

Oleochemistry potential from Brazil northeastern exotic plants

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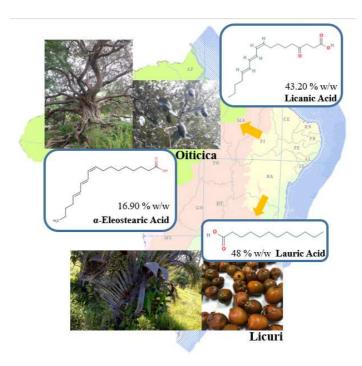
OLEOCHEMISTRY POTENTIAL FROM BRAZIL NORTHEASTERN EXOTIC

5 PLANTS

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Abstract

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Caatinga is a Brazilian semi-arid ecosystem that stands out for presenting unique environmental characteristics with a dry, spiny and deciduous shrub/forest vegetation with several species that can be renewable oil sources with potential applicability in oleochemical and nutrition. Caatinga oilseeds have a high content of unsaturated fatty acids, phytosterols and sterols, and this composition is related to its nutritional potential. The present review summarizes the knowledge on the oil contents and fatty acid profiles of seeds from six representatives caatinga species. It was observed that plants species like Caju (Anacardium occidentale L.), Favela (Cnidoscolus quercifolius Pohl), Licuri (Syagrus coronata (Mart.) Becc.), Pinhão-bravo (Jatropha mollissima Pohl Baill), Pequi (Caryocar brasiliense Camb) and Oiticica (Licania rígida Benth) contains approximately 33.1, 33.5, 49.2, 18.3, 70.16 and 57.0 % w/w of oil, respectively, on a dry weight basis. Their fatty acid profiles are mostly saturated for Licuri oil, with a high content of lauric acid (up to 40%) and unsaturated for Favela, Pinhão-bravo, Cashew nut, Pequi and Oiticica oils. Oiticica oil shows a high concentration of unusual conjugated polyunsaturated fatty acids, like α-Eleostearic and Licanic acid with 16.90 and 43.20 % w/w, respectively.

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Keywords: plant, oil, food, Brazil, Caatinga.

1. Introduction

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The number of plants for food consumption is estimated to hundred species, among which rice, wheat and maize account for 60% of the total caloric intake [1]. One alternative to recover old eating habits for health promotion is using different plant species as food [2]. This stimulates an interest in accessing plant foods in biodiversity centers, in order to find different and attractive tastes, as well as high levels of bioactive substances capable of preventing many diseases [3]. Brazil can contribute enormously in this field because the country has the most diverse flora of the world, with 33,200 different species approximately, what corresponds to 26.5% of the total known plant species [4].

In Brazil there are different types of land and climates that results in a large diversity of species distributed around six main biomes, namely the Amazon Forest, Caatinga, Cerrado, Atlantic Forest, Pantanal and Pampa, as shown in Figure 1. [5; 6; 7]. Caatinga is a semi-arid ecosystem with an area of 969.589.4 km², being an exclusively Brazilian biome that covers their northeast, composed by the states of Alagoas, Bahia, Ceará, Maranhão, Paraíba, Pernambuco, Piauí, Rio Grande do Norte and Sergipe and small portion southeastern area in the state of Minas Gerais north. The name has a Tupi-Guarani origin and means white forest. This name appropriately characterizes the physical aspect of the vegetation during the dry season, when the leaves fall and only the bright white trunks of trees and shrubs remain on the dry landscape. It corresponds to 10% of the Brazilian territory and 60% of the northeastern region [8]. Its vegetation covers a continuous area of semi-arid climate, limited by areas of typically humid climate. This area, dry and hot, is defined as the drought polygon. The species present in the Caatinga have as characteristics marked adaptations to water scarcity, i.e deciduous, annual herbaceous, succulent, the presence of acuulus and leaves transformed into thorns are constant, shrub and small trees are predominant and the canopy cover is

irregular. Its worth mentioning that there is presence of endemic species and non-endemic species. Non-endemic species occur in other areas of similar climate but are not found in humid regions that limit the biome [9]

Caatinga have an annual average rainfall that ranges from 240 to 1500 mm, restricted from January to March, with 2.000 mm of evaporation rate and high annual temperatures (around 27 ° C). Due to the low rainfall, the environment shows a shallow and stony soil with the presence of temporary rivers and streams. This periodic severe drought makes life difficult for the human inhabitants and provide adaptive challenges for the region's biota due to this unique environmental condition [8].

In this way, more than 510 genera and 5344 species of vascular plants have been identified in the Caatinga, among which 18 genera and 318 species are endemic [10]. Therefore, the climate and soil of the northeast region are determining factors of their typical vegetation [11]. Several plant species of the Caatinga are potentially useful as oil seed sources. Thus, the objective of this mini-review is to summarize the properties of oils and fatty acids that can be extracted from some representative species shown in Figure 2, of the Brazilian caatinga and present potential applications in Oleochemistry.

Among the six species selected for this review, Favela (*Cnidoscolus quercifolius* Pohl), Licuri (*Syagrus coronata* (Mart.) Becc.), Pinhão-Bravo (*Jatropha mollissima* Pohl Baill) and Oiticica (Licania rigida Benth) are endemic and naturally occur in Caatinga while Cashew (*Anacardium occidentale* L.) is a Brazillian native plant that occurs naturally on the coast and in the semi-arid region, and Pequi (*Caryocar brasiliense* Camb), naturally occurring in the Cerrado, was adapted to the northeast region and in the transition regions of the Amazon rainforest and Caatinga.

2. Cashew nut (*Anacardium occidentale* L)

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Commonly known as "Caju", belongs to the Anacardiaceae family, native from the Brazilian north and northeast regions. Cashew tree is adapted to various regions of different climates and water availability, being popular in houses backyards. It's a perennial plant, with botanical characteristics as an aerial stem with low branching; the leaves are simple, petiolate and without stipulation; the leaf is leathery, the leaves are alternate and obtuse; the inflorescence is panicle, the flowers are pentamerous, and may be complete (bisexual) and masculine (with stamens). The fruit is achene, the chestnut is the real fruit, formed by the pericarp and the seed or almond, and the peduncle is the pseudofruit [12; 13] The dispersion of cashews was carried out by Brazil colonizers in the 16th century and is currently found in various parts of the world like Vietnam, India, and Nigeria. In the 1990s, EMBRAPA (Empresa Brasileira de Pesquisa Agropecuária, in English: Brazilian Agricultural Research Corporation) started to offer small size cashew clones, to facilitate the harvest, these crops came from asexual propagation by grafting and had a high genetic quality. From these developments, it is now possible to increase the cashew productivity and rentability in Brazil [12; 14] Cashew is grown especially in small and medium-sized farms, in agricultural associations and rural settlements [12]. The Northeast region of Brazil is largely responsible for the national production of cashew nuts, with 98.8% of the total produced in Brazil. In 2017, the annual production in the Northeast region was 132 thousand tons of nuts, of which 81 thousand (60.8%) were produced in the state of Ceará [15]. Worldwide, the area occupied by cashew trees is equivalent to 3.39 million hectares,

constituting in the production of chestnuts, pseudofruit (peduncle) in natura and

derivatives such as juices, jelly and sweets [12; 14]. Cashew bark boiled in water can be used to treat non-infectious diarrhea and as an antiseptic and healing agent [16]

The fruit and pseudofruit of this species are used in the food, cosmetics and pharmaceuticals manufacturing. The oil from the nut has a high nutritional value, with a high content of oleic acid and other bioactive compounds like tocopherols and sitosterol [17 and 18]. The Soxhlet extraction yield of cashew nut oil using petroleum ether / ethyl ether 1: 1 (v/v) is approximately $33.1 \pm 0.6 \%$ w/w, but this percentage may vary according to the extraction methodology. The major acids present in cashew oil are oleic acid, followed by linoleic acid and palmitic [17].

3. Favela (*Cnidoscolus quercifolius* Pohl or *Cnidoscolus phyllacanthus*)

Belonging to the Euphorbiaceae family, Favela it is well recognized for its high drought tolerance. Its xerophilic character allows the plant to grow and reproduce, even in prolonged periods of drought, helping to maintain the balance of the ecosystem by mitigating environmental degradation [19]. Favela tree is an arboreal plant (reaches 4 meters in height) with abundant spines, with characteristic tuberous roots, also called xylopodia, specialized in storing organic matter produced in the rainy season and used during the drought. At the end of the rainy season, the leaves ripen and fall, this characteristic represents greater resistance during droughts. The leaves are long, thick, lanceolate, with the presence of stems in the limbus, the stinging spines can be constant or not. There are also thorns at the leaf insertion sites. The flowers are dioecious, with pentameric petals. The fruit is dry, dehiscent, capsule-shaped and has stinging hair on the surface [20; 21]. The propagation of the favela occurs sexually from the propagation of seeds. Although the plant is monoecious, there is a prevalence of cross-fertilization, with the dehiscence of the fruit occuring between 56 and 57 days after fertilization and

the subsequent explosive opening of the fruit launching the seeds 30 m away from the mother plant. The asexual propagation is complex, since the species has a difficult rooting process, with no records of planting fields from seedlings [22]

The seeds are brown-gray, ovoid, rigid and smooth, similar to those of castor bean (*Ricinus communis* L.), which belongs to the same family. Silva et al. (2014) [23] reported in a study of 100 species from the Caatinga Euphorbiaceae family, showing that favela is the species with the highest oil content (22.6–33.5% w/w). Favela oil is edible, and its seed has no toxic proteins, so this oilseed plant represents a potential oil source for human nutrition. However, handling and consumption must be done with care due to the toxicity generated by hydrocyanic acid [21; 22] The distribution of fatty acids showed that the favela oil is made up of fatty acids with 14–20 carbons. Unsaturated fatty acids predominated (75.49%), with linoleic (C18:2n6) and oleic acids (C18:1n9) representing 54.39 and 20.13% of total fatty acids, respectively.

Thus, Favela oil may be an alternative to similar edible oils such as sunflower oil (*Heliantus annuus* L.) and soybean oil (*Glycine max* L.). According to Arriel et al., (2005) [24] Favela dry leaves and barks are usually eaten by cattle, sheep, goats and donkeys, while the seeds are used for feeding chicken and pigs.

Besides that, Favela is a well know medicinal plant from Caatinga, being widely used in folk medicine in the treatment of injuries, urinary tract infections and inflammatory processes. Most recently Oliveira-Junior et al., 2018 [25] confirmed that compounds extracted from Favela stem barks have a great antibacterial potential against several bacterial strains tested (*E. faecalis*, *S. aureus*, *E. coli*, *K. pneumoniae* and *S. marcescens*). Reports of favela use in folk medicine is part of the popular pharmacopoeia. The species also has the presence of latex, widely used for medicinal purposes. Favela is present in the semiarid regions of Caatinga, specifically in the states

of Ceará, Rio Grande do Norte, Paraíba, Pernambuco, Alagoas, Sergipe, southwestern Piauí, some regions of Bahia and northern Minas Gerais [21]

4. Licuri (*Syagrus coronata* (Mart.) Becc.)

This highly drought-resistant palm tree from Arecaceae family, is an endemic species in semi-arid regions of the Caatinga, covering the eastern and central areas from Minas Gerais North to Pernambuco South. Licuri palm tree has a medium height measuring between 8 to 11 m. Being also called big-headed coconut, it has a stipe stem covered by old leaf sheaths. The plant is monoecious, the male flowers are long, contains six stamens and a leathery aspect. The female flowers are smaller and have a supernary ovary. The yellowish inflorescence can reach up to 1m in length.

Licuri fruit is classified as drupa for being a highly developed, divided into two very specialized parts, with the fleshy mesocarp, often edible, attractive for dispersion, and a hard endocarp, which protects the seed. This drupa fruit has a liquid endosperm that, as it ripens, it turns into a fleshy (solid) endosperm that will originate the almond. After ripening the fruits go from green to a light yellow-orange color [20; 26]. It can bloom and bear fruit for several months of the year, however the months of March, June and July are the more favorable for better fruit production. Licuri palm tree is one of the most explored native species in northeastern Brazil. The extractivism of native species is the main form of exploitation, considering that their propagation is sexual.

According to [26] the time necessary for Licuri palm tree to provide mature fruits is between 6 to 8 years old. Each tree can produce four bunches per year. Licuri bunches are 30 to 40 cm long, have an average of 1.357 small coconuts, each 2 to 3 centimeters long and approximately 1.5 cm in diameter. However, the production of

Licuri Fruits may vary according to the amount and distribution of rainfall, soil conditions and the presence of other native plants.

Through appropriate management practices it is possible to improve and maintain higher production averages. In conditions of adequate moisture, temperature and light, germination can take between 3 and 4 months. Dormancy break treatment is recommended to accelerate the germination process and optimize [27]

According to Crepaldi et al., 2001 [28], the oil is concentrated in the endosperm of the seed fruit, having 49.2 % w/w_{dry} of lipids, against 4.5% w/w_{dry} of lipids in the mesocarp. Licuri endosperm oil is an important food and feed resource for humans and animals in semi-arid zones. It is widely exploited for frying, cooking and soap production. The flavor of Licuri seeds and oil is reminiscent of that of coconut (*Cocus nucifera*) reaching few shades of taste and aroma of the almonds, probably due the high percentage of lauric acid in its composition (>40% of total fatty acids). Studies conducted by Pereira et al., 2010 [29] demonstrated that Licuri endosperm oil supplementation in goat milk led to higher acceptability scores for flavor and odor. In addition, Santos et al., (2019) [30] demonstrated that Licuri oil has antibacterial properties against *S. aureus*, thus having potential in antimicrobial product development, but so far there is no record in the pharmacopoeia.

5. Pinhão-Bravo (Jatropha mollissima Pohl Baill)

Belongs to the Euphorbiaceae family, which comprises approximately 321 genera and 8000 species. The name of the *Jatropha* genus has its origin in Latin, in which *iatrós* means "doctor" and *trophé* "food", suggesting its medicinal properties [31]. According to Sabandar et al., (2013) [32], several species of *Jatropha* have been described especially in folk medicinal uses to cure stomachache, inflammation, leprosy,

dysentery, anemia, diabetis, to treat opthalmia, ringworm, ulcers, malaria, skin diseases, bronchitis, asthma and as an aphrodisiac. Pinhão-Bravo is an endemic Caatinga species occurring exclusively in this biome. It is an easy to cultivate perennial shrub with a size less than 5m in height [31; 11]. The stem is aerial, of the trunk type and branched. The leaves are alternate, complete, with parallelobular ribs. The leaf is light green, there is hair on both sides of the leaf and on the petiole. Terminal inflorescence is classified as cimosa. The fruits are schizocarp type, measuring around 28 cm in length and 21 in diameter, have green color, simple, globose and dehiscent, with a longitudinal opening after ripening. The seed is dark in color, with thick tegument and large endosperm. The spread is sexual with the dried fruit having three explosive dehiscence that throws the seeds up to 1.8 m away from the mother plant [33; 34].

Leal and Agra (2005) [8] reported that the oil extracted from the seed is used as an animal purgative. Unlike other species of the genus *Jatropha*, the quality of the oil extracted from the seed of *Jatropha mollissima* is still little reported in the literature, especially in relation to the composition of fatty acids. According to Barros et al., (2015) [11], the mean oil content of Pinhão-Bravo is 18.3% w/w, with a higher content of unsaturated than saturated fatty acids. Indeed, Linoleic (C18:2) and oleic (C18:1) acids represent around 58-63 % and 17-19% of total fatty acids. It is important to note that depending on the origin, the oleic and linoleic acid content may vary.

6. Pequi (Caryocar brasiliense)

This kind of tree is from Caryocaraeae family, and in the Brazilian northeast it can occur in the Caatinga biome transition regions with Amazon, Cerrado and Atlantic Forest biomes, being found in the states of Minas Gerais, Maranhão and Piauí [20; 35].

Pequi is an indigenous word which means "covered with thorns", due to the prickly endocarp of its fruit [36].

Pequi tree is an arboreal plant (8 to 12 m), that has gray bark, thick and crooked branches. The leaves are composed, opposite and with leaflets covered with hair. The flowers (8 cm) are bisexual and pentamerous. The roots are deep pivoting (axial) type. The fleshy fruit is of drupa type, containing from two to six putamens inside, which are made up of seeds strongly linked to the rigid and spiny endocarp. The mesocarp is bulky, yellowish and oleaginous and the epicarp is light green [20]. Its considered semi-deciduous, as it presents partial loss of foliage in the dry period. The main form of propagation is through its seeds. However, the pequi cultivation is limited due to the presence of dormancy in the seeds. Extractivism is the main form of exploitation.

The dormancy of the pequi seed is twofold (physical or cutaneous and physiological). The physical form of dormancy is caused by the stiffness of the endocarp, while the physiological one is caused by biochemical inhibitors present in the embryo. This physiological characteristic of seeds makes propagation difficult, causing low germination rate. It is necessary to perform dormancy breaking techniques to optimize germination.

Although the extractivism of wild specimens is the main way of obtaining the fruit and seed, asexual propagation techniques, such as grafted seedlings, have been used in order to domesticate the species, obtain good quality seedlings and expand commercialization [20; 37; 38]

It is a species that has been widely explored due to the high oil content present in both pulp and seed core, which reaches around 70.16 % w/w. The oil from the seed mainly contains palmitic (34.4%) and oleic (56.1%) acids. Pequi oils (pulp and seed) have great economic relevance for local communities, being used as cooking oil and

replacing butter [36]. The oil can be used for the manufacture of sweets, ice cream and liquors, in addition to having applicability in the pharmaceutical, cosmetic and lubricant industries. Although this species has great economic potential, it is important to note that the destruction of native forests, the growth of agricultural frontiers and the extraction of fruit were factors that contributed to putting Pequi at risk of extinction [20].

7. Oiticica (*Licania rígida* Benth)

From Crysobalanaceae family, this plant is present in the riparian forests of the Caatinga found near intermittent rivers of Brazil northeastern from the watersheds of Piauí, Ceará, Rio Grande do Norte and Paraíba. In this way, the Oiticica have great value in the preservation of riverbanks and temporary streams. The tree can reach up to 20m in height, the thick trunks have a branch close to the ground, the yellow flowers branch in the bunches and the fruit has an ovoid shape measuring between 4 and 6 cm in length. Its leaves are perennial, thick, rough and covered with thick cuticles. These foliage characteristics are adaptations to drought that prevent excessive water evaporation [39].

The exploration of the Oiticica is exclusively extractivist. The production of native specimens does not occur on a regular basis, and can happen once in many years, with some plants bearing fruit and others not. The average annual production of a 10 years old tree is approximately 30 kg of almonds, while in grafted plant orchards, the production is 75 kg and can reach 100 to 200 kg if the pest control is done effectively [20].

Oiticica oil is extracted from the almond seed that can be found in the ripe fruit. The oil extraction yield can easily exceed 50% w/w_{dry}, with some variations

observed depending on the fruit's maturity level, genetic variability, and conservation status [39; 40]. Nowadays, Oiticica oil is not considered an edible oil. It is mainly being used in the production of paints, varnishes, enamels, soap industries with some research in its application as biodiesel raw material [41]. Oiticica oil is usually applied in varnishes due its fatty acid composition that contains high levels of conjugagated polyunsaturated fatty acids like α -Eleostearic acid (16.9%) and Licanic acid (43.2%).

8. Discussion

8.1. Oil content, Fatty acid composition, additional bioactive compounds and oleochemistry potential

The productiveness and applicability of oil from plants depends on several factors, such as seed oil content its proprieties and fatty acid composition. Examining the seed oil contents and proprieties, as shown in Tables 1, it is possible to have a first glimpse on the performance of the plants analyzed as oleaginous sources.

In this sense, Pequi demonstrates the highest potential as edible oil source, being followed by Oiticica. However, more research regarding Oiticia oil application for human consumption would be required, but until now, Oiticica oil is not considered as an edible oil, probably because of its high oxidability, being apply to manufacture varnishes, to coat containers for food, beverages, and medicines [49]. Despite the high amount of oil, this percentage may vary between samples according to different maturation degrees and fruit storage conditions. For instance, De La Salles et al., (2010)[46] reports a yield of oil extraction from Licuri Kernel of 39%, while Iha et al., (2014) [50] and Crepaldi et al., (2001) [51] shows 50% and 49.2%. These differences

also can be attributed to the use of fruits from different locations, being collected in the states of Bahia and Maceió.

Due to structural diversity, fatty acids are extensively used as feedstocks for food applications and the oleochemicals industry for the manufacture of soaps, detergents, lubricants, coatings, and cosmetics among other specialty products [52].

It is possible to observe that the oilcrops listed above have distinct fatty acid compositions (Table 2). Among them, Licuri oil is the only one that has more saturated than unsaturated fatty acids in its composition, and one has to take some care regarding its ingestion to obey the medical guideline recommendations for saturated fatty acids, the intake of which should not exceed 10% total daily energy [55]. On the other hand, Licuri oil is rich in the medium chain lauric acid and it could be an interesting oil source for the oleochemical industry and for the obtention of lipid-based formulations with various applications in pharmaceutical products and cosmetics [56; 57; 58]. So far, coconut and palm kernel oils are the main oil sources for these applications [57].

These oils with medium chain saturated fatty acids are particularly attractive because they are less sensitive to oxidation and they allow the synthesis of various esters and mixtures of esters with peculiar dispersion properties when mixed with water [58]. It was already proposed that Licuri oil, because of its lipophilic adjuvant and hydrating characteristics, could be used in cosmetics in replacement of traditional oils like sweet almond oil [59]

All the other oils of Caju, Favela, Pinhão-bravo and Pequi have a more unsaturated fatty acid profile and seem more adapted to nutrition. Favela and Pinhão-bravo oils are rich in the essential linoleic fatty acid, which has vital functions in the structure of the cell membrane and in metabolic processes. Linoleic acid can be metabolized into arachidonic Acid, a 20-carbon polyunsaturated fatty acids which is the

precursor of eicosanoids [60]. The increase of dietary intake of linoleic acid is associated with a reduced incidence of cardiovascular diseases (mainly coronary artery diseases) and of new onset metabolic syndrome or type 2 diabetes. However, high quality clinical trials are needed to assess both the actual amplitude and the underlying mechanisms of the health effects related to dietary intake of this essential fatty acid. Nevertheless, these types of oils, are like rapessed oil, are more sensitive to oxidation and must be processed with caution.

Caju and Pequi oils are richer in oleic acid which also provides nutritional benefit and affords oxidative stability to the oil, that like corn, soybean and sunflower oil that enables the use in cooking processes that involve high temperatures [61]. Among various functions, the intake of oleic acid elevates circulating levels of the endogenous lipid mediator ethanolamide oleoylethanolamide (OEA) that plays a role in modulation of lipid metabolism and energy intake in humans [62].

Therefore, a great diversity of fatty acids that can be found in exotic Brazilian plants. Special attention needs to be given to Oiticica oil, for containing conjugated fatty acids like α -Eleostearic and Licanic. α -Eleostearic Acid is a C18 ω -5 unsaturated fatty acid with three conjugated double bonds (18:3 Δ 9 cis, 11 trans, 13 trans) while Licanic acid is a keto derivate from α -Eleostearic Acid with an oxo (keto) group at the ω -15 carbon [63]. This fatty acid can be used for making resins [64]. Besides having industrial applications in varnishes and paints, Eleostearic acid has been documented to have anticancer properties [65]. Others conjugated fatty acids like conjugated linoleic acids (CLA) have been receiving more attention for their antioxidant, antiobesity, anticarcinogenic, antiatherogenicity, and antidiabetic activities [66].

The conjugated trienoic α -Eleostearic acid (9c,11t,13t-octadecatrienoic acid) is well known for its high levels in Tung oil (up to 70% of total fatty acids) extracted from

Aleurites fordii seeds and used in Chinese lacquers because of its drying or siccative properties [67; 68]. Licanic acid (4-keto-9c,11t,13t-octadecatrienoic acid) is a keto derivative of α -eleostearic acid. Furthermore, the conjugated triene present in α -eleostearic acid constitutes an intrinsic chromophore, which confers strong UV absorption properties to this fatty acid (λ_{max} = 272 nm) and the triglycerides and phospholipids in which it can be esterified. These properties were important for the recent development of spectrophotometric assays for testing antioxidants such as the Conjugated autoxidizable triene (CAT) assay [69], and for measuring lipase [49, 70 and 71]; and phospholipase activities [72]. Thus, the peculiar fatty acid composition of Oiticica oil offers a great potential for various applications in health and oleochemistry.

Besides oil fatty acid profile, it is also worth paying attention to the bioactive compounds that can be found in the oil and in the unsaponifiable matter, such as vitamins and sterols, among others [73]. Bioactive substances present in plants have become popular as complementary or alternative therapeutic agents to manage and/or treat chronic diseases [74]. Some authors have been using pressurized fluid to extract lipids without (or with minimal) degradation/decomposition of valuable bioactive compounds, such as vitamins, sterols, and fatty acids, among others [17; 75]

For instance, Tawa et al. 2015 [76] reported that cashew oil can produce around 1.64 mg/g of unsaponifiable matter and recently Zanqui et al., 2020 [17] showed the route to obtain 18-19 mg of tocopherols and 60-70 mg of sitosterol per 100 g of cashew oil by extraction performed using pressurized n-propane and 6% ethanol as cosolvent. While Santos et al., (2020) [75] extracted favela oil using supercritical CO_2 to obtain an oil with 40.1 mg of tocopherols and 171 mg of β -sitosterol per 100 g of favela oil.

Besides that, the use of an Pectinolitic enzymatic pretreatment in obtaining Pequi pulp oil by cold pressing by [73] proved to be very efficient to obtain more unsaponifiable matter (around 2.8%) that correspond, among others, to compounds present in oils such as sterols, tocopherols and carotenoids. Thus, enzymatic pretreatments may help improving global biorefinery processes for a better valorization of all compounds from Pequi pulp.

Likewise, the degree of fruit maturation also influences the amounts of bioactive compounds extracted, like carotenoids. Oliveira et al. (2006) [77] found values of 67.8 μ g/g of carotenoids in Pequi fruits collected from trees, 83.7 μ g/g in fruits collected on the ground and 113.4 μ g/g in fruits collected on the ground after natural fall and stored for 3 days at room temperature. Conversely, carotenoid losses due to degradation after oil extraction, such as those caused by light, can occur. The main carotenoids identified in Pequi oils were zeaxanthin, β -cryptoxanthin, and β -carotene.

Regarding Licuri oil, the presence of additional bioactive compounds has not been documented. However, Paula Filho et al., 2015 [78] studied the nutritional composition of Licuri kernel, from which the oil is obtained, and they showed the presence of α -carotene, β -carotene, β -cryptoxanthin, α -tocopherol, α -tocotrienol, β -tocopherol, β -tocotrienol, γ -tocopherol and γ -tocotrienol. No data for Oiticica and Pinhão-Bravo seed was found, reinforcing the need to better characterized these bioressources for their potential application.

8.2. Products from Brazilian semi-arid ecosystem: retrospective and novel perspectives

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Recently, the European Commission (2018) defined the Bioeconomy and circular bioeconomy (CBE) concepts to cover the production of several renewable biological resources and their conversion to various high-value bio-based products such as food, feed, biochemicals, and bioenergy [79]. The concept promises to mitigate the effects of climate change while providing a renewable carbon source (biomass) as well as creating business, employments and opportunities, especially in the rural areas. In order to fulfill these expectations, the biorefinery concept plays a key role to optimize the conversion of biomass and to achieve the goals set for CBE [80]. This concept led many countries to develop integrated biorefineries [81]. The key to the sustainability of chemical production processes is the feedstock. For bulk-chemicals the feedstock contributes to nearly 70-80% of the production cost. However, to have a higher relevance today these processes needs an environmentally friendly approach and the use of a sustainable feedstock is an essential pre-requisite for future bulk-chemical production processes [82]. There is still a huge gap between the expectations and the actual performance of biorefineries circularity. The definitive roles of stakeholders – local and international government agencies, the academic community, and private companies – as well as their inter-relationships remain to be clarified which necessitates systematic and comprehensive investigations. Policy frameworks and incentive systems need to be aligned with the most recent scientific outcomes and relayed accordingly to the concerned private sectors, which in turn, initiate the deployment of these innovations into effective practice, and later on provide immediate feedback regarding possible areas of improvement [80].

The world's agriculture and oil industries use only a few species. Some of these species have been known for centuries, but there is a growing interest in alternative oil sources from tropical floras [83; 84]. Thus, it is necessary to search for new oil crops with oleochemical potential in a sustainable way, minimizing environmental impacts due the exploration. In this context, information regarding the potential of renewable oil sources from Brazilian semi-arid ecosystem (Cattinga) can open doors to news discoveries and applications. The valorization of this biomass may suggest new models of sustainable biorefinery with biological conversions including microbial biocatalysis, enzyme biocatalysis, hybrid processes, and others [82]. The six plants species from Cattinga investigated here show potential for the production of new oleochemicals; They comply with several of the 12 principles of green chemistry such as a production based on a renewable feedstock, with a low level of potential hazards and with a generation of substances with low toxicity. Because of their bio-based nature, products obtained using natural oils and fats are often biodegradable; furthermore, the CO₂ generated from their degradation can be incorporated into next year's crop, and they are likely to be nearly CO₂ neutral [85]. The biorefinery concept implies an integrated process in which all the components that are included in the biomass are utilized as raw material [82; 86]. With respect to residues from vegetal lipids extraction, its worthy to mention the potential application of the cake generated in the end of the process, which can be used as substrate for microbes in a submerged and solid state fermentation processes. Several enzymes as biocatalysts can be produced using these processes and this includes the lipases that can be used for the biotransformation of the oil previously extracted [80; 87; 88]. Also, the cake can be used in animal feed as well as in human foods. Cavalcanti et al., 2009 [89] have shown for instance the functional properties of the delipidated Favela seed kernel proteins, that

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can be used in elaborated foods that require high solubility of ingredients, high oil emulsification performance and also modification of food texture and flavor.

Due to climate changes, it is expected that plants and derived products from the Brazilian semi-arid ecosystem will have a greater sustainability then those from current temperate regions. Among the oil-crops produced in Cattinga and reviewed here, only Cashew nut, Pequi, Licuri and Oiticica are entering in the official statistics of the Brazilian government (Table 3; retrospective between 2014 and 2018) [7], showing how overlocked are Favela and the Pinhão-Bravo. Future perspective for these raw materials depends on the correct retrospective to emphasize the need for sustainable exploration, since they are important species for the biome. For instance, the severe decline of Pequi and destruction of its populations due to land degradation and deforestation contributed to making its logging illegal in some Brazilian States [90]. On the other hand some species mentioned here can play a role in the restoration of degraded areas, like the Licuri palm tree, which can act in the maintenance of other species by hosting around 30 species of epiphytic plants mainly from the Orchidaceae, Bromeliaceae and Polypodiaceae families [91]. Favela and Pinhão-Bravo can also be easily used in this sense, by having high dissemination properties and full adaptation to the conditions of the area [92]. Technological developments and assessment of biorefinery models should be based on the regional knowledge gained from Brazilian semi-arid ecosystem, including geographical and seasonal variations in these various types of oil crops, as well as the involvement of local communities.

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9. Conclusion

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Brazilian Northeast Caatinga Forest has a rich vegetal diversity, among which species like Cashew nut, Favela, Licuri, Pinhão-Bravo, Pequi and Oiticia stand out as

potential oilseeds crops, due to their high oil contends, fatty acid composition and proprieties. However, only a small fraction of this biodiversity is known and used, probably due to climatic conditions and also because this region historically concentrated most of the rural poverty in Latin America. A sustainable management of tese bioressources using a biorefinerity strategy could help improving the valorization of these oil crops, contributing to biodiversity conservation and at the same time, to the income of local populations based on nutritional and environmental value, as well as process developments. The oleochemistry potential from brazil northeastern exotic plants can be one of the sustainability tools for establishing local biorefineries, a circular bioeconomy improving the quality of life of local population and for serving a consumer market eager for new ecofriendly products.

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504	
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506	Wiltshire: collection of data, writing of manuscript; R. L. Souza: analysis of data; A.T.
507	Fricks: analysis of data; C. Dariva: writing of manuscript; F. Carrière: analysis of data
508	writing of manuscript; Á. S. Lima: conception of the work, analysis of data; C. M. F
509	Soares: conception of the work, analysis of data, writing of manuscript. All author
510	have approved the final version of this article.

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755 FIGURE LEGENDS

Figure. 1. Brazilian Biomes Map. (Source: IBGE, 2019)

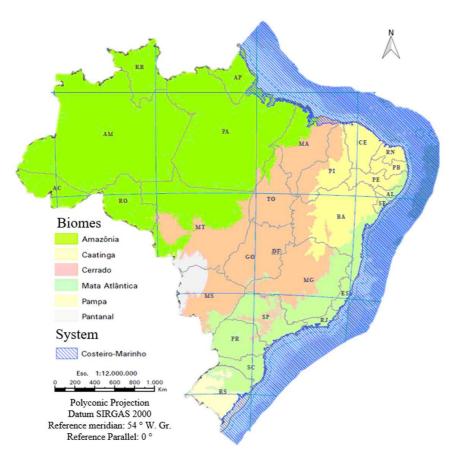
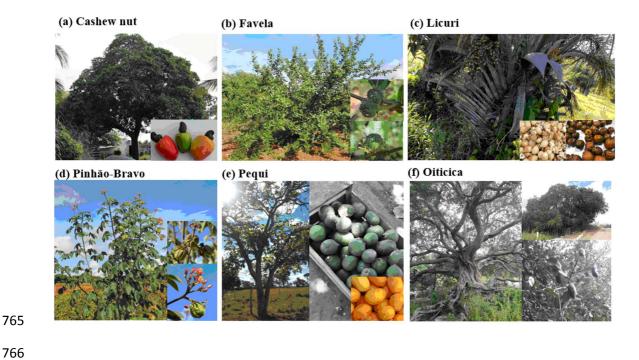


Figure 2. Representative species of the Brazilian Caatinga that can be used as a source of oil. (a) *Anacardium occidentale* L.; (author original photo collection) (b) *Cnidoscolus quercifolius* Pohl (author original photo collection); (c) *Syagrus coronata* (Mart.) Becc. (author original photo collection); (d) *Jatropha mollissima Pohl Baill* (author original photo collection); (e) *Caryocar brasiliense* (author original photo collection); *Licania rígida* Benth (author original photo collection).



767 TABLES

Table 1. Extraction techniques, yields and physical-chemical parameters of vegetable oil extracted from Caatinga oil crops. Yield of extraction and physicochemical oil parameters data are respectively from: Cashew nut [42; 43], Favela [44; 45], Licuri [29; 46], Pinhão-Bravo [11, no data available], Pequi [47; 48] and Oiticica [41].

	Fruit Part	Yield of extraction	Extraction	Acid value	Iodine value	Saponification	Peroxide value	
FeedStock			technique	(% FFA, as oleic acid)	(g of I2 per 100 g of oil)	(mg of KOH/g of oil)	(meq O2/kg of oil)	
Cashew nut	Nut kernel	33.1 ± 0.6	Soxhlet, Hexane	2.44	87.63	159.9	4.087	
Favela	Seed	33.5 ± 1.18	Cold press	4.33	109.79	121.28	6.99	
Licuri	Endosperm	49.2 ± 0.08	Soxhlet, Hexane	1.4	18.5	NA	NA	
Pinhão-bravo	Seed	18.25 ± 1.63	Soxhlet, Hexane	NA	NA	NA	NA	
Pequi	Pulp	70.16 ± 1.18	Boiling water	5.4	50.0	206.8	7.94	
Oiticica	Seed	57.0 ± 4.24	Electric press	1.52	95.4	194.0	NA	

NA: not available

Table 2. Fatty acid composition (% w/w of total fatty acids) of vegetable oils determined by gas chromatography coupled to mass spectrometry (GC-MS). All the structures are available at pubchem and chebi data bases [53; 54].

Fatty Acid	2D Structure	Cashew nut [17]	Favela [44]	Licuri [50]	Pinhão-bravo [11]	Pequi [36]	Oiticica [41]
Caprylic (C8:0)	H.0	-	-	13.00	-	-	-
Capric (C10:0)	H. 0	-	-	8.00	-	-	-
Lauric (C12:0)	H 0	-	-	48.00	-	-	-
Myristic (C14:0)	H 0	-	0.30	14.00	-	0.20	-
Palmitic (C16:0)	н 0	9.37	16.63	5.00	11.50	34.40	5.00
Stearic (C18:0)	но о	9.87	7.21	2.00	8.00	3.10	8.30
Oleic (C18:1)	H • H	66.68	20.13	7.00	18.00	56.10	10.60
Linoleic (C18:2)	H H	12.05	54.39	3.00	60.50	5.20	3.00
α-Eleostearic (C18:3 9c.11t.13t)	н _с	-	-	-	-	-	16.90
Licanic (C18:3 4- keto;9c.11t.13t)	H H O O H	-	-	-	-	-	43.20
Others	-	2.03	1.34	-	2.00	1.00	10.30

Table 3. Native species production data expressed in Brazilian local currency, reais (R\$) [7].

Application	Food				Oilseeds						
Product	Cashew nut (chestnut)		Pequi (fruit)		Licuri (coconut)		Pequi (almond)		Oiticica (seed)		
Years\Productivity	Amount (t)	Value (1.000 R\$)	Amount (t)	Value (1.000 R\$)	Amount (t)	Value (1.000 R\$)	Amount (t)	Value (1.000 R\$)	Amount (t)	Value (1.000 R\$)	
2018	1411	4189	21495	18521	1078	1562	765	2986	6	6	
2017	1421	4571	21915	21287	1151	1502	832	3098	6	7	
2016	1775	4894	17305	14766	3787	3741	1471	4042	7	7	
2015	2160	4670	18866	14236	4072	4039	2228	4897	15	9	
2014	2489	4386	19241	14589	3744	3974	1381	4059	16	10	