Differences in the essential oil composition of *Baccharis dracunculifolia* DC. (Asteraceae) from different regions of Uruguay: in the search for chemotypes

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Introduction and Aim

Uruguay is a country immersed in the Pampean-Uruguayense phytogeographical district, which also includes parts of the Eastern Argentina and Southern Brazil [1]. This country accounts for more than 2500 Angiosperm native species, 254 of them (54 families) having woody character [1]. These species occurred in vegetal communities and can be roughly divided into those coming from the forests or shrublands [1]. One of the most representative species of the last group is *Baccharis dracunculifolia* DC. (Asteraceae; Figure 1), a shrub/little tree that can reach until 5 m high, profusely aromatic, resinous, and rich in essential oils (EOs) of economic interest in perfumery [2]. Previously, our research group have studied the chemical composition (GC/MS) of the hydro-distilled EOs and volatile extracts (SDE) obtained from the aerial parts of plant material growing wild in Uruguay, considering in addition the variation according to the dioecism and seasonality [3-7]. In this contribution, as part of an ongoing project to describe *B. dracunculifolia* EOs composition in different regions of the country, we present novel data and interpreted them in the light of previous publications (1993-2021), in the search for possible chemotypes of this species.

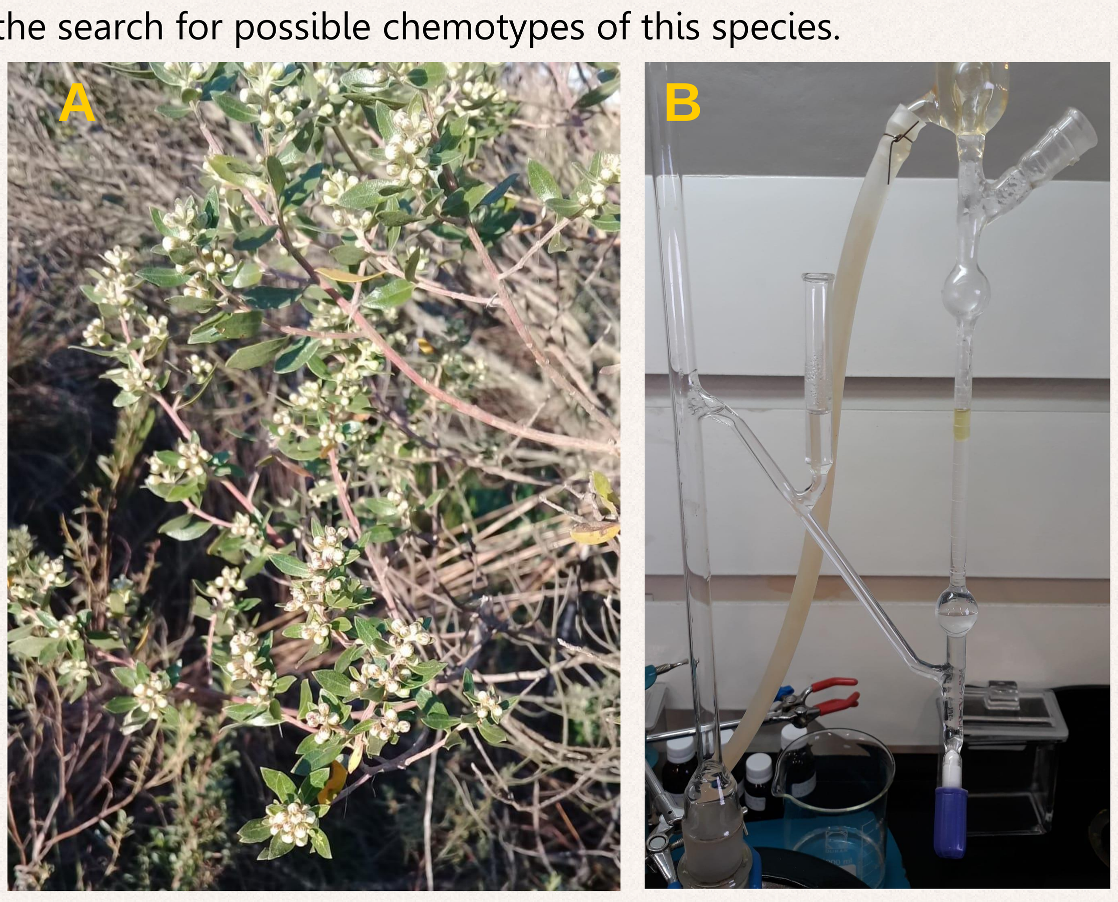


Figure 1: *Baccharis dracunculifolia* DC.: plant material (A); essential oil extracted by hydrodistillation using a Clevenger apparatus (B); a thrip (Thysanoptera) exploring the male flowers (Photos A and C: M. Abreu; B: M. Minteguiaga).

Methods

Aerial parts of *B. dracunculifolia* at flowering and vegetative stages were collected during 2021 in different seasons and places of Uruguay (in brackets the corresponding administrative divisions/Departments): "Parque Gran Bretaña" (**GB**, Rivera), "Iporá" (**IP**, Tacuarembó), "Las Flores" (**LFS**, Maldonado), "Sauce" (**SA**, Canelones) and "La Colorada" (**LC**, Montevideo). The branches were carefully separated, processed, and extracted in male and female ones (when at flowering, Figure 1). The extraction of the EOs was performed by hydrodistillation with the aid of a Clevenger apparatus (Figure 1). The chemical analyses of their composition were performed by GC/MS (Shimadzu QP2020) employing a capillary column Rxi-1MS (30 m x 0.25 mm x 0.25 µm; composition of the stationary phase: 100%-dimethylpolysiloxane). The oven program was set as follows: 50°C (5 min), 50-235°C at 5°C/min, 235°C (2 min). Injector and interface temperatures: 280°C. Ionization energy: 70 eV; scan range: 50-350 amu. Linear Retention Indices (LRIs) calculations, software match comparisons with commercial libraries, and comparison with previous literature reports [3-7] allowed for the identification of the main components of the EOs. Those bibliographic reports include other geographical sites as: "Las Brujas" (**LB**, Canelones), "La Floresta" (**LFA**, Canelones), "Cuchilla Alta" (**CA**, Canelones) [3-5], "Arenitas Blancas" (**AB**, Salto) [6], "Estación Porvenir" (**EP**, Paysandú) [7], which results were also considered for the discussion of the data.

Results and Discussion

Three effects were investigated in the search for variation in *B. dracunculifolia* EOs chemical composition: seasonality, dioecism, and geographical location where the plants grown (Figures 2 to 4).

Seasonality effect

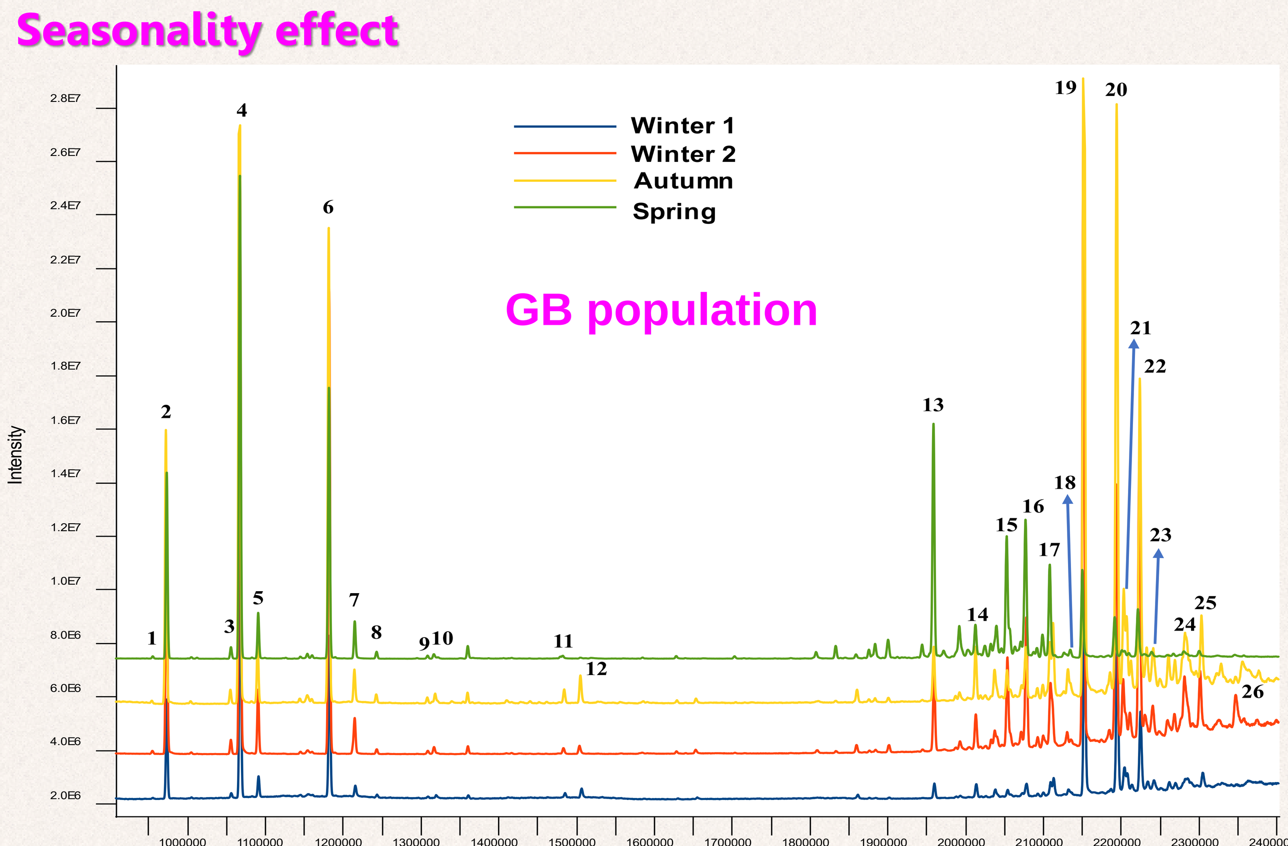


Figure 2: Effect of the seasonality on *B. dracunculifolia* EOs chemical composition (GB population).

Compound identification for the Figures 2 to 4: *B. dracunculifolia* EOs from different populations, plant genders (dioecism), and seasons analyzed by GC/MS.
1. α-thujene; **2.** α-pinene; **3.** sabinene; **4.** β-pinene; **5.** myrcene; **6.** limonene; **7.** *trans*-β-ocimene; **8.** γ-terpinene; **9.** α-terpinolene; **10.** linalool; **11.** terpinen-4-ol; **12.** α-terpineol; **13.** *trans*-β-caryophyllene; **14.** α-humulene; **15.** germacrene D; **16.** bicyclogermacrene; **17.** δ-cadinene; **18.** elemol; **19.** *trans*-nerolidol; **20.** spathulenol; **21.** caryophyllene oxide; **22.** viridiflorol; **23.** ledol; **24.** α-muurolol; **25.** α-cadinol; **26.** not identified; **27.** *iso*-bicyclogermacrenal.

All the EOs' GC/MS profiles were essentially identical, despite quantitative differences in the abundance of the compounds according to the investigated effects were evidenced (Figures 2 to 4). The chemomarker and distinctive component of *B. dracunculifolia* EO, (*trans*)-nerolidol [2] (Figure 3), was present as a main compound (14.2-20.7%) only in the specimens from the Northern regions of Uruguay while at the Southern it was absent or at trace-levels (Figures 4 and 5). These results are in line with our previous data [3-7], suggesting the presence in Uruguay of two well-differentiated chemotypes, a fact not reported previously by Frizzo *et al.* (2008) [4] (Figure 6) in their systematic study on *B. dracunculifolia* EOs chemical variation.

Other major compounds of interest also presented quantitative variations accordingly to the investigated effects, *i.e.* α- and β-pinene, limonene, spathulenol and viridiflorol.

Dioecism effect

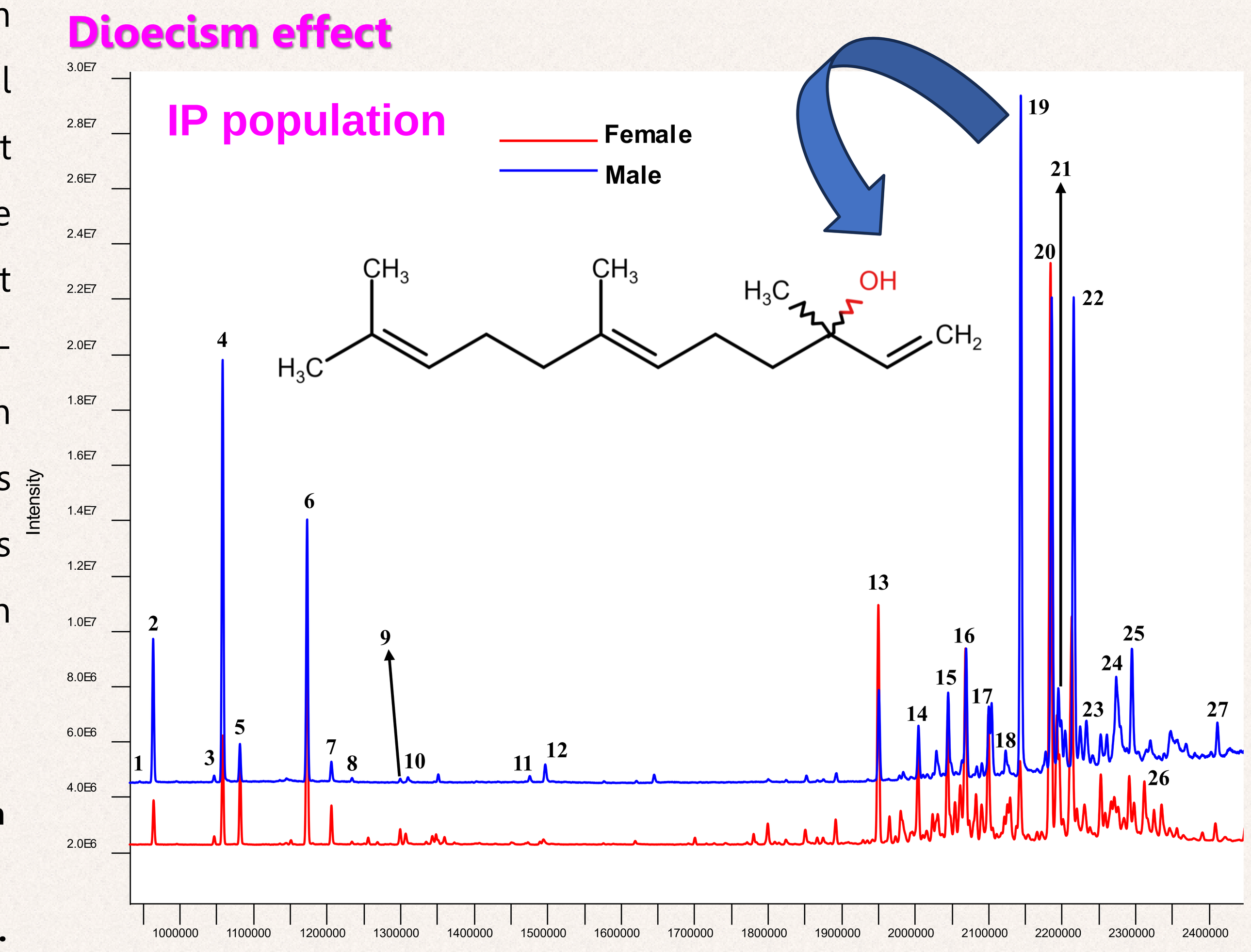
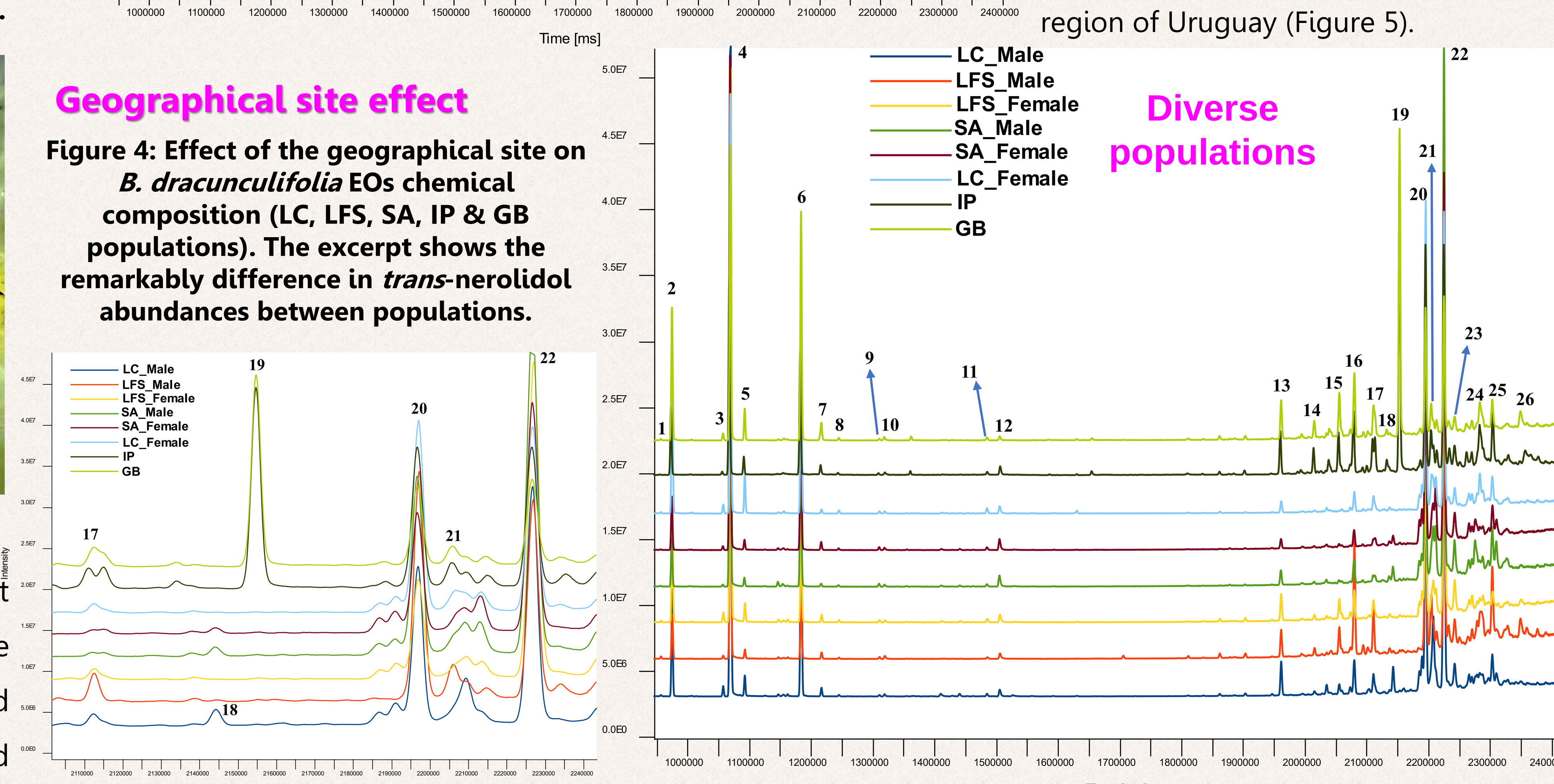


Figure 3: Effect of the dioecism (plant gender) on *B. dracunculifolia* EOs chemical composition (IP population), and chemical structure of the chemomarker *trans*-nerolidol.

These results suggests a high influence of the environmental factors on *B. dracunculifolia* EOs chemical composition, which is relevant when considering that this is an exploitable aromatic species [2]. More studies are needed to understand the reasons behind such a variation, including genetic, morphoanatomical and more detailed GC/MS analyses of the EOs (enantioselective approach), with special emphasis on the not yet studied central region of Uruguay (Figure 5).

Geographical site effect

Figure 4: Effect of the geographical site on *B. dracunculifolia* EOs chemical composition (LC, LFS, SA, IP & GB populations). The excerpt shows the remarkably difference in *trans*-nerolidol abundances between populations.

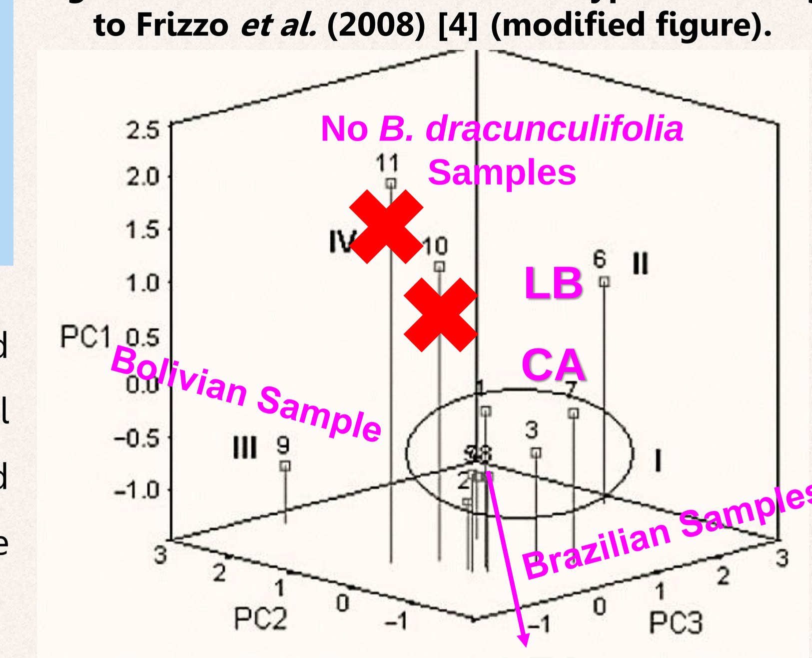


According to the studies performed to date, the presence of appreciable abundances of *trans*-nerolidol in the EOs discriminate the Northern and Southern *B. dracunculifolia* populations, as it is shown in the Figure 5.

Figure 5: Geograhical delimitation of the possible *B. dracunculifolia* chemotypes in Uruguay: presence of the chemomarker *trans*-nerolidol (abundance: 14.2-20.7%) for the Northern populations (in red) and absence or trace-level for the the Southern region (in white).

Multivariate statistical interpretations with a more extensive and robust database are also required to correctly classify the different EO samples in the reliable search for Uruguayan *B. dracunculifolia* chemotypes. In the previous analysis, Frizzo *et al.* (2008) [4] showed that the Uruguayan samples grouped differently to the Brazilian and Bolivian samples (Figure 6), but they did not consider Northern but Southern *B. dracunculifolia* populations. New samples (ongoing experiments) would shed light on this situation.

Figure 6: *B. dracunculifolia* chemotypes according to Frizzo *et al.* (2008) [4] (modified figure).



Conclusion

The experimental work and the literature revision performed allowed to suggest the existence of two well-geographical delimited Uruguayan *B. dracunculifolia* chemotypes, which would be differentiated for the expressive presence or absence of the chemomarker *trans*-nerolidol in their EOs.

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