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Composition of geranium (*Pelargonium graveolens*) essential oil from Tajikistan

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Abstract
The essential oil of *Pelargonium graveolens* from the aerial parts growing in Tajikistan was obtained by hydrodistillation and analyzed by gas chromatography – mass spectrometry. Seventy-nine components representing 95.1% of the total oil were identified. The main constituents of the essential oil were citronellol (37.5%), geraniol (6.0%), caryophyllene oxide (3.7%), menthone (3.1%), linalool (3.0%), β-bourbonene (2.7%), *iso*-menthone (2.1%) and geranyl formate (2.0%).

Keywords: *Pelargonium graveolens,* essential oil, citronellol, geraniol, caryophyllene oxide.

1. Introduction
Pelargonium graveolens L. Her. *ex* Ait. (Synonym *P. roseum* Willd.) is a species in the *Pelargonium* genus and is often called a geranium because it falls within the plant family of Geraniaceae. *P. graveolens* is an important, high-value perennial, aromatic shrub that can reach a height of up to 1.3 m and a spread (lateral growth) of 1 m. Its hairy stems are herbaceous when young and become woody with age, and the plant's leaves are deeply incised, soft to the touch, and strongly rose scented. The essential oil of *P. graveolens* is extensively used in the perfumery and cosmetic industries [1-3]. It is an indispensable aromatherapy oil since geranium oil, as well as its major constituents (citronellol, geraniol, and linalool), have shown smooth muscle relaxant (guinea pig ileum) properties [4]. Geranium oil has also become an important skin care oil because it is good in opening skin pores and cleaning oily complexions [5, 6]. This oil has also been found to have use in reducing pain due to post-herpetic neuralgia as well as treating dysentery, hemorrhoids, inflammation, heavy menstrual flows, and even cancer [5]. The French community is currently treating diabetes, diarrhea, gallbladder problems, gastric ulcers, jaundice, liver problems, sterility, and urinary stones with this oil [5, 7, 8]. Moreover, in Chinese homeopathy, it is thought to open up the liver *chakra* and promote the expulsion of toxins, helping to achieve a balanced body [9]. In Tajikistan, geranium is cultivated on an industrial scale and approximately 3.5 tons of geranium oil are produced each year. In this work, we present the chemical composition of *Pelargonium graveolens* essential oil growing in Tajikistan.

2. Materials and Methods
2.1 Plant Material
Pelargonium graveolens was grown in the Pakhtaobod Aromatic Plants Field Station, Tursunzoda region of Tajikistan. Fully grown crop plants were harvested and steam distilled in a field distillation unit. The oil decanted from distillation water was filtered to remove extraneous particles, dried over anhydrous sodium sulfate, refiltered, and measured.

2.2 Gas Chromatographic-Mass Spectral Analysis
The essential oil of *P. graveolens* was analyzed by GC-MS using an Agilent 6890 GC with Agilent 5973 mass selective detector [MSD, operated in the EI mode (electron energy = 70 eV), scan range = 45-400 amu, and scan rate = 3.99 scans/sec], and an Agilent ChemStation data system. The GC column was an HP-5ms fused silica capillary with a (5% phenyl)-polymethylsiloxane stationary phase, film thickness of 0.25 μm, a length of 30 m, and an internal diameter of 0.25 mm. The carrier gas was helium with a column head pressure of 48.7 kPa and a flow rate of 1.0 mL/min.

Inlet temperature was 200 °C and interface temperature was 280 °C. The GC oven temperature program was used as follows: 40 °C initial temperature, hold for 10 min; increased at 3 °C/min to 200 °C; increased 2°/min to 220 °C. A 1% w/v solution of the sample in CH_2Cl_2 was prepared and 1 µL was injected using a splitless injection technique.

Identification of the oil components was based on their retention indices determined by reference to a homologous series of *n*-alkanes, and by comparison of their mass spectral fragmentation patterns with those reported in the literature [10] and stored on the MS library [NIST database (G1036A, revision D.01.00)/ChemStation data system (G1701CA, version C.00.01.080]. The percentages of each component are reported as raw percentages based on total ion current without standardization. The essential oil composition of *Pelargonium graveolens* is summarized in Table 1.

3. Results and Discussion

Pelargonium graveolens (geranium) essential oil was obtained by hydrodistillation of the aerial parts. The oil from Tajikistan was analyzed by GC-MS, and 79 compounds were identified, which accounted for 95.1% of the total oil. The essential oil of *P. graveolens* was composed primarily of citronellol (37.5%), geraniol (6.0%), caryophyllene oxide (3.7%), menthone (3.1%), linalool (3.0%), β-bourbonene (2.7%), *iso*-menthone (2.1%), geranyl formate (2.0%), *cis*-rose oxide (1.9%), geranyl tiglate (1.8%), and 2-phenylethyl tiglate (1.5%) (Table 1).

Table 1: Essential oil composition of *Pelargonium graveolens* from Tajikistan

Compound	RI[a] (this work)	RI[b] (Literature)	Area (%)
(3*Z*)-Hexenol	855	859	0.1
α-Pinene	941	939	0.5
Myrcene	992	990	0.1
p-Cymene	1024	1024	0.1
Limonene	1028	1029	0.2
γ-Terpinene	1058	1059	tr
cis-Linalool oxide	1072	1072	0.2
trans-Linalool oxide	1088	1086	0.1
Linalool	1100	1096	3.0
cis-Rose oxide	1111	1108	1.9
trans-Rose oxide	1127	1125	0.8
neo-Isopulegol	1145	1148	0.1
Menthone	1154	1152	3.1
iso-Menthone	1164	1162	2.1
iso-Menthol	1182	1182	0.3
α-Terpineol	1188	1188	0.4
Citronellol	1226	1225	37.5
Neral	1240	1238	0.3
Geraniol	1251	1252	6.0
Neryl formate	1279	1282	0.1
Geranyl formate	1300	1298	2.0
Citronellic acid	1315	1313	0.1
Methyl geranate	1322	1324	0.1
8-Hydroxy-*neo*-menthol	1330	1330	0.1
Unidentified	1336	---	0.6
α-Cubebene	1348	1348	0.2
Citronellyl acetate	1354	1352	1.0
Unidentified	1362	---	0.5
α-Ylangene	1371	1375	0.1
α-Copaene	1376	1376	0.9
β-Bourbonene	1385	1388	2.7
β-Elemene	1392	1390	0.1
1-Phenylethyl isobutanoate	1396	1393	0.1
Unidentified	1404	---	0.6
(*Z*)-Caryophyllene	1407	1408	0.1
α-Gurjunene	1410	1409	0.1
(*E*)-Caryophyllene	1420	1419	1.1
β-Copaene	1430	1432	0.2
Aromadendrene	1439	1441	0.2
Citronellyl propionate	1446	1446	1.4
cis-Muurola-3,5-diene	1450	1450	0.4
α-Humulene	1454	1454	0.6
Alloaromadendrene	1461	1460	0.3
cis-Muurola-4(14),5-diene	1467	1466	0.1
Geranyl propanoate	1477	1477	0.8
α-Amorphene	1481	1484	0.2
Citronellyl isobutyrate	1486	1483	0.2
cis-β-Guaiene	1495	1493	0.2
α-Muurolene	1501	1500	0.3

Lavandulyl 2-methylbutanoate	1509	1511	0.1
γ-Cadinene	1514	1513	0.5
trans-Calamenene	1523	1522	1.3
Citronellyl butanoate	1529	1531	1.5
α-Calacorene	1543	1545	0.2
Unidentified	1553	---	0.5
Geranyl butanoate	1563	1564	0.9
Maaliol	1567	1567	0.2
Citronellyl 2-methylbutanoate	1574	---	0.1
Spathulenol	1579	1578	0.5
Caryophyllene oxide	1585	1583	3.7
2-Phenylethyl tiglate	1587	1585	1.5
Viridiflorol	1592	1592	0.5
Geranyl 2-methylbutanoate	1604	1601	0.4
Humulene epoxide II	1609	1608	1.0
1,10-di-*epi*-Cubenol	1615	1619	0.4
Junenol	1618	1619	0.2
Citronellyl pentanoate	1625	1625	0.3
1-*epi*-Cubenol	1628	1628	0.4
Caryophylla-4(12),8(13)-dien-5-ol	1635	1640	0.4
τ-Muurolol	1641	1642	0.6
α-Muurolol	1645	1642	0.3
α-Cadinol	1653	1654	0.6
Geranyl pentanoate	1657	1656	0.7
(*E*)-Citronellyl tiglate	1666	1668	1.0
14-Hydroxy-9-*epi*-(*E*)-caryophyllene	1670	1669	0.6
Cadalene	1673	1676	0.2
Geranyl tiglate	1696	1696	1.8
Geranyl ester	1712	---	0.5
Geranyl hexanoate	1750	1755	0.1
n-Pentadecanol	1774	1774	0.2
Citronellyl heptanoate	1816	1819	0.3
Geranyl heptanoate	1852	1857	0.2
Citronellyl octanoate	1918	1920	0.3
Citronellyl ester	2049	---	0.5
Unidentified	2086	---	0.6
Citronellyl ester	2287	---	1.1
Nonacosane	2900	2900	0.3

[a] Retention Indices on HP-5ms fused silica capillary column.
[b] Adams, 2007 [10].

The essential oil of *P. graveolens* is one of the most expensive essential oils used in the perfumery, flavoring, and cosmetics industries [11, 12], and therefore the plant is widely cultivated. The composition of geranium oil from Tajikistan is different from that of the commercially cultivated geranium oil reported in the literature [13-17]. There are several cultivars of geranium that are commercially grown for the production of this essential oil. The main cultivars of geranium are the Reunion Island type, the African type (Egypt, Morocco), and the Chinese type. The oil of the Reunion Island type was comprised of citronellol and geraniol (1:1) and citronellyl formate, guaia-6,9-diene, and isomenthone. The Chinese type contains high amounts of citronellol and citronellyl formate and a low concentration of geraniol. The African type contains citronellol and geraniol (1:1) as well as citronellyl formate, isomenthone, and 10-*epi*-γ-eudesmol as the major constituents. In addition, one type of geranium oil, known as "Bourbon", differs from the African type because it contains significant amounts of sesquiterpene guaia-6,9-diene, but lacks 10-*epi*-γ-eudesmol, whereas the African type contains a fair amount of 10-*epi*-γ-eudesmol and a low amount of guaia-6,9-diene.

Compared to these three main cultivars, the geranium essential oil of Tajikistan lacks characteristic components that are found in cultivated geranium essential oils, such as citronellyl formate, guaia-6,9-diene, and 10-*epi*-γ-eudesmol. In addition, the wild geranium essential oil contains a diverse range of compounds, but only citronellol appears in a significant amount (37.5%); the others appear only in low amounts.

In India, three cultivars of geranium are available: "Bipuli" (intermediate to the Reunion Island and African types), "Hemanti" (similar to the Chinese type), and a third type, "Kunti", whose oil is rich in geraniol (40–50%) and poor in citronellol (1–10%) compared to the Reunion Island type [18,19]. Gupta and co-workers [20] isolated a somaclone from the cultivar Kunti and found that its essential oil is rich in isomenthone (71%) and poor in citronellol (6%) and geraniol (3%). The geranium oil from Israel was found to have a comparable composition as African oil (Egypt, Morocco) [21]. The oil contained no guaia-6,9-diene, but was composed of 5% 10-*epi*-γ-eudesmol, which is characteristic of African type oils. Interestingly, the geranium essential oil from South Africa may not be the African type. The geranium essential oil from Johannesburg, South Africa was dominated by isomenthone, with 84.0%, and other major components, including methone (2.8%), myrcene (0.9%), δ-cadinene (0.9%), and spathulenol (0.9%) [22]. Large quantities of isomenthone (± 80%) in the oils of *P. graveolens* are responsible for their minty scent [14].

4. Conclusions

A search of the literature reveals that no *P. graveolens* essential oil contains such a diverse range of compounds as

that of the Tajik oil. The geranium oil from Tajikistan shares some common compounds with other geranium oils, but its major compounds are notably different. The perfumery value (ratio of citronellol to geraniol) of the essential oil from Tajikistan was 6.25, noting that this oil contains higher amounts of citronellol and lower amounts of geraniol. Compared to the oils examined in the relevant literature, the most notable difference was the higher quantities of caryophyllene derivatives in Tajik geranium oil, especially caryophyllene oxide (3.7%).

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6. References

1. Misra A, Srivastava NK. Value addition of essential monoterpene oil(s) in Geranium (*Pelargonium graveolens*) on leaf positions for commercial exploitation. African Journal of Agricultural Research 2010; 5(15):2077-2079.
2. Rao BRR, Kaul PN, Syamasundar KV, Ramesh S. Water soluble fractions of rose-scented geranium (*Pelargonium* species) essential oil. Bioresource Technology 2002; 84(3):243-246.
3. Rao BRR. Biomass yield, essential oil yield and essential oil composition of rose-scented geranium (*Pelargonium* species) as influenced by row spacings and intercropping with cornmint (*Mentha arvensis* L.f. *piperascens* Malinv. ex Holmes). Industrial Crops and Products, 2002; 16(2):133-144.
4. Lis-Balchin M, Patel J, Hart S. Studies on the mode of action of essential oils of scented-leaf *Pelargonium* (Geraniaceae). Phytotherapy Research 1998; 12(3):215-217.
5. Peterson A, Machmudah S, Roy BC, Goto M, Sasaki M, Hirose T. Extraction of essential oil from geranium (*Pelargonium graveolens*) with supercritical carbon dioxide. Journal of Chemical Technology and Biotechnology 2006; 81(2):167-172.
6. Fayed SA. Antioxidant and anticancer activities of *Citrus reticulate* (petitgrain mandarin) and *Pelargonium graveolens* (geranium) essential oils. Research Journal of Agriculture and Biological Sciences 2009; 5(5):740-747.
7. Weiss EA. Essential Oil Crops. Centre for Agriculture and Biosciences (CAB) International, New York, 1997.
8. Miller DM. The taxonomy of *Pelargonium* species and cultivars, their origins and growth in the wild. Geranium and Pelargoniums: The genera *Geranium* and *Pelargonium*. In: Medicinal and Aromatic Plants-Industrial Profiles. Lis-Balchin M (Ed.). Taylor and Francis, London, 2002, 49-79.
9. Higley C, Higley A. Reference Guide for Essential Oils. Abundant Health, London, 2001.
10. Adams RP. Identification of Essential Oil Components by Gas Chromatography. Mass Spectrometry, Edn 4, Allured Publishing, Carol Stream, IL, USA, 2007.
11. Gulati BC. Cultivation of geranium. Indian Oil Soap Journal 1960; 26(2):35.
12. Charlwood BV, Charlwood KA. *Pelargonium* spp. (Geranium): *in vitro* culture and the production of aromatic compounds. In: Biotechnology in Agriculture and Forestry #15: Medicinal and Aromatic Plants III. Bajaj YPS (Ed.). Springer-Verlag, Berlin, 1991, 339.
13. Teisseire P. Industrial quality control of essential oils by capillary GC. In: Capillary Gas Chromatography in Essential Oil Analysis. Sandri P, Bicchi C (Eds.). Huethig Publishing, Heidelberg, 1987.
14. Van der Walt JJA, Demarne FS. *Pelargonium graveolens* and *P. radens*: a comparison of their morphology and essential oils. South African Journal of Botany 1988; 56:617-622.
15. Demarne FE, van der Walt JJA. Composition of essential oil of *Pelargonium citronellum* (Geraniaceae). Journal of Essential Oil Research 1993; 5(3):233-238.
16. Vernin G, Metzger J, Fraisse D, Scharff C. Lab Chim. Chemicals with cas numbers 105-86-2 and 87-44-5 also play role. Parfum Cosmetiques Arômes 1983; 52:51-61.
17. Fraisse D, Sharf C, Vernin G, Metzger J. 11th International Essential Oil Congress, Singapore, Book 3, 1983, 100-120.
18. Kaul PN, Rao BRR, Bhattacharya AK, Singh CP, Singh K. Volatile constituents of three cultivars of rose-scented geranium (*Pelargonium* sp.) as influenced by method of distillation. Pafai Journal 1995; 17(4):21-26.
19. Mallavarapu GR, Prakasa Rao EVS, Ramesh S, Narayana MR. Chemical and agronomical investigations of a new chemotype of geranium. Journal of Essential Oil Research 1993; 5(4):433-438.
20. Gupta R, Mallavarapu GR, Banerjee S, Kumar S. Characteristics of an isomenthone-rich somaclonal mutant isolated in a geraniol-rich rose-scented geranium accession of *Pelargonium graveolens*. Flavour and Fragrance Journal 2001; 16(5):319-324.
21. Fleisher A, Fleisher Z. Yield and quality of essential oil from *Pelargonium graveolens* cultivated in Israel. Journal of the Science of Food and Agriculture 1985; 36(11):1047-1050.
22. Lalli JY, Viljoen AM, Van VSF. Potential interaction between the volatile and non-volatile fractions on the *in vitro* antimicrobial activity of three South African *Pelargonium* (Geraniaceae) species. Natural Product Communications 2010; 5(9):1395-1400.
23. Zhang H. A Gas Chromatographic. Mass Spectral Analysis of Aromatic Medicinal Plants from Tajikistan. M.S. Thesis (Chemistry), University of Alabama in Huntsville, 2013.
24. Strachey R. Catalogue of the Plants of Kumaon and of the Adjacent Portions of Garhwal and Tibet, Periodical Experts, New Delhi, India, 1852, 92.
25. Polunin O, Stainton A. Flowers of the Himalaya. Oxford University Press, New Delhi, India, 1984, 192.
26. Mahmood U, Kaul VK, Acharya R, Jirovetz L. *p*-Coumaric acid esters from *Tanacetum longifolium*. Phytochemistry 2003; 64(4):851-853.