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)-polydimethylsiloxane 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 CH₂Cl₂ 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.

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

| Compound | RI\(^a\) (this work) | RI\(^b\) (Literature) | Area (%)
|----------|-----------------------|------------------------|--------
| (Z)-Hexenol | 855 | 859 | 0.1
| α-Pinene | 941 | 939 | 0.5
| Myrcene | 992 | 990 | 0.1
| α-Cymene | 1024 | 1024 | 0.1
| Limonene | 1028 | 1029 | 0.2
| γ-Terpine | 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-Terpine | 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
| Citronelic 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-Murola-3,5-diene | 1450 | 1450 | 0.4
| α-Humulene | 1454 | 1454 | 0.6
| Alloaromadendrene | 1461 | 1460 | 0.3
| cis-Murola-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-Murolene | 1501 | 1500 | 0.3

### 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).
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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Index</th>
<th>Retention Index</th>
<th>Area %</th>
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<tr>
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<td>1.8</td>
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<tr>
<td>Citronellyl octanoate</td>
<td>1918</td>
<td>1920</td>
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<tr>
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<td>---</td>
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<tr>
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<tr>
<td>Citronellyl ester</td>
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<tr>
<td>Nonacosane</td>
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<td>0.3</td>
</tr>
</tbody>
</table>

*a Retention Indices on HP-5ms fused silica capillary column.
b Adams, 2007 [10]
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 oxide (3.7%).

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6. References