Chemical Composition of the Leaf and Branch Oils of *Perymenium grande* Hemsl. var. *nelsonii* (Robins. & Greenm.) Fay (Asteraceae-Heliantheae) from Costa Rica

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**Abstract:** The chemical composition of the essential oils of *Perymenium grande* Hemsl. var. *nelsonii* (Robins. & Greenm.) Fay (Asteraceae) growing wild in Costa Rica was analyzed by capillary GC-FID and GC-MS. One hundred and two and one hundred and seven compounds were identified in the leaf and branch oils, respectively, corresponding to about 94.9% and 79.3% of the total amount of the oils. The leaf oil consists mainly of sesquiterpene hydrocarbons (50.3%) and monoterpene hydrocarbons (33.8%). The major components of the leaf oil were β-caryophyllene (30.5%), β-pinene (12.4%), germacrene D (10.0%), β-phellandrene (9.8%) and α-pinene (8.9%). The branch oil consists mainly of sesquiterpene hydrocarbons (38.3%), monoterpene hydrocarbons (21.6%) and oxygenated sesquiterpenes (20.4%). The major components of the branch oil were α-isocomene (13.8%), α-pinene (7.4%), β-isocomene (5.2%), β-pinene (4.3%) and β-caryophyllene (4.3%). This is the first report of the chemical composition of the essential oils obtained from this species.

**Keywords:** *Perymenium grande*; essential oil composition; β-caryophyllene; α-isocomene; β-pinene.

1. Plant Source

   The American tropical genus *Perymenium* (Asteraceae-Heliantheae) is constituted by about 40 species mainly from Mexico [1,2]. This is apparently a monophyletic genus. Heliantheae is one of the largest and most morphologically diverse tribes of the Asteraceae family. *Perymenium grande* Hemsl. (syn. *P. latisquamum* S.F. Blake; *P. nelsonii* B.L. Rob. & Greenm.), is popularly known in Central America as “tatascán”, “tatascamite” and “taxiscobo” [3], ranging from northern Mexico to Peru in South America. In Central America it is cultivated in gardens, in small clumps of 20-30 trees in fallows and “milpas” (corn fields). It is planted as shade for coffee plantations and its characteristics are appropriate to be used in agroforestry systems. In Costa Rica, this plant is a perennial shrub or small tree with two varieties described, *P. grande* var. *grande* and *P. grande* var. *nelsonii*. The latter is

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far more widespread in the country [4]. The leaves are alternate, tripinnerved, lanceolate with cuneate to truncate base, evenly serrate and strigillose-scabrid about. The heads are in an ample and terminal cymose inflorescence [4].

Leaves and branches from *Perymenium grande* Hemsl. var. *nelsonii* (Robins. & Greenm.) Fay (Asteraceae), growing wild in Costa Rica, were collected on June, 2009, at Fraijanes (Miramar de Montes de Oro, Province of Puntarenas, Costa Rica). A voucher specimen was kept at the Herbarium of the University of Costa Rica (USJ 93915).

2. Previous Studies

Some phytochemical studies have been done on plants of the genus *Perymenium* and diterpenoids have been isolated from *P. ecuadoricum* [5] and *P. klattianum* [6]. Coumarins, flavonoids, triterpenes, and two phytane-type diterpenes have been isolated from *P. hintonii* [7]. Several sesquiterpene lactones have been isolated from *P. mendezi* [8], *P. featherstonei* [9], *P. klattianum* [6], *P. discolor* [10] and *P. berlandieri* [10]. Several sesquiterpene lactones have been isolated from *P. grande* growing in Costa Rica [12]. To the best of our knowledge, no previous reports on the composition of the essential oils of this plant have been published.

3. Present Study

The leaves and branches were dried and subjected to hydrodistillation for 3 h using a modified Clevenger-type apparatus. The distilled oils were collected and dried over anhydrous sodium sulfate, filtered and stored at 0-10°C. The yield of the light yellowish oil from the leaf was 0.3 % (v/w) and from the branches was 0.1% (v/w).

The oils of *P. grande* var. *nelsonii* were analyzed by GC-FID (gas chromatography with flame ionization detector) using a Shimadzu GC-2014 gas chromatograph. The data were obtained on a poly(5% phenyl-95% methylsiloxane) fused silica capillary column (30 m x 0.25 mm; film thickness 0.25 µm), (MDN-5S), with a LabSolutions, Shimadzu GC Solution, Chromatography Data System, software version 2.3. Operating conditions were: carrier gas N₂, flow 1.4 mL min⁻¹; oven temperature program: 60-280 °C at 3 °C min⁻¹, 280 °C (2 min); sample injection port temperature 250 °C; detector temperature 280 °C; split 1:60.

The analyses by gas chromatography coupled to mass selective detector were performed using a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 apparatus and CLASS 5000 software with Wiley 139 and NIST computer databases. The data were obtained on a poly(5% phenyl-95% methylsiloxane) fused silica capillary column (30 m x 0.25 mm; film thickness 0.25 µm), (MDN-5S). Operating conditions were: carrier gas He, flow 1.0 mL min⁻¹; oven temperature program: 60-280 °C at 3 °C min⁻¹; sample injection port temperature 250 °C; detector temperature 260 °C; ionization voltage: 70 eV; ionization current 60 µA; scanning speed 0.5 s over 38-400 amu range; split 1:70.

The oil components were identified using the retention indices (RI) on DB-5 type column [13], and by comparison of their mass spectra with those published in the literature [14] or those of the authors’ database. Integration of the total chromatogram (GC-FID), expressed as area percent, has been used to obtain quantitative compositional data.

From the hydrodistilled oils, a total of 153 compounds were identified, accounting for 79.3–94.9% of the total composition of the essential oils. The chemical composition of the oils is listed in Table 1 (see Supporting Information). The leaf oil of *P. grande* var. *nelsonii* consists mainly of sesquiterpene hydrocarbons (50.3%) and monoterpenoid hydrocarbons (33.8%). The major components of the leaf oil were β-caryophyllene (30.5%) (1) (Figure 1), β-pinene (12.4%), germacrene D (10.0%), β-phellandrene (9.8%) and α-pinene (8.9%). The branch oil consists mainly of sesquiterpene hydrocarbons (38.3%), monoterpenoid hydrocarbons (21.6%) and oxygenated sesquiterpenes (20.4%). The major components of the branch oil were α-isocoumarone (13.8%) (3), α-pinene (7.4%), β-isocoumarone (5.2%) (4), β-pinene (4.3%) and β-caryophyllene (4.3%) (1). In addition
to α- and β-isocomene, the essential oil from the branches presented the uncommon sesquiterpene hydrocarbons of the triquinane structure modheph-1-ene (5), silphin-1-ene (6), silphiperfol-5-ene (7)

Figure 1. β-Caryophyllene (1) and presilphiperfolan-8-yl carbocation (2), precursors of triquinane and related sesquiterpenes (3-8) present in the oils.

and presilphiperfol-7-ene (8) that are associated with the Asteraceae family [15-22]. The branch oil showed notable amounts (ca. 24%) of triquinane constituents and only 4.3% of β-caryophyllene. Bohlmann and Jakupovic [15] based on the co-occurrence of the triquinane sesquiterpenes (α- and β-isocomene, modhephene, silphinene, silphiperfolenes) with β-caryophyllene in Silphium roots, proposed a biogenetic pathway starting with the protonation of β-caryophyllene and the formation of the caryophyllenyl carbocation. Bohlmann et al. [23] isolated from Eriophyllum staechadifolium 8α-hydroxy-presilphiperfolene which was converted to the silphiperfol-6-ene via the presilphiperfolan-8-yl carbocation (2) and proposed a general biogenetic pathway for these compounds: [farnesol → humulyl carbocation → caryophyllenyl carbocation → presilphiperfolan-8-yl carbocation → triquinane and related sesquiterpenes]. The presilphiperfolan-8-yl carbocation (2) occupies a key position on this pathway and several chemical studies demonstrated the biogenetic relationship between compounds like (3-8) and this carbocation (Figure 1) [24-28]. Also, quantum chemical calculations have been used to propose a biogenetic pathway from farnesyl diphosphate and isomerization to neryl diphosphate to presilphiperfolan-8-ol via the presilphiperfolan-8-yl carbocation (2) [29]. P. grande var. nelsonii leaf oil showed small amounts of triquinane constituents (only 0.1%) and the presence in this oil of a higher quantity of β-caryophyllene (1) (30.5%) than in the branch oil might be indicative that, in this morphological part of the plant, protein homologues to the fungal presilphiperfolan-8β-ol synthase [30] are not as active as the ones in the leaf.
Chemical composition of the leaf and branch oils of *Perymenium grande*

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**Supporting Information**

Supporting information accompanies this paper on http://www.acgpubs.org/RNP

**References**


