FLAVOUR AND FRAGRANCE JOURNAL
Flavour Fragr. J., **13**, 389–392 (1998)

Composition of the essential oils of two isomenthone-rich variants of geranium (*Pelargonium* sp.)

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Received 15 July 1997
Accepted 9 January 1998

ABSTRACT: Two clones of geranium (nos 53 and 79) 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. 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%).

KEY WORDS: isomenthone-rich geranium clones; *Pelargonium* sp.; essential oil; α-pinene; isomenthone; 10-*epi*-γ-eudesmol

Introduction

Geranium oil of commerce is obtained by steam distillation of herbaceous parts of *Pelargonium* spp.[1] The highest quality oil possesses a delicate rose-like fragrance and is produced in the island of Reunion. It is known as 'Reunion' or 'Bourbon' geranium oil. It is used as a substitute for the expensive attar of roses.[2] Apart from 'Bourbon' geranium oil, there are two other commercial geranium oils, viz. 'Egyptian' and 'Chinese'. The 'Chinese' geranium oil is characterized by its larger citronellol : geraniol ratio, 3–4 : 1 as compared with the ratio of 1 : 1 in 'Bourbon' and 'Egyptian' geranium oils. 'Bourbon' and 'Egyptian' geranium oils are distinguished by their relative contents of guaia-6,9-diene and 10-*epi*-γ-eudesmol.[3] The best quality geranium oil is used in high-grade perfumes and flavours, while the lower quality oil is used for perfuming in creams, soaps and toiletries.

Apart from *Pelargonium* species which are used for producing commercial rose-scented geranium oil, there are several other species of the same genus and their hybrids which are reported to yield essential oils rich in different aroma compounds (Table 1).

In India, geranium was introduced in the beginning of this century, and subsequently two types called 'Algerian' or 'Tunisian' and 'Bourbon' or 'Reunion' were identified. The essential oil of the Indian cultivar 'Bourbon' resembles Reunion 'Bourbon' geranium oil for the ratio of citronellol : geraniol, but is considered as 'Egyptian' geranium oil because of its higher content of 10-*epi*-γ-eudesmol. The essential oil of the cultivar 'Algerian', resembles the 'Chinese' geranium oil in its ratio of citronellol : geraniol. Recently, introduction of another clone has been reported whose oil has a citronellol : geraniol ratio of 1 : 5.[10] Only these three clones of geranium have been reported from India. During the course of genetic improvement work on geranium, two plants with high content of isomenthone were identified from plants obtained from leaf cuttings of the Indian geranium cultivar, 'Bourbon'.[11] The present paper reports the composition of essential oils of these two clones in comparison with that of the parental cultivar.

Experimental

Plant Material

Two plants, designated nos 53 and 79, among plants obtained from leaf cuttings of the Indian geranium (*Pelargonium* sp.) cultivar 'Bourbon' showed a high content of isomenthone in their essential oil. These plants were multiplied by stem cuttings and were planted in the field along with the parental cultivar and several other selections, in a randomized complete

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 CCC 0882–5734/98/060389–04$17.50

Table 1. Major constituents of some reported *Pelargonium* species, hybrids and cultivars

Species	Major constituents of essential oils	Reference
P. graveolens	Isomenthone (75–83%)	van der Walt and Demarne[4]
P. radens	Isomenthone (80–85%)	van der Walt and Demarne[4]
P. graveolens × *P. radens*	Isomenthone (76–85%)	van der Walt and Demarne[4]
P. tomentosum	Isomenthone (61–62%) and menthone (25–27%)	Demarne and van der Walt[5]; Charlwood and Charlwood[1]
P. vitifolium	Citronellic acid (77–85%)	Demarne and van der Walt[6]
P. citronellum	Neral (27–37%) and Geranial (36–48%)	Demarne and van der Walt[7]
P. grossulariodes	Isomenthone (13%), Citronellol (12%) geraniol (16%) and methyl eugenol (11%)	Lis-Balchin[8]
P. capitatum	Citronellyl formate (23–37%) geranyl formate (8–10%)	Demarne[9]
Cultivar, 'Rose' (*P. capitatum* × *P. radens*)	Citronellol (19%), Geraniol (22%)	Demarne[9]
Cultivar 'Menthe' (*P. capitatum* × *P. radens*)	Isomenthone (54%) and α-pinene (11%)	Demarne[9]
Cultivar 'Citronelle'	Isomenthone (19%) and Citronellol (40%)	Demarne[9]

block design with three replications. Plants were harvested when they were four months old and their essential oils were obtained by hydrodistillation of the herb in a Clevenger-type apparatus.

Gas Chromatography (GC)

GC analysis of oils was performed on a Perkin-Elmer GC 8500, using two fused silica capillary columns (25 m × 0.25 mm i.d.), one coated with dimethyl siloxane (BP-1) and the other with Carbowax 20M (BP-20). Carrier gas: nitrogen, at 10 psi inlet pressure. Temperature programming: 60–220°C at 5°C/min for the dimethyl siloxane column, and 60–200°C at 5°C/min for the Carbowax column. Split ratio: 1:80.

Gas Chromatography–Mass Spectrometry (GC–MS)

GC–MS was performed on Hewlett-Packard Gas Chromatograph model 5890 coupled with a mass detector (MSD 5970 HP) using the fused HP-1 (methyl silicone) column (50 m × 0.2 mm i.d., film thickness 0.25 mμ). Carrier gas: helium. Temperature programming: 15 min at 100°C, then rising at 4°C/min to 280°C. EI mode: 70 eV.

Identification of Compounds

Compounds were identified by comparing retention indices of peaks on the two columns (BP-1 and BP-20), with literature values,[12–14] comparison of mass spectra of peaks with published data[13–15] and by peak enrichment on co-injection with authentic standards wherever possible. Relative amounts of individual components are based on peak areas obtained without FID response factor correction.

The Kovats' retention indices were obtained from the gas chromatograms by logarithmic interpolation between bracketing *n*-alkanes. The homologous series of *n*-alkanes (C-8 to C-22: Poly Science Inc., Niles, USA) were used as standards.

Results and discussion

The oil contents of the clones nos 53 and 79 were 0.20 and 0.25%, respectively, and slightly higher than that of the parental cultivar (0.15%). GC and GC–MS analyses enabled the identification of a total of 48 constituents in the oils of the three clones. The identified compounds are listed in Table 2, which shows that the essential oil composition of clones nos 53 and 79 was entirely different from that of the parental cultivar (Table 2). Both clones had isomenthone as the major constituent (64–68%), in contrast to the parental cultivar, which had citronellol (26%) and geraniol (24%) as major constituents. Citronellol, geraniol. linalol, citronellyl formate and geranyl formate, which are the main constituents of commercial 'Bourbon' geranium oil and of the parental cultivar, were present only in negligible quantities in essential oils of these two clones. Among other compounds detected in significant quantities in the essential oils of these clones, only the content of 10-*epi*-γ-eudesmol was found to be similar to that in the oil of the parental cultivar. Both the clones had a relatively higher content of α-pinene than the parental cultivar. Clone no. 79 had a considerably larger quantity (9%) of α-pinene than clone no. 53 (1%). As expected, the two oils were devoid of *cis*- and *trans*-rose oxides because of their extremely low content of citronellol (0.3–0.5%).

The essential oils of *P. graveolens*, *P. radens* and their hybrids, *P. tomentosum* and cultivar 'Menthe' are reported to be rich in isomenthone.[5,9] The essential oil composition of clone no. 79 appeared to be similar to that of cultivar 'Menthe' except for slightly lower

Table 2. Percentage composition of essential oils of the Indian variety 'Bourbon' (*Pelargonium* sp.) and its variants, clone nos 53 and 79

Compound[a]	RI		Area (%)		
	βBP-1	BP-20	'Bourbon'	Clone no. 53	Clone no. 79
cis-Hex-3-enol	831	1335	0.1	tr	0.1
α-Pinene	934	1017	0.3	1.1	8.5
Camphene	946	1042	tr	tr	0.1
Sabinene	969	1113	0.1	tr	0.1
β-Pinene	973	1105	–	tr	0.1
Myrcene	984	1155	0.7	0.4	0.7
α-Phellandrene	997	1155	0.1	0.3	0.6
p-Cymene	1013	1261	0.1	0.3	0.6
Limonene	1024	1186	0.3	1.0	1.9
(*Z*)-β-Ocimene	1028	1226	0.2	0.3	0.5
(*E*)-β-Ocimene	1040	1243	0.3	0.1	0.1
cis-Linalol oxide (f)	1062	1435	0.1	0.1	0.1
trans-Linalol oxide (f)	1071	1454	tr	0.1	0.1
Terpinolene	1081	1284	tr	0.1	0.1
Linalol	1087	1552	6.7	0.3	0.2
cis-Rose oxide	1097	1345	0.4	–	–
trans-Rose oxide	1115	1358	0.2	–	–
Menthone	1137	1454	0.1	1.7	1.2
Isomenthone	1149	1482	7.9	67.6	64.4
Terpinen-4-ol	1165	1600	–	0.1	0.1
α-terpineol	1176	1674	0.3	0.3	0.2
Citronellol +	1215	1781	26.7	0.5	0.3
Nerol		1810			
Piperitone	1231	1705	–	0.2	0.2
Geraniol	1239	1861	24.1	0.2	0.1
Geranial	1244	1739	0.5	0.2	–
Citronellyl formate	1261	1617	8.2	0.3	0.2
Neryl formate	1268	1641	0.1	0.3	0.1
Geranyl formate	1283	1698	3.1	–	tr
Citronellyl acetate	1333	1657	0.2	tr	–
α-Cubebene	1351	1453	tr	0.1	0.1
Geranyl acetate	1357	1754	0.3	0.1	–
α-Copaene	1378	1495	0.1	0.2	0.2
β-Bourbonene	1387	1495	0.5	0.8	0.6
β-Caryophyllene	1422	1581	0.5	1.2	1.0
Guaia-6,9-diene	1442	1600	0.1	tr	0.1
Geranyl propionate	1449	1817	0.5	0.2	0.1
α-Humulene	1456	1680	0.1	0.4	0.3
Germacrene-D	1480	1724	0.9	2.0	1.4
Calamenene	1519	1836	0.2	0.1	0.3
Geranyl butyrate	1534	1907	0.2	–	0.1
β-Phenylethyl tiglate	1555	2208	0.9	2.0	1.4
Furopelargone B	1567	2065	0.1	0.1	0.1
Geranyl isovalerate	1578	1880	0.3	0.8	0.5
10-*epi*-γ-Eudesmol	1618	2117	7.6	8.4	6.8
Geranyl valerate	1624	1983	0.1	0.2	0.2
β-Eudesmol	1630	2235	0.1	0.1	0.1
Citronellyl tiglate	1645	2010	1.5	1.7	1.4
Geranyl tiglate	1672	2097	1.6	–	–

tr = traces.
[a] Components are listed in the order of elution on BP-1 column.

contents of (*Z*)-β-ocimene, piperitone, geranyl formate and 6,9-guaiadiene. Cultivar 'Menthe' has been proposed to be hybrid between *P. capitatum* and *P. radens*.[9] In contrast, the cultivar, 'Bourbon' used in this study has been argued to be a hybrid between *P. graveolens* and *P. capitatum*.[16] Therefore, data only on essential oil composition are not sufficient for determining the origin or parentage of cultivars.[17,18] A simpler possibility for the origin of the Indian cultivar 'Bourbon' is that it arose as chemovariant (mutant) of *P. graveolens* (whose oil is rich in isomenthone[4,9]) and clones nos 53 and 79 were a result of independent back-mutations. A single mutation preventing further conversion of isomenthone may be involved in the origin of these clones. Such a mutation, however, does not fit into the scheme of biosynthesis of constituents of essential oil of geranium proposed by Demarne.[9]

This is the first report on an isomenthone-rich geranium oil from India. The world market for peppermint-scented essential oil of *P. tomentosum*,

which is rich in isomenthone (61–62%), has been reported to be about 2–3 tonnes annually.[5] The clones 53 and 79, therefore, may also be useful as additional sources of mint-scented essential oil.

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