Potential plastic digestor of *Euphorbia Tirucalli*

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Sandra Ávila Gaspar[1], Rayssa de Macedo Rebelo[2], Alexandre dos Santos Pyrrho[3], Simone da Silva[4], Marcia Cristina Braga Nunes Varricchio[5] and Paulo Sérgio Torres Brioso[6]

ABSTRACT

Natural products that cause oxidative stress and even local corrosion are of interest as degrading products of materials persistent in nature, such as plastic. This chapter evaluated the corrosive and shrinkage physicochemical action of total aqueous extracts of Euphorbia tirucalli, a species described as corrosive and shrinkage, from specimens with geographic variations (mangrove and mountains of Rio de Janeiro and the north coast of São Paulo) also subjected to temperature variations, on polypropylene (PP-5). This plastic is used on a daily basis and can be subjected to reuse processes. In the present experiment, aqueous extracts were prepared from temperature variations and their plant chemical productions were marked using high-performance liquid chromatography associated with the UV detection spectrum. Unlike previous tests, none of the extracts were capable of immediate extraction or digestion over 30 days. Only for the stems from Petrópolis (50%) and the north coast of São Paulo (33%) subjected to boiling was the activation of their gummy action observed, acting as glue on the PP-5. suggestive of natural polymerization for cellulose. Despite the observations regarding the potential practical, useful and cheap application of this test, it was evident that the raw latexes from the geographical regions tested at different temperatures were not capable of chemically digesting isopropylene, thus suggesting that the enzyme capable of digesting this plastic effectively participates when the endophytic fungus present in this species finds favorable conditions to develop as previously discussed. Phytopathology tests confirmed the biological effects verified through the roots of E. tirucalli and subsequently, new cultivars developed followed the variation in the release of cyanuric acid into the test environment, marking interest since cyanuric acid can play a role in recovery soil, in addition to being a herbicide, insecticide and being able to reduce contamination by gram-negative fecal coliforms in water, especially Escherichia coli. Based on this contribution, new tests will be carried out in order to investigate mechanisms of action in phytoremediation, comparing them with those already preliminarily evidenced and communicated. A specific protocol has been developed in Plant Biotechnology, as these jobs have the possibility of useful and profitable application in reuse, to be carried out by small solid waste recyclers. It will also aim at autonomy for ethnic groups in urban situations, as well as promoting environmental sustainability.

[1] Agricultural Sciences from the Federal Rural University of Rio de Janeiro (UFRJ).
Institution: Apiário Estação 4x4
E-mail: sandra.avila.gaspar@gmail.com
[2] Electronic and Computer Engineering Student at the Federal University of Rio de Janeiro
Federal University of Rio de Janeiro (UFRJ)
E-mail: rr.rayssarebelo@gmail.com
[3] PhD in Sciences (Biophysics) from the Federal University of Rio de Janeiro (UFRJ).
Institution: Laboratory of Immunoparasitology and Toxicological Analysis of the Faculty of Pharmacy (UFRJ).
E-mail: pyrrho@pharma.ufrj.br
[4] Post-Doctor in Biodiversity and Biotechnology from Federal University of Amazonas (UFAM).
Amazon Biobusiness Center (CBA); Institute of Technology and Education Galileo da Amazônia (ITEGAM).
E-mail: simonydasilva@gmail.com
[5] Post-Doctor in Intellectual Property of Brazilian Traditional Ethnic Knowledge (INPI).
PhD in Sciences (Vegetal Biotechnology) from the Federal University of Rio de Janeiro (UFRJ).
Immunology Laboratory, Institute of Biomedical Sciences and Clementino Fraga Filho University Hospital (HUCFF), Federal University of Rio de Janeiro (UFRJ).
E-mail: varichio2@gmail.com
[6] PhD in Sciences – Genetics/Agronomic Engineering at Federal Rural University of Rio de Janeiro (UFRRJ).
Official Phytosanitary Diagnostic Laboratory – Phytopathology at Federal Rural University of Rio de Janeiro (UFRRJ).
E-mail: brioso@bighost.com.br

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INTRODUCTION

Euphorbia tirucalli L. (Aveloz, fire stick) is a succulent species of African origin, with a cosmopolitan distribution. In high salinity soils, it produces diterpene esters, some with aromatic chains, which induce oxidative stress in cell membranes and plant walls (FURSTENBERGER & HECKER, 1986; BETANCUR-GALVIS et al., 2002; 2003).

However, plant chemical marking by HPLC/UV of the species from the IPPN/UFRJ garden detected the conditions where it is more active on the membrane and cell wall due to the presence of polyhydroxylated diterpenes, hydrophilic, cytotoxic and erosive, at a local level that vary in concentration according to seasonality. They were detected in root exudation, but they can be removed from the soil by leaching (VARRICCHIO, 2007; VARRICCHIO et al., 2008, a).

Natural products that cause oxidative stress and even local corrosion are of interest as degrading products of materials persistent in nature, such as plastic (SINGER et al., 2003). Thermoplastic polymers bond by weak forces. When heated, they become flexible. They return to their solid state when cooled. Heating and cooling cycles in the manufacture of PET bottles make them remoldable, an interesting advantage for environmental issues (PEREIRA & MACHADO & SILVA, 2002), since the polluting accumulation of plastic has been causing damage to public health (being found even in breast milk and placenta) and irreversible impacts on the environment (FREIRE SOUZA SILVA et al., 2019).

Among plastic materials, polypropylene (PP - 5) is a crystalline resin with high chemical resistance, with resistance to traction, acid and basic attacks, and deformation due to heat (ABREU, 2006). It can burn without the presence of a flame. It is transparent and unbreakable. Its drying time is 2 hours at 80ºC and achieves shrinkage that varies between 1.5 and 3.0%. It is found in films, syringes, biscuit and bread packaging, and it is known that even other materials with PP-5 can persist in nature.

In the literature, it is described that diterpene esters are corrosive at room temperature. DELAUNAY DE SOUZA et al. (2023, a) have already demonstrated the retractable digesting effect of raw E. tirucalli latex on isopropylene. Could E. tirucalli extracts cause corrosion or shrinkage in PP-5?

AIMS

To evaluate the corrosive and shrinkage physicochemical action of total aqueous extracts of *E. tirucalli* subjected to temperature variations on polypropylene.

SPECIFICS AIMS

- Evaluate the physicochemical action of geographically distinct total extracts of *E. tirucalli.*

- Evaluate the physical action of total extracts of *E. tirucalli* obtained by temperature variations on polypropylene.

METHODOLOGY

BOTANICAL CERTIFICATION:

Record in the Herbarium of the National Museum/UFRJ.

SOLUTIONS PREPARED FOR THE TESTS:

1 Petrópolis mineral water.

2 Total aqueous stem extract from Petrópolis/RJ, Room temperature (22 ºC).

3 Total aqueous extract of stem from Petrópolis/RJ, boiled (100ºC).

4 Total aqueous stem extract from Petrópolis/RJ cooled to -15 ºC.

5 Total aqueous extract of stem from the north coast of SP Room temperature (22 ºC).

6 Total aqueous extract of stem from the north coast of SP, boiled (100ºC).

7 Total aqueous extract of stem from the north coast of SP cooled to -15 ºC.

8 Total aqueous stem extract from IPPN/UFRJ, Room temperature (25 ºC).

9 Total aqueous extract of IPPN/UFRJ stem, boiled (100ºC).

10 Total aqueous extract of IPPN/UFRJ stem cooled to -15 ºC.

QUALITATIVE MARKER DESCRIPTION OF HPLC/UV (CHANNEL FOCUSED AT 210 AND 230 NM – VARRICCHIO, 2005)

Qualitative assessment of the corrosive and shrinkable physical effect on PP-5 using scales adjusted for this material (CÂMARA, 2003; ABREU et al., 2006; MIGUEL, 2010):

- Regarding speed: immediate, short-term (< 2 hours), medium (2 to 3 hours) and long-term (> 3 hours).

- Regarding the intensity of contraction in relation to the surface: Low (< 2.5%), Medium (2.5%), High (> 3.0%).

Polypropylene (PP - 5) was cut into 1.5 x 1.5 cm segments organized in groups of 3, arranged in quadruplicates (N = 12) per solution, making a total of 120 segments arranged in three aluminum trays. Then, 0.1mL of control solution (nº 1) and test solutions (2 to 10) were applied to each cut PP surface. Next, a time and activity curve was established.

RESULTS/DISCUSSION

PLANT CHEMICAL ANALYSIS

A qualitative analysis of the plant chemical production of E. tirucalli from IPPN/UFRJ, Petrópolis/RJ and the north coast of SP was proposed. All lattices collected between 8 am and 10 am. The HPLC/UV analysis of E. tirucalli from the municipality of Petrópolis/RJ remains similar to that from the IPPN/UFRJ garden for the channels focused on 210 and 230 nm. The production of polyhydroxylated and less esterified diterpenoids did not vary, as previously reported (VARRICCHIO et al., 2008). The solution obtained from the species from Caraguatatuba, north coast of SP evaluated by CLAE/UV demonstrated detection of a similar pattern to other samples from Rio de Janeiro.

Based on classical literature, a probable difference in plant chemical production was sought, based on geographic variation.

PROVENANCE - GEOGRAPHY REVIEW STUDY

The study of plants involves variations in their plant chemical production (secondary metabolism), also due to the environmental conditions in which the species to be studied develops: geographic regions, microclimates, soil characteristics, among others (SINGER et al., 2002) . It is also known that soils are usually the result of weathering to which rocks, with their geological characteristics, are subjected (EMBRAPA, 2004).

From this review, we returned to each plant individual we studied to establish a geographic correlation. As previously described, the soil on Governador Island, for the most part, is classified as argisol. The university campus of Ilha do Fundão is on Ilha do Governador. Between 1949 and 1952, eight islands in this region were filled in and interconnected for the construction of the University City of the University of Brazil, currently the Federal University of Rio de Janeiro/UFRJ (MENEZES et al., 2005).

The soil of *E. tirucalli*, studied by us, a plant located in the IPPN/UFRJ garden for around 35 years, is located on the shore of Guanabara Bay, whose plant group suggests it can be classified as a halophyte meadow. It was subjected to analysis in the UFRRJ Laboratory, in accordance with EMBRAPA collection recommendations at both depths, and was classified as sandy soil. In the past, Governador Island was called Paranapuãm Island, and the indigenous people who lived there were from the Maracajás tribe. Around the entire Guanabara Bay and where the city of Rio de Janeiro is located today, there was the nation of Tamoios/Tupinambás.

Petrópolis is located in the mountainous region, 68 km from Rio de Janeiro. The central urban area is located at the top of Serra da Estrela, belonging to the Serra dos Órgãos mountain range, a subsector of Serra do Mar. The municipality has extremely rugged terrain, with large differences in level. From the Itaipava district onwards, the relief decreases in altitude. The mountainous

environment, which is almost always humid, allowed the local vegetation to be characterized as Atlantic Forest forest (PMP, 2020).

Until the 18th century, the region was inhabited by the Coroados indigenous people, known by the Portuguese as "Sertão dos Índios Coroados". It was only with the discovery of gold in Minas Gerais and the consequent opening of the Caminho Novo, which passed through Petrópolis, in this century, that the region began to be occupied by non-indigenous people (PMP, 2020).

Recurrent landslides are caused by the steepness of the slopes, the thin thickness of the soil and the configuration of the rocks below the slopes. The region where the Petrópolis Mountain Region Environmental Protection Area - APA Petrópolis-RJ is located is part of the southeastern portion of the Brazilian Platform, represented by the Atlantic Mobile Belt Tectonic Domain. It is located within the Morphostructural Domain of Remobilized Folding Belts, including the Escarpas e Reversos Geomorphological Region of Serra do Mar (FNMA/INSTITUTO ECOTEMA, 2001; BAPTISTA et al., 2005; PMP, 2020).

The coastal region of São Paulo is characterized by a very rugged relief, with the Serra do Mar escarpment advancing towards the coastal plain in the area corresponding to the municipalities of the North Coast (from São Sebastião to Ubatuba), contrasting with the greater dominance of the plain in Baixada Santista and Litoral Sul. The region is marked by the relief of Serra do Mar, which acts as an important factor in orographic intensification and, associated with atmospheric flows originating from the ocean and a zone where atmospheric systems meet, provides a dynamic of high amounts rainfall, with frequent records of increased mass movements (TECHNICAL DIAGNOSIS APAM LITORAL NORTE).

According to Almeida and Carneiro (1998), Serra do Mar is a set of scarps that extends from the coast of Rio de Janeiro to Santa Catarina, where it ceases to exist as an orographic unit with a steep edge of a plateau. A large part of the territory of the North Coast of São Paulo is formed by mountainous escarpments (43%) and mountainous domains (32.4%), located predominantly in areas within the limits of Integral Protection Conservation Units (DIAGNÓSTICO TÉCNICO APAM LITORAL NORTH).

The coastal and fluvio-marine plains, together, correspond to around 15.7% of the region, with a predominance in Caraguatatuba and São Sebastião. The domains of hills and low mountains are distributed throughout the region (except Ilhabela) and predominate in Caraguatatuba (In: DIAGNÓSTICO TÉCNICO APAM LITORAL NORTE).

TEMPERATURE VARIATION OF AQUEOUS EXTRACTS OF TOTAL STEM (AERIAL PARTS AND LATEX) FROM ILHA DO FUNDÃO/RJ, PETRÓPOLIS/RJ AND LITORAL NORTE/SP OVER PP-5 (CORROSION AND SHRINKAGE)

The third context analyzed was the influence of temperature variation of aqueous extracts of the total stem (aerial parts and latex) of *E. tirucalli* from the three regions: mangrove of Guanabara Bay, mountainous region of Serra dos Órgãos and northern coast of SP (Caraguatatuba). There was no corrosive effect on PP-5 until the first 72 hours of observation of the experiment for all solutions tested. Associated with the absence of PP-5 retraction for all solutions tested, after completing the 30-day observation period.

These results with total extracts from stems of different geographic origins (geological and pedological) subjected to temperature variations are different from previous results obtained with E. tirucalli bioproducts from both the IPPN garden and Petrópolis (RJ), which were able to perform the retraction of polypropylene (PP - 5), enzymatically digesting it at room temperature from 30 days to 90 days, without apparent degradation, corrosion or damage. The retraction of the plastic surface without breaking may possibly be able to favor its remolding and reuse.

Such bioproducts were obtained from natural fermentation induced by the cultivation of *Vigna unguiculata* (cowpe beans) with elicitor extracts of *E. tirucalli* (MUSMANNO et al., 2019; FREIRE DA SILVA et al., 2019). It also suggested that there was no participation of the endophytic fungus present in E. tirucalli in this plastic digestive action (VARRICCHIO, 2005; VARRICCHIO, 2007; VARRICCHIO et al., 2008). In fact, we are interested in the oxidative stress induced by the total extract of aerial parts of E. tirucalli on the cowpea skin, which released and stimulated the growth of Fusarium spp., a fungus classically described for this bean (MUSMANNO et al ., 2019; DRAGO et al., 2019). It is known that the enzymatic digestion of plastic in nature is carried out through the enzyme phosphofructokinase 1 (PFK1).

The hypothesis of the acceleration of the chemical reaction due to the temperature variation of the extracts corresponded to a search for a solution for recycling, as it could accelerate plastic digester processing (ABIQUIM, 2010), since currently this solid waste persists in the environment for hundreds of years (FRANCHETTI & MARCONATO, 2003; CANEVAROLO JUNIOR, 2006; CANEVAROLO JUNIOR et al., 2007).

The thermal conductivity of the extracts previously tested was involved in this continuous heat exchange process and such thermal conductivity had influenced the long cooling time, leading to shrinkage and twisting (FREIRE SILVA et al., 2019). However, the physical variation in temperature of the total extracts investigated in the present experiment was not capable of interfering with the chemical bonds to exert a physical corrosive or shrinkage effect.

The aqueous extract of the crude latex of *E. tirucalli* from Petrópolis/RJ, cultivated by inserting an acupuncture needle into its main internodal segment, suggested that it was capable of stimulating the thickening of the latex and also activated its resin effect during application (0.2 ml) of the extract in chicken egg albumin, making it thick, dry, hard and resistant, like papyrus, making it difficult for sticky materials to adhere. Once again, it suggested the occurrence of natural polymerization, as a likely mechanism for the qualitative observation of this preliminary test (WENDLING DA SILVA et al., 2019, a).

In geobotany, it is known that *E. tirucalli* has been on the planet since Pangea, predominating in the supercontinent of Botswana (VALLE, 2009). Although its main correlation in studies on plant chemistry and pharmacognosy of terpenoids contained in latex, they often refer to the African continent, in a region that was once sea with soil with high salinity, attributing its toxicity to this factor (FURSTENBERGER & HECKER, 1986), the most recent studies show variations in biological activity in addition to diverse uses by indigenous peoples such as glue, rubber and resin (VARRICCHIO, 2008). As an example, the rubber product is obtained through a simple coagulation of the raw material, latex, extracted from rubber trees providing car and airplane tires, eraser rubber, balls, medical items, flooring, condoms, etc.

In the present experiment, only for the stems from Petrópolis (6/12 or 50%) and the north coast of São Paulo (4/12 or 33%) subjected to boiling was the activation of their gummy action observed, acting as glue in PP-5. This glue effect on paper had already been described using a total extract of aerial parts of E. tirucalli from Petrópolis/RJ under assisted cultivation, suggestive of natural polymerization for cellulose (SANTOS, 2001 In PINTO, 2019).

Furthermore, phytopathology tests confirmed the biological effects verified through the roots of *E. tirucalli* (VARRICCHIO, 2007) and subsequently, new cultivars developed followed the variation in the release of cyanuric acid into the test environment, a mark of interest since the Cyanuric acid can play a role in soil recovery, in addition to being a herbicide, insecticide and redactor of coliforms population (GASPAR et al., 2017).

As a reminder, phytoremediation is a technique that aims to decontaminate soil and water, using plants as a decontamination agent. It is an alternative to conventional methods of pumping and treating water, or physically removing the contaminated layer of soil, and is advantageous mainly because it has the potential for in situ treatment and is economically viable. Furthermore, after extracting the contaminant from the soil, the plant stores it for subsequent treatment, when necessary, or even metabolizes it, being able, in some cases, to transform it into less toxic or even harmless products (PIRES et al., 2003).

Phytoremediation can be used in soils contaminated by inorganic and/or organic substances. Promising phytoremediation results have already been obtained for heavy metals, petroleum

hydrocarbons, pesticides, explosives, chlorinated solvents and toxic industry byproducts. Phytoremediation of herbicides shows good results for atrazine, with the species Kochia scoparia revealing rhizospheric potential to phytostimulate the degradation of this molecule. Although still incipient in Brazil, there are already studies on some cultivated agricultural species and wild or native species from the contaminated area itself, with the aim of selecting efficient species in soil phytoremediation (PIRES et al., 2003).

The use of phytoremediation is based on the selectivity, natural or developed, that some species exhibit towards certain types of compounds or mechanisms of action. This fact is a common occurrence in agricultural and weed species, tolerant to certain herbicides. Selectivity is due to the fact that organic compounds can be translocated to other plant tissues and subsequently volatilized; they can also undergo partial or complete degradation or be transformed into less toxic compounds, especially less phytotoxic, combined and/or linked to plant tissues (compartmentalization) (Accioly & SIQUEIRA, 2000; SCRAMIN et al., 2001 apud PIRES et al., 2003).

Most organics appear to undergo some degree of transformation in plant cells before being isolated in vacuoles or binding to insoluble cellular structures, such as lignin (SALT et al., 1998). The ability to metabolize the pesticide into a non-toxic (or less toxic) compound for the plant and the environment is the principle of phytodegradation. Another possibility is phytostimulation, in which microbial activity is stimulated, promoted by the release of root exudates, which acts to degrade the compound in the soil, which characterizes, in some plants, the rhizospheric aptitude for the bioremediation of toxic compounds (PIRES et al. al., 2003).

This field of research, due to its complexity, is still very little studied and consistent references are still scarce. However, the test results that determined the beginning of our studies have been systematically repeated, highlighting the potential for phytoremediation (VARRICCHIO, 2007) in soil and water by an indirect mechanism via the release of cyanuric acid. As for water, and as an addendum, scientific research suggested the participation of cyanuric acid compromising the viability of the gram negative bacteria E. coli (CAMPOS, 2014), a microorganism with reports of adherence and multiplication in plastics through a mechanism that has not yet been established (FREIRE SOUZA SILVA et al., 2019).

To minimize the impact caused by the release of sewage into water bodies, it is necessary that they go through a disinfection stage, before their final disposal, with the aim of containing the spread of waterborne diseases. In this context, the work of Josimar Campos (2014) aimed to evaluate a chlorination system using trichlorisocyanuric acid tablets, applied to disinfect sanitary effluent from a facultative lagoon, in the municipality of Itirapuã - SP. For the evaluation, an experimental test was used, carried out in the laboratory, where concentrations of 2.5, 3.5, 5, 10, 15 and 20 mg.L-1 of total residual chlorine were tested, in the contact times of 5, 15, 30, 45 and 60 minutes, to define the

dosage; in addition to the full-scale test with the implementation of the system in the sewage treatment plant to analyze performance, which was based on the inactivation of bacteria from the coliform group.

In the experimental test, with the application of 3.5 mg.L-1 of total residual chlorine in a contact time of 30 minutes, which results in a CT factor of 105 mg.min.L-1, inactivation of 5 log and 4.5 log for total coliforms and E. coli, respectively. With the system implemented in the sewage treatment plant, at a concentration of 10 mg.L-1 of total residual chlorine applied to the effluent, the inactivation of total coliform was 4.7 log and of E. coli 4.6 log. Therefore, the results obtained demonstrated that the system was effective in disinfecting the effluent, enabling its release into class 2 water bodies without compromising bacteriological quality, in addition to being operationally simple (CAMPOS, 2014).

To conclude the evaluation of our experiment, which motivated the writing of this chapter, in fact, natural polymerization was suggestive as already described by SANTOS (2001) and CÂMARA (2003), in the observation of the glue effect of raw latex at room temperature by CAROLINE MACHADO - TUKANO with E. tirucalli from Rio Comprido, which belongs to the Tijuca Massif, in the municipality of RJ/RJ. In his project-based learning (MACHADO et al., 2019), he sought raw plant extracts that favored the conservation of stored seeds for urban indigenous crafts, for consequent financial survival, autonomy and promotion of ethnodevelopment (MACHADO et al., 2019a).

Despite all these observations regarding the potential and probable practical, useful and cheap application of this assay aimed at phytoremediation, perhaps bioremediation, on the other hand, it was evident that the crude lattices from the geographical regions tested at different temperatures were not capable of chemically digesting the isopropylene, thus suggesting that the enzyme capable of digesting this plastic effectively participates when the endophytic fungus present in this species finds favorable conditions to develop as discussed by VARRICCHIO (2005; 2007).

A specific protocol is being developed in Plant Biotechnology, as these jobs have the possibility of useful and profitable application for reuse to be carried out by small solid waste recyclers. It will also aim at autonomy for ethnic groups in urban situations, as well as promoting environmental sustainability.

Based on this contribution, new tests will be carried out in order to investigate mechanisms of action in phytoremediation (KATHAR et al., 2023), comparing them with those already preliminarily evidenced in phytoremediation (GASPAR et al., 2017; 2023; 2024) .

There is much to learn from observing nature and the traditional use of natural resources for climate change, environmental health and sustainability of the planet (VARRICCHIO & LAGE, 2020; PYRRHO et al., 2020).

CONCLUSION

The varied total aqueous extracts of *E. tirucalli* latex stem prepared at different temperatures, from different geographic, geological, pedological and climatic regions in Brazil (RJ and SP), at the concentrations/dosages tested, were not capable of triggering immediate corrosion , nor medium-term shrinkage in polypropylene (PP-5). A different result from our previous publications.

They were promising only for their potential biotechnological action as a glue applicable to paper and as a resin, both activities already described in the literature, but verified for all boiled extracts.

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