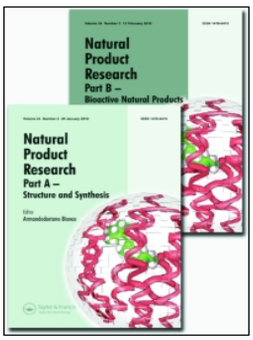

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SHORT COMMUNICATION

Artepillin C, is it a good marker for quality control of Brazilian green propolis?

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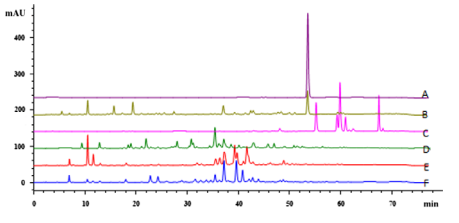
ABSTRACT

As commercialisation of Brazilian green propolis is going on, quality evaluation and authenticity are important. The result demonstrated that artepillin C found by far in Brazilian green propolis by HPLC-ESI-MS/MS analysis, while a small interferent may be mistaken as artepillin C in some propolis from China. A new HPLC quality control method as artepillin C for marker was developed, which is the primary assessment criteria for quality control of Brazilian green propolis.



Artepillin C is the marker for quality control of Brazilian green propolis: A, Standard solution of artepillin C; B, Brazilian green propolis; C, Macaranga-type propolis;D, Eucalyptus-type propolis; E, Birch-type propolis; F, Poplar-type propolis.

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HPLC; Brazilian green propolis; Artepillin C; quality control

1. Introduction

Brazilian green propolis, its plant origin is *Baccharis dracunculifolia* DC (Kumazawa et al. 2003), has been widely used in health-care, cosmetic and medicine products especially in Japan and China since 1990s. Contrary to poplar-type propolis, Brazilian green propolis has relatively low concentration of flavonoids while phenolic acids especially isoprenyl phenylpropanoids, caffeoylquinic acid and diterpenes are much richer (Salatino et al. 2005). However, indexes in quality control of Brazilian green propolis were total contents of flavonoids refer to standard of poplar-type propolis. It is important to develop a direct, fast and reliable analytical method to typify and control the quality of Brazilian green propolis.

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It is generally accepted that artepillin C is the characteristic chemical composition (Park et al. 2004) and has become an important factor in evaluating the quality of Brazilian green propolis. However, Wang (2010) identified artepillin C in Chinese propolis from Jilin province using ESI-MS/MS. Wu et al. (2013) also detected artepillin C by HPLC in Chinese propolis from Shandong, Beijing, Jiangsu and Xijiang provinces. It is necessary to know with certainty whether artepillin C only exists in Brazilian green propolis?

This study is aimed to verify if artepillin C also exist in other propolis samples and develop a simple and selective method for evaluation of artepillin C. Samples of propolis of different geographic origins were investigated. Furthermore, we compared the content of artepillin C concentrations among different Brazilian green propolis. These results will provide scientific theoretical basis for the quality control of Brazilian green propolis.

2 Results and discussion

2.1. The determination of artepillin C in propolis

The artepillin C was analysed under HPLC conditions from poplar-type propolis, birch-type propolis, ecalyptus-type and macaranga-type propolis (Figure S2). No interfering peaks were found with retention times similar to artepillin C except propolis samples from Jilin, China. There is a small peak near where artepillin C appeared. ESI-MS/MS was carried out in both positive and negative mode. The fingerprint peak in Brazilian green propolis showed very similar ESI-MS2 spectra as the artepillin C. Major negative ion markers are those of *m/z* 299.8, 255.7 and 200.5, and major positive ion markers are those of *m/z* 301.7, 283.7, 245.6, 277.5, 177.4 and 69.2 (Figures S3a, S3b). Although the fragment with [*m/z*] 301.7 in positive ion is a common ion product for artepillin C and the unknown compounds from Chinese propolis and the other major ion markers from artepillin C were not observed in Chinese propolis (Figure S3c). Another experiment revealed that the fragment with [*m/z*] 301.7 in positive ion was absent in Chinese propolis by Agilent 1200 QTOF LC/MS 6510(Figure S4).

Propolis fraction is highly complex, misidentification is very possible. This is the case of two recent papers based on HPLC (Wu et al. 2013) and ESI-MS/MS (Wang 2010). HPLC identification of artepillin C is inadequate because it can't exclude the interfering compounds. In fact, in ESI-MS/MS the unknown compound only gives the ion product with $[m/z]^-$ 300.4, 283.9 (Wang 2010), it also can't exclude the interfering compounds without more information.

2.2. The quantitative method of artepillin C by HPLC

A rapid method based on HPLC with UV detection is presented for the quantitative determination of artepillin C in propolis. The calibration curve of artepillin C was obtained by plotting peak areas vs. six known concentrations (0.05–0.5 mg/mL). The representative linear equation obtained was: $y = 9178.5x - 36.208$ ($r^2 = 0.9993$), which showed good linear relationships between the peak areas and the concentrations. The LOD and LOQ were 0.12 and 0.4 μg/mL, respectively. The obtained values for both LOD and LOQ were low, which indicated that the method was capable of detecting and quantifying trace amounts of artepillin C in samples. The RSD of inter-and intra-batch precisions were 0.35 and 0.79%, respectively; which showed good precision of the method. The repeatability of HPLC analysis for hydroalcoholic extract was exemplified by an RSD of 0.078%. The accuracy was studied through

recovery tests and obtained in the ranges of 98.46–99.20%.These results indicated that the developed method was validated and applicable for sample analysis.

Artepillin C were analysed in 56 Brazilian green propolis samples, it can be detected in all samples varying from 0.84 to 8.23%, and the average value is 3.09% (Table S1); which is in accordance with the results reported by Park et al. (2004) but lower than the values obtained in Matsuda's study (2008). The significant difference of artepillin C content among different batches might be account of geographic origins, seasonality, and storage condition and so on (Simões-Ambrosio et al. 2010; Bueno-Silva et al. 2016; Talla et al. 2016).

3. Conclusion

Propolis samples from different geographical origins were analysed, artepillin C existed by far in Brazilian green propolis. A small interferent may be mistaken as artepillin C in some propolis from China. A HPLC method was developed for quality control over quantity of artepillin C in Brazilian green propolis.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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