

Phenolic composition and extraction methods of Brazilian fruits: jabuticaba (*Plinia* spp.), açai (*Euterpe oleraceae* Mart.), jussara (*Euterpe edulis* Mart.) and cocoa (*Theobroma cacao* L.)

Composição fenólica e métodos de extração de frutos brasileiros: jabuticaba (*Plinia* spp.), açai (*Euterpe oleraceae* Mart.), jussara (*Euterpe edulis* Mart.) e cacau (*Theobroma cacao* L.)

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Nathália de Andrade Neves

ORCID: <https://orcid.org/0000-0001-6936-2171>

Universidade Federal dos Vales do Jequitinhonha e Mucuri, Brazil

E-mail: nathalia.neves@ict.ufvjm.edu.br

Maria Emília Rodrigues Valente

ORCID: <https://orcid.org/0000-0001-8824-4656>

Universidade Federal do Espírito Santo, Brazil

E-mail: maria.valente@ufes.br

Isadora Ferreira da Silva

ORCID: <https://orcid.org/0000-0003-2575-2113>

Universidade Federal de Viçosa, Brazil

E-mail: isadoraferreira85@gmail.com

Abstract

Brazil is well known for its great botanic diversity. The native fruits species of jabuticaba (*Plinia* spp.) açai (*Euterpe oleraceae* Mart.), jussara (*Euterpe edulis* Mart.), and cocoa (*Theobroma cacao* L.) stand out because of their high antioxidant capacity and diverse phenolic composition, which are the subject of several studies aiming for the extraction of phenolic fractions for their characterization and applicability. This review aimed to discuss the main phenolics identified in these four plant species, and an overview of the most recent methods of phenolic compounds extraction from these species. This work can contribute to future research projects, helping researchers to reach efficient methods of extraction.

Keywords: Deep eutectic solvent; Pulsed electric field; Supercritical fluid extraction; Ultrasound.

Resumo

O Brasil é conhecido por sua grande diversidade botânica. As espécies frutíferas nativas: jabuticaba (*Plinia* spp.) açai (*Euterpe oleraceae* Mart.), jussara (*Euterpe edulis* Mart.), and cacau (*Theobroma cacao* L.) destacam-se por sua alta capacidade antioxidante e composição fenólica diversificada, que são alvo de vários estudos visando a extração de frações fenólicas para sua caracterização e aplicabilidade. Esta revisão teve como objetivo discutir os principais fenólicos identificados nestas quatro espécies vegetais, e uma visão geral dos métodos mais recentes de extração de compostos fenólicos dessas espécies. Este trabalho pode contribuir para futuros projetos de pesquisa, auxiliando pesquisadores a alcançar métodos eficientes de extração.

Palavras-chave: Campo elétrico pulsado; Extração por fluido supercrítico; Solventes eutéticos; Ultrassom.

Resumen

El Brasil es conocido por presentar gran diversidad botánica. Las especies frutales nativas de jabuticaba (*Plinia* spp.), açai (*Euterpe oleraceae* Mart.), jussara (*Euterpe edulis* Mart.) y cacao (*Theobroma cacao* L.) se destacan por su alta capacidad antioxidante y diversa composición fenólica, que son objeto de varios estudios con el objetivo de la extracción de fracciones fenólicas para su caracterización y aplicabilidad. Esta revisión tuvo como objetivo discutir los principales fenoles identificados en estas cuatro especies de plantas y una descripción general de los métodos más recientes de extracción de compuestos fenólicos de estas especies. Este trabajo puede contribuir a futuros proyectos de investigación, ayudando a los investigadores a alcanzar métodos eficientes de extracción.

Palabras clave: Campo eléctrico pulsado; Disolvente eutético; Extracción con fluido supercrítico; Ultrasonido.

1. Introduction

Brazil has a total area of 8,514,876 Km² with a great diversity of climates, including regions with humid equatorial, dry tropical, humid tropical and humid subtropical. This variety in different climates leads to a great botanical diversity. Brazil is divided into 6 main biomes, with 46975 catalogued species of native plants, algae and fungi, of which 55% are endemic, only found in this country. The biomes are Amazon (with 13056 catalogued species), Caatinga (4963), Atlantic Forest (17150), Pantanal (1682), Pampa (2817) and Cerrado (12829) (*Flora do Brasil 2020*, 2021; Mariano et al., 2021).

Considering its biodiversity, it is not surprising that Brazil also presents native species rich in antioxidants, such as jaboticaba (*Plinia* spp.), açai (*Euterpe oleracea* Mart.), jussara (*Euterpe edulis* Mart.) and cocoa (*Theobroma cacao* L.).

The jaboticaba is a tree belonging to the *Myrtaceae* family mainly occurring in the Atlantic Forest. Among the nine species of jaboticaba, *Plinia cauliflora* (Mart.) Kausel, known as “jaboticaba paulista” and *Plinia jaboticaba* (Vell.) Kausel, known as “jaboticaba sabará” are the two mostly studied (Citadin et al., 2010). The trees are 10–15 m tall with single leaves and the leaves are simple and up to 7 cm long. They bloom in the spring and summer, producing copious fruit. The flowers and fruit grow in clusters along the trunk and branches. Its small fruits with black bark and white flesh adhere to the seeds (Gasparotto Junior et al., 2019). The pulp is sweet and slightly acid. The harvest period occurs once a year (between November and December) and lasts approximately one week. After harvest, they must be consumed in a short time because they perish quickly due to the high sugar and water content (Neves et al., 2021).

The *Euterpe* genus has about 28 species in Central and South America. The three species that occur most frequently are *E. oleracea*, *E. precatoria* and *E. edulis* (Yamaguchi et al., 2015). The fruits of the palms of the *Euterpe* genus, especially the *E. oleracea* species, popularly known as açai, and *E. edulis*, known as juçara, have a high content of the bioactive compounds anthocyanins and un-saturated fatty acids, such as oleic acid (Liz et al., 2020). The first one is native to the Amazonia biome and the second, to the Atlantic Forest regions (Baptista et al., 2021). The fruits of these palm trees are berries that cannot be consumed as fresh fruit. They require processing with the addition of water by mechanical extraction so the pulp can be removed (Baptista et al., 2021).

The *E. oleracea* is a multicaule palm, with up to 25 stems per clump. The trunks in adults have heights ranging between 3 m and 20 m and a diameter of 7 cm to 18 cm. Each stem holds, at its end, a set of 8–14 compounds, pinnate leaves, and spiral arrangement with 40–80 pairs of leaflets, opposite or sub-opposite. The inflorescence of this açai is leaf below, protected from the sun. In the first two-thirds of each rachilla, flowers are arranged in triads, with each female flower flanked by two male flowers. In the third terminal of rachilles, usually only the male flowers lie. The fruit ripening is complete in about 175 days, presenting a violet color and diameter of about 13.5 mm (Yamaguchi et al., 2015).

The species *E. edulis* Mart. is a non-stoloniferous palm with a straight, cylindrical, and slender root, sometimes exceeding 15 centimeters in diameter, and mainly found between 10 and 20 meters of height in forests. It has alternate and pinnate leaves of about 2 to 2.5 meters long and green sheaths forming a crown at the apex of the stem by the imbrication of the sheaths, where the palm heart is found, which is its main product (Borges et al., 2013; Favreto, 2010). The rachis inflorescence is approximately 70 centimeters in length; the bunches weigh about 3 kg and contain thousands of globular-shaped fruits with that weight of about 1 gram, 90% of which corresponds to the seed. When the fruit is ripe, they present a dark purple color similar to the fruits of *Euterpe oleracea* Mart. and *Euterpe precatoria* Mart. (Garcia et al., 2019; Schulz et al., 2017). The ripe *E. edulis* fruits have a sweeter flavor, are consumed as juice and pulp, and also can be used as an ingredient in many foods (Felzenszwalb et al., 2013).

Cocoa (*Theobroma cacao*) belongs to the genus *Theobroma* and is classified in the *Sterculioidea* subfamily of the *Malvaceae* family. There are 22 known species assigned to the genus *Theobroma*, of which 21 are cultivated in Brazil. *Theobroma cacao* is native to the Amazon Basin. It is the only species widely cultivated outside its native region, presenting

great economic importance. *Theobroma cacao* is generally a small tree (4 to 8 meters tall), although it can reach up to 10 meters when shaded in forests. The stalk is straight, and the fruits are usually 15 to 25 in length. The ripe fruit consists of a thick skin that contains between 30 and 50 seeds surrounded by a mucilaginous pulp. The main varieties of *T. cacao* are Forastero, Crioulo, Trinitario, which is a hybrid of Forastero and Criollo. There is another variety cultivated in Ecuador, named Nacional (Afoakwa, 2016).

The phenolic compounds are a large group of compounds formed from the secondary metabolism of plants. Molecularly, they are formed by an aromatic ring bearing one or more hydroxyl groups and can be a simple or polymerized molecule (Albuquerque et al., 2021; Lima et al., 2019). These group of molecules are one of the most studied classes of bioactive compounds and they are well-reported health benefits, because they are considered antioxidants due to the donation of hydrogen atom and/or electron to free radicals, causing the break of chain reaction of oxidation (Albuquerque et al., 2021).

There are several studies on the extraction of phenolic compounds from vegetable raw materials. It is important to characterize them, to use them in food or cosmetic formulations or even in biological tests, where the antioxidant capacity of extracts is tested for the prevention and treatment of diseases or in special diets. In this way, the description of the phenolic composition of the four Brazilian fruits discussed, as well as possible forms of extraction, can serve as a tool for future research projects that aim to use these phenolic compounds for different purposes. Regarding these four species of Brazilian botany, this review will address the phenolic composition of these four fruits, as well as the current methods of extracting phenolics used.

2. Phenolic Compounds

The phenolic compounds are a big class of compounds with more than 8000 identified structures reported (Tungmunnithum et al., 2018). Based on their structural characteristics, the phenolic compounds are divided into several groups, of which the main ones are: phenolic acids, flavonoids and non-flavonoids (Lima et al., 2019).

The non-flavonoids class include phenolic acids, stilbenes and hydrolysable tannins (gallotannins, ellagitannins and phlorotannins) (Ziauddeen et al., 2019).

The phenolic acids is a class of compounds formed by the substitution of hydrogen atoms on benzene rings by a carboxylic acid groups and at least one hydroxyl (Chen et al., 2020). They are considered important constituents of food, contributing to taste, colour and nutritional properties (Bento-Silva et al., 2020). This group is mainly divided into two sub-groups: hydroxybenzoic and hydroxycinnamic acids (Kumar & Goel, 2019). Hydroxycinnamic acids are synthesized in plants from phenylalanine via cinnamic acid or directly from tyrosine by tyrosine ammonia-lyase, producing the simplest hydroxycinnamic acid, p-coumaric acid, which can be further synthesized into caffeic, ferulic and sinapic acids. Meantime the four most common hydroxybenzoic acids are p-hydroxybenzoic, protocatechuic, vanillic and syringic acids (Bento-Silva et al., 2020; Kumar & Goel, 2019).

Flavonoids are the low molecular weight compound bioactive polyphenols which play an essential role in photosynthesizing cells (Karak, 2019). Responsible for the color, flavor and pharmacological activities in plants, they are known for their antioxidant, anti-inflammatory, antiallergic, anticancer, antiviral and antifungal properties (Karak, 2019; Kopustinskiene et al., 2020). The structure of flavonoids is composed of two benzene rings which are linked by a heterocyclic ring containing oxygen. They can be divided into different subclasses depending on the connection between the rings B and C. The subclasses include: flavonols, flavanones, flavones, isoflavones, flavonols and anthocyanidins (Maleki et al., . The flavonol include compounds like kaempferol, quercetin and myricetin. Rutin and luteolin are examples of flavones, taxifolin and hesperidin are flavonones, catechin and epicatechin are include in flavanol groups, cyanidin, delphinidin, pelargonidin and malvidin are anthocyanidins and genistein and daidzein are isoflavones examples (Karak, 2019).

Reactive oxygen species are very unstable, and react rapidly with other substances, including DNA, membrane lipids and proteins, resulting in health disorders such as diabetes mellitus, hypertension, cancer, neurodegenerative, gastric ulcers, and arthritis with increasing incidents worldwide. In this respect, the consumption of antioxidant compounds has been positively related to a reduction in the risk of developing these chronic diseases (Dibanda et al., . Antioxidants can be defined as a substance that, when present at a low concentration compared with that of an oxidizable substrate in the medium, inhibits oxidation of the substrate (Halliwell & Gutteridge, 2007 apud Granato et al., 2018). The antioxidant activity in a phenolic compound depends on the number and position of the hydroxyl groups

The antioxidant capacity of phenolic compounds is influenced by the chemical structure, which is mainly based on the ability of the phenolic ring to stabilize and delocalize unpaired electrons. This is influenced by the position and number of hydroxyl groups in the structure of phenolic compounds. In general, the antioxidant capacity is proportional to the number of hydroxyl substituents; therefore, the flavonoids have a greater antioxidant capacity when compared to other phenolic compounds (Neves et al., 2021). For instance, anthocyanins appear to be better antioxidants than other phenolic compounds, because of the presence of hydroxyl groups in ring B (Pojer et al., 2013).

3. Identification Methods

Among the various forms of separation and identification of phenolic compounds in plants, chromatographic methods are the most used. High performance liquid chromatography (HPLC) or Ultra-high performance liquid chromatography (UHPLC) are widely used for the separation of molecules. As phenolic compounds are water soluble, reversed-phase chromatography and silica-bonded C18 columns are widely used to separate this class of compounds. HPLC shows a number of advantages, for instance, it is suited for the separation of a wide range of chemicals in a great diversity of food matrices, allows analysis of thermally unstable compounds, possesses high robustness, precision, reproducibility and sensitivity (Silveira & Godoy, 2019). In addition to the chromatographic process, detection and identification of the molecules are done by methods such diode array detector (DAD) and mass spectrometry (MS) (Haminiuk et al., 2012). Besides LC-MS, Nuclear magnetic resonance spectroscopy (NMR) can also be used due to being another technique that allows unequivocal information on phenolics (Costa et al., 2015).

The diode array detector (DAD) is a wavelength detector enables simultaneous acquisition across a range of wavelengths, rather than just single one. Associated with a chromatographic tool, it can be used to perform an assessment of spectral peak purity mathematically and possible identification. Recently, DAD, through improvements such as enlarged UV–vis range, increased resolution and sensitivity, has become more informative and is a viable alternative for analytes identification. Because of the high wavelength resolution, wavelength accuracy and sensitivity, spectra measured with DAD are highly reproducible (Pragst et al., 2004; Stoev & Stoyanov, 2007).

The mass spectrometry (MS) is an analytical technique that measure the molecules masses of individual compounds and atoms precisely by converting them into charged ions (Dass, 2007). It is a very useful tool for allowing, through molecular and fragments mass, the identification of compounds. The technology of MS can be divided into three processes: ion generation, ion separation and ion detection (Seger et al., 2013). There is a variety of different ionization, mass analyzing, and detection methods. While ionization methods determine the classes of substances available for measurement, it is a combination of the mass analyzer with the detector that ultimately determines the quality and reliability of analysis. Depending on the physics of mass analysis, analyzers could belong to quadrupole, magnetic sector, ion trap, time-of-flight (TOF), or Fourier transform (FT) generic types. They could be further combined to allow analysis of both analytes and their fragments (MS/MS) (Zubarev & Makarov, 2013).

4. Phenolic Composition of Fruits

Polyphenols are one of the most abundant and widespread groups of naturally occurring substances in the plant kingdom, originating from the secondary metabolism of plants (Urbańska et al., 2019).

Jaboticaba has drawn the attention of research studies due to its phenolic composition, and therefore is the subject of several studies both with the characterization of its phenolic composition and studies involving biological assays on its antioxidant effect (Alejandro et al., 2013; Neves et al., 2021; Gurak et al., 2014; Neves et al., 2018; Pimenta Inada et al., 2020; Santos et al., 2010; Urbańska et al., 2019; Wu et al., 2012).

Regarding its phenolic composition, studies reported the presence of ellagitannins, galotannins, flavonols and anthocyanins, as shown in Table 1. The flavonols derived from quercetin, myricetin, ellagic acid and methylellagic acid are the main ones found in jaboticaba (Neves et al., 2018). The anthocyanins identified in jaboticaba species were delphinidin-3-glucoside, cyanidin-3-glucoside, pelargonidin-3-glucoside, peonidin-3-glucoside and cyanidin-3-coumaroylglucoside. From these anthocyanins Delphinidin-3-glucoside and cyanidin-3-glucoside are found mostly (Alejandro et al., 2013; Alejandro et al., 2013; Neves et al., 2021; Gurak et al., 2014; Neves et al., 2018; Santos et al., 2010). The species *P. jaboticaba* had the highest concentration of anthocyanins in its peels, whereas *P. phitrantha*, a white jaboticaba species, had the highest content of total phenolic compounds (Neves et al., 2021).

Table 1. Phenolic compounds identified on jaboticaba (*Plinia* spp).

Compound	Analised Sample	Identification method	References
Gallic acid	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS HPLC-DAD-MS-Q	Quatrin et al. (2019) Pimenta Inada et al. (2020)
	Pells and seeds of <i>M. jaboticaba</i>	HPLC-DAD-ESI-MS ⁿ	
Monogalloyl glucose	Pells, pulp and seeds of <i>Plinia</i> spp.		Neves et al. (2021)
	Pells powder of <i>Myrciaria trunciflora</i>	LC-TRAP-MS/MS	
Trisgalloyl HHDP glucose	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019) Plaza et al. (2016)
	<i>M. jaboticaba</i> pells	HPLC-DAD-ECD-CAD	
3-O-Galloylquinic acid	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. 2019
Bis-HHDP-galloylglucose (Casuarinin)	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. 2019 Plaza et al, 2016
	<i>M. jaboticaba</i> pells	HPLC-DAD-ECD-CAD	
Bis-HHDP-galloylglucose (Casuarictin)	<i>M. jaboticaba</i> pells	HPLC-DAD-ECD-CAD	Plaza et al, 2016(Plaza et al., 2016)
	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	
Trigalloylglucose	<i>M. jaboticaba</i> pells	HPLC-DAD-ECD-CAD	Quatrin et al. (2019) Plaza et al, (2016)
	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	
HHDP-digalloylglucose (Tellimagrandin I)	<i>M. jaboticaba</i> pells	HPLC-DAD_ECD-CAD	Quatrin et al. (2019) Plaza et al, (2016)
	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	
Tetragalloylglucose	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
Galloyl-castalagin	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
Pentagalloylglucose	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
HHDP-galloylglucose	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019) Pimenta Inada et al. (2020) Plaza et al. (2016)
	Pells and seeds of <i>M. jaboticaba</i>	HPLC-DAD-MS-Q	
Bis-HHDP-glucose (Casuarin)	<i>M. jaboticaba</i> pells	HPLC-DAD-ECD-CAD	Plaza et al. (2016)
	Pells powder of <i>M. trunciflora</i> and <i>M. jaboticaba</i>	LC-TRAP-MS/MS	
	<i>M. jaboticaba</i> pells	HPLC-DAD-ECD-CAD	Quatrin et al. (2019) Plaza et al. (2016)

Bis-HHDP-glucose (Pedunculagin)	<i>M. jaboricaba</i> pells	HPLC-DAD-ECD-CAD	Plaza et al. (2016)
Di-HHDP-galloyl-glucosec	Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-MS-Q	Pimenta Inada et al. (2020)
Castalin	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
Castalagin/Vescalagina	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS HPLC-DAD-MS-Q	Quatrin et al. (2019) Pimena Inada et al. (2020)
	Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2021)
Ellagic acid pentoside	Pells, pulp and seeds of <i>Plinia</i> spp	HPLC-DAD-ESI-MS ⁿ	Plaza et al. (2016)(Plaza et al., 2016)
	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS HPLC-DAD-MS-Q	
Ellagic acid	Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-ESI-MS ⁿ	Quatrin et al. (2019) Pimenta Inada et al. (2020)
	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ HPLC-DAD-ECD-CAD	Neves et al. (2018) Plaza et al. (2016)
Ellagic acid- hexoside	<i>M. jaboricaba</i> pells	LC-TRAP-MS/MS HPLC-DAD-MS-Q	Quatrin et al. (2019) Pimenta Inada et al. (2020)
	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>		
Ellagic acid rhamnoside	Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Ellagic acid acethyl-rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Ellagic acid galloyl pentoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Ellagic acid valeryl rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Ellagic acid caprylyl rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Valoneic acid dilactone	Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-MS-Q	Pimenta Inada et al. (2020)
Myricetin-hexoside	LC-TRAP-MS/MS Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
Myricetin-3-rhamnoside	Pells and seeds of <i>M. jaboricaba</i>	LC-TRAP-MS/MS HPLC-DAD-MS-Q	Quatrin et al. (2010) Pimenta Inada et al. (2020)
	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Myricetin-3-galactoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Myricetin-3-glucoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin-hexoside	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin-pentoside	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin-3-rhamnoside	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
	Pells, pulp and seeds of <i>Plinia</i> spp	HPLC-DAD-ESI-MS ⁿ HPLC-DAD-ECD-CAD	Neves et al. (2018) Plaza et al, (2016)
Quercetin-3-galactoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018))
Quercetin-3-glucuronide	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin-3-glucoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin-galloyl-pentoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)

Quercetin-caffeoyl hexoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Free quercetin	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin ρ -coumaroyl hexoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Quercetin feruloyl hexoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Methylellagic acid hexoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Methylellagic penstoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Free Methylellagic acid	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Methylellagic acid rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Methylellagic acid acethyl rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Methylellagic acid valeryl rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Methylellagic acid caprylyl rhamnoside	Pells, pulp and seeds of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2018)
Kaepferol	Pells extract of <i>P. trunciflora</i> Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i> Pells and seeds of <i>M. jaboricaba</i>	HPLC-ESI-MS LC-TRAP-MS/MS HPLC-DAD-MS-Q	Calloni et al. (2015) Quatrin et al. (2019) Pimenta Inada et al. (2020)
Delphinidin-3-glucoside	Pells, of <i>Plinia</i> spp. Pells of <i>M. jaboricaba</i> <i>M. jaboricaba</i> pells Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i> Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-ESI-MS ⁿ HPLC-MS HPLC-DAD-ECD-CAD LC-TRAP-MS/MS HPLC-DAD-MS-Q	Neves et al. (2021) (Leite-legatti et al. (2012) Plaza et al.(2016) Quatrin et al. (2019) Pimenta Inada et al. (2020)
Cyanidin-3-glucoside	Pells of <i>Plinia</i> spp. Pells of <i>M. jaboricaba</i> Pells extract of <i>P. trunciflora</i> <i>M. jaboricaba</i> pells Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i> Pells of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ HPLC-MS HPLC-ESI-MS HPLC-DAD-ECD-CAD LC-TRAP-MS/MS HPLC-DAD-ESI-MS ⁿ	Neves et al. (2021) (Leite-legatti et al. (2012) Plaza et al. (2016) Calloni et al. (2015) Quatrin et al. (2019) Neves et al. (2021)
Pelargonidin-3-glucoside	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i> Pells of <i>Plinia</i> spp.	LC-TRAP-MS/MS HPLC-DAD-ESI-MS ⁿ	Quatrin et al. (2019) Neves et al. (2021)
Peonidin-3-glucoside	Pells powder of <i>M. jaboricaba</i> Pells of <i>Plinia</i> spp.	LC-TRAP-MS/MS HPLC-DAD-ESI-MS ⁿ	Quatrin et al. (2019) Neves et al. (2021)
Cyanidin-3-coumaroyl-glucoside	Pells of <i>Plinia</i> spp.	HPLC-DAD-ESI-MS ⁿ	Neves et al. (2021)
Protocatechuic acid	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
4-Hydroxybenzoic acid derivative	Pells powder of <i>M. trunciflora</i> and <i>M. jaboricaba</i>	LC-TRAP-MS/MS	Quatrin et al. (2019)
trans-Cinnamic acid	Pells and seeds of <i>M. jaboricaba</i>	HPLC-DAD-MS-Q	Pimenta Inada et al. (2020)

HPLC- High performance liquid chromatography; TRAP – ion trap; LC- liquid chromatography; MS- mass spectroscopy; DAD- diode array detector; Q- mass spectrometry with single quadrupole; ECD- electrochemical; CAD- charged aerosol; ESI- electrospray ionization. Source: Authors.

Açaí berries are well known for their high concentration of bioactive compounds and has recently been considered a superfruit due the high concentration of anthocyanins and other nutritional properties. The anthocyanins are the most common phenolic compounds, with the predominance of cyanidin-3-glucoside and cyanidin-3-rutinoside. The açaí berries also contain other polyphenolic compounds, such as phenolic acids and the flavonoids orientin and isoorientin, both deriving from lutein. The levels of these phytochemicals in açaí fruits vary significantly between different Euterpe species, and even during fruit maturation. Other phenolics previously reported for açaí are homoorientin, catechin, epicatechin, ferulic acid, caffeic acid,

chlorogenic acid, benzoic acid, vanillic acid, gallic acid, p-hydroxybenzoic acid, syntinic acid (Yamaguchi et al., 2015), and others, as described in Table 2.

Table 2. Phenolic compounds identified in açai (*Euterpe oleracea* Mart.)

Compound	Analised Sample	Identification Method	References
Gallic acid	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)
3,4-dihydroxybenzoic acid	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)
4-hydroxybenzoic acid	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)
Catechin	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)
	Seeds extract of <i>E. oleracea</i>	HPLC-DAD-ESI-MS	(Barros et al., 2015)
	Extract from <i>E. oleracea</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	(Oliveira et al. (2021)
Epicatechin	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón, Narváez-Cuenca, Vincken, & Gruppen (2017)
	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)
	Seeds extract of <i>E. oleracea</i>	HPLC-DAD-ESI-MS	Barros et al. (2015)
Rutina	Extract from <i>E. oleracea</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	(Oliveira et al. (2021)
	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Chlorogenic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
Vanillic acid	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
	Extract from <i>E. oleracea</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Caffeic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
	Extract from <i>E. oleracea</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Syringic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
p-coumaric acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
p-Hydroxybenzoic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Hydroxyferuloyl quinic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Synapoyl deoxyhexoside	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Feruloyl sinapic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
5-Caffeoylquinic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
p-Coumaroyl hexoside	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Ferulic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Caffeoyl shikimic acid	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Isoorientin	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
Orientin	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
	Extract from <i>E. oleracea</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Homoorientin	<i>E. oleracea</i> fruits	HHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
	<i>E. oleracea</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Ferulic acid	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
Taxifolin	White açai (<i>E. oleracea</i>) juice	LC-MS/MS	Silveira et al. (2017)(da Silveira et al., 2017)
	Extract from <i>E. oleracea</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Taxifolin deoxyhexoside	<i>E. oleracea</i> fruit	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)

Protocatechuic acid	<i>E.oleraceae</i> fruits	HHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Protocatechuic acid hexoside	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Apigenin 6,8-di-C-hexoside	<i>E.oleraceae</i> fruit	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Apigenin 6-C-pentoside-8-C-hexoside	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Apigenin 6-C-hexoside-8-C-pentoside	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
(+)-Dihydrokaempferol	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Scoparin	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Quercetin 3-glucoside	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Routine	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Kaempferol 3- rutinoside	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Eriodictyol	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Quercetin	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Luteolin	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Vitexin	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Isovitexin	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Scoparin	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Isorhamnetin rutinoside	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Dihydrokaempferol	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Luteolin	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Chrysoeriol	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Chrysoeriol	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Anthocyanins	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Cyanidin 3-glucoside	<i>E.oleraceae</i> fruits	UHPLC-Uv-vis	Aliaño-González et al. (2020)
	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Cyanidin 3-rutinoside	<i>E.oleraceae</i> fruits	UHPLC-Uv-vis	Aliaño-González et al. (2020)
	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Cyanidin-3,5-hexoside-pentoside	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Pelargonidin 3-glucoside ^c	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
Pelargonidin-3-rutinoside	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Peonidin 3-glucoside	<i>E.oleraceae</i> fruits	UHPLC-Uv-vis	Aliaño-González et al. (2020)
	<i>E.oleraceae</i> fruits	RP-UHPLC-PDA-HESI-MS	Garzón et al. (2017)
	Extract from <i>E. oleraceae</i> fruits	UHPLC-DAD-LTQ-Orbitrap-MS	Oliveira et al. (2021)
Peonidin 3-rutinoside	<i>E.oleraceae</i> fruits	UHPLC-Uv-vis	Aliaño-González et al. (2020)

LC- liquid chromatography; MS- mass spectroscopy; DAD- diode array detector; ESI- electrospray ionization; UHPLC- ultra-high performance liquid chromatography; LTQ- linear ion-trap quadrupole; RP- reversed phase; PDA- photodiode array detection; HESI- heated electrospray ionization; UV-vis- Ultraviolet-visible. Source: Authors.

Although similar to açai (*E. oleracea*), some studies reported that the jucara fruit (*E. edulis* Martius) presents superior nutritional properties and higher quantities of bioactive compounds, with the majority of those belonging to the group of phenolic acids, flavonoids, anthocyanins, and stilbenes, respectively (Barroso et al., 2019), as shown in Table 3.

Table 3. Phenolic compounds identified in Jussara (*Euterpe edulis*).

Compound	Analised Sample	Identification Method	References
3,4- dihydroxybenzoic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
3,4-dihydroxyphenylacetic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
4-hydroxyphenylacetic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
Benzoic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
Ferulic acid	<i>E. edulis</i> fruit <i>E. edulis</i> extract	HPLC-PDA UPLC/ESI-MS	Vieira, Marques, Machado, Silva, & Hubinger (2017) Silva et al. (2017)
Gallic acid	<i>E. edulis</i> fruit <i>E. edulis</i> fruit <i>E. edulis</i> extract	HPLC-PDA HPLC-DAD-MS/MS UPLC/ESI-MS	Silva, Rodrigues, Mercadante, & de Rosso (2014) Vieira et al. (2017)(Vieira et al., 2017)
P-coumaric acid	<i>E. edulis</i> fruit <i>E. edulis</i> pulp extract <i>E. edulis</i> extract	HPLC-PDA HPLC-ESI-MS/MS UPLC/ESI-MS	Silva et al., (2017) Schulz et al. (2015) Vieira et al. (2017)(Vieira et al., 2017)
P-hydroxybenzoic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
Syringic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
Vanillic acid	<i>E. edulis</i> fruit	HPLC-PDA	Silva et al. (2017)
Caffeic acid	<i>E. edulis</i> extract	UPLC/ESI-MS	Vieira et al. (2017)
Sinapic acid	<i>E. edulis</i> extract	UPLC/ESI-MS	Vieira et al. (2017)
Ellagic acid	<i>E. edulis</i> extract	UPLC/ESI-MS	Vieira et al. (2017)
Aspigenin hexoside	<i>E. edulis</i> fruit	HPLC-DAD-MS/MS	Silva et al. (2014)
Taxifolin hexoside	<i>E. edulis</i> fruit <i>E. edulis</i> pulp extract <i>E. edulis</i> fruit	HPLC-DAD-MS/MS HPLC-ESI-MS/MS HPLC-PDA	Silva et al. (2014) Schulz et al. (2015) Silva et al. (2014)
Kaempferol	<i>E. edulis</i> pulp extract <i>E. edulis</i> extract	HPLC-ESI-MS/MS UPLC/ESI-MS	Schulz et al. (2015) Vieira et al. (2017)
Aromadendrin	<i>E. edulis</i> pulp extract	HPLC-ESI-MS/MS	Schulz et al. (2015)
Hispidulin	<i>E. edulis</i> pulp extract <i>E. edulis</i> fruit	HPLC-ESI-MS/MS HPLC-PDA	Schulz et al. (2015) Silva et al. (2017)
Myricetin	<i>E. edulis</i> pulp extract <i>E. edulis</i> extract <i>E. edulis</i> fruit	HPLC-ESI-MS/MS UPLC/ESI-MS HPLC-PDA	Schulz et al. (2015) Vieira et al. (2017) Silva et al. (2017)
Quercetin	<i>E. edulis</i> pulp extract <i>E. edulis</i> extract	HPLC-ESI-MS/MS UPLC/ESI-MS	Schulz et al. (2015) Vieira et al. (2017)
Catechin	<i>E. edulis</i> extract <i>E. edulis</i> fruit	UPLC/ESI-MS HPLC-PDA	Vieira et al. (2017) Silva et al. (2017)
Rutin	<i>E. edulis</i> pulp extract <i>E. edulis</i> extract	HPLC-ESI-MS/MS UPLC/ESI-MS	Schulz et al. (2015) Vieira et al. (2017)
Stillbene	<i>E. edulis</i> pulp extract	HPLC-ESI-MS/MS	Schulz et al. (2015)
Resveratrol	<i>E. edulis</i> pulp extract <i>E. edulis</i> extract <i>E. edulis</i> fruit	HPLC-ESI-MS/MS UPLC/ESI-MS HPLC-PDA	Schulz et al. (2015) Vieira et al. (2017) Silva et al. (2017)
Cyanidin-3-glucoside	<i>E. edulis</i> fruit <i>E. edulis</i> extract <i>E. edulis</i> fruit	HPLC-DAD-MS/MS UPLC/ESI-MS HPLC-PDA	Silva et al. (2014) Vieira et al. (2017) Silva et al. (2017)
Cyanidin-3-rutinoside	<i>E. edulis</i> fruit <i>E. edulis</i> extract	HPLC-DAD-MS/MS UPLC/ESI-MS	Silva et al. (2014) Vieira et al. (2017)
Cyanidin-3,5- hexose pentose	<i>E. edulis</i> fruit	HPLC-DAD-MS/MS	Silva et al. (2014)
Pelargonidin-3-glucoside	<i>E. edulis</i> fruit <i>E. edulis</i> extract	HPLC-DAD-MS/MS UPLC/ESI-MS	Silva et al. (2014) Vieira et al. (2017)
Pelargonidin-3-rutinoside	<i>E. edulis</i> fruit	HPLC-DAD-MS/MS	Silva et al. (2014)
Peonidin-3-glucoside	<i>E. edulis</i> fruit	HPLC-DAD-MS/MS	Silva et al. (2014)
Peonidin-3-glucoside	<i>E. edulis</i> fruit	HPLC-DAD-MS/MS	Silva et al. (2014)
Cyanidin-3-rhamnoside	<i>E. edulis</i> fruit	HPLC-DAD-MS/MS	Silva et al. (2014)
Dephinidin-3-glucoside	<i>E. edulis</i> extract	UPLC/ESI-MS	Vieira et al. (2017)
Malvinidin-3-glucoside	<i>E. edulis</i> extract	UPLC/ESI-MS	Vieira et al. (2017)

HPLC- high performance liquid chromatography; MS- mass spectroscopy; DAD- diode array detector; ESI- electrospray ionization; UPLC- ultra performance liquid chromatography; PDA- photodiode array detection. Source: Authors..

Cocoa, like jabuticaba, açaí and juçara, is rich in polyphenols, and these compounds account for about 15% of the dry matter of almonds. Three groups of polyphenols can be identified in cocoa beans: proanthocyanins (ca. 58%), catechins or

flavonoids (ca. 37%) and anthocyanins (ca. 4%) (Urbańska et al., 2019). However, the amount and types of the compounds found in cocoa depend on some factors such as genotype, geographic origin, harvest time, fermentation methods and further processing steps (D'Souza et al., 2017; Urbańska et al., 2019), such as drying and roasting.

The higher concentration of catechin present in cocoa beans is epicatechin, which represents 35% of the total catechin. It is a component of the cocoa tannins, which is responsible for colour changes and the astringent taste of the almonds and derived products (Urbańska et al., 2019). Cocoa procyanidins are represented by dimers, trimers or oligomers of flavan-3,4-diol. Other polyphenols include flavones (kaempferol, apigenin, luteolin and glycosides) and phenolic acids (chlorogenic, caffeic, syngaric, coumaric and ferulic acid) (Urbańska et al., 2019). Table 4 presents a list of phenolic compounds already identified in cacao, as well as the methods used.

Table 4. Phenolic compounds identified in Cocoa (*Theobroma cacao*).

Compound	Analised Sample	Identification Method	References
Caffeoyl aspartate	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
	Cocoa beans	HPLC-MS	Febrianto & Zhu (2019)
Feruloyl aspartate	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
Catechin hexoside	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
Epicatechin	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
Kaempferol-3-0-hexoside	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
Kaempferol-3-0-rutinoside	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
Luteolin	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
Quercetin	Fermented and unfermented <i>T. cacao</i> beans	HPLC-TOF-MS	D'Souza et al (2017)
	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
P-coumaryl aspartic acid	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
Clovamide	Cocoa beans	HPLC-MS	Febrianto et al. (2019)
Apegenin hexoside	Cocoa beans	HPLC-MS	Febrianto et al. (2019)

HPLC- high performance liquid chromatography; TOF- time of flight; MS- mass spectroscopy. Source: Authors.

5. Extraction Methods of Phenolic Fraction in Plants Species

Extraction is a fundamental process in separating and recovering bioactive compounds from plants. It is the first step in any medicinal plant study as it converts the real matrix into a sample suitable for subsequent analytical procedure (Vieira et al., 2017). The extraction of phenolic compounds from plant materials can be performed using various extraction procedures.

Many studies reported the use of extraction methods of bioactive compounds from fruits, vegetables and by-products for the identification/quantification or to be applied in foods, pharmaceutical products or other products and biologic analysis.

The most traditional extraction methods are the solid-liquid extraction by mechanical agitation and Soxhlet extraction, with the use of ethanolic or methanolic solutions as solvents. However, due to the long extraction time often required, these methods can cause hydrolysis and oxidation of the compounds of interest, in addition to their low efficiency and high costs of solvents. Some non-conventional methods, known as green extraction present higher efficiency and/or extraction selectivity with lower consumption of solvent, reduced operational time and energy consumption, achieving a higher yield and quality of extract.

Therefore, methods such as pressurized liquid extraction, microwave-assisted extraction, ultrasound, supercritical fluid, pulsed electric field, enzyme and deep eutectic solvent have been proposed to extract these compounds in a shorter time with higher recovery capacity (Caldas et al., 2018; Javier David Vega et al., 2017).

Regarding the extraction methods used, a number of factors including extraction time, temperature, pressure, type of

solvent, solid-to-solvent ratio, among others might affect the process efficiency (Javier David Vega et al., 2017). The extraction protocol must be consider all these factors, as the phenolic concentration extracted, and the antioxidant capacity of a given extract tend to vary with the extraction method used for the same raw material (Cádiz-Gurrea et al., 2014). The main methods of extraction reported in literature are described below.

5.1 Solid-liquid extraction

Solid-liquid extraction is considered the conventional method of extracting bioactive compounds from plant matrices. It is based on the use of conventional solvents, with or without heating. Plant matrix is initially homogenized and soaked in a solvent or mixture of solvents, often under a constant agitation, thereby the desired molecules are extracted based on diffusion and mass-transfer phenomena (Rocchetti et al., 2019). This method of extraction can require additional operation, such as subsequent column chromatography or solid-phase extraction to remove the unwanted substances (Xu, Wang, Pu, Tao & Zhang, 2017).

Some of the solvents used in the extraction methods are ethanol, methanol and acetone solutions. Ethanol is most used when extracting for food application because of its lower toxicity and high extraction efficiency.

Soxhlet extraction is based on solvent reflux, in an intermittent process. It has some advantages when compared to the use of one solvent extraction method, such as lower cost, solvent consumption and less time required, in addition to being a simpler method with high efficiency (Caldas et al., 2018).

5.2 Ultrasound-assisted extraction

Ultrasound-assisted extraction is a relatively simple process that represents a slight modification of the conventional stirred method. This method uses levels of 20kHz to 100mHz of frequency to disrupt the cells walls. The effects of ultrasound are mainly related to the cavitation phenomenon, which involves the implosion of bubbles formed in the liquid medium. This implosion generates fast adiabatic compression of gases and vapor inside the bubbles, increasing temperature and pressure that favors solvent penetration and increases the transport between the solid matrix and the liquid phase (Caldas et al., 2018).

The advantages of ultrasound-assisted extraction include less extraction time, energy and use of solvent. It is a useful and economic technology, because expensive instruments are not required for its use. Extracting efficiency is influenced not only by sonication time, temperature, and ultrasonic wave frequency, but also by the property of solvent and sample (Xu et al., 2017).

5.3 Microwave assisted extraction

In microwave-assisted extraction, electromagnetic waves penetrate materials and interact with polar groups, causing heat generation and thus promoting the heating of both the solid and the solvent. Microwave heating is based on ionic conduction and dipole rotation, which cause friction and collisions between ions and dipoles. The water in plant material absorbs the microwave energy, leading to internal superheating and cell structure perturbation, thus facilitating the diffusion of biologically active compounds from the plant matrix (Raks, Suod, & Buszewski, 2018).

The microwave assisted extraction efficiency depends on the nature of both the solvent and sample. The solubility of the different extracted compounds is influenced by the solvent's mixture ratio and temperature (Belwal et al., 2018). Solvent property is an important factor because solvents with high dielectric constants can absorb more microwave energy; methanol, ethanol, and water are commonly used to extract phenolics compounds from plants (Xu et al., 2017). Some of the advantages of this technique include quicker heating, reduced thermal gradients, an increased extracted yield and a reduction in the use of organic solvent when compared to the conventional methods (Azmir et al., 2013).

5.4 Pressurized Liquid Extraction

The pressurized liquid extraction is an effective method to recover polar extracts by applying polar solvents like ethanol and water. It involves using solvents at elevated temperature and pressure to enable the solvent to keep in the liquid state even at temperatures above the boiling point at atmospheric pressure. Higher temperatures provide higher extraction yields since temperature increases the mass transfer and the extraction rate, mostly due to the enhanced capacity to solubilize the extract, disrupt solute-matrix bonds, decrease the solvent viscosity, and reduce the surface tension. Additionally, higher pressure improves the solvent driving into the raw materials' pores and enhances the solubility of target compounds (Viganó et al., 2022).

In this technique, the sample is placed in an extraction chamber and pressurized with a solvent. The main advantages are the short time (approximately 15 min) needed to achieve an efficient extraction, and the inert extraction conditions (one atmosphere of N₂). The application of this method to extract compounds from different matrices has increased significantly in recent years and is mainly used in natural foods and plant metabolites (Barros et al., 2015).

5.5 Supercritical fluid extraction

Supercritical fluid extraction is another environmentally friendly extraction technique, which can be a good alternative to conventional organic solvent extraction methods (Capuzzo, Maffei, & Occhipinti, 2013). It is characterized by the utilization of a supercritical fluid in the extraction process. The most commonly used supercritical fluid is supercritical CO₂, but a number of other supercritical fluids, such as ethane, butane, pentane, nitrous oxide, ammonia, trifluoromethane, and water are also used. The supercritical state is achieved when the temperature and pressure of a fluid are raised above the critical point, exhibiting unique properties in terms of compressibility, density, and viscosity that differ from those of gases or liquids in a normal state (Raks et al., 2018). This technique can minimize the contamination of the sample with solvent impurities when compared to other methods. However, the high capital investment for equipment is a disadvantage associated with SFE (Khoddami, Wilkes, & Roberts, 2013).

5.6 Enzyme-assisted extraction

The bioactive compounds in the plant matrices are dispersed in the cell cytoplasm, and compounds including polysaccharides such as hemicelluloses, starch, pectin and also lignin, can reduce the accessibility of the solvent and as a result reduce the extraction efficiency (Nadar et al., 2018). Enzymes are ideal catalysts to assist in the extraction, modification or synthesis of complex bioactive compounds of natural origin. Enzyme-based extraction is based on the inherent ability of enzymes to catalyze reactions with exquisite specificity, regioselectivity and an ability to function under mild processing conditions in aqueous solutions. It also offer several advantages as opposed to the conventional methods: mild reaction conditions (processes occurring at low temperature values and for short periods of time), the possibility of using the whole plant material, processes requiring fewer numbers of steps, a substrate specificity which in turn leads to extracting a large number of bioactive compounds (by bioaccessing even anchored molecules within cellular organelles such as vacuoles and plant cell walls, otherwise inaccessible) with a high bioavailability and quality (low residue levels), while also potentially lowering production costs by replacing multiple installations used for classical extraction processes (Gligor et al., 2019; Puri et al. 2012).

5.7 Pulsed electric field assisted extraction

Pulsed electric field assisted extraction involves the application of short duration pulses (μ s to ms) of moderate electric voltage (typically 0.5–20 kV/cm) to a substrate of choice placed between two electrodes. Using high electric voltage

(5–50 kV/cm), the technology has been applied for preservation, enzyme and microbial inactivation purposes. The basic principle of pulsed electric field assisted extraction is electroporation due to dielectric disruption of cell membrane. When an electric field is applied to the membrane, it can cause its rupture through the formation of transmembrane pores, which can be reversible or irreversible depending on the field strength, pulse duration and number of pulses (Capuzzo et al., 2013).

The permeabilization of membranes through the electrical pulse can accelerate the release of intracellular compounds in addition to the increase of extraction rates and yields of components of plant matrices with low energy consumption and low environmental impact. Furthermore, it can reduce the degradation of heat-sensitive compounds and promote the purification of the extract (Khoddami et al., 2013).

5.8 Deep eutectic solvent extraction

Most solvents used in the extraction of phenolic compounds (chloroform, ethyl acetate, ethanol, methanol) cause environmental impacts, such as toxicity, volatility, flammability, non-degradability, and high cost. The deep eutectic solvent emerges as a very promising alternative as a more environmentally friendly method with the use of a class of green solvent.

Deep eutectic solvent is a low-melting mixture, consisting of two or three solvents. Like ionic liquids, these solvents are formed by a hydrogen bond interaction between hydrogen bond acceptors and hydrogen bond donors. They are usually consist of salt, mainly choline chloride, a non-toxic quaternary ammonium salt, and a polyalcohol (glycerol, ethylene glycol) or an organic acid (lactic acid, for example). The solvent has a melting point lower when compared to its individual components and has been shown to be efficient in extracting phenolic compounds from plants, as it is environmentally friendly, stable, less volatile, easy to degrade and non-toxic. Although little has still been studied and published on the use of this method, some research involving the use of deep eutectic solvent in association with other extraction techniques such as ultrasound assist-extraction have reported promising results (Gligor et al., 2019; Nadar et al., 2018).

6. Extraction of the Phenolic Fraction of Jabuticaba

Pimenta Inada et al (2020) performed the extraction of phenolic compounds from jabuticaba husks and seeds. They performed the High hydrostatic pressure processing with different pressures (200, 350 and 500 Mpa) and processing times (1, 5.5 and 10 min), drying in an air circulation oven, with different times (14, 18 and 22 h) and temperatures (55, 65 and 75°C) and lyophilization at -50°C, 0.065 mbar for 72 hours. The pressurization did not result in an increase of phenolic compounds extracted. The lyophilization and drying at 75°C resulted in similar concentrations of total phenolic compounds extracted but with different profiles, with the first rich in anthocyanins and the latter resulted in a higher concentration of ellagitannins.

In another study, 10 combinations of solvents including water, ethanol and propanone in different proportions were tested in the extraction of phenolic compounds from jabuticaba seeds (Kumari et al., 2018). The extraction was performed using 1:20 sample:solvent ratio, at 45°C for 45 minutes with constant magnetic stirring. The results showed that the combination of water and propanone (52:48 v/v) changed the polarity of the extract and increased the extraction yield.

High intensity ultrasound technology was used to extract bioactive compounds from dry jabuticaba peels, and different ultrasound intensities (1.1, 3.7, 7.3 and 13.0 W/cm²) and solvent compositions (0:100, 25:75, 50:50, 75:25 and 100:0 water: ethanol) were tested. The highest extraction was achieved at an intensity of 3.7 W/cm², using 50:50 water: ethanol. The exhaustion of bioactive compounds from dry jabuticaba peel was verified by confocal laser scanning microscopy (Barbosa-Pereira, Guglielmetti, & Zeppa, 2018).

The ultrasound assisted method was applied to study the effect of pH and the type of acid added to the extracting solution on the efficiency of extraction of phenolic compounds in freeze-dried jabuticaba peels. The hydroalcoholic solution (505 v/v) was chosen because it is more efficient when compared to the pure solvent in extracting amphiphilic or moderately

polar compounds, such as polyphenols. The phenolic compounds were extracted in an ultrasonic bath in a frequency of 40 kHz and a power of 150 W, for 60 minutes at 30°C. 0.5 g of freeze-dried jaboticaba peel were used for 25 mL of extraction solution, which had its pH adjusted to 1, 2 and 3 with formic, acetic, and phosphoric acids. The results showed that the formic acid at pH 1.0 was the best one to extract phenolic compounds, presenting the greatest antioxidant activity when compared to the other acids used (Barbosa-Pereira et al., 2018).

An innovative extraction method used microwave hydrodiffusion and gravity to obtain an extract from fresh jaboticaba peels (Wu, Li, Chen, Wang, & Lin, 2020). The jaboticaba peels (200g) were first heated in a microwave oven with 400 w of power for 20 minutes. The extract was then drained by gravity and condensed, and no solvent was used in the process. The extract obtained showed high yield (52.5±0.8%) with 1.72 mg of phenolic compounds/mL and an antioxidant capacity of 57741.67 µmol TE (Trolox equivalent)/mL. This method is considered eco-friendly as it does not use reduces the use of toxic solvents and generate lower waste with less energy consumption than the conventional methods.

7. Extraction of the phenolic compounds of açáí

A method of extracting phenolic compounds from açáí was patented by the company Amazon Dreamsand in partnership with the Federal University of Pará (PI 1003060), which consists of obtaining a lyophilized extract from the extraction with 1:0.5 (w/v) of fresh fruits/ water during 150 s followed by microfiltration using diatomaceous earth and purification (adsorption on acrylic macroporous resins and desorption with 75% ethanol) of the phenolic compounds present in the *E. oleracea* fruits. The solvent is evaporated using an industrial vacuum concentrator following a semi-industrial lyophilisation. The final extract obtained after desorption was free of fatty acid, proteins, and fibres (< 1% dry matter) and enriched in phenolic compounds (Oliveira et al., 2021).

A dynamic extraction method using pressured liquid was applied extract phenolics from açáí residues. Approximately 5.0 g of raw material were used, forming a fixed bed inside a 54.37 cm³ (3.03 cm × 7.54 cm) stainless steel column. A cylindrical piece of stainless steel was inserted (3.0 cm × 5.0 cm) into the column to reduce the empty volume of the extraction cell. The optimization of phenolic extraction was achieved by applying different temperatures (65, 90 and 115°C) and percentages of ethanol in the solvent (0, 25, 50, 75 and 99.5 wt%). The pressure was kept constant at 10 ± 0.5 MPa. The solvent flow rates were 3.0, 3.2, 3.3, 3.5, and 3.8 mL/min for 0, 25, 50, 75, and 99.5 wt% ethanol, respectively, to keep the mass flow rate constant at 3.0 g/min. The extraction time was 60 min. The solvent was pumped from the reservoir by an HPLC pump, passed through a coil in a heating bath and entered the jacketed extraction column, flowed through the sample bed where the extractable compounds were desorbed and dissolved, left the bed, and the extract-solvent mixture was collected after depressurization in a micrometer valve. The results reported that the temperature of 115°C and the ethanol proportion of 75wt% favoured the extraction of bioactive compounds from açáí residues (Viganó et al., 2022).

Another study tested different conditions for the extraction of anthocyanins and total phenolic compounds from açáí using pressurized liquid extraction. The different solvent compositions (25-75% methanol in water), temperatures (50-100°C), pressure values (100-200 atm), purge times (30 - 90s), pH (2-7) and flushing percentages (50-150%) were tested. The most significant variable in the extraction of anthocyanins was the percentage of methanol, and the optimal conditions found were: 43% of methanol, temperature of 81°C, pressure of 200 atm, time of purge of 60s, pH 7 and 50% of flushing. The optimal conditions in the extraction of total phenolic compounds were: 42% of methanol, 99.6°C, 100 atm, 65 s of purge time, pH at 3.02 and 150% of flushing. The temperature was the variable that promote the greatest influence in the extraction of phenolics (Aliaño-González et al., 2020).

In an attempt to identify the optimal green extraction method of açáí berries (ultrasound or microwaves), a study was conducted with different conditions using lyophilized açáí powder. The açáí powder was first diluted in ethanol (50% v/v)

and the phenolic compounds were extracted by sonication and using a microwave. In the ultrasound method, 37KHz of frequency and 100% of amplitude were tested for 5, 25 and 45 minutes at temperatures of 25 and 45°C. The microwave method used times of 2, 3.16 and 4.33 minutes and temperatures of 25 and 45°C. The highest values of phenolic compounds were obtained after using ultrasound at 45°C for 25 and 45 minutes and microwave for 3.16 minutes. The ultrasound method was more efficient in extracting flavonoids; however, the microwave was more efficient in extracting anthocyanins. The application of microwaves for 4.33 minutes resulted in higher values of antioxidant activity (Hanula et al., 2020).

In another study, Borges et al. (2016) aimed to obtain a protocol for extracting phenolic compounds from açai through two tests using Plackett-Burman and one using response surface methodology. In the first Plackett-Burman using 16 variables and 20 assays, the influences of the variables solid/solution ratio, extraction time (with and without sonication), ethanol proportion, methanol proportion, acetone proportion, acidification with formic acid acetic and hydrochloric were tested. In the Plackett-Burman, the variables that negatively affected the antioxidant activity of the extracts with 20% probability were discarded and another study was designed with 12 assays, 7 variables and 3 central points. The second Plackett-Burman tested the influence of the variables solid/solvent ratio (1:10 to 1:100 g:mL), acetone ratio (10 to 70%), extraction time in ethanol solution (1-59 min), ethanol (0-40%), acetic acid in ethanol solution (0.1 to 1.5M), hydrochloric acid in ethanol solution (0.01 to 1.5M), extraction time in methanolic solution (1-59 min). From the results obtained in the second Plackett-Burman, the optimization of the extraction process was carried out by a full factorial central composite design, testing the variables solid: solvent ratio, acetone (10-70%), ethanol concentration (0-40%) and time in the acidified ethanolic solution (1-59 min). As a result, two optimal extraction methods were obtained, one using aqueous acetone solution (55%) under sonication for 30 min and another using aqueous ethanolic solution (40%) acidified with 0.01M HCl under sonication for 30 min, both using the highest solid proportion: solvent (Borges et al., 2016).

8. Extraction of phenolic fraction from Jussara

Aiming to optimize the conditions of extraction of phenolic compounds from jussara by using ultrasound-assisted extraction, an experimental design was elaborated using the central composite design with three factors. The independent variables were ultrasonic extraction time (5-62 min), ethanol concentration (1-94%) and fruit to solvent proportion (3-25%); the response variables were coloration, total phenolic compounds, and total anthocyanins. The optimal conditions found were extraction time between 30 and 62 min for total anthocyanins and total phenolics, fruit: solvent ratio of 10% and 6% (w/v) for total anthocyanins and total phenolics, respectively. The ethanol concentration was non-significant ($p > 0.05$) (Rocha et al., 2017).

Jussara residues, composed of husk and pulp, were subjected to different types of extraction, using high pressures (pressurized liquid extraction- PLE and supercritical fluid extraction) and low pressures (ultrasound assisted extraction and Soxhlet extraction). The first extraction method (PLE) was tested under the conditions: 10Mpa of pressure, flow rate of 1.5mL/min, temperatures from 40, 60 to 80°C, water and ethanol (50% v/v) in pH2 and water and ethanol (99%) as solvent. Supercritical fluid extraction with co-solvent was carried out under conditions of flow rate of 2.08×10^{-4} Kg/s, pressure of 20 Mpa, temperature of 60°C. A mixture of ethanol and water (50%) acidified (pH 2) was used as co-solvent and CO₂ as solvent. The extraction by stirring bath was carried out under the conditions of acidified ethanol and water as solvent, 45 min at 60°C and the ultrasonic extraction was carried out under the conditions of 800w power, frequency of 19 KHz for 45 min, with the same solvent. The pressurized assisted extraction with ethanol and water acidified at 80°C showed the best extraction of total phenolic compounds, however, acidified water was better for the extraction of total anthocyanins. The supercritical fluid extraction obtained lower value for total phenolic compounds than the pressurized liquid, however, it was more selective for anthocyanins. Low pressure extractions did not result in significant differences for extraction, and high pressure extractions

were more efficient in extracting phenolic compounds and anthocyanins from jussara (Garcia-Mendoza et al., 2017).

Jussara pulp was submitted to ultrasound assisted extraction where the effects of temperature and ultrasonic power were studied. The conditions used were 25KHz frequency, 15 min ultrasound with 50% ethanol solvent and 15.6mL/g solution/pulp ratio. Ultrasonic powers of 0, 360 and 900W and temperatures of 25, 32, 39, 46 and 53°C were tested. The results showed that the highest extraction of anthocyanins occurred at 25°C without ultrasonic wave, however the highest values of antioxidant capacity were obtained under conditions of 360w power and 25°C of temperature (Madalão et al., 2021).

9. Extraction of Phenolic Fraction from Cocoa

Several methods to extract cocoa polyphenols to quantify polyphenols and antioxidant activity have been reported in the literature, with aqueous solutions of methanol or acetone being the most commonly used (D'Souza et al., 2017). Due to the large amount of lipids present, prior degreasing of samples with dichloromethane (Arlorio et al., 2008), hexane (Carrillo, et al., 2014; Febrianto & Zhu, 2020; Gültekin-Özgülven et al., 2016; Pedan et al., 2018; Ramos-Escudero et al., 2021) or diethyl ether (Hu et al., 2016) is often performed.

Samples containing 50 mg of dried, fermented and unfermented cocoa beans, previously ground and defatted, were mixed with 5 mL of the extraction solution, Composed of (methanol:water:acetic acid 70:28:2), this mixture being sonicated for 10 minutes, stirred for another 30 minutes, and finally filtered by syring through a PTFE membrane filter (0.45µm) in a vacuum (D'Souza et al., 2017).

In another study, 10 mL of an 80% methanol aqueous solution was used to extract previously defatted samples of dried almonds, roasted almonds, natural liquor, alkalized liquor and cocoa powder for 10 minutes at 30°C in an ultrasonic bath. In other studies (Febrianto & Zhu, 2019, 2020, 2022), 80% methanol solution was added to samples of fermented and dried cocoa and roasted cocoa, previously defatted and ground, in a proportion of 1:20 (w/v). The extraction was performed by keeping the samples added from the extraction solution on a shaker (400 rpm) for 16 h. The suspensions were then centrifuged at 2000 g/6000 rpm for 10 minutes, and the supernatants were collected and filtered to obtain the extract.

To evaluate the antioxidant activity and bioactive compounds of raw, roasted and puffed cacao beans, samples containing 1 g of previously grounded and defatted almonds were mixed with 25 mL of 70% methanol aqueous solution for 2 h in a water bath at 40 °C. The mixture was filtered through filter paper (Whatman No. 2) using a Buchner funnel (Hu et al., 2016).

In a study (Ramos-Escudero et al., 2021) with fermented and dried almonds, approximately 0.5 g of a previously peeled, grounded, and defatted sample was placed in a 15.0 mL conical plastic tube. 5.0 ml of an 80% ethanol solution was added, and the mixture was stirred for 2 h. Subsequently, the mixture was placed in an ultrasonic bath 1800 at 40 kHz frequency and 30 min extraction time at 25 °C.

Samples containing 1g of fermented and dried cocoa, previously defatted and grounded, were extracted 3 times with 3 ml of 50% aqueous acetone solution for 8 minutes at 50°C using a bench shaker. After each extraction step the mixture was centrifuged and the supernatants were combined for further analysis (Pedan et al., 2018).

Aqueous 2-propanol solution (60%, pH 9.0) was used to extract phenolic compounds from 100 mg of samples of dried cocoa beans, previously defatted and grounded. For this purpose, 1.5 mL of the extraction solution and an ultrasonic bath for 60 min were used. After extraction, the mixture was centrifuged for 10 min at 391 g at 4 °C. The supernatant was decanted and filtered through a nylon membrane (0.45 µm) (Carrillo et al., 2014).

Table 5 summarizes information about the solvent used in degreasing, as well as the solvent, or resulting combination used in the extraction of cocoa polyphenols, in addition to the sonication conditions when used.

Table 5. Solvents used in the degreasing of samples, in the extraction of phenolic compounds and Ultrasonication conditions.

Sample	Fat extraction solvent	Phenolic extraction solvent	Ultrasonication	References
Raw (fermented/Unfermented and dried) cocoa beans	Dichloromethane	Methanol:water:acetic acid (70:28:2)	10 min	D'Souza et al. (2017)
Raw (fermented and dried) cocoa beans, roasted cocoa beans, natural cocoa liquor, alkalized cocoa liquor and cocoa powder	Hexane	Methanol: Water (80:20)	10 min at 30°C	Gültekin-Özgülven et al. (2016)
Raw (fermented and dried) cocoa beans; Roasted cocoa beans	Hexane	Methanol: Water (80:20)	-	Febrianto et al. (2020)
Raw (dried) cocoa beans	Hexane	Methanol: Water (80:20)	-	Febrianto et al. (2019)
Raw (fermented and dried) cocoa beans	Hexane	Acetone:water:acetic acid (70:29.5:0.5)	-	Mayorga-Gross, Quirós-Guerrero, Fourny, & Vaillant (2016)
Raw (fermented and dried) cocoa beans	Hexane	Acetone:water (50:50)	-	Pedan et al. (2018)
Raw (fermented and dried) cocoa beans	Hexane	Ethanol:Water (80:20)	At 40 kHz of frequency and 30 min of extraction time at 25 °C	Ramos-Escudero et al. (2021)
Raw (fermented and dried) cocoa beans; Roasted cocoa beans	Dichloromethane	Methanol	-	Arlorio et al. (2008)
Raw (dried) cocoa beans	Hexane	2-propanol:Water (60:40), pH 9.0	60 min	Carrillo et al. (2014)
Raw (fermented and dried), roasted and puffed cacao beans	Diethyl ether	Methanol:Water (70:30)	-	Hu et al. (2016)

Source: Authors.

10. Conclusion

Brazil has a great botanical diversity. with fruits rich in phenolic compounds and other bioactive compounds. Dozens of phenolic ompounds were identified in jaboticaba, açai, jussara and cocoa fruits.

Many studies are published on the phenolic characterization of these compounds as well as about the different methods of extraction, exploring the differences in costs, degree of efficiency and selectivity. The extraction of bioactive compounds is a research field still under development, with still many variables to be tested and subject to many advances. Thus, this present work can make a great contribution to the field, as it is a database for researchers who are interested in studying the extraction and applicability of the phenolic fraction of Brazilian fruits.

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