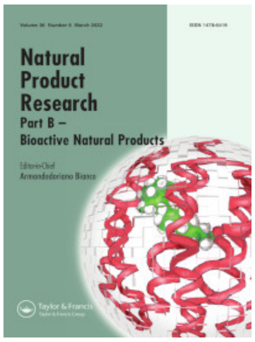

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SHORT COMMUNICATION

The chemical composition and antioxidant activity of mandaçaia *(melipona quadrifasciata)* geopropolis varies more due to region than month of collection

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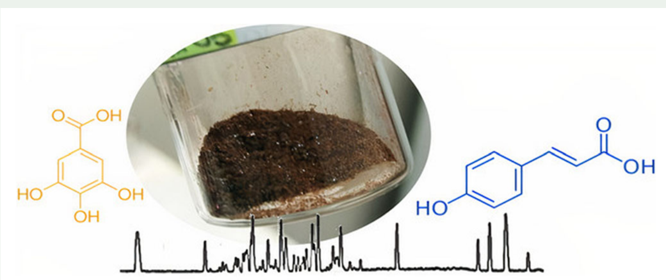
ABSTRACT

Stingless bees are responsible for pollinating up to 90% of Brazilian flora, so their study is of commercial and ecological importance. Stingless bees mix plant resins with wax and soil, forming geopropolis. Studies of the variability in composition and activity due to species, place and season of collection are lacking. Yield, total phenolic and flavonoid content, and antioxidant activity (via DPPH) of the extracts of fifteen *M. quadrifasciata* (*Mandaçaia*) geopropolis samples collected over a year in the State of São Paulo, Brazil, as well as two samples from different regions of the state of Minas Gerais in Brazil were compared. Composition was determined by ultra-high-resolution liquid chromatography and mass spectrometry, identifying 16 compounds. The month and region of collection affected the available plant resins and influenced their yield, composition and antioxidant capacity. Depending on the place of collection, *M. quadrifasciata* geopropolis is a promising natural source of antioxidant phenolic compounds.



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1. Introduction

A. mellifera propolis has been used therapeutically since ancient times; therefore, its composition and activity has been amply studied (Castaldo and Capasso 2002). Native stingless bees, which also belong to the Apidae family, are identified by stunted stings, generally small wings and hives, as well as hive entrances with distinct characteristics for each species (Venturieri, 2008). Native stingless bees are responsible for pollinating up to 90% of Brazilian flora and produce a specific type of propolis, named geopropolis, mixing plant resins with wax and variable amounts of soil. The ethanolic extract of geopropolis also presents biological activities, directly related to its chemical composition, which may vary depending on the bee species, the plant from which the resin is collected and the season (Sawaya et al. 2009).

Melipona quadrifasciata Lepeletir is popularly known as *Mandaçaia* and amply distributed in Brazil (Batalha-Filho et al. 2009). Its geopropolis shows promising antibacterial, antioxidant and antiproliferative effects, among others (Rubinho et al. 2019). Previous studies of *M. quadrifasciata* geopropolis have usually focussed on single samples and only one study collected three samples in different months (Cardozo et al. 2015). Differences in composition and activity may be due to the place and month of collection as well as the analytical method used. The purpose of this study was to evaluate the composition of *M. quadrifasciata* geopropolis from São Paulo over one year, as well as samples from two other locations, comparing their composition and antioxidant activity via DPPH assay.

2. Results and discussion

The fifteen geopropolis samples collected in Jaguariúna-SP over one year presented between 66% – 91% of insoluble residues (soil) and 1% – 6% of wax in their composition. The final yield of the dried ethanolic extracts of the samples ranged from 2% to 14%. The samples collected in Jaguariúna, SP in December 2016 and January 2017 showed a higher percentage of dry extract, possibly due to the greater supply of plant resins during the summer (Table S1). As these samples did not present the highest phenolic or flavonoid content, nor the strongest antioxidant activity, other classes of compounds were present in these resins. Cardozo et al. (2015) reported yields between 24 and 60%, but the highest yield did not produce the best antioxidant activity either. In other studies, the authors did not separate the wax from the resin as herein, so the reported yield is higher because a variable amount of wax is included in the resin (Cardozo et al. 2015; Bonamigo et al. 2017; dos Santos et al. 2017).

The geopropolis samples collected in Jaguariúna-SP presented total phenolic content from 1.75% to 3.12% and total flavonoid content of 0.15% – 0.34% of the raw geopropolis sample. The lowest results were obtained in August (winter) 2017 for both parameters (Table S1). All samples from Jaguariúna-SP presented strong antioxidant activity; EC_{50} results varied between 4.94 and 8.62 μg/mL, quite similar to pure quercetin (3.48 μg/mL) (Table S1).

No qualitative difference in the UHPLC-MS chromatograms of the samples from Jaguariúna- SP were observed, only variation in the intensity of some peaks during the year. However, qualitative difference in composition was observed between chromatograms of samples from different regions (Figure S1) as well as their total phenolic and flavonoid content (Table S1). The average total phenolic content from Jaguariuna-SP samples was 2.50%, from Inconfidentes - MG was 1.89%, and from Betim - MG 0.40%, in relation to raw geopropolis. The average total flavonoid content from the Betim – MG sample (0.08%) was similar to the Inconfidentes - MG sample (0.09%), but both were lower than the average for Jaguariúna - SP (0.21%), calculated in relation to the raw sample.

The antioxidant activity of the samples also varied significantly between regions. The samples from Inconfidentes - MG and Jaguariúna - SP presented respectively an average CE_{50} of 6.94 μg/mL ± 0.09 and CE_{50} of 6.78 μg/mL ± 0.09 (Table S1). These results were higher than the literature for this bee species and even comparable to *A. mellifera* propolis (Bankova et al. 2000), which may be related to the removal of wax from the resin. The sample collected in Betim-MG presented low antioxidant activity (CE_{50} of 385 μg/mL), probably due to the low flavonoid and phenolic contents. Other studies of propolis have encountered a correlation between phenolic content and antioxidant activity (Saral et al. 2019). The antioxidant activity of *M. quadrifaciata* geopropolis from Sta. Catarina (Brazil) also varied due to place of collection (Ferreira et al. 2019).

Aiming to identify some of the components, mass features were extracted from the chromatograms of all the samples (Jaguariúna - SP, Betim - MG and Inconfidentes - MG) using UHPLC-MS data processing software. The 119 mass features (*m/z* and retention time - Rt) were used for statistical analysis. The 16 compounds that were identified or putatively identified are shown in Table S2. Principal component analysis (PCA) was performed with the results of all chromatograms and the Bi-plot in Figure S2 shows the samples and the mass features responsible for their grouping.

The sample from Betim - MG (B0817) is separated from the others due to mass features 373/8 (**14**) and 401/8 (**16**). These were putatively identified as diterpenic acids, also found in *Tetragonisca angustula* propolis extract and *Schinus terebinthifolius* flowers (Carneiro et al. 2016), which may be a source of resins for these geopropolis samples as well. The sample from Inconfidentes - MG and one group of samples from Jaguariúna - SP, presented mass features 455/3 and 421/4, which could not be identified. Another group of Jaguariúna - SP samples collected between March and August 2017 are grouped by mass features 299/5 (**11**) and 301/7 (**12**) which were identified as diosmetin and kaurenoic acid respectively. In these samples, three other mass features were putatively identified as naringenin 271/2.5 (**10**), pinocembrin 255/7 (**13**) and 6-pentadecyl salicylic acid 347/7 (**15**) by comparison of their mono-isotopic mass and fragmentation pattern to the Metlin online database.

Three mass features found in virtually all geopropolis samples are common plant phenolics which were identified by comparison to standards: feature 169/0.7 - gallic acid (1); feature 163/1.4 - *p*-coumaric acid (4) and feature 301/1.6 - ellagic acid (7). Other features were putatively identified in comparison of their fragmentation and monoisotopic mass to Metlin data base: 121/1.1- 4-hidroxybenzaldehyde (2); 197/1.2 - syringic acid (3); 635/1.5 -a galotannin (5); 633/1.6 – corilagin (6), an ellagitannin. Features 287.1/1.7 and 613/1.9 were respectively identified as aromadendrin (8) and Di-*O*-galloyl *O*-cinnamoyl hexoside (9) by comparison to Rubinho et al. (2019).

3. Experimental (supplementary)

4. Conclusion

The greatest variation in composition and activity of *M. quadrifasciata* geopropolis occurred between samples from different regions, reflecting different available plant sources. On the other hand, seasonality had only a subtle influence over samples collected over a year in Jaguariúna-SP, with higher resin content in the summer months. With the exception of the Betim-MG sample, the geopropolis extracts contained a large number of phenolic compounds (and flavonoids) with known antioxidant activity. Six phenolic compounds were identified in geopropolis of *M. quadrifasciata* for the first time: syringic acid, corilagin, 1,2,3-Tris-O- (3,4,5-trihydroxybenzoyl) -D-glucopyranose, diosmetin and 6-pentadecyl salicylic acid. Therefore, depending on the place of collection, *M. quadrifasciata* geopropolis is a promising natural source of antioxidant phenolic compounds.

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