

Chemical Composition of the Essential Oil of *Pituranthos scoparius*

Nadhir Gourine^{a*}, Bahia Merrad^a, Mohamed Yousfi^a, Pierre Stocker^b and Emile M. Gaydou^c

^aUniversité Amar Thélidji de Laghouat, Laboratoire des Sciences Fondamentales (LSF), Équipe Chimie Organique Appliquée, B.P. 37G, (03000) Laghouat, Algeria

^bLaboratoire de Biosciences, Faculté des Sciences et Technique de Saint-Jérôme, Université Paul Cézanne, Marseille, France

^cUniversité Paul Cézanne, Faculté des Sciences et Techniques de Saint-Jérôme, UMR CNRS 6263, Institut des Sciences Moléculaires de Marseille (ISM2), AD2EM, LSCC, Groupe Phytochimie, Boîte 461, Av Escadrille Normandie Nièmen, F-13397 Marseille Cedex 20, France

n.gourine@mail.lagh-univ.dz

Received: February 6th, 2011; Accepted: April 9th, 2011

The essential oils obtained by hydro distillation of the aerial parts of *Pituranthos scoparius* were collected from different regions of Algeria and gave various yields ranging from 0.6 up to 2.8% (v/w). These samples were analyzed by GC and GC-MS showing the occurrence of monoterpene hydrocarbons and some oxygenated compounds. The major components were α -pinene (4.4-35.8%), limonene (0.8-66.5%), bornyl acetate (tr-9.6%), myristicin (tr-31.1) and dill apiole (0.4-47.3%). The aerial parts of *P. scoparius* could be either very rich or very poor in limonene, myristicin or dill apiole. Cluster analysis shows differences in essential oil compositions of samples coming from the different area collected.

Keywords: *Pituranthos scoparius*, essential oil, monoterpene, myristicin, dill apiole, cluster analysis.

Pituranthos scoparius (Coss. & Dur.) Schinz (*Umbelliferae*) (= *Deverra scoparia* Coss. & Dur), commonly known as “guezzah” is a Saharan species [1] used in traditional medicine for the treatment of asthma and rheumatism [2,3]. The Touareg people which are little communities living in the Algerian desert of Tassili and Hoggar, also use it in food as aroma for meal and bread [3]. Only a very few studies were conducted on this plant. The main previous studies deal with the antibacterial of the flavonoids [4] antibacterial activities of the essential oils [1,5], chemical composition of the essential oil of stems and seeds (Table 1) [6,7]. Two isocoumarins from the roots of *P. scoparius* were isolated [8]. Recently, the antioxidant activity of the phenolic extracts [9] and their constituents [10] were also reported.

The aim of the present study is to carry out a large scale investigation on the essential oil composition of *P. scoparius* in Algeria which involves different regions and locations never investigated to our knowledge. This is the first time that the aerial parts (mixture of stems and seeds) of the essential oil of *P. scoparius* are investigated.

Extracts of *P. scoparius* aerial parts yielded a green-yellow color oils (0.6–2.8%) (v/w) with a very characteristic odor. The aerial parts of *P. scoparius* essential oils were analyzed by GC and GC-MS. Thirty eight compounds

Table 1: Major components in seeds and stems *Pituranthos scoparius* essential oils, growing in Ghardaïa [5] and Ain-Diss [6] areas (Algeria).

Compound	Stem		Compound	Seeds	
	% [6]			% [7]	
α -Pinene	8.2	6.8	α -Pinene	11.0	34.0
β -Pinene	4.6	3.8	<i>p</i> -Cymene	1.6	3.3
α -Phellandrene	4.0	7.1	Bornyl acetate	21.0	0.2
<i>p</i> -Cymene	7.5	4.2	<i>trans</i> -Verbenol	0.2	3.6
Limonene	11.2	9.8	Apiol	52.8	15.0
Thymol	5.9	0.1			
Methyleugenol	1.6	5.9			
Germaacrene D	1.0	12.7			
Myristicin	11.1	7.2			
Spathulenol	2.5	4.5			
Dill apiole	12.2	1.1			

were identified showing high amounts in monoterpenes (45.3-83.7%), with mainly monoterpene hydrocarbons (44.4-81.9%). Some samples were also rich in oxygenated compounds such as myristicin + dill apiole (3.5-48.1%) (Table 2).

The main components identified were α -pinene (4.4-35.8%), limonene (0.8-66.5%), bornyl acetate (tr-9.6%), myristicin (tr-31.1) and dill apiole (0.4-47.3%). The samples investigated presents large variations of percentage intervals relatively to each main component; which supposes the existence of some chemotypes within the same species.

Table 2: Component identifications of *Pituranthos scoparius* aerial part of essential oils from three regions in Algeria.

Compounds	GC peaks area (%) ^a												LRI ^d	Identification
	Ghardaïa ^b							Laghouat ^b		Djelfa ^b				
	BRN ^c							SMK ^c	AMD ^c	ABD ^c		DJL ^c		
1	2	3	4	5	6	7	8	9	10	11	12			
<i>α</i>-Pinene	8.1	11.2	4.7	8.4	5.5	10.4	4.4	35.8	35.1	23.7	26.7	27.0	1029	MS, RI
Camphene	tr	tr	tr	tr	tr	tr	tr	2.4	1.2	tr	2.1	tr	1072	MS, RI
<i>β</i>-Pinene	0.5	2.9	1.2	0.5	2.0	1.2	1.7	5.2	5.2	5.3	4.1	1.7	1123	MS, RI
Sabinene	0.2	0.2	tr	0.4	0.3	0.4	0.3	2.2	1.1	1.1	0.9	4.6	1139	MS, RI
<i>δ</i> -3-Carene	tr	tr	tr	tr	tr	1.0	0.2	tr	tr	1.1	1.4	tr	1154	MS, RI
<i>β</i> -Myrcene	0.7	0.6	0.3	0.6	0.6	0.9	0.6	1.3	1.1	0.6	1.2	0.9	1168	MS, RI, AS
<i>α</i>-Phellandrene	4.6	6.4	2.1	0.7	4.1	1.7	3.6	1.0	2.0	1.2	1.9	0.8	1173	MS, RI
<i>α</i> -Terpinene	tr	tr	tr	tr	tr	tr	tr	0.2	tr	tr	tr	tr	1190	MS, RI
Limonene	66.5	49.5	32.7	45.0	37.2	58.3	34.4	7.0	30.0	0.9	7.8	4.0	1209	MS, RI, AS
<i>β</i> -Phellandrene	0.6	2.6	0.8	tr	2.0	0.4	1.9	0.6	0.7	0.9	0.6	tr	1218	MS, RI
<i>cis-β</i> -Ocimene	tr	tr	tr	tr	tr	tr	tr	tr	tr	3.2	3.8	1.2	1239	MS, RI
<i>γ</i> -Terpinene	0.1	tr	2.0	1.3	0.9	0.4	0.8	0.9	2.0	tr	1.0	2.3	1253	MS, RI, AS
<i>trans-β</i> -Ocimene	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	1257	MS, RI
<i>p</i>-Cymene	0.5	1.8	0.7	0.6	2.4	1.0	2.4	1.0	1.6	6.7	2.0	2.1	1281	MS, RI
<i>α</i> -Terpinolene	0.1	0.3	tr	tr	0.3	tr	0.3	0.2	tr	tr	tr	tr	1290	MS, RI
<i>α</i> -Copaene	0.1	tr	tr	tr	0.4	0.5	0.5	tr	tr	tr	tr	tr	1473	MS, RI
Linalool	0.1	tr	tr	tr	0.6	tr	tr	0.2	tr	1.94	tr	tr	1554	MS, RI, AS
Bornyl acetate	0.1	tr	tr	tr	tr	0.3	tr	9.5	3.0	Tr	9.6	tr	1592	MS, RI, AS
<i>β</i> -Caryophyllene	0.3	0.3	0.3	0.4	tr	0.6	0.2	tr	0.2	0.6	tr	0.3	1605	MS, RI, AS
Terpinen-4-ol	0.1	0.2	tr	tr	tr	0.4	0.2	1.1	0.4	0.9	0.6	0.6	1617	MS, RI, AS
<i>α</i> -Terpineol	0.1	0.3	0.9	tr	0.3	tr	0.2	0.2	0.1	0.4	tr	tr	1715	MS, RI, AS
Germacrene D	2.1	3.8	4.3	2.8	5.9	6.3	5.3	1.3	1.6	3.3	1.1	2.5	1723	MS, RI
Bicyclogermacrene	0.4	0.6	2.0	1.3	0.8	2.3	0.7	0.4	0.3	tr	tr	0.6	1745	MS, RI
<i>δ</i> -Cadinene	0.5	1.2	1.3	1.0	1.3	2.0	0.9	0.6	0.5	1.4	0.5	0.6	1769	MS, RI
Methyl eugenol	0.1	0.3	0.6	tr	1.4	2.7	1.9	tr	0.2	1.7	tr	0.7	2029	MS, RI
Carotol	–	1.1	tr	–	–	–	–	–	0.1	tr	–	–	2035	MS, RI
Spathulenol	0.1	0.6	0.5	0.5	0.6	1.7	0.7	0.3	0.2	1.7	0.6	1.2	2145	MS, RI
<i>α</i> -Cadinol	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	2179	MS, RI
<i>δ</i> -Cadinol	0.9	tr	3.6	3.1	tr	tr	0.2	tr	tr	0.4	tr	tr	2190	MS, RI
<i>τ</i> -Muurolool	0.2	1.0	0.4	0.5	0.7	1.7	0.2	tr	0.2	1.6	tr	0.7	2202	MS, RI
<i>α</i> -Eudesmol	tr	tr	tr	tr	tr	tr	0.8	0.3	tr	tr	0.3	tr	2221	MS, RI
<i>β</i> -Eudesmol	tr	tr	tr	tr	tr	tr	0.2	tr	tr	0.5	tr	tr	2230	MS, RI
NI	0.2	1.0	0.8	0.4	1.7	1.9	1.8	1.2	0.2	3.0	0.4	tr	2250	–
Myristicin	tr	5.2	12.4	2.6	25.1	0.4	31.1	–	1.9	18.2	2.5	tr	2288	MS, RI
Dill apiole	11.3	1.03	22.6	23.0	0.9	0.4	1.1	25.7	9.9	1.4	30.3	47.3	2384	MS, RI
Butylidene dihydrophthalide	tr	5.5	1.4	0.4	1.0	tr	1.0	0.3	tr	0.6	tr	tr	2614	MS, RI
Myristic acid	–	–	–	–	–	–	–	–	–	tr	–	–	2707	MS, RI
Palmitic acid	–	–	–	–	–	–	–	–	–	0.7	–	–	2915	MS, RI
Total identified	98.2	97.4	95.5	93.1	96.0	96.7	97.2	98.6	98.6	82.6	99.4	98.9		
Monoterpenes HC	81.9	75.5	44.5	57.4	55.3	75.6	50.5	57.7	80.0	44.6	53.6	44.4		
Oxygenated monoterpenes	0.5	0.7	1.2	0.4	1.0	1.0	0.6	10.9	3.7	3.8	10.2	0.9		
Total monoterpenes	82.5	76.3	45.7	57.7	56.3	76.6	51.1	68.7	83.7	48.4	63.7	45.3		
Sesquiterpenes HC	3.1	5.5	7.6	5.4	8.4	11.3	7.6	2.3	5.3	4.7	1.6	4.1		
Oxygenated sesquiterpenes	1.1	2.7	4.5	4.0	1.3	3.4	2.0	0.6	0.5	4.2	0.9	1.8		
Total sesquiterpenes	4.3	8.2	12.1	9.4	9.7	14.7	9.5	2.9	5.8	8.9	2.5	5.9		
Other oxygenated compounds	11.3	12.0	36.9	26.0	28.4	3.5	35.0	25.9	12.0	21.7	32.8	48.1		

^aPercentages obtained by FID peak-area normalisation; ^bRegion; ^cLocation in the region; ^dLinear retention indices relative to homologous *n*-alkanes C₈–C₄₀ obtained on UB-Wax column.

BRN: Berriane; SMK: Sidi-Makhlouf; AMD: Ain-Mahdi; ABD: Aïne-Mabed; DJL: outside the town of Djelfa; NI: not identified by GC-MS; tr: traces (<0.01%); RI retention indices; MS mass spectroscopy; AS: Identification relative to retention indices of pure authentic samples.

For the location of Berriane the *α*-pinene content ranges from 4.4 to 11.2%. For the Laghouat area (Sidi-Makhlouf and Ain-Mahdi locations) the contents of *α*-pinene are much higher than those of the Berriane location and their values are practically the same (35.8 and 35.1%). Similarly the Djelfa area is characterized by very close contents of *α*-pinene, but the contents are little lower than the last region (23.7, 26.7 and 27.0%). The *β*-pinene content is very weak in all samples except for the Laghouat area and some

samples of the Djelfa area where its content is a little bit higher (4.1–5.3%). For limonene, it appears that the highest percentages are found in Ghardaïa area (32.7–66.5%). For the other areas, the limonene content ranges from 0.9% up to 30.0%. The *p*-cymene content is very low in all samples (0.6–2.4%) except for sample 8 (Table 2), where the percentage is higher (6.7%). Similarly the bornyl acetate content was very weak in almost all samples (tr–3.0%), except for two samples: Laghouat (Sidi-Makhlouf) and

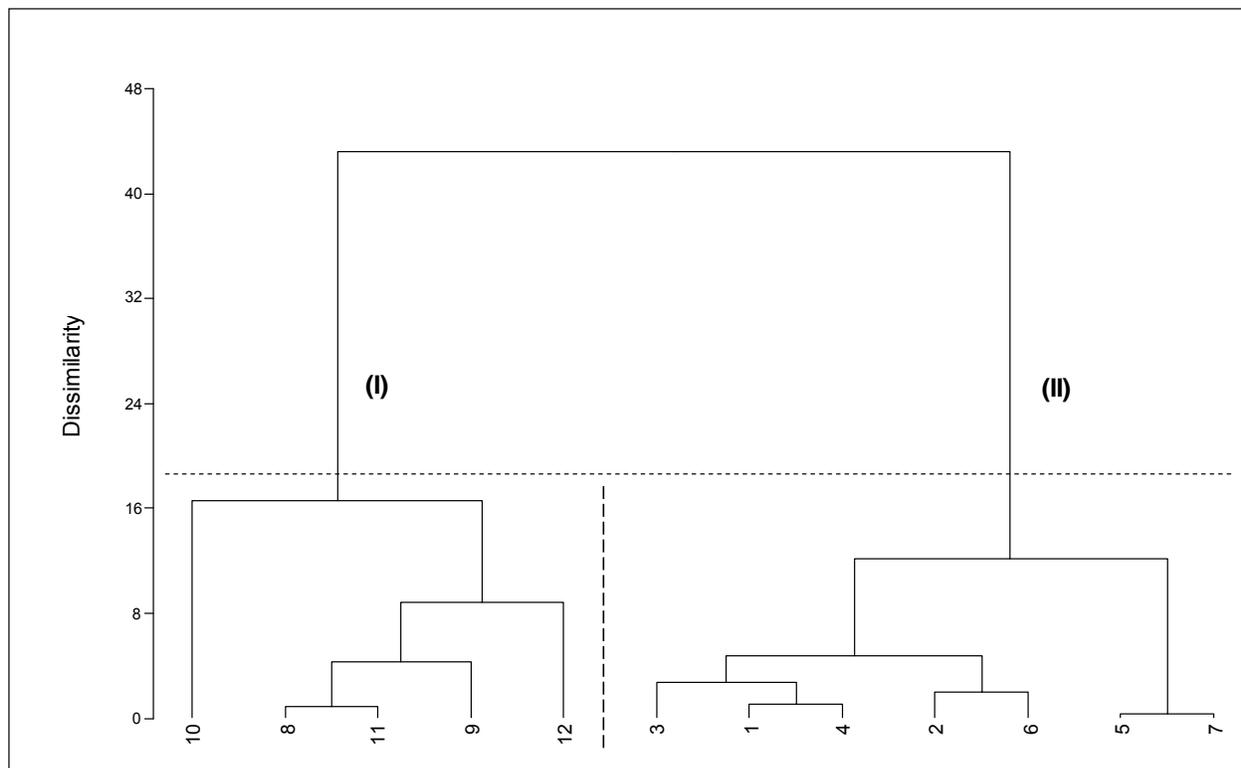


Figure 1: Dendrogram obtained from the cluster analysis of 12 essential oil samples of *Pituranthos scoparius* from three regions in Algeria. Samples are clustered using Ward's technique with a Euclidean distance measure.

Djelfa (Aïne-Mabed) with very close percentages 9.5 and 9.6%, respectively. The germacrene D content ranges from 1.1 up to 6.3%. For myristicin and dill apiole, the variation is not clear, in some samples the content is very high and in some other ones it is very weak or nil (possible presence of chemotypes). Although the α -pinene and β -pinene contents are very close for the two samples of Laghouat, the other major component of the same two samples are much more different: limonene, bornyl acetate and dill apiole. Finally it was noticed that the two samples 8 and 11, belonging to different area, are much more similar.

The results found herein our investigation, are quite in agreement with those of reported previously, for the stems and the seeds (Table 1), since the samples analyzed were found to be rich in α -pinene, limonene, bornyl acetate, and dill apiole. It is important to note that the percentages of the major compounds found in this investigation are much higher than of those reported previously, for example the percentage of limonene in the stems was 11.2%, much lower than 66.5% recorded for the first sample which belongs to the Ghardaïa region. The same observation could be extended for the myristicin and dill apiole contents. It's important to mention that our results show the absence of some minor compounds which were previously reported like thymol [6] and *trans*-verbenol [7].

Some observations related to the differentiation between the essential oils of the different studied locations have been noticed. These observations are based on the

percentage distribution of the major compounds in these essential oils. It was noticed that some samples for the same location were rich in some components; whereas in the rest of samples, their contents were weak or very poor for the same referred compound. As an example, in the Ghardaïa region, some samples have high dill apiole contents (11.6-22.9%), whereas the rest of the samples were poor in the same compounds (0.4-1.1%). This later observation confirms the potential occurrence of chemotypes in these essential oils and could explain the variability of the results reported for the same essential oil of *P. scoparius*.

In order to investigate the differences between the essential oil samples of the three different regions of our collections, we have chosen the cluster analysis using the Ward's technique. The result showed the existence of two principal clusters (I and II) within the essential oil of the individuals of *P. scoparius* (Figure 1). The group (I) is referred to the two regions of Laghouat and Djelfa and the second group (II) is referred to the region of Ghardaïa. The two types of essential oils are distinguished essentially with respect to their α -pinene, β -pinene, limonene, bornyl acetate and germacrene D contents. The chemical composition of group (I) samples is characterized by higher contents in α -pinene, β -pinene, bornyl acetate and dill apiole. The essential oil samples which belong to cluster (II) are characterized by higher content in limonene, germacrene D and myristicin.

The examination of the cluster dendrogram (Figure 1) shows some similarity between the samples in each principal cluster. The samples 8 and 11 of the group (I) are quite similar in their major compound contents (Table 2); the same observation could be generalized for samples 1 and 4, 2 and 6, 5 and 7 belonging to the second group (II). The sample number 10 is somewhat different from all the tested samples; this is due to its relatively higher content of *p*-cymene (6.7%).

The main compounds were not the same for the overall samples analyzed and coming from the different locations *i.e.* the major compound is sometimes being a minor compound and *vice-versa*. This variability of the content of the main compounds supposes the existence of different chemotypes within the same plant. Taking in account this later consideration, further studies of multivariate statistical analysis using a great number of samples are needed to determine the possible occurrence of chemotypes in the essential oil of *P. scoparius*.

Experimental

Plant material: Aerial part of *Pituranthos scoparius* were randomly collected from three different regions in Algeria: Ghardaïa (7 samples) Laghouat (2 samples) Djelfa (3 samples). The chosen numbers of samples collected from each region were roughly proportional to the availability of

the plant in each one of these regions. The main region of the current investigation is Ghardaïa, at the location of Benriane; the second region is Laghouat with two locations: Aïn-Mahdi and Sidi-Makhlouf; the last region is Djelfa with two locations: Aïne-Mabed and Djelfa. The three above regions are located 550, 400 and 300 km south the capital Algiers, respectively.

Preparation of samples: The samples of the plants (aerial parts) were air-dried in the shade at room temperature. The total number of the samples was twelve. The essential oils were obtained by hydro distillation using a Clevenger apparatus for almost 3 hours. The essential oils were obtained at different yields in the range of 0.6 to 2.8% v/w, and then they were dried over anhydrous sodium sulfate, filtered and stored at +4°C until analysis.

Gas chromatography (GC) analysis: A CP-Varian 3800 gas chromatograph was used with a flame ionization detector (FID), and a UB-Wax fused silica capillary column (60 m × 0.32 mm, 0.25 µm film thickness). Oven temperature was programmed from 50°C to 250°C at a rate of 3°C/min and held at 250°C for 10 min. Injector and detector temperatures were set at 250°C and 260°C, respectively. Helium was the carrier gas at a flow rate of 1 mL/min.

References

- [1] Boutaghane N, Nacer A, Kabouche Z, Ait-Kaki B. (2004) Comparative antibacterial activities of the essential oils and seeds of *Pituranthos scoparius* from Algerian septentrional Sahara. *Chemistry of Natural Compounds*, **40**, 606–607.
- [2] Boukef MK. (1986) Les plantes dans la médecine traditionnelle tunisienne, Agence de Coopération Culturelle et Technique, pp. 228–230.
- [3] Benchelah AC, Bouziane H, Maka M, Ouahes C. (2000) *Fleurs du Sahara*, Ibis Press, Paris.
- [4] Benmekhbi L, Kabouche A, Kabouche Z, Ait-Kaki B, Touzani R, and Bruneau C. (2008) Five glycosylated flavonoids from the antibacterial butanolic extract of *Pituranthos scoparius*. *Chemistry of Natural Compounds*, **44**, 639–641.
- [5] Dahia M, Laouer H, Chaker AN, Prado S, Meierhenrich UJ, Baldovini N. (2007) Chemical composition and antibacterial activity of *Pituranthos chloranthus* volatile oil, *Natural Product Communications*, **2**, 1159–1162.
- [6] Verite P, Nacer A, Kabouche Z, Seguin E. (2004) Composition of seeds and stems essential oils of *Pituranthos scoparius* (Coss. & Dur.) Schinz. *Flavour and Fragrance Journal*, **19**, 562–564.
- [7] Vernin G, Lageot C, Ghiglione C, Dahia M, Parkanyi C. (1999) GC/MS analysis of the volatile constituents of the essential oils of *Pituranthos Scoparius* (Coss et Dur.) Benth. et Hook. from Algeria. *Journal of Essential Oil Research*, **11**, 673–676.
- [8] Haba H, Benkhaled M, Massiot G, Lavaud C. (2004) Alkylated isocoumarins from *Pituranthos Scoparius*. *Natural Product Research*, **18**, 409–413.
- [9] Djeridane A, Brunel JM, Vidal N, Yousfi M, Ajandouz EH, Stocker P. (2008) Inhibition of porcine liver carboxylesterase by a new flavone glucoside isolated from *Deverra scoparia*. *Chemico-Biological Interactions*. **172**, 22–26.
- [10] Dahia M, Siracusa L, Laouer H, Ruberto G. (2009) Constituents of the polar extracts from Algerian *Pituranthos scoparius*. *Natural Product Communications*, **4**, 1691–1692.