INTERNATIONAL JOURNAL OF CURRENT MEDICAL AND PHARMACEUTICAL RESEARCH

IJCMPR

Available Online at http://www.journalcmpr.com

REVIEW ARTICLE

THE ANALYSIS OF CHEMICAL COMPOSITION OF SEVERAL VALUABLE MEDICINAL AND EDIBLE PLANTS VOLATILE FRACTION GROWING AND CULTIVATING IN ARMENIAN FLORA BY GC-MS METHOD

Naira Shaboyan., Nelly Ghukasyan., Vahe Hovhannisyan., Armine Moghrovyan., Hasmik Galstyan., Naira Chichoyan and Karine Dumanyan

Yerevan State Medical University after M. Heratsi 2 Koryun st., Yerevan, 0025, Armenia

ARTICLE INFO

Article History:
Received 16th January, 2016
Received in revised form 24th February, 2016
Accepted 23rd March, 2016
Published online 28th April, 2016

Key words:

GC-MS, Chaerophyllum bulbousum, Origanum vulgare, Cotinus coggigria, Valeriana cardiola, Teucrium polium.

ABSTRACT

The analysis of volatile oils` chemical composition by modern chromatographic methods is of great importance nowadays. The chemical composition of the same plants` volatile oil may be changed depending on climatic and cultivating conditions. The chemical composition of a range of plants` volatile oils (such as Smoke tree, Bulbous-rooted chervil, Oregano ordinary, Valeriana cardiola, Germander) studied by GC-MS method, proves, that by chemical composition volatile oils of plants growing in Armenian flora differ from the ones growing in other countries. Besides the chemical composition of the same plants` volatile oils growing in the same flora (Armenian floral also differ depending on cultivating conditions wild, hydroponic, soil culture).

Copyright © 2016 Naira Shaboyan et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

The Armenian flora is stood out by the variety of its medicinal and edible plants. Here small plants as well as trees and shrubs are met. Specific role plays beneficial climate. Based on world literature data, we conclude that climatic-geographical factors have a great influence on chemical composition of plants [1-5], especially on volatile oil's chemical composition [6-11]. We have studied chemical composition of several valuable medicinal plants` volatile oils, such as Bulbous-rooted chervil's herb (Chaerophyllum bulbousum), Smoke tree's leaves (Cotinus coggigria), Oregano ordinary's herb (Origanum vulgare), Germander's herb (Teucrium polium), as well as Valeriana cardiola's roots and rhizomes (Valeriana cardiola) and Teucrium polium's herb cultivated in soil conditions and Teucrium polium's herb cultivated in hydroponic conditions.

MATERIALS AND METHODS

As a material served plants from Armenian flora:

1. Bulbous-rooted chervil's herb collected from Kapan region
2. Smoke tree's leaves collected from Yerevan
3. Rhizomes and roots of Valeriana cardiola cultivated by us in Zovuni region
4. Oregano ordinary's herb collected from Lori region
5. Teucrium polium's herb collected from Vokhgaberd region
6. Teucrium polium's herb cultivated in soil and hydroponic conditions.

The primary processing and drying was carried out by WHO GACP instructions [12, 13].

Volatile oil was derived from above mentioned plants by hydro-destillation method [14] and the chemical composition of volatile oils was determined by GC-MS method.

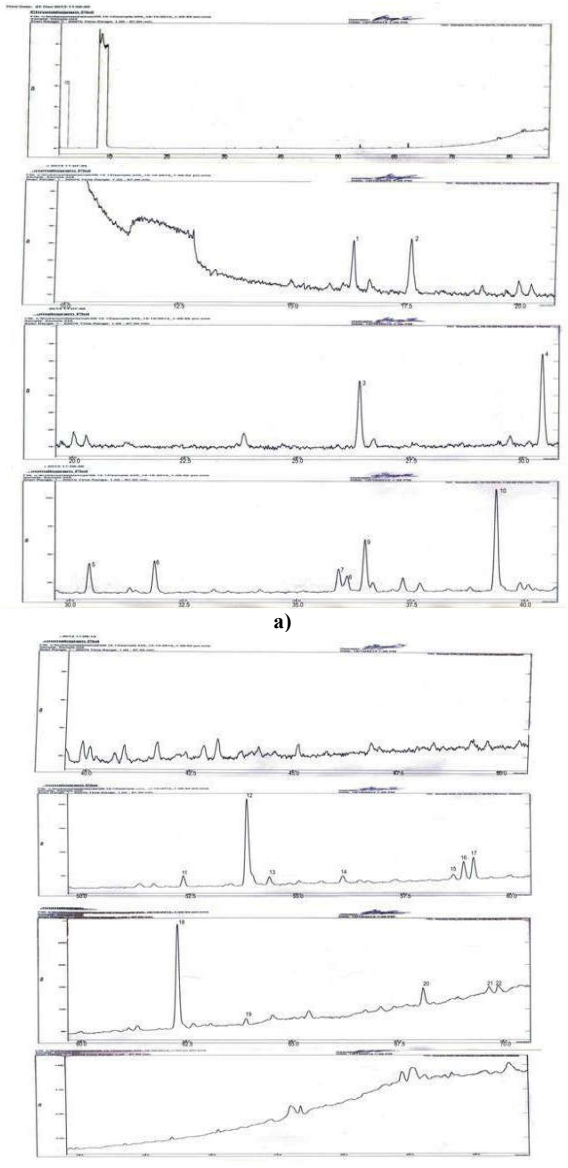
Volatile oil analysis was carried out by the gas chromatography- mass spectrometry (GC-MS) method on gas chromatograph with mass selective spectrometer from BRUKER company (USA). An OPTIMA-FFAP capillary column (0.25 mkm, 60 m*0.25 mm (ID, MACHEREY-NAGEL, Germany) was used for the separation of volatile oil compounds .Helium gas carrier flow-rate 1.0ml/min, volume of injected sample 2mkl, the oven temperature 220°C, temperature gradient 50°C (2min), split-separation -5. Compounds were identified using the NIST Mass spectral Search Program.

The content of components was calculated by GC peak's area, without correction factors. Identification of components was carried out by their retention times. Quantitative analysis of components was determined by internal normalization method.

THE RESULTS AND DISCUSSION

The analysis of the volatile fraction of Chaerophyllum bulbousum L. (Apiaceae) by capillary GC-MS method demonstrated the presence of at least 33 components. The results are shown in the pic. 1. The research has shown, that the amounts of only 15 components exceed 1% and the main components are β-caryophyllene epoxide(21.9%), 6-[(1E)-1,3-dimethyl-1,3-butadienyl]-1,5,5-trimethyl-7-oxabicyclo[4.1.0]hept-2-ene(12.9%), pulegone (10.4%), 3-methyl-5propylnonane(7.95%), eucalyptol (6.8%), β-cis-caryophyllene(5.1%), l-menthone(5%), dodecane(4.98%), spathulenol(3.35%), (+)- valeranone(2.87%). From 33 components only 9 of them are of terpenoid structure.

From sesquiterpenes β-caryophyllene epoxide, β-cis-caryophyllene, spathulenol, (+)- valeranone, α-humulene epoxide II and from monoterpenes pulegone, eucalyptol, l-menthone predominate.



Pic.1 (a, b) GC-MS spectrum of essential oil of Chaerophyllum bulbousum.

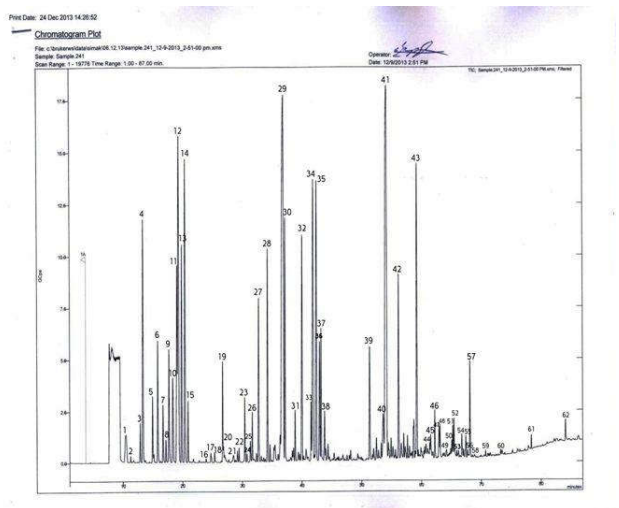
1-Dodecane (16.34*); 2-Eucalyptol (17.62*); 3-3-Methyl-5-propylnonane (26.37*); 4-I-Menthone (30.42*); 5- I-Menthone (31.86*); 6-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl acetate (35.9*); 7-Nonadecane (36.09*); 8-β-cis-Caryophyllene (36.48*); 9-Menthol (36.65*); 10-Yomogi alcohol (37.33*); 11-Patchoulene (37.7*); 12-(±)-Pulegone (39.37*); 13-3-Isopropyl-4a,5-dimethyloctahydro-2(1H)-naphthalenone (52.35*); 14-β-Caryophyllene epoxide (53.84*); 15-(±)-Globulol (54.36*); 16-α-Humulene epoxide II (56.07*); 17-Perhydrofarnesyl acetone (58.66*); 18-(+)-Valeranone (58.9*); 19-Spatulenol (59.14*); 20- 6-[(1E)-1,3-Dimethyl-1,3-butadienyl]-1,5,5-trimethyl-7-oxabicyclo[4.1.0]hept-2-ene (62.29*); 21-Spathulenol (63.9*); 22-β-Caryophyllene epoxide (68.1*); 23-Butyl 4,7,10,13,16,19-docosahexaenoate (69.66*); 24-γ-Gurjunenepoxid-(2) (69.88*).
* - Retention time (min)

The volatile oil of Oregano ordinary contains more than 70 terpenoids. The main terpenoids are aromatic terpenoids such as β-caryophyllen epoxide (13.36 %), β-caryophyllen (8.18 %) and carvacrole (2.38%). In volatile oil of Oregano ordinary sesquiterpenoids also predominate.Their total amount is 25% from general amount. From bicyclic sesquiterpenoids germacrene D (3.80%), ent-spathulenole (3.77 %), β-bisabolene (3.24%), humulene (2.68%), burbonene (2.21%), elixene (1.34 %), leden oxide (0.88 %), acyclic sesquiterpene α-trans- farnesene (1.19%), α-cadinol (0.50 %), isoaromadendrene epoxide (0.60 %), aromadendrene oxide(0.29 %), perillene (0.04 %) are present.

The amount of monocyclic monoterpenes in volatile oil is more than 9%.From which cys-β-terpineol (2.57 %), L-4-terpineol (2.34 %), eucalyptole (1.95%), dihydroedulaneII (1.93%), α-terpinolene (1.58 %), D-limonene (0.73%), β-phellandrene (0.18%), longipinocarvone (0.12 %), berbenone (0.05 %), sulkatone (0.1 %) and peryllene (0.05 %) are present.

1.3% of volatile oil are bicyclic monoterpenoids, such as sabinene (3.10 %), β-pinene epoxide (0.96 %), β-tujene (0.72 %), camphene (0.18 %), α-pinene epoxide (0.05 %).
Diterpen trans-phythole (0.057%) is also present in volatile oil of Oregano ordinary.

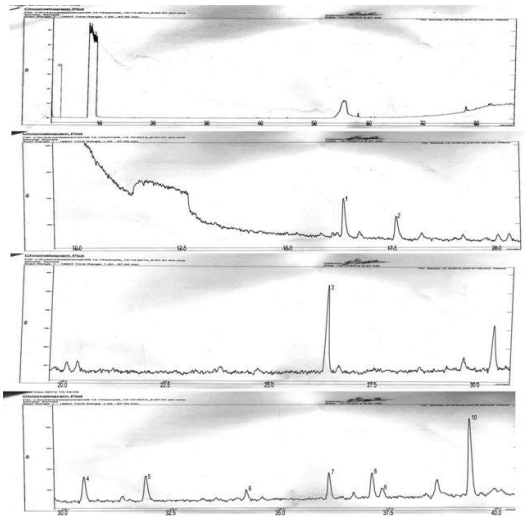
Almost 9% of volatile oil are acyclic monoterpenes, from which O-Cymene (5.22 %), trans- β - ocimene (3.81 %), β-linalool (2.90 %), cis-Geraniol (0.25 %).



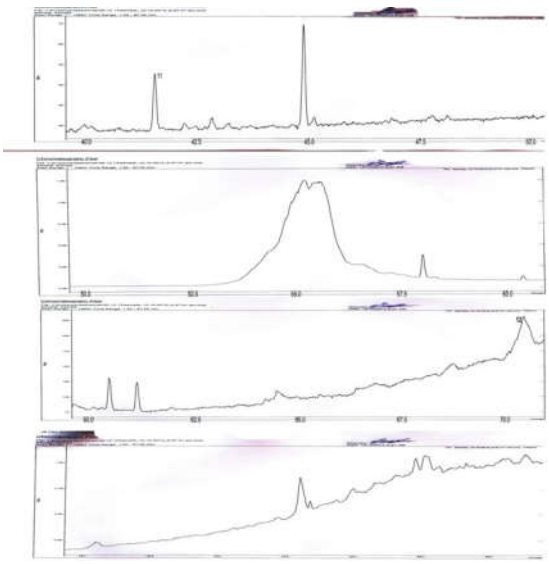
Pic.2 GC-MS spectrum of essential oil of Oregano ordinary

1- β-Thujene (10.48*); 2- camphene (11.77*); 3 - β-Pinene (12.88*); 4-(+)-Sabinene (13.36*); 5- β-Pinene (14.95*); 6- α-Terpinolene (15.82*); 7-D-Limonene (16.7*); 8-β-Phellandrene (17.18*); 9-Eucalyptol (17.7*); 10-trans-β-Ocimene (18.34*); 11- γ-Terpinene (19.07*); 12- trans-β-Ocimene (19.35*); 13- Ethyl amyl ketone (19.87*); 14- o-Cymene (20.43*); 15 - 4-methyl-3-(1-methylethylidene)-1-cyclohexene (20.9*); 16- Sulcatone (23.91*); 17- α-Pinene epoxide (24.67*); 18- cis- Geraniol (25.33*); 19 - 3-Octanol (26.69*); 20- Berbenone (26.82*); 21- Perillene (27.7*); 22-Matsuika alcohol (29.45*); 23-cis-β-Terpineol (30.42*); 24-Elixene (30.76*); 25- Dihydroedulan II (31.68*); 26-2,4-Nonadienal (31.94*); 27-(-)-β-Bourbonene (32.77*); 28- β-Linalcol (34.26*); 29- β-Caryophyllene (36.9*); 30- L-4-terpineol (37.19*); 31- Alloaromadendrene (38.86*); 32-Humulene (40.06*); 33- α-Terpeniol (41.54*); 34-Germacrene D (41.92*); 35- I-β-Bisabolene (42.47*); 36-Elixene (42.96*); 37- α-trans-Farnesene (43.22*); 38-(+)-δ-Cadinene (43.8*); 39- β-Caryophyllene epoxide (51.34*); 40-β-Caryophyllene epoxide (53.58*), 41- β-Caryophyllene epoxide (54.18*); 42-(4Z,6Z,9Z)-4,6,9-Nonadecatriene (55.83*); 43- Ent-Spathulenol (59.26*); 44- α-Cadinol (61.4*); 45- Isoaromadendrene epoxide (61.55*); 46- Carvacrol / Isothymol (62.23*); 47- Ent-Spathulenol (62.95*); 48- α-Cadinol (63.09*); 49- Longipinocarvone (64.86*); 50-Aromadendrene oxide-(2) (65.07*); 51- Ledene oxide-(II) (65.23*); 52- Tetracyclo[6.3.2.0(2,5).0(1,8)]tridecan-9-ol,4,4-dimethyl (65.43*); 53- Megastigma-4,6(Z),8(Z)-triene (65.9*); 54- Tricyclo[5.2.2.0(1,6)]undecan-3-ol, 2-methylene-6,8,8-trimethyl (67.02*); 55-6-Isopropenyl-4,8a-dimethyl-1,2,3,5,6,7,8,8a-octahydro-2-naphthalenol (67.42*); 56- β-Caryophyllene epoxide (67.69*); 57- β-Caryophyllene epoxide (68.12*); 58- cis-Z-α-Bisabolene epoxide (68.5*); 59- Lauric acid (71.3*); 60- Aromadendrene oxide-(1) (73.25*); 61-Dibutyl phthalate (78.38*); 62- Palmitic acid (84.11*)
* - Retention time (min)

In volatile oil of Smoke tree leaves 24 compounds were determined, from which 10 are of terpenoid structure. Almost all terpenoids are monocyclic monoterpenoids. Acyclic monoterpen linalool also is present (3.77 %). The predominated monocyclic monoterpen is pulegone (25.49%). From monocyclic monoterpenoids cys-cinerolone (21.81%), cys-menthone (13.30%), α- terpineol (12.94%), eucalyptol (9.04%), L-4-terpineol (8.20%), 1,4 dihydroxy-para menth-2-ene (3.72%) are present. The results are shown in pic. 3.



a)



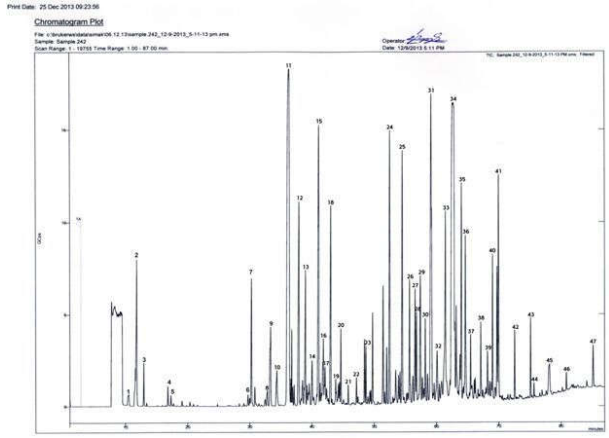
b)

Pic.3 (a,b). GC-MS spectrum of essential oil of Smoke tree

1-Tetradecane (16.39*); 2-Eucalyptol (17.64*); 3- Tetradecane (26.38*); 4-cis-Menthone (30.44*); 5- cis-Menthone (31.87*); 6-β-Linalool (34.19*); 7-2-Methyldecane (36.11*); 8-L-4-terpineol (37.1*); 9-cis-2-p-Menthen-1-ol (37.32*); 10-(±)-Pulegone (39.37*); 11-α-Terpineol (41.52*); 12-cis-Cinerolone (70.51*).
*-Retention time (min)

In Valerian volatile oil 71 compounds such as monoterpenes, sesquiterpenes and aromatic substances of other non-terpenoidal structure are determined. The results are shown in pic. 4.

65.34% of all recognized compounds are 48 sesquiterpenes .The major component is bicyclic monoterpen bornyl acetate(11.35%). 5,54% are monocyclic monoterpenes., from which P- cymene(1.59%),α- terpinolene (0.66%), D-limonene (0.45%) apple oil (0.31%), β- phellandrene (0.22%),α-terpineol acetate(0.16%),α- cyclocitrale(0.13). Also 9 bicyclic monoterpenes were determined, total amount of which was 25.58%. Some of them are camphene (6.26%), myrthenyl acetate (4.35%), camphene (1.30), β- pinene (1.12%), α-pinene (0.49%), α- tujone (0.15%).



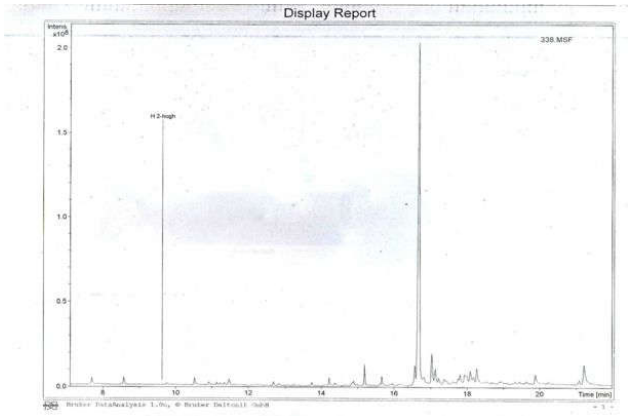
Pic. 4 GC-MS spectrum of essential oil of Valeriana cardiola.

1- d-α-Pinene (10,51*), 2- Camphene (11,81*), 3- β-Pinene (12,95*), 4- D-Limonene (16,8*), 5- β-Phellandrene (17,28*), 6- γ-Gurjunene (29,7*), 7- δ-Elemene (30,27*), 8- α-Guaiene (32,81*), 9- (-)-Aristolene (33,36*), 10- 1-Methy1-4-methylene-2-(2-methy1-1-propeny1)-1-vinylcycloheptane

(34,36*), 11- Bornyl acetate (36,33*), 12- α-Gurjunene (37,9*), 13- Alloaromadendrene (38,97*), 14- α-Caryophyllene (40,02*), 15- Myrtenyl acetate (41,1*), 16- Germacrene D (41,83*), 17- I-Zingiberene (42,09*), 18- Elixene (43,02*), 19- α-trans-Bergamotenol (44,39*), 20- Epiglobulol (44,62*), 21- (-)-Myrtenol (45,79*), 22- γ-Elemene (47,12*), 23- 3-t-Butyl-4-methoxyphenol methyl derivative (48,65*), 24- 3-lsopropyl-4a,5-dimethyloctahydro-2(1H)-naphthalenone (52,5*), 25- Viridiflorol (54,5*), 26- d-Ledol (55,65*), 27- α-Cadinol (56,54*), 28- 1,2,7,7-Tetramethylbicyclo[2.2.1Theptan-2-ol (56,76*), 29- Elemol (57,4*), 30- β-Eudesmol (58,18*), 31- (+)-Valeranone (59,15*), 32- β-Bisabolol (60,09*), 33- Patchouli alcohol (61,44*), 34- α-Neoclovene (62,77*), 35- Ent-Spathulenol (64,02*), 36- 8-Cedren-13-ol (64,65*), 37- Alloaromadendrene oxide-(2) (65,63*), 38- 2-(4a,8-Dimethyl-1,2,3,4,4a,5,6,7-octahydro-2-naphthalenyl)-2-propen-1- ol (67,12*), 39- cis-β-Guaiene (68,19*), 40- Isoaromadendrene epoxide (69*), 41- γ-Gurjunenepoxide-(2) (69,96*), 42- Drimenol (72,52*), 43- Butanoic acid, 2-methyl-, 2-methoxy-4-(2-propenyl)phenyl ester (75,09*), 44- 2-Tridecynyl pentanoate (75,62*), 45- Diisooctyl phthalate (78,12*), 46- 8S,14-Cedrandiol (80,84*), 47- 6-lsopropenyl-4,8a-dimethyloctahydro-1(2H)-naphthalenone (85,13*)

*-Retention time (min)

From sesquiterpenes α-neocloven (8.66%), valeranone (6.75%),γ- gurjunene (3.95%), 3-isopropyl-4α, 5-dimethyloctahydro-2(1H)-naphtalenon (3.87%), patchuoli alcohol (3.78%), viridifluorol (3.56%), elixene (2.68%), α-gurjunene(2.56%), drimenol (2.02%),σ- elemene(1.93%), elemol (1.76%),γ- gurjunen-epoxide (1.71%), ent-spathulenol (1.63%), 8-cedren-13ol (1.63%), α-ledol (1.22%), 6-isopropenyl, 4,8 α-dimethyl octahydro-1(2H) naphtalenone (1.20%), alloaromadendren (1.20%),β-lonone (1.18),α-cadinol (1.12%), isoaromadendren epoxide(1.11%), bisabolol (0.91%)

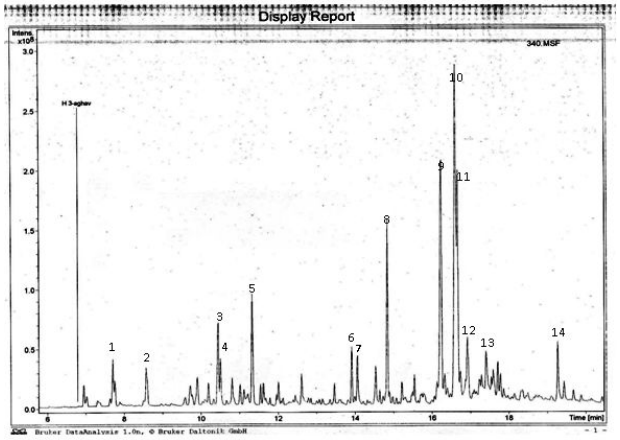


Pic. 5. GC-MS spectrum of essential oil of soil Teucrium polium.

The analysis showed, that volatile fraction of Teucrium polium, which was cultivated in hydroponic conditions contains more than 14 terpenoids and the major components are α-bisabolol (53.49%), farnesole (11.68%) and elemole (8.86%). Volatile oil of Teucrium polium, cultivated in soil conditions contains 12 compounds, from which amount of sesquiterpenes predominates-α-bergamoten (73.665), cycloisolongvifolen 8-hydroxi (5.08%) and aromatic monoterpene benzoic acid-2-(1-oxapropyl) (6.43%). In volatile fraction of Teucrium polium growing wildly 14 terpenoids are determined, from which sesquiterpenoids spathulenole (23.54%), nerulidole (17.425) and caryophyllene oxide (16.48%) predominate. In volatile fraction of all types of Teucrium polium the same terpenoids exist pinene 3-ol, farnesene and tetrahydrogeranylacetone. Hydroponic type is more rich in sesquiterpenoids and bicyclic monoterpenoids, whereas chemical composition of wild and soil types are close to each other and they contain β-pinene, limonene, germacrene D, which haven't been discovered in hydroponic type.

1- β-pinene (7.69*); 2- limonene (8.58*); 3 - pinene-3Ol (10.52*); 4 – myrthenal (11.31*); 5 - hermacren-D (13.91*); 6 – pharnesene (14.84*); 7 – elemene (16.56*); 8 - α-bergamotene (16.68*); 9 - cycloizoloncvipholene-8-hydroxi (17.03*); 10 - patchoulane (17.12*); 11 - tetrahydro-heranilaceton (19.40*); 12 – benzoic acid 2-(1-oxopropile) (21.21*).

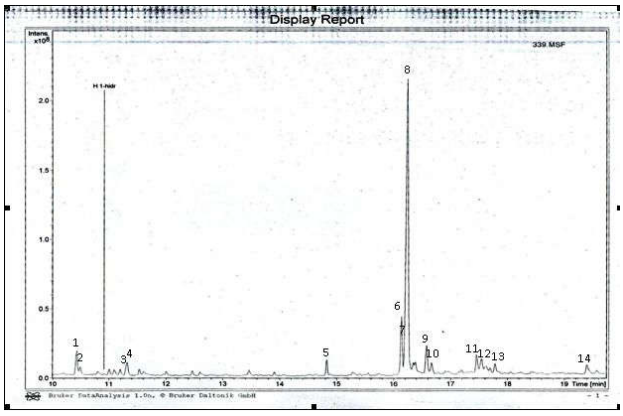
* - Retention time (min)



Pic. 6 GC-MS spectrum of essential oil of wild Teucrium polium.

1 - β-pinene (7.69*); 2 - limonene (8.58*); 3 - carveole (10.50*); 4 – pinene-3Ol (10.52*); 5 - myrthenol (11.33*); 6 – hermacren-D (13.91*); 7 – cyclobuta [1,2,3,4] dicyclopentan, decahydro-3-α.-methyl-6-methilen-1(1-methil-ethil) (14.06*); 8 - pharnesene (14.84*); 9 - pharnesole (16.22*); 10 - nerolidole (16.24*); 11 - spathulenole (16.61*); 12 - caryophilene oxide (16.66*); 13 – leden oxide (16.91*); 14 - tetrahydro-heranylacetone (19.40*).

* - Retention time (min)



Pic. 7 GC-MS spectrum of essential oil of hydroponic Teucrium polium.

1 - pinene-3On (10.43*); 2 - (E)-3-carene (10.50*); 3 -pinene-3Ol (10.52*); 4 - mirtenal (11.31*); 5 - mirtenol (11.33*); 6 – pharnesene (14.84*); 7 – elemol (16.14*); 8 - α-bisabolol (16.24*); 9 - spathulenol (16.61*); 10 - caryophylene oxide (16.66*); 11 - eudesmole (17.46); 12 – pharnesen epoxide (17.54); 13 - cyklopenta[1,3], cyklopropa[1,2] cykloheptene-

3(3ah)-On, 1,2,3b,6,7,8- hexahydro, 6,6-dimethyl (17.78*); 14 - tetrahydro-heranilaceton (19.40*).
* - Retention time (min)

CONCLUSION

1. First time the chemical composition of volatile oil of several plants of Armenian flora such us Bulbous-rooted chervil`s herb, Oregano ordinary`s herb, Smoke tree`s leaves, Valeriana cardiola`s roots and Teucrium polium`s herb was studied by GC-MS method.
2. The analysis has shown, that geographical and climatic factors influence on chemical composition of planth. Plants growing in Armenian flora are rich in sesquiterpenoids.
3. First time the chemical composition of Valeriana cardiola`s roots volatile oil was studied and the composition is close to the chemical composition of Valeriana officinalis volatile oil.
4. First time the chemical composition of Teucrium polium`s volatile oils growing in different conditions was studies and compared. And the results of analysis has shown, that the composition of Teucrium polium`s volatile oil, which is growing wildly different grown the one that is cultivated in hydroponic conditions.

References

1. Polat R1, Cakilcioglu U, Satıl F. Traditional uses of medicinal plants in Solhan (Bingöl-Turkey). J Ethnopharmacol. 2013 Jul 30; 148(3):951-63. doi: 10.1016/j.jep.2013.05.050. Epub 2013 Jun 14.
2. Shkrobothko P. Yu., Popov D.M., FursaN.S. “Quallitative identification and quantitative determination of valopotriates in officinal raw material and filter-packages of Valeriana officinalis” // Materials of international scientific-practical conference, dedicated to 75 anniversary of Perm state pharmaceutical academy, Perm PSPA, 2011, p. 258-259.
3. SotiropoulouD. E., Karamanos A.J. Field studies of nitrogen application on growth and yield of Greek oregano (Origanum vulgare ssp. hirtum (Link) Ietswaart) // Industrial Crops and Products 32.- Greece.- 2010.- P.450-457.
4. Kirkpinar F., Ünlü H.B., Özdemir G. Effects of oregano and garlic essential oils on performanse, carcase, organ and blood characteristics and intestinal microflora of broilers // Livestock Science 137.- Turkiye.- 2011.- P. 219-225.
5. El Oualidi J., Vermeau O., Puech S., Dubuisson J. Y., 1999, “Utility of RDNA ITS sequences in the systematics of Teucrium section Polium (Lamiaceae)”, Plant. Syst. Evol., 215, p. 49-70.
6. Kokkalou E, Stefanou E. The volatiles of Chaerophyllum bulbosum L. ssp. bulbosum growing wild in Greece.Pharm Acta Helv. 1989; 64(5-6):133-4.
7. Shkrobothko P. Yu., FursaN.S., Makarova D.L., Domrachev D.V., Malceva Ya.A., Panchenko C. V.”Comparative GC-MS analysis of Valeriana officalis volatile oil, growing wildly and cultivating in surroundings of Yaroslavl” // Materials of international scientific-practical conference, dedicated to 75 anniversary of Perm state pharmaceutical academy, Perm PSPA, 2011, p. 259-261.
8. Sergio Benvides, Villalobos-Carvajal R., Reyes J.E. //Physical, mechanical and antibacterial properties of alginate film: Effect of the crosslinking degree and Oregano essential oil concentration, Journal of Food Engineering 110, 2012, p. 232-239.
9. Novakovic M., Vuckobic I., Yanackovic P., Sokovic M., Filipovic A., Tesevic V., Silosavyevic S. Chemical composition, antibacterial and antifungal activity of the essential oils of Cotinus coggygria from Serbia, J. Serb. Chem. Soc. 72 (11) 1045-1051, 2007.
10. Cozzani S., Muselli A., Desjobert J. M., Bermardini A. F., Tomi F., Casanova J., 2005, “Chemical composition of essential oil of Teucrium polium subsp. Capitatum (Lamiaceae) from Corsica”, Flav. Fragr. J. 20, p. 436-441.
11. Boulila A., Bejaoui A., Messaoud C., Boussaid M., 2008, “Variation of volatiles in Tunisian populations of Teucrium polium L. (Lamiaceae)”, Chem. Biodivers 5, p. 1385-1400.
12. WHO guidelines on good agricultural and collection practices (GACP) for medicinal plants, World Health Organization, Geneva, 2003
13. Quality control methods for herbal materials, World Health Organization, 2011
14. SPh USSR, Medicine – Moscow, 1990, ed. 11, vol.1. p. 176.