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Chemotypes of *Capparis spinosa* L. Populations Growing in Eastern Algeria

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ABSTRACT

The hydro-distillation of the aerial part of Capparis spinosa gives transparent oil with a low yield (0.01%). The essential oil analysis of fifteen populations was carried out using GC-GC/MS. 89 components were identified representing an average of 92.63% of the total oil. The chemical composition of this species are dominated by n-nonanal with an average of 14.89 ± 7.59, palmitic acid (11.88 ± 5.28), isopulegyl acetate-iso (4.29 ± 4.41), heneicosane (3.32 ± 5.49) and α-pinene (2.42 ± 3.96). This study allowed us to identify within the populations several chemotypes; the chemotype to α-pinene–henecosane characterizes the populations of Tizi n'bechar and Kherrata. The chemotype to α-pinene-β-phellandrene characterizes the population of Beni Aziz. The chemotype to n-nonanal-β-anisyl alcohol characterizes the populations of Amoucha and Mansoura, while the chemotype n-nonanal-hexadecanoic acid characterizes the rest of the populations (Aftis, Allaghen, Alloune, Beni Fouad, Bibans, Bordj Zemoura, Colla, Hasnaoua, Theniet Ennasr and Tunisia) with several sub chemotypes.

Keywords: *Capparis spinosa*, Essential oil, Chemotypes, Algeria

INTRODUCTION

The genus *Capparis* is large consisting of 350 species of trees and shrubs, distributed in the world [1]. In Algeria, it is represented by a single species *Capparis spinosa* L., knowed locally as Kabar [2]. This aromatic species has an economic, ecological, and medicinal propriety [3]. *C. spinosa* grows naturally in the Mediterranean climate [4], in west and central Asia, Australia [5] and in the tropical and subtropical zones of the world. Traces and remains of *C. spinosa* have been found in many archaeological sites [6], and seed of this species were discovered in the Yanghai Tombs (China) [7]. *C. spinosa* is flexible, the stems are located on more than one meter of soil, the alternate, round leaves are glaucous green, and they appear regularly in rows on both sides of the stems [8]. It is widely cultivated for its capers, a condiment of choice; its fruits are known as caper berries.

The different parts of *C. spinosa* are largely used in traditional medicine to treat many illnesses such as headache, toothache and kidney disease [9]; they are used in pharmacological and cosmetics product [10]. The caper is used since antiquity in the kitchen; recently the beneficial effect of capers as a condiment plant was confirmed by food chemistry works [11,12]. In folk medicine, the caper is used as anti-leishmaniosis [13], antifungal [13,14], antihepatotoxic [15], anti-inflammatory [16], antimicrobial [17], antihyperlipidemic [18], anticancer and antispasmodic [19].

The fruit of the caper improves hyperglycemia and hypertriglyceridemia in type-2 diabetic patients [20]. Flower buds (capers) are known in various Mediterranean countries for their healing properties, expectorant, diuretic, anti-hypertensive, tonic, anthelmintic, emmenagogue and analgesic [16]. Caper berry, leaves and seeds possesses a high antioxidant activity [21-27]. *C. spinosa* is rich in flavonoids [20,28,29], free phenolic compounds and carotenoids [25]. The caper root contains spermidine alkaloids [30]. The chemical composition of *C. spinosa* is much studied. In Egypt the essential oil of *C. spinosa* presents the methyl isothiocyanate as the major compound [29]. The populations of Iran present the thymol as major component [31], while Ara et al. [32] found that linoleic acid and methyl ester are the major components of this species.

Chemotypes are forms of chemical, biological and botanical classifications, and refer to the molecule predominantly present in an essential oil [33]. Example *Rosmarinus officinalis* from Eastern Algeria includes several chemotypes [34]. To our knowledge, no studies of the *C. spinosa* chemotype have been performed. In the present study, the aim is to identify the chemical composition of the oils of *C. spinosa* L., the evaluation of the geographical distribution of chemotypes in Algeria and to compare our results to other compositions of this species in the world.

MATERIALS AND METHODS

Plant material

The aerial parts of *C. spinosa* were collected from 15 localities in Eastern Algeria (Figure 1). The geographic coordinates of the stations sampled are grouped in Table 1.

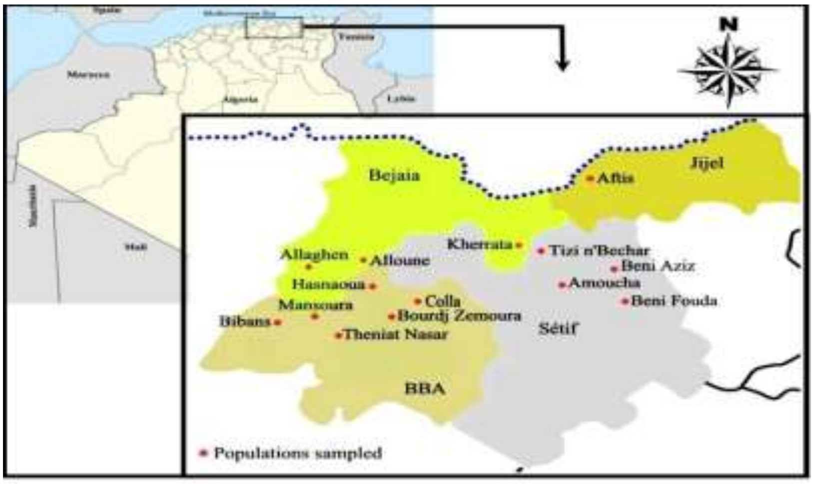

Figure 1: The populations sampled of *Capparis spinosa*

Table 1: Location of studied stations

Provinces (Wilaya)	**Localities**	**Geographic coordinates**	**Provinces (Wilaya)**	**Localities**	**Geographic coordinates**
Setif	Benifouda	36° 17′ 10″ N 5° 36′ 26″ E	Bordj Bou-Arreridj	Mansoura	36° 04′ 55″ N 4° 27′ 36″ E
	Amoucha	36° 23′ 17″ N 5° 24′ 39″ E		Hasnaoua	36° 09′ 09″ N 4° 47′ 43″ E
	Tizi n'Bechar	36° 25′ 52″ N 5° 21′ 36″ E		Bibans	36° 11' 55" N 4° 23' 50" E
	Beniaziz	36° 28′ 00″ N 5° 39′ 00″ E		Theniet Ennaser	36° 13′ 53″ N 4° 36′ 04″ E
Bejaia	Allaghen	36° 23′ 04″ N 4° 23′ 57″ E		Colla	36° 15′ 55″ N 4° 41′ 59″ E
	Kherrata	36° 29′ 34″ N 5° 16′ 39″ E		Bordj Zemoura	36° 17′ 35″ N 4° 51′ 21″ E
	Alloune	36° 33′ 51″ N 4° 42′ 45″ E	Tunisia	Beja	36° 43′ 30″ N 9° 10′ 55″ E
Jijel	Aftis	36° 23′ 17″ N 4° 27′ 41″ E			

C. spinosa is a shrub with a trunk 50-80 cm high for the oldest individuals and can reach about 1 m in a vertical position. The leaves are sub-orbicular, presence at the base of the petiole of 2 curved spines. The width of the leaves is between 2 and 4.5 cm and the length between 2.5 and 6 cm. Presence of 4 Sepals, very concave, with a large corolla (4-5 cm), and 4 petals white pink or powdery pink [2]. Caper berries are ripe fruit; they are ellipsoid (Figure 2). The seeds are 3 to 4 mm in diameter, brown, matte and smooth. The root system is moderately branched, characterized by highly developed and deeply fleshy roots.

The aerial parts of the populations sampled, were collected during the flowering period in June 2015. The harvested plant material was left to dry in a shaded and aerated place at room temperature until dried. A voucher was deposited in the herbarium of the Department of Biology and Ecology, Setif-1 University, Algeria.

Extraction of the essential oil

300 g of the air-dried materials were subjected to hydro-distillation using a Clevenger apparatus type, for 3 h with 3000 ml distilled water. The hydro distillation was repeated until obtaining a sufficient quantity of oil. The oil obtained was collected and stored in screw capped glass vials in a refrigerator at 4-5°C until analysis.

Essential oil analysis

The essential oils were analysed on a Hewlett-Packard gas chromatograph Model 5890, coupled to a Hewlett-Packard model 5971, equipped with a DB5 MS column (30 × 0.25 mm; 0.25 µm), programming from 50°C (5 min) to 300°C at 5°C/min, with a 5 min hold. Helium was used as the carrier gas (1.0 ml/min); injection in split mode (1:30), injector and detector temperatures, 250 and 280°C, respectively. The mass spectrometer worked in EI mode at 70 eV; electron multiplier, 2500 V; ion source temperature, 180°C; MS data were acquired in the scan mode in the *m/z* range 33-450.

The identification of the components was based on comparison of their mass spectra with those of NIST mass spectral library [35,36] and those described by Adams as well as on comparison of their retention indices either with those of authentic compounds or with literature values [37].

Figure 2: *Capparis spinosa* parts (Photo by Benachour, 2015)

Statistical analysis

Data were first subjected to Principal Components Analysis (PCA) to examine the relationships among the terpenes compounds and identify the possible structure of the population and study of variations in the composition of the essential oil of *C. spinosa*. Cluster analysis (UPGMA) was carried out on the original variables and on the Manhattan distance matrix to seek for hierarchical associations among the populations. The cluster analyses were carried out using Statistica v10 software.

RESULTS

The hydrodistillation of the dried aerial parts of the 15 populations of *C. spinosa* gave yellow oil with a very strong aromatic odor. The essential oil yield average is 0.01%. The analysis of essential oils of the populations by (GC-GC/MS), allowed the identification of 89 chemical components (Table 2), with a mean of (92.63% ± 4.66) of total oil. The chemical composition of this species is dominated by n-nonanal with an average of 14.89 ± 7.59, palmitic acid (11.88 ± 5.28), isopulegyl acetate iso (4.29 ± 4.41), heneicosane (3.32 ± 5.49) and α-pinene with an average of 2.42 ± 3.96. *C. spinosa* populations are very heterogeneous in the chemical composition of essential oils. The composition of the essential oils of the populations shows significant differences, the concentrations of these components show a notable inter-population variability (Figure 3). The n-nonanal with an average of 14.89 ± 7.59 is the component that exhibits the greatest variation in these populations, followed by heneicosane (3.32 ± 5.49), palmitic acid (11.88 ± 5.28), isopulegyl acetate iso (4.29 ± 4.41) and β-anisyl alcohol (1.26 ± 3.34).

The spatial three-dimensional projection of the 15 populations based on three axes (Figure 4), show that the populations of Beni Aziz, Kherrata and Tizi n'bechar are distinctly separated from the populations of Amoucha, Bibans, Allaghen, Mansoura, Tunisia, Alloune, Hasnaoua, Teniet En Nasr, Bordj Zemmoura, Aftis, Colla and Beni Fouda, which are all grouped, and whose separation is not clear.

Table 2: Chemical composition of essential oils of *Capparis spinosa*

Components		Amoucha	Bibans	Allaghen	Mansoura	Tunisie	Alloune	Hasnaoua	ThenietEnnasr	Zemmoura	Aftis	Colla	BeniFouda	Tizin'bechar	Kherrata	Beni Aziz	Average
Number of	KI	32	33	33	37	30	37	39	44	42	48	43	40	40	39	37	
Total %		**96.8**	**90.9**	**88.8**	**94**	**87**	**80.5**	**94.6**	**94.7**	**98.2**	**95.5**	**93.8**	**95.8**	**94.3**	**96.1**	**88.3**	92.63
α-pinene	933	0.41	0.51	0	0.45	0.44	1.49	0	0.92	0	2.45	0.56	0	7.27	9.18	12.7	2.42
Camphene	949	0	0	0	0	0	0	0	0	0	0	0	0	0.33	0.44	0.93	0.11
Sabinene	972	0	0	0.41	0	0	0.57	0	0	0	0.61	0	0	1.05	1.37	1.59	0.37
β-pinene	977	0	0	0	0	2.11	0.84	0	0	0	1.85	0	0	5.76	6.76	5.91	1.55
Hepten-2-one-6-methyl	986	0	0.71	0.92	0	0	1.21	0	0	0	0.48	0.45	0	0	0	0	0.25
Pentyl furan-2	990	0	0.53	0.79	1.28	0	1.06	0	1.31	1.86	0.63	1.01	0.36	0	0	0	0.59
Octanal (n)	1004	1.4	1.19	1.23	1.62	0.09	1.04	0.91	1.23	2.43	1.16	1.33	1.46	0	0	0	1.01
α-phellandrene	1006	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.86	0.12
Δ3-carene	1007	0	0	0	0	0.35	0	1.3	0	0	0	0	0	0	0	0.57	0.15
Cymene -para	1026	0.24	0	0	0	0	0	0	0	0	0	0	0	0	0	2.38	0.17
Limonene	1029	0	0	0	0.51	1.8	0	0.78	2.31	0.97	0.77	0	0	0	0	0	0.48
β-phellandrene	1031	0	0	0	0	0	0.77	0	0	0	0.98	0	0	0	4.64	5.98	0.82
β-ocimene (E)	1047	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.95	0.13
γ-terpinene	1058	0	0	0	0	0	0	0	0	0	0.55	0	0	0.32	0.49	1.4	0.18
Octanol (n)	1073	1.69	1.71	0	2	0.08	0	0	0.46	2.32	3.21	2.56	1.08	0.81	0	0	1.06
Camphenilone	1074	0	0	0	0	0	2.43	0	0	0	0	0	0	0	0	0	0.16
Nonanal (n)	1107	13.5	15.4	15.1	23.9	19.6	12.3	20.5	14.3	29.9	14.4	19.1	16	5.31	1.41	2.77	14.89
Butanoate 3M, 2-butenyl, 2M	1125	2.52	1.92	1.05	1.54	1.06	0	0.67	2.61	1.25	2.57	2.72	1.41	1.07	0.81	1.98	1.39

Nerol oxide	1152	0	1.31	0	0	0	0	0	0	0	0	0.33	0	0	0	0	0.11
Nnonanol (n)	1173	1.6	0	0	1.67	0	0	0.99	0	1.38	1.05	1.88	0.9	0	0	0	0.63
Nonen 1-al-(2Z)	1176	0	0	0	0	0	1.03	0	1.63	0	0	0	0	0	0	0	0.18
Terpinen-4-ol	1184	0	0	0	0	0	0	0	0	0	0.21	0	0	0.48	0.67	3.23	0.31
Naphthalene	1190	0	0	0	1.71	0	0	0.61	2.73	1.34	0	3.7	0	0	0	0	0.67
Methyl salicylate	1197	0	0	0	0	0	0	0	0	0	0	2.16	0	0	0	0	0.14
Safranal	1203	0	0	0	0	0	0	0	0.56	0.36	0.41	0.77	0	0	0	0	0.14
Decanal (n)	1207	1.25	1.55	1.71	2.4	1.71	1.5	2.31	1.75	3.15	1.73	2	2.26	1.28	0.51	0	1.67
β-cyclocitral	1222	1.3	1.01	1.08	1.02	1.34	1.52	0.95	1.69	1.18	2.09	1.56	1.23	0.46	0	0.79	1.15
citronellol	1258	0	0	0	0	0	0.48	0	0	0	0	0	0	0	0	0	0.03
Isopulegyl acetate	1284	0	0	0	0	0	0	0	0.68	0.43	0.3	0.22	0	0	0	0	0.11
β-anisyl alcohol	1287	7.08	0	0	11.8	0	0	0	0	0	0	0	0	0	0	0	1.26
Isopulegyl acetate	1290	0	0	0	0	9.07	0	7.78	9.25	6.94	8.77	11.5	6.52	4.64	0	0	4.3
Undicanone-2	1291	0	7.63	0	0	0	0	0	0	0	0	0	0	0	2.21	4.94	0.99
Methyl acetate	1293	0	0.71	6.69	0	0	0	0	0	0	0	0	0	0	0	0	0.49
Tridecane	1301	0	0	0.44	0	0	0	0	0.81	0.58	1.33	1.22	0.2	0	0	0	0.31
Methyl acetate iso	1303	0	0	0.49	0	0	0	0.84	0	0	0	0	0	0	0	0	0.06
Citronellyl acetate	1310	0	0	0	0	0	0	0.43	0.78	0.43	0.99	0.65	0	0.25	0	0	0.24
Carveol acetate Carvacrol	1320	0	0	0	2.13	0	0	0.67	0.68	0.46	0.08	0.95	0	0.26	0	0	0.35
Funebrene 2-epi	1359	0.37	0.61	0.61	0	0	0.44	0.38	0.5	0.24	0	0.51	0.36	0.26	0	0	0.29
β-damascenone (E)	1385	0	0.97	0.68	1.13	0	0.57	0.89	0.9	0.6	0.63	0.81	0	0.75	0	0.48	0.56
β-damascone (Z)	1386	0	0	0	0	0	0	0	0	0	0	0	0	0	0.39	3.17	0.24
α-duprezianene	1389	3.25	4.19	0	6.54	5.5	4.25	0	0	0	0	0	0	0	0	0	1.58
β-elemene	1397	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.84	0.19
Sesquithujene	1399	0.56	1	0	1.18	1.36	0.76	4.99	6.86	3.02	3.36	3.72	2.45	2.13	0.55	0	2.13
α-Ionone dihydro	1410	0	0	0	0	0	0	1.2	1.6	1.03	1.12	0	0	0.6	0	0	0.37
β-ionone	1412	0	0	0	0	0	0	0	0	0.23	0.64	1.19	0	0	0	0	0.14
Caryophyllene (E)	1423	0.44	0	0	0.62	0.89	0	0	3.95	0	0	0	0	0.82	0.65	2.93	0.69
β-ionone dihydro	1424	0	0	0	0	0	0	0	1.5	0.7	0.24	0.72	0.14	0	0	0	0.22
Thujopsene -cis	1438	0	0	0	0	0	1.73	0	0	0	2.44	0	0	0	0	0	0.28
Arbozol -endo	1440	0	0	4.99	0	0	0	1.07	0	0	0	0	0.54	0	0	0	0.44
Methyl iso eugenol	1441	0	2.42	0	0	0	0	0	0	0	0	0	0	0.58	0	0	0.2
Arbozol exo	1443	0	0	0	0	0	0	0.8	2.55	0	0	0	0.88	0	0	0	0.28
Geranyl acetone	1451	0	3.28	5.46	2.13	1.55	7.79	2.42	2.51	2.47	4.71	3.57	0.37	0.31	0	0	2.44
α-humulene	1464	0	0	0	0	0	0	0	0.59	0	0	0	0	0	0.25	1.07	0.13
Cadina 1,6,4-	1476	0	0	0	0	0	0	0	0.57	0	0	0	0	0	0	0	0.04
γ-muurolene	1481	0	0	0	0	0	0	0	0	0	0	0	0	0	0.28	1.08	0.09
β-ionone (E)	1482	0.32	1.36	2.17	1.87	0.84	2.58	2.32	2.99	1.77	1.82	1.82	0.64	0.3	0	0	1.39
Butylated hydroxytoluene	1505	0.34	0	0	0	0	0	0	0	0.83	0	0.65	0.93	0.27	0.57	0	0.24
-cadinene	1524	0	0	0	0	0	0	0	0	0	0	0	0	0.54	0.52	2.42	0.23
Hexenyl benzoate	1578	0	0	0	0.65	0	0	0	0.81	0	0	0	1.04	0	0.27	0.43	0.21
Hexyl benzoate (n)	1585	0	0	0	0.34	0	0	0	0.27	0	0.39	0	0.55	0	0	0.4	0.13
Caryophyllene	1592	0	0	0	0.99	0	0	0	0.8	0	0	0	0	0	0.28	0.37	0.16
α-muurolol -epi	1652	0	0	0	0	0	0	0	0	0	0	0	0	0.37	0.63	2.15	0.21
α-cadinol	1665	0	0	0	0	1.38	0	0	0.51	0	0	0	0	0.28	0.35	1.49	0.27
Heptadecane (C17)	1703	0	0	0	0	0	0	0.48	0	0.49	0.44	0.48	0.28	0	0.36	0	0.17
Hexadecanol (n)	1845	0	0	0	0	0	0.74	0	0	0	0.87	0	0.64	0	0	0	0.15
Nonadecane (C19)	1903	0	0.5	0.36	0	0	0	1.1	0	0.6	0.67	0.39	0.43	0	0.79	0	0.32
Farnesyl acetone (5E, 9E)	1914	0	0.79	1.42	0.23	0	1.62	0.63	0.66	0.81	1.33	0.96	0	0	0	0	0.56
Hexadecanoic acid	1987	24.8	17.8	14	10.8	11.1	6.81	7.36	9.39	11.1	13.8	8.65	16.1	14.3	9.84	2.41	11.9
Eicosane (C20)	2004	0	0.56	0.46	0.54	0	0.39	9.35	0	0.59	0.31	0.35	0.51	0.21	1.01	5.3	1.31
pseudo phytol (6Z, 10E)	2027	0	0	0	0	0	0.47	1.29	1.42	0.42	0	0	0	0	0	0	0.24
Octadecanol (n)	2080	0.48	0	0.49	0.5	3.07	0	0.62	2.74	0	0	0	0.54	0.65	0.77	0	0.65
Methyl linoleate	2098	0	0	0	1.6	0	0	0	0	0	0	0	0	0	0	0	0.1
Heneicosane (n)	2103	0.34	0.73	0.72	0	0	2.45	4.41	0	2.73	0.11	0.56	5.48	15.4	16.9	0	3.32
Linoleic acid	2157	0	5.87	4.71	2.9	3.89	3.24	2.01	3.31	0	0	0	5.89	4.58	3.55	0	2.66
Docosene-1	2158	5.73	0	0	0	0	0	0	0	2.25	0.53	2.65	0	0	0	0	0.74
Docosane	2204	0.64	0.91	1.08	0.4	0.44	0.88	1.75	0.42	1.16	0.34	0.62	1.02	1	2.23	0.21	0.87
Phytol acetate	2232	8.56	0	0	0	0	0	0	0	0	0	0	0	0.45	0.93	0	0.66
Tricosane (n)	2305	1.5	1.31	2.08	0.4	0.81	1.71	2.28	1.01	1.91	0.45	1.12	2.6	2.05	2.15	1.39	1.52
Tetracosane (n)	2406	2.02	2.04	3.09	1.5	2.19	2.23	2.05	0.89	2.18	2.98	1.72	2.93	3.43	4.1	1.15	2.3
Pentacosane (n)	2507	4.17	3.09	4.74	2.5	2.6	4.49	2.49	0	2.72	1.59	2.69	5.38	4.8	4.4	3.39	3.27
Hexacosane	2607	1.32	1.21	2.27	0.7	2.1	1.65	1.05	0.47	1.11	0.79	1.26	2.14	2.84	0	0.78	1.31
Octacosane	2642	0.69	0	0.59	0	4.02	0.41	0	0	0.39	0	0.39	5.2	0.54	0.16	0	0.83
Heptacosane	2643	0	3.72	4.39	0.4	0	0	2.34	0	0	0	0	0.9	5.8	0.33	0	1.19
Nonacosane	2710	4.48	0	0	2.2	0.65	4.81	0.9	0	0	0	2.45	0.56	1.71	0	3.08	1.39
Untriacontane	2745	2.53	1.69	1.3	0	0	1.29	0	0.56	2.22	0	0	0	0	0	0	0.64
Dotriacontane	2808	0.61	0.96	1.64	1.3	0	1.58	0.87	2.27	0.99	3.12	1.2	2.82	0	7.19	1.08	1.71
Triacontane	2849	0	0	1.61	0	2.56	1.33	0.81	0.93	0	1.03	0	0.53	0	0	0	0.59
Tritriacontane	2911	1.56	1.76	0	0.8	1.29	0	0	0	0.74	1.51	0.75	2.11	0	2.61	1.74	0.99
Tetratriacontane	3059	1.14	0	0	0	3.52	0	0	0	0	3.67	0	0.42	0	5.51	0	0.95

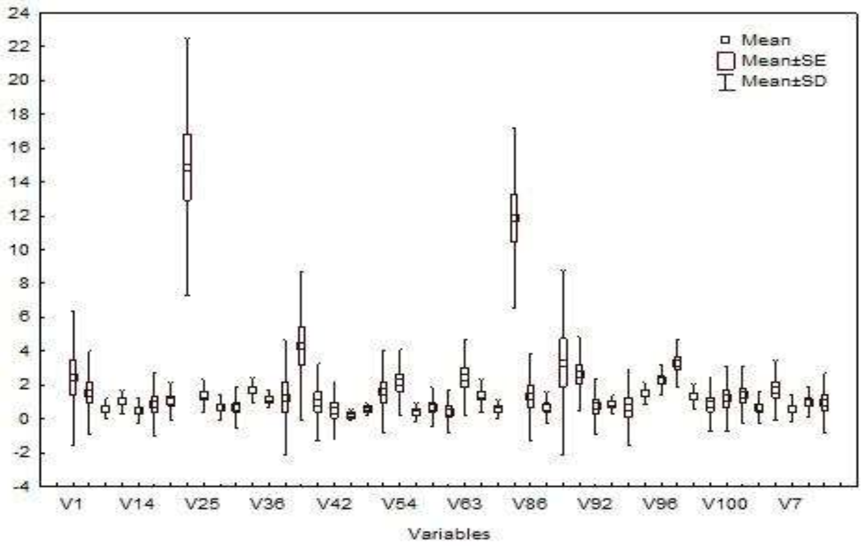

Figure 3: Variation in concentrations of essential oils compounds

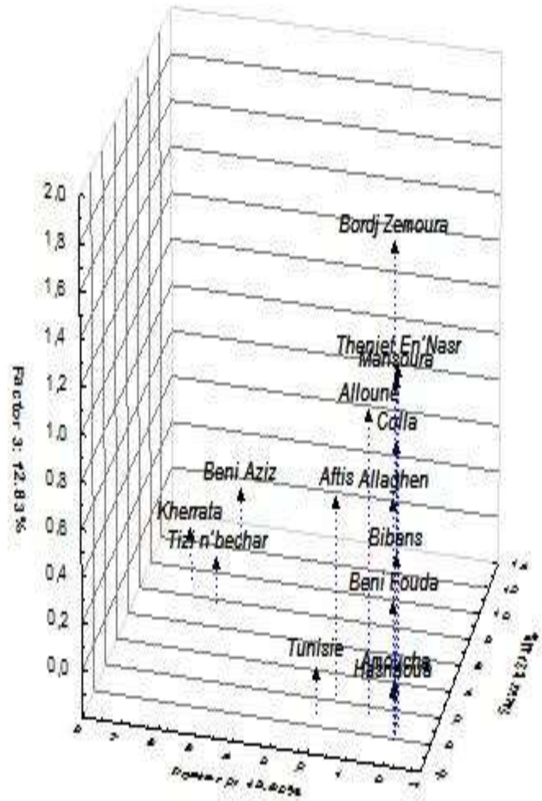

Figure 4: Spatial projection of *Capparis spinosa* populations

The UPGMA analysis, allows to construction of the phylogenetic tree, whose aim is to bring out the relations between the different populations of *C. spinosa*. This analysis based on the distance of the linkage, confirms the separation of the populations into two distinct clades (Figure 5). The first clustering separates three populations (Beni Aziz, Kherrata and Tizi n'bechar) from the other populations studied; this separation confirms that there is a difference in the chemical composition of the essential oils of the *C. spinosa* populations. The population of Beni Aziz it is separated from the populations of Kherrata and Tizi n'bechar, this separation is based on the wealth of this population in ß-phellandrene.

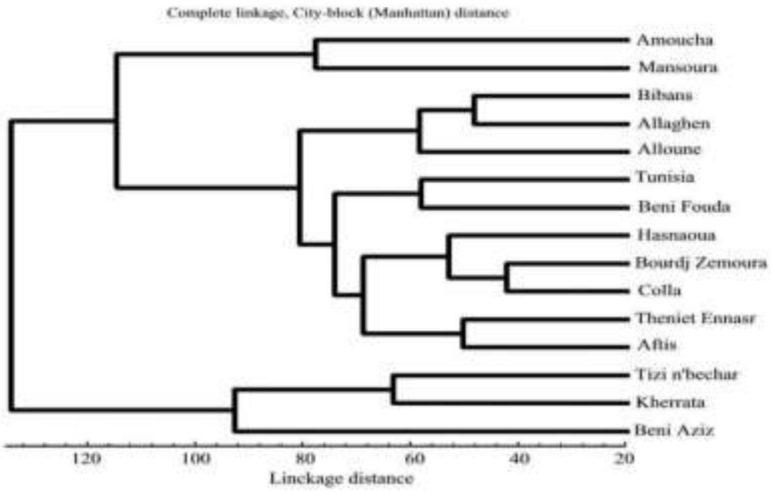

Figure 5: UPGMA of *Capparis spinosa* populations

The populations of Amoucha and Mansoura are separated from the rest of the second group populations, because they contain a single component β-anisyl alcohol with a concentration of (7.08 and 11.77%) respectively. We note that the populations of Tunisia and Beni Fouda are close by the presence of linoleic acid, while the populations of Hasnaoua, Bordj Zemoura and colla are close by the presence of sesquithujene, concerning Theniet Ennasr and Aftis are close too by the presence of dotriacontane. Based on these clustrations several chemotypes could be identified (Table 3).

Table 3: Chemotypes of *Capparis spinosa* populations in Eastern Algeria

Chemotypes	Sub-chemotypes	Populations (localities)
α-pinene-henecosane		Tizi n'bechar and Kherrata
α-pinene-β-phellandrene		Beni Aziz
n-nonanal-β-anisyl alcohol		Amoucha and Mansoura
n-nonanal-hexadecanoic acid	geranyl acetate	Bibans, Allaghen and Alloun
	isopulegyl acetate (iso) –linoleic acid	Beni Fouda and Tunisia
	isopulegyl acetate (iso)-sesquithujene	Hasnaoua, Bordj Zemoura, Colla, Aftis, and Thenit Ennaser

DISCUSSION

The chemical components of the populations studied are completely different from the components of populations studied by other researchers in other countries. According to the results of our study the mains components are n-nonanal, palmitic acid, isopulegyl acetate (iso) and heneicosane, while other authors reported only one major compound methyl isothiocyanate [29, 38-40]. The analysis of *C. spinosa* buds by Romeo et al. [21], found that aldehydes and esters represent the major components in oil. A GC/MS analysis of *C. spinosa*, from Thanjavur (India), revealed the presence of hexadecanoic acid, 1-2-benzenedicarboxylic acid and octadecadienoic acid [19]. Khanfar et al. [41], identified fifteen compounds in the *C. spinosa* oil of Jordanian origin. In Iran, the study each part of the plant separately, has shown that there is a difference in the components of the oils of leaves fruits and roots. The main components of leaves oil were thymol, isopropyl isothiocyanate, 2-hexenal and butyl isothiocyanate, but for fruits and roots, the main components are methyl isothiocyanate and isopropyl isothiocyanate [31]. The use of mature fruits of *C. spinosa* has shown that oleic acid and palmitic acid are the major components in oil [32].

CONCLUSION

Analysed by GC-GC/MS, 89 components were identified in the essential oil of *C. spinosa*. The chemical compositions of this species are dominated by n-nonanal, palmitic acid, isopulegyl acetate-iso, heneicosane and α-pinene. The results showed a great variability in the chemical composition of essential oils of the populations studied. This study allowed us to highlight the presence of several chemotypes and sab-chemotypes: α-pinene-β-phellandrene characterizes the population of Beni Aziz; α-pinene–henecosane characterizes the populations of Tizi n'bechar and Kherrata. While the chemotype n-nonanal–β-anisyl alcohol characterize the populations of Amoucha and Mansoura, hexadecanoic acid–geranyl acetone characterize the populations of Bibans, Allaghen and Alloune; the chemotype of hexadecanoic acid–Isopulegyl acetate iso characterize the populations of Tunisia, Beni Fouad, Hasnaoua, Bordj Zemoura, Colla, Theniet Ennasr and Aftis.

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