds (gallic acid, catechin, epicatechin gallate, epicatechin, siringic acid, *p*-cumaric acid and quercetin) was able to inhibit *in vitro* digestive enzymes α -amylase and α -glucosidase, and can help in the treatment of obesity, associated comorbidities and type 2 diabetes [117].

In a study by Dias et al. [118], the effect of acerola juice intake was investigated in mice with cafeteria diet-induced obesity. The results showed that acerola juice prevents weight gain (based on body weight and adiposity) and dyslipidemia (based on triglycerides), and restores inflammation to a normal range, which was attributed by the authors to the presence of phenolic compounds in the juice.

Phenolic-rich lyophilized extract of acerola bagasse was tested against the toxic action of carbon tetrachloride (CCl_4) in Wistar rats by Marques et al. [59]. According to the results, there was a decrease in the activity of aspartate aminotransferase, alanine aminotransferase and gamma glutamyl transferase, and an increase in superoxide dismutase, total antioxidant capacity and albumin content in relation to control treatment, confirming the hepatoprotective action of acerola extract.

Applications of phenolic compounds from acerola in food and pharmaceutical industries

In tropical regions such as Brazil, several native and exotic unknown or underexploited fruit species present high potential for use in the agroindustry, including acerola [41]. Acerola is a fruit with intense metabolism, characterized by very high respiration rate and ethylene-mediated molecular, biochemical and physiological changes, resulting in a high perishability and fragility after harvest [119]. Thus, the fruit processing is key to reduce acerola postharvest losses.

Fresh consumption of acerola is actually restricted to some varieties selected for high fruit sweetness and low acidity, as well as to regions close to the production area. In order to overcome limitations due to short fruit postharvest life, acerolas have been processed in several products (Fig. 4), including frozen pulp, juice, marmalade, frozen concentrate, jam, and liquor [20].

The production of frozen fruit puree is the main destination for ripe acerolas (Fig. 4). Previous studies confirmed the high amounts of phenolic compounds in acerola frozen purees, which presented the highest antioxidant activity ($\text{DPPH} = 7433.37 \mu\text{mol Trolox}/100 \text{ g fm}$ and $\text{ABTS} = 8511.84 \mu\text{mol Trolox}/100 \text{ g fm}$) among the 44 fruit pulps evaluated [42]. The processing of frozen fruit is promising in acerola industries, which enables its global distribution to consumers interested in phenolic-rich products. In recent years, the consumption of acerola frozen pulp acerola has increased in Japan, United States, and Europe [20].

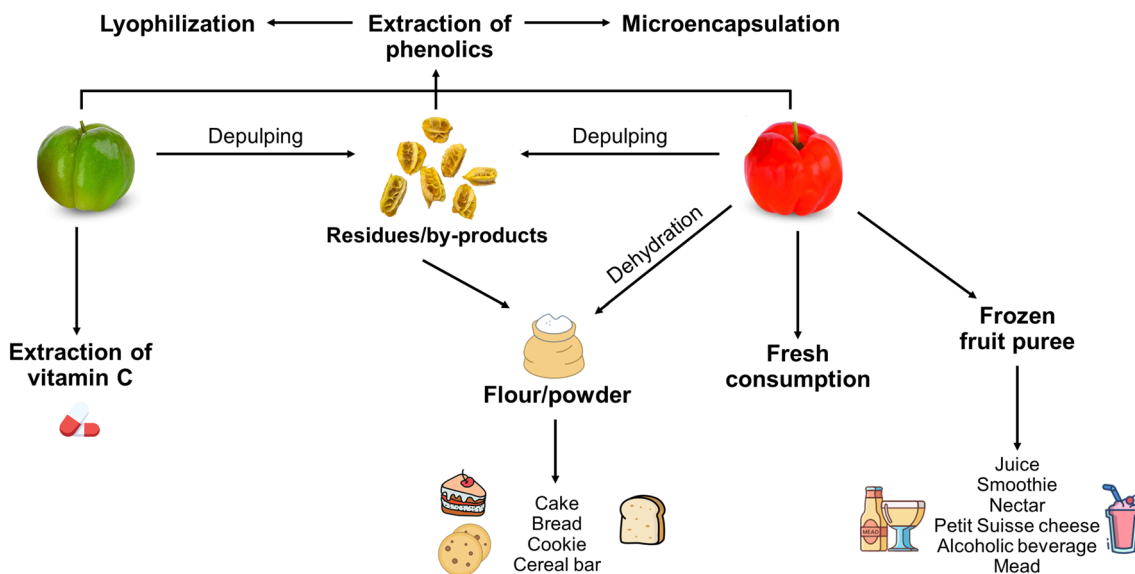


Fig. 4 Illustrative representation of potential technological processing of acerola fruit and its residue

In addition to being an alternative to reduce fruit post-harvest losses, the acerola frozen purees are versatile for the preparation of phenolic-rich products, including juices [52], smoothies [120], nectars [121], Petit Suisse cheese [122], alcoholic beverages [123], and meads [124]. Acerola is widely consumed worldwide as juice, prepared with acerola fruit [54] or in blends with other tropical fruit [125, 126]. A high diversity of phenolic compounds has been reported in acerola juices, including phenolic acids, flavan-3-ols, flavonols, and flavones, as well as resveratrol (stilbene) [52].

In recent years, some approaches have been proposed to stabilize phenolic compounds and other antioxidant compounds such as ascorbic acid and carotenoids in acerola pulps and juices, which are highly susceptible to degradation when exposed to light, moisture, heat, and oxygen. Microencapsulation is a technique that has shown positive effects in conservation phenolic compounds in acerola, using maltodextrin and gum Arabic as encapsulating agents, and dried by spray and freeze-drying [126, 127]. This technology successfully preserved bioactive compounds and antioxidant activity in acerola pulp for a period of at least 180 days [128], which demonstrates its high potential for application in functional and nutraceutical foods.

The industrial extraction of vitamin C from green unripe fruit represents an important portion of the global acerola market. With contents that can exceed 4,000 mg/100 g, green acerolas have high potential for the production of extracts, supplements, and concentrated powders of vitamin C for use in food and pharmaceutical purposes. In addition to the high ascorbic acid content, green acerolas contain several phenolic compounds, such as flavonols, flavan-3-ols, isoflavones, phenolic acids, stilbenes, and lignans [49, 55, 60]. Together, these bioactive compounds make acerola an excellent alternative for dietary supplementation and development of new functional foods. For this, processes such as microencapsulation and lyophilization can be applied to extracts of unripe acerola fruit, in order to increase the stability of these compounds, which are suitable as an antioxidant ingredient in food emulsions [8].

Acerola-based products manufacturing results in the discarding of fruit skin and seeds, constituting a residue. These fractions (also named by-products) represent between 10 and 60% of total fruit weight [91] and concentrate high levels of phenolic compounds [54, 99], suggesting their potential use in the food and pharmaceutical industries. Recent researches have focused on potential technological processes that affect phenolic composition of acerola residues, adding value to these by-products. The industrial application of acerola

residuals is an important alternative to reduce both environmental impacts and production costs [129].

The processing of acerola by-products into flour and powder results in a product with several antioxidant compounds, destined for nutritional enrichment of cakes, breads, cookies, and cereal bars [115, 130]. Some characteristics found in the flour produced from acerola residues, such as high content of dietary fibers, emulsion stability, and water and oil absorption capacity, make it ideal for incorporation into meat and bakery products [131].

The extraction of phenolic compounds from acerola by-products for use as active compounds in edible coatings is emerging in postharvest researches focusing on fruit conservation. A chitosan solution containing phenolic compounds extracted from acerola by-products was applied on guavas, being able to delay fruit ripening, preserving firmness and maintaining green color [132].

Extracts of acerola flour demonstrated high potential for several biotechnological applications, especially in the cosmetic industry, due to the presence of triterpene saponins with good surface activity and emulsifying capacity [133]. Furthermore, extracts of acerola fruit reduced the cellular melanin level and inhibited tyrosinase activity, suggesting a potential as a component in skin-whitening cosmetics [134].

Conclusions and future perspectives

Scientific evidences suggest that the acerola is a promising superfruit with great potential in the food and pharmaceutical industries. At least 76 phenolic compounds were identified using high performance liquid chromatography in acerolas, including 55 flavonoids (anthocyanins, flavan-3-ols, flavonols, flavones, flavanones, isoflavones and chalcones) and 21 non-flavonoids (phenolic acids, stilbenes and lignans).

Phenolic compounds in acerola show several biological properties, including antioxidant, antibacterial, antihyperglycemic, antihyperlipidemic, anti-inflammatory, and hepatoprotective activities. However, studies are further required to assess the seasonal and genotypic influence on the phenolics of acerola and their bioaccessibility.

Acerola is an anthocyanin-rich fruit with high potential for pigment extraction, but stabilization of anthocyanins in juice and pulp should be further elucidated and improved.

Author contributions JCV had the idea and formulated review goals and aims for the article. JCV, LFdS and TdSR performed the literature search and wrote the paper. STdF and CMV supervised and critically revised the work.

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Declarations

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