

ESSENTIAL OILS OF PLANTS FROM HISPANIOLA:
4. THE VOLATILE LEAF OIL OF *PLETHADENIA GRANULATA* (RUTACEAE).

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Adams, Robert P. (CSFAA, Box 7372, Baylor University, Waco, TX 79798, USA), Thomas A. Zanoni and Elvia Jaime Miller (Jardín Botánico Nacional, Apartado Postal 21-9, Santo Domingo, Dominican Republic). *Moscoso* 6: 223-225. 1990. The volatile leaf oil of *Plethadenia granulata* (Krug & Urban) Urban (Rutaceae) was analyzed by fused silica capillary gas chromatography/ion trap mass spectrometry (GC/ITMS). The leaves yielded 0.73% oil (fw). The principal components are: sabinene (25.41%), myrcene (10.53), trans-p-menth-2-en-1-ol (10.40), β -phellandrene (9.81), cis-p-menth-2-en-1-ol (5.13), limonene (4.91), linalool (4.73), 4-terpinenyl acetate (3.40), α -terpinenyl acetate (3.34), trans-piperitol (2.38) and trans-Sabinene hydrate (2.17). Forty four of the 47 constituents are identified.

KEY WORDS Essential oil, terpenes, *Plethadenia granulata*, Rutaceae, Ion Trap Mass Spectrometry

Plethadenia granulata (Krug & Urban) Urban is one of the two species of the genus endemic to the Caribbean (the other species, *P. cubensis* Urban is endemic to Cuba). *Plethadenia granulata* has been considered native to Cuba and Hispaniola (Leon and Alain, 1953), but in a more recent flora, Liogier (1985) considered it endemic to Hispaniola. *Zanthoxylum* is the genus most closely related to *Plethadenia*.

Plethadenia granulata is uncommon in Hispaniola. It is known from the arid coastal woodlands, on calcareous soil in Haiti and from the foothills of the Sierra de Bahoruco, along the Hoyo de Enriquillo, in the Dominican Republic (D. R.). This is an area that was coastal in earlier times when the valley from Barahona (D. R.) to Port-au-Prince (Haiti) was a sea channel. Although coastal, it is known from sea level to about 400 m elevation (D. R.). This compound-leaved, aromatic shrub is not used by the Haitians or Dominicans. Much of the volatile oil is thought to be in the glands in the leaflets.

The composition of the volatile leaf oil of *P. granulata* has not been previously reported. As a part of our on-going research on the essential oils of plants from Hispaniola (Zanoni and Adams, 1989), the composition of the leaf oil of *P. granulata* is presented in this paper.

Materials and Methods

Plant materials- The samples consisted of approximately 100 g of fresh foliage, collected from the Republica Dominicana: Sierra de Bahoruco, Prov. Independencia, approx. 2 km N of Puerto Escondido on the road to Duverge, elev. 380 m on 28 Aug. 1987. A voucher specimen (Zanoni & Pimentel 40402) is on deposit at the herbarium at the Jardín Botánico Nacional, Santo Domingo (JBSD).

The foliage was kept frozen until steam distilled using a modified Clevenger apparatus (von Rudloff, 1967). Steam distillation was performed for 2 hr and the floating oil layer collected. The oil was sealed in glass vials with teflon lined caps, sent by air to RPA where it was stored at -20°C until analyzed.

Mass spectra were recorded with a Finnigan Ion Trap (ITD) mass spectrometer, model 800, directly coupled to a Varian 6500 gas chromatograph, using a J & W DB5, 0.26 mm id x 30 m, 0.25 micron coating thickness, fused silica capillary column. The GC/ITD was operated under the following conditions: injector temperature: 220°C; transfer line: 240°C; oven temperature programmed: 60°C to 240°C @ 3°C/min; carrier gas: He @ 31.9

Table 1. Composition of the steam volatile leaf oil of *Plethadenia granulata* (Rutaceae). Compounds are listed in order of their elution on a DB5 (=SE54) column. Data expressed as % total oil based on total ion count (TIC). Unidentified components smaller than a trace (0.05%) are not reported. Compound names enclosed in parenthesis () are tentatively identified.

COMPOUND	% Total oil	COMPOUND	% Total oil
α -Thujene	0.31	cis-Piperitol	1.61
α -Pinene	0.12	trans-Piperitol	2.38
Camphene	trace	Piperitone	0.66
Sabinene	25.41	Geraniol	trace
β -Pinene	0.23	4-Terpinenyl acetate	3.40
Myrcene	10.53	Caryophyllene	0.37
α -Phellandrene	0.97	allo-Aromadendrene	1.80
3-Carene	trace	Geranyl propionate	0.29
α -Terpinene	0.73	Germacrene D	1.68
p-Cymene	0.23	Cadinene isomer, RT1635	1.05
Limonene	4.91	Cadinene isomer, RT1670	0.59
β -Phellandrene	9.81	(Geranyl isobutyrate)	0.42
cis-Ocimene	trace	1S, cis-Calamenene	trace
trans-Ocimene	0.33	δ -Cadinene	0.32
(2-Pentene, 4'-4-oxibys-)	0.09	Germacrene D-4-ol	trace
Γ -Terpinene	0.84	RT1887	0.70
trans-Sabinene hydrate	2.17	τ -Cadinol	trace
Terpinolene	0.52	τ -Muurolol	trace
cis-Sabinene hydrate	1.11	Torreyol	trace
Linalool	4.73	α -Cadinol	trace
trans-p-Menth-2-en-1-ol	10.40	cis, cis-Farnesol	trace
cis-p-Menth-2-en-1-ol	5.13	trans, trans-Farnesol	0.23
4-Terpineol	1.71	trans, cis-Farnesol	trace
α -Terpineol	3.34		

cm/sec or 1.017 ml/min (@ 210°C); injection size: 0.1 μ l (10% soln.), split 1:20, 500 ng/on column. Tuning values for the ITD were 100, 100, 100, 100 using cedrol as a tuning standard (Adams, 1989). Internal standards (n-octane and n-eicosane) were added to each sample to aid in the standardization of retention times. Identifications were made by library searches of our volatile oil library, LIBR(TP) using the Finnigan library search routines based on fit (Adams, 1989). Additional searches were made of the EPA/NIH mass spectral data base (Heller and Milne, 1983; Adams, et al, 1979)

Results and Discussion

The leaves yielded 0.73 g of oil / 100 g fresh weight (fw). The composition the leaf oil of *P. granulata* is shown in Table 1. The largest components are: sabinene (25.41%), myrcene (10.53), trans-p-menth-2-en-1-ol (10.40). β -phellandrene (9.81), cis-p-menth-2-en-1-ol (5.13), limonene (4.91), linalool (4.73), 4-ter-pinenyl acetate (3.40), α -terpinenyl acetate (3.34), trans-piperitol (2.38) and trans-Sabinene hydrate (2.17). The presence of relative large amounts of cis- and trans-p-menth-2-en-1-ol is unusual (Lawrence, 1985). Thus, *P. granulata* might be a natural source for these compounds.

Three unidentified components were present in amount greater than 0.5%. These are [(ITMS, m/z (Rel. int.)]: RT1636, 204[M] + (18), 41(93), 55(22), 67(27), 79(59), 91(92), 105(93), 119(56), 133(44), 147(7), 161(100), 176(3), 189(6), possibly a "cis"- stereoisomer of α -cadinene; RT1670, 204[M] + (23), 41(60), 55(14), 67(13), 79(24), 91(62), 105(67), 119(41), 133(26), 147(7), 161(100), possible stereoisomer of α -canadinene; RT1887, 204[M] + (4), 43(100), 55(33), 67(49), 81(40), 93(44), 107(33), 121(17), 133(11), 147(9), 161(23), 189(9), sesquiterpene alcohol.

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