

Full Paper

Variability of Two Essential Oils of *Kundmannia sicula* (L.) DC., A Traditional Algerian Medicinal Plant

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Abstract: The essential oils of the aerial parts of *Kundmannia sicula* (L.) DC collected from two Algerian localities, El Kala (near the coast) and Béjaia (from a meadow about 10 km from the coast), were analysed by GC and GC-MS. Although both samples showed similar overall chemical compositions, the major components of the Béjaia sample were identified as being spathulenol (14.8%), caryophyllene oxide (12.2%), salvial-4(14)en-1-one (10.1%), 1,5-epoxysalvial-4(14)ene (5.2%) and germacrene D (3.2%), while in the El Kala sample the main compounds were found to be salvial-4(14)en-1-one (16.4%), 1,5-epoxysalvial-4(14)ene (6.5%), chrysanthenyl acetate (5.2%) and α -amorphene (2.9%).

Keywords: Apiaceae, *Kundmannia sicula*, essential oil, GC-MS analysis

Introduction

Kundmannia Scop. is a genus of the Apiaceae family which consists of about 300 genera [1, 2]. *Kundmannia* belong to the *Oenantheae* tribe and are well represented in Spain, France, Italy, Turkey, Syria and North Africa where they grow on calcareous or siliceous soils. The genus *Kundmannia* consists of five species: *K. anatolica*, endemic of Turkey [3-4], *K. syriaca*, endemic of Syria [5], *K. insulana* (Europe) [6], *K. pastinacifolia* [Italy (Sicily)] [7] and *K. sicula* (Mediterranean basin) [8-9].

In Algeria *K. sicula* is commonly known as “Ziyata” which means “the plant that gives a lot of oil”. This species presents leaves which are not plump, and seeds joined with the pericarp. It is a herbaceous and perennial plant presenting robust and ramified stems of 40-120 cm. Inferior leaves are glabrous and gleaming. They are disposed in rosettes applied on the ground [10]. Umbels present ten radii of 8-15 cm length. Flowers are yellow [11]. Fruits are cylindrical, glabrous and 7-10 mm in length. In traditional medicine, the roots and rhizomes are used as infusions or plasters in the treatment of inflammatory pathologies [12]. To the best of our knowledge, there are no references about the oil content and chemical composition of any *Kundmannia* species, therefore, in continuation of our systematic phytochemical studies of the Algerian Apiaceae [13-14], we report here the first study on two essential oils of *Kundmannia sicula* DC., collected at Béjaia (K.s.B) and El Kala (K.s.K).

Results and Discussion

The oil was obtained by hydrodistillation of 200 g of coarsely powdered dried plant material, according to the procedure described in the European Pharmacopoeia V edition [15]. The oil obtained was stored at -4°C in a sealed vial until chemical analyses. Each distillation led us to obtain 0.7 mL of each essential oil that corresponds to yields of 0.4 % v/w .

The composition and percentages of the components are summarized in Table 1. Compounds are listed by their order of retention indice calculated on an apolar stationary phase. GC of the distilled oils revealed the presence of 27 (K.s.B) and 24 (K.s.K) components, of which 25 and 22 were identified, respectively, corresponding to 88.5% and 82.7% of the total oil compositions in each case.

The major components identified in the K.s.B essential oil were spathulenol (14.8%), caryophyllene oxide (12.2%), salvial-4(14)en-1-one (10.1%), 1,5-epoxysalvial-4(14)ene (5.2%) and germacrene D (3.9%). The main compounds in K.s.K, were salvial-4(14)en-1-one (16.4%), 1,5-epoxysalvial-4(14)ene (6.5%), chrysanthenyl acetate (5.2%) and α -amorphene (2.9%). Monoterpene hydrocarbons (0.2%) were only present in the K.s.B oil and oxygenated monoterpenes (5.2%) only appeared in the K.s.K oil. Levels of oxygenated hydrocarbons in K.s.B oil were twice as high (5.2%) as in K.s.K oil (2.3%).

The composition of the two oil samples was dominated by sesquiterpenes: 83.2% for K.s.B and 75.1% for K.s.K. Among these sesquiterpenes, the oxygenated ones represented 69.9% for K.s.B and 56.3% for K.s.K. These major compounds among them were identified as spathulenol (14.8% and 2.8%), caryophyllene oxide (12.2% and 0%), and salvial-4(14)en-1-one (10.1% and 16.4%), for K.s.B and K.s.K, respectively.

Table 1. Percentage composition of the essential oil of the aerial parts of *Kundmannia sicula* DC.

Peak no.	Chemical Component	MW	RI	K.s.B (%)FID	K.s.K (%) FID
1	β -Pinene	136	976	0.2	-
2	Octanal	128	1008	2.6	2.3
3	<i>trans</i> -2-Decenal	154	1263	2.6	-
4	Chrysanthenyl acetate	194	1264	-	5.2
5	α -Cubebene	204	1353	0.2	0.3
6	α -Ylangene	204	1377	0.1	0.2
7	α -Copaene	204	1381	1.1	1.3
8	β -Bourbonene	204	1392	0.5	0.2
9	β -Elemene	204	1396	0.7	-
10	<i>trans</i> -Caryophyllene	204	1427	1.8	1.4
11	<i>epi</i> -Bicyclophe llandrene	204	1436	0.7	0.9
12	α -Humulene	204	1462	0.5	-
13	α -Amorphene	204	1482	1.5	2.9
14	Germacren D	204	1489	3.9	-
15	γ - Muurolene	204	1500	-	0.7
16	α - Muurolene	204	1505	0.4	0.7
17	γ -Cadinene	204	1520	0.6	1.0
18	δ -Cadinene	204	1528	0.9	0.9
19	<i>cis</i> -Calamenene	202	1530	-	1.8
20	α -Calacorene	200	1552	0.5	1.5
21	C ₁₅ H ₂₄ O	220	1562	4.6	-
22	C ₁₅ H ₂₆	206	1564	-	5.0
23	1,5-Epoxysalvial-4(14)ene	220	1578	5.2	6.5
24	Spathulenol	220	1590	14.8	2.8
25	Caryophyllene oxide	220	1596	12.2	-
26	Salvial-4(14)en-1-one	220	1607	10.1	16.4
27	C ₁₅ H ₂₄ O	220	1656	5.0	7.4
28	C ₁₅ H ₂₆ O	222	1668	-	8.3
29	C ₁₅ H ₂₄ O	220	1699	16.7	14.9
30	C ₁₅ H ₂₄ O	220	1757	1.4	-
31	Unknown A	236	1783	4.2	-
32	Unknown B	234	1855	7.3	1.1
33	Unknown C	238	1921	-	9.7

Monoterpene hydrocarbons	0.2	-
Oxygenated monoterpenes	-	5.2
Sesquiterpene hydrocarbons	13.2	18.8
Oxygenated sesquiterpenes	67.0	56.3
Oxygenated hydrocarbons	5.2	2.3

MW: molecular weight

RI: retention indice

K.s.B: *Kundmannia sicula* BéjaiaK.s.K: *Kundmannia sicula* El Kala

These compounds were frequently observed in the essential oils of other Apiaceae species growing in countries of the Mediterranean basin, for example *Eryngium maritimum* grown in Turkey [16]. The percentage of sesquiterpene hydrocarbons was less abundant in K.s.B oil (13.2% or five times less than the oxygenated sesquiterpenes in the same sample) than in K.s.K oil (18.8% or three times less than the oxygenated sesquiterpenes in the sample). For the compounds listed in Table 1 as 21, 27, 28, 29, 30, whose mass spectral data are given in Table 2, the molecular weights and the retention indices led us to also identify them as oxygenated sesquiterpenoids.

Table 2. Mass spectral data (m/z (relative intensity)) of known molecular formula components.

Peak no	RI	MW	m/z (%)
21	1562	220	$[M^+]$ (12), 159 (36), 146 (37), 131 (66), 123 (100), 109 (55), 91 (60), 79 (40), 67 (22)
22	1564	206	$[M^+]$ (44), 163 (63), 145 (27), 135 (28), 123 (100), 107 (40), 93 (69), 79 (76), 67 (25)
27	1656	220	$[M^+]$ (16), 205 (22), 177 (66), 133 (31), 123 (100), 107 (38), 91 (45), 82 (68), 77 (29), 67 (45)
28	1668	222	$[M^+]$ (23), 194 (7), 179 (7), 165 (25), 151 (100), 133 (46), 111 (41), 95 (70), 81 (73), 67 (28)
29	1699	220	$[M^+]$ (60), 177 (25), 159 (100), 131 (28), 118 (30), 105 (41), 91 (47), 79 (30), 67 (25)
30	1757	220	$[M^+]$ (18), 177 (26), 159 (20), 150 (100), 135 (25), 107 (32), 91 (28), 81 (32), 67 (17)

For compound 28 (RI=1668), the molecular formula ($C_{15}H_{26}O$) and the retention index were in agreement with the literature data for a sesquiterpene containing a tertiary alcohol [17]. This is confirmed by characteristic peaks at m/z 194, 179, 165, 151 (base peak at $[M-71]^+$), 95 and 81 [18]. Compound 29 (RI=1699), an unidentified oxygenated sesquiterpene, was one of the main components in both essential oil samples. Three compounds: 31 (RI=1783), 32 (RI=1855) and 33 (RI=1921), all of which eluted in the final part of the chromatograms and amounted to 11.5% and 10.8% of the total oil for K.s.B and for K.s.K, respectively, could not be identified.

Conclusions

Our GC-MS and GC-FID studies of the essential oil from *K. sicula* from two different localities of Northeast of Algeria led us to identify 27 and 24 compounds, respectively. The major components were oxygenated sesquiterpenes, among which salvial-4(14)en-1-one, spathulenol, and caryophyllene oxide were the main ones. We note that the qualitative and the quantitative composition of the two studied essential oils are close, which seems to indicate that the two specimens present a similar chemotype. The variations in the chemical composition of essential oils can be explained by the difference in the geographic origins. The origin of changes should be sought mainly in the differences in the nature of soil on the one hand and solar radiation on the other. Both factors involve the activation or inactivation of certain enzymatic groups, leading to the predominance of a particular biosynthetic pathway [19].

Experimental

Plant Material

Aerial parts of *Kundmannia sicula* (L.) DC were collected in two different regions: El Kala (Wilaya El Taref) near the coast and in a meadow in Béjaia, about 10 kms from the coast. These two localities are situated in the eastern part of Algeria and about 400 kms from each other. The first specimen was collected in May 2002 and identified by Dr G. de Belair (Badji Moktar University - Annaba); the second was collected in June 2003 and identified by H. Laouer (Ferhat Abbas University - Setif). All samples were collected at full flowering stage and the plant material was left to dry in the shade at ambient temperature (25°C). Voucher specimen was deposited in the Herbarium of National Museum of Natural History Paris with the acquisition reference P00383263.

Gas chromatography

GC-FID analysis were performed with a Varian Star 3400 CX gas chromatograph equipped with an apolar Macherey Nagel Permabond SE 52 (50 m x 0.25 mm ID x 0.25 µm) capillary column. The carrier gas was nitrogen. Chromatographic conditions were similar to those described below. Injector and FID were maintained at a temperature of 280°C.

GC-MS analysis

GC-MS analyses were realized with an Agilent gas chromatograph 6890 equipped with an apolar Macherey Nagel Permabond SE 52 (50 m x 0.25 mm ID x 0.25 µm) capillary column. The carrier gas was helium. The oven was heated from 60°C to 280°C at a rate of 3°C/min, the final temperature was then maintained during 20 min. The injector was maintained at a temperature of 280°C. The GC apparatus was directly interfaced with a Hewlett Packard mass spectrometer 5973 operating either in EI, or in IC-CH₄ mode. The transfer line was maintained at a temperature of 280°C.

Identification of components

Compounds were identified by comparison of mass spectral data described in two libraries [NIST and Wiley 275 (1995)]. Identification was confirmed by calculating the retention indexes, determined by interpolation with retention indexes of a series of *n*-alkanes analysed with the same chromatographic conditions and compared with those described in the ADAMS library [17]. The modified Van den Dool and Kratz formula was used for the determination of retention indexes [20].

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References

1. Scopoli, J.A. *Introd. Hist. Nat.* 1777; p. 116.
2. System Simulation Ltd. *Index Kewensis. Index + for Windows version 1.8 K*; Oxford University Press: Oxford, UK, 1994-97.
3. Huber-Morath, A. Novitae Florae Anatolicae, Bauhinia. *Zeit. Bas. Bot. Gesel.* **1983**, *7*, 269-271.
4. Pimenov, M.G.; Leonov, M.V. The Asian Umbelliferae Biodiversity Database (ASIUM) with particular Reference to South-West Asian Taxa. *Turk. J. Bot.* **2004**, *28*, 139-145.
5. Boissier, P.E. *Diagn. Pl. Orient. Ser.* **1849**, *1*, 31.
6. Gandoger, M. Notes sur la flore espagnole. *Bull. Soc. Bot. France.* **1900**, *47*, 122-124.
7. Sweet, R. *Hortus Britannicus*, 2nd Ed.; J. Ridgway: London, 1830; p. 247.
8. De Candolle, A.P. *Prodromus Systematis Naturalis Regni Vegetabilis*; Treuttel et Würtz: Paris, 1830; vol. 4, p. 143.
9. Fournier, P. *Les quatre Flores de France Corse comprise*; Editions Lechevalier: Paris, 1990; p. 683.
10. Quezel, P.; Santa, S. *Nouvelle flore de l'Algérie et des régions désertiques méridionales*; Editions du Centre National de la Recherche Scientifique: Paris, 1963; p. 676.
11. Battandier, J.A.; Trabut, L. *Flore de l'Algérie*; A. Jourdan Ed: Algiers, 1888; p. 363.
12. Rimbau, V.; Cerdan, C.; Vila, R.I. Antiinflammatory activity of some extracts from plants used in the traditional medicine of North-African countries (II). *J. Phytother. Res.* **1999**, *13*, 128-132.
13. Djarri, L.; Medjroubi, K.; Akkal, S.; Elomri, A.; Seguin, E.; Vérité, P. Composition of the essential oil of aerial parts of an endemic species of the Apiaceae of Algeria, *Daucus reboudii* Coss. *Flavour Fragr. J.* **2006**, *21*, 647-649.
14. Bousetla, A.; Akkal, S.; Medjroubi, K.; Louaar, S.; Azouzi, S.; Djarri, L.; Zaabat, N.; Laouer, H.; Chosson, E.; Seguin, E. Flavonoid glycosides from *Ammoides pusilla* (Apiaceae). *Chem. Nat. Compd.* **2005**, *41*, 95-96.
15. *European Pharmacopoeia. 5th ed.* Council of Europe: Strasbourg, 2005; Vol. 2, pp. 2667-2668.
16. Aslan, S.; Kartal, M. GC-MS Analysis of *Eryngium maritimum* L. Volatile Oil. *Planta Med.* **2006**, *72*, 340-341.
17. Adams, R.P. *Identification of essential oil components by gas chromatography/mass spectrometry*, 2nd edition; Allured Publishing Corporation, Carol Stream: Illinois, 2001.
18. Waller, J.R.; Dermer, O.C. *Biochemical Applications of Mass Spectrometry*; John Wiley & Sons Inc: New York, 1995; pp. 311-406.
19. Belaiche, P. *Traité de Phytothérapie et d'Aromathérapie*. Tome-1: l'Aromatogramme; Maloine: Paris, 1979.
20. Tranchant, J. *Manuel pratique de chromatographie en phase gazeuse*; Masson: Paris, 1995.

Sample availability: Contact the authors.