An Australian Geranium Oil

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Geranium oil remains one of the most important oils employed in perfumery formulations.[1] With production declining in some countries,[2] opportunities for new suppliers are greater than they were ten years ago.[1] This article describes a comparison of the physiochemical data and chemical composition of an oil distilled from a cultivar of a *Pelargonium* sp. hybrid developed in Australia, and compares the data with that obtained from commercial geranium oils.

Experimental

Voucher specimens of this *Pelargonium* cultivar are lodged with the National Herbarium of New South Wales, Sydney (Voucher No. R94015).

Under sub-tropical conditions in the Lismore district (28°50'S, 153°20'E), living material was cultivated in well-drained Krasnozem soil at twelve trial plots, each containing fifteen plants spaced one meter apart within 9.2 square meters.

Refractive indices were measured on an Abbé Atago 15288 refractometer, optical rotations on an Atago Polax polarimeter, relative densities using 1 ml glass pycnometers and solubility in alcohol using 70% ethanol. Gas chromatography was performed on Hewlett Packard 5890 and Shimadzu 14B gas chromatographs using H_2 at 1 ml/min as carrier gas, flame ionization for detection and BP1, AT35 and BP21 m x 0.2 mm FSOT columns. Gas chromatography-mass spectrometry was performed on a Shimadzu QP 1000 using a 30 m x 0.22 mm DB17 FSOT column for both EI (70 eV and 20 eV) and CI (isobutane) determinations. GC and GC/MS determinations were programmed from 50° (1 min) to 250° (9 min) at 10°/min. GC/IR determinations used a 50 m x 0.22 mm BPS FSOT column programmed from 40° (0 min) to 290° at 4°/min with a Digilab Tracer detector. Assignments were based on Retention Indices, Mass Spectra, Infrared Spectra, Liquid Chromatography and GC peak enhancement following the coinjection of authentic constituents.

These constituents were obtained from chemical or essential oil suppliers or, for the esters, by synthesis using standard p-toluenesulfonic acid (phenylethyl tiglate), acid chloride (geranyl and citronellyl butyrates and tiglates) or acid anhydride (geranyl and citronellyl propionates) procedures.[3]

For the Australian geranium oil, fresh leaves with terminal stalks (400 g) were hydrodistilled in an all glass modified Clevenger-type apparatus to yield 0.15% (springtime growth, average from four harvests).

For the commerical samples, the following geranium oils (and suppliers) were used:

- *Reunion* (a Bourbon from Artisanar, Reunion).

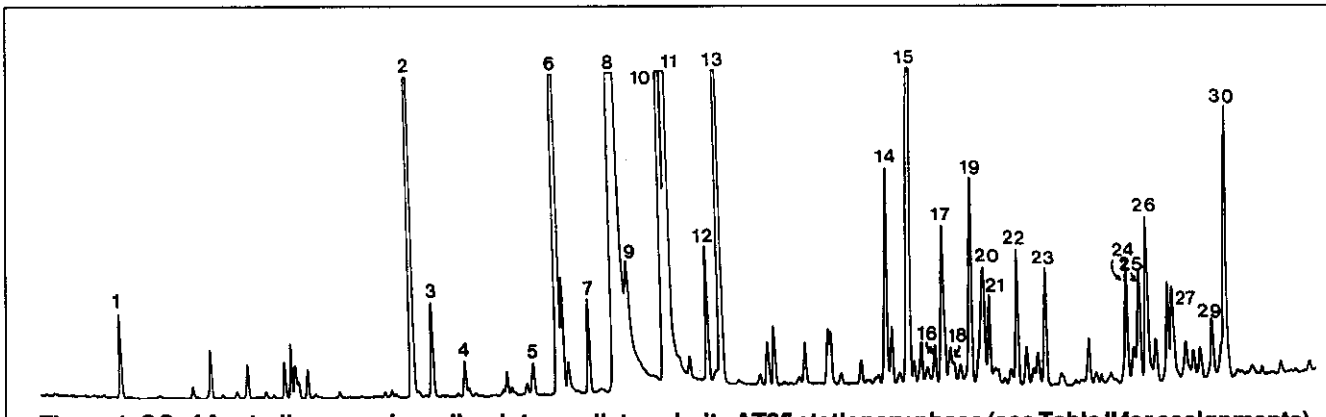

Figure 1. GC of Australian geranium oil on intermediate polarity AT35 stationary phase (see Table II for assignments)

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- *Egyptian* (Fytosan, Die, France).
- *Moroccan and Chinese* (Australian Botanical Products, Hallam, Australia).

Results and Discussion

Some thirty years ago an experiment was initiated to develop a *Pelargonium* cultivar that would be suitable for Australia's climatic conditions and still possess the characteristics of a high quality geranium oil. Specimens of *Pelargonium* hybrids and cultivars were obtained from public and private collections in gardens and nurseries. Initial selection, which was based on olfactory criteria, resulted in the establishment of a reference collection of genetic material. This collection was expanded using cuttings, cross pollination and self-pollination. Several hundred organoleptically selected cuttings were exposed to sources of x-ray, γ-ray and α,β,γ-ray irradiation. Replantings at Sydney and at Grose Vale provided a variable pool of genetic material for olfactory, gas chromatographic and oil yield evaluations.[4]

Plants producing oils with characteristics differing from Bourbon oil were eliminated. The most promising cultivar, P. *graveolens* QV1 (Stol.), although modest in oil yield (0.16%), was assessed as superior by olfactory and gas chromatographic criteria. Organoleptic evaluation (Lockwood McGrath Ltd) ranked the oil superior to Bourbon because of higher citronellol and citronellyl ester contents. A second assessor (Dragoco) suggested that, with field distillation and harvesting experience, a first-class geranium oil with a very similar odor but a tenacity superior to the desirable Bourbon oil could be produced. The perfumers of US Aromatics International found samples of this oil excellent both organoleptically and analytically. This cultivar was propagated more intensively by cuttings, and planted out at Grose Vale where it successfully withstood four to five weeks of morning frosts in winter. Examinations by taxonomists have confirmed this genotype as a P. *graveolens* sp. hybrid, probably an F1 hybrid with *P. capitatum*.[5]

This cultivar, established in trial plots in the warmer

Table I. Physical constants for oil of *Pelargonium graveolens* hybrid QV1 (Stol.) compared with those of commercial oils

Country of origin	Refractive index n_D^{20}	Optical rotation $\alpha_D^{27°}$	Specific gravity d_{20}^{20}	Solubility in 70% ethanol (vols)
Australia	1.4642	–12.0	0.8912	2.5
Reunion	1.4665	–11.9	0.8908	2.2
Egypt	1.4700	–9.6	0.8961	2.2
Morocco	1.4686	–4.4	0.9004	1.9
China	1.4652	–9.2	0.8898	2.5

Table II. Oil constituent identification and percentages of the Australian geranium genotype compared with those of commercial oils

No.	Component	Method of identification	Retention Index BP1	AT35	BP21	Reunion	Morocco	Egypt	China	Australia
1	α-pinene	KI,MS,COGC	931	963	1034	0.8	0.6	0.8	0.4	0.4
2	linalool	KI,MS,IR,COGC	1088	1153	1535	9.9	9.9	6.5	3.9	4.6
3	cis-rose oxide	KI,MS,IR	1100	1166	1368	0.6	0.8	0.9	1.4	0.4
4	trans-rose oxide	KI,MS,IR	1117	1188	1368	0.3	0.3	0.4	0.6	0.2
5	menthone	KI,MS,IR,COGC	1137	1235	1497	1.0	2.1	0.5	2.4	0.2
6	isomenthone	KI,MS,IR,COGC	1146	1252	1514	9.5	4.2	5.7	5.4	7.6
7	α-terpineol	KI,MS,COGC	1177	1273	1730	0.8	1.0	0.5	0.3	0.5
8	citronellol	KI,MS,IR,COGC	1216	1292	1778	20.6	28.0	27.7	36.5	31.7
9	nerol	KI,COGC	1219	1299	1825	0.8	0.6	0.4	0.2	0.5
10	geraniol	KI,MS,IR,COGC	1240	1329	1873	18.1	20.6	18.0	8.7	9.8
11	citronellyl formate	KI,MS,IR,COGC	1261	1332	1627	7.4	6.5	6.5	10.1	12.8
12	citronellyl acetate	KI,COGC	1337	1360	1670	0.9	0.9	0.7	0.7	0.8
13	geranyl formate	KI,MS,IR,COGC	1284	1371	1718	5.6	4.1	3.7	2.1	3.4
14	β-caryophyllene	KI,MS,IR,COGC	1422	1500	1582	1.3	0.5	1.3	1.2	1.3
15	guaia-6,9-diene	KI,MS,IR,COGC	1443	1514	1582	5.8	0.5	0.3	6.5	4.6
16	germacrene D	KI,COGC	1472	1539	1670	0.3	0.2	0.3	0.4	0.2
17	geranyl propionate	KI,MS,IR,COGC	1454	1546	1825	1.2	0.7	1.1	0.9	1.1
18	$C_{15}H_{24}$	KI,MS	1463	1552	-	0.4	-	0.5	0.3	0.4
19	$C_{15}H_{24}$	KI,MS	1480	1569	-	1.0	-	1.5	1.1	1.4
20	$C_{15}H_{24}$	KI,MS	1495	1580	-	0.6	0.8	1.0	1.7	1.2
21	citronellyl butyrate	KI,MS,IR,COGC	1518	1586	1803	0.5	0.4	0.6	0.9	0.6
22	δ-cadinene	KI,MS,COGC	1523	1606	1582	0.5	0.6	0.9	0.7	0.8
23	geranyl butyrate	KI,MS,IR,COGC	1544	1633	1897	1.0	0.4	1.5	0.6	0.6
24	sesquiterpenoid	KI,MS	1526	1700	-	0.1	1.0	0.4	0.2	0.8
25	2-phenylethyl tiglate	KI,MS,IR,COGC	1560	1714	2256	0.6	0.4	-	0.6	0.7
26	$C_{15}H_{22}O_2$	KI,MS	1571	1722	-	0.5	0.6	1.0	0.6	1.1
27	citronellyl tiglate	KI,MS,IR,COGC	1648	1745	2018	0.3	0.3	0.5	1.0	1.2
28	10-epi-γ-eudesmol	KI,MS	1625	1751	-	-	2.5	5.5	-	-
29	sesquiterpenoid	KI,MS	1670	1781	-	0.1	0.2	0.3	0.1	0.4
30	geranyl tiglate	KI,MS,IR,COGC	1678	1796	2125	1.2	1.1	1.9	1.3	1.6

Lismore district some 800 km north of the Sydney-Gross Yale region, yielded an oil with the physical constants shown in Table I. A typical gas chromatogram of this oil is shown in Figure 1.

Identification of the oil's constituents by Retention Indices, GC/MS, GC/IR and co-injection with standard compounds resulted in the identification of components shown in Table II. Percentages for oil components consistently greater than 0.5% from Reunion (France), Morocco, Egypt and China are also shown for comparison. The Australian oil was, contrary to a report on an earlier eugenol-rich oil,[9] typical in having citronellol (31.7%) as the major component. Including linalool (4.6%), geraniol (9.8%) and nerol (0.5%), monoterpene alcohols totaling 46.6% fall a few percent lower than the other commercial oils. Geraniol content (9.8%) is similar to that of the Chinese oils (8.7%) at about half of the concentration of the other oils. This is balanced by a higher ester content, especially citronellyl formate (12.8%). Isomenthone (7.6%) is higher than in the North African or Chinese oils, approaching the 9.5% of the Reunion oil. The high guaia-6,9-diene content (4.6%) and the absence of 10-epi-γ-eudesmol show similarities to the Reunion and Chinese oils. Given the varying component concentrations in oils sourced from different countries,[6-13] these GC parameters suggest a composition intermediate between Reunion (Bourbon) and Chinese oils, with the key citronellol:geraniol ratio (3:1) higher than the Bourbon (1:1) but lower than the Chinese (4:1) sample. The minor components of the Australian oil included myrcene (0.3%), α-phellandrene (0.2%), limonene (0.2%), cis-β-ocimene (0.3%), β-phellandrene (0.2%), trans-β-ocimene (0.3%), geranyl acetate (0.3%), α-humulene (0.2%) and allo-aromadendrene (0.2%). These constituent percentages are similar to Demarne's "Rose," 260/85 and 297/85 cultivars.[14]

The physical constants of the Australian oil fall within the ranges published for those from Reunion and Northern Africa.[15-16] Our measurements on the acquired commercial

oils reflect the market variations, as some constants fell outside the published ranges.

Summary

The development of an Australian geranium oil from a *Pelargonium* sp. hybrid has been followed by olfactory and gas chromatographic evaluation. The end product is a perfumery-grade rose scented oil which has been shown by gas chromatography-mass spectrometry-infrared spectroscopy to be rich in citronellol (32%), geraniol (10%) and citronellyl formate (13%), with linalool (5%), isomenthone (8%), geranyl formate (3%) and guaia-6,9-diene (5%) as secondary constituents. Comparison of this Clevenger-type, glass-distilled oil with commercial oils from Reunion, Morocco, Egypt and China indicated that the Australian oil contained more citronellol and less geraniol than all but the Chinese oil. The citronellyl formate concentration was 25-100% higher than all oils, while concentrations of guaia-6,9-diene and isomenthone approached those of the Reunion sample.

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