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Comparison of the Volatile Constituents of *Pelargonium quercetorum Agnew.* of Iran with Some of the Other *Pelargonium* Species

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In this study, the volatile constituents of the essential oil of *Pelargonium quercetorum Agnew.* were investigated and compared with some of the other species of *Pelargonium*. *Pelargonium quercetorum Agnew.* is one of the *Pelargonium* genus of that was collected from Kurdistan area in Iran. Twenty six components in the essential oil of *Pelargonium quercetorum Agnew.* representing twenty one of the total oils were identified by GC and GC/MS technique. In this herb, α-pinene (25.28 %), α-fenchyl acetate (20.63 %) have the most percentages among compounds of the essential oil. Some other components like limonene (9.94 %), β-caryophyllene (8.20 %) are located in the second level of the concentration in the essential oil.

Key Words: *Pelargonium*, *Pelargonium quercetorum*, *Pelargonium quercetorum Agnew.*, Essential oil compounds.

INTRODUCTION

Pelargonium genus that is relevant to the Geraniaceae family has over 220 species in the world. The genus *Pelargonium* is promising for such a study because members are characterized by dramatic variation in growth form (including geophytes, shrubs and stem succulents) and because growth form diversity is expressed to the greatest extent in a monophyletic group comprising 80 % of *Pelargonium* species[1-3]. *Pelargonium quercetorum* has 34 species. From the aerial parts of this herb in crude or baked form was utilized as an anti-parasite agent in local medicine in Kurdistan, Iran[4,5].

The *Pelargonium quercetorum Agnew.* was collected and reported from Ghasemlu valley in the west Azerbaijan province of Iran[4]. Confusingly, *Geranium* is the correct botanical name of the separate genus which contains the related Cranesbills. Both genera are in the Family Geraniaceae.

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Linnaeus originally included all the species in one genus, *Geranium*, but they were later separated into two genera[5] by Charles L'Héritier in 1789. Gardeners sometimes refer to the members of Genus *Pelargonium* as "pelargoniums" in order to avoid the confusion, but the older common name "geranium" is still in regular use.

EXPERIMENTAL

The *Pelargonium quercetorum Agnew.* materials of this study were collected from west of Iran (Marivan-Kurdistan province) at the end of the May. 2005-2006. This species was identified in around of the Musel and Arbil province of Kurdistan-Iraq, for the first time.

A voucher specicum has been deposited in herbarium of Research Center of Agriculture & Natural Resources, Sanandaj, Kurdistan, Iran. The local name of *Pelargonium quercetorum Agnew.* is *Gala Revaci*.

Dried aerial parts of *Pelargonium quercetorum Agnew.* were subjected to hydrodistillation for 5 h using Clevenger-type apparatus to produce a yellow oil in 0.28 % (w/w) yield. The oil of the aerial parts of *Pelargonium quercetorum Agnew.* was examined by GC/ MS (GC: HP 6890, MS: HP 5973), column (HP5-MS, 30 m × 0.25 mm fused silica capillary column, film thickness 0.32 µm) by temperature program 60 °C (3 min)-210 °C (2 min) at the rate of 6 °C/min (injection temperature 250 °C, carrier gas: helium (with purity 99.999 %), detector temperature 150 °C, ionization energy in mass was 70 eV, mass range 10-300 amu and scan time was 1 s.

The list of identified components is presented in Table-1. The identifications were confirmed by comparison of their retention indices either with those of authentic compounds or with data in the literature[6-17]. In aerial parts of *Pelargonium quercetorum Agnew.*, the major identified components and the relative amounts based on peak area were α-pinene (25.28 %), α-fenchyl acetate (20.63 %), limonene (9.94 %), β-caryophyllene (8.20 %), camphene (4.31 %), δ-cadinene (3.32 %), β-pinene (3.21 %), α-amorphene (2.80 %), valencene (2.73 %), ledene (2.25 %) and *p*-cymene (1.63 %).

RESULTS AND DISCUSSION

Plants from genus *Pelargonium* have been previously studied and reported in the literatures[3-5,18]. There are some nice studies of the chemical composition of essential oil of *Pelargonium* species[6-17,19-22]. The chemical composition of the essential oils and also antimicrobial and antioxidant properties of some *Pelargonium* species were reported[6-17,21,22].

Rose-scented geranium (*Pelargonium* species) is grown as a perennial crop for production of high value essential oil, which finds application particularly in high-grade perfumery, cosmetic products and aromatherapy. The essential oil produced in the 4 fully expanded leaves (FEL) treatments

TABLE-1
VOLATILE CONSTITUENTS OF
Pelargonium quercetorum Agnew. OF IRAN

No.	Name of compounds	K.I.*	RT**	%
1	α-Pinene	928	5.54	25.28
2	Camphene	939	5.82	4.31
3	β-Pinene	963	6.41	3.21
4	Myrcene	974	6.68	1.43
5	*para*-Cymene	1004	7.42	1.63
6	Limonene	1009	7.53	9.94
7	γ-Terpinolene	1056	8.74	0.66
8	α-Fenchyl acetate	1206	12.55	20.63
9	α-Copaene	1276	14.10	1.28
10	Thymol	1285	14.30	1.13
11	*trans*-β-Caryophyllene	1310	14.86	8.20
12	(+)-Aromadendrene	1323	15.16	1.43
13	*trans*-β-Farnezene	1329	15.31	1.19
14	α-Humulene	1333	15.39	0.80
15	α-Amorphene	1347	15.73	2.80
16	Germacrene-D	1352	15.83	1.14
17	Ledene	1361	16.04	2.25
18	α-Muurolene	1363	16.09	1.24
19	δ-Cadinene	1378	16.44	3.32
20	Unknown	1388	16.67	0.48
21	Unknown	1418	17.33	1.04
22	Valencene	1423	17.43	2.73
23	Unknown	1429	17.56	0.62
24	Unknown	1449	17.98	1.44
25	γ-Muurolene	1470	18.43	1.17
26	Unknown	1586	20.72	0.65

*Kovats index, **Retention time (min).

was found to contain higher citronellol, geraniol, citronellyl formate, *cis*- and *trans*-rose oxides and 10 epi-γ-eudesmol and lower linalool, menthone and isomenthone, than other harvest treatments. It is suggested that rosescented geranium can be harvested more frequently (six harvests per annum) on attainment of shoots with 4 fully expanded leaves in order to produce higher essential oil yield with superior quality and higher return[7].

During distillation, a part of the essential oil becomes dissolved in the distillation water (hydrosol) and is lost as this hydrosol is discarded. In an investigation, hydrosol was shaken for 0.5 h with hexane (10:1 proportion) and the hexane was distilled to yield 'secondary' or 'recovered' essential oil[15]. The chemical composition of secondary oil was compared with that of 'primary' oil (obtained directly by distilling shoot biomass of the crop). Primary oil accounted for 93.0 % and secondary oil 7.0 % of the total oil yield (100.2 mL from 100 kg green shoot biomass). Fifty-two compounds making up 95.0-98.5 % of the primary and the secondary oils were characterized through gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS). Primary oil was richer in hydrocarbons (8.5-9.4 %), citronellyl formate (6.2-7.5 %), geranyl formate (4.1-4.7 %), citronellyl propionate (1.0-1.2 %), α-selinene (1.8-2.2 %), citronellyl butyrate (1.4-1.7 %), 10-epi-γ-eudesmol (4.9-5.5 %) and geranyl tiglate (1.8-2.1 %). Recovered oil was richer in organoleptically important oxygenated compounds (88.9-93.9 %), commercial rhodinol fraction (74.3-81.2 %), sabinene (0.4-6.2 %), *cis*-linool oxide (furanoid) (0.7-1.2 %), linalool (14.7-19.6 %), α-terpineol (3.3-4.8 %) and geraniol (21.3-38.4 %). Blending of recovered oil with primary oil is recommended to enhance the olfactory value of the primary oil of rose-scented geranium. Distillation water stripped of essential oil through hexane extraction can be recycled for distilling the next batch of rose-scented geranium[8].

Two clones of geranium (nos 53 and 79) were obtained from leaf cuttings of a geranium cultivar (*Pelargonium* sp.) and later multiplied by stem cuttings were found to be rich in isomenthone (64.4 and 67.7 %) in their essential oils[10]. The detailed composition of the oils of these two clones was investigated by capillary GC and GC-MS and compared with that of the oil of the parent cultivar. Linalol, citronellol, geraniol and citronellyl formate, which are the major constituents of the parent cultivar, were found only as minor constituents in the oils of the two clones. These two isomenthone-rich clones differed from each other in their α-pinene content (1.1 and 8.5 %) although both have 10-epi-γ-eudesmol (6.8 and 8.4 %) comparable with the parent cultivar (7.6 %)[10].

Indian geranium (*Pelargonium* sp.) cultivar Bourbon was grown in agroclimatic conditions of North Indian plains at Lucknow. The herbaceous parts, on steam distillation, gave 0.13 % of oil on a fresh weight basis[11]. GC and GC-MS analysis of the oil resulted in the identification of 69 constituents, representing 97.9 % of the oil. The geranium oil produced at Lucknow is comparable to that produced in southern hills of India in terms of its citronellol and geraniol content.

The essential oils of *Pelargonium sidoides* DC. and *P. reniforme* Curt. were obtained by hydro distillation from the leaves of the plants in 0.52 and 0.71 % yields, respectively, related to the dry weight[12]. Their composition was analyzed by GLC and GC-MS. About 230 components have been detected in each of the *Pelargonium* oils, of which 102 (*P. sidoides*) and 81 (*P. reniforme*) could be unambiguously identified, accounting for about 65 and 49 % of the total peak area, respectively[12]. For both species, sesquiterpenes (*ca.* 60 %) were the dominating components, with caryophyllene (2.3 %) and caryophyllene epoxide (13 %) as the most abundant compounds of the sesquiterpene fraction of the oil of *P. sidoides* and the sesquiterpene hydrocarbons δ-selinene (4.2%) and δ-cadinene (4.0%) as the main representatives of the oil of *P. reniforme*. Other major groups of the oil of *P. sidoides* comprised monoterpenes (16 %) and phenylpropanoids (9 %), the major compounds of the latter group being methyleugenol (4.3 %) and elemicin (3.6 %). By contrast, only monoterpenes were found in reasonable amounts (4.7 %) in the related species *P. reniforme*. Detection of anacardic acids and furan-type constituents provide a rational explanation for insect deterrence by *Pelargonium* species[12].

The rose-scented geranium (*Pelargonium* sp.) cultivar Kelkar , grown in the agro climatic conditions of the western Himalayas, was processed by various hydro distillation methods, which revealed that water distillation of the herb gave a higher oil yield (0.16-0.22 %) than the water-steam distillation (0.09-0.12 %) and steam distillation methods (0.06-0.18 %)[13]. The samples were analyzed by GC and GC-MS to study and compare the essential oil compositions which revealed that the oil distilled by the water-steam distillation method contained a higher content of monoterpene hydrocarbons (1.7 %), followed by steam distillation without cohobation and without recycling (1.5 %)[13]. A higher content of sesquiterpene hydrocarbons (4.4 %) was found in cumulative oil followed by direct oil (4.2 %) obtained by steam distillation with cohobation and without recycling of hydrosol, followed by the water-steam distillation method (3.4 %). Decanted oil, recovered from redistilling the hydrosol obtained by steam distillation with cohobating and without recycling, contained maximum monoterpene cyclic ethers (1.1 %) and carbonyl content (9.9 %), closely followed by water-steam distillation method (1.1 and 7.2 %, respectively). Steam distillation without cohobating and without recycling of hydrosol yielded essential oil with a higher percentage of esters (21.1 %), followed by direct oil (16.6 %)[13]. Lower ester content (5.3 %) was noticed in decanted oil , followed by oil distilled by steam distillation with cohobating and with recycling (11.8 %) and oil distilled in a Clevenger apparatus by the water distillation method (12.2 %), whereas maximum total alcohols were found in the decanted oil (75.1 %), followed by oil from the Clevenger apparatus (72.8 %) and steam distillation with cohobating and with recycling (69.1 %). A lower alcohol content was found in the direct oil (55.2 %) closely followed by cumulative oil (55.8 %). The variation in total alcohol and ester contents in geranium oil samples, distilled by using different processing techniques on pilot scale distillation, is mainly due to hydrolysis of some volatile constituents.

In a study, the supercritical fluid extraction (SFE) of geranium essential oil from geranium (*Pelargonium graveolens*) using supercritical carbon dioxide solvent was investigated[21]. At low pressure (10 MPa) and high temperature (343 K), waxes were co-extracted with the essential oil, resulting in artificially elevated essential oil extraction yields as no method was available with the SFE apparatus used to separate co-extracted waxes and oil. At high pressure (30 MPa) and low temperature (313 K), the amount of wax co-extracted decreased. Under the optimum conditions, the extraction yield increased with decrease in flow rate giving a maximum extraction[14] yield of 2.53 %. All samples were analyzed by gas chromatography-mass spectrometry and the effect of pressure and extraction time on oil composition was studied[14]. The percentage compositions of terpene hydrocarbons, terpenols, geraniol and geranyl esters were significantly affected by pressure and extraction time. The oil samples obtained by SFE were also compared with commercially obtained steam distilled samples. All major components of the commercially obtained oils were present in the SFE-obtained oils; however, the percentage composition of the major components differed greatly between steam distilled and SFE oils[14].

Pelargonium graveolens was cultivated to evaluate the potential for geranium oil production in Israel. During the summer (April-November) the essential oil content in fresh plants increased from 0.2-0.4 %. In this period a *Pelargonium* crop can be harvested three times. A total yield of 185 litres ha^{-1} of geranium oil can be expected, including the essential oil dispersed and remaining in the distillation water. This so-called secondary oil can amount to 25 % of the total oil yield. The oudor evaluation and composition data show that oil from *P. graveolens* grown experimentally in Israel is of good quality and belongs to the African type of geranium oil[15].

In present investigation, the volatile constituents of the essential oil of *Pelargonium quercetorum Agnew.* growing wild in Kurdistan, Iran were investigated by GC and GC/MS technique. As could be seen in Table-1, two components in this herb, *i.e.* α-pinene and α-fenchyl acetate have the most percentage among the twenty-six components that were identified. Some other components like limonene (9.94 %), β-caryophyllene (8.20 %) are located in the second level of the concentration in the essential oil. Although some components *viz.*, camphene, δ-cadinene, β-pinene, α-amorphene, valencene, ledene and *p*-cymene present in the medium to low relative percentages. α-Pinene and α-fenchyl acetate (20.63 %) have the highest percentage (25.28 %) in this herb.

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REFERENCES

1. E. Schonbeck-Temesy, Wien in K.H. Rechinger, Flora Iranica, Graz (1992).
2. J. Feltwell, Geraniums & Pelargoniums, Firefly Books (2001).
3. J. Taylor, Geraniums and Pelargoniums: The Complete Guide to Cultivation, Crowood Press (1998).
4. H. Tarighi, *Iran. J. Bot.*, **5**, 101 (1992).
5. Wikipedia, the free encyclopedia, http://en.wikipedia.org/wiki/Plargonium.
6. H.J. Dorman and S.G. Stanley, *J. Essen. Oil Res.*, **16**, 145 (2004).
7. S.K. Kothari, Y.V. Kumar, A.K. Bhattacharya and S. Ramesh, *Agron. Soil Sci.*, **50**, 593 (2004).
8. B.R. Rajeswara Rao, P.N. Kaul, K.V. Syamasundar and S. Ramesh, *Bioresour. Technol.*, **84**, 243 (2002).
9. B.R. Rajeswara Rao, P.N. Kaul, G.R. Mallavarapu and S. Ramesh, *Flav. Fragrance J.*, **15**, 137 (2000).
10. R.N. Kulkarni, G.R. Mallavarapu, K. Baskaran, S. Ramesh and S. Kumar, *Flav. Fragrance J.*, **13**, 389 (1998).
11. N. Jain, K.K. Aggarwal, K.V. Syamasundar, S.K. Srivastava and S. Kumar, *Flavour Fragrance J.*, **16**, 44 (2001).
12. O. Kayser, K. Lattè, H. Kolodziej and F.-J. Hammerschmidt, *Flav. Fragrance J.*, **13**, 209 (1998).
13. K.G.D. Babu and V.K. Kaul, *Flav. Fragrance J.*, **20**, 222 (2004).
14. A. Peterson, S. Machmudah, B.C. Roy, M. Goto, M. Sasaki and T. Hirose, *J. Chem. Technol. Biotechnol.*, **81**, 167 (2005).
15. A. Fleisher and Z. Fleisher, *J. Sci. Food Agric.*, **36**, 1047 (2006).
16. B.R.R. Rao, P.N. Kaul, K. Singh, G.R. Mallavarapu and S. Ramesh, *J. Essen. Oil Res.*, 41 (2005).
17. M. Lis-Balchin, H. Steyrl and E. Krenn, *J. Chem. Technol. Biotechnol.*, **17**, 60 (2003).
18. A.M. Armitage, Seed-propagated Geraniums and Regal Geraniums: Production Guidelines and Future Concerns, Timber Press, Portland, OR (1992).
19. J. Taylor, *Geranium* and *Pelargoniums*: The Complete Guide to Cultivation, Propagation and Exhebition, Crowood Press, Ramsbury, Marlborough, Wiltshire (1998).
20. B.R. Rajeswara Rao and A.K. Bhattacharya, *Flav. Fragrance J.*, **12**, 201 (1997).
21. M. Lis-Balchin, Essential Oils from Different Pelargonium Species and Cultivars: Their Chemical Composition (Using GC, GC/MS) and Appearance of Trichomes (under EM), Medicinal and Aromatic Plants-Industrial Profiles, (*Geranium* & *Pelargonium*), Vol. 27, pp. 147-165 (2002).
22. S.G. Deans, Antimicrobial Properties of *Pelargonium* Extracts Contrasted with that of Geranium, Medicinal and Aromatic Plants-Industrial Profiles, (*Geranium* & *Pelargonium*), Vol. 27, pp. 132-146 (2002).

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