Volatile profiling of Arnicão (*Lychnophora salicifolia*), a wild medicinal species from Brazilian Cerrado

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The Cerrado is a diverse Brazilian savanna with a flora with more than 12,000 species. Arnicão (*Lychnophora salicifolia*) is an endemic species that occurs in a rocky savanna type in Central and Southeast Brazil, at higher altitudes, in sandstone and quartzite soils. It shows an aggregate distribution forming spatially defined populations, in well-delimited patches, with adaptations to Cerrado environment. *Lychnophora* species have been reported for anti-inflammatory, antioxidant, and UV protectant effects. In addition, other biological activities have been reported, e.g. trypanocide, cytotoxic, analgesic, antifungic and antibacterial. Local communities use the leaves and branches of *L. salicifolia* in the preparation of traditional medicine. These remedies, sold as either ointments or creams could have anti-inflammatory mechanisms. The aim of this work was to describe the composition of the headspace and essential oil of *L. salicifolia*, and to compare individuals harvested in preserved and non-preserved areas from four populations. Headspace–solid-phase microextraction gas chromatography-principal component analysis (HS-SPME GC-PCA) is proposed as a method to discriminate between plant populations of *L. salicifolia* from two distinct areas. Forty-eight individuals of *L. salicifolia* were randomly collected and vouchers from each population deposited at Embrapa Genetic Resources and Biotechnology herbarium (CEN). Grounded dried leaves of *L. salicifolia* were sampled by HS-SPME with a CAR/PDMS/DVB fused silica fiber. A mixture of a suitable amount of dried leaves from all individuals of each population was submitted to hydrodistillation in a microdistillation apparatus. EOs and headspace samples by HS-SPME of *L. salicifolia* dried leaves were analyzed by GC (GC/MS; GC/FID), and the results submitted to statistical analysis by PCA. The PCA obtained from *L. salicifolia* essential oil was quite similar to that of the headspace sampled by HS-SPME, both showing a similar discrimination of all populations. All samples contained a significant amount of myrcene. The most abundant compounds were tricyclene (1.3-3.4 %), myrcene (21.1-36.4 %), limonene (3.3-5.6 %), presilperfol-7-ene (0-5.2 %), butyl benzoate (1.6-12.7 %), beta-bisabolene (0.9-4.8 %), gamma-cadinene (4.7-12.6 %), caryophyllene oxide (1.8-3.6 %), *epi*-α-cadinol (5.2-11 %), and 14-hydroxy-9-*epi*-(*E*)-caryophyllene (0-18.2 %). The headspace showed a predominance of mono and sesquiterpenes hydrocarbons, varying from 34.5 to 46.9 % and 15.3 to 25.2%, respectively. It was observed a higher concentration of caryophyllene derivatives on populations from non-protected areas, usually with compounds associated to plant defense. Oxygenated sesquiterpenes were present in relatively high percentage (12-27 %), predominant in one population from a protected area. It is important to highlight that HS-SPME can successfully be used (also) for rapid in-field analysis of a large amount of samples of wild populations.

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