Rodriguésia 73: e00892021. 2022
http://rodriguesia.jbrj.gov.br
DOI: http://dx.doi.org/10.1590/2175-7860202273074

Original Paper

Assigning a value to standing forest: a historical review of the use and characterization of copal resin in the region of Santarém, Central Amazonia

João José Lopes Corrêa[1,3], *Thaís Elias Almeida*[2,4], *Manoel Roberval Pimentel Santos*[3,5]
& *Leandro Lacerda Giacomin*[2,6,7]

Abstract
Amazonia contains the largest remnant of continuous forest on the planet. In Brazil, it represents nearly 45% of the territory but contributes little to the country's economy. This work discusses the use of jutaicica copal resin extracted from tree species of the genus *Hymenaea* (Fabaceae), which once represented a considerable part of the economy of Pará state. We present a review of its historical use, explore how and for what purpose the resin is extracted, and characterize it based on thermal and spectroscopic techniques. In western Pará state, jutaicica is gathered mainly from two species, *H. courbaril* and *H. parvifolia*, and in the past was used as a valuable source for varnish production. The resins from these species are distinctive according to thermal and spectroscopic methods. Thermal analysis shows *H. courbaril* might be a better source for polymer gathering. Infrared spectra can be accurately used to differentiate sources and demonstrate more uniformity in samples from *H. courbaril*, which is corroborated by the ^{13}C-RMN spectra of the analyzed batches. Jutaicica is one of many non-timber forest products lacking investments for economic reintegration, an important contribution of income in extractive reserves, which play a key role in the conservation of Amazonia.
Key words: *Hymenaea*, jutaicica, spectroscopy, thermal analysis, varnish.

Resumo
A Amazônia contém o maior remanescente de floresta contínua do planeta. No Brasil, representa cerca de 45% do território, mas contribui pouco para a economia do país. Este trabalho discute o uso da jutaicica, resina copal extraída de espécies arbóreas do gênero *Hymenaea* (Fabaceae), produto que já representou parte considerável da economia paraense. Apresentamos uma revisão histórica de seu uso, exploramos como e com que finalidade a resina é extraída e sua caracterização térmica e espectroscópica. No oeste do estado do Pará, a resina jutaicica é obtida principalmente de duas espécies, *H. courbaril* e *H. parvifolia*, e no passado era valorizada como matéria prima para a produção de verniz. As resinas dessas espécies são distintas de acordo com métodos térmicos e espectroscópicos. A análise térmica mostra que *H. courbaril* possui maior conteúdo de matriz polimerizada. Os espectros no infravermelho podem ser usados com precisão para diferenciar as fontes e demonstram maior uniformidade nas amostras de *H. courbaril*, o que é corroborado pelos espectros ^{13}C-RMN analisados. Jutaicica é um dos muitos produtos florestais não madeireiros que carecem de investimentos em ciência e tecnologia para uma reintegração econômica, uma importante contribuição de renda nas reservas extrativistas, que desempenham um papel fundamental na conservação da Amazônia.
Palavras-chave: *Hymenaea*, jutaicica, espectroscopia, análise térmica, verniz.

See supplementary material at <https://doi.org/10.6084/m9.figshare.20452275.v1>

---

[1] Instituto Nacional de Colonização e Reforma Agrária, Superintendência Regional no Oeste do Pará, Fátima, Santarém, PA, Brazil. ORCID: <https://orcid.org/0000-0003-1378-3705>.

[2] Universidade Federal do Oeste do Pará, Herbário HSTM, Santarém, PA, Brazil.

[3] Universidade Federal do Oeste do Pará, Pró-reitora de Pesquisa, Pós-graduação e Inovação Tecnológica, Aldeia, Santarém, PA, Brazil.

[4] ORCID: <https://orcid.org/0000-0002-1611-1333>. [5] ORCID: <https://orcid.org/0000-0003-2014-4725>. [6] ORCID: <https://orcid.org/0000-0001-8862-4042>.

[7] Author for correspondence: giacomin.leandro@gmail.com

Introduction

The Northern region of Brazil is almost completely within the Amazon biome and occupies 45% (8.5 million km²) of the country (IBGE 2012). This enormous region contains the largest area of continuous tropical forest on the planet but contributes only 0.8% to the country's plant production value, including the extraction of native trees (0.6%) and non-timber forest products (NTFP) (0.2%), which are mostly related to açaí [*Euterpe oleracea* Mart., Arecaceae (1824: 29–31)] and Brazil nut [*Bertholletia excelsa* Bonpl., Lecythidaceae (1807: 122)] (IBGE 2013a, b). The small profitability of native forest products contributes to the fast expansion of alternative land uses, such as pastures and crops (preferably short cycle), especially when they are substituted for similar products of higher quality and lower cost. Revitalizing the economic contribution of Amazonian diversity in the globalized urban market depends on improving the quality, uniformity, and cost of products, which is only achievable through science, technology, changing how access to genetic heritage is regulated (Clement 2007), and, above all, the formation of an educated and skilled labor force to leverage a new development model (ABC 2008).

Considering the lack of scientific studies of many Amazonian products, the present work aims to provide an exploratory case study of copal resin, a non-timber forest product. The Amazonian copal belongs to the group of autochthonous natural resins from a remarkably diverse biome and has contributed for centuries to the extractive economy. A mega diversified biome that is intended to be preserved must offer an equally broad and diversified array of products. Autochthonous products such as copal and fixed oils, for example, are examples of non-timber forest products that are relatively little studied today. Copal still has a local use as a waterproofing internal lay of clay pots from regional crafts, an opportunity for use that has not been studied yet. Furthermore, it has applications in furniture and antique artworks restoration (Fearon 2009), and more recently in the production of precious gems (Abduriyim *et al.* 2009), suggesting that it may once again constitute one of the items in the extractive economy product basket.

The term copal is derived from the classical Nahuatl (Aztecan language) word *copalli*, which means incense or resin, and was adopted in international commerce to refer to naturally hard resins that are durable and have high melting points (Langenheim 1996). Copal is obtained from resin exuded from the trunk of various tropical tree species. In South America, the product is extracted exclusively from the genus *Hymenaea* (Fabaceae). In Africa, the main sources are species of *Copaifera* (Fabaceae), *C. demeusei* Harms (1897: 195) in the Congo and *C. copallifera* Bennett (1857: 150) Milne-Redhead (1934: 400) in western Africa, as well as *Hymenaea verrucosa* Gaertner (1791: 306) in coastal East Africa. In Asia, production is restricted to the species *Agathis alba* (Lamarck 1786: 259) Foxworthy (1910: 173) (Araucariaceae) (Howes 1949; Langenheim 1996).

The copal resin was for long used for varnish manufacturing, an old, well-established, and free of patent restrictions and related difficulties practice (Mantell *et al.* 1935). The resin is a sustainable forest product, unlike alternatives from the petrochemical industry. The earliest known references about the technique of preparing the varnish by fusing the natural resin with linseed oil are cited in a compilation of medieval techniques from the beginning of the XII century (Violette 1862 *apud* Fearon 2009). Its use as an external finish for wooden vehicles of the aristocracy, furniture, and interior decorations persisted until the beginning of the XX century in Europe when it was gradually replaced by synthetic products (Sunseri 2007; Fearon 2009).

In Brazil, the first written record of use was an official 1770 document of the king of Portugal (Elrey Dom José 1770) that announced the discovery of jutaicica resin and decree of the monopoly of its commercialization. However, the extraction and production of South American copal never reached importance in the global market. In the XIX and XX centuries, imports in the United States mainly came from Africa, such as Zanzibar on the west coast (Fearon 2009) and the Belgian Congo in the central region (Mantell *et al.* 1935; AGIA 1936). Freise (1934 *apud* Howes 1949) cites the instability of supplying Brazilian copal resin to the global market and highlights Pará state as the main region of origin of the product.

In the genus *Hymenaea*, trunk resin is secreted through two anatomical mechanisms: i) either into schizogenous pockets, formed by separation of adjacent secretory cell walls, where the resin is deposited and remains stored and isolated, or ii) into lysigenous cavities, formed by the breaking down of the walls of secretory cells (Langenheim *et al.* 1973). When the bark is ruptured by any form of injury, the liquid runs out through the cracks (Fig. 1). This process can serve to protect surfaces by engulfing small herbivores and protecting exposed surfaces from pathogenic attack, for example, by fungi (Langenheim 1969, 1996). After exudation to the outside of the trunk, the fluid resin gradually loses its volatile components, which also act as plasticizers, and reactions of polymerization of unsaturated constituents and resin solidification initiate (Cunningham *et al.* 1977; Clifford & Hatcher 1995). The final product is a vitreous matrix that keeps trapped lower molecular weight components that predominantly comprise labdanic acids (Nakano & Djerassi 1961; Cunningham *et al.* 1973, 1974).

The main sources of information about the physical and chemical properties of these resins, useful to guide its use and to compare to other available materials, come from studies about the relationships between them and the valuable amber, their fossilized form. Frequently analytical techniques are applied to solid bulk material and thus reflect an effect of all molecular constituents and provide a signature that is not dependent on the separation of components. Analyses such as Infrared spectroscopy (IR) and carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) are used to identify different types of carbon and functional groups the material has. Thermal analysis (TA) techniques such as Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) measures the decomposition mass changes and the heat flows as a function of temperature and are usually applied to investigate resins composition and resistance (*e.g.*, Langenheim 1969; Cunningham *et al.* 1983; Anderson *et al.* 1992; Clifford & Hatcher 1995; Langenheim 1996; Rodgers & Currie 1999; Martínez-Richa *et al.* 2000; Ragazzi *et al.* 2003; Feist *et al.* 2007; Guiliano *et al.* 2007; Lambert *et al.* 2008; Regert *et al.* 2008; Rao *et al.* 2013).

Figure 1 – a-d. Trunk resin exudate of *Hymenaea* spp. – a. cross-section of *H. courbaril* log; b. a hardened coating of transparent resin exuded from a two-month-old, fresh cut (21/06–26/08/2014) in *H. courbaril*; c. lumps of hard resin from a large man-made wound in *Hymenaea* sp.; d. hanging from a natural break of an *H. parvifolia* branch.

Based on available data, it is known that the basic molecules of copal are diterpenes with a labdane-type carbon skeleton, compounds with twenty carbon atoms containing a bicyclic nucleus, functionalized with acidic and alcoholic groups (see Clifford & Hatcher 1995 and Lambert *et al.* 2008 for representations of the labdatriene structures), but just a few works that consider samples from Brazil, once a practicable source of copal, are available.

In the 1930s, Rangel & Schneider (1936) described how the lack of scientific and technological knowledge of the Brazilian copal resin, which is still important nowadays, made it difficult to use. They also contributed with recommendations drawn from foreign research and with their experimental results.

As once an alternative producer of copal, Brazil had the state of Pará as the most important source of the product, where it was collected from the exudate of tree trunks of *Hymenaea* species and referred to as jutaicica (Le Cointe 1947; Rangel & Schneider 1936; Howes 1949). Considering that jutaicica copal resin once represented an important component of the economy in the state, especially in the municipality of Santarém, this study sought to verify the actual importance of the product within a regional context and its possible revitalization, considering the region as a case study.

Thus, to contribute to economic production within a standing Amazonian Forest, this work aims to provide exploratory research on jutaicica resin from the region of Santarém, Pará, including (i) a historical review of its extraction and trade and (ii) the characterization of some physical and chemical properties of local products, to better understand their diversity if in the future there is interest in pursuing of redeeming its potential as a non-timber forest product.

Material and Methods

Documentary information

Historical information about the production of jutaicica resin in Brazil, in the state of Pará, and Santarém was obtained by analyzing statistical yearbooks of plant extractive production and foreign trade monitoring for Brazil (MF 1919, 1935, 1947, 1954, 1961; INE 1936; IBGE 1976, 1979, 1981a, 1981b, 1981c, 1982, 1984, 1985, 1986a, 1986b, 1987), as well as annotated notebooks of the sale of products in the Maguari community (a supposedly important source region) between July 1986 and April 1987, preserved by Mrs. Raimunda Feitosa Pedroso (personal communication), from which an informed consent was obtained, presented in the supplementary material (available at <https://doi.org/10.6084/m9.figshare.20452275.v1>). The export value of jutaicica resin for the municipality of Santarém in 1947 was found in the 1948 publication "Álbum do Centenário da Elevação de Santarém" (Santarém 1948).

Location of botanical sources and collecting resin samples

To characterize the products available in the regional Santarém market, the collection sites were tentatively mapped. Information on the location of living specimens was obtained from former traders and residents of the communities that supplied the extractive products (see locations in Fig. 2).

Individual trees were mapped with the help of a GPS device and pieces of resin were located and collected between May and June 2014 from eight trees in the following areas: Vila Nova (n = 1), along the middle stretch of the Uruará River, in the municipality of Prainha; and Maguari (n = 3) and Jaguarari (n = 4), in the municipality of Belterra, on the right bank of the lower Tapajós River in Floresta Nacional (FLONA) do Tapajós (Fig. 2). Each specimen was labeled with a sequential code of three letters and a number. All resin accumulated on the soil and at accessible parts of the trunk was collected and quantified. The pieces of resin collected from each tree were divided into subsamples based on transparency and color and weighed.

During the fieldwork, in fragments of what was considered to be primary forest, a very large accumulation of resin pieces was found on the ground in the former site of a tree long since decayed; however, it was not possible to identify the tree species, so the resin was not included in the study.

To allow a trustable identification of the tree species from which the samples were collected, vouchers of the specimens were produced and deposited at HSTM under barcodes HSTM000007 and HSTM000008 (for specimens' details, visit <http://hstm.jbrj.gov.br/>). Duplicates were sent to experts for confirmation (R. Barbosa Pinto, UEC Herbarium, personal communication). All acronyms of herbaria cited in the text are following the Index Herbariorum (Thiers, continuously updated). Authorization for research collections was obtained from ICMBio (collection permit nº

43861-1/06/16/2014) and a registration to access genetic heritage was carried out in SisGen (study registered under # AEC109F). Approximate density and frequency estimates of the resinous specimens of *Hymenaea* spp. were calculated considering: (1) the number of resin accumulating trees (six) found in two of the areas sampled, totaling 112 hectares of primary forest in Maguari and Jaguarari communities at FLONA do Tapajós; and (2) the average density of *Hymenaea* spp. equal to 0.5

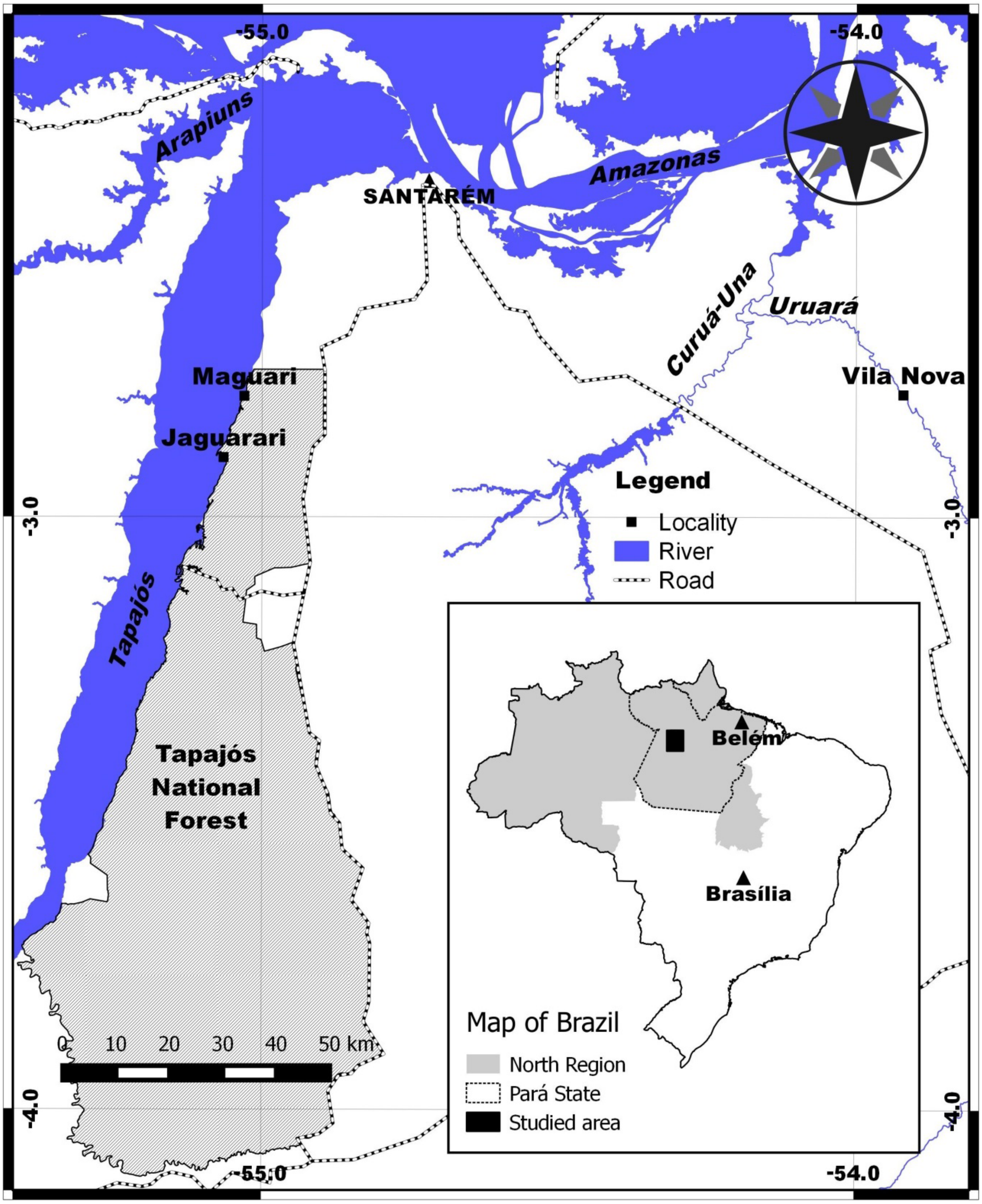

Figure 2 – Map of the studied area, showing the limits of the Floresta Nacional do Tapajós in grey, and the Tapajós river in blue. The inset at the lower right shows the location of the Lower Tapajós Basin.

trees hectare^{-1}, with an amplitude of 0.2 to 0.9 trees hectare^{-1}, and a higher relative frequency of *H. courbaril* Linnaeus (1753: 1192), according to pre-harvest forest inventories of eight annual production units located on 7,100 hectares of undisturbed areas in the FLONA do Tapajós (L. Melo, personal communication). These parameters are corroborated by a previous inventory of 144 hectares of primary forest by Silva *et al.* (1985) that found a density of 0.7 trees of *Hymenaea* spp. hectare^{-1} with a relative frequency of 67% of *H. courbaril.*

Characterization of jutaicica resin using thermal analysis

A combination of Thermogravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC) techniques were applied to characterizes four resin samples (two samples of each species). The thermogravimetric curves (TG) and their first derivative (DTG) were obtained with a thermo-microbalance (Netzsch, TG 209, Selb, Germany) at a temperate range of 22 to 700 °C and heating rate of 10 °C min^{-1}, in an atmosphere of synthetic air + argon (2:1) with a flow of 30 mL min^{-1}. The temperature (°C), time (minutes), mass (%), and DTG (% min^{-1}) values were collected every 0.05 minutes and saved as a text file.

The Differential Scanning Calorimetry (DSC) curves were obtained with a DSC module (Q20, TA Instruments, New Castle, DE, USA), from room temperature to 550 °C and a heating rate of 5 °C min^{-1}, in an atmosphere of air + argon (1:1) with a flow of 100 mL min^{-1}. The temperature (°C), time (minutes), and heat flow (mW) values were collected every 0.05 minutes and saved as a text file.

The thermal curves were analyzed using the software Origin 7.0 SRO (copyright 1991–2002, OriginLab Corporation, Northampton, Massachusetts, USA). In this study, the thermal characterization of the resins was made from the weight loss profile (TG/ DTG) and heat flow monitoring (DSC) (Ionashiro 2004).

Characterization of jutaicica resin using spectroscopic methods

Infrared (IR) spectra readings were made using the transmittance method and a spectrometer (Vertex 70, Bruker, Ettlingen, Germany), at a medium infrared spectral range (4,000 to 400 cm^{-1}), with 16 scans per spectrum and a resolution of 1 cm^{-1}, using the software Bruker Opus to control the equipment and treatment of data. For all spectra, the atmospheric H_2O and CO_2 effects were compensated for, and the baseline corrected. Two subsamples of resin collected from each of the eight trees were prepared in KBr pellets. To compare between spectra, the disc thickness and sample concentration were adjusted to obtain stronger extinction bands of around 10% transmittance (Mayo *et al.* 2003). The intensity of the peaks was described based on an arbitrary and subjective scale (strong, medium, weak). The infrared spectra curves were plotted using the software Origin 7.0 SRO (copyright 1991–2002, OriginLab Corporation, Northampton, Massachusetts, USA).

The solid-state carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR) spectra were obtained with two subsamples of resin from each of the eight trees, using a spectrometer (Avance 400, Bruker, Fällanden, Switzerland) operating at a frequency of 100.6 MHz, employing the technique of cross-polarization with magic angle spinning (CP-MAS).

The ^{13}C-NMR spectra were analyzed with the software SpinWorks 3 version 3.1.8.2 (copyright 2011, Kirk Marat, University of Manitoba, Winnipeg, Canada).

Results

According to monitoring data about non-crop plant production in Brazil, copal resin was mainly collected in Amazonia, and to a lesser extent in the Northeast and Southeast regions (Tab. S1, available on supplementary material <https://doi.org/10.6084/m9.figshare.20452275.v1>). In the first half of the XX century, the annual production of copal resin in Brazil was around 120 t year^{-1}, which is based on plant extractive production monitored in 1935 and an estimate by Rangel & Schneider (1936) of the movement of the product in Rio de Janeiro. In both cases, the state of Pará is identified as the main region of origin of the product.

Brazilian exports of copal resin sometimes surpassed 80 t year^{-1} and varied between 2.4 and 164 t year^{-1}, based on the Comércio Exterior do Brasil - COMEX, which recorded the resin as copal, jatobá, jutaicica, and goma copal. However, the quantity shipped during certain years could have been a little higher because part of the resin was included in other broadly defined groups, such as "leaves, roots and medicinal resins" and "gums, resins, and balsams," which reached 95 t year^{1} (MF 1919, 1935, 1947, 1954, 1961).

In the second half of the XX century (1974 to 1985) the average amount of copal resin extracted in Brazil decreased to 32 t year^{-1}. The state of Pará maintained its dominant participation in the activity, accounting for 80% of the national production or 25 t year^{-1} (Tab. S1, available on supplementary material <https://doi.org/10.6084/m9.figshare.20452275.v1>). Around half of this (an average of 13 t year^{-1}) was from Santarém (Tab. S2, available on supplementary material <https://doi.org/10.6084/m9.figshare.20452275.v1>).

In the municipality of Santarém, in 1947, jutaicica resin was eighth on the list of exports and contributed USD 74,000 (value corrected on 01/2021) to the economy, or a little more than 1% of the total value of the exports dominated by jute and wood (Santarém 1948). Although the physical quantity of shipped resin is not explicitly cited, it is estimated to be around 44 t based on an average historical price of USD 1.68 kg^{-1} (Tab. S2, available on supplementary material <https://doi.org/10.6084/m9.figshare.20452275.v1>).

The resale values of products from the Maguari Community from 1986–1987 allow us to estimate that the collection commercialized by the community was around 5 t year^{-1}, with a corrected unit value of USD 3.05 kg^{-1} for January 2021. These values are compatible with the total municipal production of 10 to 16 t year^{-1} and unit value of USD 1.01 to 3.11 kg^{-1} for the Santarém market between 1974 and 1985 (Tab. S2, available on supplementary material <https://doi.org/10.6084/m9.figshare.20452275.v1>).

During the period when there was commercial interest, the extracted natural resin mainly arrived in Santarém by boat. Jutaicica resin and other extract products were coming from communities along the Tapajós River, its tributaries, and other rivers near Santarém. The last large shipments of jutaicica resin were sent between 1990 and 1992 to Indústria de Tintas e Vernizes RR S.A. (CNPJ 61.576.021/0001-44) in São Paulo (personal comment, Abnatar Monteiro Marques, partner of the Souza Marques Company).

During our survey, we observed that, in the Santarém region, jutaicica is used traditionally in its raw state to waterproof clay pots and utensils used for cooking, which conserves and makes them more hygienic, as observed also by Ferreira & Sampaio (2000). In family agriculture fairs visited, the final stage of the traditional process can still be seen where resin is applied to the inside of artifacts still warm, but able to be handled (J.J.L. Corrêa, personal observation).

The interviews with former traders and people living at communities visited revealed that until the end of the commercialization period during the 1980s, extraction of resin in Santarém mainly occurred on *terra firme* formations near rivers, the main route of flow products (the definition of *terra firme* used here and beyond is following Oliveira-Filho *et al.* 2021). According to them, forests on plateaus were relatively poorly explored due to the distance to navigable waterways. In the 1970s, the modern occupation of Amazonia began with the opening of roads and the colonization of interior forests on *terra firme* far from large rivers (Fearnside 2006); however, there was not enough time to consolidate the exploration of resin due to the decline in regular trade. An estimate of the extractive capacity along historically occupied areas near rivers, which are more populated with more degraded forest resources, should be lower than that observed from 1974 to 1985 (10–16 t year^{-1}); however, there is no information about this for plateau forests in the interior.

Two botanical sources of jutaicica resin were found while mapping the trees and were both identified as species of *Hymenaea* (Fabaceae). These were *H. courbaril* and *H. parvifolia* Huber (1909: 385–386), which are the most frequent species of *Hymenaea* in the study area based on material collected and deposited in the HSTM herbarium at Universidade Federal do Oeste do Pará.

In Vila Nova, only one specimen of *H. parvifolia* producing resin was found, which was 4.46 kg (VIN01). In Maguari, three specimens were found producing 5.00 kg (MAG01), 2.70 kg (MAG02), and 2.35 kg (MAG03), all from *H. courbaril*. In Jaguarari, samples of resin were collected next to one individual of *H. courbaril*, with 3.16 kg (JAG01), and three individuals of *H. parvifolia*: 3.75 kg (JAG02), 4.12 kg (JAG03), and 0.78 kg (JAG04). The casual removal of pieces of resin was observed in all locations, generally for domestic use, such as flammable material. Resin from the JAG04 specimen, closest to the community, has been more frequently and intensively collected.

The botanical sources of the resin in the surveyed areas, *H. courbaril*, and *H. parvifolia* were found in *terra firme* forests, with a density and frequency of resin accumulating individuals estimated to be 0.05 trees hectare^{-1} or around 10% (between 6 and 25%) resinous individuals in the local undisturbed population of *Hymenaea* spp.

Regarding the characterization of the obtained resin samples in the Santarém region, the resin pieces found were frequently coated with a layer of whitish, friable material. Scraping this with a pocketknife reveals a glassy, bright, transparent, or translucent, colorless, yellowish, orange, or brownish aspect, which is sometimes variable within the same piece (Fig. 3). The collected material had, therefore, some heterogeneity in its aspect.

Our study reveals that the characteristics of the resin pieces vary based on botanical origin. Most of the pieces from *H. courbaril* are transparent (91%) and yellowish (70%), while most of the *H. parvifolia* pieces are translucent milky (83%) and orangish (55%). Some pieces of *H. parvifolia* resin are opaque and brownish and tend to adhere together more easily and give off a more intense odor.

The thermal characterization of the resins showed in the TG/DTG plots five-stages of decomposition delimited in the thermal decomposition, identified by their temperature range, characterized by mass changes and DTG peaks of maximum decomposition rate, while the heat flow measurement (DSC) identifies the absorption or release of heat by the sample due to thermal effect on physical and chemical processes, such as melting, vaporization and chemical reactions (Fig. 4).

The infrared spectra of the jutaicica samples (Fig. 5) show the pattern of a natural resin with the diterpene structure of the labdane skeleton (Regert *et al.* 2008; Guiliano *et al.* 2007). The main characteristic bands present in the spectra are as follows: (1) a very broad band of medium intensity around 3,410 cm^{-1}, associated to

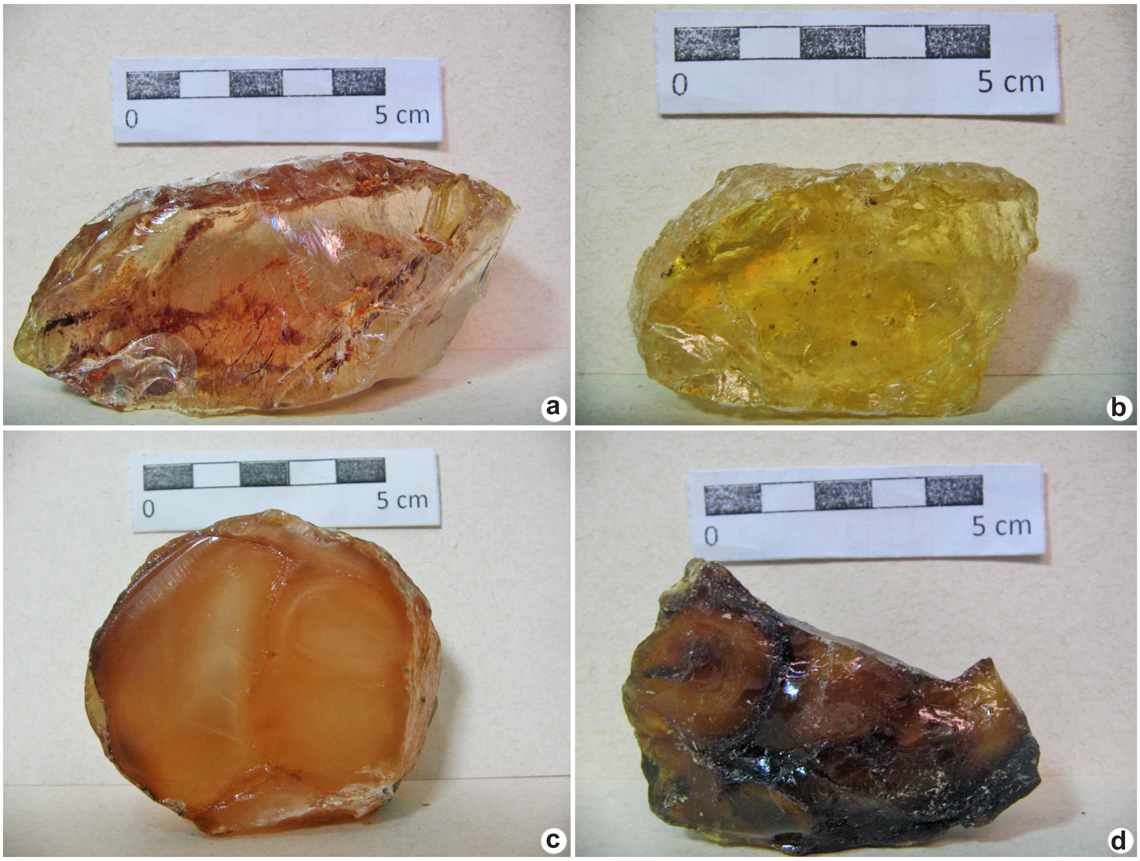

Figure 3 – a-d. The aspect of jutaicica resins – a. transparent; b. yellowish, light-colored; c. milky orangish-brown; d. dark brownish.

stretching vibration of the hydrogen-bonded OH groups in carboxylic and alcoholic groups; (2) sharp peak of medium intensity at 3,078 cm^{-1}, due to terminal olefin C-H stretch vibration; (3) strong intensity peaks related to the stretching vibration of saturated C-H bonds, with the highest intensity at 2,929 cm^{-1} (methyl group -CH3) and two adjacent peaks a little less intense at 2,865 and 2,847 cm^{-1} (methylene bridge -CH2-; sp^3 methine group >CH-); (4) strong intensity peak at 1,696 cm^{-1}, attributed to the stretching vibration of carbonyl group (C=O) in carboxylic acid (-COOH); (5) sharp peak of medium intensity at 1,641 cm^{-1}, due to the double bond stretching vibration C=C; (6) medium intensity peaks due to the bending vibrations of saturated C-H bonds - two sharp peaks close together at 1,459 and 1,444 cm^{-1} and a peak apart at 1,387 cm^{-1}; (7) medium-to-high intensity peak in the higher end of C-O single bond stretching vibration range, due to the C-O bond in a carboxyl functional group (1,271 cm^{-1}); and, (8) sharp and strong intensity spike at 886 cm^{-1}, due to the bending vibration of the C-H bond in exocyclic methylene group (=CH2). The bands that allow differentiating between the botanical sources were highlighted in Figure 5.

The ^{13}C RMN spectra of jutaicica (Fig. 6) show characteristic shifts of labdanoid resins distributed in the single-bonded (alkane), double-bonded (alkene or olefinic), and carbonyl carbon type regions, common to all spectra of copal resins (Martínez-Richa *et al.* 2000; Clifford & Hatcher 1995; Cunningham *et al.* 1983). The peaks occur among overlapping signals due to small differences in chemical shifts of similar nuclei. The region of saturated carbons, between δ 80 and 10 ppm, has the highest number and peaks intensity, with a dominant one at δ 38 ppm, attributed to sp^3 methine (>CH-) and methylene bridge (-CH$_2$-) carbons. The chemical shifts of the nuclei of the olefinic carbon between δ 150 and 100 ppm showed four peaks, the ones with the highest intensity at δ 147 and 107 ppm, which are attributed to the exocyclic double-bonded carbons (>C=CH$_2$). In the carbonyl region of the spectra of the resins of *H. courbaril* and some specimens of *H. parvifolia*, there are low-intensity peaks, the most evident one at δ 186, attributed to carboxyl carbon, and weaker ones are at δ 181 and 173 ppm.

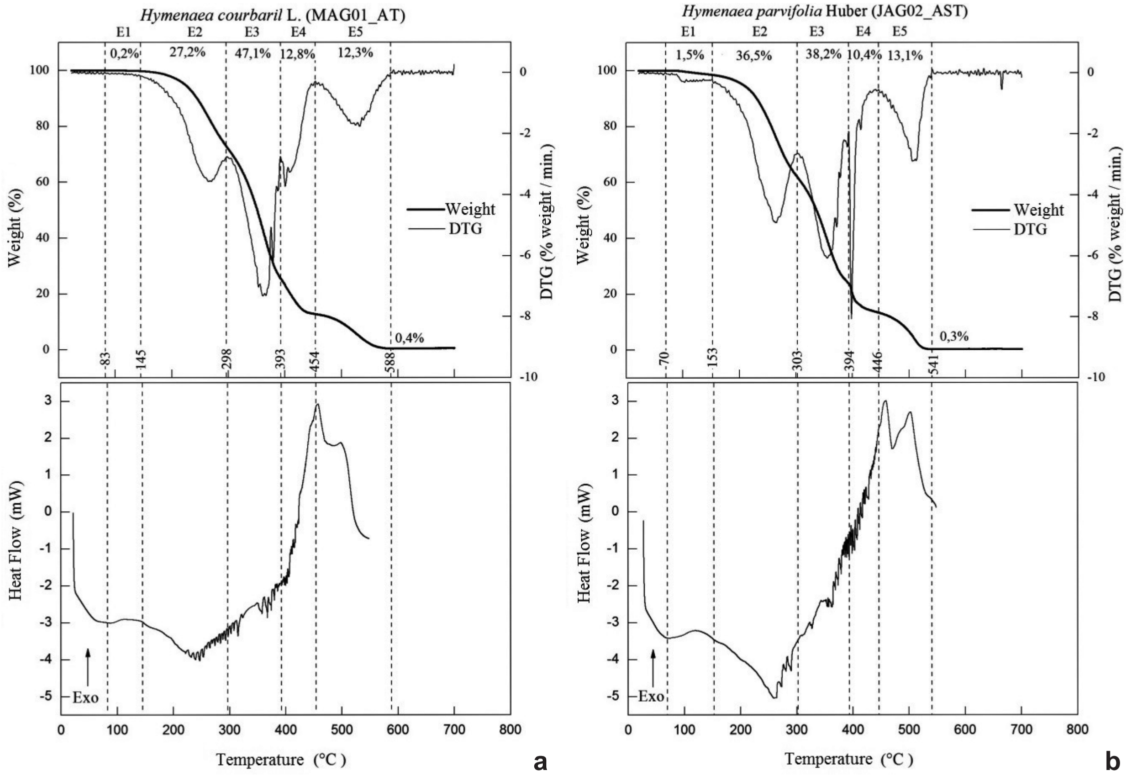

Figure 4 – a-b. Thermogravimetric (TG) and Differential TG (DTG) and Differential Scanning Calorimetry (DSC) curves for trunk resins – a. *H. courbaril*; b. *H. parvifolia*.

Discussion

Obtaining, use, and trade of copal resin in Brazil

Until the middle of the XX century, native copal resin had commercial importance in Brazil, but its exploitation and exportation were limited due to the lack of uniform batches and knowledge about its properties (Rangel & Schneider 1936 and results presented in this work). Rangel & Schneider (1936), to characterize, classify and elaborate on the use of native copal resin for making varnish, provided results of physical and chemical analyses of resin samples acquired in the Rio de Janeiro market in 1930. The information they obtained about the trade and regions of origin, the botanical sources, and the results of an analysis of the properties of the batches allowed the resins to be grouped into three typologies: "jatobá mole" from Bahia and Minas Gerais, the most soluble in oil and turpentine; "jatobá duro" from Ceará and northern Bahia, insoluble in turpentine; and "jutaicica" from the state of Pará, the most variable batches, with a higher content of impurities and, consequently, the lowest market prices (Rangel & Schneider 1936). The resin from Pará was from *H. courbaril* and *H. parvifolia* and assumed to be exuded by the roots of the trees, due to the form and impurities found in the batches (Rangel & Schneider 1936). In addition, it is possible that a mixture containing both breu (*Protium* spp.) and jutaicica resins was sold as breu-jutaicica or white breu (Silva *et al* 2013).

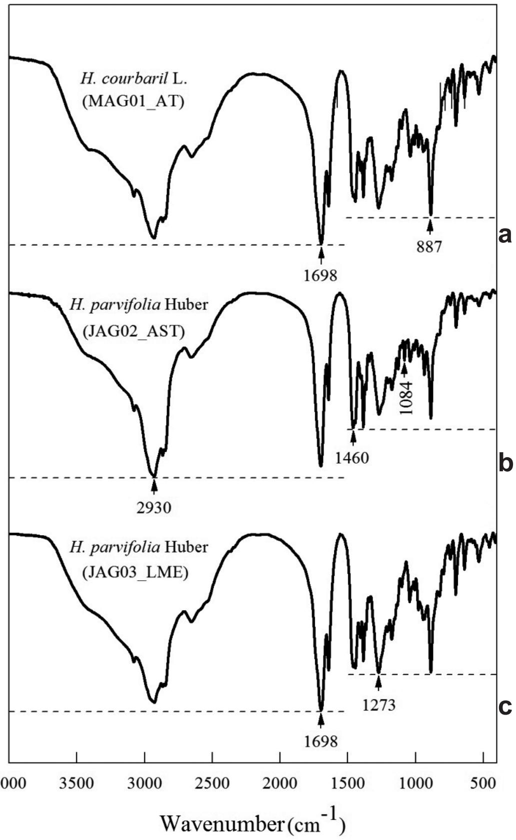

Figure 5 – a-c. Infrared (IR) curves for trunk resins – a. *H. courbaril*; b. *H. parvifolia* type I; c. *H. parvifolia* type II.

For the collections made from the eight resinous trees (six in primary forest and two in degraded, secondary forest), the maximum amount of resin obtained was 5 kg tree^{-1}. However, the quantity could be twice this if the resin was not casually collected by locals, as observed by the first author, or even three times this amount, as recorded by Ferreira & Sampaio (2000). These authors also reported: (1) failure to collect resin from longitudinal cuts in the trunk, in many areas of Amazonia and the Estação de Fruticultura Tropical of Instituto Nacional de Pesquisas da Amazônia (INPA); and (2) the natural accumulation of a maximum of 15 kg of resin per tree (over an unknown amount of time) in Reserva Ecológica de Maracá, in Roraima, and the municipality of Santarém, Pará.

In this work, we only found information (based on personal communication with traditional communities) to pieces of resin produced spontaneously by the trees, without cutting the bark to provoke exudation, which were on the ground, mixed in 10 to 20 centimeters of litter or hanging from the trunk of standing trees.

It is important to note that in this study the resin collected was exclusively from *terra firme* formations (non-flooded forests). No material was found in areas of flooded forests such as *várzea* or *igapó* or from *Hymenaea oblongifolia* Huber, a possibility suggested by Langenheim *et al.* (1973).

In the 18th century, the existence of copal resin was identified in Brazil (Elrey Dom José 1770), originating from some species of the genus *Hymenaea*, mainly in the forests of the state of Pará (Howes 1949). Resin pieces can be collected near the trees, awakening attention by lightness, hardness, sometimes transparent glassy aspect and size that reach the dimensions of the "foot of a man" (Langenheim *et al.* 1973). For the traditional population, it served and still does, in the manufacture of clay pots (Ferreira & Sampaio 2000), or simply to "make fire" due to its flammability. Until the 20th century, copal resin represented the main raw material to produce varnish, when it was progressively replaced by synthetic resin (American Gum Importers Association 1936; Sunseri 2007). At the same period, the traditional ceramic manufacturing of kitchen utensils has also declined due to the supply in the urban market and globalization of modern products with better quality and lower cost (Clement 2007). However, the available information on the use of copal resin shows that it allows the production of classic and high-quality varnish (Fearon 2009), can give rise to gemological material of great commercial value through its hot pressurized treatment (Abduriyim *et al.* 2009), and serve to waterproof porous materials that come in contact with hot foods (Ferreira & Sampaio 2000 and this work). In addition, *H. courbaril* is a woody species with high commercial value and easy multiplication (Lorenzi 1992), provides abundant nectar secretion for bees, its sap and fruits are traditionally used as medicines and foods, and it allows dense planting due to the apparent resistance to pests and diseases conferred by their secondary metabolites (Ferreira & Sampaio 2000). In an undisturbed forest environment in the Tapajós basin, we estimated the average occurrence of 1 resin accumulating tree per 20 hectares. The spontaneous accumulation of resin reaches up to 15 kg, but the accumulation rate, the most adequate extraction method, the environmental conditions, and the appropriate genotypes for production are unknown. So, the research and development of this species, for example, must begin at a very preliminary stage, although its wide use is supposedly achievable considering the above, the feasibility of the use of the resin will hardly depend on the possibility of developing extraction methods (Ferreira & Sampaio 2000).

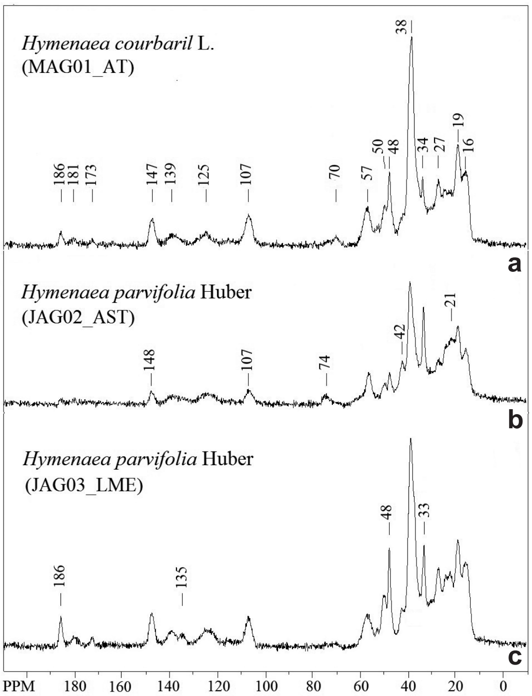

Figure 6 – a-c. Carbon 13 Nuclear Magnetic Resonance spectroscopy (^{13}C RMN) curves for trunk resins – a. *H. courbaril*; b. *H. parvifolia* type I; c. *H. parvifolia* type II.

Characterization of jutaicica resin collected in Santarém

Some thermal transformations of jutaicica resin can be macroscopically identified during use: when heated above 60 °C (to be applied by friction in clay pots) it becomes progressively soft and elastic demonstrating the characteristic of an amorphous polymer, differing from the crystalline behavior, which changes the state over a very narrow temperature range at its melting point; and in the manufacturing of classic varnish, when gradually heated to a temperature between 310 °C and 340 °C it turns permanently soluble in drying oil, and maintains properties needed to form a protective, hard, durable and transparent varnish (Rangel & Schneider 1936).

Figure 4 shows TG/DTG and DSC curves of representative samples of the two botanical sources. The thermal decomposition was solved in stages of individual components using the DTG curve. Each stage was characterized by the lower temperature at which the beginning of a mass change can be detected, the lower temperature by which the process responsible for the mass change was completed, and the temperature of DTG peak where the rate of mass change is maximum. The comparison between the mass change (TG/DTG) and energy flow (DSC) curves allows us to suggest the physicochemical process that occurs (Hatakeyama & Quinn 1999).

In the first stage (E1; 70–153 °C) weight loss begins (DTG < 0). The trunk resin of *H. parvifolia* differs by the higher weight loss (1.5–5.3%) compared to *H. courbaril* (0.2–0.3%) and by the presence of a low DTG peak in *H. parvifolia* samples. The small loss of weight of the *H. courbaril* resin samples can be attributed to a lower content of moisture and volatiles, which differs from *H. parvifolia* resin samples that contain more of these substances. In the DSC curves of all the samples, there is a broad endothermic peak (ca. 82 °C) which is mainly related to resin melt (Hatakeyama & Quinn 1999). In the second stage (E2; 153–306 °C), the loss of weight accelerates, and it is possible to discriminate between the two botanical sources. The TG/DTG curves of the *H. parvifolia* resin samples show very close to the maximum weight loss (36–45%) and rate (DTG peak), while for *H. courbaril* the weight loss (21–27%) and the rate is well below the maximum that is seen in the next stage. The mass loss and the endothermic effect can be attributed to the vaporization of components that have boiling points in this range (Hatakeyama & Quinn 1999). The descending DSC curve shows that the initial thermal event is dominantly endothermic, becoming exothermic at around 250 °C as indicated by the inflection of the curve related to a decrease of these occluded compounds and the initial cracking of the polymerized matrix (Hatakeyama & Quinn 1999; see Lambert *et al.* 2008). The thermoanalytical curves of these natural resins are due to the overlapping of thermal effects from heating their various components, mainly terpenes and their copolymers with different molecular weights. Observations made during the original manufacturing of copal varnish confirm that the main transformations occur during this temperature range, such as the distillation of volatile terpenes starting at 145 °C, where the agglutinated resin pieces in a porous solid change to a frothy fluid, followed by a clear fluid at around 310 to 340 °C, when the process is complete, and the resin becomes permanently soluble in a drying oil (Rangel & Schneider 1936; American Gum Importers Association 1936).

The third stage (E3; 306–392 °C) starts after reduction to a minimum value the rate of loss and resumes. The weight loss of the *H. courbaril* resin (47–49%) exceeds that of *H. parvifolia* (23–38%). This stage has the main peaks of the DTG curve of both species and the acceleration of exothermic flow in the DSC curve is maintained. The consolidation of the thermal degradation of the matrix of the young copal resin occurs, with the maximum decomposition rate at 360 °C (main DTG peak). Although Lambert *et al.* (2008), using gas chromatography and mass spectrometry, have identified that pyrolysis products of amber at a range of 300–360 °C result in the distillation of occluded volatile compounds, and the thermal rupture of the matured macromolecular phase occurs at higher temperatures, studies of young and fossilized diterpene resins concluded that the position of the major thermal combustion of the material is directly correlated with age and degree of maturation (Feist *et al.* 2007; Ragazzi *et al.* 2003; Rodgers & Currie 1999). In addition, observations of the process of manufacturing copal varnish indicate that heating young resin within this temperature range results in darkening and defects in the product (Rangel & Schneider 1936; American Gum Importers Association 1936), suggesting that the loss of weight at this temperature interval is mainly related to the decomposition of the polymerized matrix, differently to what occurs in the first two stages.

The fourth stage (E4; 392–450 °C) starts after a new reduction to a minimum and the rate of loss resumes, coinciding with a strong increase in exothermic flow in the DSC curve. The weight losses of *H. courbaril* (13–18%) and *H. parvifolia* (10–13%) resin samples were close. The DTG curve is characterized by sharp peaks. The boiling point of various diterpene acids, which are components of the occluded fraction (Nakano & Djerassi 1961; Cunningham *et al.* 1973, 1974), is around this temperature range. Their vaporization is related to the sequence of individual peaks in the DTG curve and short, sharp, endothermic peaks in the DSC curve, where the opposite exothermic effect predominates due to the continuity of the macromolecular phase cracking (Hatakeyama & Quinn 1999).

After a minimum inflection point that approaches zero in the DTG curve, the fifth stage (E5; 450–556 °C) starts, showing a prominent decomposition rate (DTG peak) and an endothermic peak in the DSC curve. It was not possible in this stage to differentiate weight change between samples of the two botanical sources: *H. courbaril* (11–12%) and *H. parvifolia* (13–13%). Above the average temperature of 556 °C to the end of the experiment, 0.3–1.0% of the original weight of the samples remains stable, without quantitative correlation with the botanical sources.

The measurement of the loss of mass of the resin samples through the TG/DTG technique allowed individualizing the stages of the thermal decomposition (Ionashiro 2004; Hatakeyama & Quinn 1999). Comparing the weight change and the heat flux absorbed or emitted by the samples in a program of increasing temperature, it was initially identified the resin melting and the vaporization of volatile components, followed by the cracking of the macromolecular structure (Hatakeyama & Quinn 1999). Thermal transformations characteristic of Copal type resins, whose temperatures in which they occur are directly proportional to the structural maturity, smaller in the young resins and greater in fossilized ones (Feist *et al.* 2007; Ragazzi *et al.* 2003; Rodgers & Currie 1999). In the case of the jutaicica resin samples under study, in the third stage of the thermal decomposition, initiated around 306 °C, the exothermic effect predominates, while the maximum rate of mass loss is indicated by the main DTG peak at 360 °C. The higher accumulation of mass loss at lower temperatures in *H. parvifolia* (44%) resin samples than *H. courbaril* (24%), indicating a higher content of volatile constituents in *H. parvifolia* resin, while the mass loss of the *H. courbaril* resin concentrated at higher temperature indicates its higher content of macromolecular material. The results obtained are consistent with the information on classic copal varnish manufacture, where the distillates are obtained from 150 °C and harvested as a solvent, while the maximum process temperature is limited to about 350 °C to prevent defects and the darkening unwanted (Rangel & Schneider 1936; American Gum Importers Association 1936).

Compilations and discussions of Infrared (IR) spectroscopy applied to the copal type resin are found in the classification, paleobotany, fossilization, old artworks, archeology, and gemology research (Azémard *et al.* 2014; Rao *et al.* 2013; Li *et al.* 2012; Abduriyim *et al.* 2009; Regert *et al.* 2008; Guiliano *et al.* 2007; Cunningham *et al.* 1983; Langenheim 1969; Langenheim & Beck 1965).

The IR spectra of sampled *H. courbaril* resins batches are identical in the position and relative intensity of the absorption bands and differ from *H. parvifolia* due to the variability of the relative intensity of some of them, highlighted in Figure 5. The changes in the relative intensity, although small, were consistent and allowed to discriminate the botanical sources and suggest differences in the proportion of certain functional groups in the materials, since the positions of the absorption bands are the same and the differences of intensity depend on the number of bonds responsible for absorption (Mayo *et al.* 2003). The IR spectra of the *H. courbaril* resin samples (Fig. 5) showed maximum absorption intensity at 1,698 cm^{-1} for carboxyl carbonyl group (C=O; COOH) in the region of the groups (4,000 to 1,500 cm^{-1}), and C–H exocyclic methylene group (=CH2) at 886 cm^{-1} surpassing all others in the fingerprint region (1,500 to 500 cm^{-1}) (see Mayo *et al.* 2003 for the identification of these peaks). The spectra of *H. parvifolia* resin have greater variation in relative intensity and suggest there are two more homogenous groups of signals: type I, with a maximum absorption due to saturated C–H bonds at 2,929 cm^{-1} in the region of the groups and 1,459 cm^{-1} in the fingerprint region, signaling a lower presence of unsaturated bonds (C=C), and also possessing an exclusive peak of reasonable intensity at 1,084 cm^{-1}; and type II, which is more similar to *H. courbaril*, differing by a peak of higher intensity in the fingerprint region at 1,272 cm^{-1} attributed to the simple carbon-oxygen bond (C-O) in a carboxyl functional group (Mayo *et al.* 2003). In addition, the type II resin frequently exhibits greater enlargements and loss of band resolution around 3,405 cm^{-1}, which is attributed to the effect of the hydroxyl group.

The differences in the relative intensity of the infrared absorption bands suggest differentiation between botanical sources of the resin due to the lower content of unsaturated bonds (C=C) in *H. parvifolia* for type I and higher oxidation (C-O) for type II concerning *H. courbaril*.

Compilations and discussions of carbon 13 Nuclear Magnetic Resonance (^{13}C-NMR) spectroscopy applied to the copal type resin is found in the classification, paleobotany, fossilization, old artworks, archeology, and gemology research (Li *et al.* 2012; Abduriyim *et al.* 2009; Lambert *et al.* 1999, 2008; Martínez-Richa *et al.* 2000; Lambert & Poinar 2002; Clifford & Hatcher 1995; Anderson *et al.* 1992; Cunningham *et al.* 1983).

The set of *H. courbaril* ^{13}C RMN spectra show only a slight variation among them, being characterized in the region of saturated carbons by the second more intense peak at δ 19 ppm, attributed to the methyl carbon ($-CH_3$), in the olefinic region by the prominence of the two peaks assigned to the exocyclic double bond carbons ($>C=CH_2$), and the small intensity of peaks in the carbonyl carbons (Fig. 6a). The ^{13}C-RMN spectra of the *H. parvifolia* resins are more diverse and corroborate the IR spectroscopy subdivision into two groups: type I, with the second most intense peak at δ 33 ppm, attributed to the methylene bridges ($-CH_2-$) in the region of the alkane type carbons, lower intensity of the olefinic peaks and a virtual absence of absorption in the carbonyl region, (Fig. 6b); and type II, more similar to *H. courbaril*, but with a prominent peak at δ 48 ppm, attributed to saturated carbon bound to carboxylic group (C-COOH) and δ 186 ppm, attributed to carboxylic carbon (-COOH) (Fig. 6c).

The spectroscopy of the resin samples allowed to identify that the samples of resin *H. courbaril* are more uniform, whereas the samples of resin of *H. parvifolia* can be divided into two groups: one more like *H. courbaril*, and another one differentiated by the more saturated character (lower contents of double bonds) and less oxidized (lower content of oxygen bonds), in principle useful characteristics for quality control of raw materials.

Jutaicica once was an important renewable non-timber forest product in the state of Pará, marketed for varnish production, and its trade has declined due to substitution by non-renewable derivates of the oil industry. To consider it a product to be restored it is necessary to determine more accurately the abundance and frequency of resinous specimens, and the amount and period for natural accumulation of copal resin, and for that, we suggest including this information during future forest inventories, particularly in the forest management of protected areas and settlement projects related to traditional populations and sustainable development. When comparing species sampled in western Pará state, jutaicica collected from *H. courbaril* might be a better source for polymer gathering, according to our thermal analysis findings. Locally, the botanical source of the batch can be identified by straightforward and low-cost spectroscopic methods, such as infrared, which has also shown to be an accurate method to assess sample heterogeneity, an important feature on an industrial scale. The accuracy of the IR has been corroborated by ^{13}C-RMN. Sample and batch heterogeneity might be species-specific, as shown here in the analyzed species pair. Here we present the first assessment of jutaicica as a renewable non-timber forest product, regarding a study case of its historical use and physicochemical characterization. If we aim to maintain Amazonia's diversity to keep its functionality, the local interest in the standing forest will depend on its economic valuation. The resin extracted from *Hymenaea* species is one of these products, with a possibility of market insertion, regarding the production of high-quality copal varnish. Only the need for adjustment of an old and public domain production technology to modern industrial resources is to be observed. Manufacturing copal varnish from jutaicica resin could be easily associated with distilling useful chemicals, such as a substitute to turpentine, a thinner for traditional high-quality copal varnishing. In the short and medium term, the drying oil from linseed employed in true copal varnish production, for example, could find a substitute in the immense diversity of oleaginous plant species found in Amazonia. The traditional Amazonian copal varnish (based on jutaicica resin) could be completely employed in finishing classic wood artifacts. Its productive chain could be sustainably driven and economically efficient.

Acknowledgments

The authors thanks to the following: to the Instituto Nacional de Colonização e Reforma Agrária (INCRA), for allowing the first author to finish the Master's project; the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), for awarding the study fellowship; the Universidade Federal de Sergipe (UFS) and Dr. Cristiano Teles de Menezes, and the Instituto de Física de São Carlos at the Universidade de São Paulo (USP) and Evandro Ares de Araújo, for obtaining the thermal analysis curves; the Universidade Estadual de Londrina (UEL) and Dr. César Cornélio Andrei, for obtaining the NMR spectra; Dr. Massao Ionashiro at the Instituto de Química of UNESP at Araraquara, and Dra. Gizilene Maria de Carvalho at the Departamento de Química of UEL, for encouragement and suggestions on using thermal analysis; Rafael Barbosa Pinto, for confirming the identification of the specimens; and several residents of Maguari community, for helping locating specimens and collecting the resin. Two anonymous reviewers, for their suggestions and contributions. This work is part of the first author's Master thesis.

References

ABC - Academia Brasileira de Ciências (2008) Amazônia: desafio brasileiro do século XXI. Fundação Conrado Wessel, São Paulo. 32p.

Abduriyim A, Kimura H, Yokoyama Y, Nakazono H, Wakatsuki M, Shimizu T, Tansho M & Ohki S (2009) Characterization of "Green Amber". Gems & Gemology 45: 158-177.

American Gum Importers Association Inc. (1936) Natural Resin, New York. 123p.

Anderson B, Winans RE & Botto RE (1992) The nature and fate of natural resins in the geospher - II. Identification, classification and nomenclature of resinites. Organic Geochemistry 18: 829-841.

Azémard C, Vieillescazes C & Ménager M (2014) Effect of photodegradation on the identification of natural varnishes by FT-IR spectroscopy. Microchemical Journal 112: 137-149.

Bennett JJ (1857) Description of the Kobo-tree, a new genus of Leguminosae, collected by Dr. WF Daniell, FLS, in Sierra Leone. Journal of the Proceedings of the Linnean Society, Botany 1: 149-151.

Bonpland AJA (1807) Plantes équinoxiales recueillies au Mexique, vol. 1. F. Schoell, Paris. 191p.

Clement CR (2007) Um pote de ouro no fim do arco-íris? O valor da biodiversidade e do conhecimento tradicional associado, e as mazelas da lei de acesso. Uma visão e proposta a partir da Amazônia. Amazônia Ciência Desenvolvimento 3: 177-198.

Clifford DJ & Hatcher PG (1995) Structural transformations of polylabdanoid resinites during maturation. Organic Geochemistry 23: 407-418.

Cunningham A, Gay ID, Oehlschlager AC & Langenheim JH (1983) Carbon-13 NMR and IR analyses of structure, aging, and botanical origin of Dominican and Mexican ambers. Phytochemistry 22: 965-968.

Cunningham A, Martin SS & Langenheim JH (1973) Resin Acids from two Amazonian species of *Hymenaea*. Phytochemistry 12: 633-635.

Cunningham A, Martin SS & Langenheim JH (1974) Labd-13-en-8-ol-15-oic acid in the trunk resin of Amazonian *Hymenaea courbaril*. Phytochemistry 13: 294-295.

Cunningham A, West PR, Hammond GS & Langenheim JH (1977) The existence and photochemical initiation of free radicals in *Hymenaea* trunk resin. Phytochemistry 16: 1442-1443.

Elrey Dom José I (1770) Alvará do indulto privativo, e privilégio exclusivo do commercio da goma copal, produzida nos domínios da America portugueza. Regia Oficina Tipografica, Lisboa. 3p.

Fearnside PM (2006) Desmatamento na Amazônia: dinâmica impactos e controle. Acta Amazonica 36: 395-400.

Fearon A (2009) Copal resin and the practice of oil varnishing in the second half of 19th-century America. Architectural Finishes in the Built Environment. Archetype Publications, London. Pp. 105-112.

Feist M, Lamprecht I & Müller F (2007) Thermal investigations of amber and copal. Thermochimica Acta 458: 162-170.

Ferreira CAC & Sampaio PTB (2000) Jatobá (*Hymenaea courbaril*). *In*: Clay JW, Sampaio PTB & Clement CR (eds.) Biodiversidade amazônica: exemplos e estratégias de utilização. Programa de Desenvolvimento Empresarial e Tecnológico, Manaus. Pp. 217-225.

Foxworthy FW (1910). The Almaciga tree: *Agathis alba*. Philippine Journal of Science 1910: 173-175.

Gaertner J (1791) De fructibus et seminibus plantarum. Vol. 2. Sumtibus Auctoris, Typis Academiae Carolinae, Stutgardiae. 520p.

Gentry AH & Wettach RH (1986) *Fevillea* - a new oil seed from Amazonian Peru. Economic Botany 40: 177-185.

Guiliano M, Asia L, Onoratini G & Mille G (2007) Applications of diamond crystal ATR FTIR spectroscopy to the characterization of ambers. Spectrochimica Acta Part A 67: 1407-1411.

Harms HAT (1897) Die Natürlichen Pflanzenfamilien, suppl. 2-4. Verlag von Wilhelm Engelmann, Leipzig. 84p.

Hatakeyama T & Quinn FX (1999) Thermal analysis, fundamentals and applications to polymer. John Wiley & Sons, Chichester. 180p.

Howes FN (1949) Gums and resins. chronica botanica. Company of Waltham, Massachusetts. 188p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1976) Produção extrativa vegetal (PEV) 1974. IBGE, Rio de Janeiro. 345p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1979) Produção extrativa vegetal (PEV) 1976. v.4. IBGE, Rio de Janeiro. 228p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1981a) Anuário estatístico do Brasil (AEB) 1980. v.41. IBGE, Rio de Janeiro. 226p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1981b) Produção extrativa vegetal (PEV) 1978. v.6. IBGE, Rio de Janeiro. 228p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1981c) Produção extrativa vegetal (PEV) 1979. v.7. IBGE, Rio de Janeiro. 228p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1982) Produção extrativa vegetal (PEV) 1980. v.8. IBGE, Rio de Janeiro. 245p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1984) Produção extrativa vegetal (PEV) 1981. v.9. IBGE, Rio de Janeiro. 245p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1985) Produção extrativa vegetal (PEV) 1983. v.11. IBGE, Rio de Janeiro. 234p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1986a) Anuário Estatístico do Brasil (AEB) 1985 (1982-84). v.46. IBGE, Rio de Janeiro. 759p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1986b) Produção extrativa vegetal (PEV) 1984. v.12. IBGE, Rio de Janeiro. 236p.

IBGE - Instituto Brasileiro de Geografia e Estatística (1987) Produção extrativa vegetal (PEV) 1985. v.13. IBGE, Rio de Janeiro. 234p.

IBGE - Instituto Brasileiro de Geografia e Estatística (2012) Manual Técnico da Vegetação Brasileira. 2ª ed. IBGE, Rio de Janeiro. 272p.

IBGE - Instituto Brasileiro de Geografia e Estatística (2013a) Produção Agrícola Municipal - Culturas Temporárias e Permanentes 2012. v. 39. IBGE, Rio de Janeiro. 98p.

IBGE - Instituto Brasileiro de Geografia e Estatística (2013b) Produção da extração vegetal e da silvicultura 2012. v. 27. IBGE, Rio de Janeiro. 58p.

INE - Instituto Nacional de Estatística (1936) Anuário Estatístico do Brasil (AEB). Ano II. Instituto Nacional de Estatística, Rio de Janeiro. 890p.

Ionashiro M (2004) Fundamentos de termogravimetria, análise térmica diferencial e calorimetria exploratoria diferencial. Editora Giz, São Paulo. 82p.

Lamarck JBAPM (1786) Encyclopédie méthodique, botanique. Vol. 2. Panckoucke, Plomteux, Paris. 774p.

Lambert JB & Poinar Jr GO (2002) Amber: the Organic Gemstone. Accounts of Chemical Research 35: 628-636.

Lambert JB, Shawl CE, Poinar Jr GO, Santiago GO & Santiago-Blay JA (1999) Classification of modern resins by solid state Nuclear Magnetic Resonance spectroscopy. Bioorganic Chemistry 27: 409-433.

Lambert JB, Santiago-Blay JA & Anderson KB (2008) Chemical signatures of fossilized resins and recent plant exudates. Angewandte Chemie 47: 9608-9616.

Langenheim JH (1969) Amber: a botanical inquiry. Science 163: 1157-1169.

Langenheim JH (1996) Biology of amber-producing trees: focus on case studies of *Hymenaea* and *Agathis*. *In*: Anderson K & Crelling JC (eds.) Amber, resinite, and fossil resins. ACS Symposium Series, American Chemical Society, Washington DC. Pp. 1-31.

Langenheim JH and Beck CW (1965) Infrared spectra as a means of determining botanical sources of amber (Report). Science 149: 52-54.

Langenheim JH, Lee Y & Martin SS (1973) An evolutionary and ecological perspective of Amazonian Hylaea species of *Hymenaea* (Leguminosae: Caesalpinioideae). Acta Amazonica 3: 5-38.

Le Cointe P (1947) Amazônia Brasileira III - Árvores e plantas úteis (indígenas e aclimadas): nomes vernáculos e nomes vulgares, classificação botânica, habitat, principais aplicações e propriedades. Livraria Clássica, Belém. 524p.

Li H, Wang X, Zhu Y & Ren Q (2012) Identification of amber and the copal under heat pressurized process. Advanced Materials Research 554-556: 2112-2115.

Linnaeus C (1753) Species plantarum. Vol. 2. Impensis Laurentii Salvii, Holmiae. 1232p.

Lorenzi H (1992) Árvores brasileiras: manual de identificação e cultivo de plantas arbóreas nativas do Brasil. Ed. Plantarum, Nova Odessa. 384p.

Mantell CL, Allen CH & Sprinkel KM (1935) Natural resins for the varnish industry. Industrial & Engineering Chemistry Research 27: 1369-1373.

Martínez-Richa A, Vera-Graziano BR, Rivera CA & Joseph-Nathand P (2000) A solid-state ^{13}C-NMR analysis of ambers. Polymer 41: 743-750.

Martius KFP (1824) Historia Naturalis Palmarum. Vol. 2. T.O. Weigel, Lipsiae. 172p.

Mayo DW, Miller FA & Hannah RW (2003) Course notes on the interpretation of infrared and raman spectra. John Wiley & Sons, New Jersey. 600p.

MF - Ministério da Fazenda do Brasil (1919) Diretoria de Estatística Comercial. Comercio Exterior do Brasil (COMEX) 1917-1918. Ministério da Fazenda, Rio de Janeiro. 146p.

MF - Ministério da Fazenda do Brasil (1935) Diretoria de Estatística Econômica e Financeira do Tesouro Nacional. Comercio Exterior do Brasil (COMEX) 1930-34. Ministério da Fazenda, Rio de Janeiro. 145p.

MF - Ministério da Fazenda do Brasil (1947) Serviço de Estatística Econômica e Financeira do Tesouro Nacional (membro do Instituto Nacional de Estatística). Comercio Exterior do Brasil (COMEX) 1941-42. Ministério da Fazenda, Rio de Janeiro. 210p.

MF - Ministério da Fazenda do Brasil (1954) Serviço de Estatística Econômica e Financeira do Conselho Nacional de Estatística - IBGE. Comercio Exterior do Brasil (COMEX) 1949-50. Ministério da Fazenda, Rio de Janeiro. 226p.

MF - Ministério da Fazenda do Brasil (1961) Estatística do Comercio Exterior do Brasil (COMEX) 1960. Ministério da Fazenda, Rio de Janeiro. 285p.

Milne-Redhead EWBH (1934) New combinations under *Copaifera*. Bulletin of Miscellaneous Information 1934: 400.

Nakano T & Djerassi C (1961) Terpenoids. XLVI. Copalic Acid. The Journal of Organic Chemistry 26: 167-173.

Oliveira-Filho A, Dexter KG, Pennington RT, Simon MF, Bueno ML & Neves DM (2021) On the floristic identity of Amazonian vegetation types. Biotropica 00: 1-11.

Ragazzi E, Roghi G, Giaretta A & Gianolla P (2003) Classification of amber based on thermal analysis. Thermochimica Acta 404: 43-54.

Rangel JL & Schneider HS (1936) Copaes do Brasil: resinas de jatobá, trapoca e jutahycica. Ministério do Trabalho, Indústria e Comércio, Rio de Janeiro. 41p.

Rao ZF, Dong K, Yang XY, Lin JC, Cui XY, Zhou RF & Deng Q (2013) Natural amber, copal resin and colophony investigated by UV-VIS, infrared and Raman spectrum. Science China Physics, Mechanics & Astronomy 56: 1598-1602.

Regert M, Devièse T & Le Hô A-S (2008) Reconstructing ancient Yemeni commercial routes during the Middle Age using structural characterization of terpenoid resins. Archaeometry 50: 668-695.

Rodgers Ka & Currie S (1999) A thermal analytical study of some modern and fossil resin from New Zealand. Thermochimica Acta 326: 143-149.

Santarém (1948) Álbum do centenário da elevação de Santarém a categoria de cidade. Prefeitura Municipal de Santarém, Santarém. 106p.

Silva JN, Oliveira DR, Leitão SG, Assis IM, Veiga-Junior VF, Lourenço MC, Alviano DS, Alviano CS, Bizzo HR (2013) Essential oils of *Protium* spp. samples from Amazonian popular markets: chemical composition, physicochemical parameters and antimicrobial activity. The Journal of Essential Oil Research 25: 171-178.

Silva JNM, Carvalho JOP & Lopes JCA (1985) Inventário Florestal de uma área experimental na Floresta Nacional do Tapajós. Boletim de Pesquisa Florestal 10/11: 38-110.

Sunseri T (2007) The political ecology of the copal trade in the Tanzanian Coastal Hinterland, c. 1820-1905. Journal of African History 48: 201-220.

Thiers B (continuously updated) Index Herbariorum: a global directory of public herbaria and associated staff. New York Botanical Garden's Virtual Herbarium. Available at <http://sweetgum.nybg.org/science/ih/>. Access on 1st April 2021.

Area Editor: Dra. Viviane Kruel
Received in April 21, 2021. Accepted in October 18, 2021.